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NOTES

Observation of Interpenetrated Spherulites by Confocal Laser Scanning Microscopy

Satomi HIRANO, Yasuhiko TERADA, Takayuki IKEHARA, and Toshio NISHI

Department of Applied Physics, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Poly(butylene succinate)/poly(vinylidene chloride-*co*-vinyl chloride) (PBSU/P(VDC-VC)) is a miscible semicrystalline/semicrystalline polymer blend system in the melt state. The small difference of melting temperature between the two components enables them to crystallize simultaneously over a wide range of compositions and isothermal crystallization temperatures. In general, when two spherulites collide with each other, they stop growing and a clear boarder is observed by polarizing optical microscopy (POM).[1,2] In PBSU/P(VDC-VC) blend systems, however, PBSU lamellae continue to grow along P(VDC-VC) lamellae after PBSU spherulites collide with P(VDC-VC) spherulites, and interpenetrated spherulites are observed by POM. POM also shows that the birefringent pattern of a PBSU spherulite in certain crystallization conditions is neither positive nor negative; it is rotated by about 45° from positive or negative spherulites.

The investigations of these blends by atomic force microscopy (AFM)[3] showed the following results. The lamellar direction in PBSU spherulites with neither a positive nor negative pattern was not parallel to the radial direction but inclined by about 45°. This explains its birefringent pattern. In addition, the population-density of the lamellae in P(VDC-VC) spherulites was lower than that in PBSU spherulites. This enables PBSU lamellae to penetrate into P(VDC-VC) spherulites. The penetration was characterized by the change in the lamellar direction of PBSU and the absence of depression in the height profile on the spherulitic border between PBSU and P(VDC-VC).

POM is one of the most common methods to observe the time evolution of spherulites. However, the spatial resolution of POM restricts detailed investigations on the microstructure down to the lamellar level. On the other hand, AFM has high resolution sufficient to observe individual lamellae though its narrow scan area (~20 μm×20 μm) and long scan time (~min) are sometimes inconvenient.

Confocal laser scanning microscopy (CLSM) needs no special treatment on samples. Its resolution is intermediate between AFM and POM, and its scan time is short (~sec). Therefore CLSM is appropriate for both static and dynamic observations of spherulites though few have been reported.[4]

In the present work, our purpose is to observe the interpenetrated spherulites in PBSU/P(VDC-VC) blends by CLSM and compare the results with those by POM and AFM. We also show the potential of CLSM in visualizing the morphology of polymer spherulites.

EXPERIMENTAL

PBSU (M_w=140000, T_m=387 K, T_g=241 K) was supplied by Showa High Polymer. P(VDC-VC) (M_w=100000, T_m=421 K, T_g=279 K) supplied by Asahi Chemical is a random copolymer of vinylidene chloride: vinyl chloride=80:20. In this study, we used PBSU/P(VDC-VC)=60/40 (wt/wt) blend films. Blends were prepared by dissolving the two components in *N*,*N*-dimethylformamide at about 380 K. The solution was then cast on glass plates and dried *in vacuum* at room temperature for 3 days to remove the residual solvent. The films were approximately 1 μm in thickness. These films were premelted at 433 K for 3 min and then quenched to the crystallization temperature T_c=373 K at a rate of -100 K min^{-1} using a temperature controller (Linkam LK-600 PM). Isothermal crystallization process was observed by POM (Olympus BHP-P) equipped with a first order retardation plate. Samples were crystallized isothermally for 2569 min, which was sufficient for PBSU to fill the whole space, and then held in air. No morphological change was observed by POM in this process.

We used reflective CLSM (Lasertec VL 2000) to observe these films. The confocal light source was the violet laser diode with a wavelength of 410 nm. It had resolutions of 0.15 μm in space and 1/30 s in time. The differential interference method was used to increase the contrast of the images. POM and AFM observations of the same area of a sample were also performed to compare morphology.

AFM (Jeol JSPM-4200) observations were carried out in the non-contact mode. The cantilevers (Jeol datum NSC 12/15) had a spring constant of 0.25—0.65 Nm^{-1} and a resonance frequency of 20—40 kHz.

RESULTS AND DISCUSSION

Figure 1 is a POM photograph of the blend. It shows two types of spherulites (A and B). As shown in the previous paper,[2] PBSU (A) had large birefringence which is

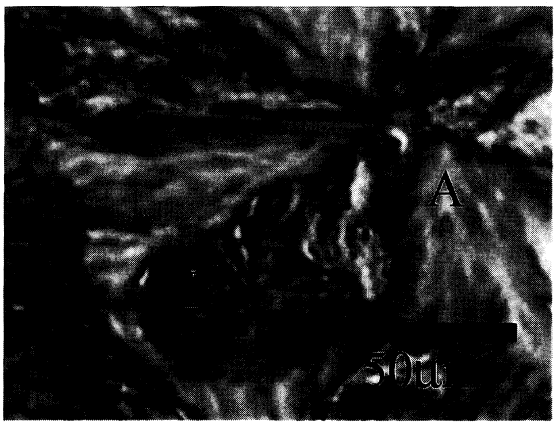

Figure 1. POM image of PBSU/P(VDC-VC)=60/40 (wt/wt) blends crystallized at 373 K. The PBSU spherulite (A) grew through the P(VDC-VC) spherulite (B).

