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Miscibility and crystallisation of polypropylene–linear low density polyethylene blends

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Abstract

Crystallisation, morphology and miscibility of polypropylene (PP) and linear low density polyethylene (LLDPE) blends were studied by polarised optical microscopy connected to a computer with digital image processing and analysis. In particular the effects of LLDPE and its melt flow index (MFI) on the kinetics of PP crystallisation was investigated through establishing a relationship between nucleation density, spherulitic growth rate and overall crystallisation growth rate. All the blends contained 20% by mass of PP and the LLDPEs used were of the similar grades. The crystallisation of PP was controlled to occur isothermally at temperatures where LLDPEs were in molten state. It was found that, the PP crystallised as open-armed diffuse spherulites, similar to those observed in the miscible blends, suggesting that the PP and the LLDPE may be miscible at some temperatures. The nuclei density, spherulite growth rate and overall crystallisation rate of PP decreased significantly in the blends, indicating that the LLDPE retarded crystallisation of PP, possibly due to various reasons such as the dilution of PP by LLDPE (LLDPE as a solvent in molten state), hindrance of viscous LLDPE to the PP crystallisation front, and decreased supercooling degree because of the miscibility between the PP and LLDPE. This provided further evidence that the PP and the LLDPE could be miscible at crystallisation temperatures selected.

In addition, the spherulite growth rate of PP decreased with a decrease in MFI of LLDPE while the MFI of LLDPE had negligible effect on the nuclei density, showing that the diffusion process controlled overall crystallisation rate when the nucleation density were similar for blends with various MFI. This further confirmed that PP and LLDPE were miscible at elevated temperatures since the more viscous LLDPE (lower MFI) reduced the crystallisation rate of PP at a greater degree.

Keywords: Polypropylene–polyethylene blends; Spherulite growth; Miscibility

1. Introduction

Crystallisation of a homopolymer is controlled by nucleation, spherulite growth rate, the degree of supercooling and the rate of cooling. The crystallisation behaviour of a blend is more complex due to the existence of a second crystallising or non-crystallising component [1].

The crystallisation of polypropylene (PP) and polyethylene (PE) blends has been studied extensively. In a differential scanning calorimetry (DSC) study of a PP and high density PE (HDPE) blend, Martuscelli et al. [2] revealed three different types of crystallisation behaviour at three ranges of crystallisation temperatures. Below 125°C, simultaneous crystallisation of PP and HDPE was observed. From 125 to 127°C, two crystallisation peaks were observed with PP crystallising first. Above 127°C, HDPE could not crystallise and the crystallisation of PP was from a melt mixture of PP and PE.

Studies on isothermal crystallisation of PP–HDPE and PP–low density PE (LDPE) blends at a temperature high enough to prevent PE crystallisation were reported by various authors [3–8]. From optical microscopic observations, it was found that the spherulite growth rate of PP in PP–PE blends was only dependent on temperature, and it was unaffected by the presence of PE for blends up to 40% [8] or 50% of PE [3–7]. Theoretical prediction by Galeski et al. [3] also illustrated that the reduction of the spherulite growth rate caused by PE was negligible for PE concentrations up to 50%.

The optical microscopic studies [3–8] also showed that, two-phase structures were observed in the blends with less than 50% of PE, and droplets of LDPE and HDPE were occluded by the growing PP spherulites. Theoretically, the difference in interfacial energy decides whether the droplets of PE were engulfed or rejected by the growing PP spherulites. Bartczak et al. [9] predicted that only the rejection required

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Table 1
Characteristics of polymers

Materials	Descriptions	MFI[a]	Density (g cm^{-3})[b]	Initial T_c (°C)[c]
PP2.5	Homopolymer	2.5	0.905	134
PP8.5	Homopolymer	8.5	0.905	135
PP40	Homopolymer	40	0.905	131
LLDPE0.78	Superhexene copolymer	0.78	0.920	121
LLDPE1	5% hexene copolymer	1	0.919	119
LLDPE2.5	5% hexene copolymer	2.5	0.918	117

[a] Supplied by manufacturers, refer to ASTM D1238, load of 2.16 kg at 230°C for PP, and 190°C for LLDPE.

[b] Supplied by manufacturers.

[c] The initial crystallisation temperatures for the polymers were measured as the initial appearance of nuclei under the polarising microscope for a cooling rate of 2°C min^{-1}, after melting at 200°C for 5 min.

additional work to be done by the crystallisation front. This dissipation of energy would induce a considerable depression in the spherulite growth rate. In all the above cases [3–8], the droplets were engulfed in the PP spherulites, therefore no energy was consumed and the spherulite growth rate was unaffected. The theoretical prediction concurred with the experimental observations.

It was also found in the above studies that the overall crystallisation rate of PP was strongly reduced by the addition of PE [3–8]. The reduction in the overall rate was attributed to a decrease in the nucleation density as the effect of the spherulite growth rate was found to be negligible [3,4,7]. Similar results were reported on PP–linear low density PE (LLDPE) blends by Long et al. [10,11].

The decrease in nucleation density was found predominantly caused by the nuclei migration from PP to PE, which was in turn caused by an interfacial energy difference. This was demonstrated by Galeski et al. [4] and Bartczak et al. [7] through a specially designed experiment, where nucleating agent was added into one component and then the blends were melt mixed several times. The nuclei density was measured for pure samples and blends after each mixing and was found decreased in PP phase after blending.

In contrast with the above findings, Avalos and co-workers [12] reported that the isothermal growth rate of PP spherulites was one-third of pure PP on the addition of LDPE for concentrations less than 10%. Blom et al. [13] reported recently that, the presence of small amount of HDPE was able to delay the nucleation and subsequent crystallisation of the PP phase. They concluded that, the decreased spherulite growth rates in the blends were caused by the miscible behaviour between PP and LDPE (and HDPE) at low PE concentrations. Their findings also suggested that the decrease in spherulite growth contributed to a decrease in the overall crystallisation rate.

