Unique Morphology of Poly(ethylene succinate)/Poly(ethylene oxide) Blends

Zhaobin Qiu,* 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

Received July 19, 2002
Revised Manuscript Received August 26, 2002

The miscibility of polymer blends has been studied extensively. Most of the investigated systems represent mixtures of two amorphous polymers or mixtures in which one of the components is crystalline. However, blends in which both components are crystalline polymers have received much less attention than fully amorphous or amorphous/crystalline systems. It is more complicated and interesting to investigate this special kind of blends of two crystalline polymers since both components are able to crystallize and provide various conditions to study the crystallization behavior and morphology in polymer blends. Up to now, only a small number of works are reported on miscible polymer blends of two crystalline polymers with different chemical structures.[1−5] However, the melting points T_m of the two components in these studies were usually about 100 °C apart, and the high T_m component crystallized first. The low T_m component crystallized in the constrained space in the spherulites or on the interspherulitic boarders on lowering the crystallization temperature, which was confirmed by the increase in the brightness of the spherulites observed with a polarizing microscope under crossed polars. It indicated that the two components crystallized sequentially, not simultaneously. However, it is interesting to investigate whether the two components can crystallize simultaneously and which kind of morphology will arise from the simultaneous crystallization since both of them are crystallizable.

Interpenetrated spherulites are occasionally formed in a few miscible pairs of two crystalline polymers.[6−10] Spherulites of one component continue to grow in the spherulites of the other component after they contact with each other. In our previous work, we reported the interpenetrated spherulites formation process of poly(butylene succinate) (PBSU)/poly(vinylidene chloride-*co*-vinyl chloride) (PVDCVC) blends and poly(ester carbonate) (PEC)/poly(L-lactic acid) (PLLA).[7−10] From the previous studies, we propose that the important factors in realizing interpenetrated spherulites are the difference in the lamella population density in the different spherulites of the two components, the sufficient amount of the melt of one component inside the spherulites of the other component, and the simultaneous spherulitic growth of both components.

Poly(ethylene succinate) (PES) and poly(ethylene oxide) (PEO) were miscible, and the crystallization kinetics and semicrystalline morphology have been investigated by optical microscopy and small-angle X-ray scattering.[11] Because of the small difference in the melting points of the two components (∼35 °C), PES/PEO might be an ideal system to study the possibility of simultaneous crystallization and the formation of interpenetrated spherulites. However, such kind of work has not been reported in the literature so far. In this communication, the morphology of PES/PEO blends was investigated by optical microscopy, and the formation of interpenetrated spherulites was found.

Both PES (M_w = 10 000, T_g = −11 °C, T_m = 103 °C) and PEO (M_w = 100 000, T_g = −55 °C, T_m = 67 °C) samples used in this study were purchased from Scientific Polymer Products, Inc. (Ontario, NY). PES/PEO blends were prepared with the mutual solvent chloroform. The solution of both polymers (0.01 g/mL) was cast on glass plate at room temperature. The solvent was allowed to evaporate in a controlled air stream for 1 day, and the resulting films were further dried in a vacuum at 50 °C for 3 days. In this way, blends were prepared with various compositions ranging from 80/20 to 20/80 in weight ratio, the first number referring to PES.

The spherulitic growth was observed under crossed polars with a polarizing microscope (Olympus BHA-P) equipped with a first-order retardation plate and a temperature controller (Linkam LK-600PM). The sample was first melt at 130 °C for 3 min to destroy any thermal history and then quenched to crystallization temperature 50 °C at a cooling rate of 100 °C/min.

The isothermal crystallization temperature chosen in this work was 50 °C, which was below the melting point temperatures of both PES and PEO, to study the possibility of simultaneous crystallization of the two components. Both neat PEO and neat PES showed negative birefringence after complete crystallization at 50 °C. Because of the low supercooling, the PEO spherulites were very large, and the diameter could reach ∼1 mm. The high supercooling resulted in smaller size of PES spherulites. Figure 1 shows the spherulitic morphology of neat PEO, neat PES, and PES with various weight fractions of PEO (80/20−40/60), which were obtained just after the space was volume-filling. Down to the composition of PES/PEO = 40/60, PES crystallized so quickly that PEO could not nucleate before the whole space was filled with PES spheulites (see Figure 1c−e). It could be observed that the spherulites of PES became larger after blending with PEO, indicative of a decrease in nucleation density. The coarseness of PES spherulites increased with increasing PEO content in the blends, too. It should be noted that given a sufficient time PEO could crystallize within the PES spherulites, too, though it was difficult to be perceptible with optical microscopy. The melting point temperature of PEO was observed in PES/PEO blends by differential scanning calorimetry when the same experimental condition was used as in optical microscopy experiments. This indicated that PEO was first rejected into the interlamellar and interfibrillar regions of PES spherulites during the crystallization process of PES and then crystallized after the complete crystallization of PES.

