

Critical Crystallization Temperature for the Occurrence of Epitaxy Between High-Density Polyethylene and Isotactic Polypropylene

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ABSTRACT: The crystallization behavior of high-density polyethylene (HDPE) on highly oriented isotactic polypropylene (iPP) at elevated temperatures (e.g., from 125 to 128°C), was studied using transmission electron microscopy and electron diffraction. The results show that epitaxial crystallization of HDPE on the highly oriented iPP substrates occurs only in a thin layer which is in direct contact with the iPP substrate, when the HDPE is crystallized from the melt on the oriented iPP substrates at 125°C. The critical layer thickness of the epitaxially crystallized HDPE is not more than 30 nm when the HDPE is isothermally crystallized on the oriented iPP substrates at 125°C. When the crystallization temperature is above 125°C, the HDPE crystallizes in the form of crystalline aggregates and a few individual crystalline lamellae. But both the crystalline aggregates and the individual crystalline lamellae have no epitaxial orientation relationship with the iPP substrate. This means that there exists a critical crystallization temperature for the occurrence of epitaxial crystallization of HDPE on the melt-drawn oriented iPP substrates (i.e., 125°C). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2029–2034, 1997

INTRODUCTION

Epitaxy is defined, most generally, as the crystals of one phase (guest crystal) growing on the surface of a crystal of another phase (host crystal) in one or more strictly defined crystallographic orientations.¹ In the past 10 years, increasing interest has been seen in studying heteroepitaxy between polymers because of the unusual crystalline morphologies. It was found that epitaxial interfaces between noncompatible semicrystalline polymers can be formed.^{2,3} Because the epitaxial interfaces between polymers are bonded by van

der Waals forces, good adhesion is obtained between the components.⁴ Additionally, the special structure has led to the peculiar properties, such as the synergism of the mechanical properties of the blends or complex films. Therefore, epitaxial interaction may provide a valuable way for improving the mechanical property of noncompatible polymer blends. In regard to this aspect, kinetic studies of the epitaxial process are of great importance for its processing.

Among the studies of polymer heteroepitaxy, the epitaxial crystallization between zigzag chain polymers [such as polyethylene (PE), polyesters, and polyamides] and helical chain polymers [such as isotactic polypropylene (iPP) as well as syndiotactic polypropylene (sPP)]^{5–14} was studied extensively, including their epitaxial orientation relationship,¹⁵ synergism in their mechanical properties caused by epitaxy,^{16,17} and crystallization

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kinetics.^{18–20} The kinetic study of the PE/iPP system indicated that the epitaxial crystallization of PE on the highly oriented iPP substrates can occur only in a thin layer contacted directly with the iPP substrates. The critical epitaxial layer thickness depends not only on the branching of the PE samples,¹⁹ but also on its crystallization temperature.²⁰ It decreases from ca. 250 nm, when the layered high-density polyethylene (HDPE)/iPP films were heated to 150°C for 10 min and then cooled directly to room temperature on air, to ca. 80 nm, when the HDPE was isothermally crystallized from the melt on the iPP oriented films at 124°C. Also, 124°C was the highest temperature performed for the HDPE/iPP epitaxial system until now. The purpose of this article was to present some experimental results about HDPE isothermally crystallized on the highly oriented iPP substrates at temperatures above 124°C.

