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Miscibility and isothermal crystallisation of polypropylene in polyethylene melts

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Abstract

Three blends were made, consisting of 20% polypropylene (PP) homopolymer and 80% high density polyethylene (HDPE), low density polyethylene (LDPE) or linear low density polyethylene (LLDPE). Isothermal crystallisation of PP, at temperatures where the PE remained molten was studied by differential scanning calorimetry (DSC) and hot-stage optical microscopy (HSOM) with polarised light. The resulting semi-crystalline morphology was studied by transmission electron microscopy (TEM). It was observed by HSOM that the PP crystallised as open armed, diffuse spherulites in the PP–LLDPE blend, similar to the crystal morphology observed in miscible blends, while in the PP–LDPE and PP–HDPE blends, PP crystallised in phase separated droplets. The crystallisation rate of PP decreased significantly in the PP–LLDPE blend, but in PP–LDPE, PP–HDPE blends, it was similar to that of the pure PP. The difference in crystallisation rates indicated that PP was much more dispersed in the LLDPE melt, either by dissolution, or greater dispersion of droplets without nuclei, or both. The DSC and HSOM results suggested that the PP was miscible with the LLDPE at elevated temperatures at a PP composition of 20%, while the PP was immiscible with the HDPE and LDPE at these temperatures. However, TEM showed that there was phase separation in the PP–LLDPE (20:80) blend as well, though the droplets were much finer. Nevertheless, the form of spherulitic growth implies a substantial amount of PP dissolved in the molten LLDPE.

Keywords: Polypropylene and polyethylene blends; Miscibility; Crystallisation

1. Introduction

There is more than one aspect in selecting polymers for blending. From a purely scientific viewpoint, the main characteristic is thermodynamic miscibility of the components [1]. Thermodynamically miscible polymers are homogeneous down to the molecular level, demanding a decrease in free energy of mixing (ΔG), $\Delta G = \Delta H - T\Delta S < 0$, which results in a single-phase polymer blend, at specified temperatures and compositions.

From a practical viewpoint, miscibility can be defined as the degree of dispersion of phases. This means that the systems may or may not appear to be homogeneous, according to the type of test method used. Different methods each measure a certain range of scale. For example, optical microscopy has the potential of resolving details down to 1 μm, while transmission electron microscopy (TEM) can distinguish phase separations down to 1 nm in size. Differential scanning calorimetry (DSC), mechanical testing and X-ray scattering permit the assignment of parameters such as interatomic ordering and chain packing, but these are not real space methods and so can be model dependent.

The preparation of scanning electron microscopy (SEM) and TEM specimens can be time consuming and often requires experience. In particular, since polymer specimens are beam sensitive, TEM requires either staining of sections or etching and surface replication. The techniques for studying polymers by SEM and TEM are still developing and X-ray instruments do not give information on the scale of phase separation in incompatible blends. DSC and hot-stage optical microscopy (HSOM) have been widely used, since they are fast and readily available. However, the results from one or two methods cannot give a full picture, so a combination of methods generally provides better insight into the phase morphology of polymers.

The miscibility of polypropylene (PP) and polyethylene blends has been studied extensively. However, there are debates on their miscibility. Phase separation has been detected in PP and linear polyethylene (high density polyethylene, HDPE) melts using light microscopy [2], SEM [3], neutron scattering [4,5] and TEM [6]. However, recently

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Table 1
Characteristics of polymers

Polymer	Comonomer	MFI[a] (g (10 min)$^{-1}$)	Manufacturer
PP	–	28	ICI
LLDPE	5 mol% hexene	1	ICI
LDPE	–	20	Kemcor
HDPE	–	22	Mobil

[a] According to manufacturers, refer to ASTM D1238: 2.16 kg load at 230°C for PP and 190°C for PE.

Blom et al. [7] reported that HDPE was able to penetrate the PP phase sufficiently at low HDPE contents to reduce the number and size of high segment-density regions, delaying the nucleation and subsequent crystallisation of the PP phase. They claimed there was a certain degree of interaction between PP and HDPE at HDPE concentration below 20%.

PP has also been found to be of limited miscibility with highly branched polyethylene (low density polyethylene, LDPE). Phase separation was observed by TEM, but with evidence of a small portion of PP being dissolved in the LDPE [8]. Another study on PP–LDPE blends has shown that a small addition of LDPE (10%) caused the depression of spherulite growth rate of PP and increased the chain folding energy in PP crystallisation [9]. This was interpreted as partial miscibility of PP and LDPE in the melt.

In the case of PP and linear low density polyethylene (LLDPE) blends, both polymers are linear chain hydrocarbons with no long chain branching, providing structural similarity. The compatibility in tensile and impact properties for these blends has been reported by various authors [10–17]. Dumoulin et al. [10–13] studied the blends in the solid state by DSC and dynamic mechanical thermal analysis (DMTA), and investigated mechanical properties as well as melt rheology. These results indicated that the blends containing a small proportion of LLDPE (below 5%) were miscible. On the contrary, Hill et al. [18] studied PP–LLDPE blends by TEM on samples quenched from 190°C and found that there was liquid–liquid phase separation in PP and LLDPE blends at 190°C between PP composition of 1 and 99%.

From DSC and HSOM studies, we previously reported that PP was miscible with LLDPE and immiscible with LDPE and HDPE [19]. Whereas most techniques only gave indirect evidence of dissolved PP, HSOM allowed the observation of developing structures, starting from an initially crystallised droplet and in which neighbouring droplets were observed to crystallise implying that crystallisation was somehow bridging between the droplets [19]. This was confirmed more recently, when Dong et al. [20] studied PP–LLDPE blends by TEM and observed PP lamellae in the PE-rich phase, indicating that a fraction of PP dissolved in the LLDPE even though phase separation was obvious. In order to see whether these blends are miscible or not by another method, PP–LLDPE, PP–LDPE, PP–HDPE blends were investigated by TEM as well as DSC and HSOM in this work. The miscibility of the PP and PE will be discussed.

