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The nucleation effect of linear polyethylene lamellae over the crystallization of branched polyethylene

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Summary

The isothermal crystallization of branched polyethylene (BPE), when it takes place in the presence of linear polyethylene (LPE) lamellae was found to occur above the highest crystallization temperature of the pure BPE. A standard state formed by isothermally crystallized LPE lamellae at 122°C was used to provide surfaces for the crystallizing BPE at various seeding temperatures (117, 118, 119 or 120°C). Isothermal treatments were carried out in a thermostatic oil bath, and evidence on the progress of crystallization of BPE was obtained by differential scanning calorimetry and transmission electron microscopy after quenching from the seeding temperature.

Introduction

The morphology and crystallization behavior of blends of linear polyethylene (LPE) with branched polyethylene (BPE) has been the subject of much research over the last few years (1-8). Early work on this area was carried out by Clampitt (9) who investigated whether the two types of polyethylene would form homogeneous crystals on cooling from the melt. Results though showed a small range of compatibility between both components.

Norton and Keller (1) and Michler *et al.* (2) investigated the lamellar morphology of blends of LPE with BPE by transmission electron microscopy (TEM). The former studied the conditions of segregation with crystallization temperature and the latter carried out lamellar thickness measurements for slow cooled blends from the melt. Alamo *et al.* (3) using well characterized fractions of LPE and BPE determined the molecular constitution requirements for cocrystallization in blends using differential scanning calorimetry (DSC) and extraction techniques. The authors found that BPE with an ethyl branch content greater than 3% mol did not cocrystallize with LPE. Stein and coworkers (6) found that the extent of crystal segregation depended upon the crystallization conditions and the relative concentration of the two species in the blend by performing a series of scattering experiments.

It is usual to find in blends of commercial LPE with BPE that the linear polyethylene is the higher melting component, however, conditions of cocrystallization in blends of low molecular weight LPE and high molecular weight BPE in which the BPE is the high melting component have also been studied by Conde Braña *et al.* (5).

The degree of mixing of LPE and BPE in the melt has not been possible to assess in situ due to the similarities in the physical properties of both components. Evidence obtained using indirect techniques developed by Barham *et al.* (4) to study these systems showed that segregation in the liquid state occurs for some blend compositions. Recent small angle neutron scattering experiments by Alamo *et al.* (7) on blends of deuterated LPE and BPE in the melt, however, showed homogeneity for all concentrations.

Puig *et al.* (8) have recently reported how the lamellar thickening that usually takes place in polyethylene on isothermal crystallization is suppressed when LPE is blended with BPE, lowering its melting temperature.

The present paper reports on the isothermal crystallization of BPE, when is blended with LPE, at temperatures above the highest crystallization temperature of the pure BPE. LPE crystals were first isothermally grown in order to create a standard state of lamellae that would serve as nuclei of the crystallization of BPE on subsequent treatment. Preliminary results, obtained by DSC and TEM, showed that crystallization of BPE takes place at temperatures that it would not normally occur if LPE lamellae were not present. Moreover, it was observed in a series of blend compositions that the amount of BPE that crystallized depended upon the LPE content in the blend, being a 1% LPE blend where the BPE showed greater crystallization.

Experimental

The LPE was BP Rigidex HD6070, density 960 kgm^{-3} (Mw ≈ 72,000, Mn ≈ 12,000). The BPE used was a low density polyethylene, density 918 kgm^{-3} (Mw ≈ 208,100, Mn ≈ 25,300) (10). Blends with 0.5, 1, 3, 5, 10 and 15% LPE content were prepared by dissolving the two polymers in xylene at 1% (w/v) and precipitating by pouring into cold acetone, a non-solvent. After filtering, blends were dried under vacuum at 50°C for 2 days.

