

SPHERULITIC STRUCTURE AND MORPHOLOGY OF POLY(ETHYLENE SUCCINATE)/POLY(ETHYLENE OXIDE) (PES/PEO) BLENDS WITH ONE-STEP CRYSTALLIZATION*

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Abstract The spherulitic structure and morphology development of poly(ethylene succinate)/poly(ethylene oxide) (PES/PEO) blends with one-step crystallization behavior were observed by means of polarizing optical microscope. It was found that the pure PES spherulite in which the adequate quantity of PEO melt existed in the interlamellar regions, and the blending spherulite formed by both PES and PEO lamellae could form simultaneously. When the two types of spherulites contacted with each other the front of the blending spherulite could penetrate into the pure PES spherulite to grow continually. This penetration growth behavior was also observed when the mini-crystal particles of the PES component were formed at lower crystallization temperatures. The kinetics analysis showed that the penetration growth rate was faster than that in the original melt. It was evidenced that the increasing of growth rate and the formation of new growth site should be the typical characteristics of interpenetrated growth in binary crystalline polymer blends.

Key words: PES/PEO blend; One-step crystallization; Penetrated growth; Structure and morphology.

INTRODUCTION

The melt miscible binary crystalline polymer blends have attracted more attention of polymer physicists due to the unique supermolecular morphologies and physical properties of these blends^[1–14]. Normally, the crystallization of binary crystalline polymer blends can be divided into two different crystallization processes with two-step crystallization [two components crystallize individually at two different crystallization temperatures (T_c), the low T_c component (LTC) can dwell in the interlamellar, interfibrillar and interspherulitic regions of the high T_c component (HTC)] and one-step crystallization (two components can crystallize simultaneously at the same crystallization temperature). Two-step crystallization has been observed in the blends of poly(ethylene oxide) (PEO)/poly(3-hydroxybutyrate) (PHB)^[6, 7] and poly(vinylidene fluoride) (PVDF)/poly(butylene adipate) (PBA)^[8, 9], for which the melting-point (T_m^0) difference of the two components is large [T_m^0 (PVDF) = 210°C; T_m^0 (PBA) = 60°C; T_m^0 (PEO) = 69°C; T_m^0 (PHB) = 180°C]. It occurs also in blends for which the melting points of the components are close to each other, but the crystallizabilities are quite different, as in PVDF/PHB^[10–12] blends. One-step crystallization processes have been observed in the blends for which the melting points of two components are very close, such as poly(butylene succinate) (PBSU)/poly(vinylidene chloride-co-vinyl chloride) [P(VDC-DC)]^[15, 16] [T_m^0 (PBSU) = 115°C; T_m^0 [P(VDC-VC)] = 148°C], poly(ethylene succinate) (PES)/poly(ethylene oxide) (PEO) [T_m^0 (PES) = 103°C]^[17] and poly-(butylene succinate-co-butylene carbonate) (PBSC)/poly(L-lactide acid) (PLLA)^[11] [T_m^0 (PBSC) = 106°C; T_m^0 (PLLA) = 140°C]. The so-called interpenetrated or interlocked growth was found in these systems. The spherulite of one

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component continued to grow inside a spherulite of the other component instead of termination of spherulitic growth when they impinged on each other^[18, 19]. In fact, the occurrence of one-step crystallization process in a binary crystalline polymer blend depends strongly on the crystallization temperature, composition and melting points of components. That means the system may crystallize with one-step or two-step crystallization characteristics depending on crystallization conditions and compositions.

Poly(ethylene succinate)/poly(ethylene oxide) (PES/PEO) is a very useful polymer pair for studying the structure and morphology development of binary crystalline polymer blends due to their miscibility and availability^[17, 18]. The crystallization behaviors and spherulitic growth of PES/PEO blends have been studied under isothermal crystallization conditions, and an interpenetrated crystallization behavior has been observed^[18]. In our previous work^[20], spherulitic growth and morphology of PES/PEO blends in non-isothermal crystallization processes were investigated by means of differential scanning calorimetry and polarizing optical microscopy. PES and PEO can crystallize as one-step or two-step crystallization depending on cooling rate and compositions. In the one-step crystallization process, the growth front of PES followed that of PEO to grow with different growth rate in the same spherulite with the same nucleus, and the PES lamellae developed along the preexisting PEO lamellae radically, which resulted in the change of spherulitic morphology. In this paper, the isothermal crystallization behaviors of PES/PEO blend were studied, and the structure and morphology development and kinetic behavior of spherulitic growth were discussed.