The above-mentioned studies on kinetics of PP crystallisation were all based on PP as the major component. In addition, the effects of melt flow index of PP and PE on the kinetics of PP crystallisation in the blends have not been considered. In this research, we used blends containing 20% by mass of PP. Various PEs, namely HDPE, LDPE, LLDPE, and very low density polyethylene (VLDPE) have been used to blend with PP. The kinetics of PP crystallisation in the blends, the crystal structure of PP, the miscibility and morphologies of the blends, and the mechanical properties of the blends after heat-time treatment were investigated. In this paper, the kinetics of PP crystallisation rate, particularly the influence of LLDPE and its MFI on spherulite growth rates and overall crystallisation rates of PPs is reported. The miscibility of PP–LLDPE blends in the melt will also be discussed.

2. Experimental

2.1. Materials and blend preparation

Three isotactic PP homopolymers were used to blend with three similar grade LLDPEs (5% hexene copolymers), respectively. Table 1 lists characteristics of the materials and the polymers were labelled according to their MFI. The composition of all the blends studied was 20% of PP and 80% of LLDPE.

The blends were mixed in an Axon BX-12 single screw extruder (Axon Australia Pty Ltd, Australia) with a Gateway screw diameter of 12.5 mm and a length to diameter ratio of 26:1. The operating temperature for the feeding zone, metering zone, compression zone and die-end were 170, 200, 200 and 180°C, respectively. The screw speed was 80 rpm. The blends were pelletised before sampling.

2.2. Hot-stage polarised optical microscopy

Polarising light microscopy is the study of the microstructure of materials using their interactions with polarised light. Under polarised light, the spherulite appears as circular areas showing a dark distinctive pattern in the shape of a Maltese cross [14]. Types and boundaries of spherulites have been investigated widely by polarised optical microscope. However, the measurement of number and size of spherulites is time consuming.

With the development of digital image analysis [15], a complete quantitative study by hot stage optical microscopy (HSOM) has become convenient. The calculation of numbers of spherulites in a larger area and average size of spherulites with different shapes has become easier. In addition, an advantage of polarising microscopy over other methods such as DSC, FTIR and dilatometry, is that the nucleation and spherulite growth rate can be measured independently from the overall transformation of crystallisation. The direct relationship between the micro scale change and the overall transformation can then be easily related.

In this study, optical microscopy was performed using a Nikon Labophot II microscope with a Mettler FP90 hot stage, a specimen holder with a temperature controller. Images were captured using a Sony camera and video monitor connected to a Macintosh 7500 computer with IPLab image analysis software. Specimens of 20 μm thickness were prepared with 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 between 120 and 130°C, at which PP was able to crystallise in molten PE. The pre-set temperature on the hot-stage can be kept constant to ±0.1°C and the maximum cooling rate is 20°C min^{-1}.

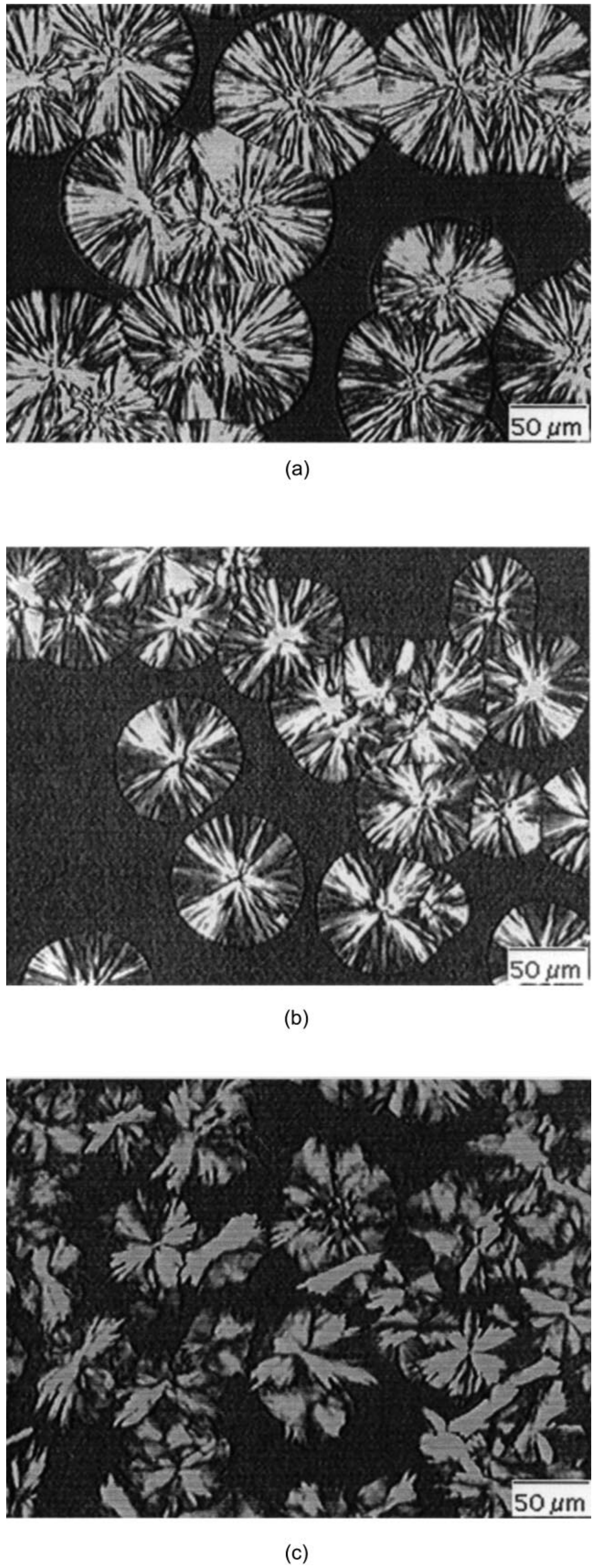

Fig. 1. (a) PP 2.5 spherulites after isothermal crystallisation at 128°C for 8 min. (b) PP 8.5 spherulites after isothermal crystallisation at 130°C for 10 min. (c) PP40 spherulites after isothermal crystallisation at 126°C for 22 min, magnification ×100.

