Absence of isothermal thickening for a blend of linear and branched polyethylene

C. C. Puig*, M. J. Hill and J. A. Odell
H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK
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In this paper we investigate the effect on melting stability of blending linear with branched polyethylene. Linear polyethylene (LPE) was blended in solution with branched polyethylene (BPE) at a concentration of 10% LPE. Both homopolymers and the blend were held at 126°C, for 80 h. At this temperature solid–liquid phase separation takes place in pure LPE and in the blend; pure BPE remains molten. The melting point of the isothermally crystallized blend lamellae was lower than the melting point of pure LPE lamellae crystallized under the same conditions. This depression in melting temperature has previously been explained in two ways: by the inclusion of BPE into the LPE crystals, and because of the different environment of the crystals. We assess these two factors and find them insufficient to explain the decrease in melting temperature observed. We discuss another important factor, the dimension of the crystals in the chain direction. By transmission electron microscopy we show that crystals isothermally grown in the blend are thinner than LPE crystals grown under the same conditions. This difference in crystal thickness is sufficient to explain the observed depression in melting temperature. We believe that the lamellae in the blend fail to thicken during the initial stages of crystallization. We envisage three mechanisms that explain the suppression of thickening present in the blend, and one of these is eliminated.

(Keywords: linear polyethylene; branched polyethylene; blend; melting point; crystal thickness)

INTRODUCTION

Much recent interest has centred on blends of linear polyethylene (LPE) and branched polyethylene (BPE). Conditions of co-crystallization and/or segregation during isothermal crystallization and phase segregation in the liquid state have been studied by a wide range of techniques[1–9].

Liquid–solid phase segregation in a blend of semicrystalline polymers is achieved by maintaining the melt at a temperature (T_c) where only one of the components crystallizes. It is usually the LPE that crystallizes at T_c, with the BPE in the liquid state. This is the case for the pair of polymers under investigation in this work, for which the 'phase diagram' has already been determined; details are given in ref. 10, but in that paper the main interest is in liquid–liquid phase separation, not in liquid–solid phase separation, which is our interest here.

When a blend of LPE and BPE segregates during isothermal crystallization (liquid–solid phase segregation), two endotherms are observed on subsequent heating after quenching: the high-temperature peak corresponding to the species which crystallize at T_c, and the low-temperature peak to those which crystallize on quenching. The higher-temperature peak seen on remelting a blend is often found to occur at lower temperatures than the main melting peak of the pure LPE crystallized under the same conditions[1]. The magnitudes of such variations have been found to depend on the concentration of BPE[8], the crystallization conditions[7] and on the branch content[10].

In the case of semicrystalline polymer blends, the stability of the crystal could be affected by the presence of the second component in four different ways. First, the crystals are melting in an environment (in our case BPE) that acts as a diluent[8]. Secondly, if some of the second component is included (co-crystallized) in the lattice, defects will be introduced. This will reduce the enthalpy of fusion and, therefore, the melting temperature. Co-crystallization could not take place unless the second component is able to crystallize in the same lattice pattern as the first, as is the case for LPE and BPE. The incorporation of BPE into the crystals growing at T_c has been proposed to explain the depression in melting temperature[7,8]. Thirdly, the melting point could be depressed by an increase in surface free energy, σ_e, in the blend; however, published results show that σ_e is in fact either unchanged or reduced[5]. Lastly, if the final crystal thickness of the first component is affected by the presence of the second component, a change in the melting temperature will be observed due to the increase in the surface area of the crystals.

It is not obvious why there is a variation in crystal thickness, since the crystallization conditions are the same for the LPE and for the blend. Reduction of crystal thickness has been reported to occur when irregularities in the form of branches (copolymers) are introduced to the main chain of the polymer[11]. Here a decrease in crystal thickness would be expected since the linear sequences between branch points, available for

* To whom correspondence should be addressed
0032-3861/93/163402-06

crystallization, are decreased. In the blends however, there is no modification of the main crystallizing component (LPE); nevertheless, a reduction in the crystal thickness is observed.

In this paper we show that all three factors are present, but we identify the third, the difference in crystal thickness, as being the dominant factor. TEM studies show that the final crystal thickness of the dominant lamellae in the blend is lower than that of the LPE lamellae crystallized under the same conditions, although initially both populations are of similar thickness.

