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Influence of Teflon Substrate on Crystallization and Enzymatic Degradation of Polymorphic Poly(butylene adipate)*

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Abstract Oriented and non-oriented Teflon films, which were found to have the same crystalline structure, but different surface morphologies, were used to sandwich poly(butylene adipate) (PBA) films during isothermal crystallization. It was found that both the Teflon surface structure and the PBA polymorphic structure are the determining factors to induce epitaxial crystallization. The oriented Teflon film was able to induce epitaxial crystallization of PBA α crystal, while the non-oriented Teflon did not induce any epitaxial crystallization of PBA. Epitaxial crystallization did not occurred for PBA β crystals between neither the oriented nor the non-oriented Teflon films. The enzymatic degradation rate of PBA films was not determined by the epitaxial crystallization, in fact it was still dependent on the polymorphic crystal structure of PBA. The morphological changes of PBA films after enzymatic degradation confirmed again that the epitaxial crystallization only occurred for the PBA film with α crystal structure which was produced by being sandwiched between oriented Teflon films, and it happened only on the surface of PBA films.

Keywords: Poly(butylene adipate); Epitaxial crystallization; Polymorphic crystals; Enzymatic degradation; Morphology.

INTRODUCTION

Biodegradable polymers have received increased focus during the last decade because of the increasing waste problems from conventional polymers[1−3]. Compared to conventional polymers which have to be burned or stored and thus damage the environment or cause an inevitable buildup of waste, biodegradable polymers, however, alleviate the problems of waste management because of their degradability. As a result, the exact biodegradation behavior of an individual polymer is of monumental importance for application.

By changing the chemical and physical structure of polymers, the degradation rate is adjustable in a wide range. The most used chemical alteration is to copolymerize two degradable polymers[4, 5], or to copolymerize a degradable polymer with a nondegradable polymer[6, 7]. For changing the physical structure of the polymer, the stereochemistry[8, 9], crystalline structure[10, 11], crystallinity[12, 13] and lamellar thickness[14, 15] can be used to control the rate of degradation[16, 17].

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Polymorphism is an interesting phenomenon for polymers of which the polymer chains with the same chemical structure form several crystal lattices with different packing ways[18–20]. The crystals with the same packing way can also form different morphological structures, such as an ordered deposition *via* epitaxial crystallization or spherulites[21–23]. All polymorphic crystal forms except one are metastable[24, 25]. Poly(butylene adipate) (PBA) was found to have polymorphic crystals. Two crystal forms, *i.e.* α and β forms, were found in stretched and annealed films around the year of 1980[26, 27]. Our previous work reported that the PBA polymorphic crystals can be formed simply by changing the isothermal crystallization temperature[28]. The β-form crystals are formed at temperatures below 31 °C, while the α-form crystals are formed above 29 °C, and the thermodynamic stability, phase transformation, morphology and degradation of PBA polymorphic crystals have also been studied[29, 30]. The results on the enzymatic degradation revealed the complex influence of PBA polymorphic crystal structure. The enzymatic degradation of either α- or β-form crystals depends on lamella thickness, *i.e.* the degradation rate decreases with increasing lamella thickness. However, the thermodynamic stable α crystals showed a higher degradation rate even though they always have a larger lamella thickness than the metastable β crystals[30]. This degradation behavior of PBA polymorphic crystals has been discussed in terms of the morphology, chain packing and chain mobility. It was found that the PBA films corresponding to α and β crystal structures show very different morphology after degradation. Oriented "lines" appeared on the surface of PBA α crystal films at the initial degradation stage. Such "lines" were not seen in the PBA films with β crystal structure. The primary results indicated that the oriented "lines" are epitaxial crystals induced by the film used during film preparation[21, 30]. The epitaxial crystallization of PBA has been further confirmed in our recent work[31, 32]. However, some problems still remain such as the influences of epitaxial crystallization on the degradation of PBA polymorphic crystals.

The aim of this work is to elucidate the influence of the Teflon substrate on the epitaxial crystallization of polymorphic PBA crystals and the influence of the epitaxial crystallization on enzymatic degradation of the PBA films with different polymorphic crystal structure. Oriented and non-oriented Teflon films were used to sandwich PBA films for melt crystallization. The structure and morphology of PBA films were investigated by wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) and polarized optical microscopy (POM). The morphologies before and after degradation were observed by SEM to study the influence of the epitaxial crystallization on the degradation of PBA polymorphic crystals.