2. Materials and methods

2.1. Materials and blend preparation

An isotactic PP was blended with an LLDPE, an LDPE and an HDPE. The characteristics of the polymers are listed in Table 1. The blends were mixed in an Axon BX-12 single screw extruder (Axon Australia Pty., Australia) with a screw diameter 12.5 mm and a length to diameter ratio of 26:1, operating at a screw speed of 80 rpm. The temperatures for feeding zone, melting zone, compression zone and die were 170, 200, 200 and 180°C, respectively. The blends were extruded with a strand die and pelletised prior to sampling. All the blends were made with mass ratio of PP:PE = 20:80.

2.2. Differential scanning calorimetry

A Perkin–Elmer DSC-7 with nitrogen purge was used to analyse the thermal properties and overall crystallisation kinetics of the PP. Samples around 5 mg were accurately weighed and sealed in aluminium pans. Crystallisation and melting temperature measurements were performed by melting samples at 200°C for 2 min followed by cooling to 40°C and subsequent reheating to 200°C. A program rate of 10°C min^{-1} was applied.

For isothermal crystallisation, samples were melted at 200°C for 5 min and quenched to an isothermal crystallisation temperature. The selected isothermal crystallisation temperatures were between 119 and 130°C, where PP crystallised from PE melts. Samples were kept at these temperatures for the necessary time for complete crystallisation. The heat evolved during isothermal crystallisation (ΔH_c) was recorded as a function of time. The crystalline conversion (X_t) at constant temperature is related to the generated heat ratio at time t and at infinite time t_∞ according to the equation:

$$X_t = \frac{Q_t}{Q_\infty} = \frac{\int_0^t (\mathrm{d}H/\mathrm{d}t)}{\int_0^\infty (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t} \tag{1}$$

in which dH/dt is the rate of heat evolution.

The isothermal crystallisation is analysed using the Avrami equation [21–23]:

$$\ln[-\ln(1 - X(t,T))] = \ln k(T) + n \ln t \tag{2}$$

in which $X(t,T)$ is the volume fraction of crystalline material at time t and isothermal crystallisation temperature T, n, the Avrami exponent which is related to the nucleation type and crystal growth geometry, the crystallisation rate coefficient, k, a parameter of crystallisation growth rate

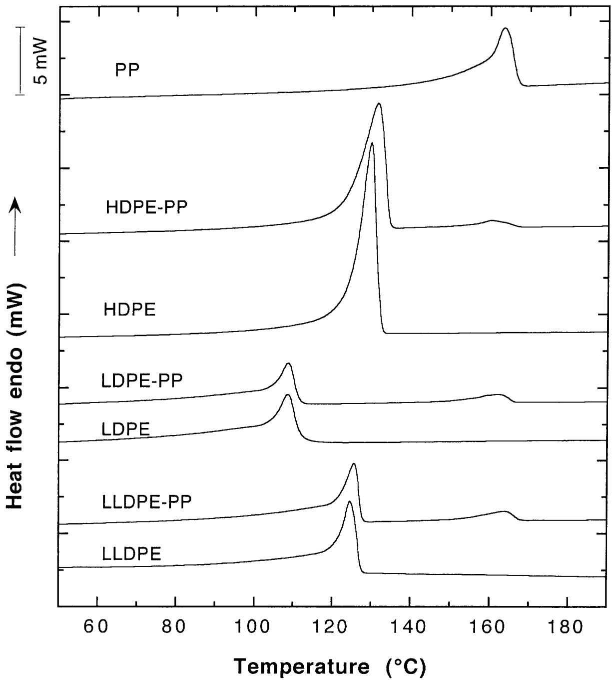

Fig. 1. DSC melting curves of pure polymers and the blends.

and related to the nucleation type, crystal growth geometry and crystallisation temperature.

From a correlation of $\ln[-\ln(1-X)]$ versus $\ln t$, the Avrami exponent (slope of the straight line) and the crystallisation rate coefficient (intersection with the y-axis) were calculated. Based on these two values, the crystallisation half-time, which is a measure of crystallisation rate, can be obtained from the equation:

$$t_{1/2} = \frac{\ln 2}{k^{1/n}} \tag{3}$$

2.3. Hot-stage optical microscopy

A Nikon Labophot II microscope with polarised light equipped with a Mettler FP90 hot stage was used to study the morphology and crystallisation of the blends and the PP. Images were captured using a Sony camera and video monitor connected to a Macintosh computer with IPLab image analysis software. Specimens of 20 μm thickness were prepared by a microtome. The films were heated between glass slides and cover slips in the hot stage to 200°C for 5 min prior to rapid cooling to the isothermal crystallisation temperature. The selected isothermal crystallisation temperatures were between 124 and 130°C, at which temperatures, PP crystallised while PE remained molten. After a time long enough for PP to crystallise completely (typically 6 h and longer), the glass slides were taken out of the hot stage and the blends were cooled naturally whereupon the PE crystallised.

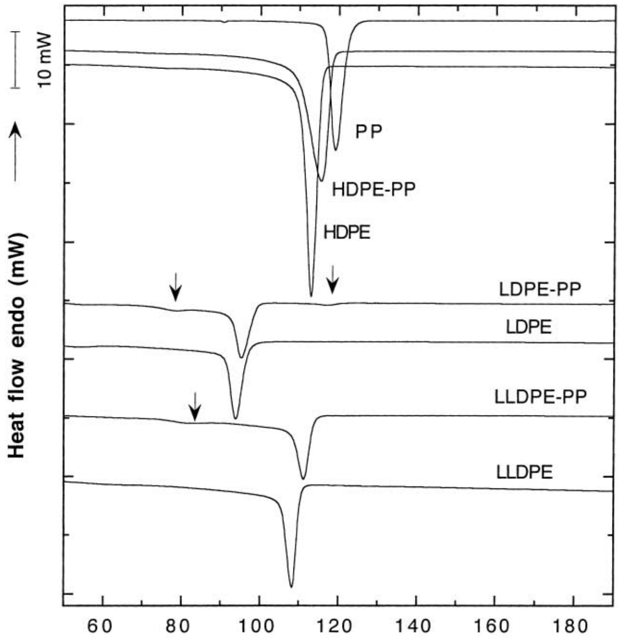

Fig. 2. DSC crystallisation curves of pure polymers and their blends.