EXPERIMENTAL

The LPE was BP Rigidex 50 ($M_w = 72\,000$, $M_n = 11\,000$). The BPE used was BP PN220 ($M_w = 208\,100$, $M_n = 25\,300$) with 10 long branches and 16 short branches per 1000 carbon atoms. A blend of 10% (w/w) LPE was investigated. The blend was prepared by dissolving the two polymers in xylene at 1% (w/v) and precipitating by pouring into acetone at $-20°C$.

Isothermal crystallizations were carried out in a silicone oil bath. The samples were put in the oil bath at 150°C for 30 min to ensure an equilibrium melt and then the temperature was decreased to 126°C for a crystallization time of 80 h. Finally, the samples were quenched into cold acetone. The phase diagram has already been determined for this LPE/BPE pair[10]. It has been shown that LPE-rich material is phase-separated in a matrix of BPE-rich material at both 150 and 126°C; LPE-rich crystals grow in roughly spherical clusters at 126°C[10,12].

Thermal behaviour of the isothermally crystallized samples was determined using a Perkin–Elmer DSC-7. The weight of the samples was about 2 mg, the heating rate was, unless otherwise stated, chosen to be 10°C min^{-1} (see 'Results and discussion' section) and the melting temperature was taken as the peak of the endotherm. Calibration was checked against the onset temperature for a pure indium sample.

Following the technique introduced by Kanig[13], TEM samples were treated with chlorosulfonic acid at 22°C. Samples gave consistent results over a wide range of treatment times; typical lengths of treatment were between 150 and 200 h. After chlorosulfonation samples were sectioned at room temperature using an LKB microtome and the thin sections stained with uranyl acetate. Transmission electron micrographs were obtained using a Philips 301 electron microscope operated at 80 kV. Construction of histograms of distribution of crystal thickness was based on 200 measurements from TEM negatives. The amorphous region becomes stained and appears black in prints of micrographs; the crystal layer does not stain, and appears white.

In order to evaluate any effects of TEM sample preparation we have also investigated the long spacing of the isothermally crystallized LPE by small-angle X-ray scattering (SAXS). A Rigaku–Denki low-angle camera was used in conjunction with an Elliot rotating-anode generator. The operating voltage used was 39 kV and a tube current of 39 mA. Cu Kα radiation was used with a distance of 0.347 m from the sample to the detector (film). Lorentz correction was applied to determine the position of the maxima.

To study the effect of melting crystals of LPE in a matrix of BPE, we grew single crystals of LPE from solution; these were then mixed into a suspension of BPE crystals. By doing this we avoided co-crystallization between the two polymers.

LPE single crystals were grown from 0.05% (w/v) solution in xylene at 84°C for 3 days. Then the single crystals of LPE were added to the suspension of BPE and put into an ultrasonic bath for 5 min to ensure mixing between the two components. The concentration corresponded to 10% (w/w) of LPE. After mixing, the suspension was filtered and put to dry under vacuum. Then the single crystals were pressed to ensure intimate contact between the two polymers. D.s.c. analysis was done at a heating rate of 5°C min^{-1} to enhance any environmental effects, which we expect will increase with slower heating rates.

RESULTS AND DISCUSSION

Figure 1, curves a and b, shows the thermal behaviour of isothermally crystallized samples. In both cases the high melting peaks correspond to material which crystallized at T_c and the low melting peaks to the material which crystallized on quenching. The low melting peak in curve a is composed of about 15% of lower-molecular-weight LPE, segregated at T_c. The low melting peak in curve b is composed of BPE that did not crystallize at T_c, together with the 15% of low-MW LPE. The presence