EXPERIMENTAL

Materials

Poly(butylene adipate) (PBA) was provided by BASF AG company. The polymer was purified by dissolving in chloroform and precipitation from methanol. The precipitate was dried by vacuum before use. The number average molecular weight (M_n) was determined as 40000 with a polydispersity index (M_w/M_n) of 1.7 which was measured by gel permeation chromatography (GPC) using narrow molecular weight distributed polystyrene as standard and chloroform as eluent. Oriented and non-oriented Teflon films were supplied by Tonghe Plastic Institute, China and were used as received. Pseudomonas species type XIII purchased from Sigma Aldrich was used as received, a concentration of 1 mg/mL lipase in double distillated water was used as lipase solution.

Preparation of PBA Films with Different Polymorphic Crystals

PBA films used for enzymatic degradation and further studied by WAXD and SEM, denoted thick PBA films, were prepared using the method described in an earlier paper[30]. Briefly the PBA sample was "sandwiched" between two oriented or non-oriented Teflon films with a 0.1 mm thick Teflon spacer. The PBA films for epitaxial growth investigations by POM were prepared using the same method only no spacer was used, resulting in a much thinner film, denoted thin PBA film. The sample was treated under a pressure of 50 kg/cm^2 and a temperature of 75 °C for 5 min to get a uniform smooth PBA film without any thermal history. After heat treatment the sample was transferred directly to a water bath with a preset temperature (T_c) for isothermal crystallization.

Polarized Optical Microscopy

The morphology of the thin PBA films was observed by an optical microscope (Leica DMLP) under crossed polarizers with a sensitive tint plate. The images were recorded by an attached digital camera and transferred to the computer (View finder 3.0).

Enzymatic Degradation of PBA Films

Thick PBA films were sliced into 10 mm × 10 mm × 0.1 mm samples for the enzymatic degradation. A piece of thick PBA sample was weighted and placed in a vial with 1 mL phosphate buffer solution (0.1 mol/L, pH 7.4) and 20 μl lipase solution. The vials were placed on a mechanical shaker with a speed of 150 r/min at 28 °C. After every 3 h the vials were removed from the shaker and the buffer and lipase solutions were renewed for all the vials in which the PBA samples needed further degradation. One vial was removed every 3 h and the PBA film sample was thrice washed with double distillated water before drying overnight under vacuum. After then the samples were weighted to determine the weight loss and degradation rate. All degradation experiments were repeated twice to insure accuracy except for T_c 25, 30 and 35 °C which were repeated six times.

Scanning Electron Microscopy

The morphological change of PBA film was investigated by SEM before and after enzymatic degradation. The PBA samples after enzymatic degradation were coated with gold in vacuum beforfe observation by a Hiachi s-530 scanning electron microscope.

Wide Angle X-ray Diffraction

The WAXD spectra was recorded at room temperature by using a Rigaku D/max-25000 system with a nickel-filtered Cu Kα radiation (wavelength λ = 0.154 nm, 40 kV and 110 mA) in the 2θ range of 6° to 60° with a scanning step of 0.02°. The WAXD spectra were normalized before comparison of the peak area.

RESULTS AND DISCUSSION

The Oriented and Non-oriented Teflon Films

The epitaxial crystallization of a polymer is strongly depended on substrates[21, 33]. For PBA with polymorphic crystal structures, the situation of epitaxial crystallization is much more complicated. In order to demonstrate the influences of substrate and polymorphism on PBA epitaxial crystallization, it is necessary to investigate the structure and morphology of Teflon films, which were used to sandwich PBA film for inducing epitaxial crystallization of PBA on their surfaces. Two types of Teflon films, *i.e.* oriented and non-oriented films, were used in this work.

Figure 1 shows the WAXD patterns of the oriented and non-oriented Teflon films. It is apparent that the crystal structure of two Teflon films is identical, even though the films are processed differently.

