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Studies on simultaneous crystallization of polypropylene/nylon 12 blends

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The effect of the morphology of polypropylene (PP)/nylon 12 (PA12) blends on their crystallization behaviour is studied using differential scanning calorimetry and scanning electron microscopy. In PP/maleated polypropylene (PP-MA)/PA12 = 65/10/25 blend, simultaneous crystallization of the PP/PA12 blend occurs under some conditions. When the diameter of the dispersed phase (PA12) is smaller than 0.5 μm, PP crystallizes first and its crystals induce the crystallization of PA12. When some of the PA12 particles are larger than 0.5 μm, this part of PA12 crystallizes first. Then this part of the PA12 crystals induces the crystallization of PP, and PP crystals induce the crystallization of PA12 fine droplets in turn.

(Keywords: crystallization; blends; differential scanning calorimetry)

Introduction

The morphology and crystallization behaviour of incompatible polymer blends are intricate and subtly interconnected problems. Blends with one component in suspension as finely dispersed droplets sometimes exhibit 'fractionated crystallization' as a result of crystallization of isolated melt particles nucleated by various nucleating species[1–3]. Frensch and Jungnickel studied the fractionated crystallization of nylon 6 (PA6)/poly(vinylidene fluoride) (PVF_2) and poly(butylene terephthalate) (PBT)/PVF_2 blends[4]. For blends of PA6/PVF_2 = 15/85, vigorous mixing brought forth only one d.s.c. exothermic peak at 140°C, the crystallization temperature of pure PVF_2. They thought that PVF_2 crystals induced the simultaneous crystallization of PA6 in the blends of PA6/PVF_2 fine dispersion.

The present authors[5] noticed a similar phenomenon in blends of maleated polypropylene (PP-MA)/PA6 at <50% PA6. It is probable that PA6 crystals induced the crystallization of PP-MA. In this paper, we demonstrate the significant influence of morphology on the crystallization behaviour of polypropylene (PP)/nylon 12 (PA12) blends.

Experimental

Isotactic polypropylene (PP) (*MW* 26000) was from Daqing Petroleum Chemical Co. Nylon 12 (PA12) (*MW* 8500) was purchased from Polysciences Co. (courtesy of Professor Zhiliu Feng). Maleated PP (PP-MA) (*MW* 19000, degree of grafting of MA 2.46 wt%) was synthesized in this laboratory.

Blends of PP/PA12 were prepared via the following steps. In a 1000 ml three-necked flask equipped with a nitrogen inlet, PP and PP-MA were dissolved in a mixed solvent of xylene/phenol = 3/1 (v/v) at 130°C. When the dissolution was complete, a solution of the required amount of PA12 in the same solvent mixture at 130°C was added. The solution was vigorously stirred for 10 min. The polymer blends were precipitated in a hexane/ether = 3/1 (v/v) mixture and collected after 24 h, washed several times with acetone, and dried in vacuum at 60°C for 96 h.

The above blends in test tubes in argon atmosphere were subjected to heat treatment in a thermostatted oil bath (180°C) for a specified period of time. After heat treatment, sheets of the blend samples were fractured in liquid nitrogen and the fractured samples were immersed in phenol at 100°C for 10 h to make PA12 on the fractured surface dissolve completely. The etched fractured surfaces were washed with phenol and acetone and dried in vacuum. The morphology of the etched fractured surfaces of PP/PA12 blends was observed with a Hitachi S-570 scanning electron microscope after coating with gold.