2.4. Etching and transmission electron microscopy

Specimens were cooled in a Mettler Toledo FP82HT hot stage with FP90 controller, from 200 to 40°C at 10°C min^{-1}. They were then etched in a 1% solution of potassium permanganate in a 10:4:1 mixture of concentrated sulphuric acid — phosphoric acid (85%) — water [24]. Replicas of the etched surface were prepared by a two-stage procedure using a cellulose acetate cast on which tantalum–tungsten shadow and carbon coating were applied. The final replicas were extracted and then examined by TEM.

3. Results and discussion

3.1. Melting and crystallisation

Fig. 1 shows DSC melting curves of pure polymers and blends. The blends displayed two single melting peaks at temperatures corresponding to the pure polymers, indicating separate melting in all blends.

Interpretation of the cooling exotherms in Fig. 2 is complicated by two facts. Firstly that in a normal cooling regime, the main crystallisation temperature of PP is close to that of HDPE so that the two peaks overlap; secondly, PP gives rise also to some lower temperature crystallisation peaks. Accordingly, the PP–HDPE (20:80) blend showed only a single peak between the crystallisation temperatures of PP and HDPE, which was broader compared with the peaks of pure PP and HDPE. A new exothermic peak appeared in the PP–LDPE (20:80) blend at around 80°C in addition to the normal crystallisation peaks of PP and LDPE. Similarly, the peak at the normal crystallisation

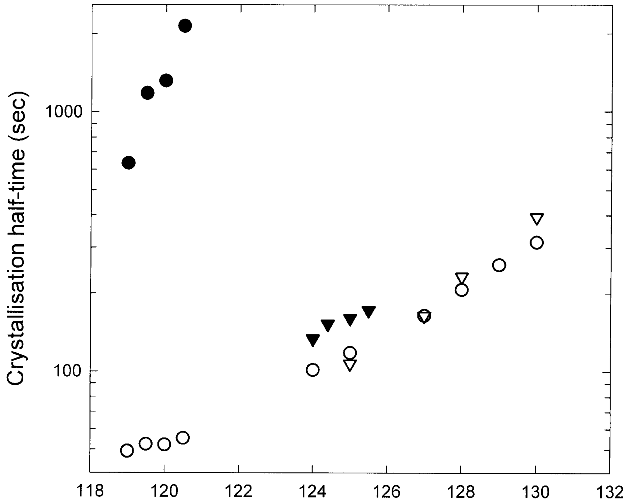

Fig. 3. Crystallisation half-time versus crystallisation temperature for PP and blends. PP (○), PP–HDPE (▼), PP–LDPE (▽), PP–LLDPE (●).

temperature of PP disappeared in the PP–LLDPE blend, while again a new peak appeared at 88°C, which is in the same temperature range as the additional peak in the PP–LDPE blend.

The additional lower-melting peaks in PP–LDPE and PP–LLDPE blends, which have been identified as the crystallisation of PP [8] and further confirmed in by our experiment [25], admit of two possible interpretations. The first is that the PP was able to dissolve in the LLDPE in the molten state. On constant cooling to the temperature range of PP crystallisation, the concentration of PP in the PE-rich matrix is too low to form nuclei, and hence the crystallisation of this PP is delayed. Only immediately upon crystallisation of LLDPE, the concentration of PP in the melt increases to the point where PP is able to crystallise at a lower temperature. Furthermore, the crystalline LLDPE could act as nuclei for the crystallisation of PP. The additional lower temperature peaks in the PP–LDPE blend could be explained in the same way, with this dissolved fraction of PP crystallising after LDPE as in the PP–LLDPE (20:80) blend, while the undissolved fraction in the PP–LDPE blend was observed to crystallise at the normal higher temperature.

A second interpretation for this lower melting peak was given by Dong et al. [8], where its origin was attributed to the smaller droplets of dispersed PP, which did not contain heterogeneous nuclei so as to crystallise at the usual temperature along with the LDPE used here. Instead, these PP droplets required a lower temperature, either for homogeneous nucleation or as a result of stress imposed on the droplet by the complete crystallisation of the LDPE. In the present work, from the size of the spherulites in the unblended PP, it appears that roughly 10^6 heterogeneous nuclei per mm^3 are present, i.e. one per $(10\ \mu m)^3$. If the droplets are of this size or larger, then on average most droplets will contain at least one nucleus, and would crystallise at the normal temperature, along with the LDPE or LLDPE. However, if the diameter of the droplets were halved, then on average only one in eight droplets would be nucleated, and the majority of the material would crystallise at lower temperature by the proposed homogeneous nucleation mechanism. However, it was also observed that the apparent volume of the dispersed PP was lower than expected, so it is probable that in their system also some of the PP was dissolved in the LDPE. However, the PP was in too low concentration and not mobile enough to observe the kind of segregation at the spherulitic growth front observed in some other blends [26]. These mechanisms are not mutually exclusive, but a choice between them can be made by referring to the results of Dong et al. [8] where it was found that as the concentration of PP increased from 10 to 30%, while the higher crystallisation peak arising from heterogeneous nucleation increased, the lower peak decreased almost to vanishing point. The concentration of PP in the PE phase would not be expected to decrease in the same way, so in this case, the droplet size effect appears to be operating. From the dimensions of PP droplets in three polyethylenes and the crystallisation curves, it seems that heterogeneous nucleation dominated in the PP–HDPE and PP–LDPE blends and homogeneous in the PP–LLDPE blend.

3.2. Crystallisation half-time

Fig. 3 shows the crystallisation half-times of PP for PP and its blends. The crystallisation half-time of PP in the PP–HDPE and PP–LDPE blends were of the same magnitude as that of pure PP. However, the half-time of PP in the PP–LLDPE blend was more than 10 times greater than that for pure PP at the same crystallisation temperature. With an increase in crystallisation temperature, the difference between half-times in the PP–LLDPE blend and in pure PP increased.

The interpretation of this difference in half-times in the three blends depends to some extent on which of the previous two interpretations of the lower melting DSC peak is favoured. If the lower temperature crystallisation exotherm arises from dissolved PP, then the variation would be caused by different miscibility levels between PP and LDPE, HDPE and LLDPE. However, if the second interpretation were dominant, then droplet size would be important. If the PP is found in fewer but larger droplets, most of these would contain a nucleus active at any given temperature, while if the droplets are finely dispersed, nucleation would be delayed, because some droplets may not contain nuclei.

