

Polypropylene–polyethylene blend morphology controlled by time–temperature–miscibility

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Received 1 January 1999; received in revised form 16 April 1999; accepted 25 May 1999

Abstract

Isotactic polypropylene (PP) has been blended with various types of polyethylene, high density (HDPE), low density (LDPE), linear low density (LLDPE), very low density (VLDPE) and ultra low density (ULDPE). Each blend contained 20% by mass PP. The blends were cooled from the melt to temperatures where PP could crystallise, but not the polyethylene. When the two polymers were immiscible, or immiscible at the crystallisation temperature where liquid–liquid phase separation occurred on cooling, then the two phases crystallised independently. Under these conditions the crystallisation rate (half-time) for PP was very similar to that of pure polypropylene. When the polymers were miscible, crystallisation of PP took place from a solution in the molten polyethylene. Under these conditions the crystallisation rate of PP was greatly decreased since it was in dilute solution. The significant change in rate of crystallisation of PP was a detection of miscibility. After PP had crystallised the blend was cooled to ambient temperature and the polyethylene quickly crystallised in the intervening spaces.

When PP crystallised from a homogeneous solution, which was the case with only LLDPE, broad diffuse spherulites formed and PP became a continuous phase. Crystallisation under these conditions took 5–10 h and a unique co-continuous structure resulted even though PP was only present at 20%. PP was found to be immiscible in HDPE, LDPE and VLDPE. A combination of DSC and hot stage polarised optical microscopy was used to study the crystallisation of the blends. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Polyolefin blend; Polypropylene; Polyethylene

1. Introduction

Blending of polymers is now regarded as an economical alternative to the development of new polymers. Materials with improved end use properties can be obtained by blending two or more polymers having different molecular characteristics. It is well known that morphologies of a partially miscible polymer blend depend on its composition, morphology and processing conditions. For most homogeneous systems an important characteristic of the phase diagram is that a change of temperature leads to a phase change, i.e. the existence of an upper critical solution temperature, UCST and/or a lower critical solution temperature, LCST.

When selecting polymers for blending, two important characteristics of the components need to be taken into consideration: whether they are thermodynamically miscible or mechanically compatible [1]. Thermodynamically miscible polymers are homogeneous at the molecular

level. The mixing process must produce a decrease in free energy (ΔG), $\Delta G = \Delta H - T\Delta S \leq 0$. This results in a single-phase polymer blend, at a specified temperature, and therefore the majority of the properties of the blend will be an average of the properties of the individual polymers. Very few polymer blends belong to this case. A vast majority of polymers form heterogeneous blends on mixing. Compatibility is used to describe polymers that are not thermodynamically miscible, but having similar structures resulting in useful properties in practice [2].

Polyethylene (PE) has been used to modify the physical and mechanical behaviour of isotactic polypropylene (PP) by forming physical blends. Four varieties of PE, namely low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), very low-density polyethylene (VLDPE) and ultra low-density polyethylene (ULDPE) are commonly used in physical blends with PP or PP copolymers.

PP and PE blends are compatible but thought to be only partially miscible. The polymer pairs tend to separate into two liquid phases. Each phase is a solution of a minor

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Table 1
Description of the polyolefins used in the blends (Z–N = Ziegler–Natta, M = metallocene)

Polymer	Description	Source	MFI
Polypropylene	Homopolymer	Orica	28
LLDPE1	5% hexene, Z–N gas phase	Orica	1
LLDPE2	5% hexene, Z–N gas phase	Orica	2.5
VLDPE	6.3% butene, M gas phase	Kemcor	27
ULDPE	20% butene, M gas phase	Kemcor	10
LDPE	—	Kemcor	22
HDPE	—	Mobil	20

component in a major component and the phases separate into sub-microscopic domains. The polymer with the major proportion forms the continuous matrix and contributes most towards properties while the minor polymer forms small discrete domains, which contribute synergistically to certain specific properties. PP and LLDPE are compatible polymers but they are thought to be only miscible at some compositions and at elevated temperatures [3]. PP and LDPE or HDPE are generally considered immiscible in the liquid state. The miscibility of PP with metallocene VLDPEs has not been widely studied, though such blends are considered potentially important for toughened PPs. Most polyolefins are immiscible in the liquid state since small differences in the shape of the molecules give rise to unfavourable intermolecular forces [4,5]. A further immiscibility arises as the polyolefins crystallise into different crystal domains.

