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ORIGINAL CONTRIBUTION

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Epitaxial behavior of HDPE on the boundary of highly oriented iPP substrates

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Abstract The epitaxial crystallization behavior of high-density polyethylene on the boundary of highly oriented isotactic polypropylene (iPP) substrates has been investigated by means of atomic force microscopy (AFM) and transmission electron microscopy (TEM). The results obtained from AFM and TEM indicate that the epitaxial nucleation of HDPE on the highly oriented iPP substrates occurs earlier than that in the pure HDPE phase, i.e., homogeneous nucleation. Therefore the epitaxially grown HDPE lamellae can grow across the boundary of the iPP substrate into the HDPE spherulitic phase with the epitaxial orientation relationship remaining.

Key words Epitaxial crystallization – high-density polyethylene – isotactic polypropylene – morphology

Introduction

Epitaxy is defined as the crystallization of one material (guest crystal) on the surface of a crystal of another material (host crystal) in one or more strictly defined crystallographic orientations [1]. In the past 10 years heteroepitaxy between some semicrystalline polymers has been of particular interest because of both the unusual crystalline morphology and the synergism of their mechanical properties [2–4]. A number of publications have appeared on the epitaxial crystallization of isotatic polypropylene (iPP) with some zig-zag chain polymers, such as polyethylene (high-density, linear low-density, low-density) [5–10], polyoctenamer [11, 12], *trans*-1,4-polybutadien [13], and polyamides, in which the zig-zag chains are inclined ± 50° to the iPP chain direction. This kind of epitaxial orientation relationship has been explained in terms of the alignment of the zig-zag chain segments along methyl group rows in the (010) lattice plane of iPP with a 0.5-nm intermolecular distance for a chain-row matching [14], and a 15% disregistry between the matching lattice spaces of the two crystals is considered as an upper limit [15]. According to this explanation, it can be deduced that the (010) lattice plane of iPP plays a determinative role in this kind of epitaxy. However, in our experiments the melt-drawn iPP oriented substrate film has a fiber texture, which contains only a small number of exposed (010) lattice planes in the top surface. Therefore the epitaxial crystallization of the above mentioned zig-zag chain polymers on the surface of the melt-drawn oriented iPP substrate is hard to understand. This paper presents some experimental results regarding the epitaxial crystallization behavior of high-density polyethylene (HDPE) on the boundary of a highly oriented iPP substrate.

Experimental

The polymers used in this work were isotactic polypropylene and polyethylene (type Novolene, and Lupolen 6021 DX, both from BASF Ludwigshafen, Germany). Uniaxially oriented thin films of iPP and HDPE were prepared according to a technique introduced by Petermann and

Gohil [16]. According to this method, a small amount of a 0.5% solution of the polymer (iPP and HDPE) in xylene was poured and spread on a preheated glass slide where the solvent was allowed to evaporate. After evaporation of the solvent the remaining thin polymer film was then picked up by a motor driven cylinder with a drawing speed of approx. 20 cm/s. The temperatures for preparing the melt-drawn films of iPP and HDPE were 140° and 130 °C, respectively. The resulting highly oriented films, which are about 50 nm thick, can be mounted on copper grids or a freshly cleaved surface of mica, and directly used for transmission electron microscopy (TEM) or atomic force microscopy (AFM) observations, respectively. For the AFM observations of the crystallization behavior of HDPE on the boundary of the oriented iPP substrate the thin HDPE film was floated on top of the surface of distilled water and mounted onto the surface of the mica, which was covered only partially by an oriented iPP film, then heated to 150 °C for 15 min and quickly cooled to room temperature. For TEM observations the double-layered film of HDPE with iPP was prepared as follows. The thin HDPE film was transferred onto the surface of a glass slide, which was covered partially by an iPP film, and then heat-treated at 150 °C for 15 min. After cooling quickly to room temperature the film was detached from the glass slide onto the surface of distilled water with help of a poly(acrylic acid) layer and mounted on copper grids. A Philips CM200 TEM operated at 200 kV was used in this study. Bright-field (BF) micrographs were obtained by defocus of the objective lens. AFM experiments were carried out with a DME Rasterscope 3000. The pictures were obtained with a contact mode scan head (maximum scan range: 9 × 9 μm^2). Si_3N_4 tips attached to a microfabricated cantilever (200 μm, triangular base) were used. The force constant of the cantilever is 0.22 N/m. The scanning line frequency is 1 Hz. All images presented here are raw data.