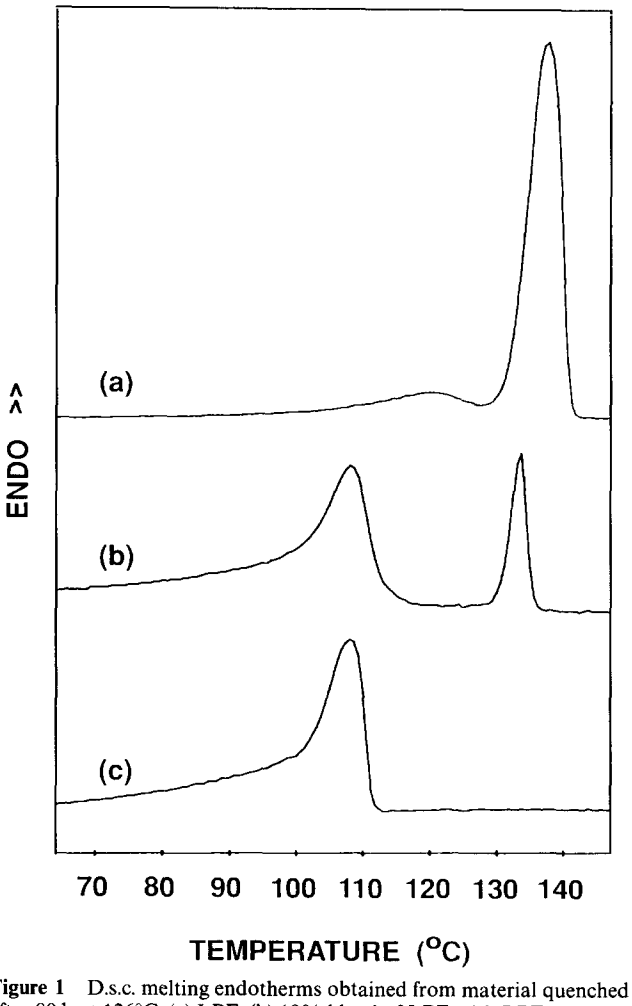

Figure 1 D.s.c. melting endotherms obtained from material quenched after 80 h at 126°C: (a) LPE; (b) 10% blend of LPE with BPE; (c) BPE. Heating rate 10°C min^{-1} in each case

of LPE in the low-temperature peak in curve b is confirmed by the tail seen at the high-temperature end of the lower endotherm of the blend (compare with pure BPE treated under the same conditions, curve c).

Figures 2a and *2b* show TEM micrographs of the LPE and the blend, respectively. Populations of thick crystals grown at T_c and the thinner ones crystallized on quenching can be seen in both micrographs.

Now we direct our attention to the main point of this paper: the high-temperature melting peak of the blend (*Figure 1*, curve b) is located at a lower temperature than the high-temperature melting peak of pure LPE (curve a).

Figure 3 shows the temperatures of the start, the peak and the end of high melting d.s.c. endotherms for the LPE and for the blend. From these values it is possible to see that the peak and end of the endotherms are 3.5–5°C higher in pure LPE, but the endotherms start at the same temperature in both cases. In order to rule out anomalies due to heat transfer effects and to assess possible differences in the annealing rates of the two samples, experiments were conducted over a heating rate of 5–30°C min^{-1}.

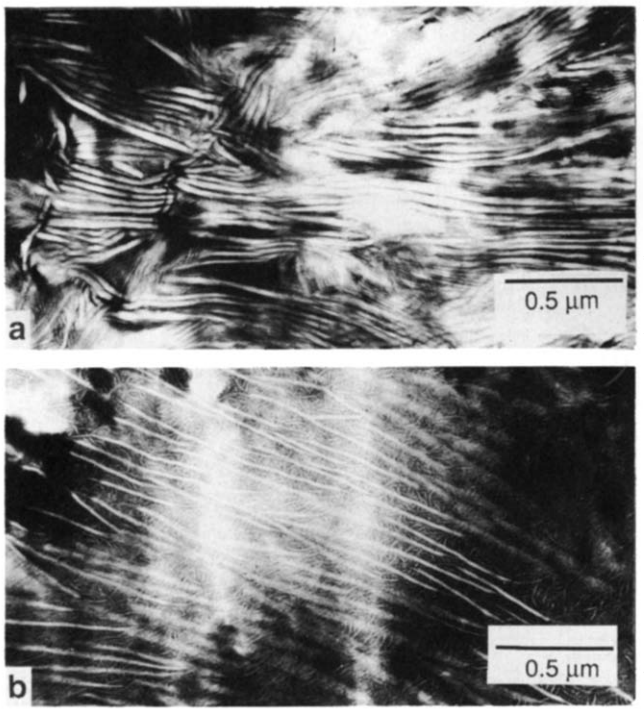

Figure 2 Micrographs showing sections of PE chlorosulfonated after crystallizing at 126°C for 80 h; sections stained with uranyl acetate for 2 h after sectioning: (a) LPE; (b) 10% blend of LPE with BPE