A blend of PP and PE may be miscible or immiscible in the melt at processing temperatures (about 200°C). If the blend is immiscible droplets of the minor phase, PP in our study, will exist as droplets in the major phase (PE in our study). If a blend of PP and LLDPE is cooled from a miscible melt it may separate into two phases. On cooling

further each phase will crystallise (solidify) and the structure will be determined by the previous two-phase liquid structure. Both PP and PE can be the continuous phase or domains. This is dependent on their composition in the blend and the comonomer composition of PE.

If the blend of PP and PE is cooled and remains miscible, it can be held at a temperature such that PP crystallises from the molten blend. This temperature must be such that PE will not crystallise over the longest time PP takes to crystallise. After a time long enough for PP to completely crystallise the blend is further cooled and the remaining PE will crystallise. This phenomenon results in PP forming a continuous phase in PE, leading to a co-continuous morphology [3,6], even when PP is the minor phase. This will give a unique phase structure to the blend and it is expected that physical and mechanical properties will be unique to this microstructure. This project aims to form such blends, which separate only by crystallisation, and study their crystallisation kinetics and morphology. It is also proposed to investigate the miscibility of polypropylene in each of the types of polyethylene (HDPE, LDPE, LLDPE, VLDPE and ULDPE).

2. Experimental

Throughout the experiments polypropylene homopolymer (MFI 28 g/10 min, 230°C, 2.16 kg load, according to manufacturer) and six types of polyethylene were used. Table 1 lists the polymers; MFI of polyethylenes was obtained from the manufacturers and refers to 190°C and 2.16 kg load. The blends were mixed using an Axon single Gateway screw extruder at 200°C. The composition of the blends was PP:PE (20:80) by mass.

Table 2
Crystallisation and melting temperatures of PP, PEs and their blends

Sample	Crystallisation						Melting					
	Peak (°C)			ΔH (J/g)			Peak (°C)			ΔH (J/g)		
	1	2	3	1	2	3	1	2	3	1	2	3
PP	119.8			–101.4			162.9			106.7		
LLDPE1	107.1			–87.0			124.3			99.4		
LLDPE2	107.0			–89.7			124.9			105.2		
VLDPE	65.9			–50.8			89.78			54.7		
ULDPE	—			—			—			—		
LDPE	92.4			–80.9			108.6			89.4		
HDPE	112.5			–178.7			130.6			190.5		
LLDPE1–PP	110.4			–32.9			125.4	163.2		86.8	14.8	
LLDPE2–PP	111.4			–89.0			125.7	162.3		82.5	17.8	
VLDPE–PP	74.4	100.9	118.5	–42.8	–5.8	–2.85	90.3	122.2	160.5	40.5	0.6	18.7
ULDPE–PP	96.7	109.7		–1.8	–0.10		123.1	161.9		0.5	4.9	
LDPE–PP	94.7	117.6		–72.7	–3.5		109.0	161.8		78.5	17.6	
HDPE–PP	114.8			–170.5			131.1	159.5		174.4	7.1	

Table 3
PP crystallisation half-times (per second) for the pure PP its blends at various isothermal temperatures

T_c (°C)	PP	LLDPE1-PP	LLDPE2-PP	VLDPE-PP	LDPE-PP	HDPE-PP
115	33.64			36.89		
118	45.30			46.20		
119	49.23	635.48	385.70			
119.5	50.73	1177.94	559.82			
120	52.05	1313.70	841.23	49.14		
120.5	55.20	2139.93	1599.35			
121	59.41		1961.13			
121.5	64.12		2677.81			
122	72.87			65.39		
124	101.3			95.15		133.35
124.5	108.53					152.04
125	117.97			129.53	107.04	160.30
125.5	126.75					171.71
126						214.16
127	164.01			140.07	163.65	
128	207.12				231.65	
129	260.47			240.56		
130	323.12			1955.56	392.86	

2.1. Differential scanning calorimetry study of melting and crystallisation

A Perkin–Elmer DSC-7 was used to determine the melting and crystallisation behaviour of the polymers and their blends. For crystallisation and melting temperature measurement, PP, PE and their blends were melted at 200°C, held isothermally for 2 min, then cooled to 40°C and heated to 200°C again. The scanning rate was 10°C/min. For isothermal analysis, samples were quench cooled from 200°C to an isothermal temperature between 115 and 136°C.

