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Polymer 46 (2005) 819–825
polymer
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Origin of various lamellar orientations in high-density polyethylene/isotactic polypropylene blends achieved via dynamic packing injection molding: bulk crystallization vs. epitaxy

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Received 24 September 2004; received in revised form 3 November 2004; accepted 15 November 2004
Available online 19 December 2004

Abstract

Epitaxial growth of high-density polyethylene (HDPE) onto lamellae of isotactic polypropylene (iPP), with HDPE chains inclined about 50° to that of iPP, has been achieved for the first time in their blends via dynamic packing injection molding. Even more, the epitaxial growth was found to be dependent on composition of the blends. The sequence of crystallization is not the dominant factor, but the fact that iPP crystallizes before HDPE is prerequisite for epitaxial growth of PE. Various lamellar orientations with composition can be explained by the competition between bulk crystallization and epitaxy at interfaces (i.e. iPP lamellae). In 20PP (20 wt% iPP by weight in blends), HDPE can readily crystallize in the bulk as a result of shear, and no epitaxial growth of PE is observed. For 80PP, however, bulk crystallization of HDPE can be depressed due to lack of nuclei in its bulk, resulting from a much finer droplets dispersed in the iPP matrix, and then epitaxial growth prevails.

Keywords: Bulk crystallization; Epitaxy; HDPE/iPP blends

1. Introduction

C-axis orientation parallel to shear direction can be usually encountered in an individual semi-crystalline polymer (e.g. high-density polyethylene or isotactic polypropylene) subjected to shear [1–5]. When high-density polyethylene (HDPE) crystallizes on highly oriented isotactic polypropylene (iPP) substrate or vice versa, however, no *c*-axis orientation occurs [6–12]. Instead, a well-defined crosshatched morphology develops due to heteroepitaxy originated from helical pattern of iPP interact with zigzag chain conformations of PE. High-density polyethylene or isotactic polypropylene chains are inclined about 50° to the substrate chain axis. The contact planes are (100) HDPE and (010) iPP. It is a straightforward interpretation that epitaxially grown high-density polyethylene chains interact with rows of methyl groups that populate the (010) planes of the isotactic polypropylene alpha crystal, since polyethylene chains fit exactly into the valleys formed by the methyl groups. Epitaxial growth is related to the nucleation of polymer chains on the substrates, dependent of crystallization temperature and cooling rate [13]. Only when the lamellar thickness is less than that of the substrate along lattice matching direction can epitaxy occur. Moreover, thickness of deposited film is critical for epitaxial growth and thicker film can give rise to twisted lamellae.

Epitaxy between high-density polyethylene and isotactic polypropylene can improve mechanical performances due to the bridging of the amorphous interlamellar phase of one component by the crystalline lamellar component of the other phase. Heteroepitaxy of polymers is an active way for improving the mechanical properties of polymer blends, especially for incompatible systems [14,15]. However, up to now, well defined epitaxial growth can only be achieved by either (a) annealing of drawn blends of HDPE/iPP or

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0032-3861/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2004.11.110

sandwiched films of HDPE/iPP or (b) vacuum deposition or cast film crystallization of HDPE or iPP onto single crystals or oriented film of iPP or HDPE, respectively. No well-defined heteroepitaxy has been encountered in polymer blends submitted to conventional processing methods (such as extrusion and injection molding), although there are some indications in literature [16,17]. Achieving heteroepitaxy in PE/iPP blends processed by conventional methods has not only significant theoretical value but also important practical applications.

In this paper, samples of HDPE/iPP blends are prepared with the aid of the so-called dynamic packing injection molding, which relies on the application of shear stress fields to melt/solid interfaces during the packing stage by means of hydraulically actuated pistons. The mutual lamellar orientation between HDPE and iPP is characterized with two-dimensional small angle X-ray scattering (2D SAXS), one and two-dimensional wide angle X-ray scattering (1D/2D WAXS), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). Moreover, the origin of epitaxial growth of HDPE onto iPP with respect to compositions is also discussed.