3.3. Isothermal crystallisation of PP in the PE melts

Optical microscopy can give further evidence, which may help to decide which of these two mechanisms is operative. Fig. 4 shows typical PP spherulites, with variations from the

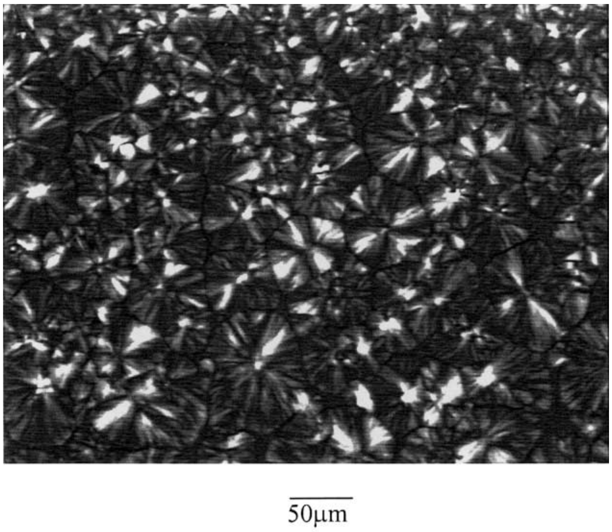

Fig. 4. HSOM image of PP spherulites after isothermal crystallisation at 130°C for 20 min, magnification ×100.

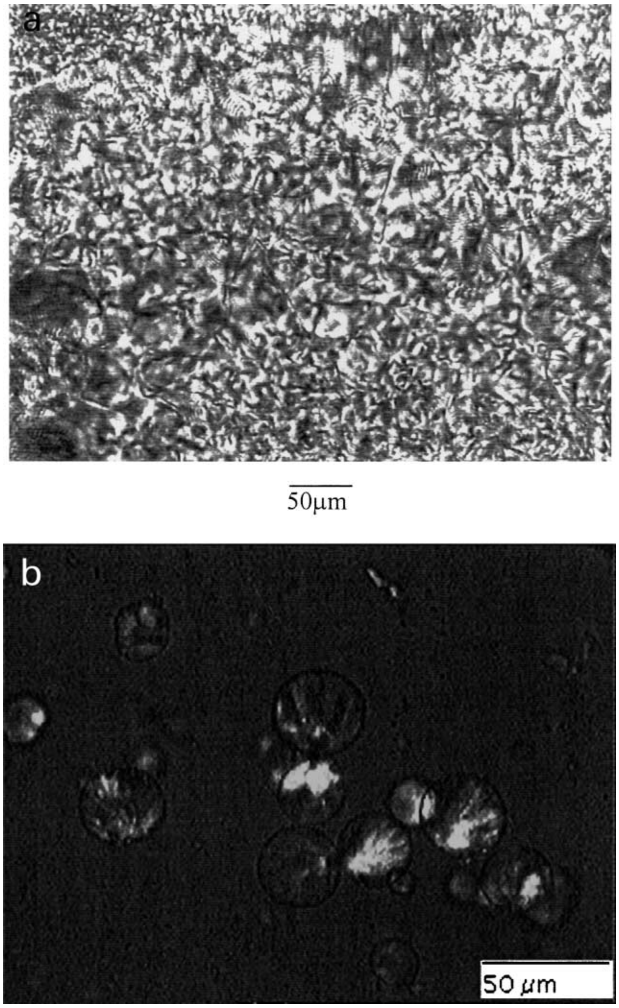

Fig. 5. HSOM images of (a) HDPE; (b) PP–HDPE after isothermal crystallisation at 130°C for 30 min showing PP droplets, magnification ×100.

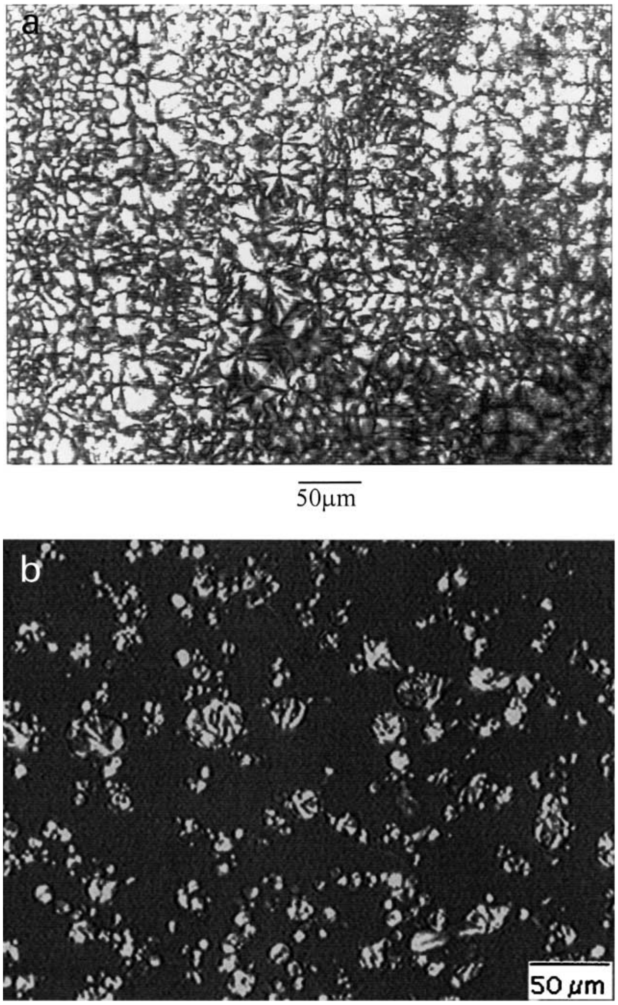

Fig. 6. HSOM images of (a) LDPE; (b) PP–LDPE (20:80) after isothermal crystallisation at 126°C for 21 min showing PP droplets with different sizes, magnification ×100.