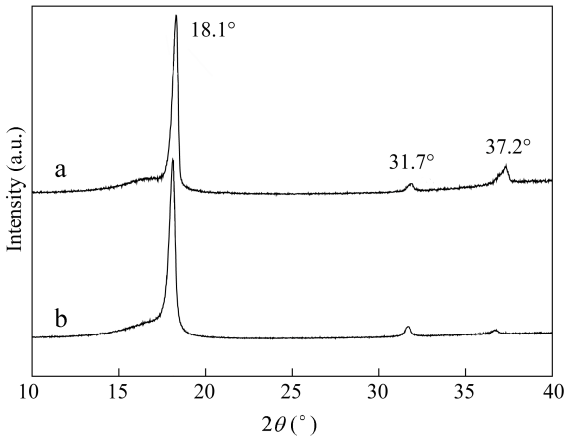


Fig. 1 Wide angle X-ray diffraction patterns of oriented (a) and non-oriented (b) Teflon films

Figure 2 shows the surface morphology of two types of Teflon films. It was found that the surface of the oriented and non-oriented Teflon films is different. The oriented Teflon film has many parallel "lines" on the surface which originate from an orientation during processing. In contrast the non-oriented Teflon films have a smooth and featureless surface. From the results of Fig. 1 and Fig. 2, it is clear that the Teflon films used in this work have the same crystal structure, but different surface morphology. Therefore when these two different substrates were used to sandwich PBA between them for melt crystallization, any differences observed in PBA films are solely due to the different morphology of the surface as it is the only difference between the oriented and non-oriented Teflon films.

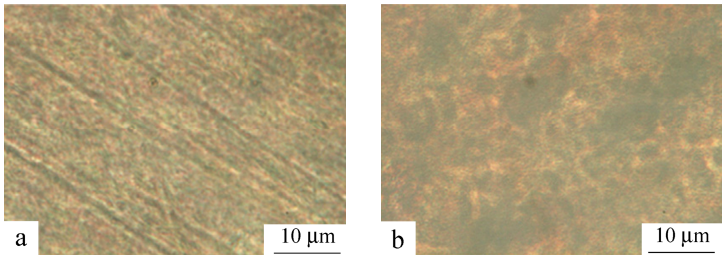


Fig. 2 SEM micrographs of the surface of oriented Teflon (a) and non-oriented Teflon (b)

Epitaxial Crystallization of PBA Chains Induced by Teflon

The epitaxial crystallization of PBA chains was investigated by sandwiching PBA samples between the Teflon films. After melt-crystallization between the Teflon films, the PBA films were stripped from the Teflon films and their morphologies were observed. In this experiment, the influences of both the substrates (oriented and non-oriented Teflon films) and the PBA polymorphic crystals on the epitaxial crystallization were considered.

Figure 3 shows the optical micrographs of PBA films with α crystal structure melt-crystallized between Teflon films. It is clear that when the oriented Teflon films were used for sandwiching PBA films, parallel oriented "lines" can be observed in all the PBA films after melt-crystallization at 35, 40 and 45 °C, respectively. While when the non-oriented Teflon films were used, no "lines" are observed in melt-crystallized PBA films. These results suggest that only the oriented Teflon films are able to induce the epitaxial crystallization of PBA with α crystal structure.

