

Effects of Crystallization Temperature and Blend Ratio on the Crystal Structure of Poly(butylene adipate) in the Poly(butylene adipate)/Poly(butylene succinate) Blends*

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Abstract The effects of crystallization temperature and blend ratio on the polymorphic crystal structures of poly(butylene adipate) (PBA) in poly(butylene succinate) (PBS)/poly(butylene adipate) (PBS/PBA) blends were studied by means of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (XRD) and atomic force microscopy (AFM). It was revealed that the polymorphism of PBA can be regulated by the blend ratio even in a non-isothermal crystallization process. The results demonstrate that high temperature favors flat-on α crystals, while low temperature contributes to edge-on β crystals. It was also found that the effect of blend ratio on the crystallization mechanism of PBA is well coincident with that of the crystallization temperature. The increment of PBS content in the PBS/PBA blend gives rise to more β -form crystals of PBA. For those PBS/PBA blends with low PBA content, the interlamellar phase segregation of PBA makes its molecular chains so difficult to diffuse from one isolated microdomain to another that high crystallization temperature and sufficiently long crystallization time will be required if the PBA α -type crystals are targeted.

Keywords: Blends; Crystallization; Poly(butylene adipate); Poly(butylene succinate).

INTRODUCTION

The method of blending one polymeric material with another, especially for cases of crystalline/crystalline binary polymer blends, has aroused great scientific interest as a means for developing new polymeric materials with desirable property combinations. The differences in melting points and crystallization temperatures of the two components could result in complicated phase structures and various properties. Till now, many crystalline/crystalline polymer blend systems have been widely studied^[1–14]. For these binary polymer systems, the confined and sequential crystallization behavior has been paid more attention and studied by differential scanning calorimetry, small-angle X-ray scattering and wide-angle X-ray diffraction^[15, 16].

The confined crystallization phenomenon arises when a crystalline polymer is finely dispersed in isolated domains whose number exceeds that of existent heterogeneities which normally promote crystallization^[17].

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Frensch^[18] has given overviews of the phenomenon in a variety of immiscible polymer blends. However, researchers have turned their interest to the confined and sequential crystallization in the miscible polymer blends like PBS/poly(ethylene oxide) (PEO) blend^[15]. The different crystallization processes of the two components will cause a variety of morphological patterns. During the crystallization process of PBS, the molten PEO can be expelled into interlamellar, interfibrillar or interspherulitic domains, some of which contain heterogeneities with differing efficiency to induce the nucleation. Consequently, PEO will crystallize at different temperatures, which is called sequential crystallization. Although the causes of the sequential crystallization have been analyzed, there are few reports of microscopic observations of the confined or sequential crystallization process at the lamellar scale. Therefore, we present here a real-time morphological observation of confined and sequential crystallization process of PBS/PBA blends by hot-stage atomic force microscopy (AFM).

Recently, considerable research attention has been paid to the deterioration of our environment due to solid waste pollution. Owing to the potential application in environment-friendly materials, aliphatic biodegradable PBA has aroused increasing interests in both fundamental and technical researches^[19, 20]. PBA can form two types of crystals (α - and β -forms). The α -form crystals are thermodynamically more stable and have faster degradation rate. Both α - and β -forms can be prepared by melt-crystallization at different temperatures. The former is formed at temperatures above 31 °C, while the latter appears below 29 °C^[21]. In the temperature region between 29 °C and 31 °C, the mixture of both α - and β -forms develops. What's more, the β -type can transform into α -type through annealing at higher temperatures^[22]. As the polymorphism of PBA affects its thermal stability and biodegradability, it is important to control the polymorphism of PBA. As another kind of aliphatic biodegradable polyester, PBS has similar chemical structure to that of PBA. Blending PBS with PBA is an effective way to reduce the overall cost of the biodegradable material and modify the desired properties and degradation rates. The mechanical properties of such crystalline polymer blends depend strongly on their crystal structures and phase separation mode. In our previous work, it was first reported that the crystallization temperature and blend ratio greatly affect the morphologies of the PBS/PBA blends by AFM^[23]. For a blend with PBA as a minority phase, mainly interlamellar segregation of PBA occurs. For a blend with medium PBA content, interlamellar and interfibrillar phase segregations take place simultaneously. For a PBA-rich blend, the interfibrillar mode is the main phase separation process. Besides, the sequential crystallization and polymorphic crystal structure of PBA in the PBS/PBA blend have been studied by Yang *et al.*^[24]. Their findings show that PBS is favorable for the formation of the PBA α -crystal in the PBS/PBA blends with $W_{\text{PBS}} < 70\%$. However, as in other similar blends, microscopy was not performed to directly verify the confined crystallization.