Maltese cross-pattern imposed by their mixed birefringence [27] and the orientation of their quadrite centres [28]. Turning to the blends, it is necessary to keep the PE molten in order to observe the PP structure, since on cooling the PE will develop its own morphology, as in Fig. 5a where the HDPE has formed banded spherulites. In the PP–HDPE blend, PP appeared as large droplets dispersed in the HDPE melt which under the given conditions appear to have all crystallised as shown in Fig. 5b, so that inside the droplets, the spherulite structure can easily be seen. Fig. 6a shows how the LDPE crystallises in the form of much smaller spherulites, while Fig. 6b displays PP droplets in the PP–LDPE blend, similar to those in the PP–HDPE blend. However, the size of PP droplets in PP–LDPE blend was smaller than that in the PP–HDPE blend, indicating more dispersed distribution of PP phase in the LDPE, which may be a consequence of the better compatibility between LDPE and PP.

Fig. 7a shows LLDPE spherulites similar to those of HDPE: when large enough these display a banded

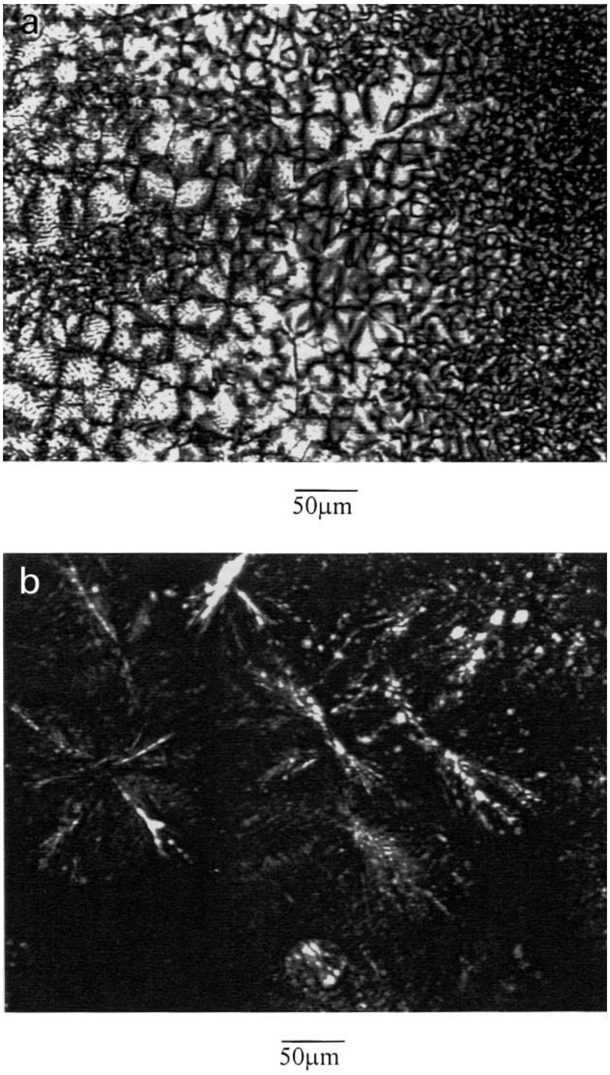

Fig. 7. HSOM images of (a) LLDPE; (b) PP–LLDPE (20:80) after isothermal crystallisation at 126°C for 190 min showing diffuse PP spherulites and small droplets of PP, magnification × 100.

morphology, which is best seen at the left of the picture. In the PP–LLDPE blend, PP appears to be open armed, diffuse spherulites growing in the molten LLDPE at 126°C, although small droplets around 1 μm in size were also observable (Fig. 7b). These are in fact open clusters of droplets connected by bridging lamellae as reported under TEM [20], and they have an appearance of bunches of small birefringent grapes. These are different from the open armed, diffuse spherulites observed in highly diluted miscible or partially miscible blends such as isotactic PP-atactic PP blend [29], ethylene–propylene rubber (EPR) [30], PP (10–20%)–LLDPE [25] blends. However, the development of bridging lamellae has shown that PP dissolves to a certain extent in the LLDPE at the crystallisation temperatures. This growth is only occurring in an isolated part of the specimen, which would account for the much slower crystallisation in the isothermal DSC experiments.

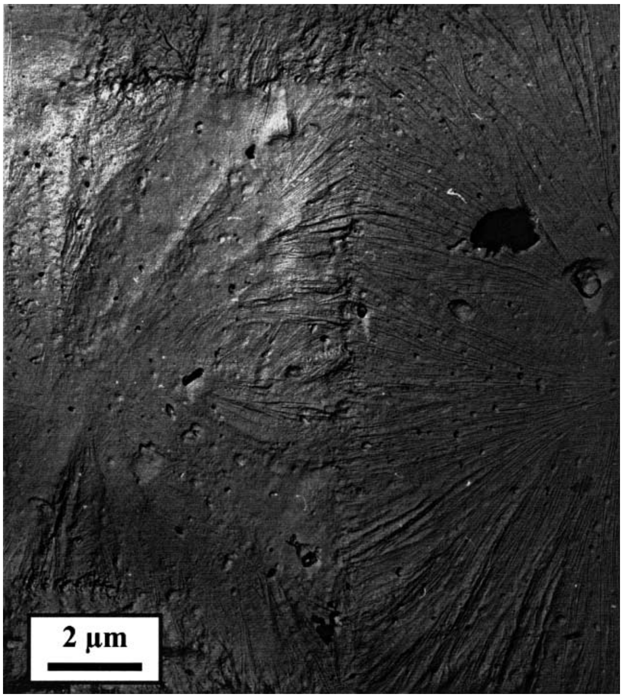

Fig. 8. TEM of PP showing PP lamellar structure with spherulites.