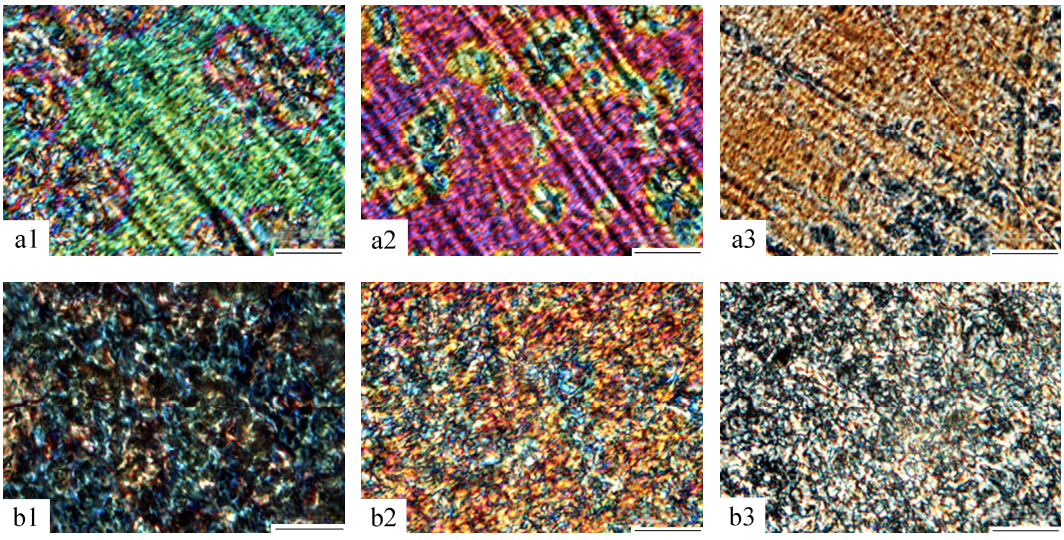


Fig. 3 Polarized optical micrographs of PBA films after isothermal crystallization between oriented and non-oriented Teflon sheets: (a1), (a2) and (a3) PBA films after isothermal crystallization at 35 °C, 40 °C, and 45 °C, respectively between oriented Teflon sheets; (b1), (b2) and (b3) PBA films after isothermal crystallization at 35 °C, 40 °C, and 45 °C, respectively between non-oriented Teflon sheets (The scale bar is 10 μm.)

The observed parallel "lines" in PBA films are very similar to those of oriented Teflon when comparing the morphology in Fig. 2 and Fig. 3. Further observation on the "lines" in PBA films indicated that many smaller fine "lines" are running perpendicular to the large oriented "lines", as shown in Figs. 3(a1), 3(a2) and 3(a3). To further reveal the structure of the two kinds of "lines", controlled enzymatic degradation was performed to PBA films and the morphological changes were observed by SEM, as shown in Fig. 4. It was found that the surface of as-prepared PBA films shows the parallel 'lines" (Fig. 4a). These "lines" are in the same size scale as the "lines" observed by POM in Fig. 2(a). Therefore, these "lines" are the replica of the oriented Teflon surface on PBA films during PBA film preparation. However, after enzymatic degradation, only the smaller fine "lines" perpendicular to the large parallel "lines" are observed, as seen in Fig. 4(b). These results indicate that the small fine "lines" may grow from those large "lines".

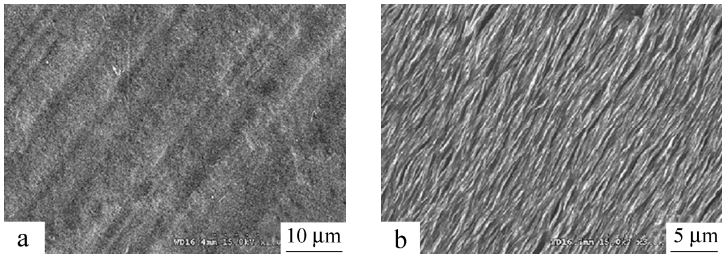


Fig. 4 SEM images of PBA film before (a) and after enzymatic degradation (b) The PBA film was melt-crystallized at 35 °C and then degraded for a short period to remove the amorphous surface layer.

The PBA α crystals are formed at small degree of under cooling[28, 29]. According to the viewpoint of crystallization kinetics, the nucleation is the controlling step for the overall crystallization. The large "lines" in the as-prepared PBA films act as the nucleation sites to induce the epitaxial crystallization of PBA. Accordingly, the smaller fine "lines" as seen in Fig. 4(b) are the epitaxial crystals which grow with the large "lines" as nucleation sites. The non-oriented Teflon films do not induce the epitaxial crystallization of PBA even though they have the same crystal structure as that of oriented Teflon films. The main reason for the absence of epitaxial crystallization is that the featureless and smooth surface of non-oriented Teflon films cannot provide the nucleation sites for PBA crystallization.

Figure 5 shows the optical micrographs of PBA films with β crystal structure after melt-crystallization between the oriented and non-oriented Teflon films. No "lines" are seen in the PBA films which were sandwiched between the two types of Teflon films. Compared to the results in Fig. 3, it can be concluded that the PBA with β crystal structure cannot epitaxially crystallize on the surface of Teflon films no matter the film is oriented or not. One reason for epitaxial crystallization of PBA with only α crystal form between the oriented Teflon films is the crystal match of PBA α crystal and Teflon crystal structures, which does not match with PBA β crystal. However, it has been reported that the PBA with β crystal structure can epitaxially crystallized on polyethylene (PE), which is explained by the match of the orthorhombic crystal structure of PE and the orthorhombic unit cell of PBA β crystal form[1, 3]. As a result, it is clear that both the PBA with α and β crystal forms are able to form epitaxial deposits depending on the substrate used.

