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A comparison of the crystallization behavior of HDPE on oriented iPP and sPP substrates

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Abstract

The crystallization behavior of high-density polyethylene (HDPE) on highly oriented isotactic or/and syndiotactic polypropylene (iPP or/and sPP) substrates at various conditions was studied by means of transmission electron microscopy and electron diffraction. The results indicate that HDPE crystals always grow epitaxially on the iPP substrates under the conditions performed, while on the oriented sPP substrate epitaxially grown HDPE can only be observed when quenching the HDPE-melt directly to room temperature. The reason for this phenomenon results from the thinner lamellae of sPP compared to iPP, and consequently smaller critical nucleus size of HDPE is required for the occurrence of its epitaxial crystallization on the sPP substrate. It is further found that the melt-drawn oriented polymer films are ideal substrates for conducting comparative studies of polymer hetero and graphoepitaxy. By comparing the hetero and graphoepitaxies of HDPE–iPP and HDPE–sPP systems, it is concluded that the heteroepitaxial interaction between polymers is stronger than their graphoepitaxial counterpart. Therefore, heteroepitaxy of polymers takes place prior to their graphoepitaxy © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Isotactic polypropylene; Syndiotactic polypropylene; Polyethylene; Heteroepitaxy

1. Introduction

Since the first synthesis and characterization of stereoregular polypropylenes, i.e. isotactic and syndiotactic polypropylenes (iPP and sPP, respectively), by Natta et al. in the 1960s [1–4], the morphological studies of iPP were followed extensively [5–7], and sophisticated understanding on the molecular level has been achieved [8–11]. The sPP, due to the difficulties in its synthesis, has received much less attention, and the earlier work had not been continued for almost three decades. Very recently, the development of the new metallocene catalyst systems has made it possible to produce sPP with high stereoregularity [12]. As a result, the interest in the structural and morphological studies of sPP increased in the past few years, and the understanding of its structure has raised drastically.

The same situation has happened in the field of polymer epitaxy. Epitaxial crystallization between iPP and polymers having zigzag chain conformations, such as polyethylene (PE) [13–15], polyamides [16], as well as polyesters [16,17], was studied in detail for many aspects. The epitaxial behavior between sPP and other polymers was, however, less documented. Only four publications dealing with the epitaxial events of sPP have appeared until now [18–21]. The purpose of this work is to exhibit a comparison of the crystallization behavior of HDPE on highly oriented iPP and sPP substrates at various conditions.

2. Experimental

The polymers used in this work were high-density polyethylene (HDPE), type Lupolen 6021 DX, and isotactic polypropylene (iPP), type Novolene 1050FP, both produced by BASF AG Ludwigshafen, Germany. The highly syndiotactic polypropylene (sPP), having a melting temperature of about 160°C, was supplied by Prof. Dr Kaminsky of the University of Hamburg, Germany. Highly oriented polymer films were prepared according to a melt-drawn technique outlined by Petermann and Gohil [22]. While the highly oriented iPP and sPP films were used as the substrates for HDPE, melt-drawn HDPE films were used as the layered material due to better uniformity compared to solution cast films. The double layered HDPE–iPP and HDPE–sPP films were prepared by transferring the HDPE thin films onto the TEM grids, which were covered by highly oriented iPP or sPP films. In order to compare the nucleation effects of iPP and sPP on the HDPE crystals, sandwich samples with the HDPE film in between the oriented iPP and sPP films were also made. All samples were heat-treated at a temperature of

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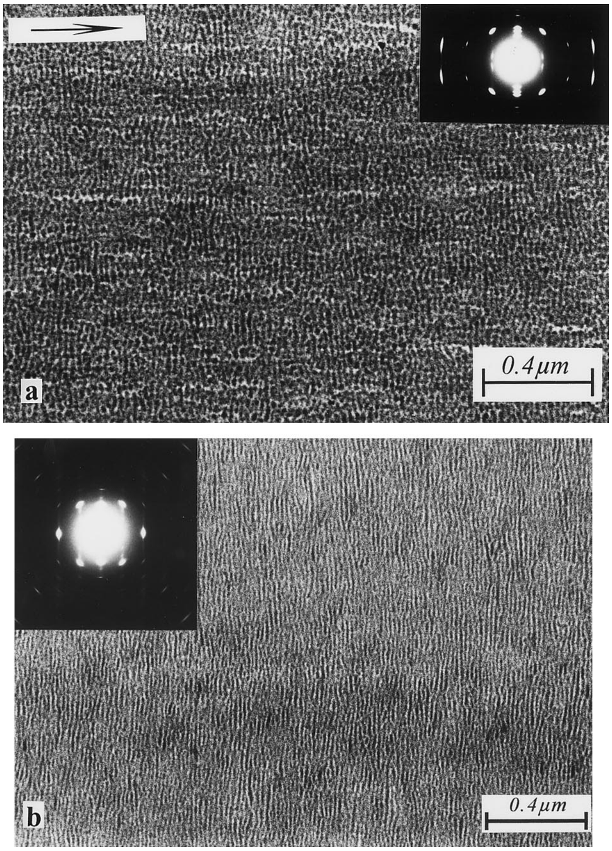

