Morphological studies of PE crystallized between iPP and PTFE oriented films

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Abstract

The crystallization behavior of polyethylene (PE) between oriented isotactic polypropylene (iPP) and poly(tetrafluoroethylene) (PTFE) substrates in sandwich triple layered samples at various crystallization conditions was studied by means of transmission electron microscopy and electron diffraction. It is well known that both iPP and PTFE oriented substrates are active nucleation agents for PE, but result in different crystallization manners of PE. While the iPP substrate leads to an epitaxial crystallization of PE in a way, with the molecular chain directions of both polymers ±50° apart, an oriented overgrowth of PE on the PTFE substrate with parallel chains of both polymers is identified. By using sandwich samples with the PE in between the two different substrates, i.e. iPP and PTFE, the nucleation efficiency of both polymers for PE can be compared. The results indicate that at high undercoolings, the iPP and PTFE oriented crystals have about the same nucleation ability onto PE, but at lower undercoolings, the PE crystallizes all on the PTFE side. This indicates unambiguously that the nucleation of PE on the PTFE substrate starts at a higher temperature than that on the iPP oriented substrate. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Heterogeneous nucleation is a commonly encountered phenomenon of polymer crystallization which has been an interesting research topic for a long time [1–4]. Even though, great effort and progress have been made in the past few decades towards a full understanding of it, except for the epitaxial crystallization of polymers, little is known about the mechanism of its heterogeneous nucleation process.

Epitaxial crystallization of polyethylene (PE) on the oriented isotactic polypropylene (iPP) [5–7] and poly(tetrafluoroethylene) (PTFE) [8,9] is well documented in the literature. When the PE is epitaxially crystallized on the iPP substrate, both polymer chain directions are ±50° apart. On the PTFE substrate, their molecular chain directions align parallel to each other. Both epitaxial orientation relationships have been explained in terms of some geometrical matching [9,10]. Keeping the different orientation of PE layers on iPP and PTFE substrates in mind, a direct comparison of the nucleation efficiency of iPP and PTFE on

PE is possible by placing the PE in between the two different substrates.

It is the purpose of this presentation to report some experimental results on the crystallization behavior of PE embedded between iPP and PTFE substrates.

2. Experimental

The polymers used in this work are iPP, Novolene 1050FP; high-density PE, Lupolen 6021DX, both from BASF AG Ludwigshafen, Germany; and commercial grade PTFE. Uniaxially oriented thin films of iPP and PE were prepared according to a technique introduced by Petermann and Gohil [11]. The as-prepared oriented films are 30–50 nm thick, and can be used directly for transmission electron microscopic observation. Highly oriented PTFE films were prepared with the help of the friction transfer process [12]. Triple layered sandwich samples of iPP/PE/PTFE with the PE embedded between the two different substrates were made by using a PTFE covered glass slide and collecting at first a layer of melt-drawn PE film and then a layer of melt-drawn iPP film on it. The triple layers were heat-treated at 150°C (above the melting temperature of PE but below the melting temperatures of both the substrates) for 10 min and subsequently cooled

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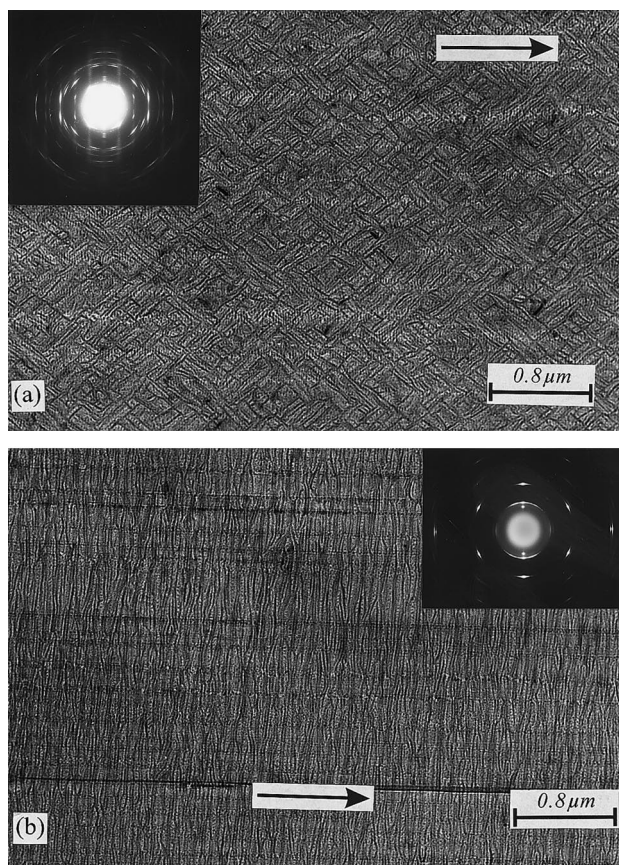*E-mail address:* petermann@ct.uni-dortmund.de (J. Petermann).