In the PP–HDPE blend, PP and PE were mostly immiscible, not only in the thermodynamic sense but also practically, with the PP forming large phase separated droplets in which a nucleus might be available for crystallisation and might be available at the start of the isothermal time. In these droplets, the concentration of PP was close to 100%, and the crystallisation mechanism of PP in droplets was like that in pure PP. Similar considerations apply to the PP–LDPE blends. On the contrary, in the PP–LLDPE blend, a significant quantity of PP was dissolved in the LLDPE, while the phase separated PP was much more finely dispersed. The LLDPE has much smaller MFI than that of HDPE and LDPE, and if rheology were the deciding factor, the opposite effect should be seen, and the PP should be better dispersed in the HDPE and LDPE. In the system as it is, two effects may be combining to reduce the rate of PP crystallisation. One is that the amount of phase separated PP will be less than the original PP concentration of 20%. The growth rate of PP inside the PE matrix will be significantly diminished by the LLDPE dilution. The other is that very few of the tiny PP droplets will be nucleated. It might be thought that PP should be somewhat soluble in the LDPE also, however, the larger droplets would all have crystallised and might be consuming the remaining PP dissolved in the matrix, preventing bridging growth.

The remaining figures show TEM images of etched specimens: these were all crystallised by cooling in the Mettler hot stage and so correspond to the DSC treatments of Fig. 2 rather than the HSOM specimens. Fig. 8 shows a TEM image of PP spherulites and lamellae. One characteristic of PP is that the lamellar structure grows more distinct,

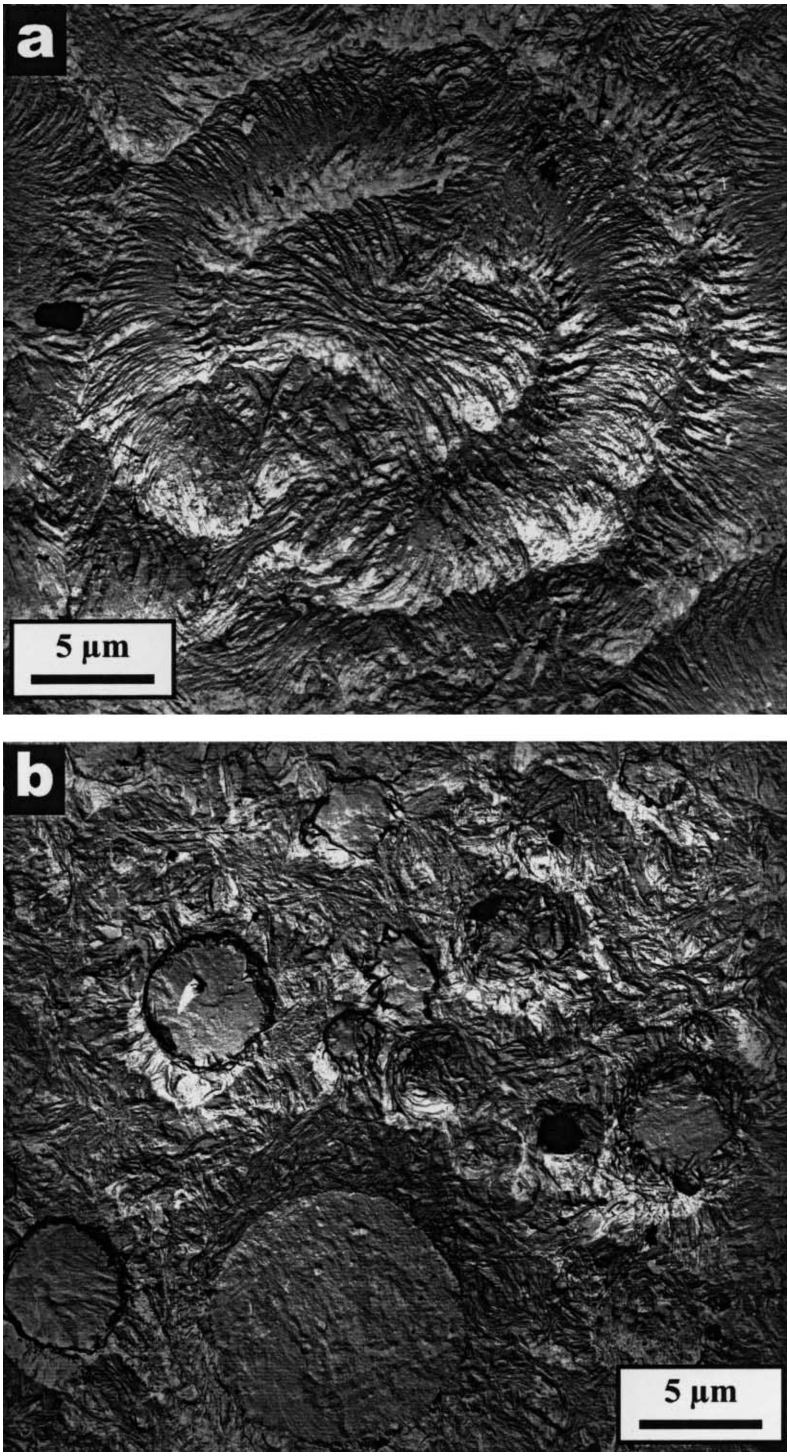

Fig. 9. TEM of (a) HDPE; (b) PP–HDPE (20:80) blend showing dispersed PP droplets.

the further from the centre of the spherulite; one would generally expect to see the most pronounced lamellar morphology in larger droplets where there is sufficient room for this kind of development. The straight line between spherulites indicated that nucleation occurred at the same time and the nucleation is heterogeneous. This also gives an idea of the average spherulite radius, only a few microns, so it is quite reasonable to expect that the large PP droplets which are formed in the blends with, especially HDPE as in Fig. 5b, but also LDPE as in Fig. 6b, would almost all be heterogeneously nucleated. HDPE spherulites displayed a banded structure under TEM (Fig. 9a) as well as under HSOM (Fig. 5a). Fig. 9b shows PP droplets in the HDPE matrix, but banded structure is not observed, which