Fig. 1. BF electron micrographs and electron diffraction patterns (inset) of highly oriented (a) iPP and (b) sPP films. The arrow shows the orientation direction of the films.

150°C, below the melting point of iPP and sPP but above the HDPE melting point, for 10 min and then cooled with different rates to various temperatures. The thermal treatment of HDPE–iPP and HDPE–sPP systems for each chosen condition was carried out simultaneously in order to provide the exactly same thermal history of HDPE on the iPP and sPP substrates. 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. In order to minimize radiation damage of the polymer samples caused by the electron beam, focusing of the sample was carried out on one area, the specimen film was then translated to its adjacent undamaged area and the image was recorded immediately.

3. Results

3.1. Basic structure of oriented iPP and sPP substrates

Fig. 1 shows the BF electron micrographs and electron diffraction patterns (inset) of the highly oriented iPP and sPP substrate films. The arrow in the micrograph indicates the drawing direction of the film during preparation. The dark lines represent the crystalline lamellae of the corresponding polymers, while the bright regions between the crystalline lamellae reveal their amorphous areas. It can be seen that both iPP and sPP oriented films consist of highly oriented lamellar crystals arranged perpendicular to the drawing direction. The average thicknesses of the crystalline lamellae, i.e. the length of the fold stems of the polymer chain, are about 16 and 10 nm for iPP and sPP, respectively. The electron diffraction patterns demonstrate that both iPP and sPP melt-drawn films exhibit a high degree of fiber orientation with the *c*-axis (molecular chain direction) oriented parallel to the drawing direction, while the *a*- and *b*-axes rotate about the *c*-axis randomly.

The morphology of HDPE as prepared highly oriented films has been described in details elsewhere [23], and is not important here because they are melted and recrystallized before the electron microscopic observation.

3.2. Morphologies of HDPE crystallized on highly oriented iPP and sPP substrates at isothermal crystallization conditions

Fig. 2 shows the BF electron micrographs of HDPE–iPP and HDPE–sPP double layered films, which were heated to 150°C for 10 min, and then crystallized isothermally at 122°C for 2 h. The arrows in the micrographs represent the molecular chain directions of the iPP and sPP substrates, which can be clearly seen with their lamellae arranged perpendicular to their chain directions, especially in the high magnification images (Fig. 2(c) and (d)). The HDPE on the iPP as well as on the sPP substrates crystallize in form of edge-on lamellar crystals, but create quite different morphologies. While epitaxially aligned on the iPP substrate with lamellae ±40° apart from the chain direction in the iPP crystals and forming a cross-hatched lamellar texture, the HDPE lamellae crystallized on the sPP substrate do not display any preferred orientation. Moreover, the sizes of HDPE lamellar crystals grown on the iPP and sPP substrates are different. Except for the same lamellae thickness (ca. 24 nm), which is expected because of the exactly same thermal treatment of both samples, the lateral width of HDPE lamellae on sPP substrate is much larger than on the iPP substrate. These differences clearly imply that unlike the iPP, the sPP substrate crystals exhibit no specific nucleation effect on the HDPE crystals at the present condition. Consequently, the nuclei density of HDPE on sPP is lower than on iPP. As a result, larger HDPE lamellae are formed on the sPP substrate. The results of the corresponding electron diffraction (Fig. 3) are in good agreement with the BF observation. Fig. 3(a) gives the information of HDPE crystallized on the iPP substrate and displays the epitaxial crystallization of HDPE on the iPP substrate with the chain directions of both polymers inclined at angles of ±50°, and the contact plane of HDPE with the iPP substrate is the $(100)_{\mathrm{HDPE}}$ lattice plane. In Fig. 3(b), the appearance of discontinuous reflection rings of the HDPE superimposed on sharp sPP reflections results from the fact that the lamellar width is