Fig. 1. BF electron micrographs and the corresponding electron diffraction patterns (insets of the BF images) of (a) PE/iPP; and (b) PE/PTFE double layered samples, which were heat-treated at 150°C for 10 min and subsequently cooled to room temperature. The arrows show the chain directions of the corresponding substrate crystals.

with different rates to various temperatures. After the heat-treatments, the corresponding triple layers were detached from the glass slide with the help of a thin polyacrylic acid layer, which was subsequently dissolved in water. For electron microscopy observation, a Philips CM200 TEM operated at 200 kV was used in this study. Bright-field (BF) electron micrographs were obtained by defocusing the objective lens.

3. Results and discussion

The morphologies of the melt-drawn iPP and PE films were described in detail in previous work [13,14]. They consist of oriented lamellae aligned perpendicular to the drawing direction and exhibit a fiber orientation with their molecular chains arranged parallel to the drawing direction. The friction transfer PTFE thin films also possess a uniaxial chain orientation as described elsewhere [15,16].

Although the morphologies of PE crystallized on oriented iPP and PTFE substrates are well described in the literature [5–9], two BF electron micrographs with their corresponding electron diffraction patterns inserted are presented

here in order to give the reader a better understanding. When PE crystallizes on oriented iPP substrates, as in Fig. 1(a), an epitaxial orientation with the PE chain directions ±50° apart from the iPP chain direction is observed. The substrate induced morphology of the PE on friction transfer oriented PTFE films is displayed in Fig. 1(b). On the BF electron micrograph, a parallel aligned PE crystalline lamellar structure can be seen. The PE chain direction is oriented parallel to the chain direction of the PTFE substrate as also deduced from the inserted electron diffraction pattern (Fig. 1(b)).