Isothermal crystallizations were carried out in a thermostatic silicon oil bath where the temperature was controlled to ± 1°C. The pure BPE and the blends were melted at 160°C for 30 minutes, samples were then rapidly transferred to a silicon oil bath at 122°C and left for 40 hours in order to ensure complete crystallization of the LPE component while the BPE remained molten. In order to investigate whether the isothermally grown LPE lamellae were able to nucleate the growth of BPE crystals, various seeding temperatures were examined by decreasing the temperature of the bath from 122°C to: 117, 118, 119 or 120°C. The length of treatment varied between 80 and 120 hours according to the seeding temperature used. Finally, samples were quenched into cold acetone.

Thermal behavior was determined using a Perkin-Elmer DSC-7. The weight of the samples was about 3 mg and the heating rate was 10°Cmin^{-1}. The melting temperatures were identified with the maximum in the endothermic peak. Calibration was checked against the onset melting temperature for a pure indium sample.

TEM was carried out using a Philips 301 electron microscope operated at 80kV. Kanig´s technique (11) was used as a method of preparation of sample for TEM. Samples were treated with chlorosulphonic acid at 25°C for 35 hours, long enough to avoid crystal shrinkage along the chain direction during microscopy observations (12) but short enough to prevent lamellar degradation (13,14). After chlorosulphonation samples were sectioned at room temperature using a LKB ultramicrotome and the thin sections stained with a dilute aqueous solution of uranyl acetate.

Results and discussion

The thermal behavior on heating of pure BPE and a 1% blend is shown in Figure 1. Pure BPE (curve c) and a 1% blend (curve a) were held at 122°C and then at 117°C after melting at 160°C and before being quenched, while in curve b a 1% blend was only held at 122°C. Curve c clearly shows the absence of an endotherm of fusion above 117°C, which indicates that for the pure BPE no crystallization had occurred during isothermal treatment at 117°C for 80 hours. The commercial pure BPE used was unable to develop any crystallinity at such low supercooling, it only shows a broad endotherm with a peak located at ~109.5°C corresponding to the melting of species that crystallized on rapid cooling from 117°C. Curve b shows the characteristic behavior found in polyethylene blends when crystallized above the melting temperature of the BPE component (8); the endothermic peaks at 126.4 and 107.9 represent the melting of LPE lamellae formed after 40 hours at 122°C and the melting of BPE lamellae formed on quenching from this temperature, respectively.

The melting transitions observed in curve a are explained by the different crystal populations formed upon the three crystallization stages used (isothermal treatments at 122°C and 117°C, and quenching). The high and low temperature endotherms correspond to the melting of LPE and BPE lamellae, respectively. Annealing of LPE lamellae, formed at 122°C, on storage at 117°C for 80 hours shifts their melting transition to higher temperatures (~129.1°C). The third or intermediate peak, just above the seeding temperature, is attributed to the melting of BPE lamellae whose growth was favored by the presence of preexistent LPE crystals at 117°C. The small size of the intermediate endotherm indicates that little BPE can crystallize, i.e. there are only a few crystallizing BPE segments (presumably the most linear chain segments) in its complex molecular structure that meet the requirements for nucleation on the surface of LPE lamellae. Recent experiments on fractionation of pure BPE during isothermal crystallization have also suggested the presence of such linear sequences in its structure (15).

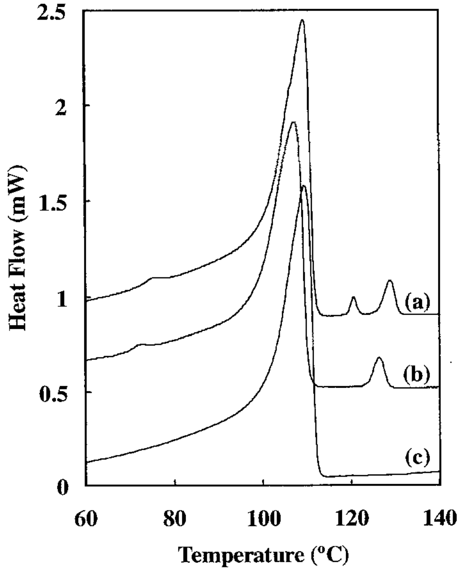


Figure 1:
DSC melting endotherms obtained from material quenched after various isothermal treatments: (a) 1% blend crystallized at 122°C and 117°C. (b) 1% blend crystallized at 122°C. (c) BPE held at 122°C and 117°C.

