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# Enhanced crystallisation in branched polyethylenes when blended with linear polyethylene

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**Abstract**

The enhanced crystallisation behaviour exhibited by branched polyethylene (BPE) when blended with a commercial linear polyethylene (LPE) was studied. Two commercially available BPE were examined, one was a low-density polyethylene type and the other a 1-octene copolymer produced by Dow using its constrained geometry catalysts technology. Low LPE content blends were investigated. Enhanced crystallisation in BPE, as revealed by shifts in crystallisation temperature peaks obtained using differential scanning calorimetry, was found after blends were fast cooled from the melt. A 3% LPE content blend in both types of mixtures was found as the blend composition where enhancement of BPE crystallisation was largest. When both BPE are compared the larger shift in $T_c$ was found for the more crystalline BPE material. © 2001 Published by Elsevier Science Ltd.

*Keywords*: Enhanced crystallisation; Polyethylene; Blends

## 1. Introduction

During a dynamic experiment on cooling from the melt, polyethylene exhibits a crystallisation process whose transition temperature is a function of molecular weight, its branching content and the intramolecular distribution of branches. In a recent article, it was reported that it is possible to increase the crystallisation temperature of a low density polyethylene (LDPE), for a given cooling rate (1°C/min), by up to ~3°C, when it is blended with linear polyethylene (LPE). For low LPE content blends (less than 10%) quenched from the melt, two separate melting endotherms are found on subsequent heating. The crystallisation behaviour of the low melting material (LDPE), when assessed by heating the quenched blend to a temperature just below the beginning of the high melting endotherm and then cooled, an increase in the transition temperature recorded on cooling is observed when compared with the pure LDPE [1].

Blends of LPE and branched polyethylene (BPE) attract industrial and scientific interest. An issue, which has been debated over the last decade, is whether the commercial components are completely miscible in the melt. Barham et al. had earlier suggested by looking at the solid state morphology of quenched low LPE content blends by transmission electron microscopy and differential scanning calorimetry that they were partially miscible [2]. Recent results by Alamo et al. showed, however, using ultra-small-angle neutron scattering and working with a spatial resolution of ~30 μm, that deuterated HDPE/LDPE mixtures for all compositions are homogeneous in the melt. In addition, it was shown that scattering from blends of deuterated HDPE with a highly BPE, hydrogenated polybutadiene (with 10.6 mol% of ethyl branches), corresponded to that of a phase-separated melt [3]. Using micro-Raman imaging, Morgan et al. then showed that for quenched blends there was no detectable variation in the deuterium content across the sample [4].

In the solid state, cocrystallisation between LPE and BPE is expected because of the similarities in their crystal structures. Cocrystallisation in these blends was proposed in the early work by Clampitt to explain the presence of an intermediate melting peak in a binary blend after annealing at 120°C [5]. Sato and Takahashi associated the presence of an intermediate melting peak, found on cooling from the melt at various rates and then heated at 16°C/min, with the presence of hybrid crystallites of LPE and BPE [6]. Alamo et al. studied the solid state morphology of rapidly crystallised blends of LPE and hydrogenated polybutadiene, with ethyl branch contents ranging from 2 to 5.5 mol% of branch points. By using differential scanning calorimetry and solvent extraction techniques, cocrystallisation in quenched blends was found for branching contents less

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than 4 mol% [7]. Recently, Galante et al. working with several LPE/BPE blends studied cocrystallisation under both isothermal and slow-cooling crystallisation conditions. Two melting peaks were found on heating after isothermal crystallisation from the melt, the lower was assigned to a 'cocrystal' peak and the higher was associated with the melting of pure LPE crystals. Cocrystallisation occurred preferably at low crystallisation temperatures. In addition, cocrystallisation was less favoured with increasing concentration of the linear component in the blend [8]. Ueda and Register, in contrast, showed that no cocrystallisation had occurred in a lower molecular weight LPE ($M_n$ = 3000 g/mol) and short-chain BPE blends, even for rapid cooling conditions from the melt [9].

