

On the cocrystallization phenomenon in blends of high density polyethylene and low density polyethylene

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Summary

A large increase in the crystallization temperature of low density polyethylene (LDPE) when blended with high density polyethylene (HDPE) is reported. Such behavior is observed for quenched LDPE rich blends when the low melting component is cooled from 119°C under controlled conditions in the differential scanning calorimeter. It is suggested that the presence of the most linear LDPE methylene segments within the HDPE-rich crystals (cocrystallization phenomenon) facilitates the nucleation of the more branched LDPE segments on cooling. On reheating, a depression in the low melting temperature component (LDPE) is observed with increasing HDPE content in the blend.

Introduction

The study of the solid state morphology of melt crystallized blends of linear polyethylene (LPE) and branched polyethylene (BPE), the latter with a variety of molecular structures, has been performed over the years using several experimental techniques. The occurrence of cocrystallization in these blends has been proposed by various authors to explain several experimental observations. These are, the presence of a third intermediate peak located between the melting points of the pure polyethylenes (1-3), a depression in the LPE melting point with an increasing BPE content (4-6), a uniform fine-grained morphological appearance (4,7), the presence of a single melting endotherm (8-13), an increase in the dimensions of the crystal lattice (8,9), the presence of single diffraction and scattering peaks (6,10), incomplete removal of the low melting component by solvent extraction (6), a decrease in the amorphous interlayer (14), and the absence of isothermal thickening of LPE lamellae (15). Cocrystallization phenomena between deuterated linear polyethylene and hydrogenous branched polyethylenes are also being currently investigated (16-18).

In this article cocrystallization between LDPE and HDPE is assessed by studying the thermal behavior on cooling of the branched component in the blend and its subsequent melting behavior. A large increase in the crystallization temperature of LDPE

when blended with HDPE is reported; this effect is indicative of cocrystallization between the components when blends are rapidly cooled from the melt.

Experimental

The LPE used, a HDPE, was a BP HD6070 (density 960 kgm^{-3}) with $M_w \approx 72000$ and $M_n \approx 12000$, whereas the BPE was a LDPE, BP PN220 (density 918 kgm^{-3}) with $M_w \approx 200000$ and $M_n \approx 15000$ (21). The PN220 branching content was 10 long branches and 16 short branches per 1000 carbon atoms (22).

Blends were prepared by dissolving the linear and branched polyethylene in xylene (1% w/v) at 140°C and precipitating into cold acetone ($\sim -12^\circ\text{C}$), followed by filtering and drying under vacuum at 50°C for 48 hours (7). The HDPE content in the blends was 3, 5 and 10 wt%. The pure polymers went through the same dissolving and drying procedure. Samples were compression molded at 170°C to obtain discs $\sim 1 \text{ mm}$ thick and $\sim 4 \text{ mm}$ diameter.

Quenching experiments were carried out by encapsulating samples in aluminum pans, heating to 170°C for 20 minutes in a hot plate, and quenching into acetone at $\sim -80^\circ\text{C}$. In addition, isothermal crystallizations were carried out in a thermostated silicon oil bath; samples, wrapped with aluminum foil, were immersed in the bath at 170°C for 20 minutes, then the temperature was decreased to 125°C for 3 days before quenching into cold acetone ($\sim -12^\circ\text{C}$).

The thermal behavior of melt crystallized samples ($\sim 6\text{mg}$), under an inert atmosphere, was studied using a Perkin Elmer differential scanning calorimeter (DSC-7) instrument. All heating experiments were carried out at $10^\circ\text{C}/\text{min}$ from 40°C to 150°C , whereas cooling runs from 119°C to 40°C took place at $1^\circ\text{C}/\text{min}$. Melting and crystallization temperatures were taken from the peak of the endotherms and exotherms, respectively. Calibration was carried out by taking the onset melting temperature of a pure indium sample.

