

Review

TIME-DEPENDENT MORPHOLOGY OF POLYETHYLENE-POLYPROPYLENE BLENDS

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Abstract The effect of time-temperature treatment on morphology of polyethylene-polypropylene (PE-PP) blends was studied to establish a relationship between thermal history, morphology and mechanical properties. Polypropylene (PP) homopolymers were used to blend with various polyethylenes (PE), including high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and very and ultra low density polyethylene (VLDPE and ULDPE). The majority of the blends were prepared at a ratio of PE:PP = 80:20, while blends of PP and LLDPE were prepared at various compositions. Thermal treatment was carried out at temperatures between the crystallization temperatures of PP and PEs to allow PP to crystallize first from the blends. On cooling further, PE crystallized too. A very diffuse PP spherulite morphology in the PE matrix was formed in some partially miscible blends when PP was less than 20% by mass. Droplet-matrix structures were developed in other blends with either PP or PE as dispersed domains in a continuous matrix, depending on the composition ratio. The scanning electron microscopy (SEM) images displayed a fibrillar structure of PP spherulite in the LLDPE-PP (80:20) and large droplets of PP in the HDPE-PP (80:20) blend, providing larger surface area and better bonding in the LLDPE-PP (80:20) blends. This explains why the blends with diffuse spherulite morphology showed greater improvement in tensile properties than droplet-matrix morphology blends after time-temperature treatment.

Keywords Polypropylene and polyethylene blends, Thermal history, Spherulite, Morphology, Mechanical properties

INTRODUCTION

It is well known that the morphology of an immiscible polymer blend depends on its components, miscibility and processing conditions. For most immiscible heterogeneous systems one phase distributed in another phase has been widely observed. For example, in the polypropylene-linear low density polyethylene (PP-LLDPE) blends the morphologies are dependent on the compositions, both PP and LLDPE can be a continuous phase. Figure 1 shows the morphologies of different components of PP-LLDPE blends. It is seen that when the PP content is high, PP spherulites were clearly identifiable and LLDPE appeared as domains in the PP matrix (Figs. 1b and c). When the PP content was low the PP spherulites disappeared and LLDPE became the continuous phase (Figs. 1d and e).

A characteristic feature of most heterogeneous systems is that change of temperature leads to phase changes, *i.e.* the existence of upper critical solution temperature (UCST) and lower critical solution temperature (LCST). Figure 2 shows a schematic representation of UCST and LCST. PP and PE blends usually display an UCST.

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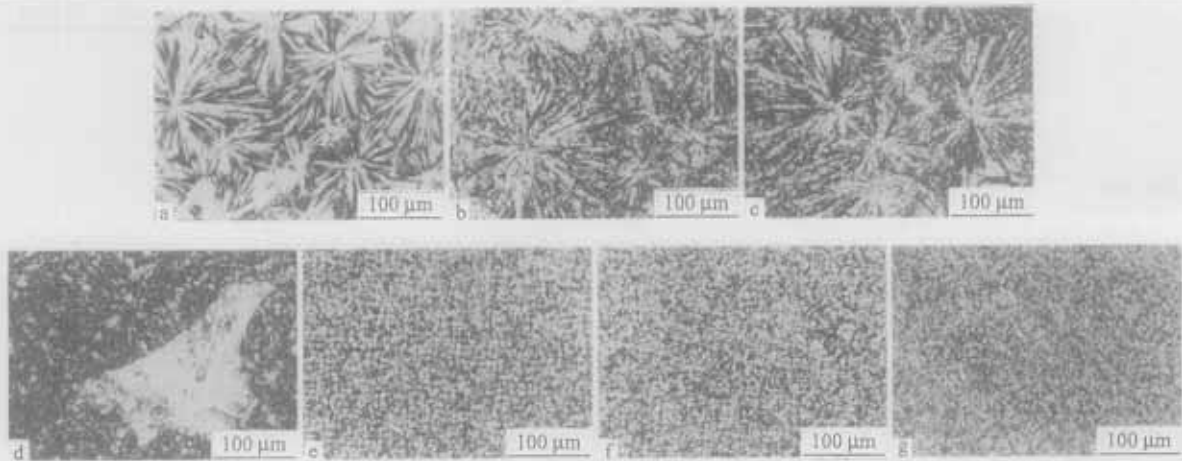