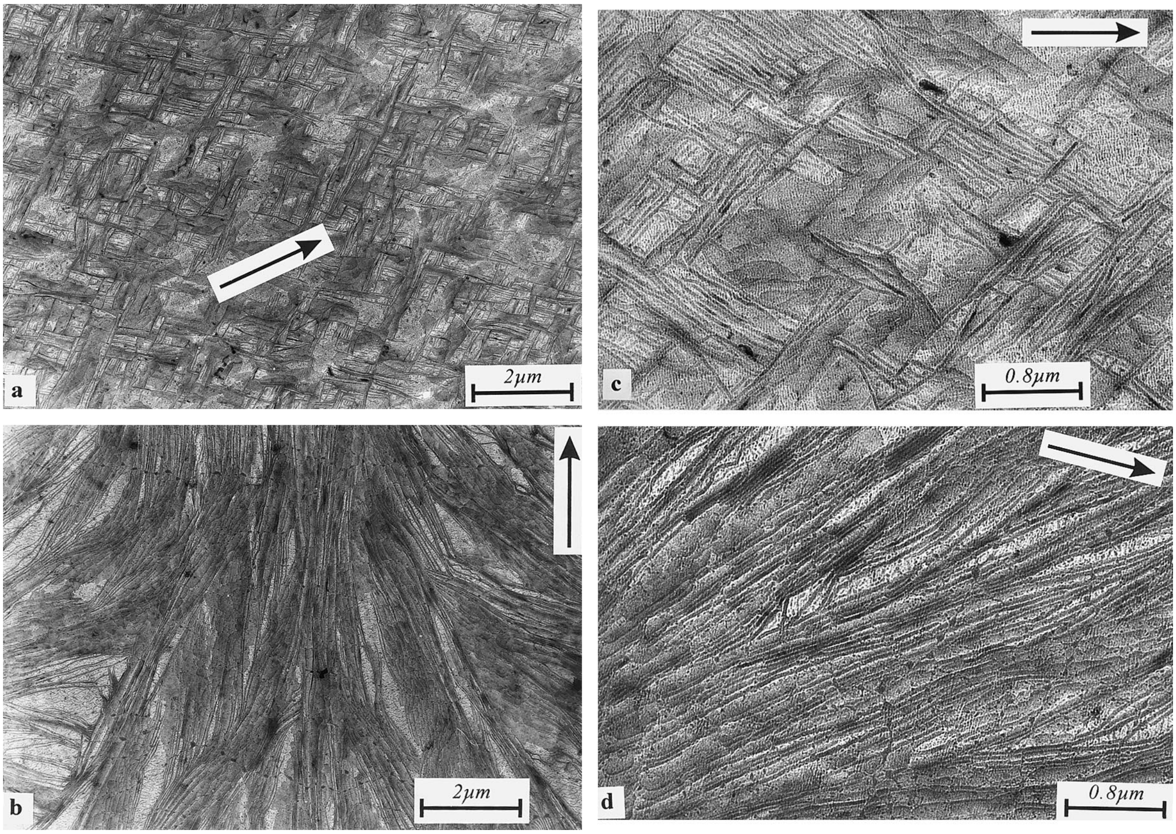

Fig. 2. BF electron micrographs of HDPE/iPP and HDPE/sPP double layered films, which were heat-treated at 150°C for 10 min and subsequently crystallized at 122°C for 2 h. The molecular chain directions of iPP and sPP substrates are indicated by the arrows in the micrographs. (a) and (c) HDPE/iPP system; (b) and (d) HDPE/sPP system.

larger than the diffraction aperture. Lowering the crystallization temperature of HDPE can reduce the lamellae size not only in the chain fold direction, i.e. lamellar thickness, but also in the crystal growth direction, i.e. the lateral width. The structural relationships of HDPE with iPP and sPP substrates remain the same: no epitaxial crystallization of HDPE on the sPP substrate at isothermal crystallization conditions and epitaxially oriented cross-hatched lamellar structure on the iPP substrate.