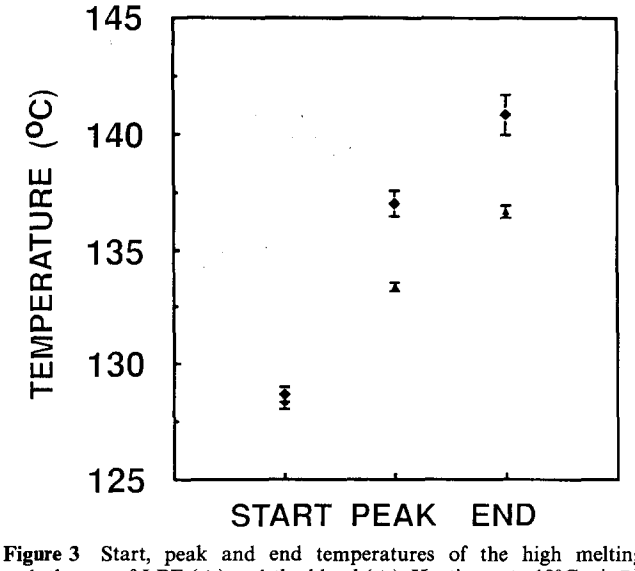

Figure 3 Start, peak and end temperatures of the high melting endotherms of LPE (◆) and the blend (▲). Heating rate 10°C min^{-1}

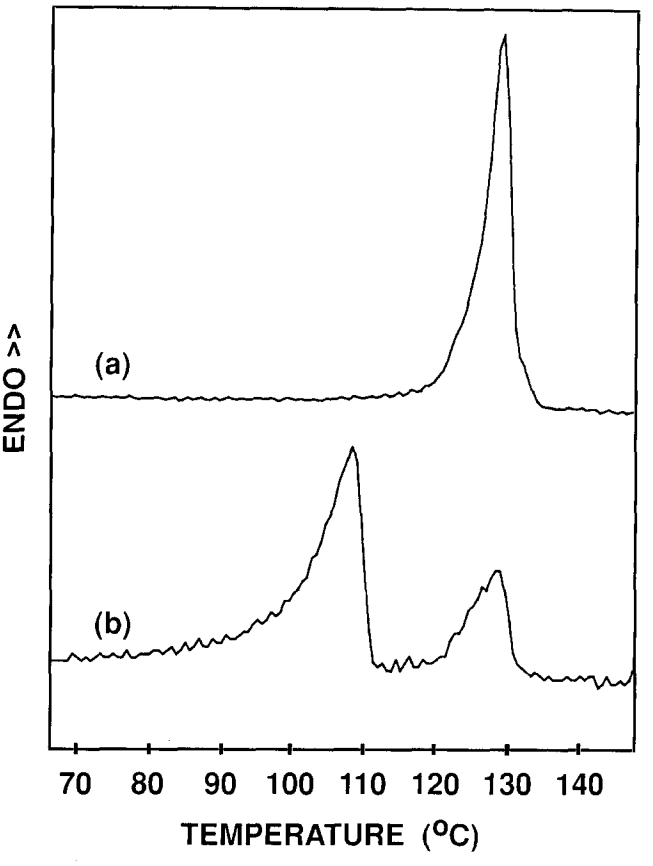

Figure 4 D.s.c. melting endotherms of (a) LPE single crystals, (b) a mixture of 10% LPE single crystals with 90% BPE single crystals. Heating rate 5°C min^{-1}

Little difference in peak temperature was observed for heating rates of 5–15°C min^{-1}. Beyond 20°C min^{-1} we observed a slight increase in depression, which can be attributed to differential thermal lag. There was no change in onset temperature with the heating rate. We conclude that, at our chosen heating rate of 10°C min^{-1}, we record the genuine melting-point depression.

