Formation of Interpenetrated Spherulites Based on Miscible Crystalline Polymer Blends

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SUMMARY: The morphology and formation process of interpenetrated spherulites of poly(butylene succinate)/poly(vinylidene choloride-*co*-vinyl chloride) (PBSU/PVDCVC) blends were investigated by confocal laser scanning microscopy (CLSM). CLSM images showed that the dense fibrils of PBSU spherulites penetrated into the sparse PVDCVC spherulites. For a blend with PBSU content 50% and crystallization temperature T_c = 368 K, the simultaneous growth of PBSU and PVDCVC spherulites was observed. After PBSU fibrils collided with PVDCVC spherulites, they kept growing through PVDCVC spherulites. For a blend with PBSU content 30% and T_c = 363 K, PBSU started to nucleate after PVDCVC spherulites filled the whole space.

Introduction

There have been many studies on polymer blends both from scientific and engineering view points[1]. Miscibility between two amorphous polymers have been studied intensively especialy in relation to phase diagram and phase separation dynamics. Miscibility between crystalline and amorphous polymers has also been examined and a number of miscible blends are known. In this case, melting point depression and crystallization dynamics of crystalline polymer in the blends have been studied intensively.

However, few studies have been reported on the miscibility and crystallization behavior of polymer blends between two crystalline polymers. A miscible crystalline/crystalline polymer blend is still a rare phenomenon and only a few pairs have been reported so far where melting temperature T_m difference for each polymer is more than 100 K. In this case, the higher-T_m component crystallizes first in the crystallization process and the other component crystallizes in the constrained condition[2,3].

Our group has been looking for miscible crystalline/crystalline polymer blends with different chemical structures with less T_m difference and almost simultaneous spherulitic growth rate for each polymer. Recently, we have found such pairs and they are poly(butylene succinate) (PBSU)/poly(vinylidene fluoride) (PVDF) with T_m difference about 45 K[4] and PBSU/poly(vinylidene choloride-*co*-vinyl chloride) (PVDCVC) with T_m difference about 35 K[5-7]. In particular, PBSU/PVDCVC blends have been found to show interpenetrated

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spherulites. We investigated their structures in detail by polarizing optical microscopy[5,6] and atomic force microscopy[7] (OM and AFM). OM and AFM studies revealed that PBSU spherulites were dense and PVDCVC spherulites were sparse. This causes the penetration of PBSU lamellae into PVDCVC spherulites.

In this invited lecture article, we report the formation process of the interpenetrated spherulites by OM and confocal laser scanning microscopy (CLSM).

Experimental

The characteristics of the samples are displayed in Table 1. The constituent polymers were dissolved into a mutual solvent N,N-dimethylformamide at about 370 K. Cast films were prepared on a glass plate and they were dried in air before the removal of the solvent in a vacuum chamber for several days at room temperature.

The spherulitic growth was observed under crossed nicols with a polarizing microscope (Olympus BHA-P) and by a blue laser confocal microscope (Lasertec VH2000). The samples were isothermally crystallized with a temperature controller (Linkam LK-600PM). After melted at 443 K for 10 min, the samples were quenched to crystallization temperatures T_c at -100 K/min. A test plate of 530 nm and a differential interference prism were used for OM and CLSM measurements, respectively, to increase contrast of the images.

Table 1. Characteristics of the samples: source, weight average molecular weight M_w, glass transition temperature T_g, and melting temperature T_m.

Sample	Source	M_w	T_g (K)	T_m (K)
PBSU	Showa Denko	140,000	241	387
PVDCVC[a]	Asahi Chemical	100,000	279	421

[a]vinylidene chloride/ vinyl chloride = 80/20.

Morphology

Figure 1 shows a CLSM image of a blended sample. Based on the birefringent pattern in an OM image, the spherulite A is assigned to a PBSU spherulite. S1 and S2 are assigned to PVDCVC spherulites which were penetrated by A (PBSU) [6]. The lamellar stacks (fibrils) were observed in Fig. 1, though the resolution was not high enough to visualize individual lamellae. The spherulites A and S1 are distinguished from each other by the population-density of fibrils; A consisted of thin and dense fibrils while S1 consisted of thick and sparse ones. This enables PBSU to penetrate into PVDCVC.