Blends of various LPE contents were examined following the isothermal treatments described above, i.e. 122°C for the crystallization of LPE and 117°C as the seeding temperature. Figure 2 only presents the endotherms associated to the melting of species crystallized on isothermal treatments. The decrease in size of the intermediate endotherm in Figure 2 as the LPE content in the blend goes from 1% to 15%, when it disappears, is attributed to the gradual diminution in the number of BPE segments available for crystallization at 117°C. Heats of fusion obtained from the area under those intermediate endotherms that present well defined peaks are shown in Figure 3. Results do not only corroborate what was observed in Figure 2, but reveal a lower heat of fusion for a 0.5% blend than for a 1% blend. Such behavior can be explained by the absence of enough nuclei (LPE lamellae) to activate the crystallization of BPE, i.e. there is a blend composition in which crystallization of BPE is maximum.

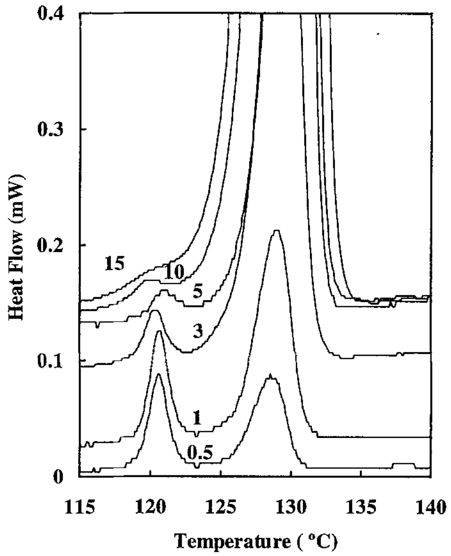


Figure 2:
DSC endotherms of the species crystallized at 122°C and 117°C for blends with various LPE contents.

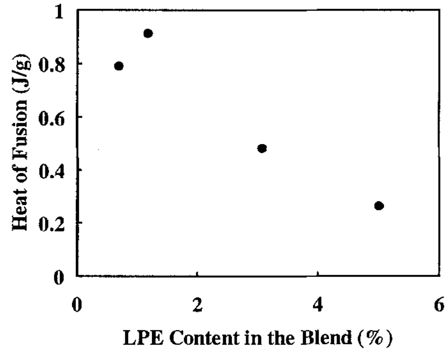


Figure 3:
Variation of heat of fusion of the intermediate endotherm with LPE content in the blend.

A 1% blend was used to investigate how an increase in the seeding temperature would affect the crystallization of BPE; three additional temperatures were studied: 118, 119 and 120°C. Figure 4 shows the melting endotherms of species crystallized on isothermal treatments. It can be observed from Figure 4 that an increase in the temperature causes a decrease in the size of the intermediate endotherm till it disappears for a seeding temperature of 120°C. These results could well be explained by the heterogeneity of the BPE, higher the seeding temperature longer have to be the linear sequences in the BPE chain to be able to crystallize.