EXPERIMENTAL

Materials

Poly(ethylene oxide) ($M_w = 1.0 \times 10^5$, $T_m = 67^\circ\text{C}$) and poly(ethylene succinate) ($M_w = 1.1 \times 10^4$, $T_m = 103^\circ\text{C}$) used in this paper were purchased from Acros Organics. The blended samples were dissolved in the desired ratios in *N,N*-dimethylformamide (DMF) to form 10% dilute solutions at about 80°C . The solvent was evaporated slowly at room temperature in a Petri dish to form a homogeneous film, which was further dried in vacuum for two weeks.

Instruments and Measurements

The measurements of melting temperature, glass transition temperature and crystallization temperature were carried out in a differential scanning calorimeter of Netcszh DSC 204F1. The blended samples with different compositions were heated to 130°C with a heating rate of 10 K/min for 10 min and then cooled to -70°C with a cooling rate of 10 K/min. Three phase transition temperatures were recorded for making phase diagram of the samples. The DSC measurements were calibrated by using standard indium, and the experiments were performed under a flowing nitrogen atmosphere.

The spherulitic morphology observations were carried out on a polarizing optical microscope of Nikon Eclipse E400 with a hot stage of Instec STC200. The thin film samples with thickness of 10–20 μm sandwiched between two optical glass slides were put on a hot stage and heated to 130°C in atmospheric ambience for 10 min to get a equilibrium melt, then the sample was shifted as quickly as possible to the microscope hot stage where its temperature was preset to a fixed crystallization temperature for isothermal crystallization. The spherulitic morphologies were observed at different crystallization temperatures, and the growth rates of the spherulites were recorded.

RESULTS AND DISCUSSION

Figure 1 shows the isothermal crystallization process of PES/PEO blend with composition of 40/60 at 56°C . It is found that, (1) two types of spherulites are formed with different morphologies and growth rates under the same crystallization conditions, (2) the spherulite with fast growth rate can penetrate into the other one to grow continually, while the spherulite with slow growth rate stops growing when the growth fronts of two spherulites contact with each other, (3) the growth rate of penetration is faster than that in the original melt of this spherulite, and a new growth site is formed when the penetrating growth takes place as shown in Fig. 1(d) which results in the formation of a sector region in the spherulite.

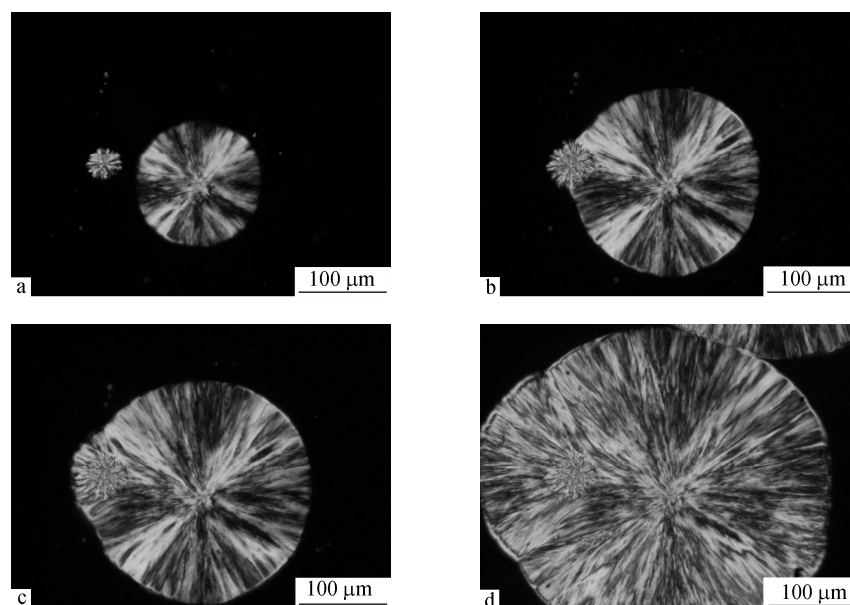


Fig. 1 Isothermal crystallization process of a PES/PEO blend with composition of 40/60 at 56°C
a) $t = 18.72$ min; b) $t = 28.85$ min; c) $t = 35.52$ min; d) $t = 57.59$ min