Figure 2. CLSM image of the same area of a sample as Figure 1. A and B are PBSU and P(VDC-VC) spherulites, respectively.

neither positive nor negative. P(VDC-VC) had small and positive birefringence. The crystallization process of Figure 1 was as follows: PBSU and P(VDC-VC) nucleated almost simultaneously. Nucleation frequency of P(VDC-VC) was higher than that of PBSU. The radial growth rates of PBSU and P(VDC-VC) spherulites were 0.25 μm min^{-1} and 0.12 μm min^{-1}, respectively. When the PBSU spherulite (A) collided with the P(VDC-VC) spherulites (B), PBSU lamellae continued to grow beyond the spherulitic border along P(VDC-VC) lamellae. After penetration, the region of the P(VDC-VC) spherulite became brighter and its birefringent pattern changed.

Figure 2 is a CLSM image of the same area as Figure 1. It shows corrugations in the whole area. This can be ascribed to lamellae and/or fibrils. We compared Figure 2 with AFM images of the same area. Figures 3a and 3b are the magnified CLSM images of the rectangular areas a and b in Figure 2, respectively. Figures 3a′ and 3b′ are the AFM images of the same areas. It is obvious that the structures of AFM images in Figures 3a′ and 3b′ are finer than those of CLSM images in Figures 3a and 3b. To show it in more detail, the intensity profile of CLSM image and the height profile of AFM topography in Figures 3a and 3a′ along the arrows are shown in the inset of (a) and (a′), respectively. The intensity profile of Figure 3a, however, does not indicate the height of the surface since it is a differential interference image. The periods in the profiles of (a) (CLSM image) and (a′) (AFM image) are about 400—500 nm and 100 nm, respectively. In Figures 3a′ and 3b′, the AFM topographic contrast is caused by lamellae. In contrast, CLSM could not resolve each lamella in Figures 3a and 3b. However, the directions of the corrugations in the CLSM images were identical to those of lamellae observed by AFM. Therefore, one possibility is that these corrugations are caused by fibrils each of which consists of stacked lamellae.

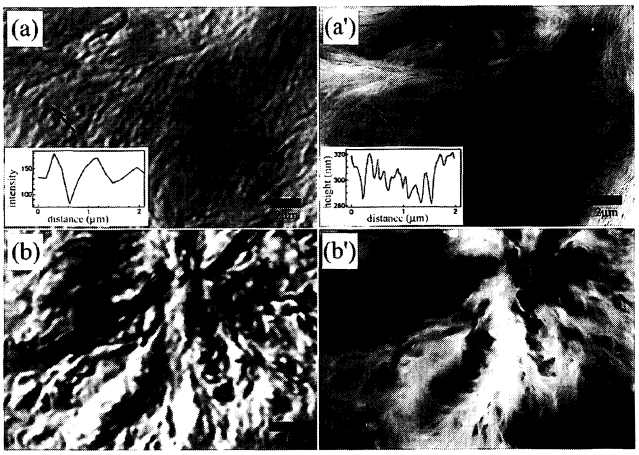

Figure 3. (a) and (b) are the magnified CLSM images of the rectangular areas a and b in Figure 2, respectively. (a′) and (b′) are the AFM images of the same areas. Intensity profile of CLSM image and height profile of AFM topography in (a) and (a′) along the arrows are shown in the inset of (a) and (a′), respectively.

The feature of CLSM image of PBSU spherulite (A) was different from that of P(VDC-VC) (B). CLSM images of PBSU spherulites had finer corrugations and smaller contrast than those of P(VDC-VC) spherulites. In the previous paper,[3] the population density of the lamellae in PBSU spherulites was larger than that in P(VDC-VC) spherulites. The corrugations and contrast in CLSM images reflected the population density of lamellae. In Figure 2, the growth direction of PBSU fibrils was inclined from the radial direction. This is consistent with the previous studies.[3] Though CLSM could not resolve individual lamellae, its images reflected the density and growth direction of lamellae in spherulites.

CONCLUSION

We examined the morphology of interpenetrated spherulites of PBSU/P(VDC-VC)=60/40 (wt/wt) blend films crystallized isothermally at 373 K by CLSM, and compared the CLSM images with POM and AFM images. Although CLSM could not resolve individual lamellae for its limit of spatial resolution, structures on the scale of 400—500 nm in width were observed. These structures could not be observed by POM. One possibility is that they are fibrils. The corrugations in CLSM images reflected the population density of lamellae and lamellar growth direction. Dense PBSU lamellae made the corrugations finer and the contrast smaller than sparse P(VDC-VC) lamellae. The direction of corrugations observed by CLSM was identical to the lamellar growth di-

rection observed by AFM. CLSM is a useful technique for observation of polymer spherulites.

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