2. Experimental

2.1. Materials and sample preparation

Isotactic polypropylene (iPP), supplied by the Duzisan Limited Company, had a melt flow index (MFI) of 1 g/10 min and a density of 0.91 g cm^{-3}. High-density polyethylene (HDPE), supplied by Yansan Petrochemical Corp., had a MFI of 5 g/10 min and a density of 0.968 g cm^{-3}. All compositions were quoted as weight percentages and were labeled by the percentage of iPP. Thus 20, 50 and 80PP represent 20, 50, 80 wt% of PP in HDPE/iPP blends, respectively. Melt blending was conducted using TSSJ-25 co-rotating twin-screw extruder with a barrel temperature of 160–190 °C. After pelletiation and drying, blends were injected into a mold with the aid of a SZ 100 g injection-molding machine with barrel temperature of 190 °C and injection pressure of 900 kg cm^{-2}. Dynamic packing injection molding technology was applied. Its main feature was to introduce shear to the cooling melt during the packing stage by two pistons that moved reversibly with the same frequency. Shear rate was about 10 s^{-1} calculated from the geometry of the mold. Detail descriptions can be found elsewhere [18].

2.2. Two-dimensional small angel X-ray scattering (2D SAXS)

2D SAXS measurements were carried out using an in-house setup with a rotating anode X-ray generator (Rigaku RU-H300, 18 kW) equipped with two parabolic multilayer mirrors (Bruker, Karlsruhe), giving a highly parallel beam (divergence about 0.012°) of monochromatic Cu Kα radiation ($\lambda = 0.154$ nm). The SAXS intensity was colleted with a two-dimensional gas-filled wire detector (Bruker Hi-Star). A semitransparent beamstop placed in front of the area detector allowed monitoring the intensity of the direct beam. The SAXS intensities were normalized to the intensity of the direct beam. Azimuthal scans of 2D SAXS were made with 1° step from −90 to 270°.

2.3. Two-dimensional wide angle X-ray scattering (2D WAXS)

The 2D WAXS experiments were conducted using a Rigaku Denki RAD-B diffractometer. Monochromated Cu Kα radiation (0.154 nm) and reflection mode were used. The samples were placed with the orientation (flow direction) perpendicular to the beams. All the 2D WAXS patterns shown in this article have extracted the background, which allows a qualitative comparison between the 2D WAXS patterns. Azimuthal scans of 2D WAXS were made for the (110) planes of both HDPE and iPP with 1° step from 0 to 360°.

2.4. Differential scanning calorimetry (DSC)

The thermal analysis was performed with a Perkin–Elmer DSC Pyris 1, indium calibrated. Melting endotherms were obtained at 10 °C/min with 4–5 mg of sample in a nitrogen atmosphere.

2.5. Scanning electron microscope (SEM)

The specimens were firstly etched chemically by 1% solution of potassium permanganate in a 10:4:1 (by volume) mixture, respectively, of concentrated sulphuric acid, 85% orthophosphoric acid and water [19]. The surface was coated with gold and subsequently examined by an X-650 Hitachi scanning electron microscope at 20 KV.

3. Results

Fig. 1 shows the 2D SAXS patterns, obtained at 25 °C, of samples 20, 50 and 80PP, respectively. Corresponding azimuthal scans of 2D SAXS are also included. The shear direction is vertical. To distinguish lamellae of HDPE and iPP in the scattering patterns, similar measurements have been carried out at 135 °C, the lamellae of HDPE are melted and only PP lamellae remain. The result is shown in Fig. 2. Combining information in Figs. 1 and 2, it is clear that for 20PP the preferred lamellar growth is perpendicular to the shear direction for both HDPE and iPP. To the contrary, for50 and 80PP, the two diffraction spots on the meridian are due to iPP (lamellae perpendicular to shear direction) and the other four spots, indicating here the lamellae of PE, are titled by about ±50° to the meridian.