Fig. 1 Morphology of PP-LLPDE blends cooled at 5 K/min

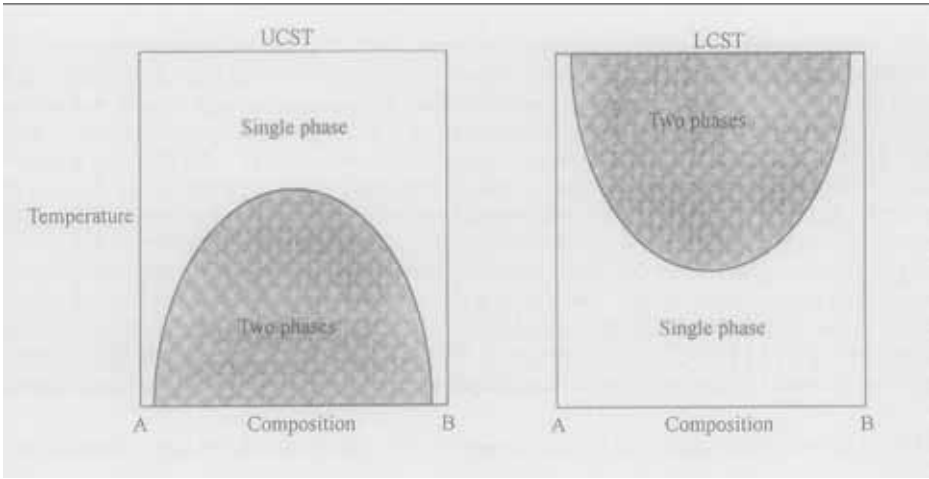


Fig. 2 Schematic phase diagrams for binary blends showing upper critical solution temperature (UCST) and lower critical solution temperature (LCST) behavior

Figure 3 shows a schematic representation of a temperature and component dependent phase diagram for PP-LLDPE blends. It is shown that above the UCST line the system is homogenous. Previous studies have shown that at temperatures high enough to prevent crystallization, PP and PE are miscible with supercritical propane in all proportions^[1, 2]. The morphologies of a solid blend depend on the ratio of the components, A:B. Generally, the major component forms a continuous matrix phase and the minor component forms discrete domains^[3], as illustrated in Fig. 4(a). A co-continuity semi-IPN morphology may be formed at around 50:50 composition ratio^[3] shown in Fig. 4(b).

However, this general phase diagram does not consider another important factor, time. Yu *et al.*^[4, 5] first reported that, if the time was long enough, isothermal crystallization of PP in molten PE could develop a diffuse spherulite morphology, although PP was only 20% in the blend. Such isothermal crystallization was achieved by cooling the blends to a particular temperature just above the UCST line and holding the blends at this temperature for an extended period. At this temperature, only PP was able to crystallize and PE was in the molten state. Therefore, a new factor, time, has to be taken into consideration in the study of the phase diagram and morphology of blends.

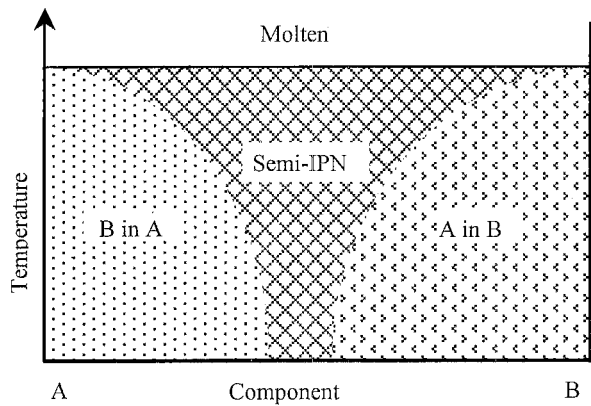


Fig 3 Schematic representation of temperature and component depend phase diagram for PP-LLDPE blends

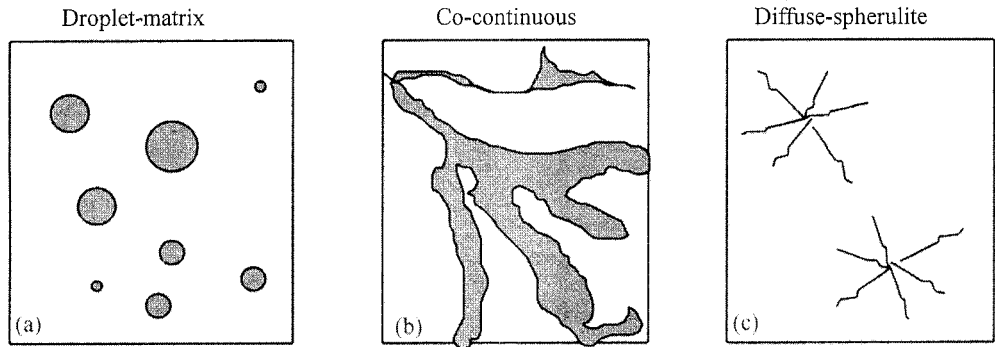


Fig. 4 Illustration of three different morphologies of polymer blends

The morphology of diffuse spherulites formed under this condition is illustrated in Fig. 4(c). Such a spherulitic structure leads to a unique phase structure in the blend, in which the minor component can develop an extended spherulitic structure instead of small crystals confined in droplets. These diffuse spherulites are also different from the compact spherulites that are usually observed in pure PP.

In this paper, the detailed study of various PE's and the effect of melt flow index (MFI) of both PP and PE on the morphologies under different thermal treatments will be reported. The effect of the morphologies on mechanical properties will also be discussed.