Results

Microstructure of highly oriented iPP and HDPE films

Figure 1 shows TEM and AFM images of the highly oriented iPP substrate film. The arrows in the micrographs indicate the drawing directions of the films. On the BF electron micrograph (Fig. 1a) small lamellae of iPP are visible which are aligned perpendicular to the drawing direction of the film. The corresponding electron diffraction pattern (insert in Fig. 1a) reveals a high degree of chain-axis orientation. On AFM (Fig. 1b) highly oriented iPP lamellae can be clearly seen.

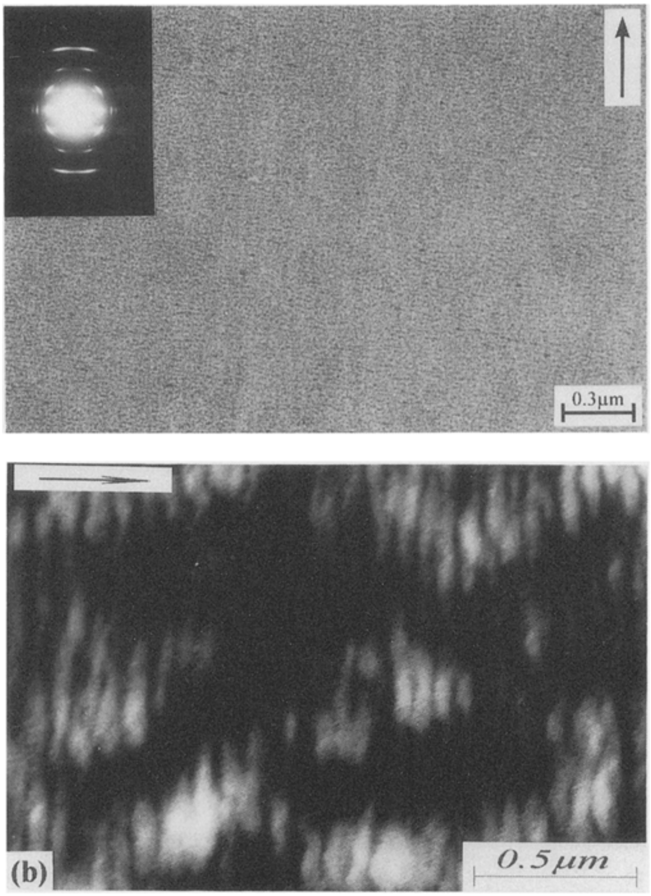

Fig. 1A TEM and **B** AFM of iPP oriented film. *Arrows*, molecular directions

The BF electron micrograph and AFM of HDPE oriented films (Fig. 2) show that the HDPE film consists of oriented lamellae and needle crystals, i.e., shish-kebab morphology. The electron diffraction pattern (insert in Fig. 2) indicates a high degree of crystalline orientation with the a-axis perpendicular to the film plane and the c-axis parallel to the drawing direction of the film [17].

AFM observations of the crystallization behavior of HDPE on the boundary of oriented iPP substrate film

Figure 3a shows an AFM of a HDPE-iPP double-layered film which was heat-treated at 150 °C for 15 min and then cooled rapidly to room temperature. The molecular direction of the iPP substrate film is horizontal (as indicated by an arrow). It can be clearly seen that a cross-hatched lamellar structure of HDPE arises with the HDPE lamellae being inclined at ± 40° with respect to the c-axis of the iPP substrate. This is the typical epitaxial morphology of the HDPE-iPP system. The peculiar arrangement of the