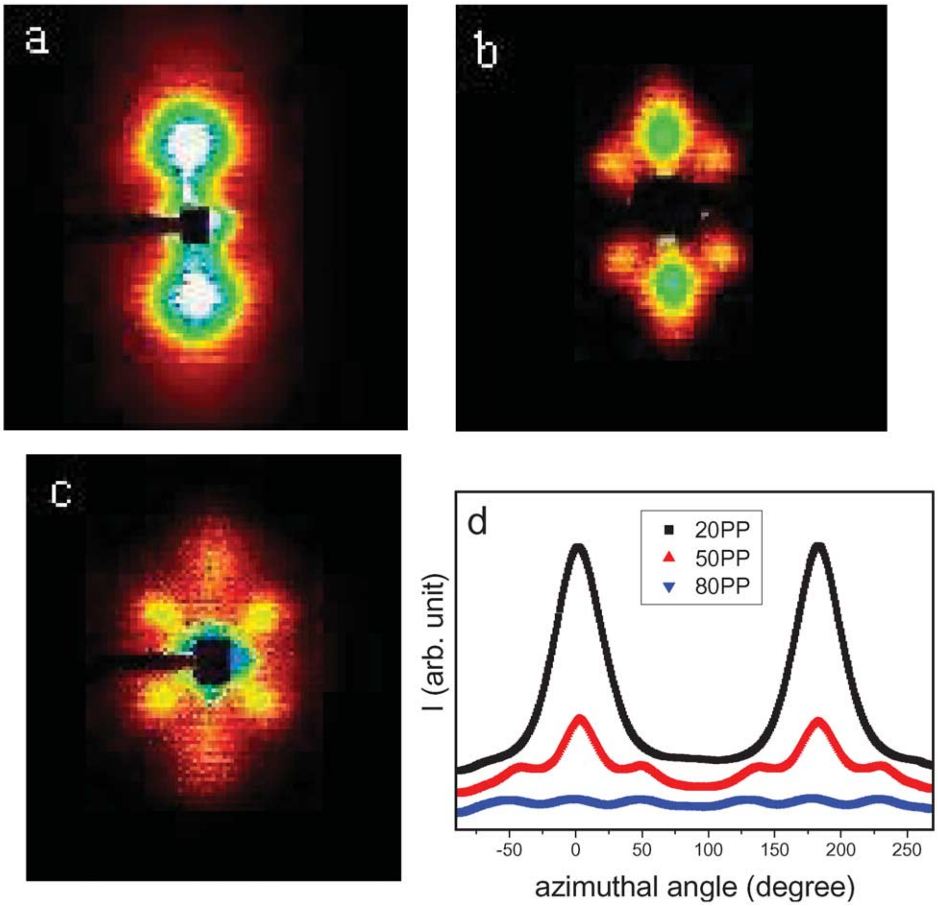

Fig. 1. Scattering patterns of 2D SAXS at 25 °C of (a) 20PP, (b) 50PP, (c) 80PP and (d) corresponding azimuthal scans of 2D SAXS. Shear direction is vertical.