The differential scanning calorimetry (d.s.c.) measurements were carried out under nitrogen with a Perkin–Elmer DSC-2C. The temperature programme was as follows:

$$40^\circ\mathrm{C} \xrightarrow{10^\circ\mathrm{C\,min^{-1}}} 200^\circ\mathrm{C}\ (\text{kept for } 7\,\text{min}) \xrightarrow{-10^\circ\mathrm{C\,min^{-1}}}$$

$$40^\circ\mathrm{C} \xrightarrow{10^\circ\mathrm{C\,min^{-1}}} 200^\circ\mathrm{C}$$

Results and discussion

Our previous results demonstrate that PP-MA improves the compatibility of incompatible PP/PA12 blends, and the change in interfacial behaviour influences the crystallization behaviour of the blends. Addition of PP-MA to a blend of PP/PA12 = 75/25 gives a smaller PA12 crystallization peak on the d.s.c. trace than in an uncompatibilized blend[6].

In the present work on the compatibilized blend of PP/PP-MA/PA12 = 65/10/25 (SPA-0), there is no PA12 crystallization peak on the d.s.c. thermogram (*Figure 1*). Annealing at 180°C for 2 h, however, gives a small PA12

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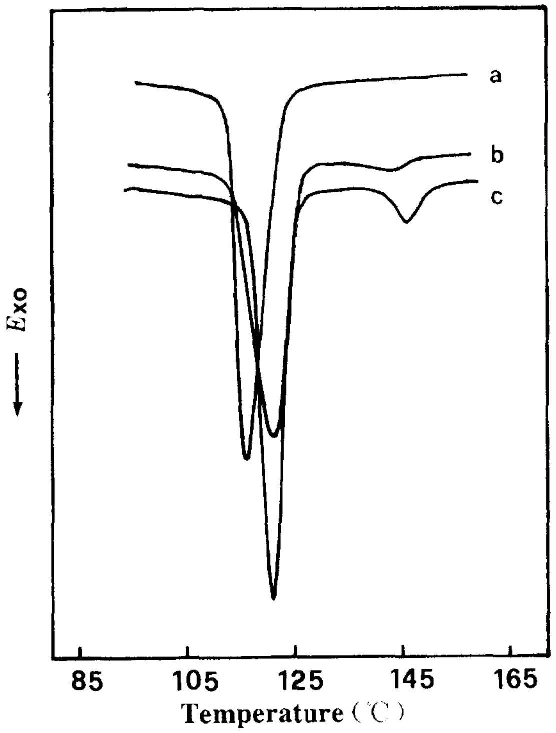

Figure 1 Effect of annealing on the crystallization behaviour of PP/PP-MA/PA12 = 65/10/25 blend: (a) original sample (SPA-0); (b) annealed for 2 h at 180°C (SPA-1); (c) annealed for 4 h at 180°C (SPA-2)

crystallization peak at 145°C, while the crystallization peak of PP widens and shifts to a higher temperature (a shift of about 6°). Longer annealing at 180°C (4 h) further increases the intensity of the PA12 crystallization peak, shifting to an even higher temperature.

When the morphology of the etched fracture surface of the blends is observed by scanning electron microscopy (SEM) (*Figure 2*), the average diameter of the dispersed phase in sample SPA-0 is at a minimum as compared to the annealed samples (SPA-1 and SPA-2), and all the particles are round in shape. Annealing for 2 h makes the fine particles partly coalesce into larger and sometimes elliptical particles. On annealing for 4 h at the same temperature, all the particles of the dispersed phase are elliptical and the average dimension increases further.

From these experimental results from d.s.c. and SEM, it is obvious that the crystallization behaviour of the blends is related to the morphology of the blends. At a small (<0.5 μm) average diameter of the PA12 particles, as in SPA-0, the normal crystallization of PA12 particles is completely suppressed, probably resulting from the fact that the number of heterogeneous nuclei that could induce normal crystallization of PA12 is smaller than that of PA12 particles. The PA12 particles in the form of supercooled liquid droplets would then not crystallize until the second-order nucleating impurity comes into play, or when homogeneous nucleation occurs. However, the melting behaviour of PP and PA12 in the above blends did not change, no matter how the PA12 phase was dispersed. Even in the case where the normal crystallization peak of PA12 was completely suppressed, the melting peak of PA12 was the same as that of binary PP/PA12 blends[6].