2.2. Hot-stage optical microscopy

A Nikon Labophot polarising optical microscopy equipped with a Mettler FP-90 hot-stage was used to observe phase transformation. The experimental procedure consisted of preparation of 20 µm thick films using a microtome [8,9]. The films were heated to 200°C for 5 min between a glass slide and cover slip; this was followed by cooling rapidly to an isothermal temperature between the temperatures for PP and PE crystallisation.

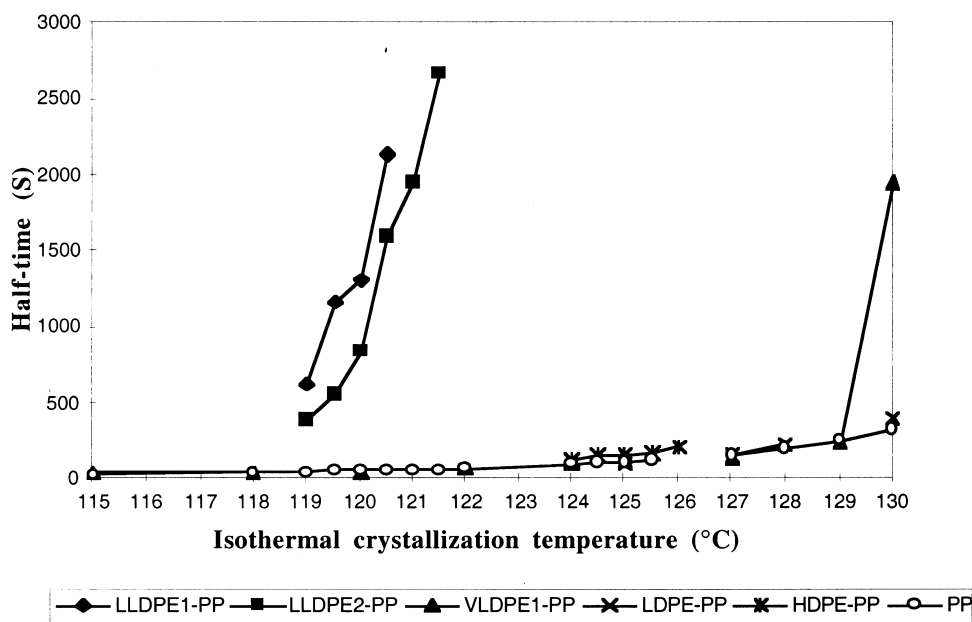


Fig. 1. PP crystallisation half-time versus isothermal temperature for PP and its blends.

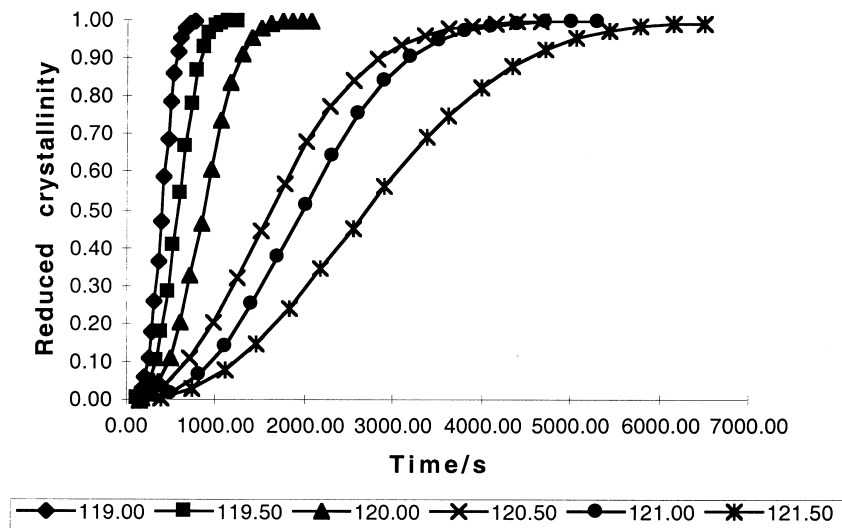


Fig. 2. Reduction fraction of crystallised PP in LLDPE1 versus time at 119.0–121.5°C.