Tashiro et al. using blends of deuterated HDPE and LLDPE (1-butene copolymers) investigated cocrystallisation between both components, by tracing the change in infrared bands of $CH_2$ and $CD_2$ species. The authors showed that depending on the branching content, cocrystallisation could be found even for slow cooling conditions from the melt. Cocrystallisation was also studied by X-ray scattering techniques; it was shown that in the blend where cocrystallisation is not favoured, because of the larger branching content, more LLDPE could be accommodated in the HDPE lamellae by decreasing the linear component content in the blend. On isothermal crystallisations, the degree of cocrystallisation is very much influenced by kinetic factors as well as by the thermodynamic stability of the pure components [10–14].

Morgan et al. showed, working with deuterated HDPE/LDPE blends and using Tashiro's method for studying cocrystallisation, that the inclusion of LDPE in the first formed crystal population (HDPE) decreased for slower cooling rates. However, even for a cooling rate of 1°C/min some cocrystallisation was still found. It was concluded that the lower melting point of LPE-rich crystals in the blend compared with that in the pure LPE, is a result of LDPE material inclusion in the LPE lamellae rather than a dilution effect [15].

Wignall et al. studied the solid state morphology of blends of LPE with long-chain BPE as well as with short-chain BPE [16,17]. In both types of blends, cocrystallisation was more extensive when they were quenched from the melt. It was determined for slowly cooled blends that up to 15–20% LDPE was contained within HDPE lamellae for rich LDPE content blends. In short-chain BPE blends, the authors found that more mixing occurs with increasing concentration of the branched component.

There has been few studies that deal with the nucleation of low melting BPE by LPE lamellae. It was shown that on isothermal crystallisation, at a temperature that the pure BPE does not crystallize and for long times (about three days), only a few LDPE segments were nucleated by pre-existing LPE lamellae surfaces [18].

In this article, the enhanced crystallisation behaviour of two types of BPE blended with a LPE was studied further. Both sets of blends showed that the shift in crystallisation temperature ($T_c$) is greater for 3% LPE content blends. The shift in $T_c$ does not seem to depend on the cooling rate used to record the transition but on the sample previous thermal treatment. When both blends are compared, the blend that contains the more crystalline BPE, exhibits a larger shift in $T_c$.

## 2. Experimental

Three commercial polyethylene samples were used. A LPE, BP HD6070, was used along with two BPE. One was a LDPE that contains long as well as short branches (lBPE), BP PN220, and the other was Dow's Affinity PL1840 (sBPE), which is a 1-octene copolymer prepared by Dow's INSITE constrained geometry catalysts technology. The densities and melt flow indexes for LPE, lBPE and sBPE are 960, 918 and 907 kg/m$^3$; 7.6, 0.6 and 1.1 g/10 min, respectively.

Binary LPE/BPE blends were prepared by dissolving both components (total weight 0.5 g) in 50 ml xylene at 160°C. After mixing, the components in the solution were precipitated by pouring the hot solution into 100 ml of chilled acetone, the blend precipitated immediately. Then, filtration and drying under vacuum for 48 h at 50°C followed. The pure LPE and BPE were also subject to the same dissolution process. LPE/BPE blends were prepared with the following composition (wt/wt): 0.5/99.5, 1/99, 2/98, 3/97, 4/96, 5/95, and 10/90. Disc shaped samples 4 mm diameter and ~300 μm thick were prepared by compression moulding at 160°C.

Samples (~3 mg) were encapsulated in aluminium DSC pans and held at 160°C for 30 min in a hot stage. Then the samples were rapidly dropped into acetone at its freezing point (~ − 80°C).

The quenched samples were transferred to a differential scanning calorimeter where their melting and crystallisation behaviours were studied. A Perkin-Elmer DSC-7 was used throughout the experiments. The quenched samples were first heated from 0 to 160°C at various rates (5, 10 and 20°C/min). In addition, quenched samples were also heated to 118°C at 40°C/min where they were left for 30 min before being cooled to 0°C at various rates (2, 5, 10 and 20°C/min). The melting behaviour of controlled cooled samples from 118°C was then examined at 10°C/min. Crystallisation and melting temperatures were taken as the peaks of the exotherms and endotherms, respectively.

