Epitaxial Crystallization of Poly(butylene adipate) on Highly Oriented Polyethylene Thin Film

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ABSTRACT: The crystallization behavior of PBA on highly oriented PE substrate from solution as well as melt was studied by optical microscopy, transmission electron microscopy, and X-ray diffraction. The results show that the PE exhibits very strong nucleation ability toward PBA as reflected by the occurrence of heteroepitaxy and transcrystallization of PBA on the PE substrate. The epitaxial crystallization of PBA on PE substrate results in the formation of β-PBA crystals at any crystallization conditions. This is associated with the perfect lattice matching between the β-form PBA and PE crystals and can provide us a simple way to control the crystalline modification of PBA during different processing process in order to regulate its crystal size.

Introduction

In recent years, increasing interest in biodegradable polymeric materials, owing to their environmental and ecological advantages, stimulates numerous studies on the properties and structure characterization of biodegradable polyesters, such as poly(butylene adipate) and poly(L-lactide), etc.[1,2] For this kind of material, biodegradability is one of the most essential properties. The biodegradation rate is another important parameter for specific applications. Therefore, great effort has been made on modulating the biodegradation rate of biodegradable polymers. It is well-known now that the biodegradation rate of a polymer depends not only on its chemical structure but also on its supermolecular structure. Abe and co-workers reported that the degradation rate of semicrystalline polyesters is inversely proportional to the lamellar thickness.[3] The dependence of degradation rate on crystal size makes it possible to control the degradation rate of a semicrystalline polyester simply through regulating its processing condition. This is, however, not quite sufficient enough since many of the polyesters exhibit pronounced polymorphisms depending on thermal treatment, which show also strong influence on their biodegradation behaviors. For example, poly(butylene adipate) (PBA), an aliphatic biodegradable polyester, exhibits two different modifications designated as α and β.[4−7] Experimental results on enzymatic degradation of melt-crystallized, α- and β-PBA films indicated that the α-PBA degraded relative faster than its β-counterpart, even though the α-crystals have larger crystal size than the β-crystals.[8] Taking this into account, a successful domination of the crystalline structure while regulating the crystal size during thermal process is of great importance.

Epitaxial crystallization provides a useful way to control the crystalline structure, e.g., orientation and modification, of semicrystalline polymers.[9−18] Lotz et al. have successfully modulated the melt-crystallization of isotactic poly(1-butene) in different modifications through regulating the crystalline structure of the substrate polymers.[16,17] Among many others, another example is that Lovinger has skillfully controlled crystallization of PVDF from melt in its piezoelectric and pyroelectric β-form at atmospheric pressure through polymer epitaxy.[18] Keeping all of those in mind, epitaxial crystallization may find potential application in dominating the crystalline structure of biodegradable polyesters during different thermal processes for regulating their crystal sizes.

In this work, the epitaxial crystallization of PBA induced by the oriented high-density polyethylene (PE) was studied. The purpose of this paper is to present some experimental results regarding the epitaxial behavior between PBA and PE as well as its controlling effect on PBA crystalline structure.

Experimental Section

The PBA and PE materials used in this work were produced by BASF AG Ludwigshafen, Germany. The weight-average molecular weight of PBA is about 4×10^4, with a polydispersity of 1.7. Its melting temperature is measured to be 57 °C. Before sample preparation, the PBA was purified by precipitating from its chloroform solution.

Highly oriented PE thin films were prepared according to a melt-drawing technique frequently described in detail elsewhere.[19−21] The resulting PE films (30−50 nm thick) are suitable for transmission electron microscopy (TEM) observations.

Layered samples for polarized optical microscopy (POM) and TEM observations were prepared by dipping glass slides covered with oriented PE thin films into 2 and 0.1 wt % PBA/chloroform solutions, respectively. Thick films, ca. 10 μm, were used for POM observation after evaporation of the chloroform and removing the PBA layer on the backside (without PE substrate) of the glass slide. Samples for TEM observation were floated on the surface of distilled water and mounted onto 400 mesh TEM copper grids. The prepared samples were either

