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On morphology and the competition between crystallization and phase separation in polypropylene–polyethylene blends

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Blends of polypropylene (PP) and low density polyethylene (LDPE) have been examined for a series of compositions using differential scanning calorimetry and permanganic etching followed by transmission electron microscopy. Thermal analysis of their melting and recrystallization behaviour suggests two possibilities, either that below 15 wt% PP the blends are fully miscible and that PP only crystallizes after LDPE because of compositional changes in the remaining melt, or else that the PP is separated, but in the form of droplets too small to crystallize at normal temperatures. Microscopic examination of the morphology shows that the latter is the case, but that a fraction of the PP is nevertheless dissolved in the LDPE. © *1998 Kluwer Academic Publishers*

1. Introduction

Blends of polypropylene (PP) and linear polyethylene (PE) are known to behave as effectively immiscible systems [1], and such deviations in crystallization behaviour as do occur can often be attributed to secondary phenomena such as migration of heterogeneous nuclei from one phase into another [2] or in the case of solution blended high molecular materials, entanglements [3]. In contrast, blends with branched PE do give evidence of a certain range of miscibility, especially where PP is the minor component. However, the degree of miscibility is very limited, even with high branch contents normally encountered in practice. Microscopic examination of the morphology has shown that even in blends containing only 1% of either component, phase-separated droplets of the minority component are still visible [4], although such miscibility as is found is greater than in blends of PP and linear PE [5]. However, complete miscibility has been reported for ethylene-hexene statistical copolymers containing 51 mol% hexene, but 33 mol% hexene (much larger than encountered in any commercial very low density PE (VLDPE)), is still not enough to give complete miscibility [6–8].

In blends with typical PE copolymers, however, the most cogent evidence for the presence of a small amount of PP dissolved in a majority PE phase is the growth, albeit very slow, of PP spherulites in the blend consisting of 90% PP and 10% PE [9] at 130 °C, above the melting temperature of the PE. There does, therefore, appear to be some contradiction between the various reported results. Both blend components are crystalline polyolefines whose morphology can be simultaneously examined in a specimen by permanganic etching, as for example when they occur together in so-called propylene–ethylene ‘block’ copolymers [10, 11], which gives an opportunity to examine the resulting blend morphologies at the resolution provided by the transmission electron microscope (TEM). In our own investigation, which resolves this ambiguity, we have solution blended PP with low density PE (LDPE; Alkathene, ICI) in various concentrations. Permanganic etching followed by replication and TEM have been used to reveal the morphology of the blends after various thermal treatments.

2. Experimental

2.1. Materials

The polypropylene used was the grade GWE 26 manufactured by ICI, who kindly provided us with a specimen, of which the molecular number and weight were determined by polystyrene calibration calculated PSCC, Shawbury, England to be $M_n = 36400$, $M_w = 296000$. The polyethylene was the low density material Alkathene Grade WNF 15 from ICI, of medium mlecular weight with a broad distribution.

2.2. Preparation of PP–LDPE blends

The two polymers were solvent blended according to the following procedure. Pellets of PP and LDPE, in weight proportion adding up to 2 g together with 0.24 g butylated hydroxytoluene BHT antioxidant,

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were dissolved in 200 ml boiling xylene heated in a flask in a mantle with a magnetic stirrer. After 2 h, the mixed solution was poured into 400 ml of methanol cooled over dry ice, with vigorous stirring. The precipitated polymer was filtered and washed with isopropanol, then dried under vacuum at 60 °C.

2.3. Specimen preparation

The blends, in the form of a fine powder, were compressed on a Kofler hot bench between a glass microscope slide and a piece of Kapton film to give discs of approximately 0.2 mm thickness. They were melted at the appropriate temperature in a Mettler hot stage, and either cooled in this at a controlled rate or removed while molten and quenched in liquid nitrogen.

2.4. Etching and microscopy

Specimens were etched for 1 h in a reagent consisting of 1% w/v potassium permanganate in an acid mixture made from 1 vol concentrated sulphuric acid and 3 vol dry orthophosphoric acid (prepared from the Merck reagent, min. 85%, by boiling off water to at a boiling point (b.p.) of 260 °C).

Replicas of the etched surface were prepared by a two stage procedure involving taking a first cast with cellulose acetate, shadowing with tantalum–tungsten and coating with carbon, and extracting the final replicas which were then examined by TEM.