All DSC runs, under a high purity nitrogen atmosphere, were previously calibrated for each heating rate with the onset melting temperatures and heats of fusion of Indium and Tin.

## 3. Results and discussion

Fig. 1 shows the DSC heating traces for the lBPE blends (Fig. 1(a)) and sBPE blends (Fig. 1(b)), recorded at 10°C/min,

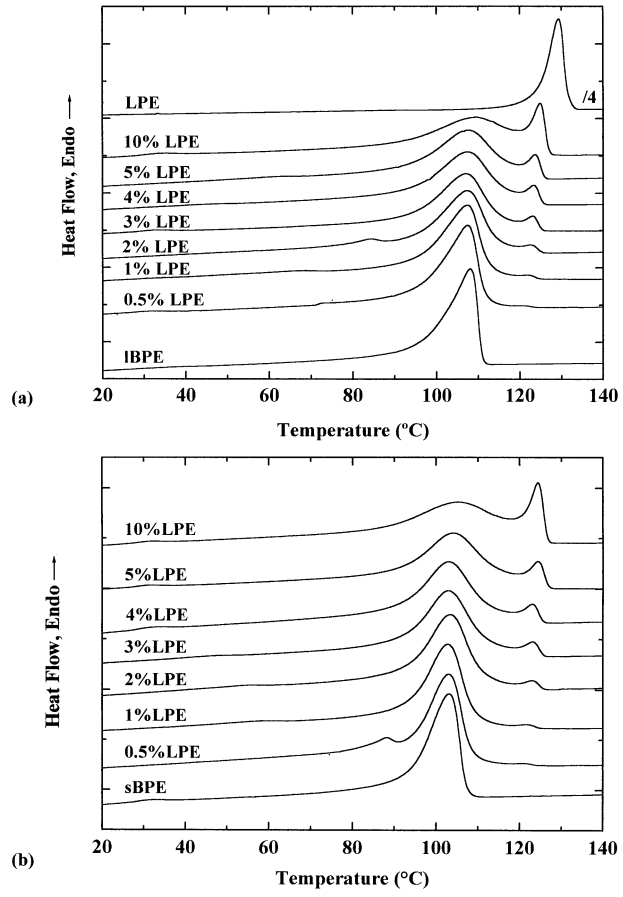


Fig. 1. DSC heating traces of LPE/BPE blends quenched from the melt. (a) lBPE blends; (b) sBPE blends.