THERMAL PROPERTIES OF THE BLENDS

Melting and Crystallization of Blends

Figure 5 shows melting curves of polymers and blends, at 10 K/min heating condition. 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. 6 is complicated by two facts. Firstly that in a normal cooling regime the main crystallization temperature of PP is close to that of HDPE so that the two peaks overlap; secondly PP gives rise also to some lower temperature crystallization peaks. Accordingly, the HDPE-PP (80:20) blend showed only a single peak between the crystallization temperatures of PP and HDPE, which was broader compared with the peaks of PP and HDPE. A new exothermic peak appeared in the LDPE-PP (80:20) blend at around 80°C in addition to the normal crystallization peaks of PP and LDPE. Similarly, the peak at the normal

crystallization temperature of PP disappeared in the LLDPE-PP (80:20 and 90:10) blends, while again a new peak appeared at 88°C, which is in the same temperature range as the additional peak in the LDPE-PP (80:20) blend.

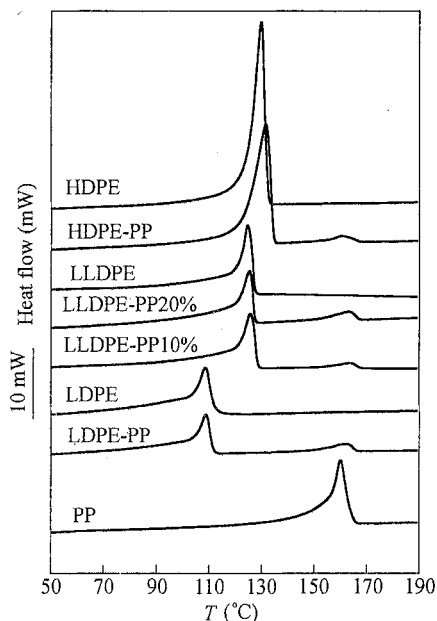


Fig. 5 DSC melting curves of polymers and blends, at a heating rate of 10 K/min

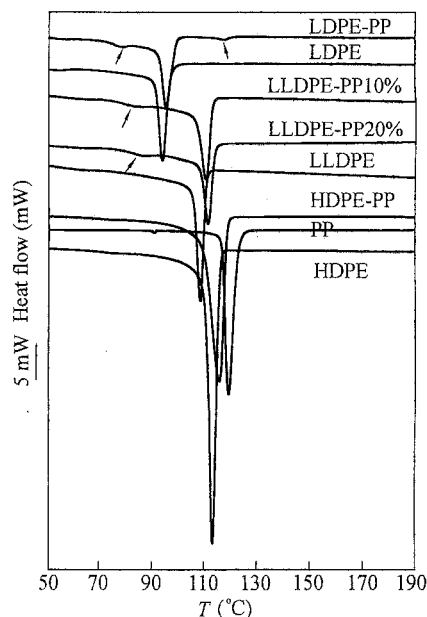


Fig. 6 DSC crystallization curves of polymers and blends, at a cooling rate of 10 K/min

The additional lower-melting peaks in LDPE-PP (80:20) and LLDPE-PP blends, which have been identified as the crystallization of PP^[6,7] admit two possible interpretations. The first is that the PP was able to dissolve in the molten LLDPE. On cooling to the temperature range of PP crystallization, the concentration of PP in the PE-rich matrix is too low to form nuclei, and hence the crystallization of this PP is delayed. Only immediately upon crystallization of LLDPE, the concentration of PP in the melt increases to the point where PP is able to crystallize at a lower temperature. Furthermore, the crystalline LLDPE could act as nuclei for the crystallization of PP. The additional lower temperature peaks in the LDPE-PP (80:20) blend could be explained in the same way, with this dissolved fraction of PP crystallizing after LDPE as in the LLDPE-PP (80:20) blend, while the undissolved fraction in the LDPE-PP (80:20) blend was observed to crystallize at the normal higher temperature.

A second interpretation for this lower melting peak was given by Dong *et al.*^[6] where its origin was attributed to the smaller droplets of dispersed PP, which did not contain heterogeneous nuclei so as to crystallize 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 crystallization of the LDPE. These mechanisms are not mutually exclusive, but a choice between them can be made by referring to the results of Li *et al.*^[7] where it was found that as the concentration of PP increased from 10% to 25%, while the higher crystallization 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 polyethylenes and the crystallization curves, it seems that heterogeneous nucleation dominated in the HDPE-PP (80:20), LDPE-PP (80:20) blends, and LLDPE-PP (25% and more PP) blends, and homogeneous in the LLDPE-PP (10% and 20%) blend.

In a blend of PP with very low density polyethylene (VLDPE), the stronger peak of VLDPE shifted to a higher temperature (approximately 2 K higher) and a small shoulder appeared in the lower temperature region,

the weak peak of VLDPE remained in its original position and the crystallization temperature of PP shifted slightly towards VLDPE (Fig. 7). As a change in crystallization temperature is a typical indication of the partially miscible behavior, it can be postulated that the PP was miscible with this VLDPE at elevated temperatures.

Another possibility causing changes in crystallization temperatures could be the migration of nuclei from the PP to the VLDPE^[8,9]. The VLDPE was able to crystallize at a much higher temperature because of abundance in heterogeneous nuclei, which migrated from PP phase to the VLDPE phase during blending.