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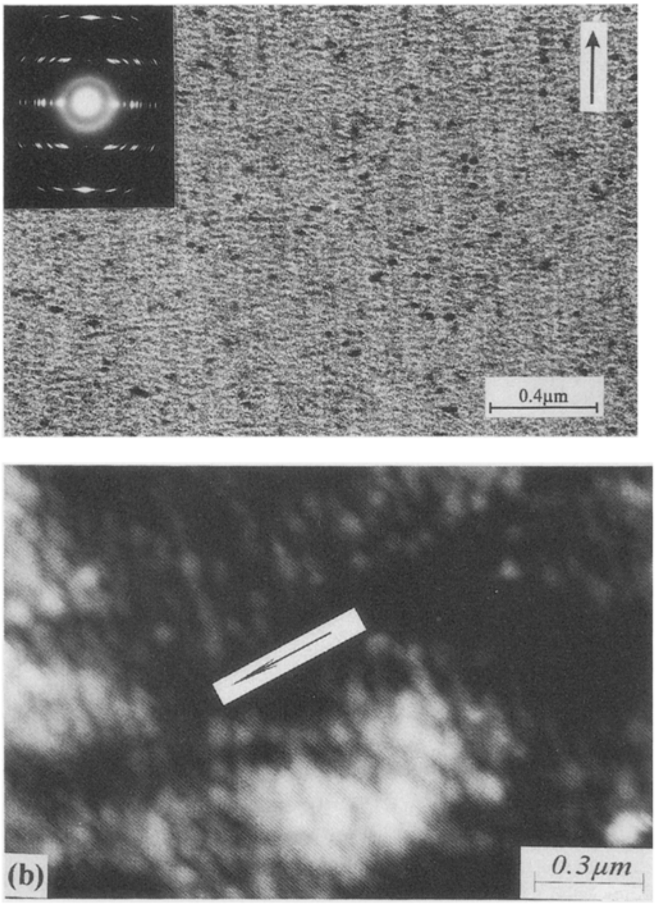


Fig. 2A TEM and **B** AFM of HDPE oriented film. *Arrows*, molecular directions

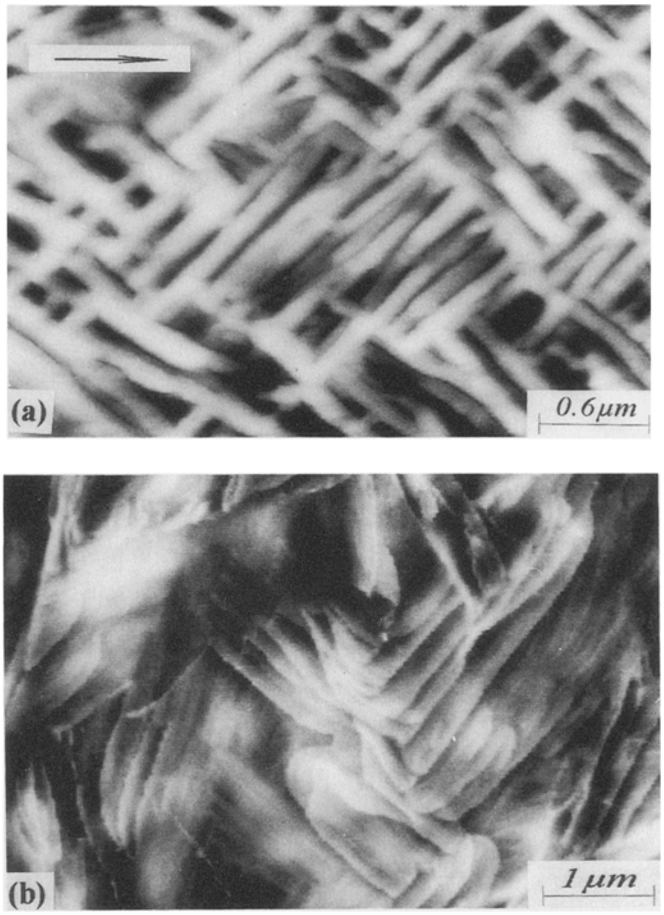


Fig. 3 AFM of HDPE **A** on the top surface of oriented iPP film and **B** on the top surface of freshly cleaved mica. The samples were heat-treated at 150 °C for 15 min and then quickly cooled to room temperature. *Arrow*, molecular directions of oriented iPP substrate in **A**

HDPE crystals was explained with the epitaxial crystallization of HDPE on oriented iPP substrate in terms of the alignment of the zig-zag HDPE chains in (100) lattice plane along the methyl group rows of iPP in the (010) lattice plane [14]. The HDPE which is on the neat surface of the mica, creates a normal spherulitic structure after melting and recrystallization (Fig. 3b). The crystallization behavior of HDPE on the boundary of the oriented iPP substrate is shown in Fig. 4. The difference between Fig. 4a and 4b is the molecular directions of the oriented iPP substrates, which are located in the bottom part of the pictures. As indicated by the arrows, the molecular direction of iPP substrate in Fig. 4a is vertical to the boundary line, while in Fig. 4b it is parallel to the boundary line of the iPP film. The top parts of both Fig. 4a and 4b lack iPP substrate. Therefore the morphology of the HDPE in these parts of the pictures is the same as that in Fig. 3b. On the boundaries (Fig. 4a, b) a special morphology arises where the HDPE lamellae grow epitaxially across the boundary of the iPP substrate and extend into the area without the iPP substrate.