2.3. Measurement of spherulite growth, overall crystallisation growth and nuclei density

Images of PP spherulites, which appear as bright areas under polarised light in the dark background, were recorded at appropriate intervals (up to a second) as digitised computer files. The area of spherulite was calculated using IP Lab image analysis software and later used to calculate spherulite growth rate. The spherulite growth rate is described by its radius at successive time [16]. Since $s = \pi r^2$, two methods can be used to measure spherulite growth rates based on the area of spherulites. One from the slope of the plot of individual radii versus time, and the other from the slope of average radius versus time. Individual spherulite growth rate, $\dot{g}$, is determined by randomly chosen spherulites:

$$\dot{g} = \dot{s}\frac{1}{2\sqrt{\pi s}} \tag{1}$$

In which $\dot{s} = \mathrm{d}s/\mathrm{d}t$ and s is the area of the measured spherulite. The individual growth, $\dot{g}$, is determined by plotting $\sqrt{s/\pi}$ versus t. the average growth rate, $\dot{G}$, is determined by measuring the crystallised fraction and the number of the spherulites in the field of view, then plotting $\sqrt{X/n\pi}$ versus t.

Errors brought by impinged spherulites were moderated in calculation. As the program only considers spherulites as particles, with broken boundaries as one, it may falsely consider impinged spherulites as one particle. In this case, joined particles were separated manually by drawing lines on the computer screen. Another way to remove these errors is to set a threshold value to remove all clearly impossible data. For example, the size of PP spherulite in our study is less than 100 μm across. Particles that are greater than

100 μm could be impinged spherulites and will be recognised by the computer and be removed. It is noted that the scale has to be properly calibrated when calculating spherulite radius and growth rate.

The overall or bulk crystallisation rate in the field of view can be measured directly through the area fraction of crystalline material:

$$X = A\mathrm{d}X(t, T)/\mathrm{d}t \tag{2}$$

This is based on the assumption that the volume fraction of particles or of phases is equal to the area function, measured on some intersecting surface [17]

$$V_\mathrm{f} = A_\mathrm{f} = \frac{\text{area contained in particles}}{\text{total area of plane}} \tag{3}$$

The reduced crystalline fraction was calculated by dividing the crystalline area at different times by the crystalline area at the finish time.

Nuclei numbers were counted after isothermal crystallisation finished and then calculated by nuclei per unit area. Detailed image processing and analysis have been described by Long et al. [15].

The isothermal crystallisation kinetics is analysed using the Avrami equation [18–20]:

$$\ln(-\ln(1 - X(t, T))) = \ln k(T) + n \ln t \tag{4}$$

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

From graphic representation 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) was calculated. Based on these two values, the crystallisation half-time, which is a measure of crystallisation rate, can be obtained from the equation:

$$t_{1/2} = \ln 2/(k^{1/n}) \tag{5}$$

3. Results and discussion

3.1. Morphologies of PP and blends under controlled crystallisation

Fig. 1 shows typical PP spherulites with the Maltese cross pattern. Fig. 1(a) and (b) display the most common α-form crystals, while Fig. 1(c) shows β-form crystals [14]. In a PP 8.5 (20%)–LLDPE1 blend, the PP 8.5 crystallised as open-armed diffuse spherulites in the LLDPE1 melt (Fig. 2), where the lamellae were coarser and further apart. Similar spherulite structures were also observed in other PP–LLDPE blends studied.

The spherulites of PP in molten LLDPEs were not as sharp or as well defined as in the pure PP, however they could still be easily distinguished. The spherulite structure was irregular because the supply of PP in the matrix was diminished due to the small proportion of PP present (20%), and the consumption of crystallisation. In contrast, the homopolymer formed compact spherulites (Fig. 1).

The open armed, diffuse spherulites are often observed in highly diluted miscible or partially miscible blends, such as *isotactic* PP (*i*PP)–*atactic*(*a*PP) PP blend [21] and PP–ethylene propylene rubber (EPR) [22]. The reason for formation of such diffuse spherulites has been proposed [22]. During crystallisation, the PP intended to crystallise on its own, rejecting foreign components. Because the concentration of non-crystallisable foreign components (molten LLDPE) was high in the 20% PP blends, additional work has to been done by the growing spherulites to reject