In addition, the different kinetics for the two polymorphic crystals of PBA is another reason for epitaxial crystallization of PBA with only α crystal form. The PBA β crystals formed at larger degree of undercooling with fast nucleation rates. Therefore the oriented "lines" on the surface of oriented Teflon, which induce the nucleation and epitaxial crystallization of PBA with α crystal form, do not have enough time to induce the epitaxial crystallization of β crystals.

Figure 6 shows the polarized optical micrographs of PBA films with mixed crystal of α and β structure after melt-crystallization between the Teflon films. The parallel "lines" of epitaxial crystals can only be indistinctly seen in the PBA films after melt-crystallizing at 32 °C between oriented Teflon sheets (Fig. 6a3). This is due to

the epitaxial crystallization of PBA α crystals which is dominant in the mixture at 32 °C. When the crystallization temperature is below 32 °C, *e.g*. 28 °C or 30 °C, the parallel "lines" are hard to be seen in PBA films prepared between either oriented or non-oriented Teflon films due to the increased amount of β crystal forms in the mixture.

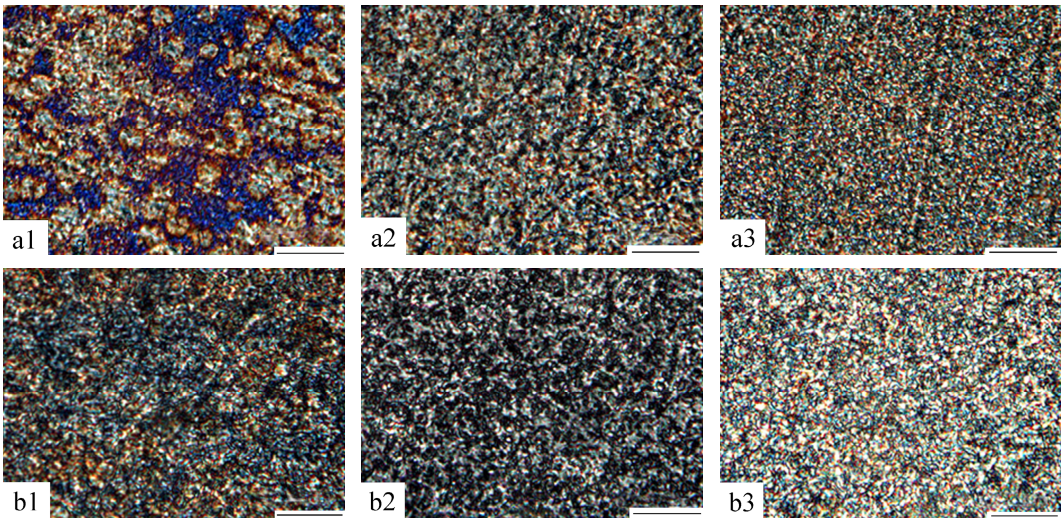


Fig. 5 Polarized optical micrographs of PBA films after isothermal crystallization between oriented and non-oriented Teflon films: (a1), (a2) and (a3) PBA films after isothermal crystallization at 15 °C, 20 °C and 25 °C, respectively between oriented Teflon sheets; (b1), (b2) and (b3) PBA films after isothermal crystallization at 15 °C, 20 °C and 25 °C, respectively between non-oriented Teflon sheets (The scale bar is 10 μm.)