Double PP exotherms were observed in a ULDPE-PP (80:20) blends (Fig. 8). The double PP peaks in the ULDPE-PP blend may be caused by the different solubility of fractions of PP molecules in the ULDPE, which are separated by either an isotacticity difference or variations in the molecular weight distribution. The ULDPE may dissolve the less isotactic (or smaller PP) molecules more easily than the more stereoregular (or larger) molecules during blending and in the molten state. On cooling the PP molecules with more stereoregular (or larger) molecules can crystallize first, whereas the less isotactic (or smaller) molecules would only crystallize at a lower temperature after they were released by the ULDPE.

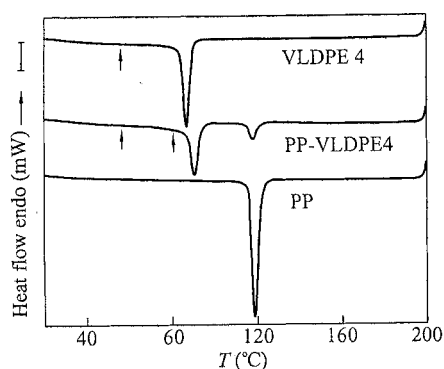


Fig. 7 DSC crystallization curves of PP, VLDPE and their blend, at a heating rate of 10 K/min

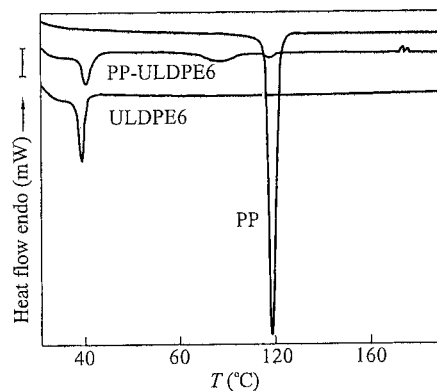


Fig. 8 DSC crystallization curves of PP, ULDPE and their blend, at a cooling rate of 10 K/min

Isothermal Crystallization Rate of PP in Molten PE

Figure 9 shows the crystallization half-time values of PP for the PP and five blends. This crystallization kinetics study was carried out in a temperature range of 119°C to 130°C by differential scanning calorimetry (DSC). Over this range, the PEs either did not crystallize, or their crystallization rates were too slow, not comparable to the crystallization rate of PP. The isothermal crystallization results were analyzed by the Avrami equation.

It can be seen that the type of PE used in the blends affected the crystallization rate of PP (Fig. 9). The crystallization half-time of PP in the HDPE-PP (80:20) and LDPE-PP (80:20) blends were of the same magnitude as that of pure PP. However, the half-time of PP in the LLDPE-PP (80:20) blends was more than ten times greater than that for the pure PP at a given crystallization temperature. With an increase in crystallization temperature, the difference between half-times in the LLDPE-PP (80:20) blends and in the PP increased.

The crystallization rate of PP in a VLDPE-PP (80:20) blend changed significantly with temperature. Between 124°C and 128°C, the rate in the VLDPE-PP blend was the same as that in the pure PP. However, the crystallization rate decreased drastically when the temperature increased above 130°C.

The melt flow index (MFI) was also found to influence the crystallization rate of PP in the molten PEs. Figure 10 shows the crystallization half-time versus crystallization temperature for a PP and its blends with three LLDPEs. The half-time of the PP crystallization increased with decreasing MFI, indicating that the more viscous LLDPE retarded PP crystallization to a greater degree.

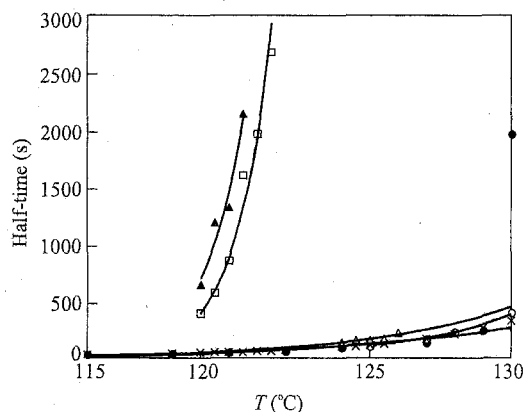


Fig. 9 Crystallization half-time of PP in pure PP and its blends with various PEs

[×] Refer to PP; [▲] PP-LLDPE1; [□] PP-LLDPE2; [○] LDPE-PP (80:20); [△] PP-HDPE; [●] PP-VLDPE1

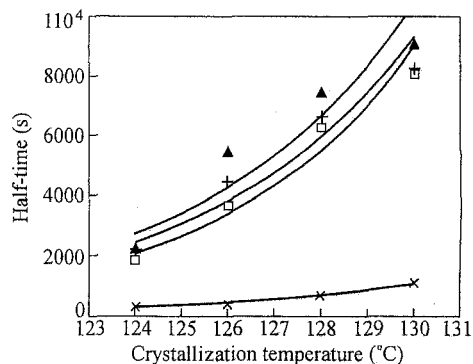


Fig. 10 Crystallization half-time of PP versus isothermal crystallization temperature for the pure PP8.5 and its blends with LLDPEs

[×] PP8.5; [▲] PP8.5-LLDPE0.78; [+]
PP8.5-LLDPE1; [□] PP8.5-LLDPE2.5.