Evaluation of factors contributing to the lower melting temperature

Environmental effect on the melting of LPE crystals. By examining a mixture of 10% isothermally crystallized LPE single crystals in a matrix of BPE we have tried to evaluate any change in the melting point due to the crystals melting in a different environment. We used a mixture of single crystals in order to avoid any possibility of co-crystallization between the two polymers and any change in the crystal thickness of the first component due to the presence of the second component. *Figure 4* shows the melting behaviour for the pure LPE, curve a, and for the mixture, curve b. It can be seen that there is no appreciable difference in the melting temperature of the LPE crystals.

In order to satisfy ourselves that intimate contact between the components of this mixture was achieved,

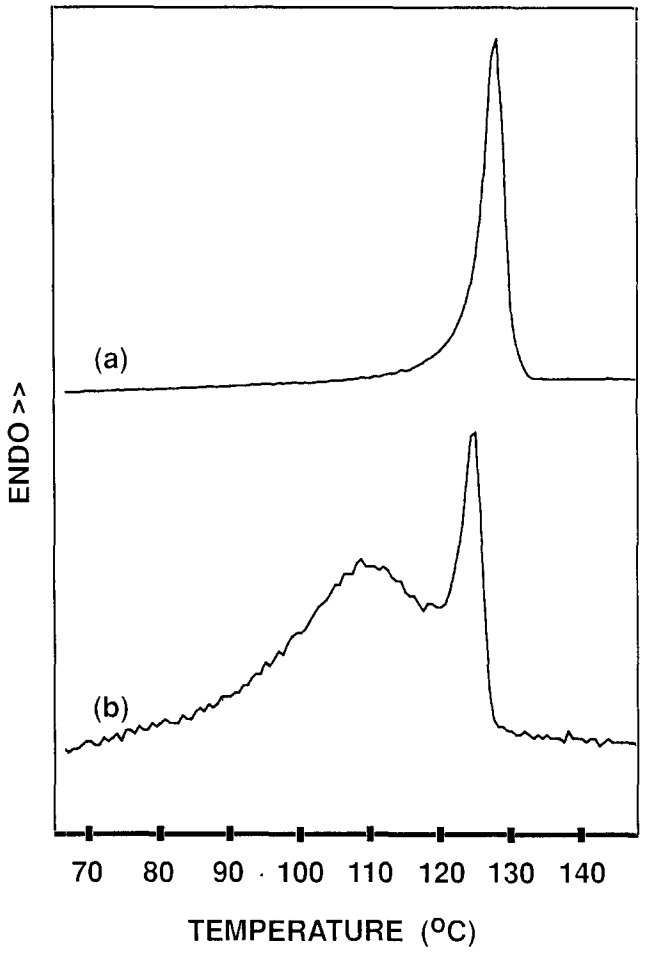

Figure 5 D.s.c. melting endotherms obtained on remelting the samples in *Figure 4* after storage for 10 min at 150°C before quenching. Heating rate 10°C min^{-1}

we held it in the melt at 150°C for 10 min and then quenched. On subsequent heating we observe a marked depression in the melting point (*Figure 5*). We believe that there has been diffusion, partial mixing and co-crystallization between the two components[12]. This rapid change would not have been possible if good mixing had not been achieved.

Martinez-Salazar *et al.*[8] also reported that the level of depression in melting temperature was higher in melt-crystallized blends than in the mixtures of single crystals of LPE and BPE.

Co-crystallization effect on the melting of LPE crystals. Some depression of melting temperature due to a decrease in the enthalpy of fusion might be expected. Measurements of heats of fusion from d.s.c. traces give a 5% decrease in the heat of fusion of the upper peak. A reduction in the enthalpy of fusion could be caused by the incorporation of BPE into the LPE crystals growing from the melt, since this would generate defects. We estimated that no more than 0.8% of BPE present in the blend can be co-crystallized, corresponding to 9% of the material in the crystal*. We expect that it is predominantly the linear parts of BPE, between the branches, that are included in the crystals.

Co-crystallization would be expected since BPE is semicrystalline, its structural unit is the same as that of LPE, and when it crystallizes it does so in the same crystal lattice. Furthermore, the components are known to be partially miscible under our crystallization conditions[10].