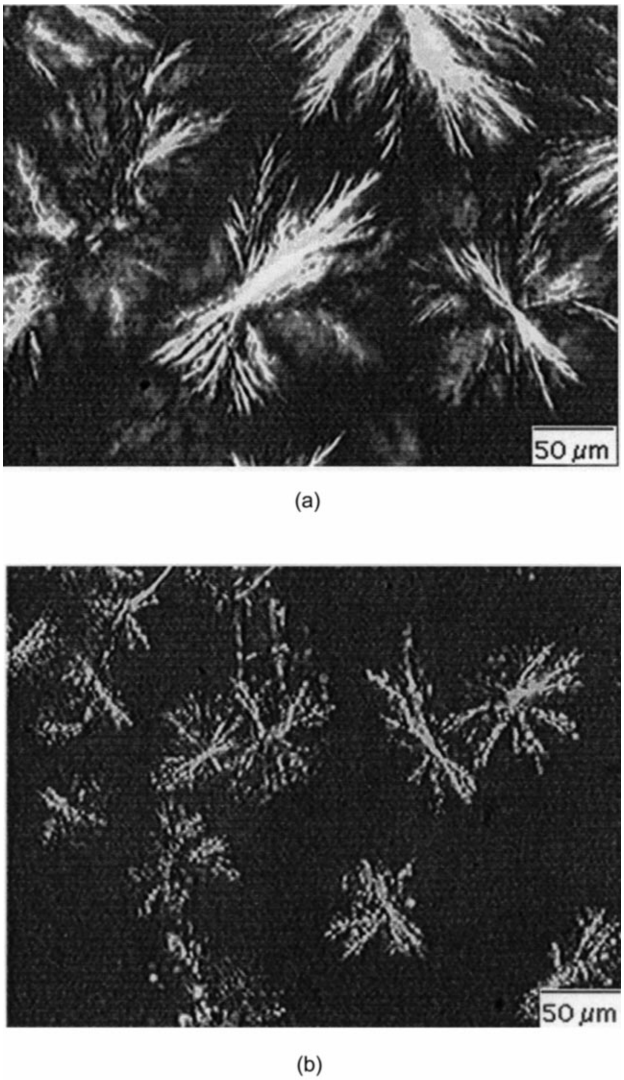

Fig. 2. (a) PP8.5 spherulites in a blend with LLDPE1 (80%) after isothermal crystallisation at 128°C for 20 h, magnification ×100. (b) PP8.5 crystals in a blend with LLDPE1 (80%) after isothermal crystallisation at 124°C for 25 min, magnification ×100.

Table 2
Spherulite growth rates (nm s^{-1}) of PPs in the pure PPs and their blends

Sample	Isothermal crystallisation temperature (°C)			
	124	126	128	130
PP2.5	185	150	115	81
PP8.5	215	180	121	59
PP40	222	160	114	76
LLDPE0.78–PP2.5	10	9	6	3
LLDPE1.–PP2.5	16	14	9	5
LLDPE2.5–PP2.5	23	18	16	12
LLDPE0.78–PP8.5	13	9	7	3
LLDPE1–PP8.5	20	16	11	8
LLDPE2.5–PP8.5	35	29	20	13
LLDPE0.78PP40	25	15	7	–
LLDPE1–PP40	33	22	15	–
LLDPE2.5–PP40	39	33	23	–

LLDPE, and therefore the formation of new lamellae was sacrificed in favour of thickening of the existing lamellae. Thus the lamellae were coarser and further apart. The coarser lamellae were also the result of decreased supercooling degree caused by a lower equilibrium melting temperature of PP in the miscible blend [23].

3.2. Effect of LLDPE on spherulite growth rate of PP

Table 2 lists the spherulite growth rates of PP for the pure PPs and their blends. It was seen that the growth rates decreased as the temperature increased both in the pure PP and in the blends. Blending with the LLDPE reduced the spherulite growth rate of PP significantly. Furthermore, the effect of varying LLDPE on the growth rate was also different. Particularly the spherulite growth of PP decreased with a decrease in MFI of LLDPEs (Fig. 3). In addition, the PP with lowest MFI exhibited the slowest growth rate for a given LLDPE (Fig. 4), although the spherulite growth rate of the pure PP did not follow the same trend.

3.3. Effect of LLDPE on overall crystallisation rate of PP

The overall crystallisation rates were measured by capturing spherulite images at appropriate intervals of time until the growth of spherulites stopped (typically, at least 5–6 h). Fig. 5 shows the crystalline fraction versus time at various temperatures for the pure PP 8.5. The crystallisation rates of PP were decreased as the crystallisation temperature increased.

Based on Figs. 5 and 6 was plotted according to the Avrami equation, displaying a linear relationship. The Avrami exponent and the rate constant were calculated for all the materials according to this linear relationship. It was found that the values of *n* varied slightly but they were all close to 2 (Table 3), indicating that the crystallisation process was heterogeneous and took place within two dimensions [24]. The growth of spherulites were confined in two dimensions although initial nucleation and crystallisation may take place in three dimensions, because the specimens were 20 μm in thickness and were sandwiched between glass slides and cover slips. The heterogeneous nucleation was confirmed by HSOM observations (Fig. 1(a) and (b)). All the spherulites were approximately the

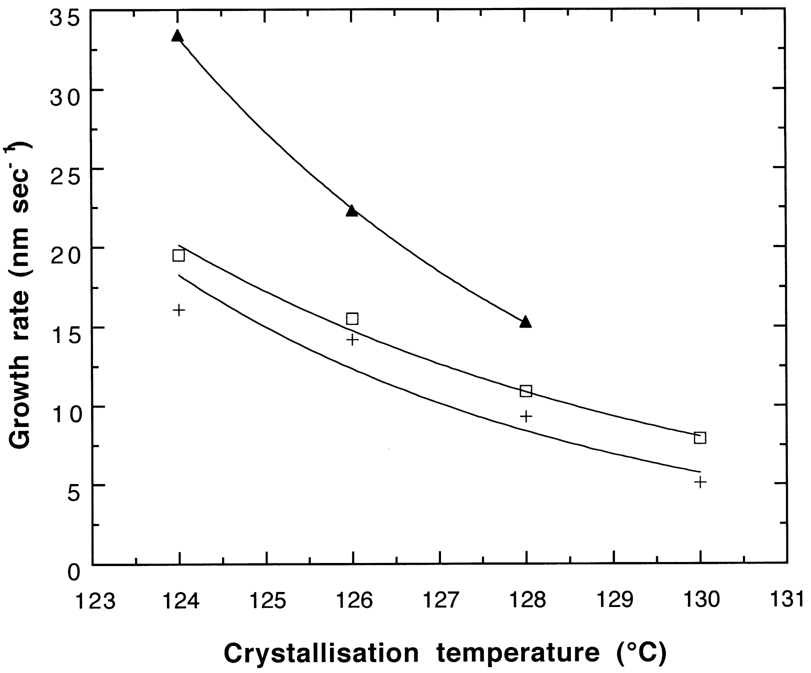

Fig. 3. Spherulite growth rates of PPs verses crystallisation temperatures for the blends with LLDPE1: [▲] — LLDPE1–PP40; [□] — LLDPE1–PP8.5; [+] — LLDPE1–PP2.5.