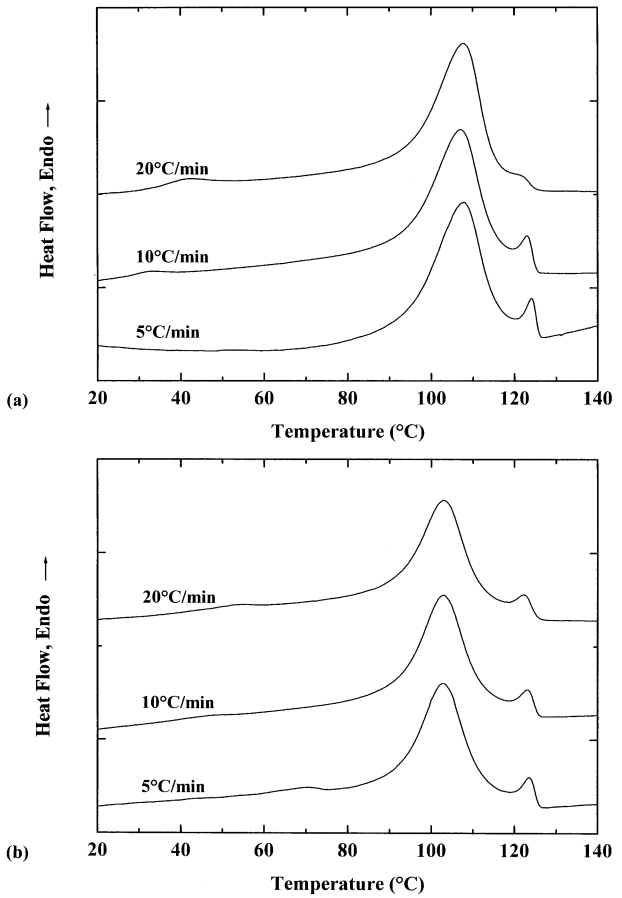


Fig. 2. DSC traces at various heating rates of 3%LPE blends quenched from the melt. (a) lBPE blend; (b) sBPE blend.

after quenching from the melt into acetone at its freezing point. The melting behaviour shown in Fig. 1 resembles that already reported for low LPE content blends [2]. Two melting endotherms are observed for all blend compositions studied. The origin of the melting endotherms has been associated with the presence of two lamellar populations. The lamellar populations formed on fast cooling from the melt can be explained either by the presence of a phase-segregated melt prior to the cooling process or by the difference in crystallisation kinetics between the linear and the branched component. The LPE crystallizes at temperatures that are high enough for BPE molecules to solidify. Due to similarities in chemical structures between both components, methods to study phase segregation in the melt are difficult to implement [19]. Recent results by ultra-small-angle neutron scattering at a temperature above the melting point of a deuterated HDPE/LDPE (25/75) blend have shown that they are completely miscible [3].

In Fig. 1, the high melting temperature peaks are associated with the melting of the LPE component whereas the low melting peaks with the BPE component. The quenched pure LPE melting temperature, ~129.3°C, is reduced by several degrees in both sets of quenched blends (Fig. 1), its magnitude depends slightly on the blend composition. The observed depression in melting temperature for the quenched materials is explained by the inclusion of BPE segments into the LPE lamellae, lowering their thermal stability LPE-rich crystals. For example, a 3% LPE blend in both sets of materials shows a high melting temperature peak at about 123.2°C, ca. 6.1°C depression in melting temperature.

A recent study showed that during heating severe recrystallisation occurs in quenched crystallised LPE/BPE blends [20]. Morgan irradiated 5%LPE/95%BPE quenched blends with up to 30 Mrad of gamma radiation and showed that changes in melting behaviour occur as a function of radiation dose. The high temperature peak decreased in area and shifted to lower temperatures with an increase in dose level. The melting trace of a sample irradiated to 30 Mrad consisted mainly of a broad peak.

Fig. 2 shows the heating traces for quenched 3% LPE blends (Fig. 2(a), lBPE blend; Fig. 2(b), sBPE blend) heated inside the DSC at different rates (5, 10 and 20°C/min). The heat flow in the DSC traces was corrected by heating rate. Results show that in these blends some degree of crystal reorganisation occurs over pre-existing lamellar populations. In both 3% LPE blends, the high melting endotherm decreases in area and shifts to lower temperatures with