3.3. Morphologies of HDPE crystallized on oriented iPP and sPP substrates at different cooling rates

Fig. 4 shows the BF electron micrographs of HDPE–iPP and HDPE–sPP double layers, which were heat-treated at 150°C for 10 min and subsequently cooled at a rate of 50°C/min to room temperature. A perfect cross-hatched lamellar structure of HDPE crystals arises for the HDPE–iPP system with their lamellae being inclined at angles of ±40° with respect to the chain direction of iPP substrate. The average thickness of the cross-hatched HDPE lamellae is approximately 20 nm. Similar to the isothermally crystallized samples, no preferred orientation occurs on the sPP substrate. The corresponding electron diffraction patterns are shown in Fig. 5. The diffraction pattern of HDPE–iPP layers (Fig. 5(a)) has a close resemblance with that shown in Fig. 3(a). The electron diffraction pattern of HDPE–sPP double layers (Fig. 5(b)) is somewhat different from Fig. 3(b). It shows almost continuous HDPE reflection rings superimposed on the diffraction pattern of the sPP substrate due to the smaller width of the HDPE lamellar crystals.

Cooling the HDPE melts on the iPP and sPP substrates still faster by quenching the composite layers from 150°C directly into air at room temperature, results in even smaller HDPE lamellar crystals. As shown in Fig. 6, the HDPE lamellae are only approximately 13 nm thick. At the same time their lateral width reduces remarkably. Besides the change in crystal size, the morphology of the HDPE on the sPP substrate changes completely, while the orientation relationship between HDPE and iPP substrate remains unchanged. A cross-hatched lamellar structure of HDPE arises now on the sPP substrate with their lamellae being inclined at angles of ±53° with respect to the chain direction of the sPP substrate. A small amount of HDPE lamellae arrange perpendicular to the chain direction of the sPP. This means that at this cooling rate the sPP crystals can serve as the nucleation agent for HDPE and an oriented overgrowth of HDPE results.

The corresponding electron diffraction pattern of

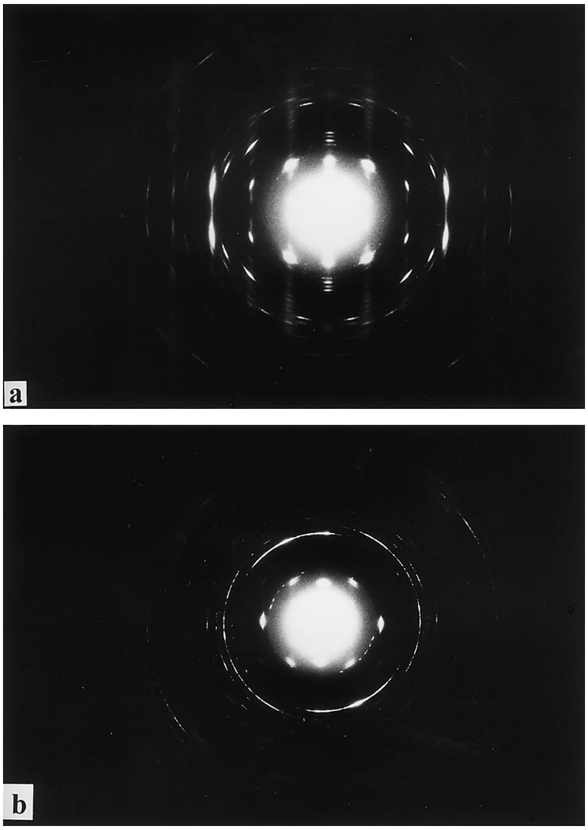

Fig. 3. The corresponding electron diffraction patterns of (a) HDPE/iPP and (b) HDPE/sPP double layered films as shown in Fig. 2.

HDPE–iPP double layers is identical to those shown in Figs. 3a and 5a. Therefore, only the electron diffraction pattern of HDPE–sPP double layers under the present cooling condition is presented here (Fig. 7(a)). A sketch with main reflections of the HDPE crystals being indexed is shown in Fig. 7(b). The electron diffraction pattern consists of sharp reflection spots related to the oriented sPP substrate (solid ellipses in the sketch) and the oriented overgrown HDPE crystals (hollow ellipses in Fig. 7(b)). As subscribed by I, II, and III, there are three different sets of HDPE oriented reflection spots. Sets I and II correspond to the cross-hatched lamellar structure with their chain directions ±37° apart from the chain direction of sPP crystals. In the HDPE–sPP system, the $(110)_{\mathrm{HDPE}}$ lattice plane is in contact with the sPP substrate. The third reflection set reveals the alignment of HDPE on the sPP substrate with both polymer chains parallel, and corresponding to the lamellae arranged perpendicular to the chain direction of sPP. The existence of $(110)_{\mathrm{HDPE}}$ and $(020)_{\mathrm{HDPE}}$ reflections on the equator indicates that this set of HDPE lamellae has a fiber texture and no fixed contact plane with sPP substrate. This oriented overgrowth could be caused by graphoepitaxy [24].