The purpose of this paper is to probe the effects of temperature and blend ratio on the crystallization process of PBA confined in the PBS lamellae scaffold by AFM. The polymorphic crystal structure of PBA formed at different temperatures was further investigated by DSC and WAXD. On the basis of the observed morphologies and polymorphic crystal structure, the temperature-dependent crystallization process of the PBA component was discussed as well.

EXPERIMENTAL

Materials

PBA with a number-average molecular weight M_n of 3.5×10^4 was produced by BASF AG. The poly(butylene succinate) (PBS) ($M_w = 2.0 \times 10^5$) was purchased from Aldrich Chemical. The melting points of PBS and PBA were measured to be 114 °C and 60 °C, respectively.

Preparation

Blends of PBS and PBA were prepared by solution blending in chloroform. Both of them were dissolved in chloroform with desired mass proportions (total polymer concentration was 10 mg/mL). Various PBS/PBA blend weight ratios were applied as 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100. The films (300 ± 10 nm in thickness) for the AFM experiments were obtained by dip-coating onto a freshly-cleaved mica substrate.

Characterizations

Differential scanning calorimetry (DSC) runs were performed on a Mettler DSC under ultra pure nitrogen purge with 5 mg samples encapsulated in aluminum DSC pans. Wide-angle X-ray diffraction (WAXD) experiments were performed on a Rigaku D/Max 2500 VB2 + /PC X-ray diffractometer at 40 kV and 200 mA. Tapping-mode AFM images were obtained using a NanoScope III MultiMode AFM (Digital Instruments) equipped with a high-temperature heater accessory (Digital Instruments). The scan rate varied from 0.7 Hz to 1.2 Hz. The scanning density was 512 lines/frame.

RESULTS AND DISCUSSION

Non-isothermal Crystallization and Crystal Structures

In order to better illustrate the effects of crystallization temperature on the crystal structure, the non-isothermal crystallization process and crystal structure of PBA were investigated using DSC and WAXD.

The DSC cooling curves at a cooling rate of 10 K/min (before the cooling, the samples were molten at 150 °C for 5 min to erase the thermal history) are summarized in Fig. 1 for the PBS/PBA blends. In the temperature range shown in Fig. 1(a), the exothermal peaks correspond to the crystallization of PBS. With the increment of PBS content, the crystallization peak of PBS is almost composition-independent. Only when the PBS content is below 40%, its crystallization temperature significantly reduces, suggesting the excess of PBA hinders the crystal growth of PBS. Figure 1(b) shows the exothermal peaks of PBA. When the PBA content is over 50%, only one crystallization peak of the PBA component at about 36 °C is observed, which is similar to that of neat PBA. However, two crystallization peaks of PBA are detected for the 60/40 (*W/W*) PBS/PBA blend, suggesting the occurrence of sequential crystallization^[18]. When the PBA content is reduced to 20%, again one crystallization peak appears, but the temperature is then 19 °C, suggesting the occurrence of confined crystallization. This indicates the nucleation or lamellar growth of PBA is hindered by PBS. Similar phenomenon of multiple crystallization peaks at different degrees of supercooling has also been found in PBS/PEO blends with low or middle PEO contents^[15].