Fig. 3 shows the 2D WAXS patterns, obtained at 25 °C, of 20, 50 and 80PP, respectively. Corresponding azimuthal scans of the (110) diffraction ring for both HDPE and iPP component are also shown. Expectedly, the crystal modifications are orthorhombic for HDPE and monoclinic (alpha) for iPP. Moreover, all reflections are arced rather than circles, indicating significant molecular orientation. Strong reflections of (*hk*0) planes of iPP on the equator indicate that the molecular chains of iPP are preferentially oriented along the shear direction, for all compositions. Four (110) reflections around the meridian also emerge in the (110) plane of iPP, indicating a lamellar branching through homoepitaxy between α-crystals of iPP [10,20]. These reflections arise from the iPP component daughter regions and related (*a*-axis parallel to the meridional direction) to the parent component iPP regions (*c*-axis parallel to the meridian). The epitaxial orientational relationship was first established in α-crystal quadrate some years ago and later explained on a molecular basis by Lotz et al. [10]. One needs first determine relative amounts of the epitaxially related iPP components having their *c*-axis (parent) and *a*-axis (daughter), respectively, parallel to the meridian in the PP and PP/HDPE samples whose WAXDs are shown in Fig. 3(a)–(c). It is difficult to judge the relative amounts of the two epitaxially related iPP orientations just by visual comparison of the equatorial and meridional reflection from (110) plane of iPP. However, peculiar scattering patterns develop for (110) plane of HDPE with respect to compositions, namely (a) Two (110) reflections of HDPE are on the equator for 20PP. (b) Six arcs, with two still on the equator and four other about ±50° apart from shear direction, for 50PP, and (c) only four arcs, about ±50° apart from shear direction, for 80PP. The (200) reflections of HDPE change little for the three compositions and remain on the equator. Clearly, the *c*-axis orientation is along the shear direction for 20PP. As for 50 and 80PP, however, the situation is different. Some authors have suggested that these special reflections result from the *b*-axis orientation along shear direction [21,22]. The *b*-axis orientation along shear direction stresses the space confinement due to fastest growing *b*-axis in orthorhombic crystal of HDPE. There is no *b*-axis orientation for HDPE, however, since the diffraction angle between shear direction and the normal of (110) plane should be about 35°, according to the parameters of unit cell of orthorhombic crystal of HDPE, rather than about 50° in this case. Moreover, the lamellar orientation of HDPE should be 35° apart from shear direction rather than 40° in this case, if the *b*-axis orientation