TEM observations of the crystallization behavior of HDPE on the boundary of the oriented iPP substrate

Figure 5 shows a BF electron micrograph of HDPE crystallized on the boundary of the iPP substrate. The thermal history of the sample used here is the same as that used in the AFM experiment. The HDPE, which is located in the bottom part of Fig. 5, is supported by an oriented iPP film, and the molecular direction of the iPP substrate is horizontal (as indicated by an arrow). The top part of Fig. 5 reveals a spherulitic morphology of the pure HDPE.

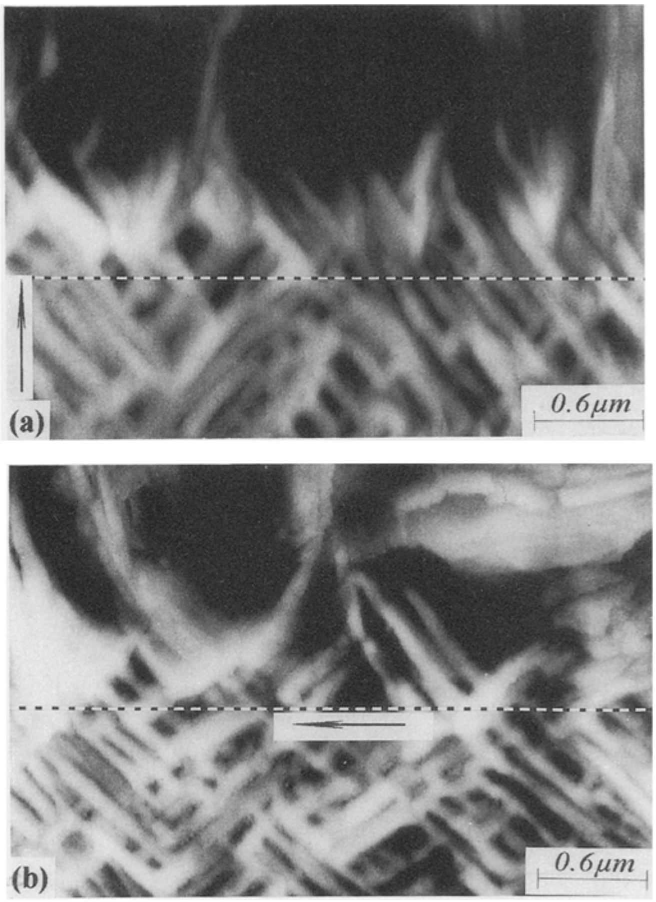
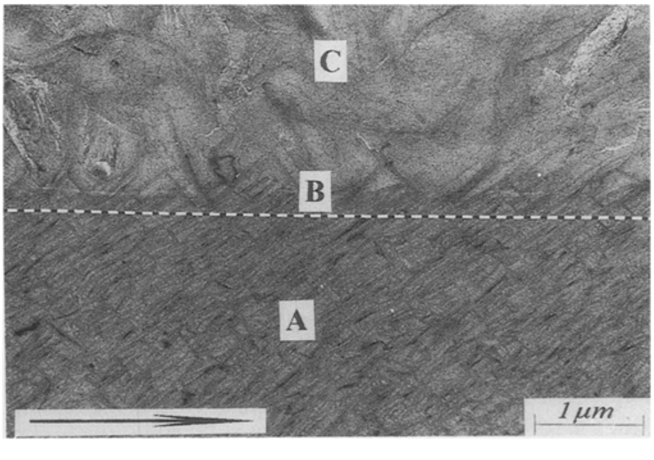


Fig. 4 AFM micrograph of HDPE on the boundary of the oriented iPP substrate *bottom* iPP substrate; *arrows*, molecular directions of iPP. The samples were heat-treated as in Fig. 3

Fig. 5 TEM of HDPE on the boundary of the oriented iPP substrate. *A* iPP substrate; *arrow*, molecular directions of the iPP substrate; *B* boundary; *C* only pure HDPE. The thermal history of the sample used here is the same as used in AFM experiments.