EXPERIMENTAL

The polymers used in this work were isotactic polypropylene (iPP) and high-density polyethylene HDPE, (type Novolene and Lupolen 6021 DX, both from BASF Ludwigshafen, Germany). Uniaxially oriented thin films of iPP and HDPE were prepared according to a melt-drawn technique introduced by Petermann and Gohil.²¹ According to this method, a small amount of a 0.5% solution of the polymer (iPP or HDPE) in xylene was poured and uniformly spread on a preheated glass slide, where the solvent was allowed to evaporate. After the evaporation of the solvent, the remaining thin polymer film was then picked up by a motor-driven cylinder with a drawing speed of approximately 20 cm/s. The temperatures for preparing the melt-drawn iPP and HDPE films were 140 and 125°C, respectively. The resulting highly oriented films of 30–50 nm thickness were mounted onto copper grids and directly used for transmission electron microscopy (TEM) observations. The double-layered HDPE/iPP films were prepared as follows: The highly oriented thin HDPE films were floated on the surface of distilled water and transferred onto the TEM grids, which were covered by the highly oriented iPP films. The double-layered films were then heated to 150°C (above the T_m of the HDPE, but below the T_m of iPP oriented films) for 10 min, cooled slowly (at a rate of 0.1°C/min) to the desired temperatures (125–

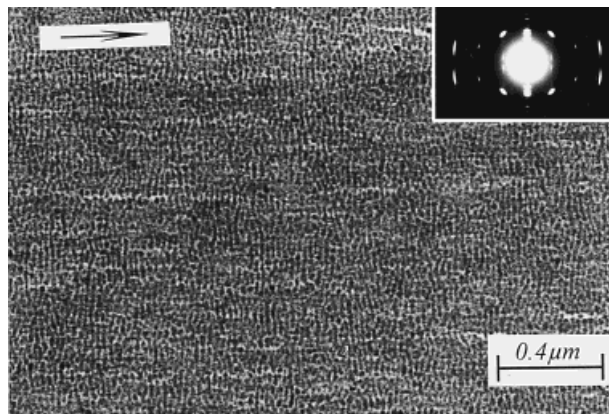


Figure 1 BF electron micrograph and electron diffraction pattern (inset) of highly oriented iPP substrate films, which have been annealed at 150°C for 30 min. The arrow shows the drawing direction of the film.

128°C), and crystallized isothermally at those temperatures for 5 h. The above thermal treatment of the samples were carried out in a DSC (TA DSC 2910) apparatus in order to obtain an accurate temperature ($\pm 0.1^\circ\text{C}$). After heat treatment, the double-layered films were used for TEM observation with the electron beam perpendicular to the film plane. A Philips CM200 TEM operated at 200 kV was used in this study. Brightfield (BF) micrographs were obtained by the defocus of the objective lens. To minimize radiation damage of the polymer samples caused by the electron beam, focusing of the sample was carried out on one area and the specimen film was then transferred to its adjacent undamaged area and the image recorded immediately.

RESULTS AND DISCUSSION

Morphologies of the iPP Oriented Films

Figure 1 shows a BF electron micrograph of the highly oriented iPP substrate films. The arrow in the micrograph indicates the drawing direction of the film during preparation. The dark lines represent the iPP crystalline lamellae, while the bright regions between the crystalline lamellae reveal the amorphous areas. It can be clearly seen that the iPP crystals are now oriented with their lamellae aligned perpendicular to the drawing direction. The average thickness of their lamellae is about 15 nm. The corresponding electron diffraction pattern (inset of Fig. 1) confirms that the

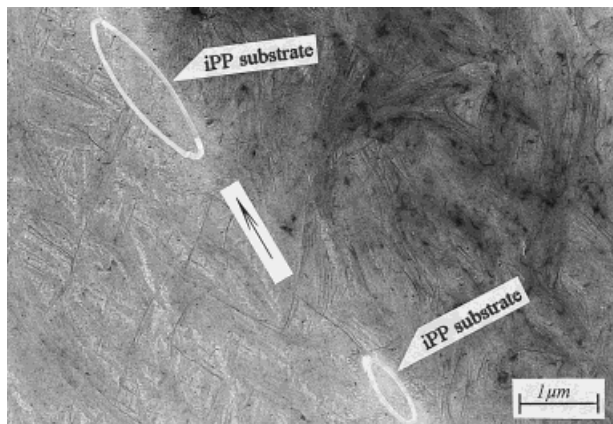


Figure 2 BF electron micrograph of HDPE/iPP double-layered films, which were heat-treated at 150°C for 10 min, cooled at a rate of 0.1°C/min to 125°C, then crystallized isothermally at this temperature for 5 h, and finally cooled at a rate of 10°C/min to room temperature in air. The molecular direction of the iPP substrate is indicated by an arrow.

melt-drawn iPP films exhibit a high degree of chain-axis orientation.