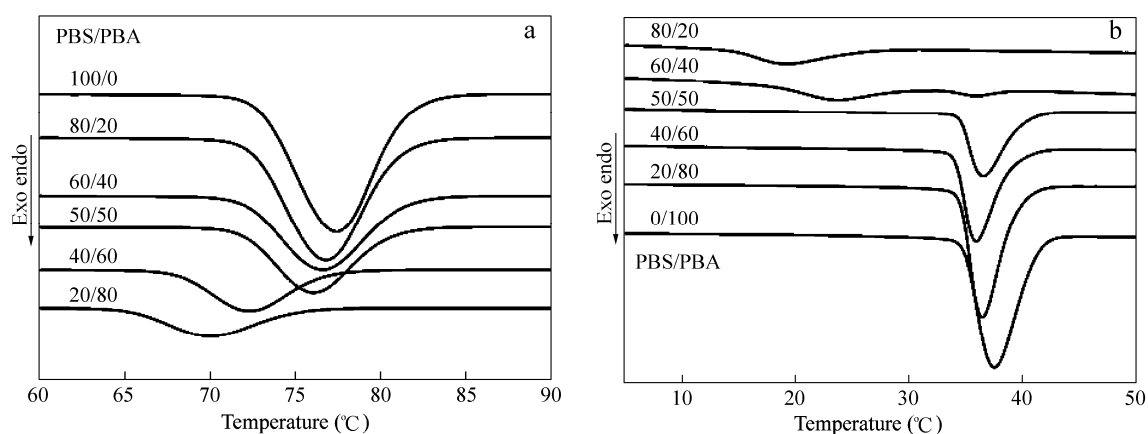


Fig. 1 DSC cooling curves of PBS/PBA blends with different PBS/PBA weight ratios in the temperature range of (a) 60–90 °C and (b) 10–50 °C (The cooling rate is 10 K/min.)

The WAXD patterns of pure PBS, PBA and their blends with the same thermal history are depicted in Fig. 2. Interestingly, the patterns of the blends are not just the superimposition of the pure PBS and PBA patterns. In Fig. 2, the characteristic peaks at 19.7° and 22.8° were assigned to (020) and (110) planes of the PBS crystal in the monoclinic unit cell, respectively. What's more, they keep unaltered regardless of the blend ratio, revealing that the crystal structure of PBS is not related to the blend ratio.

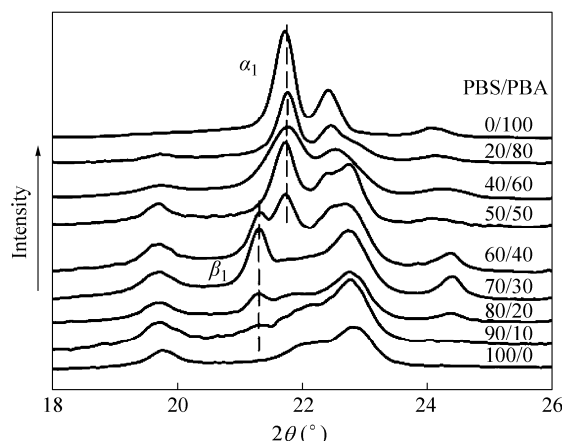


Fig. 2 WAXD patterns of pure PBS, pure PBA, and their blends with different blend ratios. Before the measurement, the samples were molten at 150 °C for 5 min and then cooled to the room temperature at a cooling rate of 10 K/min.

However, the diffraction peaks of PBA crystals change greatly with blend ratio. The WAXD peaks of pure PBA are seen at $2\theta = 21.75^\circ$ [α (110)], 22.4° [α (020)] and 24.0° [α (021)], indicating that only α -form crystals are formed in pure PBA in non-isothermal process. With the content increment of PBS, the strong diffraction peak α of PBA becomes smaller in size and disappears until PBS reaches 70%. In the PBA-rich blends, PBA forms α -crystal, implying that the lower amount of PBS crystal can not impact the formation of PBA α -form crystallization. For those PBS-rich blends, however, PBA shows a strong diffraction peak at 2θ of 21.2° [β (110)] and a weak one at 24.3° [β (020)], indicating that the higher amount of PBS causes the β -form crystallization. In addition, polymorphic crystals of PBA are formed in 60/40 blend. The present results clearly illustrate that the polymorphism of PBA can be regulated by blend ratio not only in the isothermal crystallization as in previous reports but also in the non-isothermal crystallization process.