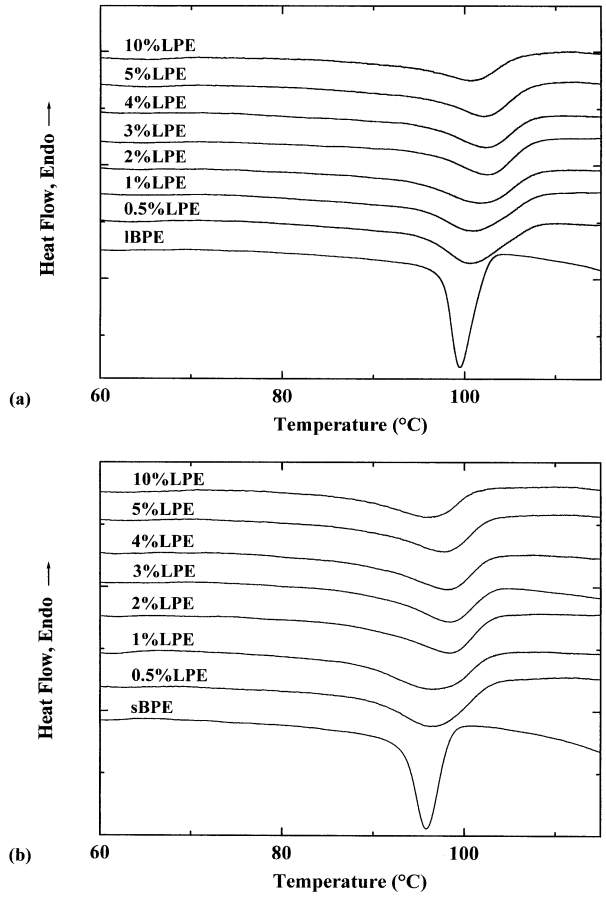


Fig. 3. DSC cooling traces from 118°C of LPE/BPE blends that previously were quenched from the melt. Cooling rate 2°C/min. (a) lBPE blends; (b) sBPE blends.

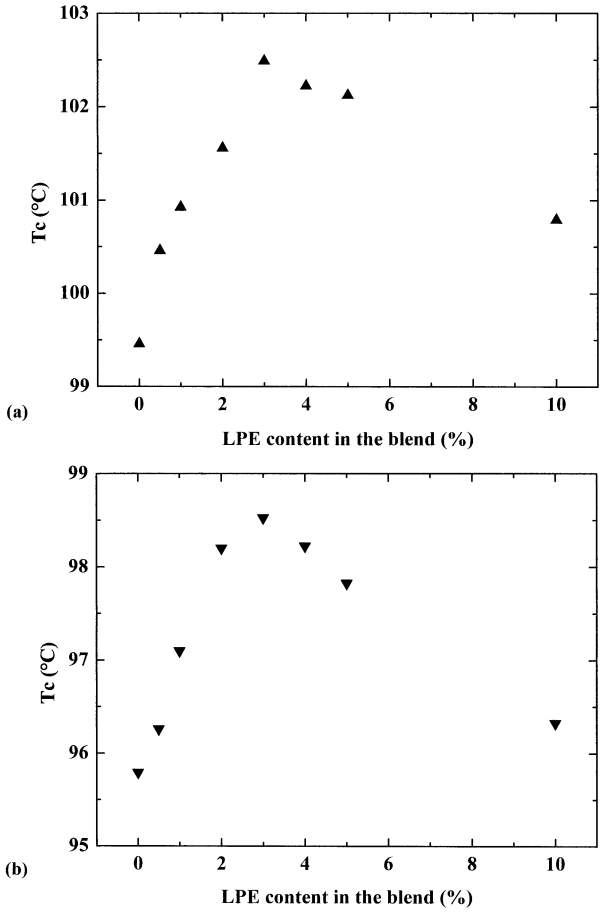


Fig. 4. Variation in $T_c$ as a function of LPE blend composition. $T_c$ were recorded on quenched blends by cooling from 118°C at 2°C/min. (a) lBPE blends; (b) sBPE blends.

increasing heating rate. The melting peaks broaden with increasing heating rate due to thermal lag effects.

Our main concern is the crystallisation behaviour of the low melting material while preserving the high melting populations of crystals that were formed on quenching. Morgan et al. showed, using micro-Raman imaging to examine spatial variation of composition in deuterated-LPE/BPE blends with a resolution of about 1 μm, that rapidly quenched blends exhibit homogeneous Raman images [4]. The results suggest that some inclusion of LPE within BPE lamellae when the blends are rapidly quenched from the melt is also expected (BPE-rich lamellae). Both sets of quenched blends and both pure BPE were heated to 118°C at 40°C/min. The rate used to take the quenched sample to 118°C is fast enough to minimize reorganisation processes that may occur on heating. The high under-cooled LPE molecules that had earlier formed part of the BPE-rich lamellae after rapid cooling, now melted, crystallize rapidly at 118°C, leaving a melt that is composed by BPE molecules.