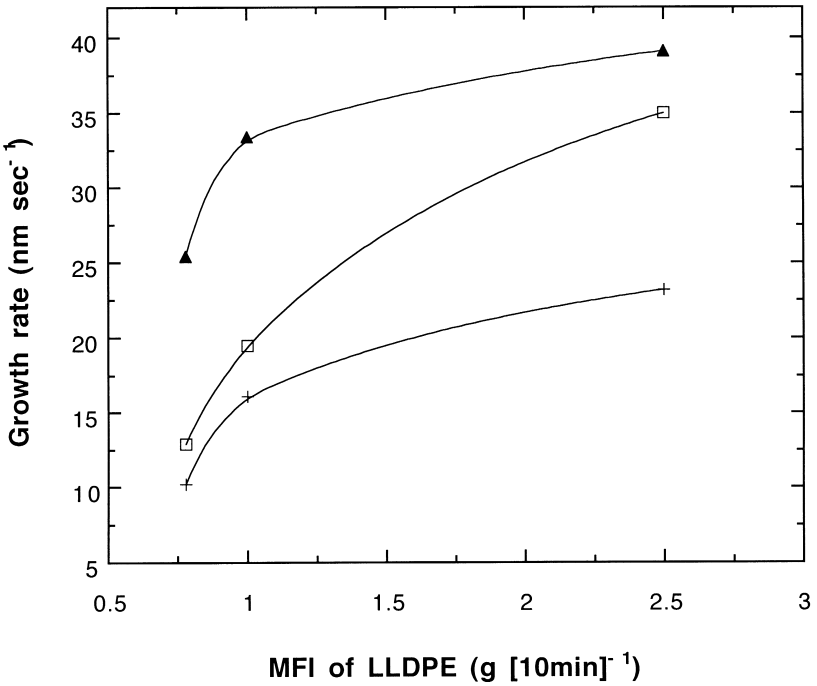

Fig. 4. The PPs spherulite growth rate in the blends plots against MFI of LLDPEs at a crystallisation temperature 124°C: [▲] — PP40; [□] — PP8.5; [+] — PP2.5.

same size, indicating that they grew at the same time, which was the result of heterogeneous nucleation.

The rate constants (k) at various temperatures were plotted in Fig. 7 for the PP 8.5 and its blends. Similar results were obtained for the PP 2.5, PP40 and their blends with LLDPEs. It was found that the value of k decreased significantly in the blends and the effect of different LLDPEs on the k value varied. The lower the MFI of LLDPE, the smaller was the value of k, indicating that the LLDPE with higher molecular weight (lower MFI) further slowed

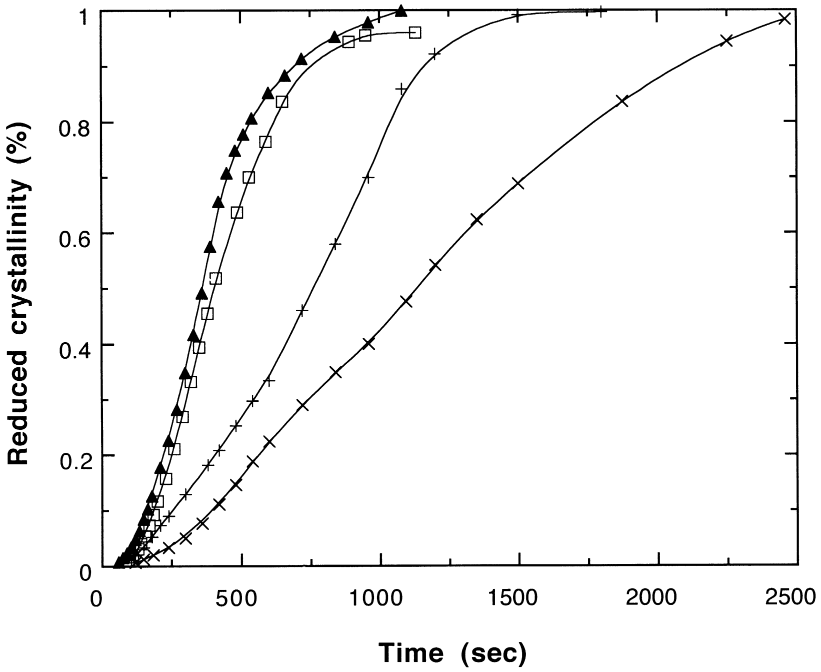

Fig. 5. Reduced fraction of crystallised material, $X(t, T)$, versus time for pure PP 8.5 at various crystallisation temperatures: [▲] — 124°C; [□] — 126°C; [+] — 128°C; [×] — 130°C.

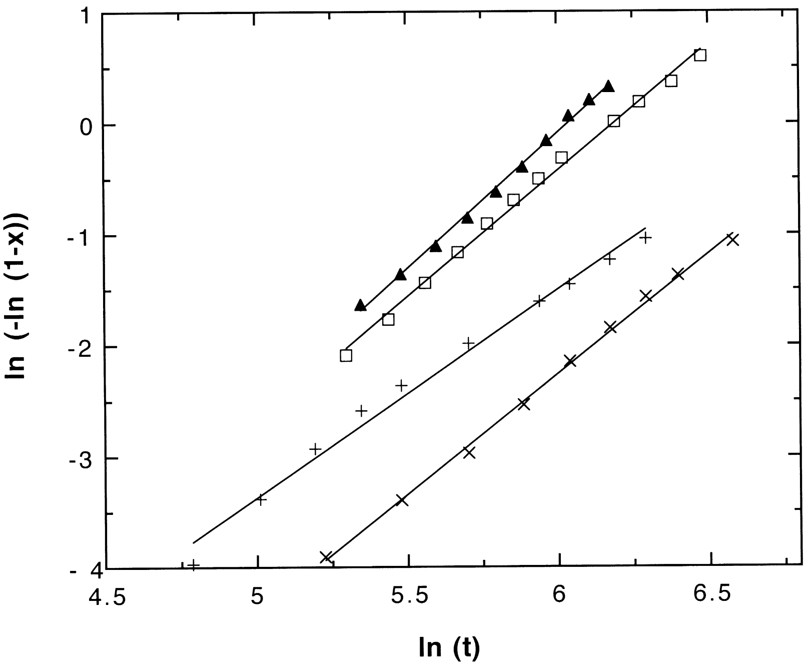

Fig. 6. A plot of data from Fig. 5 according to the Avrami equation: [▲] — 124°C; [□] — 126°C; [+] — 128°C; [×] — 130°C.