The above DSC and WAXD experimental results demonstrate that the nucleation or crystal growth pattern of PBA in PBS-rich blends is different from that in PBA-rich blends or neat PBA, which is consistent with the Yang's results^[24]. Here, the different crystallization temperatures presented in Fig. 1 and crystal structures shown in Fig. 2 were analyzed and compared. It must be mentioned that PBA is miscible with PBS in the amorphous phase over the whole composition range^[23]. Therefore, the phase separation morphology is induced by the crystallization process in PBS/PBA blends.

When the temperature was above T_m (PBS), the melt PBS/PBA blend was homogeneous. Lowering the temperature to T_m (PBA) $< T < T_m$ (PBS), PBS crystallized and simultaneously segregated from the mixture. In this temperature regime, the PBS/PBA blend is semicrystalline/amorphous. During the crystal growth process of PBS, crystallization was accompanied with the segregation of the temporary amorphous PBA. According to our previous report, the amorphous PBA is mainly located in the interlamellar regions of PBS in a PBS/PBA blend with PBA as a minority phase. For a PBA in-rich blend, PBS forms only a spherulitic framework filled in with PBA, that is, the interfibrillar mode is the main phase separation process. For a blend with medium PBA content, interlamellar and interfibrillar phase segregations take place simultaneously^[23]. For PBS, its crystallization temperature significantly decreased in the PBA-rich blends ($W_{\text{PBS}} < 40$ wt%), suggesting the excess of PBA hinders the crystal growth of PBS. However, it does not affect the crystal structure of PBS, as shown in Fig. 2.

Further lowering the temperature to $T < T_m$ (PBA) at the cooling rate of 10 K/min, PBA begins to crystallize, leading to a three-phase morphology in which two distinct crystalline phases coexist with a mixed amorphous phase. The DSC and WAXD results shown in Fig. 1 and Fig. 2 have demonstrated that non-isothermal crystallization leads to the formation of PBA crystals, whose crystal type (α - or β -type) depends on the blend ratio in PBS/PBA blends. PBA crystallized into α -form crystal at 36 °C in the PBS/PBA blends with higher W_{PBA} . In the PBS/PBA blends with lower W_{PBA} , PBA crystallized at 19 °C and β -type crystals were

obtained. In the PBS/PBA blends with the middle PBA content, PBA crystallized at 36 °C and 23 °C, respectively, and the mixture of α -type and β -type crystals was formed.

The crystallization capacity of PBA is dependent on different phase segregation structures. Especially for those PBS/PBA blends with low PBA contents ($W_{\text{PBA}} < 40$ wt%), the interlamellar phase segregation of PBA makes its molecular chains difficult to diffuse from one isolated micro-domain to another^[23]. For this reason, during the fast cooling process, PBA located in interlamellar regions can only crystallize at low temperature and then form β -type crystal structure. However, those expelled into the interfibrillar or interspherulitic regions in high PBA content blends can crystallize at high temperature and form α -type crystal structure.

Isothermal Crystallization and Crystal Structures

The previous DSC and WAXD results emphasize that the non-isothermal crystallization of PBA is profoundly influenced by the presence of PBS. To further clarify temperature effects on the PBA structure, the isothermal processes were carried out.

Figure 3(a) shows the typical melting behavior of neat PBA crystallized at different isothermal temperatures. Obviously, both α and β crystals have double melting behaviors, however, the dependence of melting peaks on the crystallization temperature is obviously different^[21]. Thus it is easy to determine the exact crystal type of PBA by the melting peaks. Figure 3(b) shows the melting behavior of PBA in the PBS/PBA (80/20 wt %) blend. It can be seen that PBA forms α -crystal at high temperature but β -crystal at low temperature. The above experimental results clearly demonstrate that PBA in blends of PBS/PBA as a minority phase can still crystallize even at high temperature and form α -crystal. Thus, it can be concluded that no matter what the blend ratio is, only α -form crystal will be formed if the isothermal crystallization temperature is high or the cooling rate is low enough.