When the HDPE–iPP and HDPE–sPP double layered films were quenched from 150°C direct into ice water, the resulting HDPE crystals are too small to be resolved in our micrographs. Fig. 8 shows the electron diffraction patterns of the HDPE–iPP and HDPE–sPP layered films, which were quenched from 150°C directly into ice water and subsequently annealed at 115°C in order to improve their crystallinity. On the diffraction pattern of the HDPE–iPP system (Fig. 8(a)), the HDPE reflection arcs with clearly distinct diffraction maxima located in the same places as in Fig. 5(a), reflect the heteroepitaxial orientation of the microcrystals. The extra $(002)_{\mathrm{HDPE}}$ reflections appeared on the meridian direction of the iPP diffraction pattern, which have never been observed at other sample heat-treatment conditions (compare Fig. 8(a) with Figs. 3(a) and 5(a)), imply the occurrence of an additional graphoepitaxy [25]. The electron diffraction pattern of the HDPE–sPP double layers (Fig. 8(b)) indicates that almost no preferred orientation of the HDPE crystals exists any more.

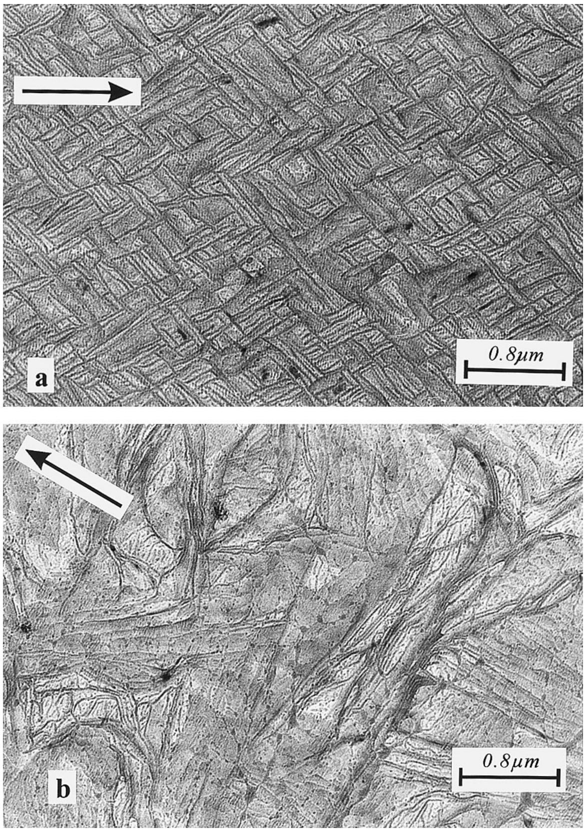

Fig. 4. BF electron micrographs of (a) HDPE/iPP and (b) HDPE/sPP double layered films, which were annealed at 150°C for 10 min and cooled at a rate of 50°C/min to room temperature. The arrows represent the molecular chain directions of iPP and sPP substrate crystals.

3.4. Melting and recrystallization behavior of HDPE in iPP–HDPE–sPP sandwich form multilayers

Fig. 9 shows the BF electron micrograph and electron diffraction pattern of an iPP–HDPE–sPP sandwich triple layer, which was air-cooled from 150°C to room temperature. The arrow in the micrograph represents the molecular chain direction of the iPP and sPP oriented films. The contrast of the BF electron micrograph is now poorer than