The most interesting crystallization behavior was observed for the 20/80 blend sample. The crystallization of both PES and PEO spherulites could be observed simultaneously, and the interpenetration of PES spherulites by PEO spherulites was also found. The interpenetration process is shown in Figure 2. The micro-

* Corresponding author: e-mail zqiu@west.t.u-tokyo.ac.jp.

10.1021/ma025599x CCC: $22.00
Published on Web 09/24/2002

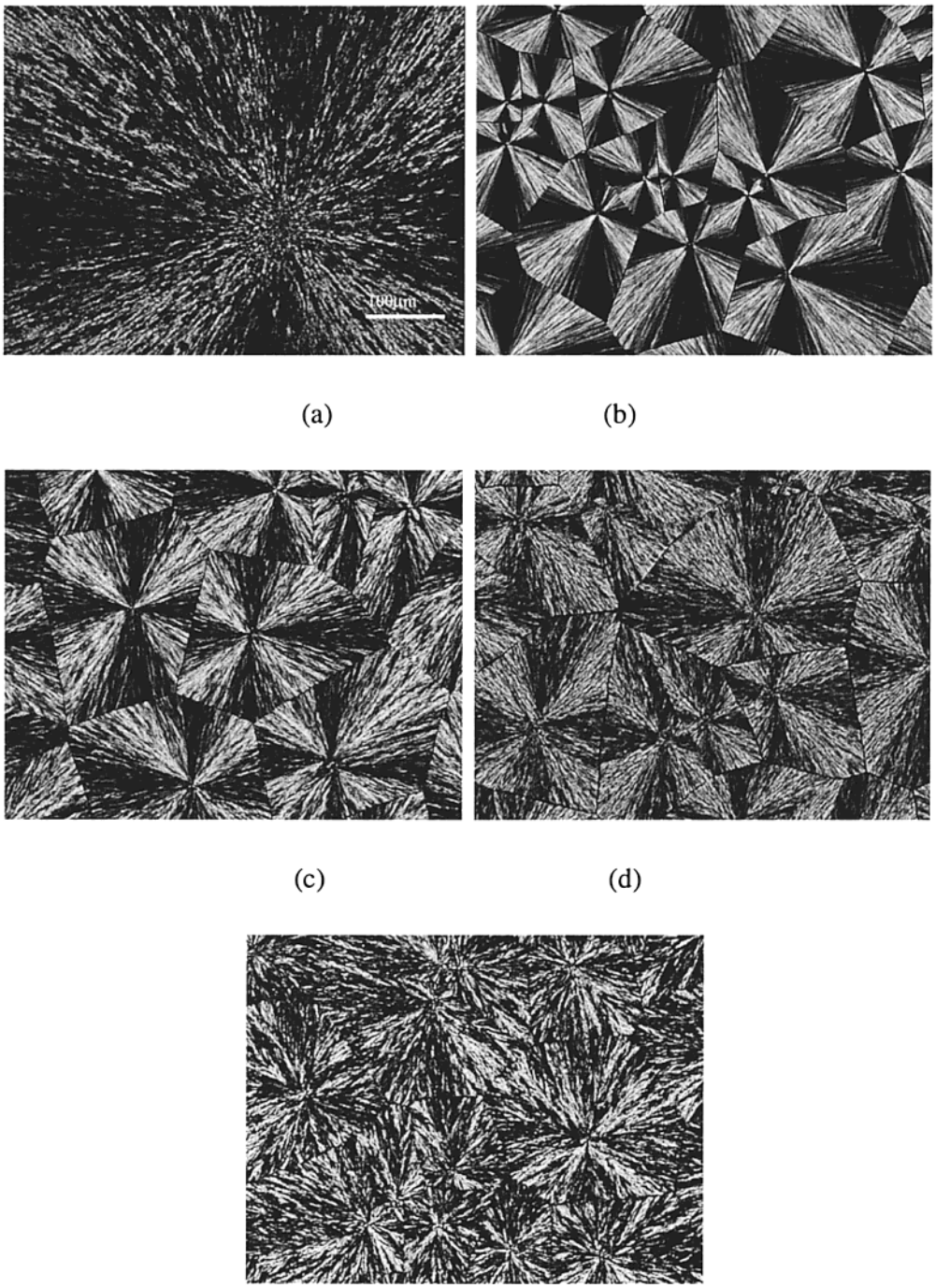

Figure 1. Polarized optical micrographs of the spherulitic morphology of PES/PEO blends after complete crystallization at 50 °C: (a) 0/100, (b) 100/0, (c) 80/20, (d) 60/40, (e) 40/60.

graphs were obtained under crossed polars with the use of a first-order retardation plate and are reproduced here in color to emphasize the observed phenomenon. Two different types of spherulites could be observed during the crystallization of this blend sample. The large and compact spherulites were attributed to be PEO type spherulites, and the small and open ones were PES type spherulite. This was confirmed by heating the sample to the temperature, which was just above the melting point of PEO while below that of PES. The PEO type spherulites disappeared, but PES type spherulites still existed. As shown in Figure 2a, PES and PEO crystallized simultaneously with PEO spherulite generally growing faster than PES spherulite. Instead of growth being