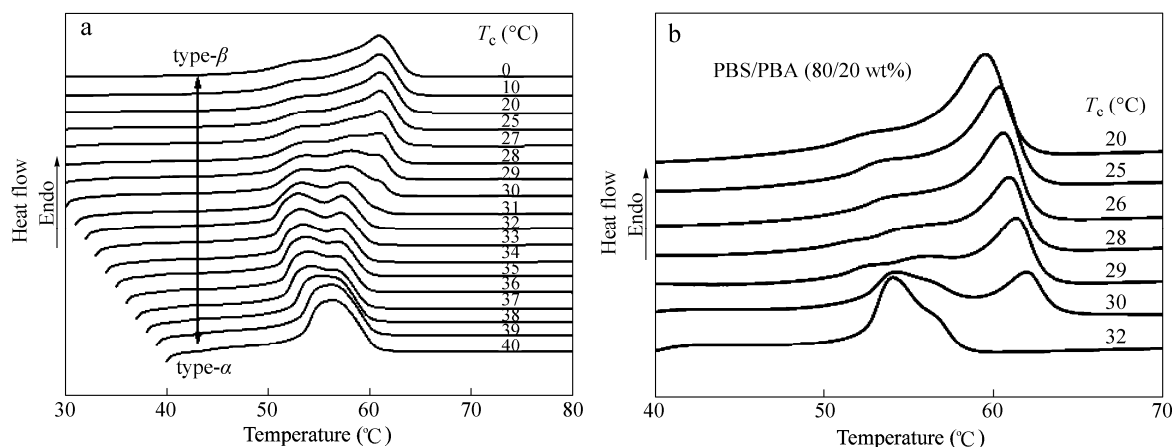


Fig. 3 DSC melting curves of (a) neat PBA and (b) the PBA component in PBS/PBA (80/20 wt%)
PBS was crystallized at 75 °C and PBA was isothermally crystallized at different temperatures.

The DSC results (Fig. 1b and Fig. 3b) reveals that although the confined crystallization occurs in the PBS/PBA blends with very low PBA content, PBA can still crystallize at high temperature and form α -crystal. To further support the conclusion that crystallization temperature plays a major role in the formation of PBA crystal structures, the morphological details of confined crystallization were examined by AFM. Figure 4(a) shows a representative AFM phase image of an 80/20 PBS/PBA blend in which the PBS was crystallized isothermally at 75 °C prior to crystallization of the PBA. As shown in Fig. 4(a), PBS forms mainly edge-on lamellae which align parallel for a long distance. The increased distance between PBS lamellae indicates that the melt PBA is expelled into the PBS interlamellar regions. Figure 4(b) illustrates the morphological change after cooling the blend to 35 °C and then held for 6 h. It can be found that some flat-on PBA lamellae have grown along the direction of the PBS lamellae in the PBS interlamellar regions. Such morphological observation clearly

shows that the PBA will form flat-on α lamellae in the blends with a minority PBA component, which is well coincident with the DSC results shown in Fig. 3(b).

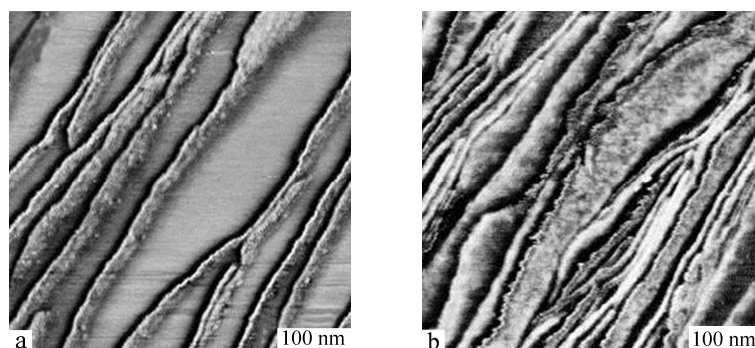


Fig. 4 AFM phase images of a 80/20 PBS/PBA blend under two-step crystallization conditions. (a) PBS crystallized isothermally at 75 °C and (b) after crystallization of PBA at 35 °C for 6 h

However, the lamellae grow so slow at 35 °C that some of the widened regions remain amorphous even 6 h later. This indicates that for those PBS/PBA blends with low PBA contents, the interlamellar phase segregation of PBA makes its molecular chains very difficult to diffuse from one isolated micro-domain to another. To make PBA crystallize at low content in PBS/PBA blends, a lower crystallization temperature or sufficiently long crystallization time is needed. So it is almost impossible for PBA in a PBS/PBA blend with low W_{PBA} to crystallize above 32 °C when the blend is cooled at a fast cooling rate, *e.g.* 10 K/min. As a result, PBA forms β crystal in blend with PBA as a minority phase during the non-isothermal crystallization process as depicted in Fig. 1.