Oriented HDPE films were used, as the films exhibit uniform thickness in comparison to the solution-cast films. Their morphologies are described elsewhere,¹⁴ but are not important in the context of this investigation, because they are heated above the melting point of the HDPE and used as a thin molten film, whose crystallization behavior on the oriented iPP substrate was investigated.

Isothermal Crystallization of HDPE on the Oriented iPP Films at 125°C

Figure 2 shows the BF electron micrograph of an HDPE/iPP double-layered film, which was heat-treated at 150°C for 10 min, cooled at a rate of 0.1°C/min to 125°C, and crystallized isothermally at this temperature for 5 h. The underlying iPP substrate is covered by the HDPE film. However, there are some areas, in which no HDPE films exist, where the highly oriented iPP substrate can be clearly seen, as indicated by the ellipses. The molecular direction of the iPP substrate is indicated by an arrow. Now, two kinds of morphologies of HDPE crystals are observed. In the area with very thin HDPE film (not more than 30 nm), as shown in the lower-left corner of Figure 2, the HDPE crystallizes epitaxially on the oriented iPP

substrate and creates a cross-hatched lamellar structure with their lamellae $\pm 40^\circ$ apart from the chain direction of the iPP substrate. But in the region with a thicker HDPE film (about 50 nm) (upper-right corner of Fig. 2), no epitaxial relationship between HDPE and the oriented iPP substrate can be observed. The HDPE crystals are randomly oriented.

The corresponding electron diffraction patterns taken in the different areas of Figure 2 are shown in Figure 3. In the electron diffraction pattern corresponding to the lower-left corner of Figure 2, except for the electron diffraction spots of the oriented iPP substrate, there are two sets of HDPE reflection spots, each having a single crystalline orientation with [020] and [002] lattice directions in the film plane [Fig. 3(a)]. The angle between the [002]_{HDPE} direction and chain direction of the iPP substrate is 50°. This confirms that the HDPE crystals grow epitaxially on the ori-

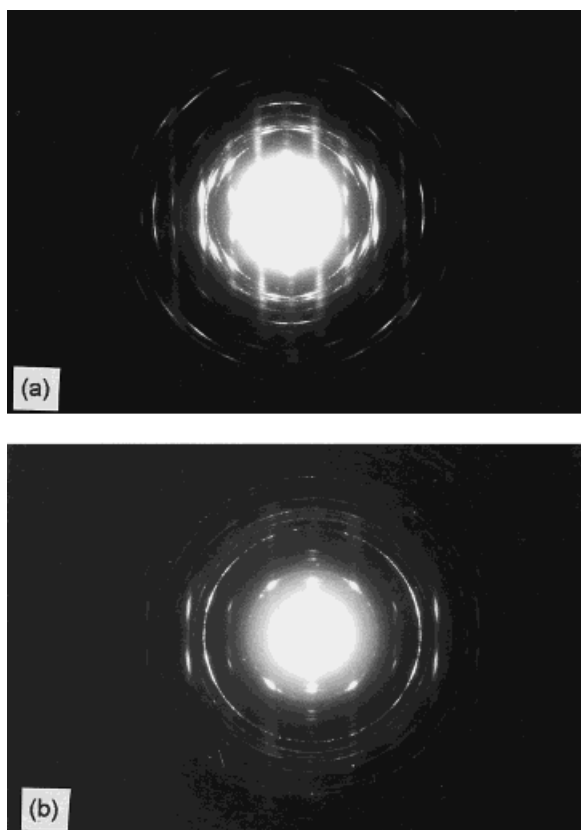


Figure 3 The corresponding electron diffraction pattern of HDPE/iPP double-layered films taken in different areas of Figure 2: (a) of the lower-left corner and (b) of the upper-right corner.