The different orientations of PE in the PE/iPP and PE/PTFE systems are helpful for studying the crystallization behavior of the PE embedded between the oriented iPP and PTFE substrates with respect to the nucleation abilities of both substrate materials. On the BF electron micrograph of an iPP/PE/PTFE triple layered sample, which was heat-treated at 150°C for 10 min and subsequently quenched into air at room temperature, the PE crystals appear as too small lamellae for analyzing their orientation. But a detailed analysis can be fulfilled with the help of the electron diffraction pattern. Fig. 2 shows the electron diffraction pattern (Fig. 2(a)) and its corresponding sketch of an air quenched iPP/PE/PTFE triple layered sample with the main diffraction spots being indexed (Fig. 2(b)). The molecular chain directions of the iPP, PTFE, and PE are indicated by arrows labeled with iPP, PTFE and PE, respectively. There are totally five reflection sets belonging to different chain orientations. Among them, one set belongs to the oriented iPP substrate, which is illustrated with gray ellipses in Fig. 2(b). The contribution of the oriented PTFE film is illustrated with the black ellipses. The remaining three reflection sets, as subscribed with PE_I, PE_{II} and PE_{III}, are identified as the reflections of the oriented overgrown PE crystals. When taking the reflection spots of PTFE and PE_{III} from the overall diffraction pattern, the remaining electron diffraction pattern (as shown in Fig. 3(a)) has a close resemblance to the diffraction pattern inserted in Fig. 1(a) (90° rotation to get the same chain direction). Therefore, the PE sets I and II are generated by the epitaxial crystallization of PE on the iPP substrate with the c-axes ±50° apart from the chain direction of iPP crystals. The PE set III, Fig. 3(b), exhibits then the epitaxial overgrowth of PE on the PTFE friction transferred film. According to these electron diffraction patterns, it is concluded that with the crystallization condition used, the PE crystals are nucleated on both iPP as well as PTFE surfaces. On a BF micrograph of a sample, which has been taken from an iPP substrate film with a few remaining PTFE fibers, the above mentioned orientations of PE can clearly be seen (Fig. 4). The four strips are the PTFE oriented film fragments, localized on top of a PE/iPP double layer, which had the same heat-treatment as the sample in Fig. 2. In the vicinity of the PTFE fibers, both epitaxial arranged PE lamellae generated by iPP and the PTFE strips are observed, as indicated by the different arrows described with PE/iPP and PE/PTFE,
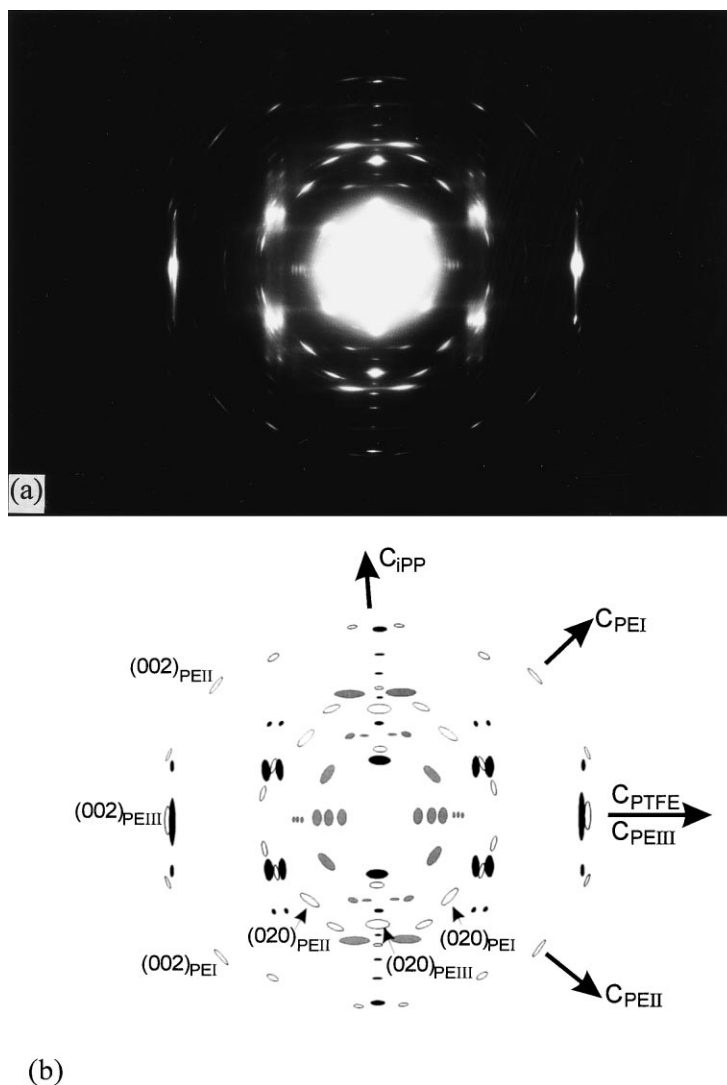
Fig. 2. (a) electron diffraction pattern; and (b) its corresponding sketch with the main reflections being indexed of iPP/PE/PTFE sandwich triple layers, which has been annealed at 150°C for 10 min and then quenched directly to room temperature. The arrows represent the chain directions of the iPP, PTFE, and PE crystals, respectively. The gray ellipses indicate the diffraction pattern of the oriented iPP; the black ellipses are associated to the reflections of the oriented PTFE substrate; the remaining hollow ellipses exhibit the diffraction spots of the oriented overgrown PE crystals.

respectively. Therefore, a similar nucleation ability of both substrates under quenching conditions of the PE can be concluded from the Figs. 2 and 4.

Fig. 5 shows the electron diffraction pattern of an iPP/PE/PTFE triple layered sample, which was heat-treated by cooling it from 150°C at a rate of 20°C/min to room temperature. The arrows represent the chain directions of the iPP and PTFE substrates, respectively. The diffraction patterns shown in Figs. 2 and 5 are very similar. This means that as in quenching condition, iPP and PTFE display still a similar nucleation ability for PE by cooling the PE melt with a rate of 20°C/min, although the lower nucleation efficiency (larger lamellar size) due to a relatively lower undercooling is concluded by comparing the PE crystal sizes created both on iPP and PTFE substrates as shown in Fig. 6(a) and (b) with Fig. 1(a) and (b).