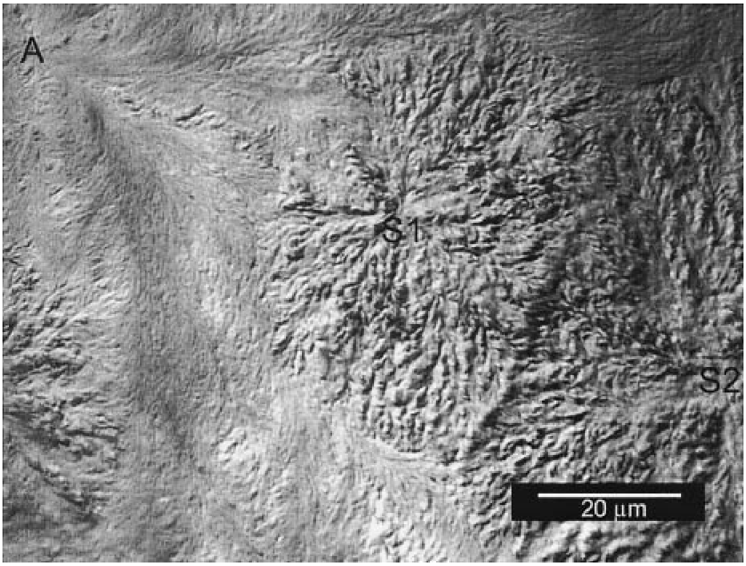

Figure 1. CLSM image of a PBSU/PVDCVC = 60/40 blend showing a dense PBSU spherulite (A) which penetrated through sparse PVDCVC spherulites (S1 and S2). T_c = 373 K.

The penetration is characterized by the spherulitic borders; The border between S1 and S2 are clearer than that between A and S1 in Fig. 1. The high contrast at the border between S1 and S2 is caused by the depression due to collision[7]. The depression characterizes the termination of fibrillar growth after collision. In contrast, Fig. 1 shows that the border between A and S1 was unclear. This indicates that A kept growing when it collided with S1.

Interpenetration process

The interpenetration process is shown in Fig. 2. When the spherulites A1, A2, and the others nucleated almost simultaneously, A1 and A2 were high contrast and the others were low contrast spherulites in Fig. 2(a). As mentioned above, A1 and A2 are assigned to PBSU and the others are PVDCVC spherulites. When the fast-growing A1 (PBSU) collided with the slowly-growing B1 (PVDCVC) in Fig. 2 (b), the border of B1 became clearer. Then, the high contrast area spread toward the opposite border through B1 (Figs. 2(c) and 2(d)). The fibrils of A1 grew along those of B1. After the fibrils of A1 penetrated through B1, it continued to grow as indicated by the arrow in Fig. 2(e). A1 and A2 stopped growing when they collided with each other (Fig. 2(e)).