3. Results and discussion

3.1. Evidence from differential scanning calorimetry (DSC)

One of the most popular techniques for characterizing polymer blends is DSC. In binary blends of non-crystalline polymers compatibility is often assessed by the observation of single or separate glass transitions, but where one or both components are able to crystallize the interpretation can be more complicated. For the present PP–LDPE blends, Fig. 1a shows cooling curves at 10 K min^{-1} for a series of compositions. A crystallization peak for LDPE is observed between 93 and 89 °C for all compositions except pure PP. Blends containing between 85 and 20 wt % PP with LDPE show a PP crystallization peak between 115 and 110 °C but at 15 wt % PP this peak is hardly discernible, and is not seen at all for 10 wt % PP. On the other hand, as the proportion of PP comes down to 20 wt %, another peak appears at 83–81°C, and is more marked for 15 and 10 wt % PP. This peak is absent from the pure LDPE cooling curve, and so it may be assigned to a different PP crystallization process (note that both processes are present in the 20 wt % PP blend).

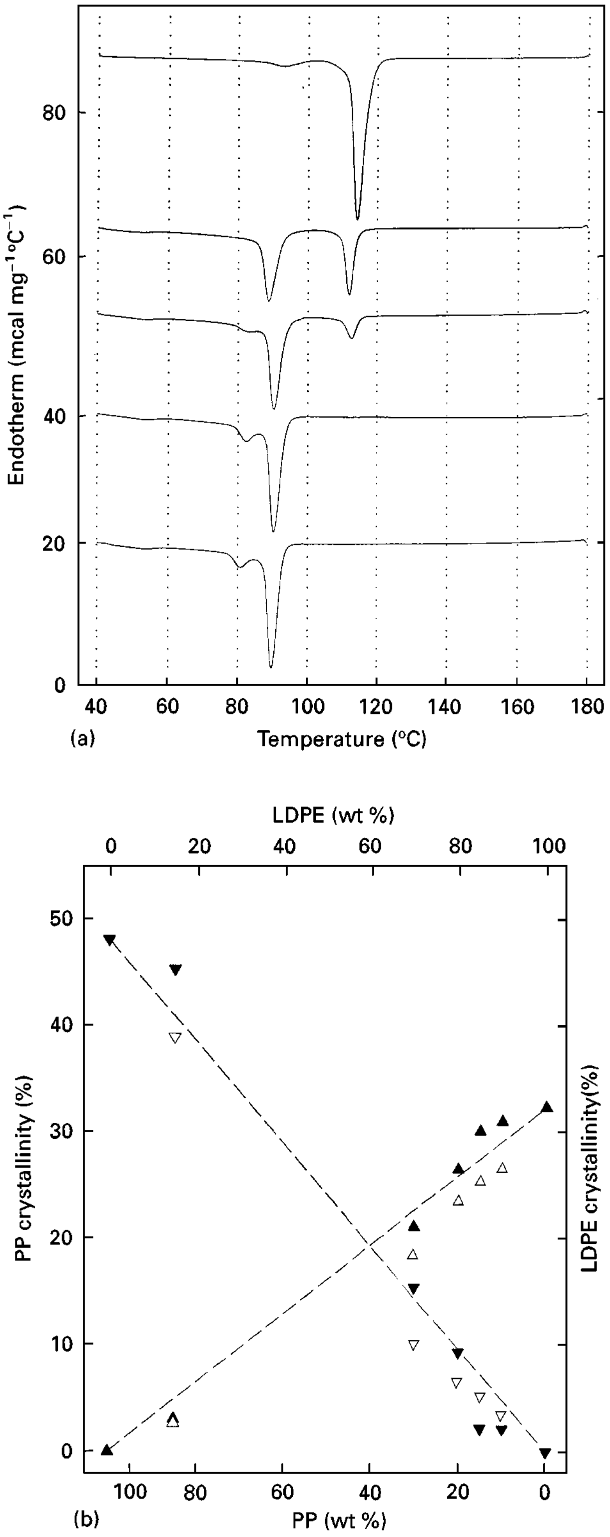

Figure 1 (a) DSC traces of cooling of a series of PP–LDPE blends ((i) 10, (ii) 15, (iii) 20, (iv) 30, and (v) 35 wt % PP, respectively), showing crystallization exotherms; (b) PP and LDPE crystallinites derived from these (▼) PP cooling exotherm, (△) PP remelting endotherm; (▲) LDPE cooling exotherm, (△) LDPE remelting endotherm.