Cooling the iPP/PE/PTFE triplex from 150°C with a rate of 10°C/min to room temperature, a different result is obtained. As shown on the BF electron micrograph (Fig. 7(a)), in which only a ribbon of PTFE friction transfer film exists in the bottom part of the picture, even larger PE lamellae are observed. Moreover, in the area of the PTFE ribbon, parallel arranged PE lamellae perpendicular to the chain direction of PTFE are observed. This implies a higher nucleation ability of the PTFE than the iPP substrate. In the boundary area of the PTFE substrate, the PE lamellae align perpendicular to the boundary line of the PTFE, i.e. their molecular chain direction, and form a transcrystallization zone rather than a cross-hatched lamellar structure relating to the iPP substrate. Some transcrystalline PE lamellae are as long as 1.5 μm. This further confirms that now the PTFE has a much higher nucleation ability onto PE.
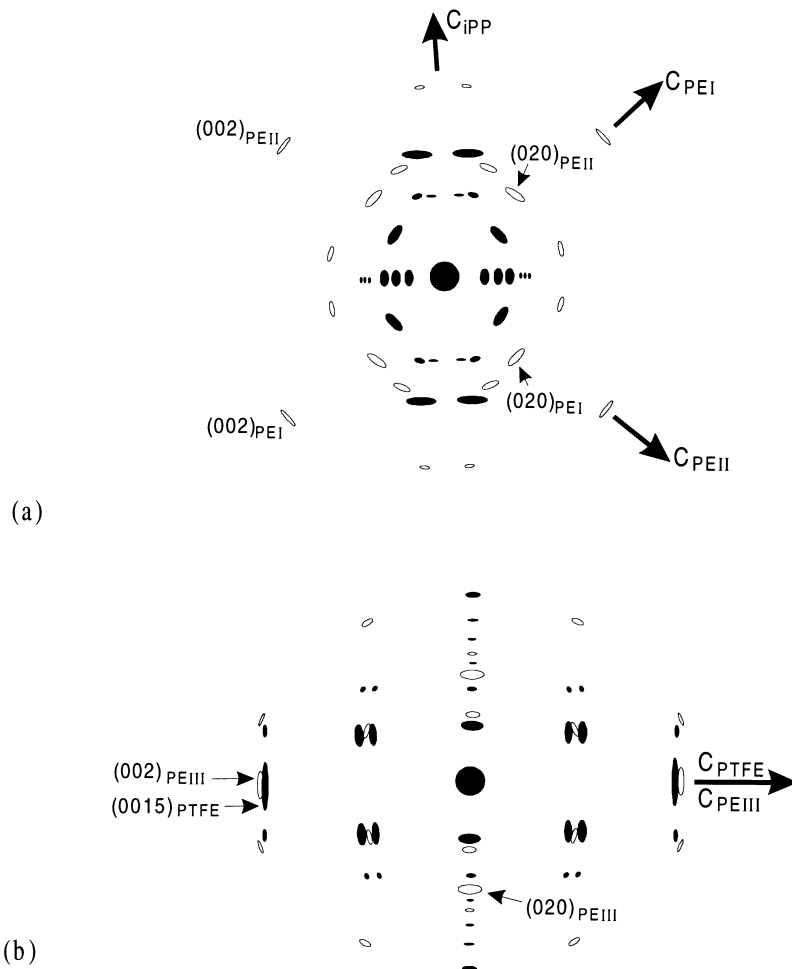
(a)

(b)

Fig. 3. The electron diffraction pattern of Fig. 2 divided into (a) the part corresponding to the PE/iPP epitaxial crystallization; and (b) the epitaxial crystallization of PE/PTFE.
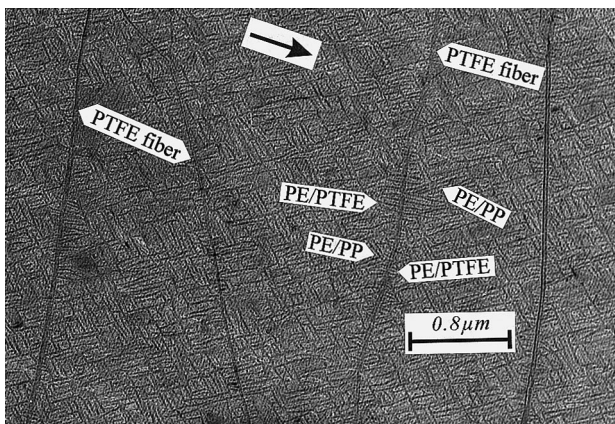