MORPHOLOGY OF THE BLENDS

Spherulite Structure of PP in the Blends

Figure 9 shows a polarized optical image of PP crystals, following isothermal crystallization at 130 °C. Typical PP spherulites with the Maltese cross pattern were observed. It was also observed that, under isothermal crystallization at 130 °C, the PP spherulites occupied the whole area after approximately 20 min, and the amorphous regions were in the inter-spherulitic areas.

PP displayed a range of crystal morphologies in PE-PP blends at isothermal crystallization temperatures above the crystallization temperatures of PEs. In contrast, the homopolymer formed compact spherulites (Fig. 11). The PP appeared as large droplets in the HDPE melt as shown in Fig. 12. Inside the droplets, the spherulite pattern was still well distinguished. Similar PP droplets were also observed in the LDPE-PP (80:20) blend^[5, 10, 11]. However, the droplets were smaller than those in the HDPE-PP (80:20) blend, showing a more dispersed distribution of the PP phase in the LDPE, and indicating better compatibility between the LDPE and the PP. The optical microscope observation indicated that HDPE-PP (80:20) and LDPE-PP (80:20) blends were immiscible at crystallization temperatures, because the PP crystallized in phase-separated domains in these blends.

The PP crystallized as open-armed, diffuse spherulites in molten LLDPEs in the LLDPE-PP (80:20) blends with less than 20% of PP present (Fig. 13)^[7]. The spherulites of PP in molten LLDPEs were not as sharp or as well defined as in the pure PP, but 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 in the blend, and the consumption of previous crystallization.

The reason for formation of such diffuse spherulites has been proposed^[12]. During crystallization, the PP intended to crystallize on its own, rejecting foreign components. The concentration of non-crystallizable foreign components (molten LLDPE) was high in the less than 20% PP blends. Additional work has to be done by the growing spherulites to reject LLDPE, and the formation of new lamellae was sacrificed in favor of thickening of the existing lamellae. Therefore, 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^[13].

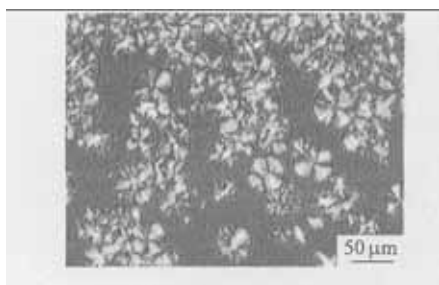


Fig. 11 PP spherulites after isothermal crystallization at 130°C for 5 min



Fig. 12 PP droplets in HDPE-PP blend after isothermal crystallization at 128°C for 44 min

The open armed, diffuse spherulites are often observed in highly diluted miscible or partially miscible blends, such as *isotactic* PP-*atactic* PP blend^[14] and PP-ethylene propylene rubber^[12]. However, the diffuse spherulites observed under an optical microscope are in fact open clusters of droplets connected by bridging lamellae as reported under a transmission electron microscope (TEM)^[11], and they have an appearance of bunches of small birefringent grapes.

Crystal morphology observed in a PP-VLDPE blend was dependent on the temperature^[15]. At 124°C, the PP crystallized in droplets in the PP-VLDPE blend, similar to those in the PP-HDPE blend. However, the droplets are much smaller so that the spherulite pattern could not be observed. When the crystallization temperature was raised above 130°C, the PP crystals were diffuse, similar to those in LLDPE-PP with less than 20% PP present. The optical microscope observations indicated that the PP was immiscible with this VLDPE at temperatures below 130°C, but miscible with the VLDPE at temperatures above 130°C.

The PP crystals were observed to be fine in an ULDPE-PP (80:20) blend by the optical microscope (Fig. 14). The crystals were not as bright as in the other blends. The crystalline fraction of PP in this blend was significantly smaller compared with those in other blends. The image of a ULDPE-PP (80:20) blend at room temperature after crystallization at 115°C for 21 h, reveals very diffuse PP crystals in a dark amorphous background, showing that this ULDPE was non-crystalline although at room temperature.

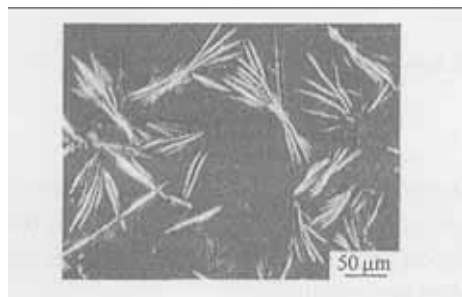


Fig. 13 Diffuse PP spherulites in LLDPE-PP (15%) blend after isothermal crystallization at 126°C for 160 min

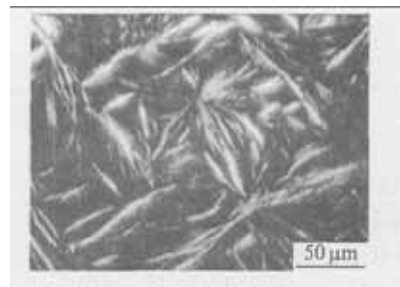


Fig. 14 Crystal structure of a ULDPE-PP blend at room temperature after isothermal crystallization at 115°C for 21 h