PP and LDPE crystallinities derived from the cooling exotherms (180–40 °C) are plotted in Fig. 1b as percentage relative to total mass of blend. By comparison with the extreme values for the unblended polymers, both PP (▼) and LDPE (▲) show little deviation from a linear addition diagram (dotted lines), except that the value of heat of crystallization of PP at 15 wt % seems anomalously low. However, immediate remelting from 40 °C of the same DSC specimens gives clearly separated endotherms for LDPE at 105 °C and PP at 160–163 °C, whose size displays no such anomaly for either PP (▽) or LDPE (△). This suggests that in this case some PP crystallization may be masked by the much larger LDPE exotherm.

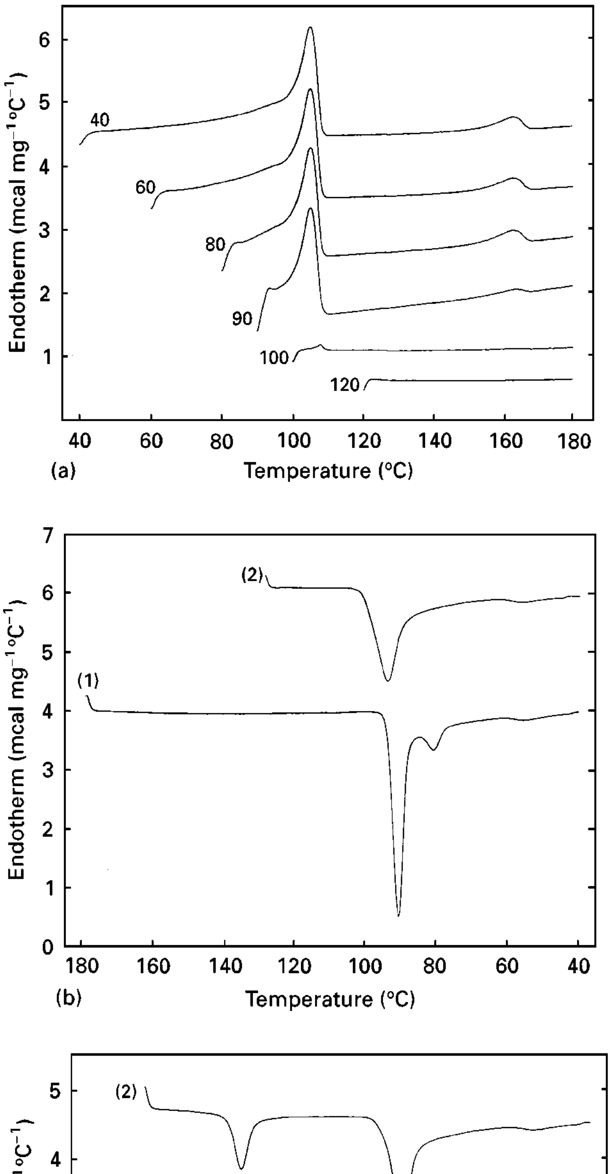

Figure 2 (a) DSC traces of remelting of a 10 wt % PP–90 wt % LDPE blend, from a series of marked temperatures; (b) cooling (1) from melting at 180 °C and (2) after remelting to 130 °C; (c) 20 wt % PP blends showing recrystallization (1) from a melt at 180 °C and (2) after partial melting at 163 °C.

By taking a blend with 10 wt % PP, cooling from 180 °C from a series of intermediate temperatures and immediately rescanning, it is possible to observe in the melting endotherms of Fig. 2a what has crystallized at any given stage [12]. It is apparent from the development of the LDPE melting peaks at around 105 °C that, as suggested above, this component does crystallize mostly between 100 and 90 °C, whereas the crystallization of the PP, which melts between 150 and 160 °C, takes place subsequently between 90 and 80 °C.

It is possible to remelt the LDPE at 130 °C, while leaving any crystallized PP still solid. On cooling from this state the putative PP crystallization peak is no longer seen (Fig. 2b), confirming the interpretation that the lower exotherm also represents PP crystallizing from the liquid state in some form. The LDPE exotherm is broadened and raised slightly in temperature, suggesting that the solid PP is then nucleating the LDPE.

By reheating the 20 wt % PP material to 163 °C, it is possible largely to melt out any PP, whether it crystallized in processes A or B. However, such a low melting temperature leaves a large number of PP nuclei available for an enhanced nucleation process [13, 14] by which it recrystallizes on subsequent cooling as in Fig. 2c at the much higher temperature of 147 °C. Together, the above experiments indicate that PP crystallizes by one of two processes, of which the lower temperature one becomes predominant at lower PP concentrations.