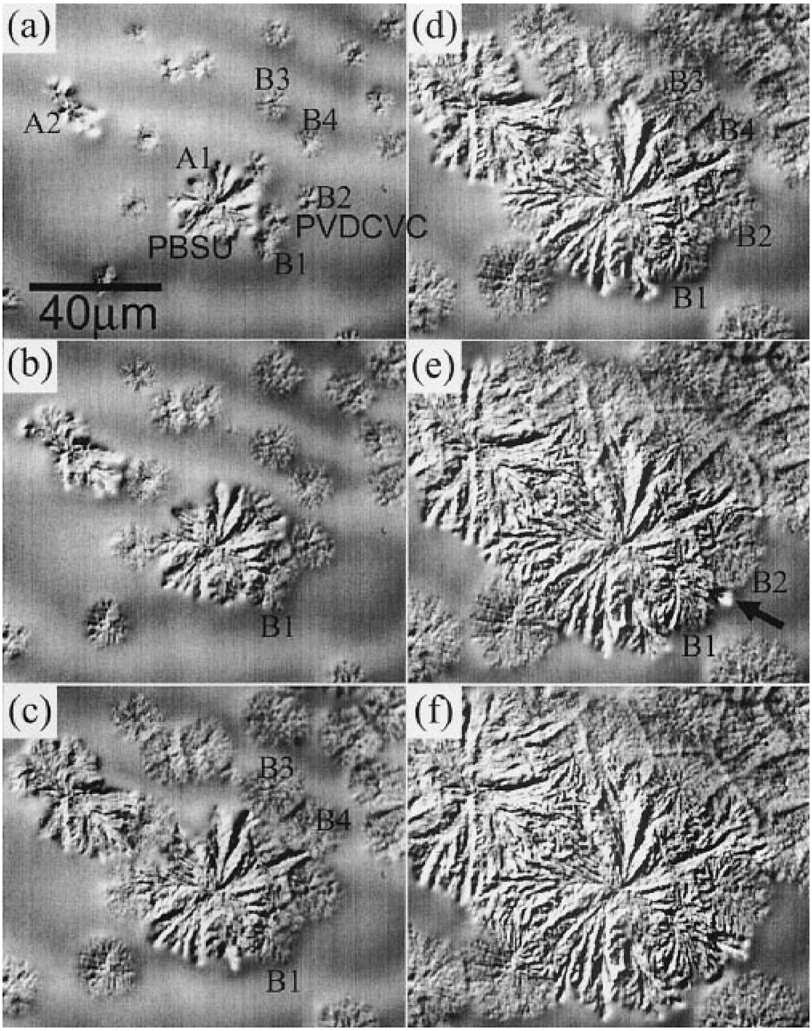

Figure 2. The process of interpenetration of a PBSU/PVDCVC = 50/50 blend crystallized at 368 K. (a) Crystallization time t = 40 min, (b) 60 min, (c) 80 min, (d) 100 min, (e) 120 min, and (f) 140 min. A1 and A2 are assigned to PBSU spherulites. B1, B2, B3, and B4 are assigned to PVDCVC spherulites.

The crystallization of PBSU in PVDCVC spherulites occurred because the PVDCVC spherulites contains a sufficient amount of amorphous PBSU in the interfibrillar regions before collision. However, the crystallization process was different between the inside and outside areas of PVDCVC spherulites. The growth rate of A1 fibrils in the inside area of B1 was slightly slower than that in the outside area of B1 (Figs. 2(d) and 2(e)). Moreover, that in the inside area of B2 was quite slow. In the inside area of PVDCVC spherulites, the PBSU fibrils grew slowly possibly because they crystallized in the restricted region between PVDCVC fibrils.

The penetration of PVDCVC into PBSU was not observed, as discussed in the previous work[6,7]. This can be explained by the difference in crystallinity of the two specimens. Since CLSM images of PBSU spherulites showed that they have few interfibrillar gaps observable by CLSM before collision, the formation of the lamellae of PVDCVC in PBSU spherulites would hardly occur.

When T_c is close to T_m, the interpenetration process is quite different[6]. Figure 3 shows OM images of a PBSU/PVDCVC = 30/70 blend crystallized at 363 K. The dark and bright spherulites are assigned to PVDCVC and PBSU spherulites, respectively[6]. In this case, the high-T_m component PVDCVC nucleated first and filled the whole space (Fig. 3(a)). Then, the low-T_m component PBSU started to crystallize (Fig. 3(b)). Finally, PBSU spherulites filled the whole space.

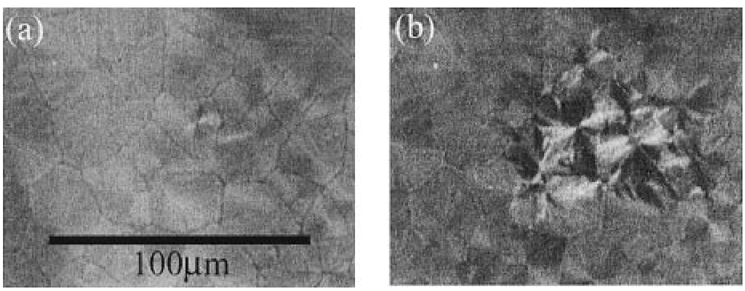

Figure 3. OM images of a PBSU/PVDCVC = 30/70 blend crystallized at 363 K. Crystallization time: (a) $t = 120$ min and (b) $t = 400$ min. The dark and bright spherulites are assigned to PVDCVC and PBSU spherulites, respectively.

Conclusion

We investigated the morphology and formation process of interpenetrated spherulites in PBSU/PVDCVC blends by CLSM. CLSM images visualized the fibrils of PBSU and PVDCVC spherulites. As in the previous study[6,7], the fibrillar population-density of PBSU spherulites was higher than that of PVDCVC spherulites in blends. This enables the PBSU fibrils to penetrate into PVDCVC spherulites. For a blend with the PBSU content of 50% and $T_c = 368$ K, two components nucleated almost simultaneously. After collision, the PVDCVC spherulites were penetrated by the PBSU fibrils. The growth rate of PBSU fibrils in the inside area of the PVDCVC spherulite was slower than that in the outside area of the PVDCVC spherulite. This is possibly because PVDCVC fibrils are obstacles to crystallization of PBSU fibrils. For a blend with the PBSU content of 30% and T_c = 363 K, PBSU started to nucleate after PVDCVC spherulites filled the whole space.

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