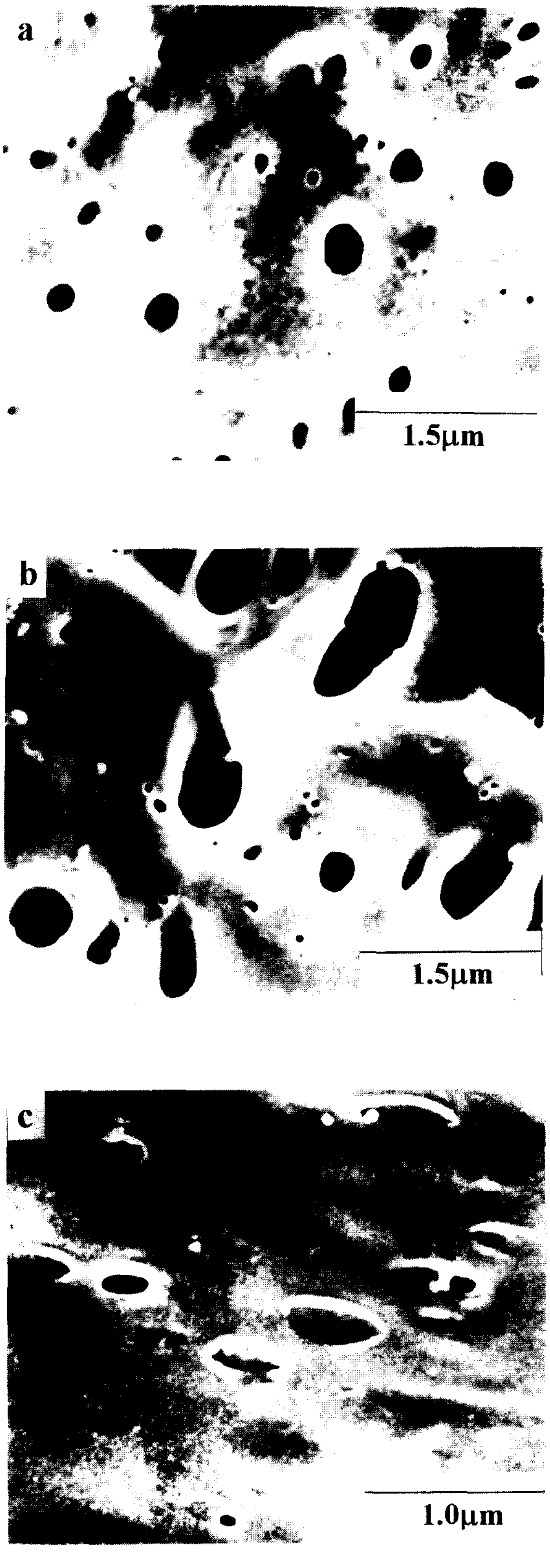

Figure 2 Effect of annealing on the morphology of PP/PP-MA/PA12 = 65/10/25 blend: (a) original sample (SPA-0); (b) annealed for 2 h at 180°C (SPA-1); (c) annealed for 4 h at 180°C (SPA-2)

It is not clear from the d.s.c. endothermic curve which component crystallizes first in the simultaneous crystallization of PP and PA12 in the unannealed compatibilized sample (SPA-0). Matching of crystallization peaks of pure PP (114.5°C) and SPA-0 (115°C, under the same