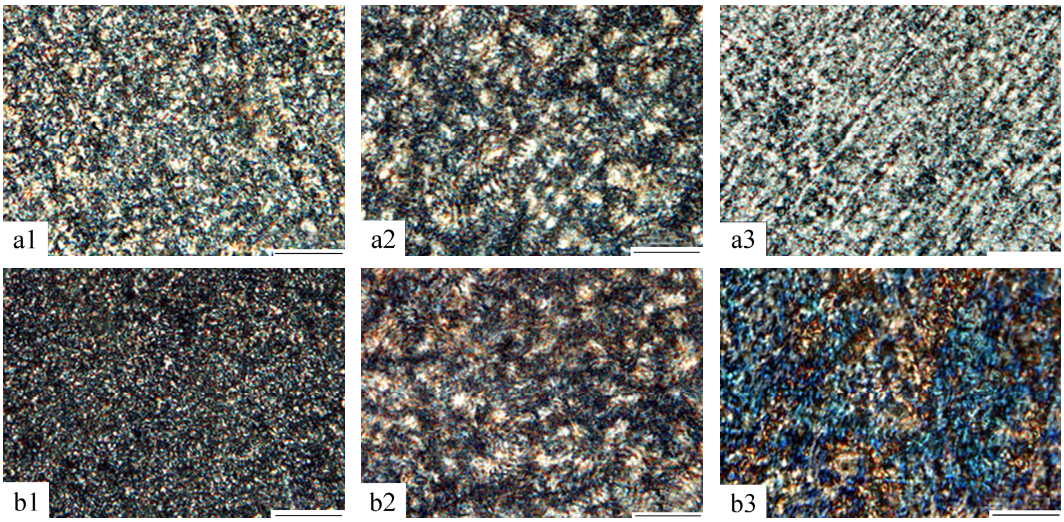


Fig. 6 Polarized optical micrographs of PBA films after isothermal crystallization between oriented and non-oriented Teflon films: (a1), (a2) and (a3) PBA films after isothermal crystallization at 28 °C, 30 °C and 32 °C, respectively between oriented Teflon sheets; (b1), (b2) and (b3) PBA films after isothermal crystallization at 28 °C, 30 °C and 32 °C respectively between non-oriented Teflon sheets (The scale bar is 10 μm.)

Based on the above results, it can be concluded that both the polymorphic crystal structures and the substrate surface morphology have great influences on the epitaxial crystallization of PBA on the Teflon substrates. Only the oriented Teflon films can induce the epitaxial crystallization of PBA with α crystal structure, while the PBA β crystals have no ability to form epitaxial crystals on either oriented or non-oriented Teflon films. The essential reasons are because of the crystal match of PBA α polymorphic crystal and Teflon

crystal structures as well as the different crystallization kinetics, *e.g.* the nucleation at different undercooling degrees for the PBA polymorphic crystals.

Influence of Epitaxial Crystallization on Enzymatic Degradation of PBA Polymorphic Crystals

The enzymatic degradation rate of PBA films was calculated according to the following equation:

$$R_d = W_l/(A_s \times t)$$

where W_l is the weight loss of PBA sample, t is the degradation time and A_s is the surface area of PBA sample. Figure 7 shows the enzymatic degradation rates of PBA after melt-crystallized at different temperatures between oriented and non-oriented Teflon sheets. The PBA films with either α or β crystal structure show the same tendency that the degradation rate decreases with increased crystallization temperature (T_c) *i.e.* lamella thickness[29]. These results are the same as our previous results[30].

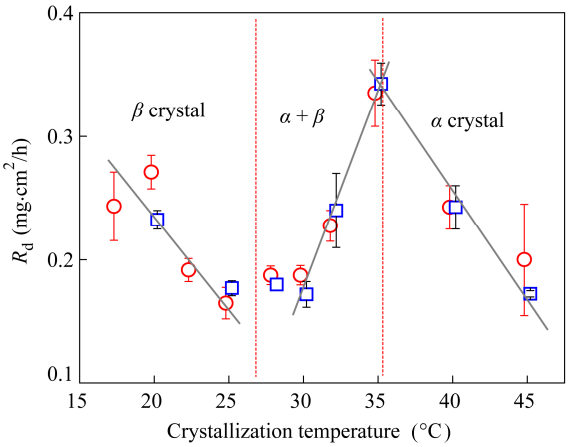


Fig. 7 The degradation rate R_d of PBA films as a function of crystallization temperature T_c
The symbols (○) and (□) represent the degradation rates of PBA films which were prepared by sandwiching between oriented and non-oriented Teflon films, respectively.

The attention we have to pay is to the comparison of enzymatic degradation between the PBA α crystal-form films with and without epitaxial crystals in the film surface. As seen in Fig. 7 when the crystallization temperature is higher than 32 °C, the PBA films with α crystal structure prepared between oriented and non-oriented Teflon films show almost the same degradation rate. This means that the degradation of the PBA films with epitaxial crystals on the surface has the same degradation rate as PBA films with no epitaxial crystals on the surface. From this evidence, it is clear that the epitaxial crystals formed between oriented Teflon films have no influence on the degradation of PBA films. Therefore, the chain packing manner in polymorphic crystal lattices and the chain motion inside them may be responsible for the different degradation behavior of PBA with polymorphic crystal structure.