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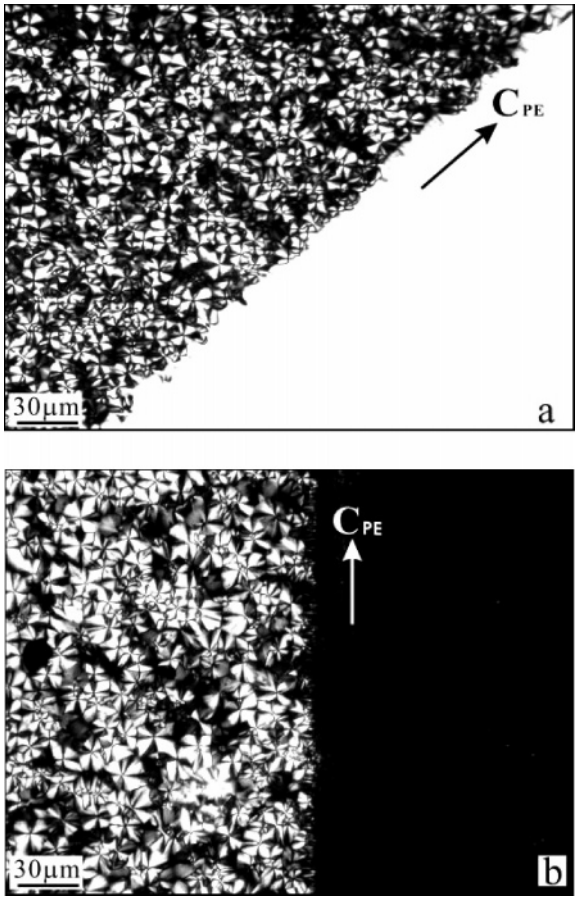

Figure 1. (a) A POM micrograph shows a boundary region of PBA crystallized from solution on glass slide, which is partially covered with highly oriented PE substrate. The PE substrate is located in the lower right corner of the picture. The arrow indicates its molecular chain direction. (b) A POM micrograph taken from the same area as in (a) but rotated 45° anticlockwise about the light beam.

used directly for POM or TEM observations or heat-treated at 75 °C (below the melting point of PE but above the melting point of PBA) for 10 min and then cooled to desired temperatures for isothermal crystallization.

For TEM observations, a JEM GEOL-100CX operated at 100 kV was used in this study. Bright-field (BF) phase contrast micrographs were obtained by defocus of the objective lens. For POM observation, an Olympus BH-2 optical microscope equipped with a LTS350 hot stage was used. All of the optical micrographs shown in this paper were taken under polarized light with the polarization direction horizontal.

Wide-angle X-ray diffraction (WAXD) experiments were carried out using a 12 kW rotating-anode generator (Cu KR) in combination with a Geigerflex D/max-RB diffractomter. The reflection peak positions and widths were calibrated with silicon powder ($2\theta > 15°$) and silver behenate ($2\theta < 10°$). Powder patterns were taken in reflection mode at a scan rate of 10°/min within the 2θ angle region of 15−30°.

Results and Discussion

Crystallization from Solution. The crystallization behavior of PBA from solution on highly oriented PE substrate was at first checked by polarized optical microscope (POM). Figure 1a presents a POM micrograph of the as prepared PBA/PE double layers, which was observed directly after the evaporation of the solvent. For a direct comparison, a boundary region was chosen with the thin PE film located at the lower right corner of Figure 1a. The boundary line of PE substrate can be clearly recognized. The arrow indicates the

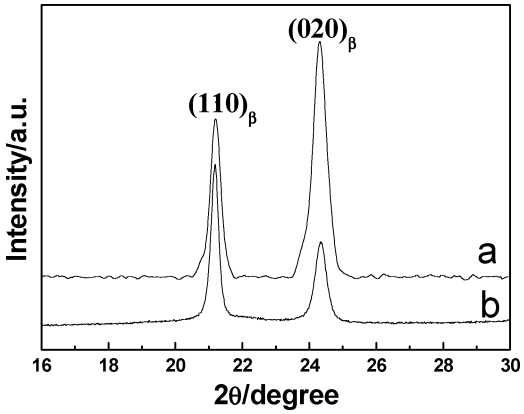

Figure 2. WAXD patterns of PBA crystallized from solution on (a) PE and (b) glass substrates.