Fig. 4. BF electron micrograph of a PE/iPP double layered film with four PTFE fibers on the PE side of the film. The thermal history of the sample is the same as that shown in Fig. 2. The black arrow indicates the chain direction of the oriented iPP substrate. The white arrows noted with PE/iPP and PE/PTFE are used to indicate the PE lamellae, which are generated by iPP or PTFE substrates, respectively.
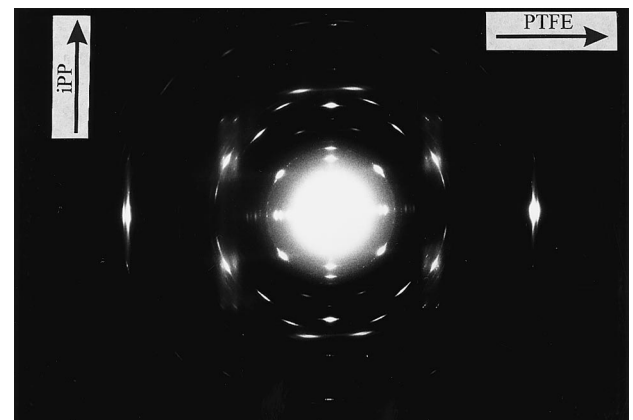

Fig. 5. Electron diffraction pattern of an iPP/PE/PTFE triple layered sample, which has been heated to 150°C for 10 min and cooled at a rate of 20°C/min to room temperature. The arrows indicate the chain directions of the iPP and PTFE substrate crystals, respectively.
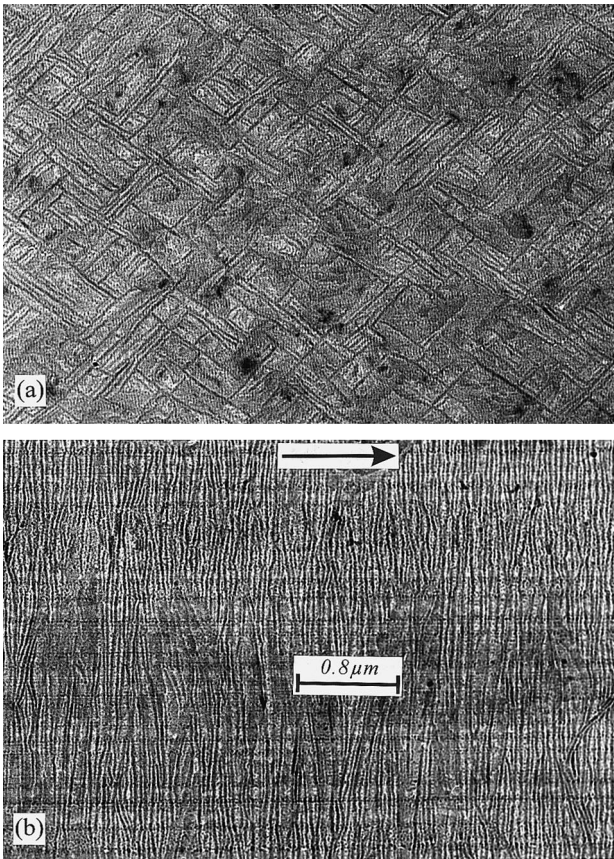
Fig. 6. BF electron micrographs of (a) PE/iPP; and (b) PE/PTFE double layered samples which have subjected the same thermal history as that shown in Fig. 5. The arrows represent the chain directions of the iPP and PTFE substrates.
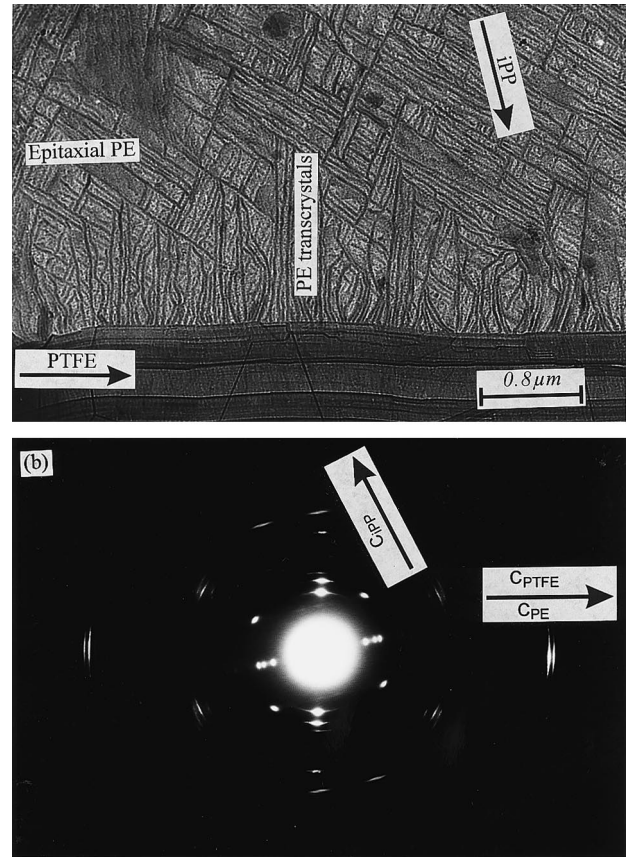