A scenario that immediately suggests itself is where the lower temperature PP crystallization is induced by compositional changes. A system that behaves this way is binary blends of polycaprolactone (PCL) and low M_w polystyrene (PS) [15]; as the PCL crystallizes, it is withdrawn from the blend liquid into the crystalline phase, so increasing the concentration of PS in the liquid, until the PS separates by a liquid–liquid mechanism at the boundaries of the growing PCL spherulites. In our present system the LDPE crystallizes but the PP would also be able to crystallize after being thus released. If such were the mechanism it raises the possibility that compositions with less than 15 wt % PP are fully miscible. Another scenario whereby the two PP crystallization processes are observed is that even as low as 10 wt % PP, there is still some phase separated PP. At concentrations of less than 50 wt % PP, the PP should exist as isolated regions, in the form of droplets of increasingly smaller size as the concentration of PP is reduced. The first (higher temperature) crystallization process takes place in those droplets of PP that contain heterogeneous nuclei, while the lower temperature one might be a homogeneous process. In order to test this rigorously, it would be necessary to perform isothermal droplet crystallization experiments at several temperatures as has been done for polyethylene [16]. However, there is evidence to suggest that in bulk PP. Homogeneous nucleation starts to predominate over heterogeneous nucleation when the temperature falls below 80 °C [17].

3.2. Morphological evidence

In order to determine, as well as possible, the structure of the material in the liquid phase at 180 °C, sheets of blends taken to this temperature and quenched were etched and examined by TEM (Fig. 3). In these specimens the PP droplets are in the smectic phase [18], indicative of very rapid quenching. If this rapid procedure does not allow any significant further phase

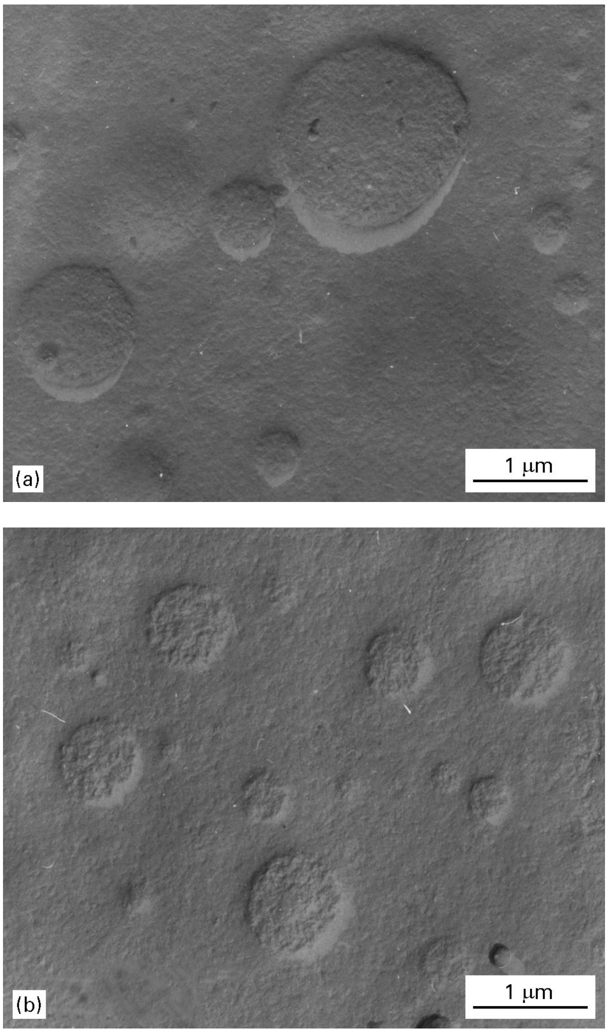

Figure 3 TEM morphologies of quenched blends: (a) 20 wt % PP, and (b) 10 wt % PP.

separation, then the micrographs reveal that, contrary to any impression derived from the DSC, both 20 and 10 wt % PP (Fig. 3a and b, respectively) blends are phase-separated, though the droplets in the 10 wt % PP material are much smaller. If the number of heterogeneous nuclei is limited, then with the finer dispersion of the droplets at 10 wt % PP, the proportion of the total phase separated PP in contact with a heterogenous nucleus would be greatly reduced, and many of the droplets, especially the smaller ones, would be still liquid until sufficiently cooled when the second, possibly homogeneous, process sets in.