drawing direction of highly oriented PE substrate during preparation, i.e., its chain orientation. Considering that the PE film is too thin to provide birefringence contribution at present condition, it is the PBA layer that contributes the birefringence in POM micrograph. From Figure 1a, it can be clearly seen that the supermolecular structures of PBA crystallized on glass and PE surfaces are quite different. On the glass substrate, irregular spherulitic structure of PBA can be recognized. This is typical for polymer crystallized from solution on glass slide. On the other hand, the PBA crystals on the PE substrate show very strong birefringence with respect to those on glass surface. Moreover, no individual PBA crystals can be identified. This implies that the PE substrate exhibits very strong nucleation ability toward PBA, which results in the formation of abundant microcrystallites, which cannot be resolved under optical microscope. Another feature of the PBA crystals formed on PE substrate is that they exhibit exceptional extinction phenomenon during the rotation of the sample about light beam axis. Every ±45° rotation of the sample leads to a complete contrast inversion of the PBA crystals on PE substrate. As an example, Figure 1b shows a POM micrograph taken from the same region as Figure 1a with only a 45° anticlockwise rotation about the beam axis. The extinction phenomenon of PBA crystals on PE substrate during the rotation process indicates that these crystals are preferentially oriented. According to the role of light extinction under polarized optical microscope, it can be concluded that the chains of PBA are oriented in the film plane and aligned either parallel or perpendicular to the chain direction of PE substrate crystals. From the above observations, it can be concluded that heteroepitaxial crystallization of PBA on oriented PE substrate takes place during the evaporation process of the solvent.

To check the crystalline structure of the PBA crystallized from solution on neat glass slide and PE substrate, wide-angle X-ray diffraction measurement was performed on the sample used for Figure 1. Figure 2 shows the X-ray diffraction patterns of PBA solution grown on neat glass side as well as PE substrate. From Figure 2, it can be evidently seen that in both cases the PBA crystallizes in the same modification. The observed peaks can be indexed as the (110) and (020) reflections of PBA crystal in its β-modification, reflecting the crystallization of PBA from solution in β-form regardless of the substrate. The diffraction peak intensity of the PBA crystallized on neat glass slide and PE substrate is, however, different. On the PE substrate, the intensity

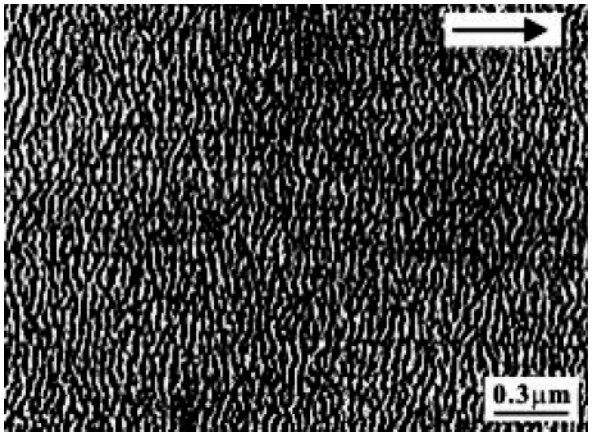

Figure 3. A BF electron micrograph of PBA crystallized on PE substrate from solution. The arrow shows the chain direction of PE substrate.

of the (020) β-PBA reflection increases remarkably. This may be related to the preferred orientation of PBA on PE substrate results from heteroepitaxy, as reported by Wittmann and Lotz et al. on many other aliphatic polyester systems.

To get more detailed structural information on PBA crystallized on PE surface from solution, TEM observation was conducted using ultrathin films. The structure of melt-drawn PE films, which exhibit a high degree of fiber orientation with the edge-on lamellae aligned perpendicular to the drawing direction, has been described in detail elsewhere and will not be repeated here.[19−21] Figure 3 shows the bright field (BF) phase contrast electron micrograph of the PBA crystallized from solution on highly oriented PE surface. The arrow in the picture indicates the drawing direction of the PE film during preparation. It is evident that the PBA film consists of highly oriented edge-on lamellae aligned perpendicular to the chain direction of PE substrate. This implies that heteroepitaxy of PBA on PE substrate takes place with both polymer chains parallel. The corresponding electron diffraction pattern of the PBA/PE double layers and a sketch of it with the main reflections being indexed are shown in parts a and b of Figure 4, respectively. The appearance of sharp and well-defined reflection spots of both PBA and PE on the electron diffraction pattern (see Figure 4a) confirms that both PBA and PE substrate layers are highly oriented. The alignment of [00*l*] of PBA along [002] of PE reflects a parallel orientation between PBA and PE chains. This kind of mutual orientation has been frequently reported for many other epitaxial systems with PE.[22−24] Moreover, all of the PBA reflection spots in Figure 4a are accounted for by its orthorhombic unit cell in β-form. This confirms the occurrence of epitaxial crystallization of PBA from solution on PE substrate in its β-form. The absence of (020) and appearance of strong (110) and weak (210) reflection spots of β-PBA in the equator (see Figure 4a) indicates that the (110) lattice plane of the PBA crystals are preferentially in contact with the PE substrate. One may note that the electron diffraction is somewhat different from the wide-angle X-ray diffraction. These results are actually in good accordance considering reflection mode was used for X-ray diffraction.