the rate of PP crystallisation. The reason for such phenomenon will be discussed later.

Fig. 8 shows the crystallisation half-time versus crystallisation temperature for PP40 and its blends with LLDPE. The half-time of the PP crystallisation increased significantly in the blends, showing a drastic decrease in the crystallisation rate after blending. Again, the effect of different LLDPE on PP was different. This result was in agreement with the changes in the rate constant, *k*.

Two factors that would contribute to a decrease in the overall crystallisation rate in the blends are nuclei density and spherulite growth rate. A decrease in the nuclei density was proposed as the only reason for the decreased overall crystallisation rate in the immiscible PP–PE blends, because the change in the spherulite growth rate of PP was negligible for up to 80% of PE in their blends [3–10].

In this study, the crystallisation of PP in molten LLDPE was both a nucleation and spherulite growth controlled process. Fig. 9 shows the nuclei density as a function of MFI value of the LLDPE.[1] Point A in the figure represents the nuclei density in the pure PP 8.5. It can be seen that the nuclei density decreased dramatically in the blends for a PP concentration of 20%, compared with that of pure PP. However, the change of nuclei density with the MFI of LLDPE is negligible. In contrast, the half-time increased with a decrease in the MFI of LLDPE (Fig. 8). As discussed previously, the spherulite growth rate also decreased with a decrease in the MFI of LLDPE. The negligible change in the nuclei density, the simultaneous decrease in the spherulite growth rate and the overall crystallisation rate with a decrease in the MFI of LLDPE implied that the change in the spherulite growth rate contributed to the change in overall crystallisation rate.

The relationship between the overall crystallisation rate and the spherulite growth rate is shown in Fig. 10. It can be seen that the overall crystallisation rate increased (decreased half-time) continuously with an increase in the spherulite growth rate.

3.4. Relationship between spherulite growth rate and miscibility

The spherulite growth rate of PP decreased significantly in the PP–LLDPE (20:80) blends, implying that the PP and the LLDPE studied were miscible to some extent.

Crystallisation involves nucleation and diffusion of crystallisable segments to the crystal growth front. The

Table 3
Avrami exponents for PP2.5, PP8.5 and their blends

Sample	122°C	124°C	126°C	128°C	130°C
PP2.5		1.9	1.9	2.0	2.1
LLDPE0.78–PP2.5		2.0	2.0	2.0	1.9
LLDPE1–PP2.5	2.1	2.0	2.0	2.0	2.0
LLDPE2.5–PP2.5	2.1	1.9	2.0	2.0	2.0
PP8.5		2.0	2.0	2.0	2.0
LLDPE0.78–PP8.5		2.0	2.1	2.1	2.1
LLDPE1–PP8.5		2.0	2.1	2.1	2.1
LLDPE2.5–PP8.5		2.0	1.9	1.9	2.0

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[1] The nuclei number was counted after completion of crystallisation, and the nuclei density was calculated as the number per unit area.

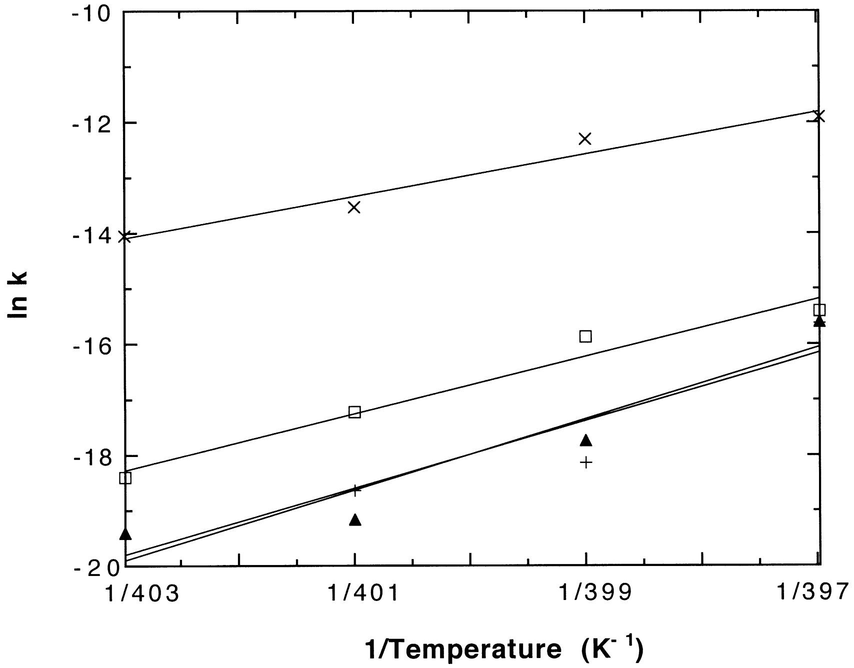

Fig. 7. ln *k* versus temperature for PP8.5 and its blends: [×] — PP8.5; [▲] — LLDPE0.78–PP8.5; [+] — LLDPE1–PP8.5; [□] — LLDPE2.5–PP8.5.