3. Results

3.1. DSC results

3.1.1. Properties of pure polymers and blends

Table 2 lists crystallisation and melting temperatures of PP, various grades of PE and their blends. Crystallisation and melting for ULDPE was too low ($T_m = 45^\circ\text{C}$) to measure accurately using the DSC with water cooling. The crystallisation of PP occurred at varying temperatures depending on its miscibility, though it always melted in the range 159–163°C. The polyethylenes crystallised at various temperatures depending on their structure, with the highest temperature being 112°C for HDPE. These temperatures

were measured after scanning at 10°C/min. Under isothermal conditions the crystallisation could take place at higher temperatures over longer times, but during the times used the polyethylenes always crystallised at temperatures below 124°C (for HDPE), so PP could be crystallised at temperatures of 124°C and higher in a HDPE liquid. Other PE crystallisation required much lower temperatures. PP will either be soluble in the PE liquid or exist as a dispersed liquid phase.

3.1.2. Isothermal crystallisation in the DSC

Table 3 shows the crystallisation half-times for PP and its blends with each of the PEs at a concentration of PP(20):PE(80). The lowest temperature for isothermal

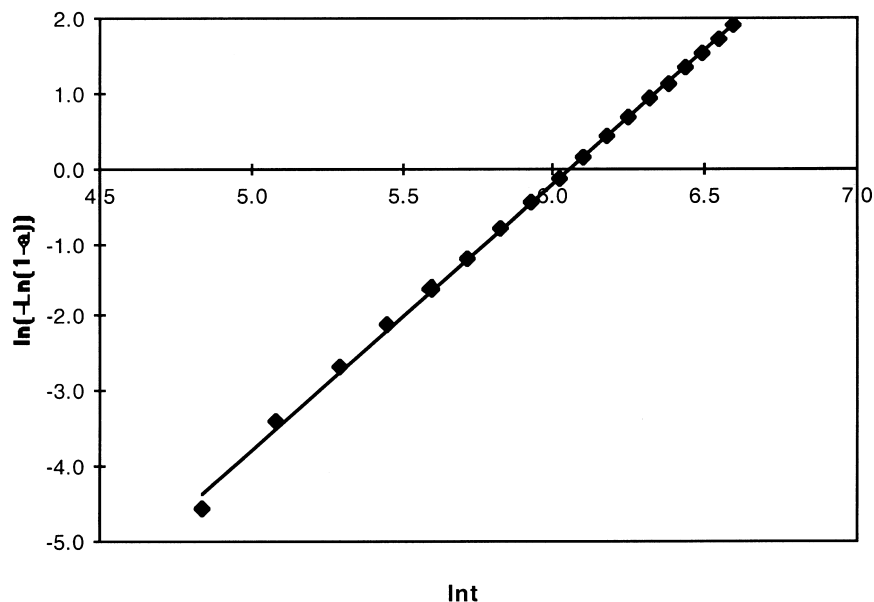


Fig. 3. A plot of data for crystallisation of PP in LLDPE1 at 120°C from Fig. 2 according to the Avrami equation.

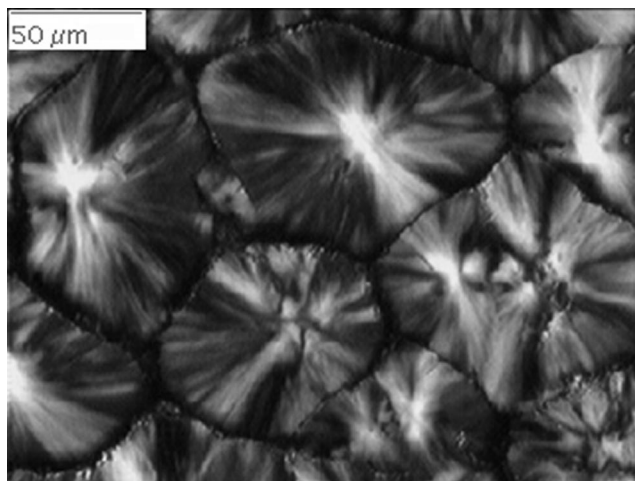


Fig. 4. PP crystals in pure PP after isothermal crystallisation at 124°C for 2 h, 200 ×.

crystallisation was chosen to be above the highest temperature at which the polyethylene was able to crystallise. For example isothermal crystallisation of LLDPE1 could not be detected at 119°C using DSC. A calculated half-time extrapolated from lower temperatures, using the Avrami equation, was found to be 1500 s. This was 2.5 times the half-time for polypropylene shown in Table 2. The absence of polyethylene crystallisation was confirmed by the hot stage optical microscopy results. Based on Table 3, Fig. 1 shows a plot of the isothermal crystallisation half time versus isothermal temperature. It can be seen that different kinds of PE and different MFI affect the PP crystallisation rate. The polypropylene crystallisation was faster in polyethylene with higher MFI, and also, at a higher temperature, the polypropylene did not crystallise in polyethylene with lower MFI while it crystallised in polyethylene with higher MFI. No polypropylene crystallisation was observed in the blend ULDPE2–PP at these isothermal temperatures.