Crystallization from Melt. Figure 5 illustrates the morphologies of melt-crystallized PBA on glass and PE surfaces. The samples prepared in the same way as in

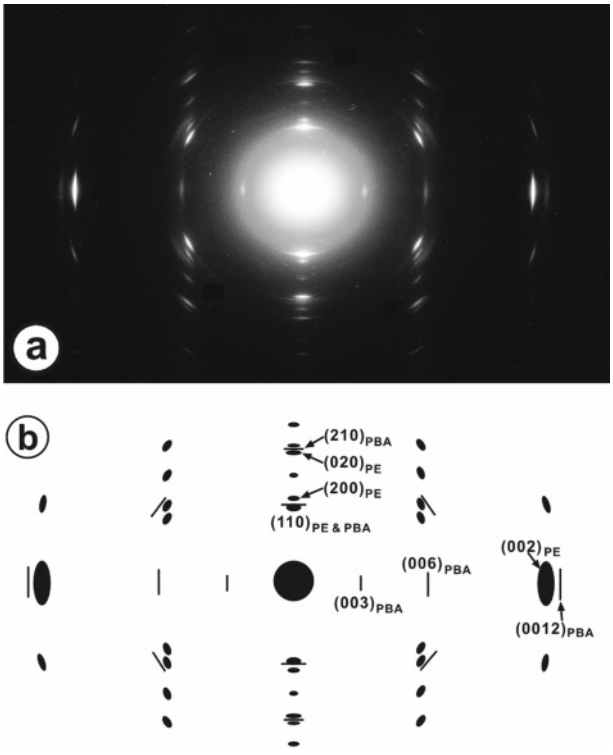

Figure 4. (a) An electron diffraction pattern and (b) its sketch with main reflections being indexed of PBA/PE double layers as shown in Figure 3. The solid ellipses represent the electron diffractions of PE, while the lines represent the reflection spots of PBA.

Figure 1 were heated to 75 °C for 10 min and subsequently cooled at a rate of 30 °C/min to (a) 35, (b) 30, and (c) 25 °C for isothermal crystallization. In Figure 5, boundary regions were used to reflect the exact same thermal conditions for the PBA crystallized on glass slides and PE substrates. The PE substrates are located at the lower right corners in the pictures. The chain directions of PE substrates are parallel to the boundary lines as indicated by the arrows. The morphologies of PBA crystallized on PE substrates have close resemblance with that shown in lower right part of Figure 1a, and no noticeable difference between the samples crystallized on PE substrates at different temperatures could be recognized under optical microscope. Both X-ray diffraction and electron microscopy observations confirm the occurrence of heteroepitaxy of PBA on PE substrate in β-form at all used crystallization temperatures.

On the contrary, evident changes were observed for the PBA crystallized on the neat glass surface at different temperatures. Crystallizing the PBA at 35 °C on a glass slide (see upper-left corner of Figure 5a) results in the formation of relatively larger spherulites. When crystallizing the PBA at 30 °C (upper-left corner of Figure 5b), except for the reduction of spherulite size, the morphology of the spherulites also changes as can be judged from the appearance of regular banding, which can be more clearly seen in the enlarged image as inserted in the upper left corner of Figure 5b. With further decrease of crystallization temperature, e.g. 25 °C, the banded structure disappears (see Figure 5c). The banded structure can only be observed in PBA samples crystallized in temperature range of 27−32 °C. Moreover, apparent transcrystallization layers can be observed in Figure 5 under any crystallization conditions.