Fig. 3 shows the cooling traces, recorded at 2°C/min, from 118°C for both sets of blends and the pure BPE (Fig. 3(a), lBPE blends; Fig. 3(b), sBPE blends). In all traces, an exotherm is found that reflects the crystallisation of BPE melt. Despite their different origin both BPE show similar behaviour. The crystallisation behaviour of BPE that was not incorporated within the LPE lamellae changes with blend composition. The crystallisation temperature peak ($T_c$) shifts to higher temperatures with increasing LPE content in the blend up to a blend composition when it starts to lower. The high temperature end of the exotherms in the DSC traces also follow the same trend. The variation in $T_c$ with blend composition is shown in Fig. 4 (Fig. 4(a) and (b) are for lBPE and sBPE blends, respectively). The highest increase in $T_c$, ~3°C, is obtained for 3% LPE blends in both sets of materials. It is believed, as proposed in a previous study, that such level of increase in $T_c$ is only possible because of the existence of some BPE segments already included within the LPE lamellae [1]. The same shift in $T_c$ for a quenched 3%LPE/97%lBPE blend is found even when storage time at 118°C is varied between 5 and 60 min. The results also indicate that the increase in $T_c$ is higher for the blend that contains the more crystalline BPE, longer methylene sequences between branch points (lBPE).

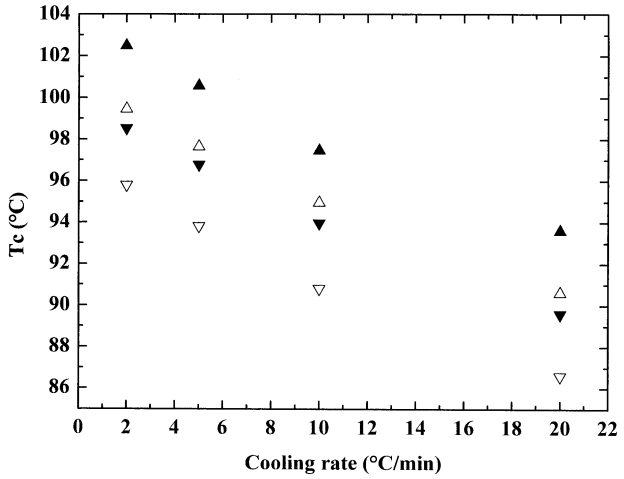


Fig. 5. Crystallisation temperature peaks as a function of cooling rate from 118°C for quenched 3%LPE blends and for both pure BPE. ▲ lBPE blend; △ pure lBPE; ▼ sBPE blend; ▽ pure sBPE.

In addition, a 3%LPE/97%lBPE blend was taken to the melt at 160°C in the DSC and then cooled at 40°C/min to 118°C. Further cooling at 2°C/min, after 30 min at 118°C, shows a peak at 99.9°C. This $T_c$ is much lower than that reported in Fig. 4(a) for the same blend composition but quenched from the melt. The above results further support the enhanced crystallisation behaviour in BPE as a result of the cocrystallisation present in LPE-rich crystals.

It was shown in Fig. 2 that reorganisation processes in both 3% LPE blends are more severe when a heating rate of 5°C/min is used. We also examined whether the heating rate used to take the quenched samples to 118°C has any influence on the observed enhanced crystallisation behaviour of BPE obtained later on further cooling. No changes in $T_c$ were recorded by either heating both quenched 2% LPE blends to 118°C at 40 or 5°C/min.

The crystallisation behaviour of pure BPE and in the blends was also recorded on cooling from 118°C at other rates (5, 10 and 20°C/min). Fig. 5 shows $T_c$ values for both pure BPE and for both 3%LPE blends as a function of cooling rate. As the cooling rate is increased the crystallisation temperature decreased, however, the shift in $T_c$ observed in both pairs of 3% LPE blend and pure BPE is about the same magnitude in all cases. This suggests that the observed increase in $T_c$ is related with the LPE-rich crystals, already present at higher temperatures (above 118°C), and not on the dynamic conditions used to record the crystallisation behaviour.