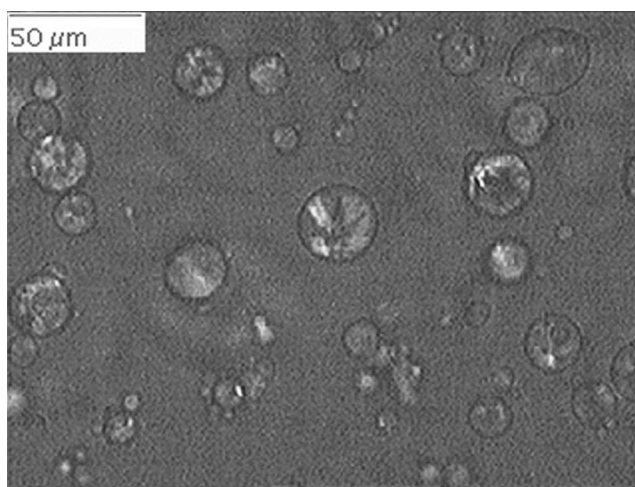


Fig. 5. PP crystals in a blend with HDPE, MFI = 20 (80%) after isothermal crystallisation at 130°C for 98 min, 200 ×.

3.1.3. Avrami analysis

The simplest way to study the kinetics of crystallisation is based on the measured isothermal crystallisation rates [7,10,11]. Such isothermal crystallisation can be described by the Avrami equation:

$$\ln(-\ln(1 - X(t, T))) = \ln k(T) + m \ln(t)$$

where $X(t, T)$ is the volume fraction of crystalline material at time t and constant temperature T , m the so-called Avrami exponent which characterises the nucleation type and the crystal growth geometry, $\ln(k)$, the crystallisation rate coefficient which is a parameter of the crystallisation growth rate.

The crystallisation rates for the blends were measured as a function of time at various crystallisation temperatures. Fig. 2 is an example of the results which show crystallisation of the PP fraction in the blend LLDPE2–PP at 120°C. Based on the data from Fig. 2, Fig. 3 shows a typical plot of the crystallisation rate versus time according to the Avrami equation.

The PP crystallisation half-times were readily calculated from the Avrami k and m values. Table 3 lists PP crystallisation half-times for the blends and pure PP. Fig. 3 is a plot of half-time versus isothermal temperature. The values of half-time were found to increase with increasing crystallisation temperature for all the polymer samples and with the addition of PE and the effects of different PE on PP crystallisation were different. The half-times for miscible blends were very large because PP was crystallising from a dilute solution. The half-times for phase-separated blends were similar to the half-time of pure PP since PP was in a high concentration in the phase-separated droplets. The half-times serve as a good guide to miscibility of PP with the various polyethylenes in the liquid state. The half-time conclusions could be confirmed by the optical microscopy observations. However in situations where the phase structure is not clear or too small to be observed by microscopy the half-times will provide a good evidence for the liquid–liquid phase structure.

3.2. Optical microscopy results

The initial crystallisation for PP, HDPE, LDPE, LLDPE1, LLDPE2, VLDPE and ULDPE were observed, under a polarising microscope with hot-stage, at temperatures of 136, 124, 100, 119, 117, 106°C, respectively. Fig. 4 is the image of PP crystals in pure PP after isothermal crystallisation for 2 h. These are typical PP spherulites where the crystals finally occupy the whole area and the amorphous regions are in the interspherulitic space. Figs. 5–9 are the images of PP crystals in the blends, HDPE–PP, LDPE–PP, VLDPE–PP, LLDPE1–PP, LLDPE2–PP, respectively. Each of the blends was crystallised isothermally in a temperature range, 124–126°C, where only PP could crystallise. The pictures were captured at the temperature of crystallisation so that the background is uniformly dark.