condition for the formation of nuclei of critical size can be described by a nucleation theory. The driving force for crystallisation is the free energy change due to the loss of free energy from the change of a certain amount of material from the liquid to solid and the gain in surface free energy from the creation of an area of solid–liquid interface. The diffusion of chain segments in a viscous melt regulates the crystal growth rate. The spherulite growth rate can be described by the Turnbull–Fisher equation [25]:

$$G = G_0 \exp(-(E_0 + \Delta G^*)/RT) \qquad (6)$$

where G is the spherulite growth rate, G_0 is a constant, E_0 is the activation energy for transport across the liquid–solid

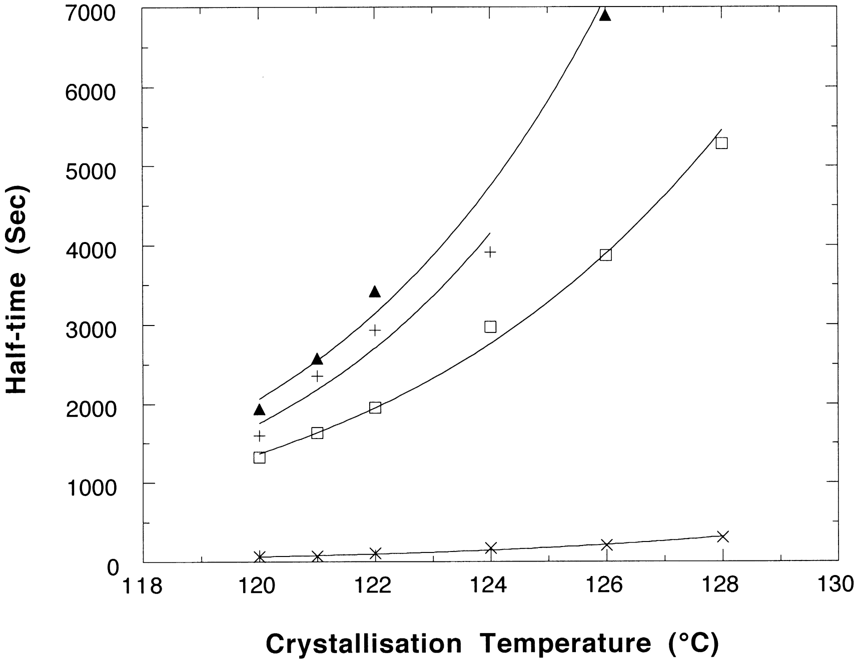

Fig. 8. Crystallisation half–time versus isothermal crystallisation temperature for pure PP40 and its blends with LLDPEs: [×] — PP40; [▲] — LLDPE0.78–PP40; [□] — LLDPE2.5–PP40; [□] — LLDPE1–PP40.

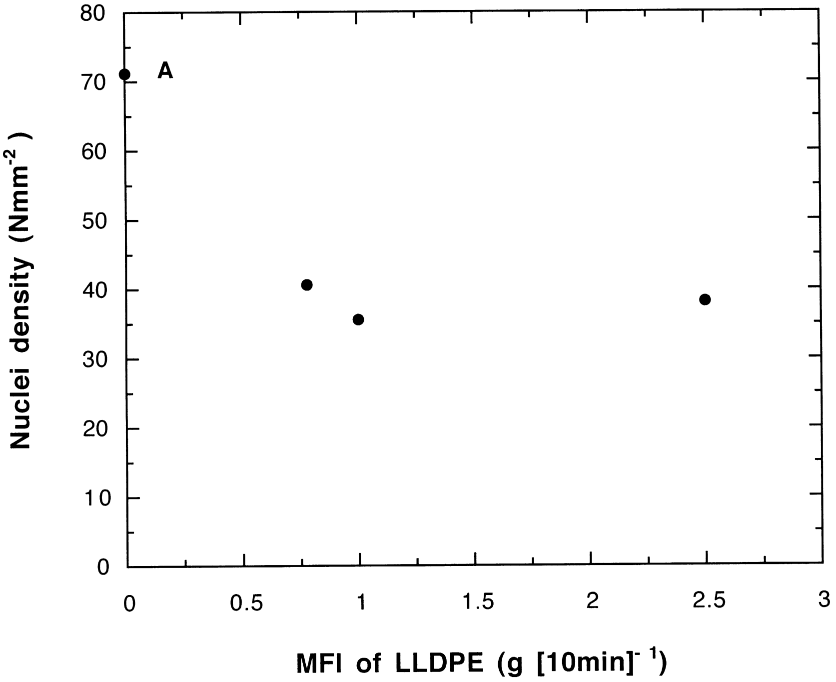

Fig. 9. The nuclei density in blends of PP8.5 with LLDPEs at isothermal crystallisation temperature 130°C.

interface and ΔG^* is the free energy for forming a nucleus with a critical size.

In the blends at molten state, the LLDPE may act as a solvent and dilute the PP concentration in the matrix. The segment density of PP was diminished significantly in a 20% solution, and the free energy for the formation of nuclei of critical size increased (ΔG^* increased). Therefore, the crystallisation of PP was retarded in the PP–LLDPE (20:80) blends (G decreased).