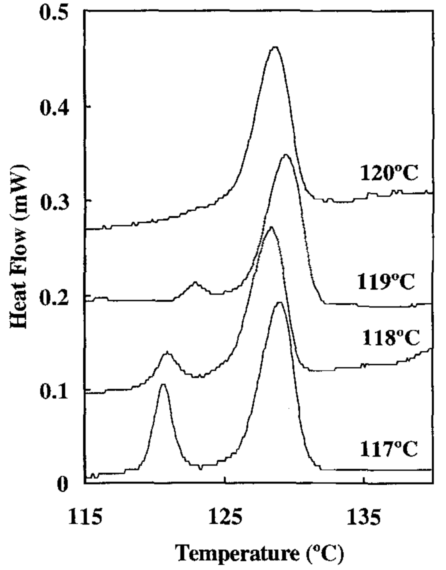
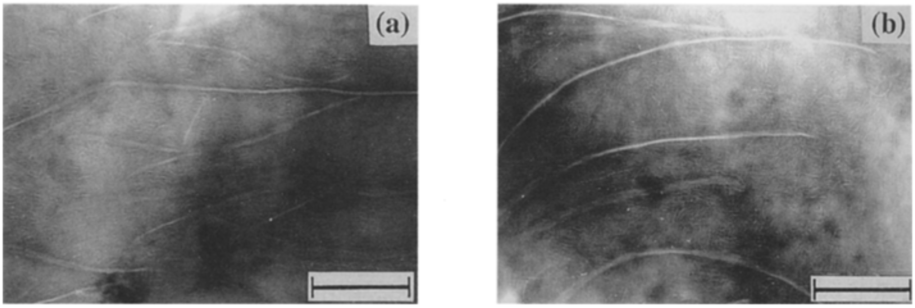


Figure 4:
DSC endotherms of species crystallized at 122°C and at various seeding temperatures for a 1% blend.

The lamellar morphology of melt crystallized pure LPE (16-18), BPE (19,20) and their blends (2,5) has been extensively studied by electron microscopy using chlorosulphonated sections. Figure 5 shows the crystallite morphology of a 0.5% blend (Figures 5(a) and 5(b)) and of a pure BPE (Figure 5(c)).

The lamellar morphology of quenched pure BPE after being held at 122°C and 117°C is shown in Figure 5(c). The micrograph shows short, curved, thin lamellae (*ca.* 6 nm thick), randomly oriented, which is indicative of crystallization of BPE on cooling and not on isothermal treatments.

The micrographs given in Figures 5(a) and 5(b) clearly show two populations of lamellae, thicker and longer crystals are associated with lamellae being formed on isothermal crystallization whereas shorter and thinner lamellae are formed on quenching. The lamellar morphology of a 0.5% blend crystallized at 122°C is shown in Figure 5(b). Longer and thicker lamellae (up to *ca.* 16 nm thick) are associated with LPE crystals whereas thin lamellae correspond to BPE crystals. Figure 5(a) shows the lamellar morphology of a 0.5% blend crystallized at 122°C and 117°C. Comparing Figures 5(a) and 5(b), the blend crystallized at 117°C has a larger number of lamellae which constitutes further evidence of crystallization of BPE at the seeding temperature. Furthermore, crystal branching is more pronounced in (a) than in (b), the presence of shorter and thinner isothermally grown crystals at 117°C whose growth was nucleated by the thicker and longer dominant lamellae grown at 122°C is observed in Figure 5(a). This suggests that crystallization of BPE in the blend at temperatures above the highest crystallization temperature of the pure BPE occurs because of the existence of LPE crystals that provide the surfaces on which BPE segments nucleate.



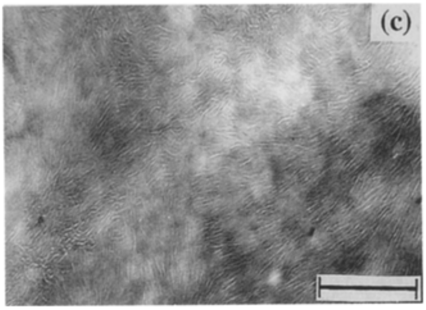


Figure 5:
Transmission electron micrographs showing sections of PE after chlorosulphonation. (a) 0.5% blend crystallized at 122°C and 117°C. (b) 0.5% blend crystallized at 122°C. (c) BPE held at 122°C and 117°C. Scale bar represents 0.5μm.

Conclusions

It was shown in blends of LPE with BPE that isothermally grown LPE lamellae are able to nucleate the crystallization of some segments of BPE at temperatures above the highest crystallization temperature of the pure BPE. An optimum LPE content in the blend was found in which the crystallization of BPE was maximum.

Acknowledgments

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