Interpretations based on the crystallization behaviour observed by DSC are, therefore, seen not to be sufficient, by themselves, to determine the phase diagram. On the basis of DSC evidence alone, crystallization of material segregated by phase separation, induced by changes in composition of the melt, such as has been seen in PCL–PS [15] and other systems, would seem to be a most likely explanation, but the morphological evidence so far suggests that the crystallization of PP observed in the DSC is actually that of pre-existing supercooled droplets [16]. The position of a crystallization peak so immediately subsequent to the main LDPE exotherm raises the possibility that strains set up as the majority LDPE solidifies initiate the crystallization of the droplets.

Besides the quenched specimens, others cooled in the hot stage under conditions equivalent to the DSC specimens were studied. In order to do a reheating experiment in the hot stage, a slightly different cooling procedure was adopted, namely rapid cooling from 180 to 120 °C followed by cooling at 5 K min^{-1} from 120 to 40 °C (this is because the processor loses control at lower temperatures if the cooling rate is too rapid). Observed at lower magnification as in Fig. 4a, a 10 wt % PP specimen is seen to contain crystallized droplets similar in size to those in the quenched specimen, but no evidence of any other structures. It would be expected that any PP droplets formed by phase separation would accumulate on inter-spherulitic boundaries, and give rise to a concentration of pits there due to the greater etchability of PP, but this is not seen. In a similar specimen at higher magnification (Fig. 4b), there are found PP droplets in a wide range of sizes, around one of which the LDPE spherulite has nucleated, but even the smallest droplets are randomly distributed and not concentrated in the way one would expect for crystallization-induced phase separation. Note that in this specimen the first stage of the replication has also removed the PP out of the larger droplets, so that it appears as black electron-absorbing material in the final replica. It is possible to take such a specimen and carry out a morphological parallel study to the DSC reheating procedure of Fig. 2b. On reheating to 150 °C (Fig. 4b) and rapid quenching as in Fig. 4c, the LDPE is seen to have been melted and transformed to an almost featureless matrix. Within this, there is a scattering of sizes of PP droplets which retain the appearance of their original morphology, although it is probable that a small amount of crystalline reorganization would have occurred during the annealing process. But although the distribution of PP is made much clearer, there is still no evidence of phase separated droplets concentrated at where the LDPE spherulite boundaries were, and so that, if not present in the original melt, they are more likely to have arisen by simple liquid–liquid phase separation as the melt was being cooled to the crystallization temperature.

The morphological evidence therefore qualifies the impressions given by a cursory analysis of the DSC data. On the one hand, the impression of a considerable degree of miscibility has to be toned down, because much of the separated PP hidden from the DSC by its inability to crystallize is, in fact, observed microscopically. On the other hand, both in DSC and under the microscope, there are features that suggest the possibility of the existence of PP dissolved in LDPE that can, under appropriate circumstances, be induced to crystallize. Of the two possible ways in which this could come about, the one already suggested, of phase separation followed by crystallization, must be very limited in extent. There is another mechanism, whereby the dissolved PP might crystallize directly without prior liquid–liquid phase separation, and this has been demonstrated. An example is shown in Fig. 5 where a blend of 10 wt % PP in LDPE has been allowed to crystallize for 16 h at 130 °C, well above the melting point of the LDPE. From droplets of crystallized PP