In the past, the melting behaviour of BPE using differential scanning calorimetry has been assessed in order to characterize the branch distribution content among molecules [21]. Those calorimetric based methods are valid if lamellar crystals reorganisation processes are minimised on heating. After slow cooling at 2°C/min from 118°C, it would be expected that on subsequent heating reorganisation processes are minimal. Fig. 6 shows the melting behaviour

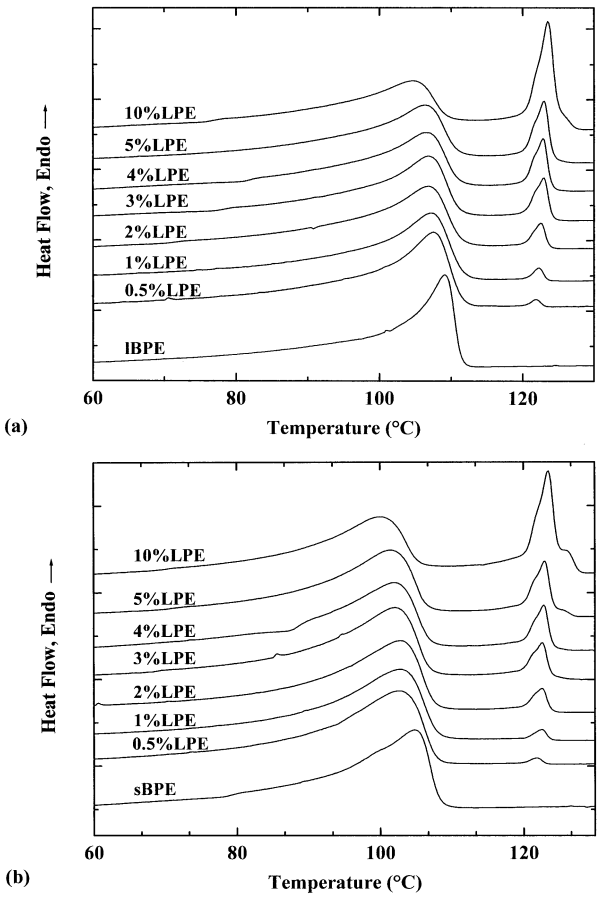


Fig. 6. DSC heating traces of quenched blends that were later controlled cooled at 2°C/min from 118°C. (a) lBPE blends; (b) sBPE blends.

of the quenched blends and the pure BPE, recorded at 10°C/min, after holding them at 118°C for 30 min and then cooled at 2°C/min (Fig. 6(a), lBPE blends; Fig. 6(b), sBPE blends). When compared with the melting behaviour of quenched blends (Fig. 1) significant changes are observed. The heat of fusion of the high melting crystals increased after thirty minutes at 118°C. It is thought that there are at least two contributing factors to the higher heat of fusion of the high melting endotherm. One comes from the annealing of the already existing quenched LPE-rich crystals and the other is based on the crystallisation at 118°C of LPE molecules that were earlier included within the quenched formed BPE lamellae. By holding at 118°C the LPE molecules that had earlier been included within the BPE lamellae are allowed to crystallize and to separate from the BPE molecules. The asymmetry observed in the high temperature peaks may well then be related with the various origins of the lamellar populations.