The Thomson–Gibbs equation (1) relates the melting temperature to the various thermodynamic constants:

$$T_m = T_m^\circ - \frac{2T_m^\circ \sigma_e}{\Delta H^\circ l} \quad (1)$$

where ΔH°, σ_e and T_m° are the bulk enthalpy, the surface free energy and the equilibrium melting temperature of an infinite crystal and T_m is the melting temperature of a crystal of thickness l, and the equation assumes constant entropy change. The values of the thermodynamic data are: $T_m^\circ = 418.8$ K, $\Delta H^\circ = 280 \times 10^6$ J m^{-3} and $\sigma_e = 0.0905$ J m^{-2} (ref. 15). Using this equation we find that the observed change of enthalpy, due to co-crystallization, would only account for a reduction in melting temperature of 0.5°C.

Reduction in crystal thickness. The melting temperature in a given sample of polymer is determined by the dimension of the crystal in the chain direction. We used TEM to obtain the thicknesses of the crystals. *Figure 6* presents the distributions of crystal thickness, of the thicker lamellar populations only, for LPE and for the blend crystallized at 126°C. It is these crystals which are responsible for the higher melting endotherms observed in each case (*Figure 1*, curves a and b).

It is clear, from *Figure 6*, that the lamellae crystallized from the blend are considerably thinner. We estimate that the peaks of the distributions of crystal thicknesses are at 21.9 nm for the LPE and 15.8 nm for the blend. These values give a difference in crystal thickness of 28%. The maximum observed values are also less in the blend, the highest measured for LPE being 36.4 nm and the highest for the blend 18.2 nm. However, the lowest values

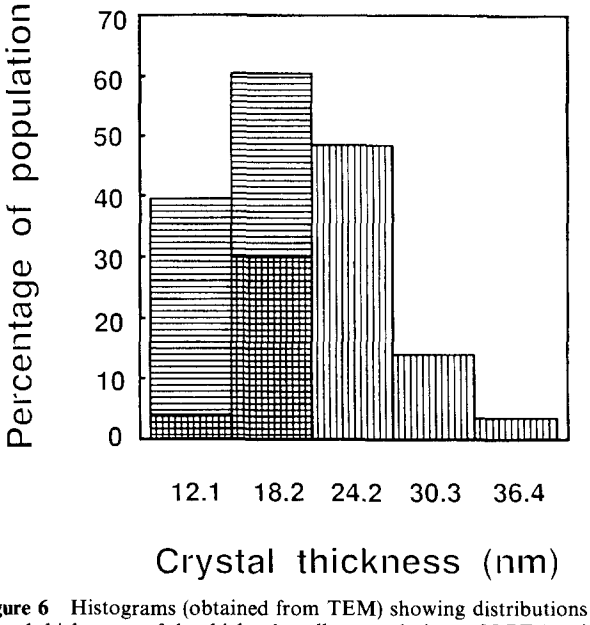

Figure 6 Histograms (obtained from TEM) showing distributions of crystal thicknesses of the thicker lamellar populations of LPE (vertical hatch) and the blend (horizontal hatch) after crystallization at 126°C

* In ref. 10 Hill *et al.* estimate that a larger amount of BPE is included in crystals of this same system, isothermally crystallized at 126°C. Liquid–liquid segregation of the melt was the main concern of these authors, who did not make such a thorough study of co-crystallization; the figure quoted here is more accurate than that in their paper[14]

of crystal thickness for both materials are the same, 12.1 nm.

We are aware of the precautions that have to be taken in working with chlorosulfonic acid as a means of preparation of samples for electron microscopy either by an insufficient acid treatment[16] or by an excessive acid treatment[17,18]. Under our treatment conditions the modification of lamellar thickness was minimized. Furthermore, SAXS was used to confirm that the long spacing of the LPE was not affected by the staining method. The value of long spacing was 32 nm, after Lorentz correction, whereas the average value obtained from the histogram of distribution of long spacing (*Figure 7*) was 30.9 nm.