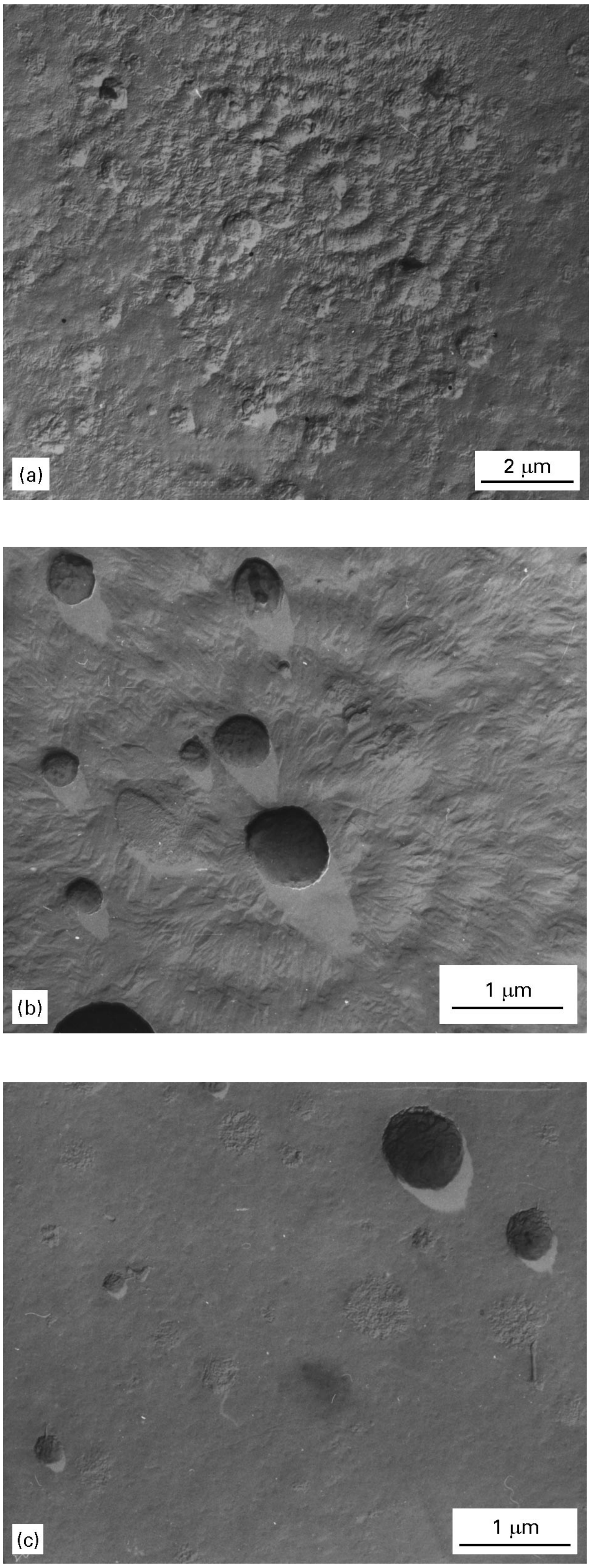

Figure 4 TEM morphologies of a slowly cooled blend with 10 wt % PP at (a) medium magnification, (b) a similar specimen at high magnification, and another (c) after reheating to 150 °C and quenching.

majority phase, lamellae of PP (here seen flat-on, down their *c*-axes) are observed growing out into the LDPE-rich phase. A succeeding paper [19] will discuss how the crystalline morphology of the PP is affected by changes in its supercooling as a minority component.

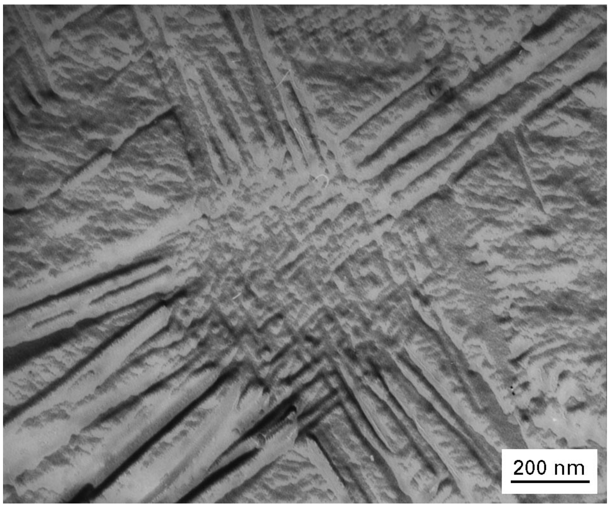

Figure 5 TEM morphology of a blend with 10 wt % PP after crystallization at 130 °C for 16 h.

One way in which it would be possible for PP to dissolve to several per cent in the LDPE, and yet from phase separated droplets at 1 wt % PP, is through fractionation. Under such a system, the higher M_w species of the PP would tend to concentrate in the droplets, while the lower M_w material would be more readily soluble in the LDPE. This we consider to be the most likely scenario.

4. Conclusions

1. Suitable design of DSC experiments can give considerable information about phase separation processes in systems such as PP–LDPE.
2. Nevertheless, there are ambiguities in determining the phase diagram, which can be resolved by additional evidence from morphology.
3. No evidence has been found for crystallization-induced phase separation processes in the system LDPE–PP.
4. A significant degree of solubility of PP in LDPE has been confirmed.
5. Fractionation must be taken into account when interpreting the phase behaviour of polymer blends.

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