Fig. 7. (a) BF electron micrograph of a PE/iPP double layered sample, which is partially covered with a PTFE oriented ribbon on the PE side. The chain directions of the oriented iPP and PTFE substrate crystals are represented by the arrows labeled with iPP and PTFE, respectively. The sample was heated to 150°C for 10 min, and cooled at a rate of 10°C/min to room temperature. (b) An electron diffraction pattern corresponding to the part of the picture having both iPP and PTFE substrates.

The corresponding electron diffraction pattern taken from the area with both iPP and PTFE substrates, as shown in Fig. 7(b), exhibits only PE reflection spots associated to the epitaxial overgrowth of PE on PTFE, and reflects that all the PE in the sandwich sample crystallized on the PTFE side. A further increase of the crystallization temperature does not change the crystallization behavior of the PE melt anymore; i.e. all PE crystallizes first on the PTFE side.

The occurrence of the epitaxial overgrowth of PE on both the iPP and PTFE substrates at higher undercooling indicates that iPP as well as PTFE oriented substrates can serve as active nucleation surfaces for PE. As mentioned in Section 1, the epitaxial crystallization of polymers is usually explained in terms of certain geometrical matching, e.g. a chain-row matching for the PE/iPP system and an intermolecular distance matching for the PE/PTFE system. The mismatching between PE–iPP [5] and PE–PTFE [9] are calculated as 2 and 12%, respectively. Combining the results obtained here that the nucleation efficiency of iPP and PTFE towards PE is about the same at high undercoolings, but PTFE possesses a higher nucleation ability onto PE than the iPP crystals at lower undercoolings, it is concluded that close matching is not a necessary requirement
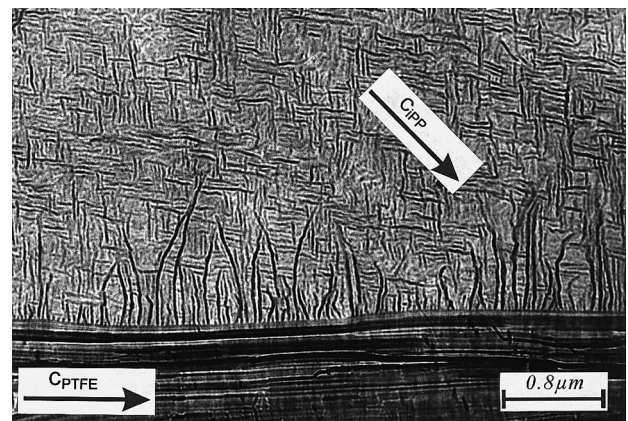

Fig. 8. BF electron micrograph of a PE/iPP double layered sample, which is partially covered with a PTFE oriented ribbon on the PE side. The PTFE oriented ribbon is located in the bottom part of the picture. The chain directions of the oriented iPP and PTFE substrate crystals are represented by the arrows labeled with iPP and PTFE, respectively. The sample was first heated to 150°C for 10 min, then cooled at a rate of 1°C/min to 122°C and kept there for 5 min, and finally quenched to room temperature.