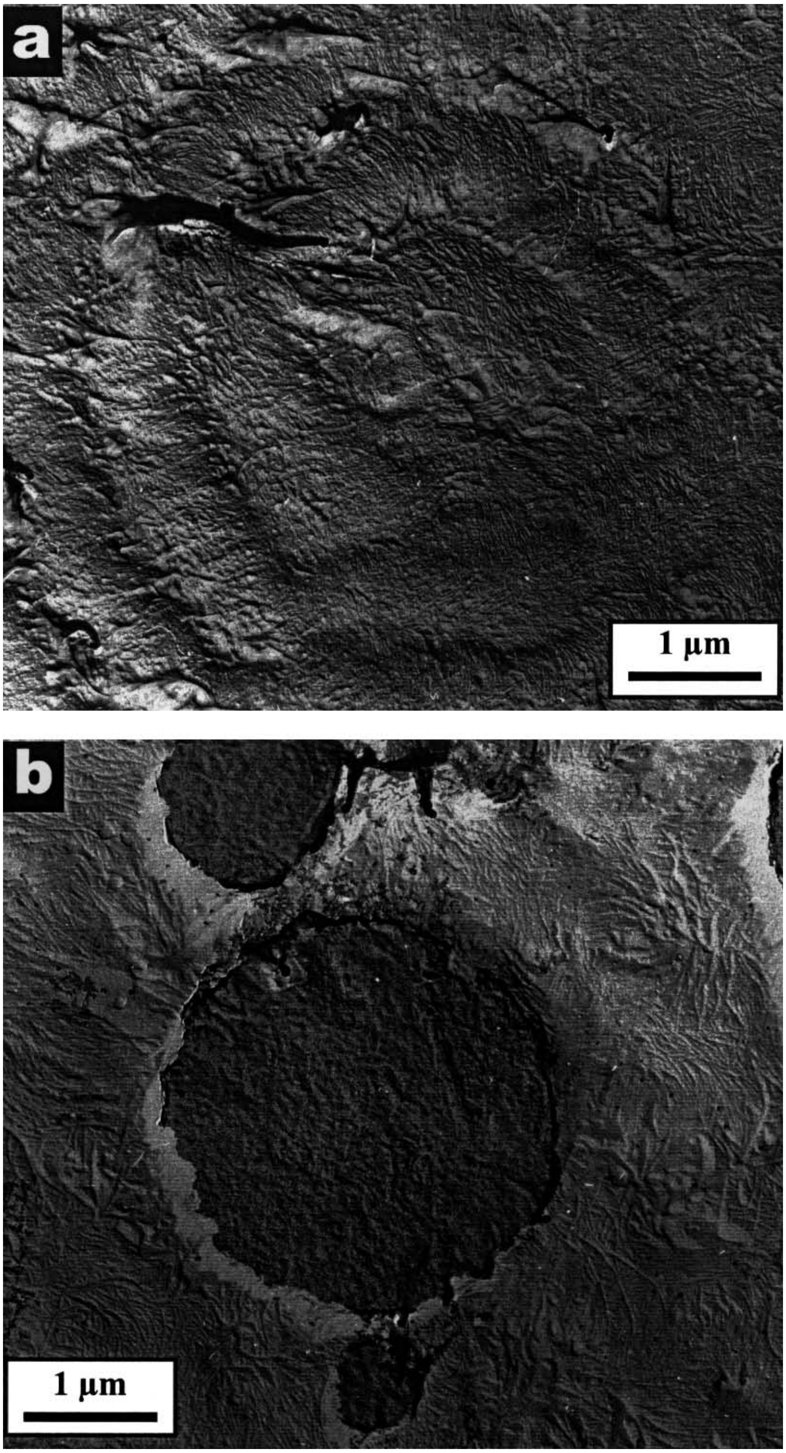

Fig. 10. TEM of (a) LDPE; (b) PP–LDPE (20:80) blend showing dispersed PP droplets.

suggests that PE has nucleated on the surface of the PP droplets. The largest droplet at the bottom of the picture shows pronounced lamellar morphology, as does the one to its left: these must have been nucleated by a heterogeneous process. However, the most distinct feature is that most droplets appear to be surrounded by a dark ‘collar’. This is a replication artefact, indicating a discontinuity between the two phases, which the replicating material has penetrated, implying that the bond between the PP and HDPE is mechanically weak and easily penetrated by the etchant. On its own, LDPE also forms banded spherulites (Fig. 10a) although the pitch of the banding is too fine for easy observation under the optical microscope. In the blend (Fig. 10b), there is less evidence of nucleation of PE on the PP surface. The lamellar texture of the LDPE is, as expected, much finer than that of the HDPE.