α - and β -Crystal Growth Processes of the PBA Component

Recently, a couple of studies have been reported on the crystal structure of PBA. Gan *et al.* have investigated the morphological structure of PBA crystals^[25]. They found that in PBA banded spherulites, two polymorphic crystals are mixed in each of lamellar crystals. The flat-on lamellae consist of α -type crystals, while the edge-on domains are composed of β -type crystals. In our previous study, it was also found that flat-on lamellae are the predominant structures in the PBA spherulite grown at high temperature. For isothermal crystallization at low temperature, PBA forms mainly edge-on lamellae^[23]. The findings enable us to identify α - or β -type crystal structure of PBA by means of lamellar morphology.

According to the above DSC and WAXD experimental results, it is concluded that PBA can form β crystal at 25 °C, $\beta + \alpha$ crystals at 28 °C and α crystal at 35 °C. Based on the results, the AFM study was made focusing on α and β crystal growth processes of the PBA component at different temperatures. The 20/80 PBS/PBA blend was chosen for the observation of the PBA crystallization process at 25 °C, 28 °C and 35 °C respectively.

Figure 5 shows the β crystal growth process of PBA at 25 °C. The image area was 2 $\mu\text{m} \times 1 \mu\text{m}$ and the time interval between two successive images was about 14 min. Figure 5(a) shows a representative AFM phase image of a 20/80 PBS/PBA blend in which PBS was crystallized isothermally at 75 °C. AFM observation revealed that the PBS grows dominantly in edge-on lamellar form at 75 °C. Because of the high content of PBA, the PBS crystalline lamellae only construct a scaffold framework. Figures 5(b)–5(h) show the lamellar growth process of PBA at 25 °C in the PBS lamellar scaffold. As shown in Fig. 5(b), the morphological development first took place at the position away from the lamellae of PBS and edge-on lamellar sheaf was formed. Once formed, it kept growing into the scaffold framework until it was stopped by the PBS lamellae. Li *et al.*^[26] have investigated the heterogeneous nucleation and homogeneous nucleation. They observed that heterogeneous nucleation is identified by lamellae growing in all directions normal to the surface of the nucleus. But for homogeneous nucleation, lamellae were observed to grow in two directions. Their results help us to identify the

nucleation mode of PBA. As shown in Fig. 5(b), PBA keeps growing at both growing tips, suggesting that the nucleation mode of PBA is homogeneous nucleation. The founding lamella of PBA is more than 1 μm in length before induced nucleation occurs (Fig. 5c). The secondary lamellae nucleate close to existing mother lamellae and fill up the space between the founding ones. The whole crystallization process of PBA is restricted either in the interlamellar or interfibrillar regions of PBS.