It was not possible to use SAXS to assess the effect of the staining on blend samples due to the lack of regular stacking (as can be seen in *Figure 2b*). But the possibility of an underestimate of lamellar thickness due to insufficient chlorosulfonation was eliminated, since no change in average crystal thickness was observed on staining for between 12 and 240 h. (In ref. 16 it is shown that low values for lamellar thickness are obtained if the PE is not stained for long enough.)

In order to assess whether this depression in crystal thickness is enough to explain the observed depression in the melting temperature, we have again used the Thomson–Gibbs equation. Using the estimated peak crystal thicknesses mentioned earlier (21.9 nm for the LPE and 15.8 nm for the blend) in equation (1), a difference in melting temperature of 4.4°C is obtained. This level of depression of melting point falls in the range measured by d.s.c. (*Figure 3*).

From the three factors analysed above, we conclude that, although all are present, it is the depression in the lamellar thickness that is the principal cause for the melting temperature of the blend lamellae being lower than that of the pure LPE.

Suppression of thickening in blend lamellae

We have seen that the thinnest lamellae are of the same thickness, and that the lowest melting temperatures are equal in the blend and in the LPE. It thus appears that the crystals initially form at similar thickness in both cases, but that those in the blend fail to thicken. We now address the mechanisms whereby thickening of the blend material is suppressed.

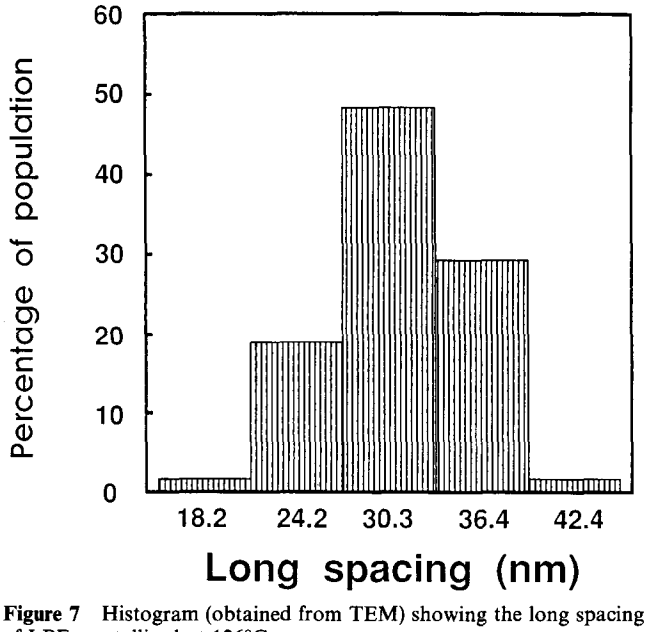

Figure 7 Histogram (obtained from TEM) showing the long spacing of LPE crystallized at 126°C

The dependence of crystal thickness upon the crystallization temperature is predicted by kinetic theories of crystallization[19]. This dependence has been corroborated in solution-grown single crystals of PE, where crystal thickness was shown to increase with T_c (ref. 20). Difficulties are found in trying to obtain the same information in melt-grown crystals, where, owing to the presence of multilayers, a fast process of thickening takes place during the early stages of crystallization. However, experimental methods were developed to follow the thickening process. The dependence of initial crystal thickness (l_g^*) on T_c was the same as is observed in solution-grown single crystals[21].

The increase in lamellar thickness is faster at higher T_c, and occurs at a logarithmic rate with time in the early stages of crystallization[22]. A mechanism has been proposed to explain the rapid initial thickening; it involves the doubling, tripling and quadrupling of lamellae[23], and is only possible where lamellae are stacked in close proximity. At later stages of growth, thickening is still present, but at much lower rates[24].

Dlugosz *et al.*[24] found that in isothermal crystallization the nucleation density has a dramatic effect on the time required for the completion of crystallization. They worked with a range of LPEs with different nucleation densities. The samples with the higher nucleation densities consistently produced thicker lamellae under the same crystallization conditions. They propose that lamellae in all samples were of the same initial thickness but, at the end of the crystallization period, the sample with the larger number of growth centres contained crystalline material which was, on average, older and had therefore thickened more than the sample with the smaller number of growth centres.