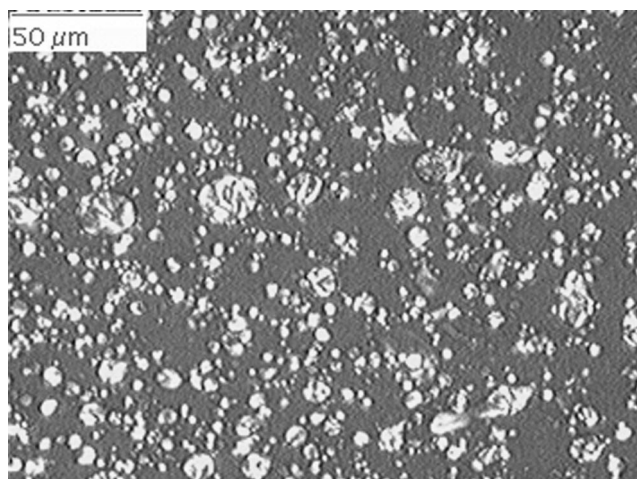


Fig. 6. PP crystals in the blend with LDPE, MFI = 22 (80%) after isothermal crystallisation at 126°C for 61 min, 200 \times .

Upon cooling, the respective PE crystallised and the background became filled with crystals of PE.

The pictures of the spherulites of PP in molten LLDPEs were not as sharp or well defined as pure PP spherulites and were not as perfect, but they could still be easily distinguished.

4. Discussion

The half-times shown in Fig. 1 can be divided into two groups: those the same as pure PP and those with very much slower times. The one exception is the half-time for the PP–LDPE blend, which crystallises with the same rate as PP until at 130°C when it crystallises much slower. The blends which crystallise with the same half-times as PP do so because they are immiscible; so PP will be a dispersed phase which will consist of all or mostly PP and so will

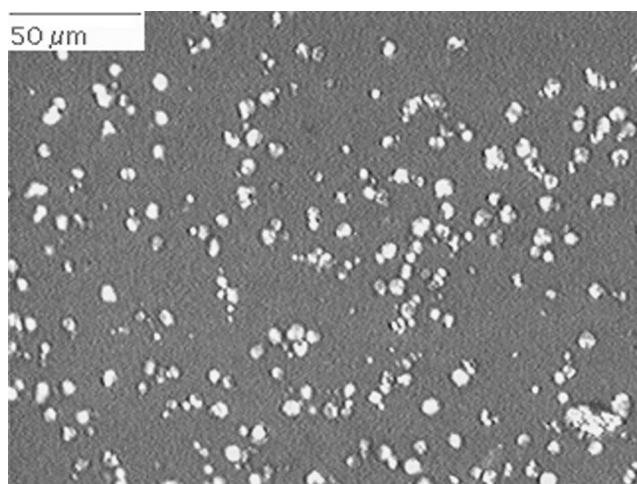


Fig. 7. PP crystals in the blend with VLDPE, MFI = 27 (80%) after isothermal at 126°C for 4 min, 200 \times .

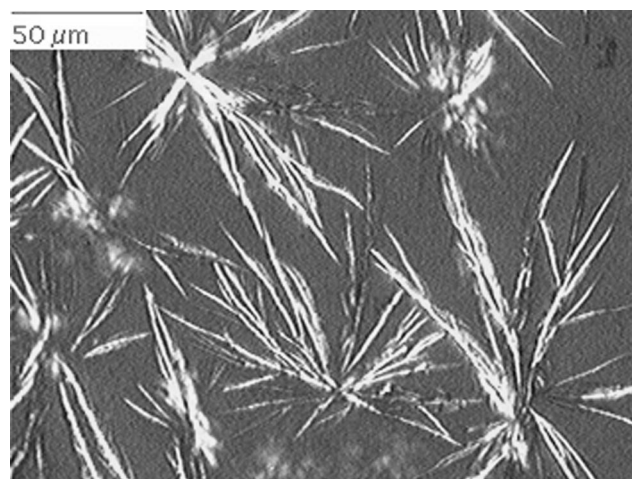


Fig. 8. PP crystals in a blend with LLDPE1, MFI = 1.0 (80%) after isothermal crystallisation at 124°C for 15 h, 200 \times .

crystallise at the same rate as pure PP. The crystallisation of PP from an immiscible dispersed phase can be seen clearly in Fig. 5 where the characteristic spherulite patterns caused by the polarised light can be seen in the droplets. Similar observations are provided in Figs. 6 and 7, although the droplets are much smaller.