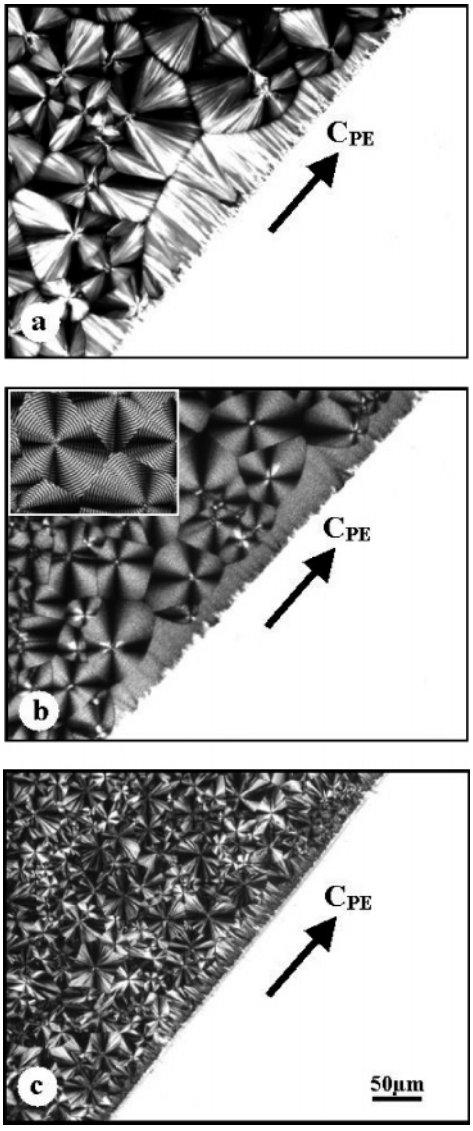

Figure 5. Optical micrographs showing the morphologies of PBA crystallized from melt on PE and glass substrates. The crystallization temperatures were (a) 35, (b) 30, and (c) 25 °C. The arrows indicate the chain direction of PE substrates.

This is different from the solution grown samples, comparing Figure 5 with Figure 1. The difference originates from the different nucleation process. For solution crystallization process, nucleation and crystal growth of PBA can only proceed when the PBA precipitated out from the solution as solvent evaporated. This leads to almost simultaneous occurrence of PBA crystallization regardless of the substrate, even though different substrate may affect the resulting morphology. On the other hand, melt crystallization of polymers is a supercooling driven process. An active nucleation agent may result in the crystallization of a polymer at a temperature several degrees higher than its bulk crystallization. In present case, the crystallization of PBA on PE takes place while its bulk crystallization is hardly realizable. The densely spaced nuclei on the boundary line of PE substrate initiate the transcrystal growth of PBA owing to spatial confinement.

Wide-angle X-ray diffraction measurements were used to characterize the crystalline structures of the PBA crystallized on glass at each temperature. As shown in Figure 6, the crystalline structure of PBA crystallized on neat glass surface depends strongly on

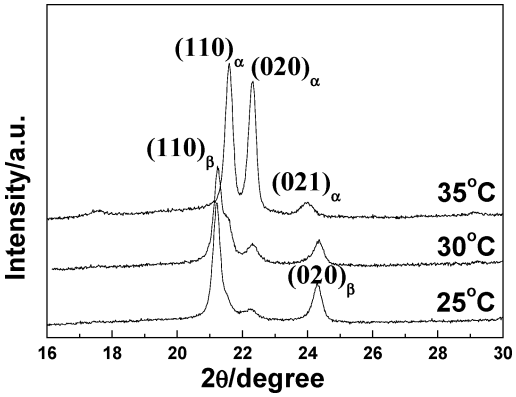

Figure 6. X-ray diffraction patterns of PBA crystallized from melt on glass substrates at different temperatures.

the crystallization temperature. It is clear that the PBA crystallizes in its α-form on the glass slide at high temperature, e.g. 35 °C, whereas mainly β-PBA crystals are observed at lower temperature, for example 25 °C. Crystallizing the PBA at moderate temperature leads to the formation of a texture with α- and β-PBA crystals coexist. This is in good agreement with that reported in ref 25.

From the above experimental results, it is concluded that based on the similar orthorhombic unit cell of β-PBA ($a = 0.506$, $b = 0.735$, and $c = 1.467$ nm) and PE ($a = 0.74$, $b = 0.494$, and $c = 0.2534$ nm)[26] epitaxial crystallization of PBA on PE substrate results in the formation of β-PBA crystals from both solution and melt, regardless of the crystallization temperature.

Conclusions

The crystallization behavior of PBA from solution and melt on highly oriented PE substrates and glass slides at exactly same conditions was directly compared. The results clearly indicate that the PBA can crystallize epitaxially on the oriented PE substrate. This means that the PE exhibits very strong nucleation ability toward PBA, which is also reflected by the transcrystallization of PBA at the boundary of PE substrate. The epitaxial crystallization of PBA on PE substrate results in the formation of β-PBA crystals from both solution and melt, regardless of the crystallization temperature. This is associated with the perfect lattice matching between the β-form PBA and PE crystals and provides us a simple way to control the crystalline modification of PBA during different processing process in order to regulate its crystal size.

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