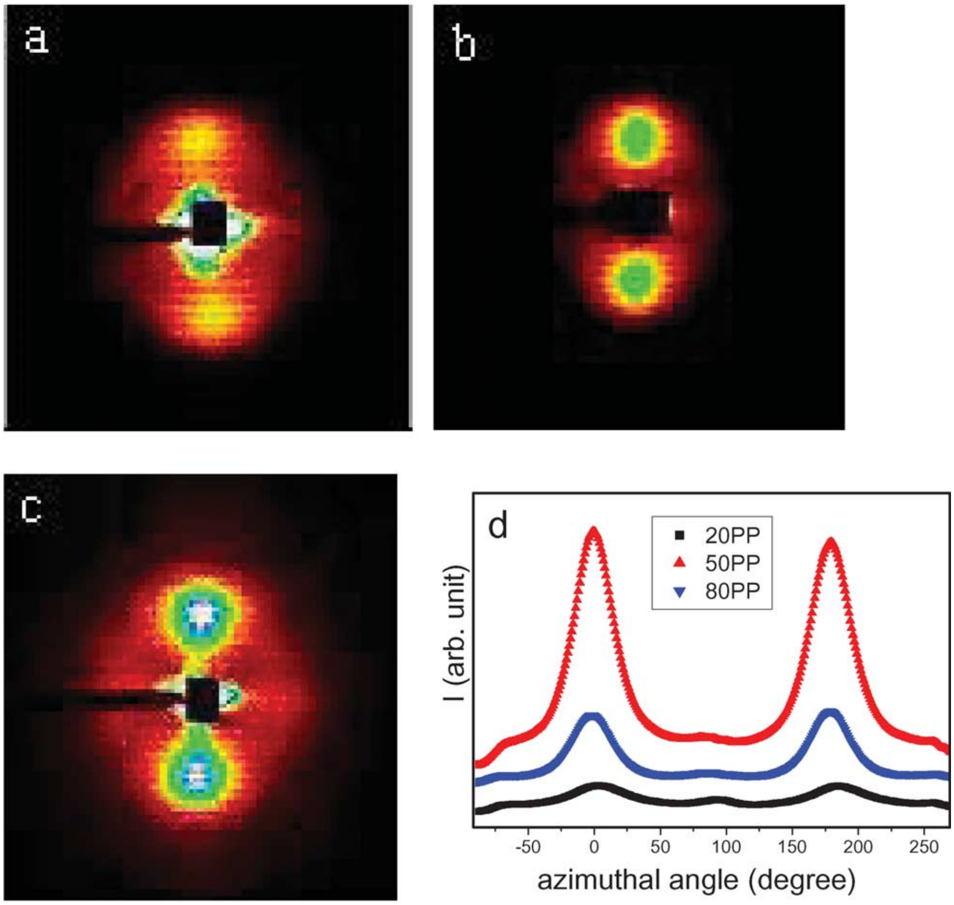

Fig. 2. Scattering patterns of 2D SAXS at 135 °C of (a) 20PP, (b) 50PP, (c) 80PP and (d) corresponding azimuthal scans of 2D SAXS. Shear direction is vertical.

of HDPE along shear direction exists. According to Lotz and Wittmann [10,11], there exists epitaxial growth of HDPE lamellae onto that of iPP or vice versa by the molecular mechanism $(100)_{\mathrm{HDPE}}//(010)_{\mathrm{iPP}}$. The HDPE or iPP chains are inclined about 50° to the substrate chain axis, based on the lattice matching between HDPE (010) and iPP (101) planes. Undoubtedly, for 80PP the HDPE lamellae grow epitaxially onto that of iPP by the contact plane $(100)_{\mathrm{HDPE}}//(010)_{\mathrm{iPP}}$ and HDPE lamellae are oriented 40° away from the shear direction. However, for 20PP there is no epitaxy and lamellar orientation of both HDPE and iPP is perpendicular to shear direction. As for 50PP, both above lamellar orientations coexist. In a word, the lamellar orientations may differ for HDPE depending on the PE/iPP compositions. They are schematically represented in Fig. 4.

4. Discussion

From the foregoing results, it is clear that the epitaxial growth of HDPE lamellae on iPP is strongly related to the composition of the blend. Then, what is the dominant factor affecting the epitaxial growth in HDPE/iPP blends? Obviously, the sequence of crystallization of HDPE and iPP is necessary for epitaxy, since for epitaxial growth of HDPE lamellae to take place on iPP is that iPP has crystallized first and provides a template for growth of HDPE. Under quiescent crystallization conditions, indeed HDPE crystallizes around 125 °C, and that of iPP around 115 °C, obtained by cooling the melt down at a rate of 10 °C/min. However, the situation is different for blends subjected to shear. The crystallization temperature of HDPE increases only slightly under shear, since the melting temperature of HDPE is much lower than that of iPP. IPP can crystallize at much higher temperatures, actually before PE. In other words, the introduction of shear accelerates crystallization for both PE and iPP, but has more impact on iPP than on HDPE. This is quite natural since the temperature window for PE is only a couple of degrees, as expected somewhat 25 °C for iPP. Then, is it that iPP crystallizes before HDPE in 80PP and vice versa in 20PP? However, the situation is not so. The onset crystallization temperature of iPP is about 140 °C for 20PP and about 127 °C for 80PP, obtained by cooling the melt down at a rate of 10 °C/min [23]. Meanwhile, for both 20 and 80PP the crystallization temperature of HDPE is almost same, about 120 °C. Clearly, in this case, iPP crystallizes before HDPE