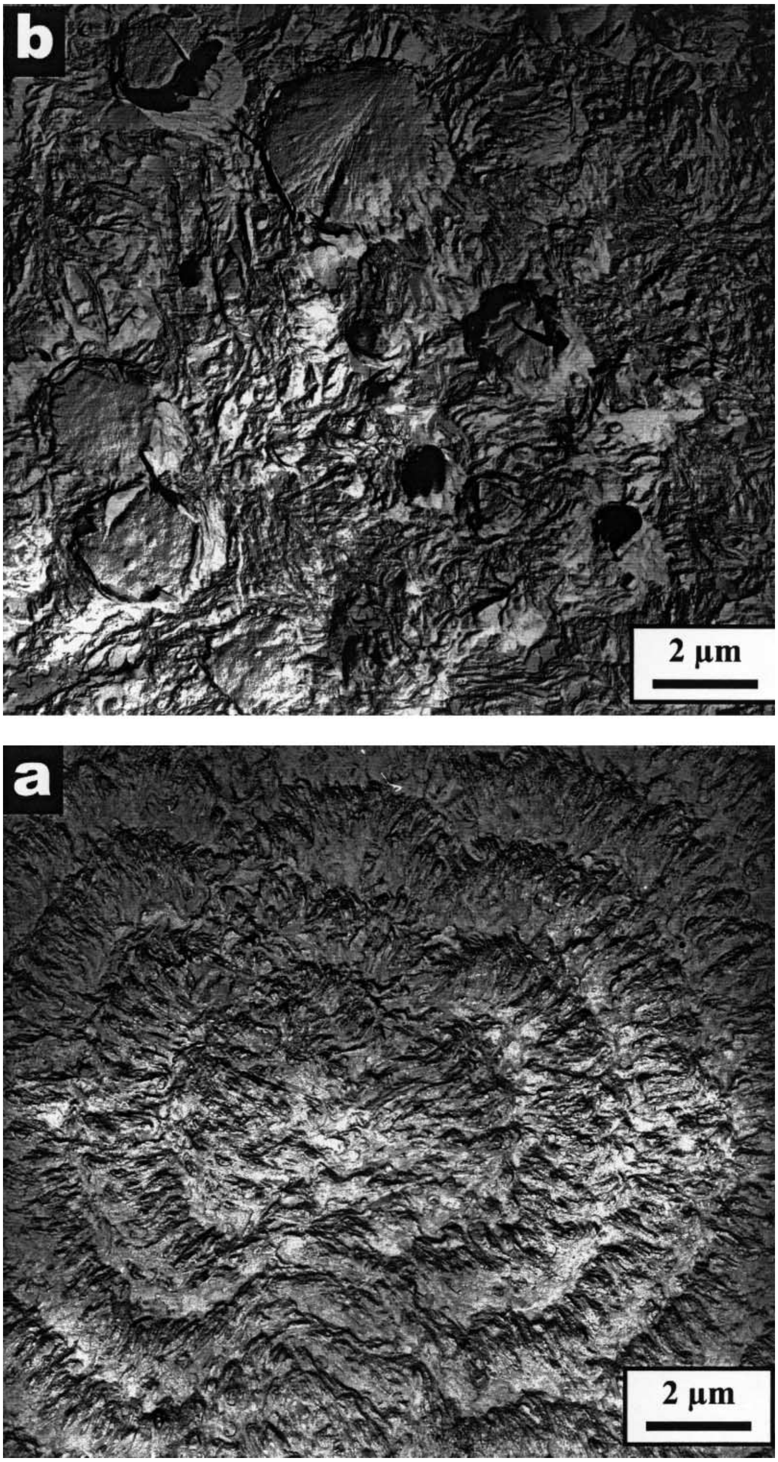

Fig. 11. TEM of (a) LLDPE; (b) PP–LLDPE (20:80) blend showing dispersed PP droplets and PP crystals growing in the LLDPE phase.

Fig. 11a shows LLDPE spherulites, also banded on a scale intermediate between that of the HDPE and LDPE spherulites. Lamellar texture is also intermediate in scale. In a PP–LLDPE blend (Fig. 11b), PP also appeared as droplets in the LLDPE matrix. The size of droplets is finer, but here again, the phase boundary appears rough. On the lower right of the larger droplet located in the upper middle of Fig. 11b, there is an appearance that PP lamellae seem to have grown out from the droplet into the LLDPE phase. This would be an indication of a significant quantity of PP dissolved in the PE matrix. However, one would not expect to see this to any great extent, since these are rapidly cooled specimens, and fringes of PP lamellae forming round droplets generally take half an hour or more to develop [20]. There is no suggestion of large extended PP spherulitic developments as in Fig. 7b, because these samples were fast cooled and extended structure would take several hours to grow. This appearance here is not typical, and may simply result from the etchant penetrating the gap between the droplet and matrix and bringing the PP lamellae into relief.

4. Conclusions

It was found by DSC and HSOM that PP was miscible with LLDPE and immiscible with HDPE and LDPE. However, a TEM study showed phase separation occurred in the PP–LLDPE (20:80) blend as well and that there was some solubility of PP in LDPE. Nevertheless, most of the PP dissolved in the LLDPE at crystallisation temperatures. These solubilities are temperature dependent. The methods being used require that the temperature be restricted to the range where PP can crystallise, while high enough that the PE remains liquid. DSC and HSOM are easy and quick methods to study crystallisation of PP and PE. Incorporation of this TEM study with DSC and HSOM has provided a further depth of understanding on morphology and crystallisation of the blends.

References

[1] Utracki LA. Polymer alloys and blends, Munich: Hanser, 1989. p. 1–47.
[2] Blackadder DA, Richardson MJ, Savill NG. Macromol Chem 1981;182:271.
[3] Noel III OF, Carley JF. Polym Eng Sci 1984;24:488.
[4] Wignall GD, Child HR, Samuels RJ. Polymer 1982;23:957.
[5] Lohse DJ. Polym Eng Sci 1986;26:1500.
[6] Montes P, Rafiq YA, Hill MJ. Polymer 1998;39:6669.
[7] Blom HP, Teh JW, Bremner T, Rudin A. Polymer 1998;39:4011.
[8] Dong L, Olley RH, Bassett DC. J Mater Sci 1998;33:4043.
[9] Avalos F, Lopez-Manchado MA, Arroyo M. Polymer 1996;37:5681.
[10] Dumoulin MM, Farha C, Utracki LA. Polym Eng Sci 1984;24:1319.
[11] Dumoulin MM, Carreau PJ. Polym Eng Sci 1987;27:1627–33.
[12] Dumoulin MM, Utracki LA, Carreau PJ. In: Utracki LA, editor. Two phase polymer systems, Munich: Hanser, 1991. p. 185–212.
[13] Utracki LA. ACS Symp Ser 1989;395:153.
[14] Yeh PL, Birley AW. Plast Rubber Process Appl 1985;5:249–52.
[15] Flaris V, Stachurski ZH. Polym Int 1992;27:267.
[16] Flaris V, Stachurski ZH. J Appl Polym Sci 1992;45:1789.
[17] Muller AJ, Latorre C, Mendez G, Rotino J, Rojas JL. ANTEC 1994:2418.
[18] Hill MJ, Oiarzabal L, Higgins JS. Polymer 1994;35:3332.
[19] Shanks RA, Li J, Long Y. Polymer 2000;41:2133.
[20] Dong L, Bassett DC, Olley RH. J Macromol Sci, Phys 1998;B37:527.
[21] Avrami MJ. Chem Phys 1939;7:1130.
[22] Avrami MJ. Chem Phys 1940;8:212.
[23] Avrami MJ. Chem Phys 1941;9:177.
[24] Shahin MM, Olley RH, Blissett MJ. J Polym Sci, Phys 1999;37:2279.
[25] Li J, Shanks RA, Long Y. J Appl Polym Sci (in press).
[26] Shabana HM, Olley RH, Bassett DC, Jungnickel B-J. Polymer 2000;41:5513.
[27] Varga J. J Mater Sci 1992;27:2557.
[28] Olley RH, Bassett DC. Polymer 1989;30:399.
[29] Keith HD, Padden FJ. J Appl Phys 1964;35:1270.
[30] Lustiger A, Marzinsky CN, Muller RR. J Polym Sci, Phys 1998;36:2047.