arrested, the PEO spherulite continued to crystallize inside the PES spherulite, and the growth front of the PEO type spherulite became distorted when it reached the PES type spherulite. Meanwhile, the brightness increased in the part of PES spherulite where the crystallization of PEO had occurred and did not change where the crystallization of PEO had not occurred (see Figure 2b). These results indicated that PES spherulite was penetrated by PEO spherulite. However, it can also be observed that the outline of the brighter area is not

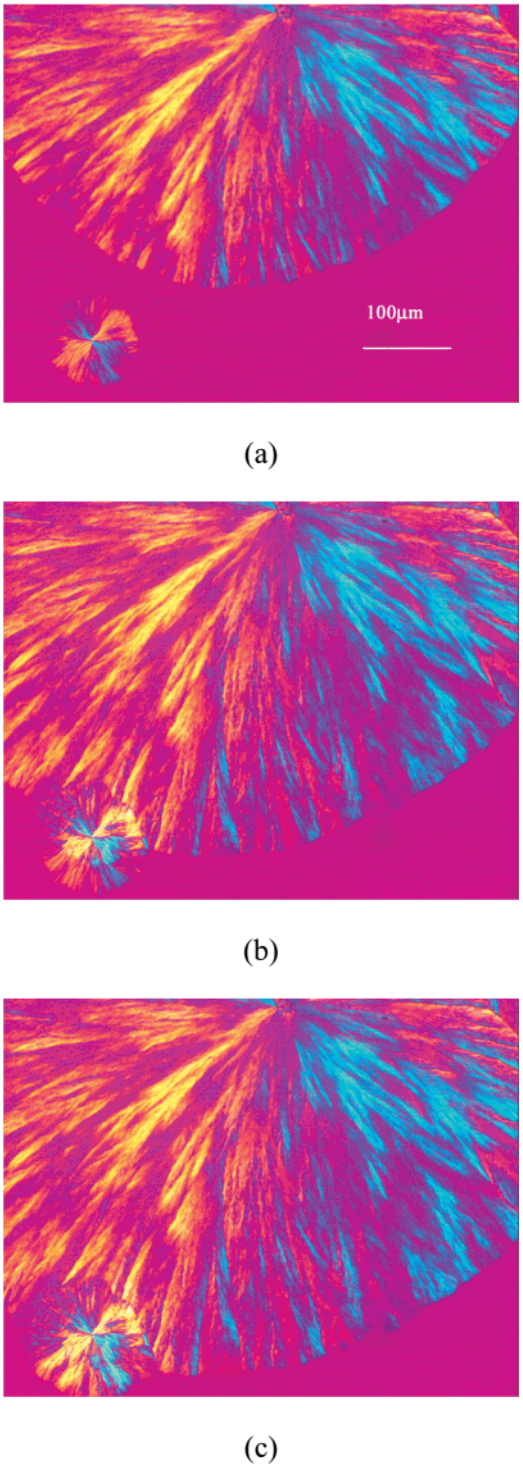

Figure 2. Process of interpenetration in 20/80 blend at 50 °C: (a) 3 min, before interpenetration; (b) 5 min, during interpenetration; (c) 6.5 min, after interpenetration.

consistent with the shape of the rest of the PEO spherulite, and the brighter area seems too large. It can be reasoned that the PEO fibrils grew faster inside the PES spherulite because the PEO content in the amorphous regions of the PES spherulite would be expected to be higher than the nominal melt concentration due to rejection of PEO from PES crystals. On the other hand, the PES spherulites stopped advancing toward the PEO spherulites. However, it could be observed in Figure 2 that a relatively clear boundary was seen as a line (the upper right part in each micrograph) upon the impingement of two PEO spherulites, indicative of the growth arrest.