Secondly, the LLDPE may affect the diffusion speed of

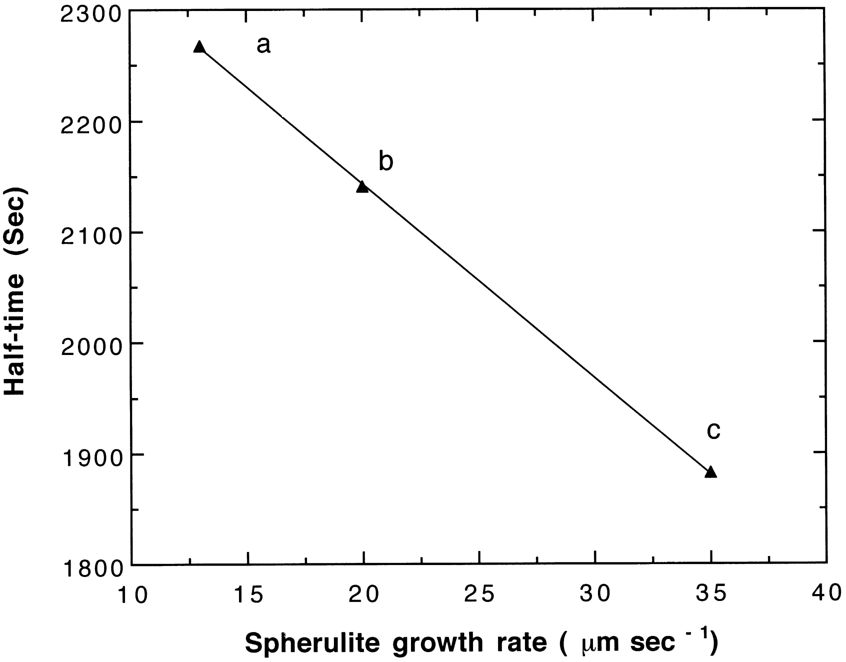

Fig. 10. Crystallisation half-time of PP8.5 versus spherulite growth rate of PP8.5 for the blends of PP8.5 with LLDPE at 124°C. (a) PP8.5–LLDPE0.78, (b) PP8.5–LLDPE1, (c) PP8.5–LLDPE2.5.

the PP chain segments during crystallisation. In the PP–LLDPE blends, the diffusion environment of the chain segments of PP was a solution of PP and LLDPE melts, instead of the PP melt in the pure PP. The diffusion speed of PP chain segments was affected not only by the PP itself but also by the characteristic of the LLDPE. The movement of PP chain segments was slowed by the viscous LLDPE (E_0 increased) and thereby the spherulite growth rate decreased (Eq. 6).

Both the reasons proposed that the PP was miscible with the LLDPE, because both the dilution and the hindrance to diffusion could only happen when the PP and the LLDPE were in one phase. We previously reported that in PP–LDPE and PP–HDPE systems the crystallisation rate of PP was the same as that in the pure PP because PP and LDPE (or HDPE) were immiscible in the liquid state [26]. The PP crystallised in phase separated domains, in which the concentration of PP was almost 100%. The crystallisation of PP in these blends was like that in the pure PP. Under this condition, the existence of PE did not disturb the crystallisation of PP because they were in two separated phases.

Finally, the decrease in equilibrium melting temperature in the miscible blends reduced the spherulite growth rate, due to the decreased supercooling degree.

The effect of MFI on the spherulite growth rate was further evidence of the miscible behaviour between the PP and the LLDPE. In a solution of LLDPE with higher viscosity (low MFI), the molecular weight of LLDPE was greater and the mobility of LLDPE chain segments was slower. As the hindrance from the LLDPE to the diffusion of PP chain segments was greater, more energy was dissipated in the transport process (E_0 increased). Therefore, the diffusion speed of PP was slower in the LLDPE with a lower MFI and so was the spherulite growth rate (Eq. 6).

A decrease in PP spherulite growth rate in the miscible blends has also been observed previously. Keith and Padden [27] reported that the spherulite growth rate of *i*PP was reduced by the addition of *a*PP, and decreased with the increasing molecular weight of *a*PP, while blends of *i*PP and *a*PP were typically miscible systems.

A study on a PP–LDPE blend showed that the addition of LDPE (10%) caused a depression in the spherulite growth rate of PP and increased the chain folding energy for PP crystallisation [12]. This was attributed to the miscible behaviour of PP and LDPE. Blom et al. [13] reported that, the HDPE was able to penetrate the PP phase sufficiently at lower HDPE contents to reduce the number and size of high segment-density regions, thereby delaying the nucleation and subsequent crystallisation of the PP phase.

The microscopic observations confirm the miscibility conclusions. In Fig. 2, the PP spherulites grew diffusely in the liquid LLDPE solution, even though the PP was only 20% by mass. These spherulite structures were often observed in the miscible blends. In an immiscible blend such as a PP–HDPE blend, the PP crystallised in the small droplets at a PP composition of 20% [26].

However, the miscible range of the PP and the LLDPE is limited. As shown in Fig. 2(b), small droplets were observed in the PP 8.5–LLDPE1 blend at a lower crystallisation temperature (124°C). It can also be seen that the small droplets attempted to connect together, forming the shape of crystal arms and diffuse spherulites. The droplets were also observed in other blends at lower crystallisation temperatures. The number of droplets and the temperature where droplets could be observed varied from blend to blend.

4. Conclusion

The nuclei density, spherulite growth rate and overall crystallisation rate of PP were strongly influenced by the LLDPE and its MFI for a PP composition of 20% in the PP–LLDPE blends. Particularly, the spherulite growth rate of PP was significantly decreased in the blends and was affected by the MFI of LLDPE. The lower the MFI of LLDPE, the slower was the spherulite growth rate of PP. The decrease in the spherulite growth rate of PP in the PP–LLDPE blends could be caused by a number of reasons. Firstly, the LLDPE diluted the PP concentration in the matrix and retarded the crystallisation of PP. Secondly, the viscosity of LLDPE regulated the diffusion speed of PP chain segments and hence the spherulite growth rate of PP. Lastly, the spherulite growth rate would decrease due to the decreased supercooling degree in the miscible blends. Therefore, it can be concluded that these observations suggested that the PP was miscible with the LLDPE, which is confirmed by the open-armed diffuse PP spherulites in the PP–LLDPE blends. In addition, the decrease in both the nuclei density and the spherulite growth rate contributed to the drastic decrease in the overall crystallisation rate in the partially miscible blends. The crystallisation of PP in the PP–LLDPE (20:80) blends was both nucleation and diffusion controlled.

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