ented iPP substrate with the $(100)_{\text{HDPE}}$ lattice plane being in contact with the iPP substrate and the chain directions being $\pm 50^\circ$ apart from the molecular direction of the iPP substrate. This kind of epitaxy has been explained in terms of the parallel alignment of HDPE chains onto the oblique methyl group rows in the lateral contact plane of iPP with a 0.5 nm intermolecular distance for a chain-row matching.¹⁵ The electron diffraction pattern taken in the area of the upper-right corner of Figure 2 shows several discontinuous Debye–Scherrer rings of HDPE crystals superimposed on the well-oriented iPP reflections [Fig. 3(b)], but the arrangements of HDPE crystals are not epitaxially oriented as in Figure 3(a). This is in accordance with the BF observations.

The above results confirm our previous observations,^{19,20} i.e., that the epitaxial crystallization of HDPE on the oriented iPP substrate occurs only in a certain layer which is in direct contact with the iPP substrate surface and that the epitaxial layer thickness of HDPE crystals decreases considerably with increase of the crystallization temperature. When the HDPE is isothermally crystallized from the melt on the oriented iPP substrate at 125°C, the critical epitaxial layer thickness reduces to less than 30 nm. The HDPE crystals formed from the melt beyond the above-mentioned critical layer have no epitaxial relationship with respect to the iPP substrate.

Isothermal Crystallization of HDPE on the Oriented iPP Films at Temperatures Above 125°C

Figure 4(a) shows the BF electron micrograph of an HDPE/iPP double-layered film, which was heat-treated at 150°C for 10 min and subsequently crystallized isothermally at 126°C for 5 h. Obviously, the HDPE crystals are now more randomly dispersed on the iPP substrate. In the bright regions where no HDPE crystals exist, the parallel aligned crystalline lamellae of the iPP substrate are clearly visible and the chain direction of the iPP substrate is indicated by an arrow. The HDPE crystals exhibit now mainly large crystalline aggregates with random orientation, even in the area with the very thin HDPE part, where the underlying parallel aligned iPP crystals can be seen through the overlying HDPE crystals. A few individual HDPE lamellae can be identified, having an average thickness of about 25 nm. These lamellae have also no epitaxial orientation relationship with the iPP substrate. The corre-

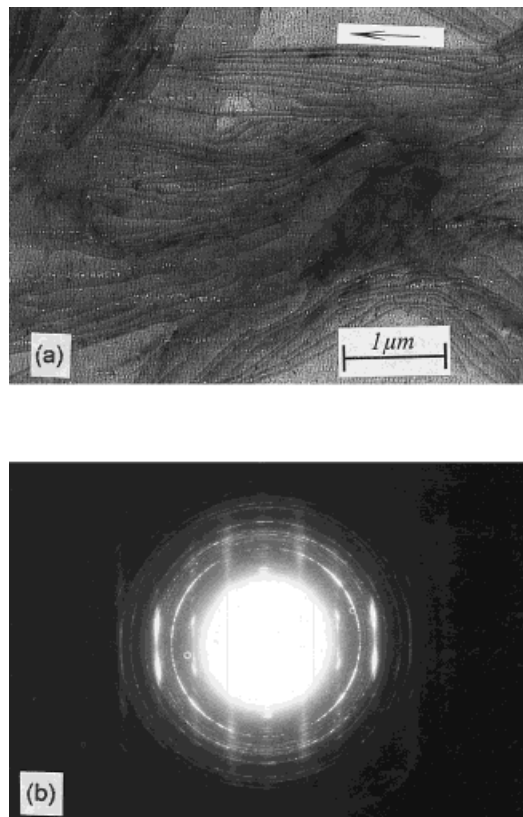


Figure 4 (a) BF electron micrograph and (b) the corresponding electron diffraction pattern of HDPE/iPP double-layered films, which were heated to 150°C for 10 min, then crystallized isothermally at 126°C for 5 h and finally cooled to room temperature. The molecular direction of the iPP substrate is indicated by an arrow.