Two additional possibilities are considered for the simultaneous crystallization of PES and PEO. One is the formation of PES spherulite inclusion surrounded by PEO spherulite, like α-spherulite inclusions surrounded by *β*-spherulite formed during the crystallization of isotactic polypropylene.[12] In this case, the growth front of PEO spherulite should be observed to advance outsides PES spherulite, and both PES and PEO should keep the original brightness after collision. However, this is not consistent with our results. The other is that PES spherulite and PEO spherulite merely superposed on each other as two separate layers in a film. In this case, the observed image should be the superposition of the birefringent patterns of PES and PEO spherulites. The retardation should increase where they have the same birefringence and should decrease where they have the opposite birefringence. The wavelength of the transmitted light would change with a test plate with the change of the retardation (see the model proposed in our previous work).[10] However, the experimental results showed the increase in light intensity of the PES spherulite and the unchanged color of the spherulite.

The fact that PEO penetrated into PES spherulites but PES did not penetrate into PEO spherulites may be explained as follows. The structures of PEO and PES spherulites were compact and open, respectively, indicating that the density of lamellae, namely the number of lamellae per unit volume, in PEO spherulites may be higher than that of PES. Furthermore, the sparse spherulites of PES contained a sufficient amount of amorphous PEO, which enabled the fibrils (stacks of lamellae) of PEO spherulites to continue to crystallize in the interfibrillar region of PES spherulites on contact. On the other hand, advance of PES spherulites into PEO spherulites stopped because the PEO spherulites were very compact and could not afford enough space for the fibrils of PES to continue to grow in the interfibrillar region of PEO spherulites on contact. Analogous cases have been found for PBSU/PVDCVC blends and PEC/PLLA blends in our previous work.[7−10] The detailed study on the crystallization process of PES/PEO blends by atomic force microscopy and real-time in-situ SAXS is currently underway and will be reported soon to get direct evidence for the difference in lamellar density of the two components.

Acknowledgment. Part of this work is supported by Grant-in-Aid for Scientific Research on Priority Areas (A), "Dynamic Control of Strongly Correlated Soft Materials" (No. 413/13031012) from the Ministry of Education, Science, Sports, Culture, and Technology, Japan. Z. Qiu thanks the Japan Society for the Promotion of Science for providing the fellowship and grant-in-aid to do this research at the University of Tokyo. The authors thank the reviewers for valuable suggestions.

References and Notes

(1) Avella, M.; Martuscelli, E. *Polymer* **1988**, *29*, 1731.
(2) Penning, J. P.; Manley, R. St. J. *Macromolecules* **1996**, *29*, 77.
(3) Cheung, Y. S.; Stein, R. S. *Macromolecules* **1994**, *27*, 2512.
(4) Liu, A. S.; Liau, W. B.; Chiu, W. Y. *Macromolecules* **1998**, *31*, 6593.

(5) Lee, J. C.; Tazawa, H.; Ikehara, T.; Nishi, T. *Polym. J.* **1998**, *30*, 327.
(6) Blümm, E.; Owen, A. J. *Polymer* **1995**, *36*, 4077.
(7) Lee, J. C.; Tazawa, H.; Ikehara, T.; Nishi, T. *Polym. J.* **1998**, *30*, 780.
(8) Ikehara, T.; Nishi, T. *Polym. J.* **2000**, *32*, 683.
(9) Terada, Y.; Ikehara, T.; Nishi, T. *Polym. J.* **2000**, *32*, 900.
(10) Hirano, S.; Nishikawa, Y.; Terada, Y.; Ikehara, T.; Nishi, T. *Polym. J.* **2002**, *34*, 85.
(11) Chen, H. L.; Wang, S. F. *Polymer* **2000**, *41*, 5157.
(12) Varga, J. *J. Mater. Sci.* **1992**, *27*, 2557.

MA025599X