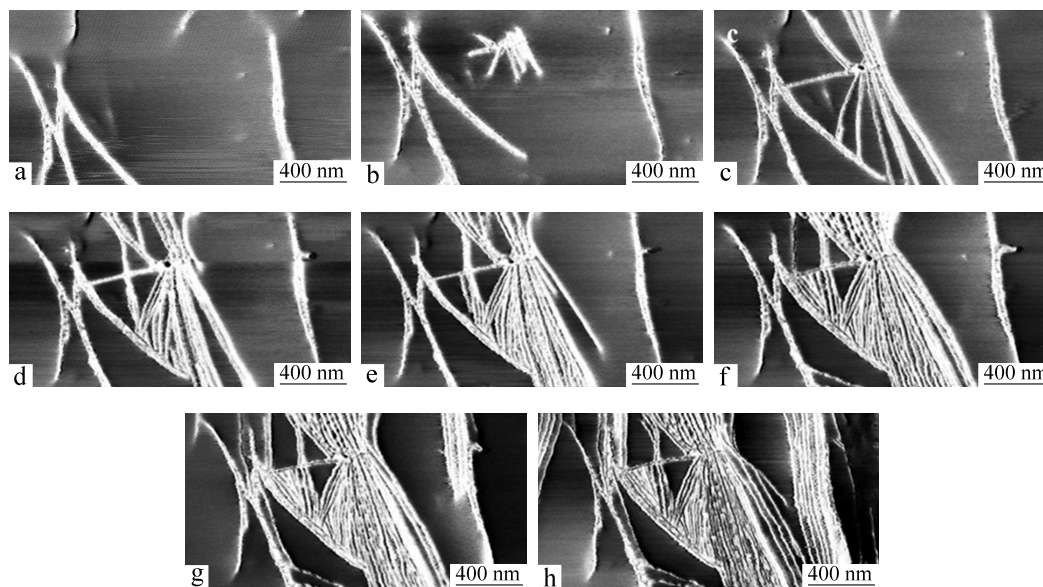


Fig. 5 A series of phase images of the lamellar growth of PBA in a PBS/PBA 20/80 blend in a consecutive time sequence: (a) PBS crystallized isothermally at 75 °C for 3 h, and (b) – (h) PBA lamellar growth at 25 °C

Consecutive phase images obtained in real time at 28 °C show the $\alpha + \beta$ crystal growth process of PBA in a PBS/PBA 20/80 blend, as revealed in Fig. 6. It is seen that both edge-on and flat-on lamellae of PBA grow simultaneously in different isolated microdomains. These edge-on and flat-on lamellae are probably made up of β -PBA crystals and α -PBA crystals^[23, 25], respectively. The nucleation and crystal growth of the two polymorphic crystals took place in different regions divided by the PBS lamellae.

Similar to the crystal structures of other crystalline polymers, the flat-on lamellae of PBA have a two-dimensional layered structure. For the second or third layer of α -form lamellae, the late growth rate became slow due to the lack of sufficient crystallizable material. The growth process of edge-on lamellae at 28 °C is similar to that at 25 °C, that is, the founding lamellae are formed first and then the branching occurs. It should be mentioned that the edge-on and flat-on lamellae are present in different microdomains, but do not twist into one another. This phenomenon differs from that in the previous papers^[20, 25], where lamellar twisting was reported. As shown in Fig. 7, during isothermal crystallization at 35 °C, only flat-on lamellae are observed, which further confirms that PBA will form flat-on α lamellae at high temperatures.

In summary, *in situ* AFM study of PBA crystal growth clearly shows that the crystallization temperature substantially influences the crystal structure and lamellar morphologies of PBA. High temperature favors flat-on α -form lamellae, while low temperature contributes to edge-on β -form lamellae. Furthermore, the results obtained in the AFM study show that the PBS lamellae cannot induce the crystallization of PBA. On the contrary, they hinder the PBA lamellar growth and reduce its crystallization rate, which leads to the situation that the growth direction of PBA lamellae follows that of the preexisting PBS lamellae.