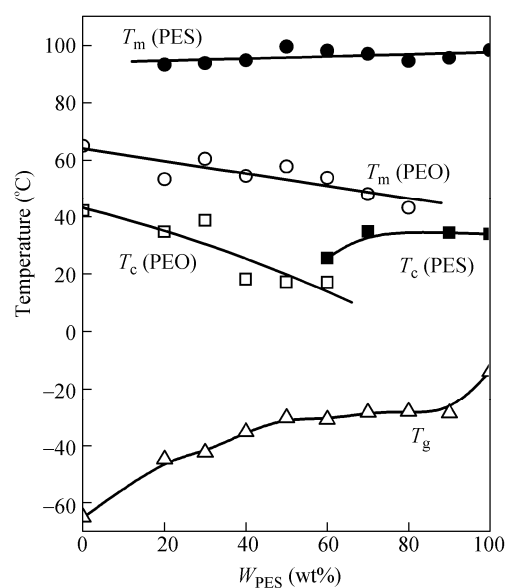


Fig. 2 Phase diagram of PES/PEO blends

Figure 2 shows the phase diagram of PES/PEO blends. The melting point depression and the single glass transition temperature indicate the compatibility of PES and PEO components in the experimental compositions. When the temperature is higher than PEO melting point but lower than PES melting point, the PES crystals, PEO melt and amorphous PES should coexist in their blends. The melting process of spherulites crystallized completely (shown in Fig. 1) was observed and shown in Fig. 3. It can be seen that the morphology of the larger spherulite (with fast growth rate) is changed when the temperature is higher than the melting point of PEO, but the shape and size of the spherulite are not changed. This result indicates that only parts of lamellae in these spherulites are melted at this temperature, and the melted lamellae should be formed by PEO component. When

the temperature approaches to the melting point of PES the small and large spherulites are melted completely. It is considered that the small spherulite in Fig. 1(a) is formed by PES component, and the large spherulite is formed by both PES and PEO components.

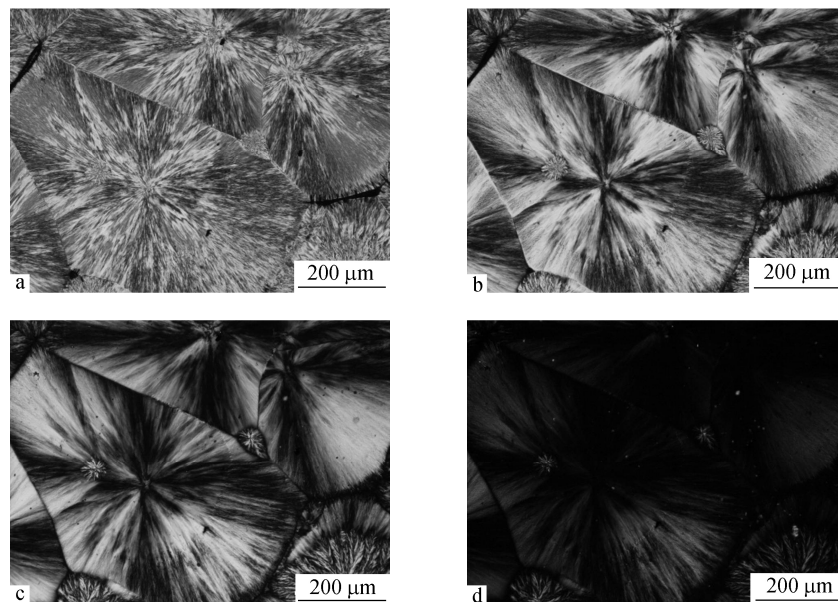


Fig. 3 Melting process of PES/PEO spherulites with composition of 40/60 formed at 56°C
a) $T = 56^{\circ}\text{C}$; b) $T = 68.8^{\circ}\text{C}$; c) $T = 98.5^{\circ}\text{C}$; d) $T = 105.9^{\circ}\text{C}$