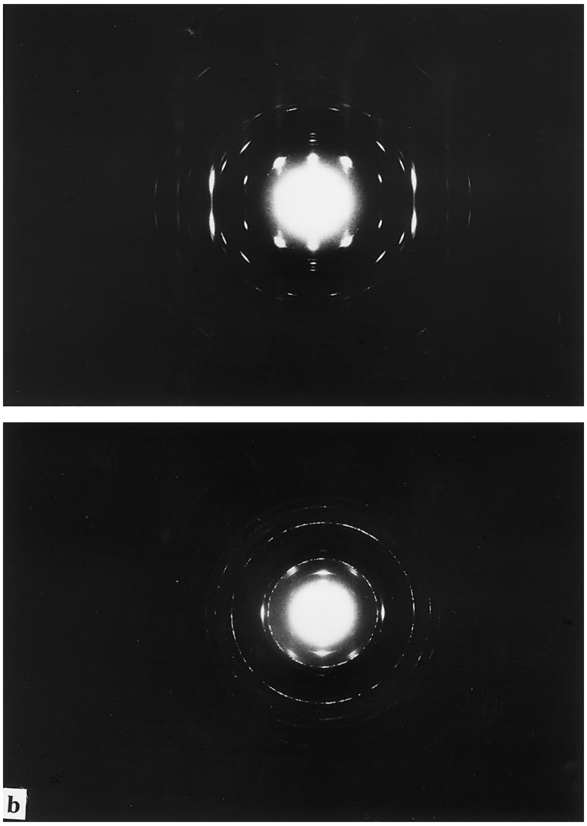

Fig. 5. The corresponding electron diffraction patterns of (a) HDPE/iPP and (b) HDPE/sPP double layered films as shown in Fig. 4.

those taken from HDPE–iPP or HDPE–sPP double layered films due to the lamellae overlap in a thicker sample (compare Fig. 9(a) with Fig. 6(a) and (b)). Nevertheless, the lamellar structure can still be observed clearly. The highly oriented iPP and sPP crystalline lamellae cannot be distinguished from each other due to their same orientation direction. Now the HDPE lamellae take the same orientation as in the HDPE–iPP double layered system, which can also be concluded from the electron diffraction pattern (Fig. 9(b)). This means, that the sandwiched HDPE film is only nucleated by the iPP layer, confirming that the iPP has a much higher nucleation ability to the HDPE than sPP.

4. Discussion

For both the HDPE–iPP and HDPE–sPP systems, the heteroepitaxial orientation relationships are well documented in the literature [13,19]. However, two questions could be answered according to our experimental results: (i) why the HDPE crystallizes epitaxially only on the iPP substrate, when crystallization is performed isothermally above room temperature or at lower supercoolings, and (ii) which of the two substrate polymers (iPP and sPP) has stronger nucleation influence onto the HDPE.

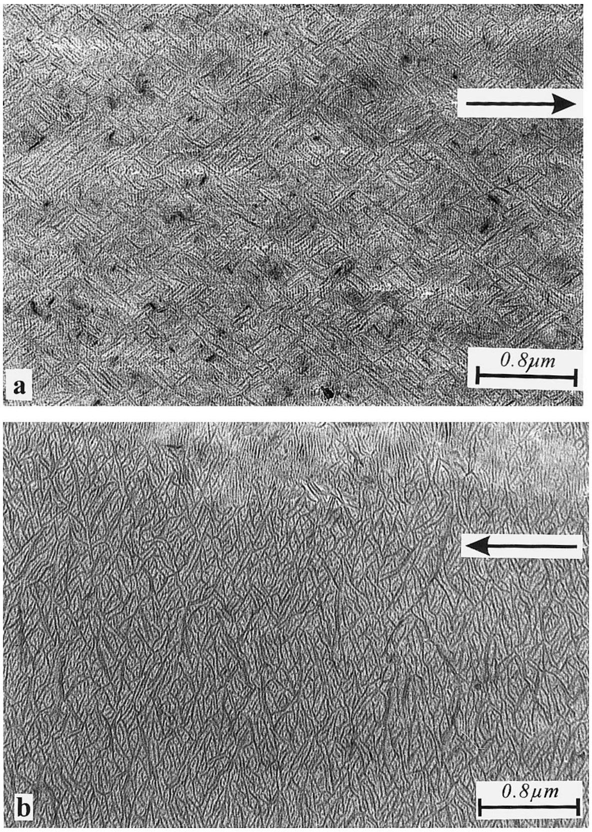

Fig. 6. BF electron micrographs of (a) HDPE/iPP and (b) HDPE/sPP double layered films, which were quenched from 150°C directly to room temperature. The molecular chain directions of iPP and sPP substrates are shown by the arrows.