for a substrate serving as a strong nucleation agent. It was demonstrated earlier that the crystal size of the substrate plays a very important role in polymer epitaxy. The larger dimension of the substrate crystal in matching direction than that of the critical nuclei of the layered polymer is a prerequisite for the occurrence of the epitaxial crystallization [17,18]. Fig. 7(a) demonstrates that the crystallization of the PE which is embedded in between the oriented iPP and PTFE substrates is initiated by the PTFE substrate. The area close to the PTFE ribbon, where the PE is only supported by the iPP substrate, instead of the cross-hatched epitaxial structure relating to the iPP substrate a transcrystallization zone of PE is generated by the PTFE. The PE further away from the boundary of the PTFE substrate forms a cross-hatched epitaxial orientation and reflects the nucleation effect of the iPP substrate. This means that the prerequisite of crystal size of both PTFE and iPP is fulfilled for the epitaxial crystallization of PE. By checking the crystal size of iPP and PE, we find that the lamellar thickness of PE in Fig. 7(a), about 25 nm, is about the same as that of the iPP crystal dimension in PE chain direction, $16/\cos 50° \approx 25$ nm (measured from Fig. 6(a)). This implies that the iPP substrate reaches its limit capacity for serving as epitaxial substrate of PE cooled at a rate of 10°C/min. But the crystal size of PTFE in its chain direction is much larger than the PE lamellar thickness according to the dark-field electron micrographs. Therefore, one can speculate that the small crystal size of iPP may be responsible for the decrease of its nucleation ability. In order to attest this speculation, the sandwich sample was heated to 150°C for 10 min, cooled at a rate of 1°C/min to 122°C for 5 min, and subsequently quenched to room temperature. As shown in Fig. 8, unlike that shown in Fig. 4, now only transcrystalline lamellae on the boundary of the PTFE strip are observed. Moreover, the dimension of the transcrystalline PE lamellae is larger than the iPP induced epitaxial PE lamellae, especially their lateral width. This demonstrates that the nucleation and consequently the crystal growth of PE on the PTFE substrate start earlier than those do on the iPP substrate under low undercoolings. In other words, the nucleation and crystal growth of PE on the PTFE substrate take place at a higher temperature than those do on the iPP substrate. This results from the influence of the substrate crystal size on the nucleation of the deposit polymer.

4. Conclusions

By following the crystallization behavior of PE in the sandwich form triple layers with the PE in the middle, the heterogeneous nucleation efficiency of iPP and PTFE towards PE is compared. The results show that both iPP and PTFE oriented films are active nucleation surfaces for PE, and influence the PE to crystallize in particular ways, i.e. epitaxial orientations. These two substrates exhibit about the same nucleation ability towards PE at high undercooling, but the PTFE shows higher nucleation ability onto PE than the iPP at low undercooling. The change of the relative nucleation for PTFE and iPP on PE may result from the fact that PTFE substrate crystals are larger than the iPP crystals in the PE chain direction.

References

[1] Chatterjee AM, Price FP, Newmann S. J Polym Sci, Polym Phys Ed 1975;13:2369.
[2] Chatterjee AM, Price FP, Newmann S. J Polym Sci, Polym Phys Ed 1975;13:2385.
[3] Chatterjee AM, Price FP, Newmann S. J Polym Sci, Polym Phys Ed 1975;13:2391.
[4] Seth KK, Kenpster CJE. J Polym Sci, Polym Symp 1977;58:297.
[5] Wittmann JC, Lotz B. Prog Polym Sci 1990;15:909.
[6] Petermann J. In: Karger-Kocsis J, editor. Polypropylene: structure, blends and composites, London: Chapman & Hall, 1995. p. 140.
[7] Yan S, Yang D, Petermann J. Polymer 1998;39:4569.
[8] Takahashi D, Teraoka F, Tsujimoto I. J Macromol Sci, Phys B 1976;12(3):303.
[9] Fenwick D, Smith P, Wittmann JC. J Mater Sci 1996;31:128.
[10] Wittmann JC, Lotz B. J Polym Sci, Polym Phys Ed 1986;24:1559.
[11] Petermann J, Gohil RM. J Mater Sci Lett 1979;14:2260.
[12] Wittmann JC, Smith P. US Patent Appl, 1989, No. 361.
[13] Yang D, Thomas EL. J Mater Sci 1984;19:2098.
[14] Yan S, Petermann J, Yang D. Acta Polym 1996;47:285.
[15] Wittmann JC, Smith P. Nature 1991;352:414.
[16] Katzenberg F, Liebertz H, Petermann J. Sen'i Gakkaishi 1997;52(12):549.
[17] Greso AJ, Phillips PJ. Polymer 1994;35:3373.
[18] Yan S, Petermann J, Yang D. Polym Bull 1997;38:87.