Obviously, PES and PEO can crystallize simultaneously as shown in Fig. 1. Normally, PEO and PES formed the so called open-spherulites with PES and PEO melts inside them, respectively. According to the experimental results, the PES component inside the PEO spherulite can crystallize simultaneously with PEO spherulite growth to form a kind of blending spherulite. Therefore, the growth front of PES spherulite stopped growing when they contacted with the front of PEO spherulite because the PES component has crystallized in the PEO spherulite (cf. Fig. 1). In this case, the separated PES lamellae formed inside the PEO spherulite and developed along with PEO lamellae. The lamellae of both components were interlocked by each other to form the blending spherulites. Therefore, the PEO lamellae in the blending spherulites could be melted firstly when the temperature is higher than the melting point of PEO, which resulted in the change of morphology of the spherulites shown in Fig. 3.

However, the crystallization of PEO component inside the PES spherulite is different with that of PES inside the PEO spherulite. Only when the growth front of the blending spherulite contacts with PES spherulite the PEO component inside the PES spherulite starts to crystallize following the growth front to form so called interpenetrating crystallization. Figure 1 shows the whole process of a PEO spherulite interpenetrating a PES spherulite, *i.e.*, PEO component continues to grow inside the PES spherulite instead of the termination of spherulitic growth when they impinge on each other. According to Qiu *et al.*^[18], penetration of spherulites requires several conditions. First, the difference in melting temperature (T_m) of the two constituents must be sufficiently small when both components crystallize simultaneously. Second, the content of the higher- T_m component should be smaller than that of the lower- T_m component to realize the simultaneous development of the spherulites of both components. Third, the spherulites of the penetrated component must contain a sufficient amount of interlamellar amorphous regions that contain an adequate quantity of the penetration component. Obviously, the PES component forms a kind of open spherulite with a great number of PEO melt inside the spherulites which causes the penetrated growth of PEO spherulites. However, the PES spherulites can not

penetrate PEO spherulites to grow continually due to the PES melt inside the PEO spherulites has crystallized to form blending spherulites.

As shown in Fig. 1 a protruded sector is formed after the PEO spherulite penetrated through the PES spherulite. That means the spherulitic growth rate of penetration of PEO is faster than that of free growth in the melt. The polarizing optical microscopy observation showed that the growth rate of PEO in the original melt was $3.77 \mu\text{m}/\text{min}$ and the penetrating growth rate inside the PES spherulite was $4.34 \mu\text{m}/\text{min}$. The fast penetrating growth rate resulted in the formation of new growth site inside the PES spherulites, and the growth front of PEO that passed through the PES spherulite preceded the other portion of the growth front as shown in Fig. 1(d). Normally, the spherulitic growth rate is dependent on crystallization temperature and composition of blends as shown in Fig. 4. The spherulitic growth rate of PEO increases with increasing of PEO content. It was evidenced that the spherulite growth of one component in polymer blends could result in composition non-uniform distributions^[21]. When PEO was engulfed inside the PES spherulite, the PEO concentration inside the PES spherulites should be higher than the original concentration in the melt due to the PES crystallization solidification, which resulted in the increasing of growth rate of penetration. The experimental results showed that the growth rate of pure PEO spherulites crystallized at temperature of 56°C was $8.4 \mu\text{m}/\text{min}$, which indicated that the melt inside the PES spherulite was still a blend formed by PES and PEO, but the concentration of PEO component was higher than that of originals.