Effect of Time on Morphology

Figure 15 presents two images of a PP-VLDPE blend at different times during isothermal crystallization at 130°C. Both droplets and solution grown PP crystals were present at a crystallization time of 80 min (Fig. 15a). With an increase in the crystallization time, the number of droplets increased and the solution grown spherulites became less distinguishable. After 115 min, the solution-grown spherulites were not observable and more droplets appeared as shown in Fig. 15(b). The increase in the number of droplets with time indicated that the degree of phase separation increased with time. This phenomenon was also observed in a LLDPE-PP (30%) blend, while crystallization competed with phase separation at an early stage of crystallization, finally phase separation dominated^[7].

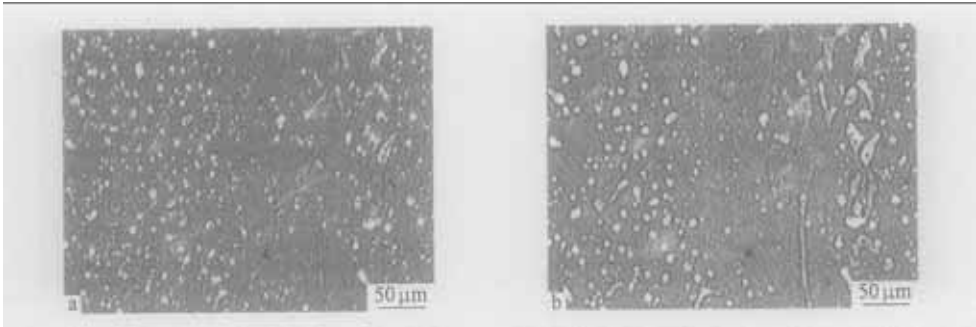


Fig. 15 PP droplets and spherulites in a VLDPE-PP (80:20) after isothermal crystallization at 130°C for (a) 80 min, (b) 115 min

Effect of MFI on Spherulite Growth Rate

The effects of varying LLDPE on the PP spherulite growth rate were different. The same PP grew slower in the LLDPEs with a smaller MFI (Fig. 16). In addition, the PP with lowest MFI exhibited the slowest growth rate for a given LLDPE^[16] although the spherulite growth rate of the PP did not follow the same trend.

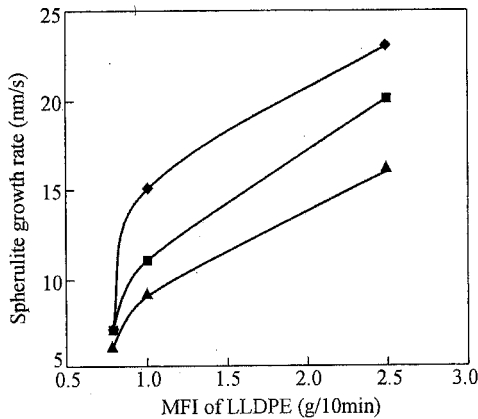


Fig. 16 Spherulite growth rate of PP in the PP-LLDPE blends as a function of MFI of LLDPE at a crystallization temperature of 124°C
[◆] PP40; [■] PP8.5; [▲] PP2.5

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. Therefore, the diffusion speed of PP was slower in the LLDPE with a lower MFI and so was the spherulite growth rate.

A decrease in PP spherulite growth rate in the miscible blends has also been observed previously. Keith and Padden^[14] 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 *isotactic* PP (*i*PP) and *atactic* PP (*a*PP) were typically miscible systems. The influence of MFI on spherulite growth rate of PP suggests that PP and LLDPE are partially miscible.

Lamellar Structure of the Blends

Figure 17(a) shows a fibrous structure of PP spherulites and small PP droplets less than 1 μm diameter in a LLDPE matrix, located in the upper-left side of the image. It is seen that the fibrillar structure of the PP grew out of the PP phase and penetrated into the LLDPE phase. The LLDPE was distributed in between and around the arms of PP spherulites. However, small droplets were also present, which could be barely seen by the optical microscope. Nevertheless, the diffuse spherulite structure was the dominant feature, because the crystalline

volume of long crystals was much larger than that observed in the droplets. Figure 17(b) shows larger PP droplets with rounded and smooth edges in the HDPE matrix, displaying a smoother and smaller interface between the PP and HDPE than that observed between the PP and LLDPE.