sponding electron diffraction [Fig. 4(b)] further proves that there is no epitaxial relationship between the HDPE crystals and the iPP substrate. The same results were obtained by heating the HDPE/iPP double-layered films to 150°C for 10 min and then crystallizing them isothermally at 128°C for 5 h.

From the above observations, it can be concluded that there is a critical crystallization temperature for the occurrence of epitaxial crystallization of HDPE on the oriented iPP substrate, i.e., 125°C. At the critical crystallization temperature, the critical layer thickness of the epitaxially crystallized HDPE crystals on the oriented iPP substrates is about 30 nm or less, while above the critical crystallization temperature, no epitaxial crystallization of HDPE on the oriented iPP substrates takes place.

These results are so far surprising, as epitaxial crystallization is expected to form most efficiently at low supercoolings according to the traditional lattice matching theory. In comparing the crystal thickness of HDPE and iPP, we can notice that, besides the large crystalline aggregates, even the individual HDPE lamellae are much thicker than are the crystal lamellae of the iPP substrate. According to the arguments of Greso and Phillips²² that epitaxy can occur only when the crystal dimension of the substrate in the matching direction is larger than the critical nucleus size of the deposit crystal, which has a similar size to that of the lamellar thickness, we can explain the above obtained results. The lamellar thickness of the iPP substrate measured from Figure 4 is about 15 nm. Therefore, the dimension of the iPP crystals in the matching direction is about $15 \text{ nm} / \cos 50^\circ \approx 23 \text{ nm}$. To fit the requirement deduced by Greso and Phillips, the dimension of epitaxial HDPE crystals, i.e., the lamellar thickness, should be equal to or smaller than 23 nm. As the lamellar thickness of the HDPE crystals (about 25 nm) is thicker than is the lamellar thickness of the iPP substrate in the matching direction, no epitaxy of HDPE on the oriented iPP substrate can occur.²³

It should be pointed out that the aforementioned critical crystallization temperature, i.e., 125°C, is obtained when the melt-drawn iPP films having lamellae about 15 nm thick are used as the substrates. On the basis of the Greso and Phillips' argument, it is reasonable to assume that the critical crystallization temperature should change upon varying the lamellar thickness of the iPP substrate crystals.

CONCLUSION

The experimental results obtained from TEM and electron diffraction confirm our previous observations that epitaxial crystallization of HDPE on the oriented iPP substrates occurs only in a thin layer, which is in direct contact with the iPP substrate. The epitaxial layer thickness of HDPE depends strongly on the crystallization temperature. The higher the crystallization temperature, the thinner the epitaxial layer. When the HDPE is crystallized at 125°C, the critical epitaxial layer is not more than 30 nm thick. With further increase of the crystallization temperature, e.g., at 126° or 128°C, there is no epitaxial orientation

relationship between HDPE and iPP at all. This leads to the conclusion that there is a critical crystallization temperature for the occurrence of polymer heteroepitaxy. For the HDPE/iPP epitaxial system, the critical crystallization temperature was demonstrated to be 125°C when the iPP oriented films with lamellae of about 15 nm thick were used as the substrates. In crystallizing the HDPE melt on this kind of iPP substrates at temperatures above the aforementioned critical temperature, i.e., 125°C, no epitaxial crystallization of the HDPE on the oriented iPP film can be observed. But as the critical temperature depends only on the substrate crystal dimensions and critical nucleus size of the layered crystals, this temperature may change through using different preparation conditions for the substrate iPP films or different HDPE materials, such as branched PE.

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