Results and discussion

Figure 1 shows heating thermograms of the various quenched samples. Both pure polyethylenes show single melting endotherms whereas all blends present two melting endotherms. The high melting peak is associated with the melting of HDPE-rich lamellae and the low melting endotherm corresponds to LDPE-rich crystals (4). The origin of double melting endotherms in quenched polyethylene blends is still being argued. Some authors, using indirect techniques, claim that such behavior is due to partial miscibility in the molten state (4,19); others, however, maintain that both components are completely miscible over the entire concentration range and explain double melting by crystallization effects that had occurred on cooling (20). A marked depression in the high melting temperature with increasing LDPE content in the blends is observed in Figure 1. The inclusion of some LDPE segments into the HDPE-rich crystals reducing the thermal stability of the crystals, a phenomenon usually referred as cocrystallization, has been proposed to explain the lowering of melting temperature (6). In relation to the low melting endotherm, however, no clear trend is observed. Cocrystallization in quenched samples is not only present within the HDPE-rich crystals but it also occurs within the LDPE-rich lamellae by incorporating HDPE segments, as was recently reported by Wignall *et al.* (16).

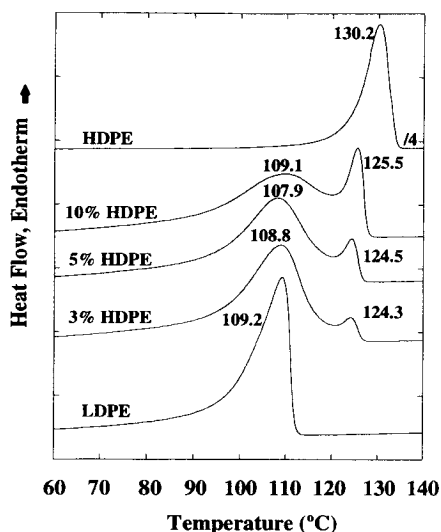


Figure 1: DSC heating traces obtained at 10°C/min for materials quenched from 170°C.

In order to gain additional information that could contribute to clarify the cocrystallization phenomenon that occurs in quenched polyethylene blends, the crystallization behavior of LDPE segments not incorporated into HDPE-rich lamellae was investigated. Quenched samples were taken to 119°C for 30 minutes in DSC-7, high enough temperature to melt the LDPE-rich lamellae but low enough to prevent the melting of HDPE-rich crystals, and then cooled under controlled conditions (1°C/min). Figure 2 shows thermograms on cooling from 119°C for the blends and the pure LDPE. The crystallization temperature of LDPE in the blends is greater than for the pure LDPE, and its value depends on the HDPE content in the blends, being greater as the linear component content in the blend decreases.

On reheating, all blends and the pure LDPE exhibit two well separated endotherms and one endothermic peak, respectively (Figure 3). Two observations can be made: First, when the melting behavior of a blend slowly cooled from 119°C is compared with that obtained from a quenched blend (Figure 1), a large increase in the heat of fusion of the high melting endotherm is found. For a 3% blend there is a *ca.* 2.8 J/g (~65%) increase in the enthalpy of fusion of the HDPE-rich lamellae. Two factors may contribute to the higher heat of fusion on subsequent heating, one, though small, is due to the annealing of HDPE-rich lamellae at 119°C while the other is given by the separate crystallization of HDPE segments that had earlier cocrystallized on quenching within the LDPE-rich lamellae. Second, a clear depression in the low melting temperature with increasing HDPE content in the blend is now observed.

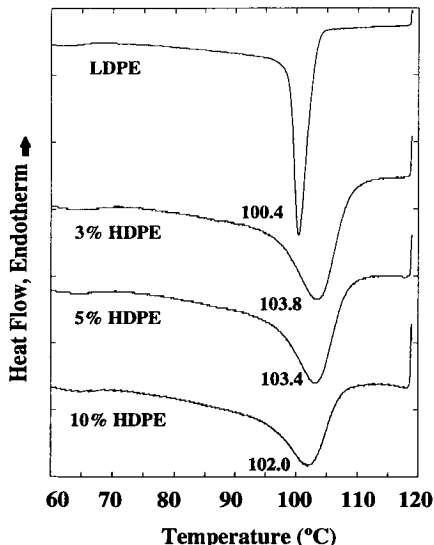


Figure 2:

DSC cooling traces obtained at 1°C/min for quenched materials and after holding at 119°C for 30 minutes

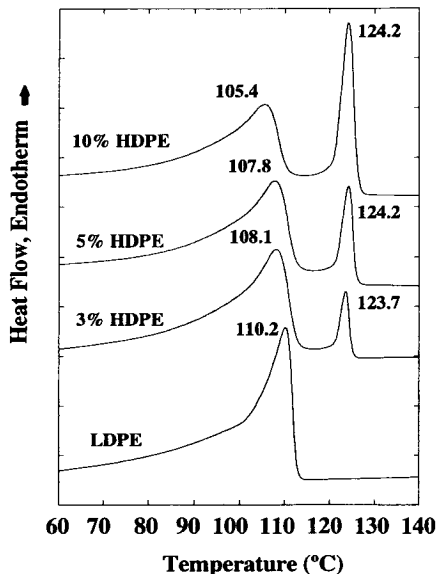


Figure 3:

DSC heating traces obtained at 10°C/min for quenched material and cooled from 119°C.