Fig. 6 also shows significant changes in the DSC traces that are relevant to the studies that are carried out here, it involves the melting of the material that crystallised on cooling from 118°C. A continuous depression in melting temperature for the low melting material with increasing LPE content in both sets of blends is now observed

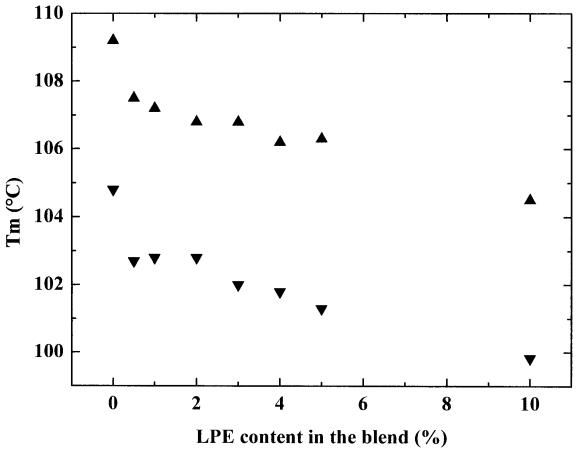


Fig. 7. BPE melting temperature peaks as a function of LPE blend composition. The materials were quenched from the melt and then were slowly cooled from 118°C at 2°C/min. $T_m$ were recorded at 10°C/min.

(Fig. 7). The melting behaviour of BPE lamellae must be little influenced by reorganisation processes during heating, since their formation occurred at a low cooling rate (2°C/min). The melting behaviour, therefore, must reflect the melt state of the BPE composition at 118°C. The observed melting behaviour suggests that the most linear methylene sequences present in BPE are incorporated within LPE lamellae. These results confirm that cocrystallisation is a segregation process throughout which the most branched methylene sequences are excluded from the LPE-rich lamellae, a phenomenon, which is also governed by the blend composition.

It has been reported that the degree of cocrystallisation between LPE and BPE is dependent on the cooling rate used from the melt [20]. By cooling the previous samples in acetone at its freezing point, cocrystallisation for a given blend composition is maximised. It is also believed, as stated earlier, that the enhanced crystallisation observed in BPE is a result of the cocrystallisation already present within the high melting LPE lamellae. The composition of the cocrystals can be varied by using different cooling treatments from the melt. 3% LPE blends were cooled from 160°C into water at room temperature. In addition, they were also held at 160°C for 30 min in a thermostatic oil bath and then the heater was switched off, leaving them to cool down to room temperature rather slowly. The samples were then studied by DSC using the same heating and cooling conditions as for the quenched samples.

By slowly cooling the samples from the melt the degree of incorporation of BPE segments within LPE lamellae is lowered. For slow cooled lBPE and sBPE blends, the $T_c$ recorded after heating to 118°C for 30 min and then cooled at 2°C/min are 99.7 and 96.6°C, respectively. These are much lower values than those obtained for quenched lBPE and sBPE blends, having the same LPE content (Fig. 4). When the blends are cooled into water at room temperature (milder conditions) the $T_c$ values obtained are 102.2 and 98.1°C for lBPE and sBPE blends, respectively. These are higher than the previous ones but still slightly lower than those for the cold acetone quenched blends.

When the melting behaviour of the 3%LPE blends cooled in various ways and additionally treated by cooling from 118°C at 2°C/min is assessed, the results confirm previous conclusions. When cocrystallisation is larger such as in the rapidly cooled blends then a lower melting temperature for the BPE component should be expected in those blends quenched from the melt. The low melting temperatures for water cooled and slowly cooled lBPE blends, both cooled later at 2°C/min from 118°C, are 107 and 108.2°C, respectively. Both $T_m$ agree well with the expected trend for a given blend composition. The same behaviour was also found for the sBPE blends, $T_m$ values are 102.2 and 103.8°C for water and slow cooled samples, respectively. As pointed out earlier the 3%LPE blends treated as the others but quenched into acetone showed melting temperatures of 106.8 and 102°C for lBPE and sBPE blends, respectively.

## 4. Conclusions

An enhancement in the crystallisation behaviour of BPE is found when some BPE segments are already included within the high melting LPE-rich crystals. This behaviour is favoured by quenching low LPE content blends from the melt. Enhanced crystallisation behaviour in BPE when blended with LPE responds to the samples previous thermal treatment. Shifts in $T_c$ are not dependent on the cooling rate used from 118°C but on the degree of crystallinity of the BPE.

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