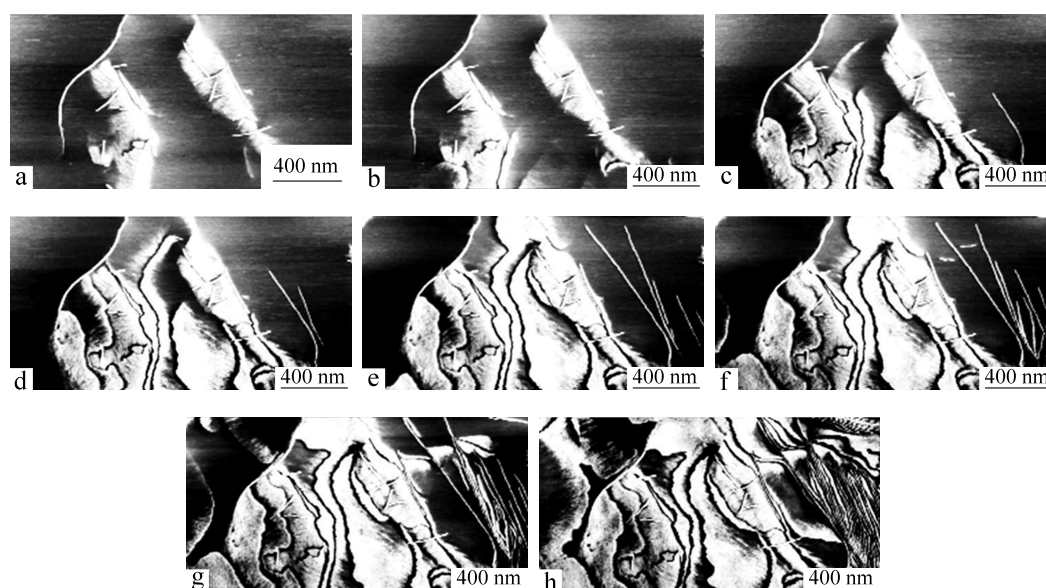


Fig. 6 A series of phase images (a) – (h) of the lamellar growth of PBA at 28 °C in a PBS/PBA 20/80 blend in a consecutive time sequence

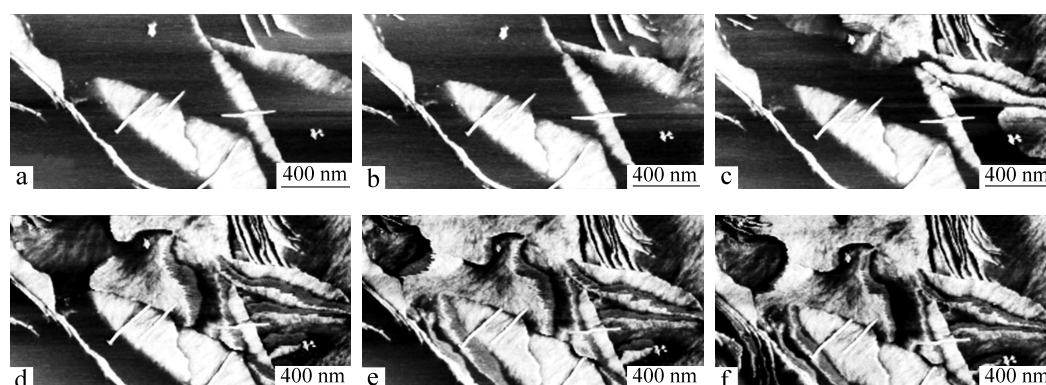


Fig. 7 A series of phase images (a) – (f) of the lamellar growth of PBA at 35 °C in a PBS/PBA 20/80 blend in a consecutive time sequence

CONCLUSIONS

We have investigated the effects of the crystallization temperature and blend ratio on the polymorphic crystal structures of PBA in PBS/PBA blends by means of DSC, WAXD and AFM. It was found that blend ratio controls the crystal structures of PBA during the non-isothermal crystallization. The higher amount of PBS crystals ($W_{\text{PBS}} \geq 70$ wt%) causes the PBA β -form crystallization, but the lower amount of PBS ($W_{\text{PBS}} \leq 50$ wt%) gives the PBA α -form crystallization. It was further found that the crystallization temperature plays a major role in the formation of PBA crystal structures during the isothermal crystallization process, for all PBS/PBA blend compositions. The flat-on α -form crystals are formed at high temperatures, *e.g.* 35 °C, while the edge-on β -type crystals appear at low temperatures, *e.g.* 25 °C. At medium crystallization temperatures, *e.g.* 28 °C, both α -form and β -form lamellae grow simultaneously in different isolated microdomains. Apart from what is stated above, the PBA crystallization ability was found to be dependent on different phase segregation structures. Especially for those PBS/PBA blends with low PBA content, the interlamellar phase segregation of PBA makes its molecular chains so difficult to diffuse from one isolated micro-domain to another that lower crystallization temperature or sufficiently long crystallization time is needed if the PBA α -type crystal is targeted.

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