It has been known that the PBA forms crystal structure with mixed α and β crystal forms after melt-crystallization at temperatures between 27 °C and 32 °C[28]. At this temperature range it was found in Fig. 7 that the degradation rate increases with crystallization temperature. As revealed by our previous WAXD results[29, 34], the α crystal becomes the dominant chain packing and its content increased with increasing crystallization temperature. So it is clear that the degradation of the mixture depends on the content of α and β crystal forms, while the lamella thickness does not play the decisive role in this temperature range. As a result the degradation for PBA with mixed crystal forms provides evidence that the polymorphic crystal structure and the chain packing determine the degradation of polymorphic crystals.

The above results have revealed that only the oriented Teflon film can induce the epitaxial crystallization on the surface of melt-crystallized PBA films with α crystal structure, and that the epitaxial crystals on the film

surface have no influence on the degradation rate of PBA films. However, the PBA α crystal films with or without surface-existing epitaxial crystals may show different surface morphology after enzymatic degradation. Due to the faster degradation of amorphous regions, the crystalline morphology will be clearly emerged after degradation.

Figure 8 shows the surface morphological change as a function of degradation time for the PBA films with α crystal structure prepared by sandwiched between Teflon films and melt-crystallized at 35 °C. After degradation for 3 h, the aligned "lines" are clearly seen on the surface of PBA films (Fig. 8 a1) with epitaxial crystals on the surface, while no "lines" are seen but only spherulites are exposed for the PBA films (Fig. 8 b1–8 b4) without epitaxial crystallization. The epitaxial crystal lines observed by the SEM are in the same size scale as the fine lines running perpendicular to the large lines as observed by the optical microscope as shown in Fig. 3. The degradation results confirmed again that the fine "lines" observed by polarized optical microscopy on melt-crystallized PBA films are the epitaxial crystals.

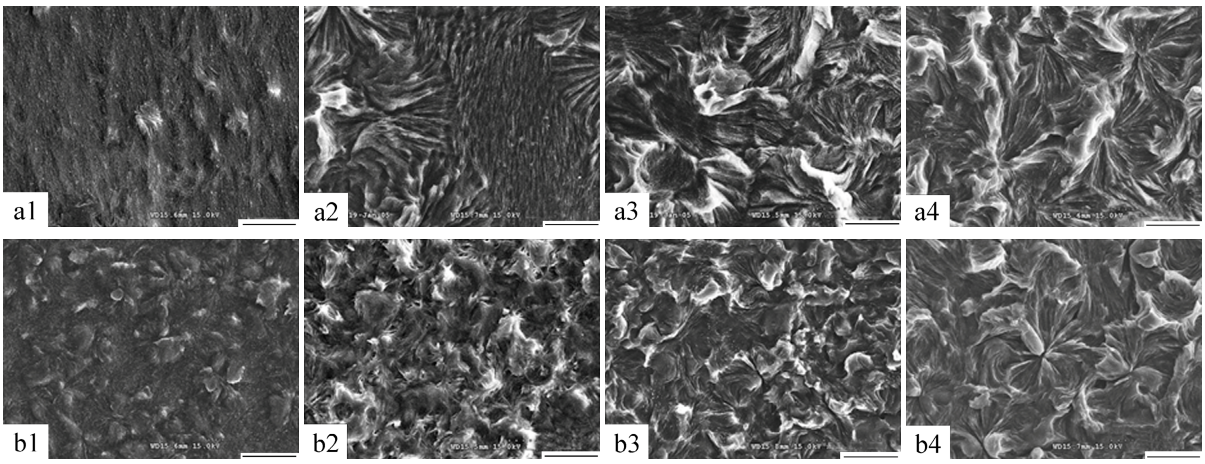


Fig. 8 SEM images of surface morphological changes of PBA films with α crystal structure (T_c = 35 °C) during enzymatic degradation; (a1), (a2), (a3) and (a4) PBA films prepared by sandwiching between oriented films and then degraded for 3, 6, 9 and 12 h, respectively; (b1), (b2), (b3) and (b4) PBA films prepared by sandwiching between non-oriented films and then degraded for 3, 6, 9 and 12 h, respectively (The scale bar is 20 μm.)