As from crystallization theory well known, the critical nucleus size (having the similar order with the lamellae thickness) depends remarkably on the supercooling, e.g. the lamellar thickness of HDPE changed from 24 nm when crystallizing it at 122°C isothermally to 13 nm as quenching its melt from 150°C directly to room temperature. When performing the heteroepitaxial crystallization between polymers, the substrate crystals are usually edge-on lamellae, such as iPP and sPP used here. As pointed out by Greso and Phillips [26], for realizing the heteroepitaxial crystallization of polymers, the mutual dimension of substrate crystals (lamellar thickness of the substrate crystals divided by the cosine of the chain inclination angles of the deposit polymer, which are 50° for the HDPE–iPP system and 37° for HDPE–sPP system) has to be larger than the critical nucleus size of the layered polymer crystals. These mutual crystal dimensions of iPP and sPP are $16/\cos 50° \approx 25$ nm and $10/\cos 37° \approx 13$ nm, respectively. For the HDPE–iPP system, the mutual crystal size (25 nm) is larger than the critical nucleus size of HDPE crystals under all crystallization conditions performed in this work and consequently heteroepitaxy of HDPE occurs at every crystallization conditions chosen here. However, not so for the HDPE–sPP system, where only under rapid quenching

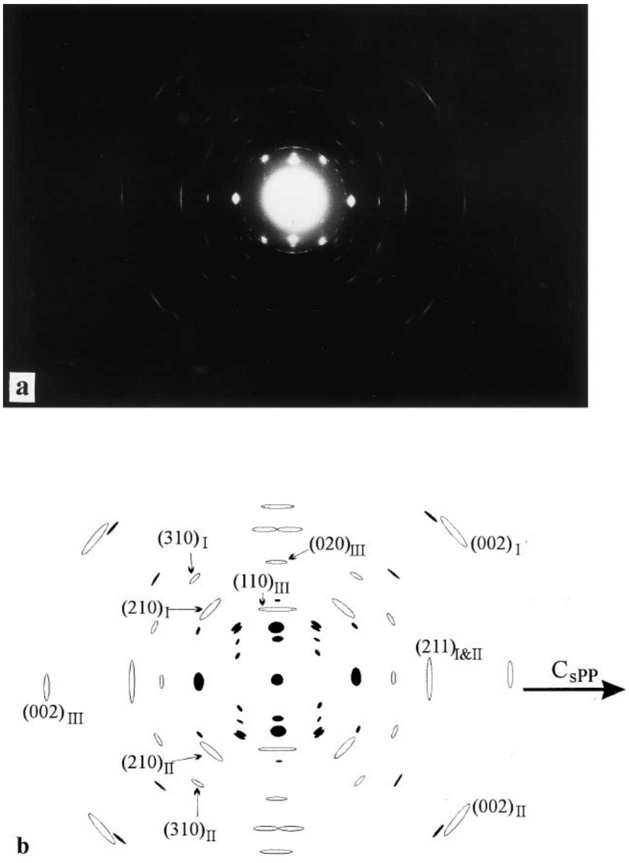

Fig. 7. (a) the corresponding electron diffraction patterns of HDPE/sPP double layered films as shown in Fig. 6 and (b) a sketch of it with main HDPE reflections being indexed.

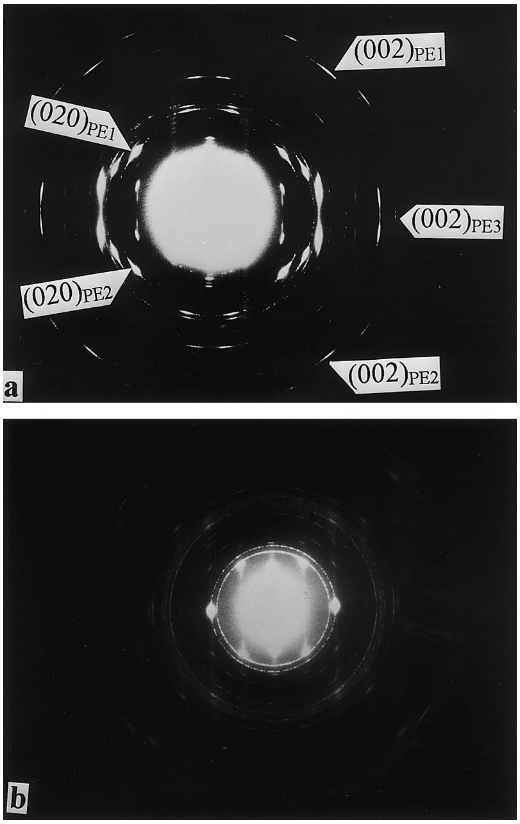

Fig. 8. Electron diffraction patterns of (a) HDPE/iPP and (b) HDPE/sPP double layered films, which were quenched from 150°C directly into ice water. The molecular directions of both iPP and sPP substrates are horizontal.

condition a HDPE nucleus size as small as 13 nm can be reached in order to create heteroepitaxy.