Isothermal crystallizations from the melt at 125°C were carried out to segregate both types of polyethylene on crystallization of the linear component as was carried out by Norton and Keller (7). Figure 4 shows the thermal behavior of the isothermally crystallized 5% blend. Figure 4a shows the melting behavior of the blend after quenching from 125°C: Two well defined endotherms are observed, the high melting and the low melting peaks correspond to the melting of HDPE that crystallized at 125°C and LDPE that crystallized on cooling, respectively. The isothermally crystallized blend was taken to the DSC and cooled at 1°C/min after thirty minutes at 119°C (Figure 4b): The LDPE component in the blend shows a crystallization temperature of 101.2°C, just above the crystallization temperature of pure LDPE (Figure 2). On reheating the blend at 10°C/min two endotherms are again found (Figure 4c), the low melting endotherm shows a melting point similar to that obtained for the pure LDPE in Figure 3.

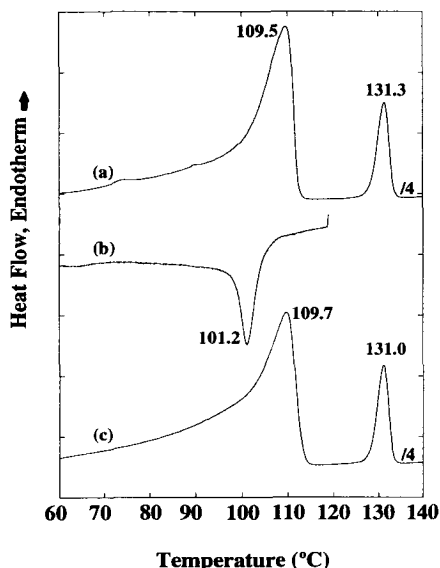


Figure 4:
DSC traces for a 5% blend crystallized at 125°C and quenching. (a) Heating trace at 10°C/min. (b) Cooling trace at 1°C/min from 119°C. (c) Heating trace at 10°C/min after cooling at 1°C/min.

It is expected from the cocrystallization phenomenon that the most linear methylene sequences of LDPE are incorporated within the HDPE-rich crystals, leaving the most branched segments to crystallize separately at a later stage. Alamo and Mandelkern reported that the melting temperatures of branched polyethylene represent meaningful melting temperatures and are not product of melting-recrystallization processes that occur during heating (23). Thus, the observed depression in the low melting temperature in Figure 3 constitutes evidence of segregation on cocrystallization, i.e., the more branched material melt at lower temperatures. As the HDPE content in the blend increases, a greater proportion of LDPE linear sequences are incorporated within the larger number of HDPE-rich lamellae, leaving the more branched segments (lower melting component) to crystallize later. Thus, the low melting endotherm, on subsequent heating, is only given by the fusion of the most branched material in LDPE since its more linear material is incorporated within the HDPE-rich lamellae.

In a branched polyethylene sample, the most branched chains must exhibit a lower crystallization temperature than its most linear chains. However, such behavior is not observed in Figure 2: When pure LDPE is compared with the blends an increase in the crystallization temperature for the LDPE in the blends is found. This can not be explained by nucleation effects of first formed HDPE lamellae over the crystallization of LDPE, since the shift in crystallization temperature for the 5% segregated blend (Figure 4b) is small compared with that obtained in Figure 2 for the quenched 5% blend. Small nucleation effects of HDPE lamellae over the crystallization of LDPE on isothermal conditions were also recently shown by Puig (24). Thus, the observed variation in crystallization temperature, when cocrystallization is present, must be explained by a nucleation mechanism throughout which the more LDPE linear segments, already incorporated within the HDPE-rich lamellae, are able to favor the crystallization of those branched segments.

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