With longer degradation time, it was founds that the amount of oriented "lines" becomes less in PBA films and spherulites appear (Fig. 8a2). After degradation for 9 h, all the oriented "lines" disappeared, and both the PBA films with and without epitaxial crystals on the surface show the same morphology with spherulites exposed on the film surface. These results indicate the epitaxial crystals exist only on the surface layer of the melt-crystallized films, and that it is the Teflon films that induce the epitaxial crystallization of PBA on its melt-crystallized film surface.

Figure 9 shows the change of surface morphology for melt-crystallized PBA films with mixed α and β crystals in the course of enzymatic degradation. It has already been found in the previous results that the PBA films with mixed crystal structures only show the epitaxial crystallization in the mixed crystal structures with higher α contents (*e.g.* T_c = 32 °C), while most PBA films with mixed crystal structures do not shown epitaxial crystallization due to the insufficient amount of α crystals in the mixture. As seen in Fig. 9, it was found that no matter whether the PBA films were prepared by sandwiching between oriented or non-oriented Teflon films and melt-crystallized at 30 °C, they show the same morphological changes without any aligned "lines" during enzymatic degradation.

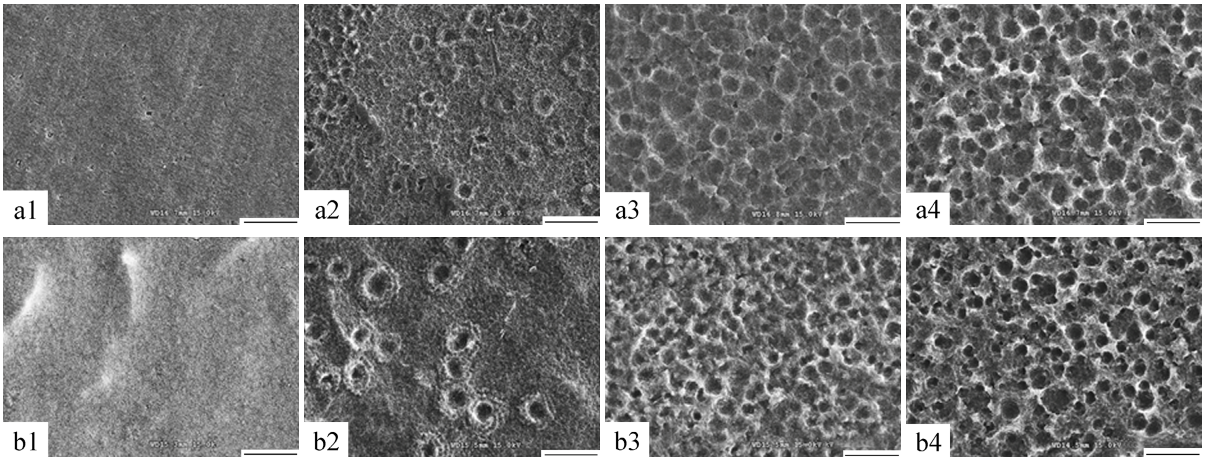


Fig. 9 SEM images of the surface morphological changes of PBA films with mixed α and β crystals (T_c = 30 °C) during enzymatic degradation: (a1), (a2), (a3) and (a4) PBA films prepared by sandwiching between oriented films and then degraded for 3, 6, 9 and 12 h, respectively; (b1), (b2), (b3) and (b4) PBA films prepared by sandwiching between non-oriented films and then degraded for 3, 6, 9 and 12 h, respectively (The scale bar is 20 μm.)

CONCLUSIONS

PBA films with polymorphic crystal structure were prepared by sandwiching between two Teflon sheets. Only the PBA films with α crystal structure were able to form epitaxial crystals only on the oriented Teflon, but not on the non-oriented Teflon films. This is due to the induction by the oriented "lines" on the surface of Teflon films. While epitaxial crystallization did not occur for PBA with β crystal form between neither the oriented nor the non-oriented Teflon films. The epitaxial crystals did not affect the degradation rate of PBA films with polymorphic crystal structures, but did give a different surface morphology after enzymatic degradation. The degradation results confirmed that the epitaxial crystallization occurred on the surface of PBA films with α crystal structure.

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