We propose three possible causes that could explain the absence of thickening in the blend. They are: (i) younger average age of lamellae, (ii) lamellae not stacked and (iii) the thickening of co-crystals would require branches to be pulled into the lattice.

Average age of lamellae. If lamellae are not formed at the same time, they will not have the same final age and, therefore, crystal thickness at the end of the treatment.

We have followed the development of endothermic peaks for different crystallization times at 126°C by d.s.c. (*Figure 8*). It is clear that after only 20 min of isothermal crystallization there is an endotherm on heating the pure LPE, showing that lamellae are already present. But, for the blend, the endotherm is not observed until after 100 min. Clearly, there is a delay in the onset of crystallization for the blend (probably due to the diluent effect and to the diffusion rates involved). However, the difference in time is negligible in comparison with the long isothermal crystallization time used (80 h). Hence we do not consider this to be the cause of the lack of thickening present in the blend.

Lack of stacking lamellae. *Figure 2b* shows that the isothermally crystallized lamellae in the blend are well separated, not stacked. The space between them is filled by thin lamellae (mainly composed of BPE), which crystallized on quenching.

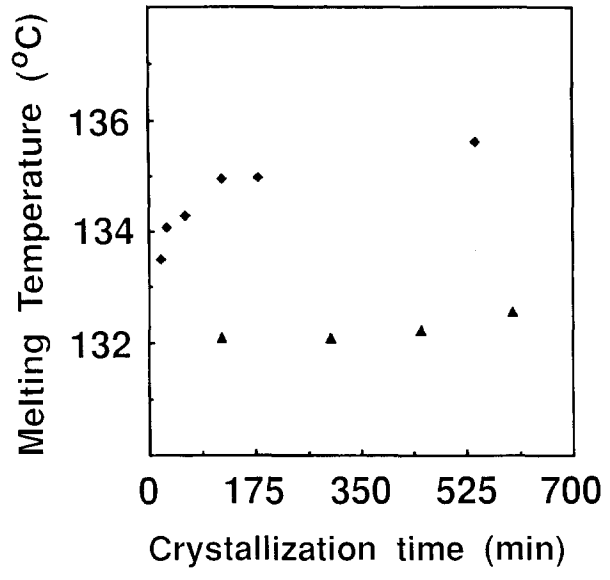

Figure 8 Variation of melting temperature with crystallization time for LPE (◆) and the blend (▲) after the initial stages of crystallization at 126°C. Samples were held at 126°C for the times indicated and then heated to 160°C at 10°C min^{-1}

As explained above, rapid isothermal thickening has been shown to take place in the early stages of crystallization when crystals are found stacked in close proximity[23]. Such thickening leads to a sharp increase in melting temperature with crystallization time, as is observed for the pure LPE (*Figure 8*). However, the lack of stacking in the blend would not allow the lamellae to thicken by this mechanism. In *Figure 8* we see that the melting temperature of the blend remains constant in the early stages of crystallization. This would be the expectation if stacking is a necessary condition for this rapid thickening[23].

Presence of BPE in the LPE crystals. We mentioned earlier the presence of some BPE in the LPE crystals. This represents 9% of the material that melts in the high-temperature peak. During isothermal crystallization we expect that it will be the linear sequences, between branches, which are included in the growing crystals. If the branches are distributed randomly, there are enough sequences of the length of initial crystal thickness for inclusion of only linear portions.

We propose that the thickening process could be limited if there is this type of co-crystallization, with branches located outside the crystal. Any thickening would involve dragging branches into the lamellae, causing energetically unfavourable lattice disruption.

CONCLUSIONS

We have suggested three possible reasons for the observed lower melting temperature of lamellae isothermally crystallized from a blend of LPE with BPE as compared with those crystallized from a pure LPE melt under the same conditions:

(a) melting in an environment of BPE;

(b) co-crystallization of BPE into the LPE-rich lamellae; and

(c) a lower lamellar thickness.

We have shown that all three effects are present, but the third is much the most important.

Further, we have shown that the lamellae form at the same initial thickness in both preparations, but that those in the blend fail to thicken. We envisage three possible reasons why thickening should not take place in the blend and eliminated one of these. Studies are continuing to see which of the other mechanisms is more important.

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