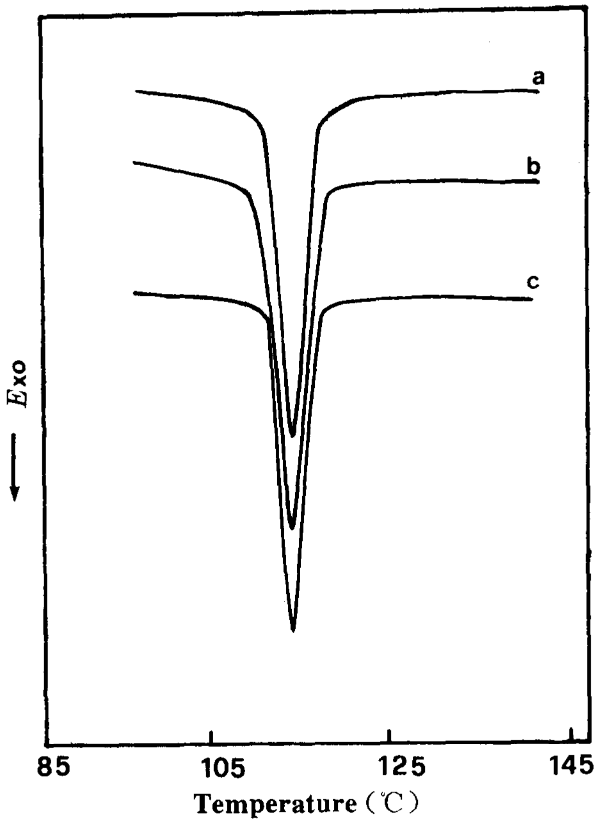

Figure 3 Effect of annealing on the crystallization behaviour of PP-MA/PA12 = 75/25 blend: (a) original sample (SPA-3); (b) annealed for 2 h at 180°C (SPA-4); (c) annealed for 4 h at 180°C (SPA-5)

testing conditions) shows that PP crystallization in SPA-0 is not influenced by the presence of PA12.

However, PA12 crystals should have a nucleating effect on PP crystallization if a part of PA12 crystallizes first in a blend of PP/PA12, just as in the SPA-1 and SPA-2 blends. Lotz and Wittmann[7] showed that the epitaxy between PP and polymers with aliphatic sequences in their chemical structure and a planar zigzag chain conformation provided a structural basis for the known, hitherto unexplained, nucleating efficiency of polyamide crystals towards PP melts. In the blends of SPA-1 and SPA-2, this expitaxial interaction results in a strong nucleation by PA12 in PP crystallization, and the crystallization temperature of PP rises.

Therefore, our experimental results show that the normal crystallization of PP occurs first in the SPA-0, and the PP crystals formed induce the crystallization of PA12 droplets. In annealed samples SPA-1 and SPA-2, PA12 crystallizes in two steps. The larger particles of PA12 formed upon annealing in the two samples crystallize first at 143 or 145°C, and then these large crystallized PA12 particles induce the crystallization of PP. PP crystals in turn induce the crystallization of PA12 fine droplets.

In the case where PP is replaced by PP-MA in SPA-0, the blend PP-MA/PA12 should have better compatibility owing to more reaction between maleic anhydride and amine groups[8]. A blend of composition PP-MA/PA12 = 75/25 (sample SPA-3) indeed has only one exothermal peak (*Figure 3a*). Annealing at 180°C for 2 h (SPA-4) or 4 h (SPA-5) does not bring about further coalescence of the dispersed phase with diameter <0.3 μm. All three samples have a crystallization peak at 114°C (*Figure 3*), the same as that of PP-MA itself. This further proves that normal crystallization of PA12 would not occur when the diameter of the dispersed phase is smaller than 0.5 μm, where the crystallization of PA12 is only induced by PP crystals.

In summary, an unusual fractionated crystallization occurs in PP/PA12 blends. The matrix (PP + PP–MA or PP–MA) and the dispersed phase (PA12) crystallize concurrently due to mutual nucleation of both components in some cases. The morphology of the blends has an important effect on the crystallization behaviour of the blends. When the diameter of the dispersed phase (PA12) is less than 0.5 μm, PP crystallizes first and its crystals induce the crystallization of PA12. When a part of PA12 particles is larger than 0.5 μm, this part of PA12 crystallizes first, then this part of the PA12 crystals induces the crystallization of PP, and PP crystals in turn induce the crystallization of PA12 fine droplets.

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