It is clearly to recognized that Fig. 5 has a close resemblance to Fig. 4. On the boundary are epitaxially grown HDPE lamellae, which extend over the boundary of the iPP substrate into the spherulite area.

The corresponding electron diffraction patterns of the different areas, defined as A, B and C in Fig. 5, are shown in Fig. 6. Obviously, in Fig. 6a there are both electron diffractions of the HDPE and iPP. The molecular direction of the iPP substrate is horizontal. Figure 6a exhibits a typical epitaxial orientation relationship between HDPE and iPP. The c-axes of the two crystals are ± 50° apart, whereas two sets of HDPE lamellae have each a single crystalline orientation with the [020] and [002] lattice directions in the plane of the film. The contact planes of the two crystals are (100) for HDPE. The corresponding electron diffraction pattern of the HDPE in C of Fig. 5 shows a set of Debye–Scherrer rings characterized by the spherulitic morphology (Fig. 6c). Figure 6b shows the corresponding electron diffraction pattern of the boundary area of Fig. 5 (indicated by a B in Fig. 5). Although there are no diffraction spots of the iPP substrate in this area, the two sets of epitaxially oriented HDPE diffraction patterns remain the same as in Fig. 6a. Furthermore, it should be pointed out that a weak (110) Debye–Scherrer ring is attributed to a small amount of randomly oriented HDPE crystals. This result strongly confirms that the HDPE, which is on or near the boundary of the iPP substrate can grow epitaxially across the boundary into the area with pure HDPE.

Combining the above results obtained by AFM and TEM investigations, a model of the crystallization behavior of HDPE on the boundary of the oriented iPP substrate can be proposed. As shown in Fig. 7, after melting and recrystallization the HDPE, which is direct on the top of the iPP substrate, recrystallizes epitaxially on the iPP substrate and forms a cross-hatched texture. On the boundary the epitaxially grown HDPE lamellae grow through the boundary into the pure HDPE area with the epitaxial orientation relationship remaining. Farther away from the boundary of the iPP substrate the pure HDPE crystallizes in a spherulitic morphology.

Discussion

In all TEM studies of the polymer/polymer epitaxial interfaces until now the substrates and the layers have been investigated with the electron beam perpendicular to the sample surfaces, as also in our investigations. However, having a sharp boundary between a substrate, which creates epitaxy of the layer, such as oriented iPP, and a substrate which does not initiate epitaxy, such as a glass surface or nonoriented iPP, the nucleation and growth