Not much is known regarding the occurrence of graphoepitaxy in polymer–polymer system [27], and a detailed discussion of it on the basis of our results may lead to many speculations. Anyhow, especially in very rapidly quenched samples, graphoepitaxy is observed frequently when using a topological structured (ridges and grooves) substrate film. The preferred orientations may result from an increased nucleation with the chain directions oriented into the directions of the ridges or grooves.

The higher nucleation ability of iPP than sPP for HDPE is unambiguously demonstrated with the crystallization of the triple layered samples, in which HDPE is sandwiched between two oriented substrate films of iPP and sPP. When quenching HDPE on separated sPP and iPP films to room temperature, both systems exhibit epitaxy. For the triple layered samples, only epitaxial orientation of the HDPE caused by iPP substrate is seen, confirming that the HDPE starts to crystallize on the iPP substrate first and growth with this orientation to the sPP substrate, on which the crystallization of the HDPE has not even started.

5. Conclusion

By comparing the crystallization behavior of HDPE on the oriented iPP and sPP substrates, it is found that the crystal size of the substrate polymer plays a very important role in the polymer heteroepitaxy. It is a critical requirement for the occurrence of polymer heteroepitaxy. Until the lamellar thickness of the deposit polymer created at the chosen conditions is smaller than the dimension of the substrate crystals in the orientation direction of the deposit polymer, no heteroepitaxy will take place.

The melt-drawn polymer films with uniaxial fiber orientation show their advantages in the parallel studies of hetero and graphoepitaxy. Under certain conditions, hetero and graphoepitaxies can happen simultaneously between the same polymer pairs. From the experimental results obtained in this work, it is concluded that the heteroepitaxy takes place prior to the graphoepitaxy. Only when the nuclei created by heteroepitaxial nucleation are not sufficient for the crystallization process, can the graphoepitaxial nucleation become an active event, and thus graphoepitaxy occurs.

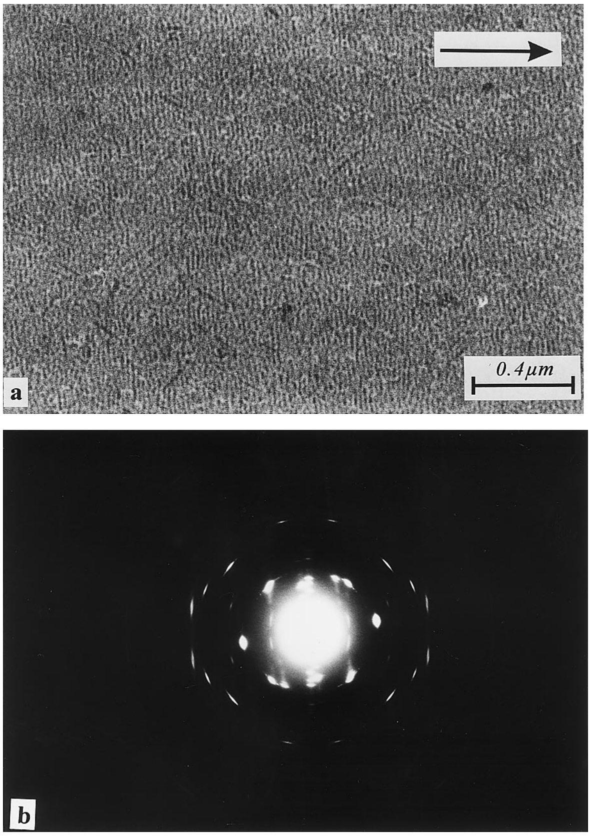

Fig. 9. (a) BF electron micrograph and (b) electron diffraction pattern of iPP/HDPE/sPP triple sandwich layers, which were heated to 150°C for 10 min and quenched directly to room temperature. The arrow represents the chain direction of iPP and sPP substrate crystals.

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