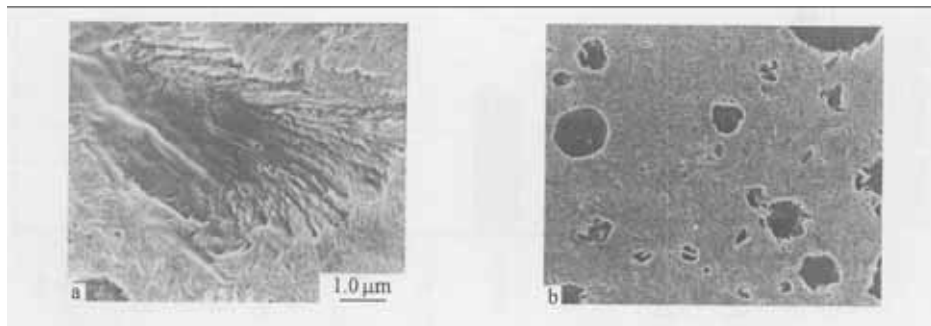


Fig.17 a) SEM of the LLDPE1 (80%)-PP (20%) blend, magnification $\times 2000$
b) SEM of the HDPE (80%)-PP (20%) blend, magnification $\times 1200$

Effect of Thermal Treatment on the Mechanical Properties

Figure 18 shows the tensile test results of polymers and the blends both after oven thermal treatment and conventional cooling. Thermally treated samples were melted at 200°C for 10 min and left for PP to crystallize at 130°C for 5 h, followed by normal cooling. It can be seen that thermal treatment improved tensile properties for most materials.

Young's modulus and strain at break are clearly seen to increase for all the materials except the PP. The most significant increases were seen for the two LLDPE-PP (80:20) blends. The Young's modulus and the strain at break increased by approximately 40% for two LLDPE-PP (80:20) blends, and approximately 20% for the VLDPE-PP (80:20) blend, but by a smaller amount for PP blends with the LDPE and HDPE.

Considering the experimental errors, the yield strength was unchanged for most blends and pure polymers except the PP, VLDPE, and the blends of PP with the HDPE and VLDPE (Fig. 18). The effect of thermal treatment on the yield strength was not as significant as on the modulus and strain at break. It is interesting to note that the yield strength of the VLDPE-PP (80:20) blend increased by almost 20%, although the yield strength of both the PP and the VLDPE decreased after thermal treatment.

Since the work by Schotland^[17] on pure PP, the idea that thermal treatment increases the tensile properties (modulus and yield strength) of pure polymers has been widely accepted. In this study, the reason for the decreased strain at break and strength for the PP was that the thermally treated PP samples broke before they reached a maximum value. The reasons for decreased yield stress in the VLDPE and the HDPE-PP (80:20) blend after thermal treatment were complex. Possible reasons could be larger crystal size, which was caused by coalescence of phase-separated droplets with increasing annealing time^[18] and weak interfacial boundaries after annealing^[19].

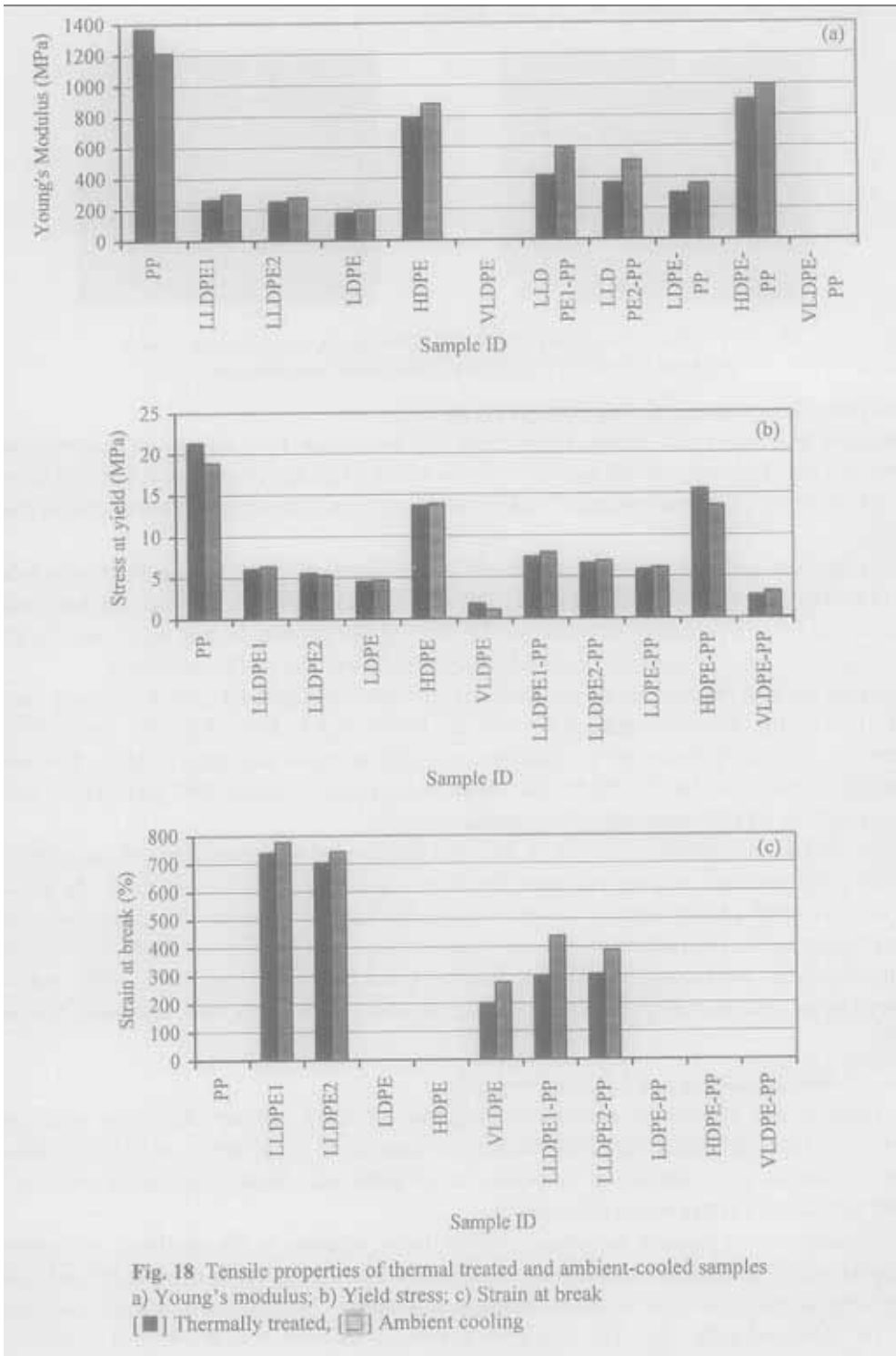
Correlation between Morphology and Tensile Properties