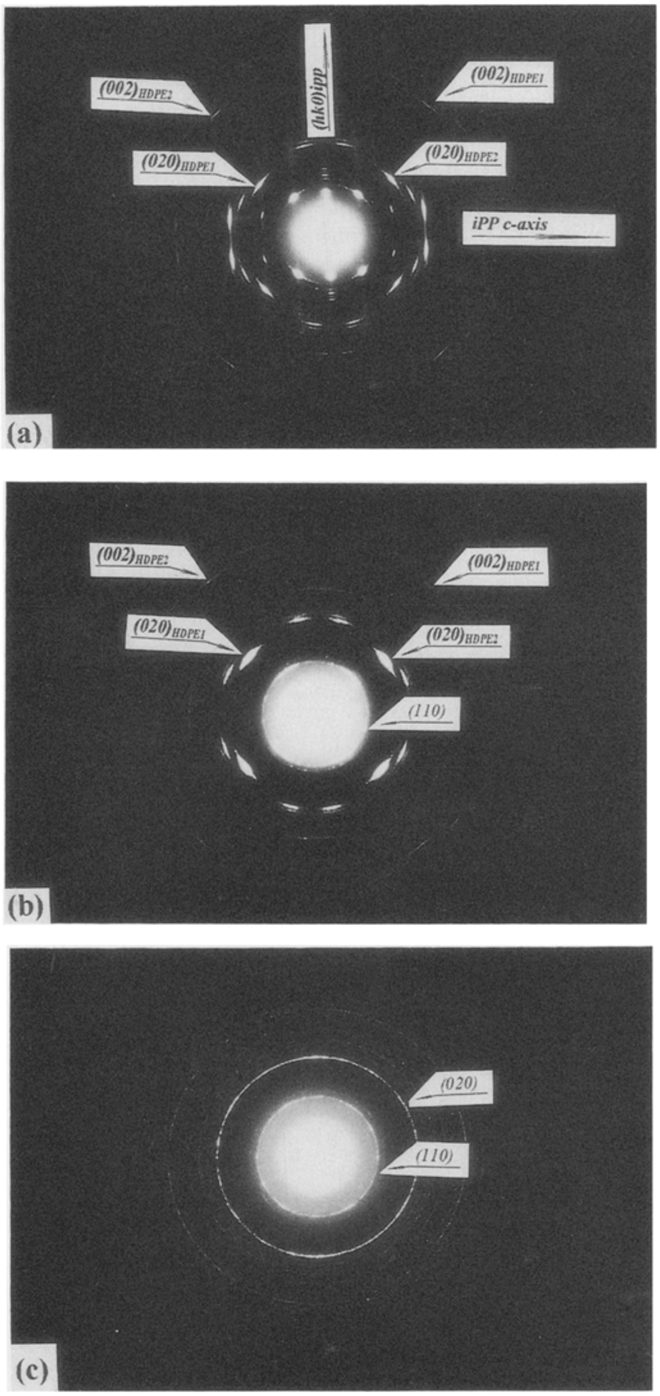


Fig. 6 The corresponding electron diffraction patterns of the different areas in Fig. 5

behavior of the layer on the boundary can be investigated and new results expected.

There are still some open questions about the origin of the epitaxial growth. Wittmann et al. [14] explained the epitaxy between PE and iPP by an alignment of PE chains along the methyl side groups of the iPP chains in the (010) plane and into the [101] direction of the iPP and a molecular matching of those row distances with distances of (200) lattice planes of the PE crystals. Petermann et al. [10] also proposed the alignment of the PE chains along the methyl side groups of the iPP but suggested that this alignment is nucleation induced, and that the epitaxy results from the growth of those nuclei with their fastest growth direction (for PE the [010] direction) in the film plane. Phillips et al. [18] suggested an epitaxial nucleation and proposed that at low supercooling the critical nucleus size of the HDPE can be larger than the iPP substrate crystal, and that consequently no epitaxial crystallization of HDPE on iPP substrate occurs, as it is observed at low supercooling [10].

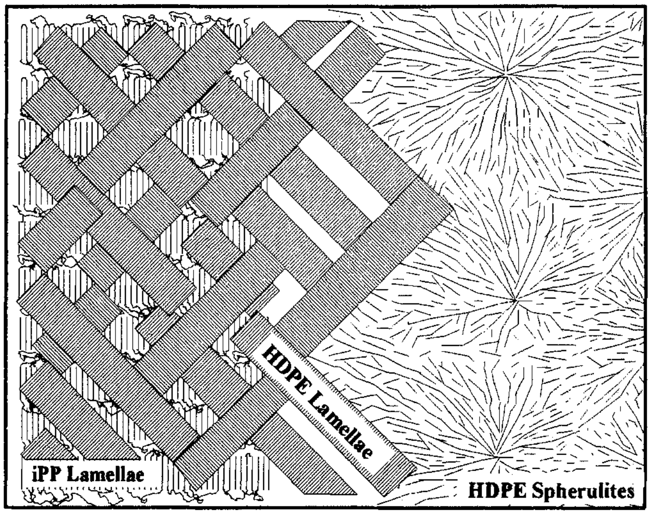


Fig. 7 Model of HDPE crystallized on the boundary of the iPP substrate

From the fact that the epitaxially grown HDPE lamellae can extend over the boundary of the oriented iPP substrate into the pure HDPE area, it can be concluded that the epitaxial crystallization of HDPE on oriented iPP substrate is caused by oriented nucleation of HDPE on the surface of the iPP substrate, and that the growth of HDPE crystals occurs along their fastest directions, i.e., their b-axes. Therefore, the HDPE lamellae, which are produced by the oriented nuclei on or near the boundary of the oriented iPP substrate, can grow epitaxially across the boundary of the iPP substrate into the pure HDPE area.

Conclusion

The experimental results obtained from AFM and TEM show that the HDPE lamellae can grow epitaxially across the boundary of the iPP substrate into the pure HDPE area. From these results it can be concluded that the epitaxy between HDPE and oriented iPP substrate results from the oriented nucleation effect of iPP substrate on the HDPE crystals and the growth of the HDPE crystals along their fastest directions, namely their b-axes. The chain-row matching may be only a controlling factor for the creation of the oriented nuclei of HDPE on the iPP substrate, but it may not control the whole epitaxial crystallization process.

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