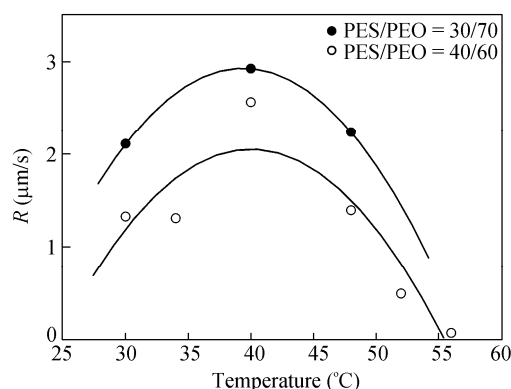


Fig. 4 Spherulitic growth rate of PEO component in the PES/PEO blends

The observation of crystallization morphology of PES/PEO blend with PES/PEO = 40/60 crystallized isothermally at 30°C is shown in Fig. 5. It can be seen that the PES forms very small crystal particles (mini-spherulites) due to the lower crystallization temperature. When the growth front of a PEO spherulite impinges on these crystal particles, it was observed that new growth sites are formed even the new primary nucleus are formed by these crystal particles. However, as shown in Fig. 6, this phenomenon has not been observed for the 10/90 sample crystallized at 56°C , only all the PES spherulites are engulfed in PEO spherulites. It has been reported that, for binary crystalline polymer blends with two-step crystallization, such as PBS/PEO blend^[22, 23], the crystallization behavior of the low T_c component is significantly affected by the crystallization condition of the high T_c component, the low T_c component can dwell in the interlamellar, interfibrillar and interspherulitic regions of the high T_c component. It can be considered that an adequate quantity of PEO melt exists between PES lamellae in Fig. 5, and the interpenetrating growth occurs when the growth front of PEO spherulites passes through these PES crystals, and the growth rate increases, and the new growth sites form. For PES/PEO = 10/90 sample crystallized at 56°C , the PEO melt may be excluded from interlamellar regions of PES spherulites, and no penetration growth occurs under this condition. Therefore, it can be concluded that the increasing of growth rate and the formation of new growth site should be the typical characteristics of interpenetrated growth in binary crystalline polymer blends.

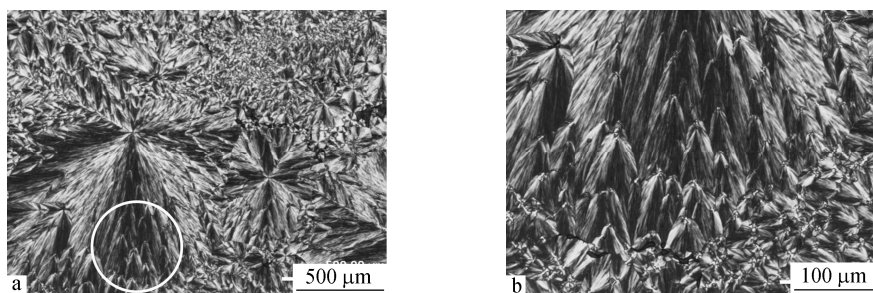


Fig. 5 (a) Crystallization morphology of PES/PEO blend with PES/PEO = 40/60 crystallized isothermally at 30°C, (b) the zoom image circled in (a)

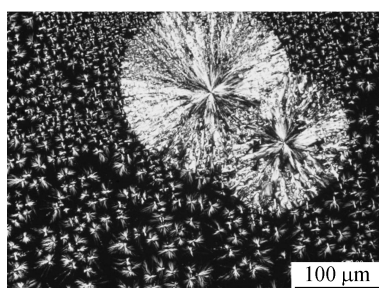


Fig. 6 Spherulitic morphology of PES/PEO blend with ratio of 10/90 crystallized at 56°C

CONCLUSIONS

PES and PEO in their blends can crystallize through one-step or two-step crystallization process controlled by crystallization temperature and composition. When one-step crystallization process occurs two types of spherulites are formed with different morphologies and growth rates under the same crystallization conditions. One is PEO spherulite in which the PES melt is included into the interlamellar regions. The other is a kind of blending spherulite in which PES forms an open-spherulite, and the PEO melt inside the PES spherulite crystallizes simultaneously. The melting experiments of spherulites evidenced this result. When the growth fronts of two spherulites contact with each other the growth front of PEO spherulite penetrates into the PES spherulite to grow continually while the PES spherulite stops growing. The growth rate of penetration is faster than that in the original melt, and the growth front of PEO that passed through the PES spherulite precedes the other portion of the growth front, and a new growth site is formed. The increasing of penetration rate results from the composition non-uniform distribution during solidification. When PEO is engulfed inside the PES spherulite, the PEO concentration inside the PES spherulites should be higher than the original concentration in the melt, which results in the increasing of growth rate of penetration. It can be concluded that the increasing of growth rate and the formation of new growth site should be the typical characteristics of interpenetrated growth in binary crystalline polymer blends.

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