Blends of PP with LLDPE 1 and 2 showed very long crystallisation half-times compared with the half-time for pure PP. The crystallisation of PP in these blends could only be observed at temperatures between 119 and 120.5°C; since at higher temperatures the time required became excessively long and at lower temperatures the LLDPE would be able to crystallise. In these blends with LLDPEs, PP was miscible and so was crystallising from solution. The LLDPE is a very viscous hydrocarbon solvent under these conditions. It is also apparent that the half-time for PP in LLDPE 2 are about half of those for PP in LLDPE 1. This can be related to the relative MFI of the polymers.

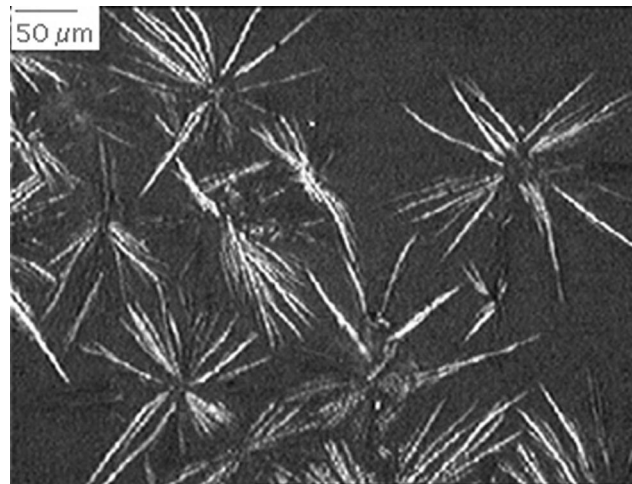


Fig. 9. PP crystals in a blend with LLDPE2, MFI = 2.5 (80%) after isothermal crystallisation at 126°C for 105 min, 100 \times .

LLDPE 2 has an MFI of 2.5 g/10 min whereas LLDPE 1 has an MFI of 1 g/10 min, so the melt of LLDPE 2 will be of lower viscosity. In the lower viscosity solution diffusion of PP to the crystal faces will be faster thereby decreasing the half-times.

The explanation of the long half-times for PP crystallising from solution in LLDPEs is confirmed by the optical microscopy pictures shown in Figs. 8 and 9. No PP droplets were observed in these blends. The PP crystals can be seen to grow from the solution in a very wispy form. The long crystallites form very open crystals which mesh together to form a sparse co-continuous phase of PP within the LLDPE. Upon cooling to ambient temperature the PP morphology will be fixed in a crystalline LLDPE matrix. This morphology is unique to this time–temperature pathway. If the blend was to be cooled continuously then the LLDPE, which crystallises faster than PP, can crystallise first or simultaneously with PP. If the LLDPE crystallises then PP will be excluded from the crystalline LLDPE matrix and form a separate phase before it then crystallises, and so a phase-separated crystalline morphology results. The unique co-continuous type PP morphology requires that PP crystallises while the LLDPE remains a liquid, thus maintaining its solvent properties.

The measurements by DSC and polarised optical microscopy can be used to determine the solubility of PP in blends with PEs, in addition to creating the unique co-continuous morphology in the solid state. Future papers will study the effect of the PP type and further expand on the types of LLDPE and the effect of other concentrations of PP.

5. Conclusion

This research has demonstrated the crystallisation of PP in different types of PE and indicated that PP is only soluble in the LLDPEs. Blends have been prepared where

crystallisation of the polypropylene takes place from a homogeneous melt, or solution in molten polyethylene; or from a phase-separated mixture. The morphology is distinctly different in each case and the rates of crystallisation clearly show whether a homogeneous or phase-separated blend is present. Crystallisation of polypropylene in the phase-separated blend is similar to phase separation of bulk polypropylene, though each phase is expected to contain some amount of the other polymer. The crystallisation of polypropylene from solution in LLDPE is very slow as would be expected from a relatively dilute solution. Polypropylene is present as a minor component in the solution yet when slowly crystallised over several hours the crystals can grow throughout the volume forming a co-continuous structure of very fine sparse crystals. This unique morphology is expected to have different properties to those of a rapidly cooled melt where the polyethylene will crystallise first.

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