The three elements that dictate the mechanical properties of these polymer blends are total crystallinity, morphology and interfacial properties. Deterioration of mechanical properties is a result of the two-phase structure of the blends. Low mechanical properties of the polyolefin blends are a result of poor interfacial adhesion and poor stress transfer between the phases.

Thermal treatment can promote the inter-crystalline links (adhesion at the interface), as demonstrated by Varin and Djokovic^[20]. Their SEM images showed that there were 'ridging' bonds between PP and HDPE phases in annealed samples, which were not found in unannealed samples. Upon thermal treatment, the entanglements of PP and PE increased with time. The improved interfacial adhesion also provided a contribution to the improved tensile properties of treated samples in this study.

Thermal treatment is also expected to promote the crystallinity^[20]. An increase in crystallinity would contribute to an increase in modulus but lower strain at break due to thicker lamellae. In this work, the thermal

treatment improved the overall crystallinity of the blends and the perfection of PP crystals^[10], and therefore provided an enhancement of modulus as well as strength.



The formation of the diffuse spherulite-matrix morphology played an important role in the significant improvement of tensile properties of the LLDPE-PP (80:20) blends. This morphology strengthened the interface

between the PP and LLDPE phases by the presence of diffusely crystallized PP spherulites and a fibrillar structure. Not only the modulus and yield stress but also the ductility was significantly improved after thermal treatment in these blends.

The diffuse spherulite-matrix morphology exhibited significantly improved strain properties after annealing, and this morphology only developed in LLDPE-PP (80:20) blends because PP was miscible with LLDPE at elevated temperatures. In the miscible blends, the growth of PP spherulites in the PE phase was possible and PP could crystallize as open-armed spherulites in the LLDPE. The PP had a very large surface in contact with the LLDPE, so this would increase the interfacial bonding, leading to better strain properties. In the immiscible blends, there were already two phases prior to crystallization, the PP could only crystallize in the phase separated domains. The phase boundary in the droplet-matrix was smooth as shown in Fig. 17(b), indicating that the bonding between PP and PEs was much weaker in the PP-HDPE blend.

Moreover, the fibrous crystals (Fig. 17a) penetrating into the LLDPE reinforced the LLDPE like stiff fibrous filler particles (the Young's modulus of the PP was 5–6 times of that of the LLDPEs). Clearly, the greater increase in the modulus and strain at break for the PP-LLDPE blends compared with all other blends demonstrated that this unique solution grown morphology (Fig. 13) and fibrillar structure (Fig. 17a) provided mechanical properties analogous to those observed in a fibrous reinforced composite.

CONCLUSION

Isothermal crystallization of PP in molten PE formed different PP crystal structures in a range of blends. PP crystallized as open-armed diffuse spherulites in LLDPE-PP (80:20) blends when the PP concentration was below 20%, and in some VLDPE-PP (80:20), ULDPE-PP (80:20) blends, while in LDPE-PP (80:20) and HDPE-PP (80:20) blends, PP crystallized in phase separated droplets.

Blends with controlled morphologies, which were developed by isothermal crystallization of PP in molten PE, showed improved Young's modulus and elongation at break over the same blends with a continuous cooling history. In particular, the open-armed diffuse spherulitic structure displayed significantly superior tensile properties to the droplet-matrix morphology. The reason is that the diffuse spherulitic structure strengthened the interface between PP and LLDPE, and the fibrillar-like lamellae reinforced the blends similar to a fibrillar filler.

The diffuse spherulite morphology was only developed in the partially miscible blends while PP was crystallizing from a dilute solution. This morphology displayed significant improvement in the mechanical properties and provided important information for further applications. If crystallization of PP was performed by continuous cooling instead of isothermal treatment, a conventional droplet-matrix morphology would have formed in the LLDPE-PP (80:20) blends. Therefore, time-temperature treatment is important in the control of the morphology of blends.

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