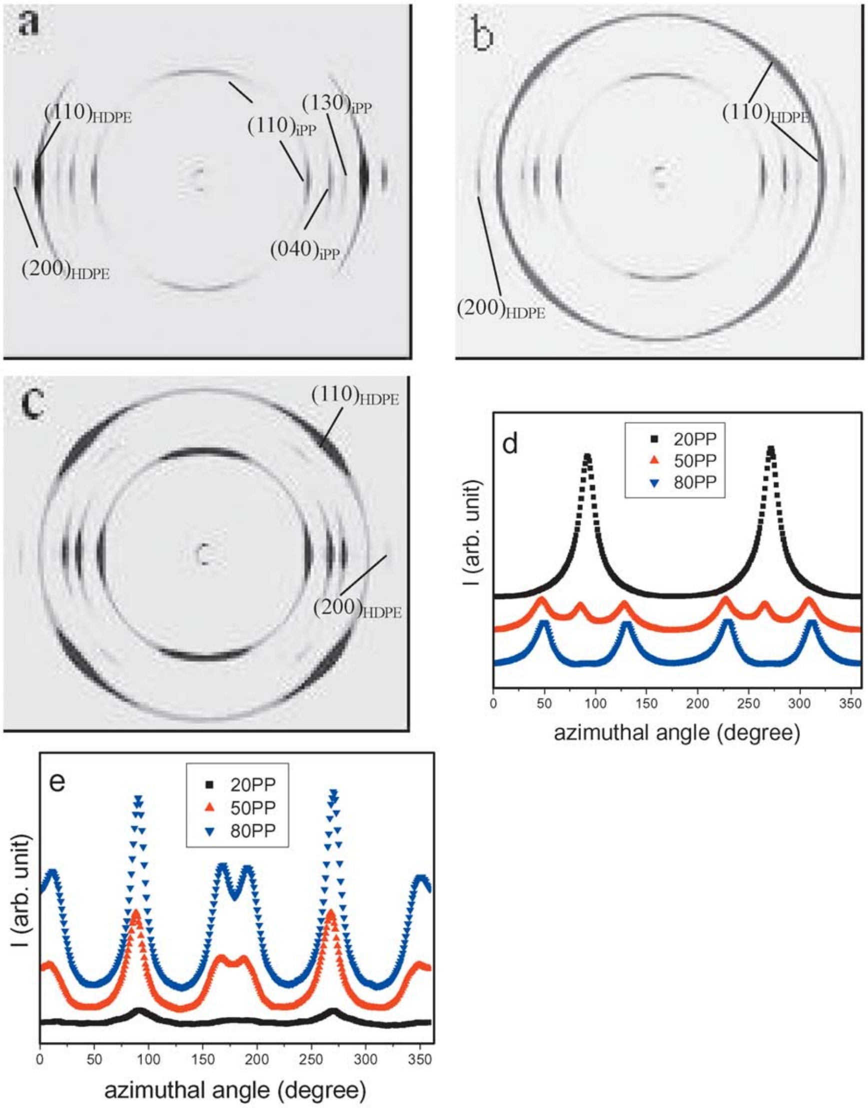

Fig. 3. Scattering patterns of 2D WAXS at 25 °C of (a) 20PP, (b) 50PP, (c) 80PP and corresponding azimuthal scans of (110) plane for both HDPE (d) and iPP (e) Shear direction is vertical.

for both 20 or 80PP and thus the sequence of crystallization between HDPE and iPP is not the dominant factor though it is the precondition for epitaxial growth of HDPE onto iPP. Moreover, in another experiment [24], even after subjected to annealing at 160 °C for 30 min, (the iPP component remains unmelted), upon cooling, no epitaxial growth occurs in the blends with HDPE as a major component, just like 20PP, whereas well defined one is realized in the blends with HDPE as a minor component, just like 80PP. Therefore, it is clear that there is another mechanism dominating the lamellar orientation with respect to compositions, rather than the sequence of crystallization between HDPE and iPP.

Epitaxial growth, as a specific case of surface-induced crystallization, is controlled by nucleation at interfaces. Therefore, the epitaxial growth must involve the necessary requirements for the formation of critical nucleation. A major requirement (but which turns out not to be entire in the present case) for the formation of nuclei is that the crystal dimension of iPP in the matching direction must be larger than the critical lamellar thickness of HDPE. To favor epitaxial growth of HDPE lamellae onto that of iPP is either to increase the lamellar thickness of iPP or to reduce that of HDPE. In our experiments, the lamellar thickness of iPP in 20, 50 and 80PP is almost the same, as deduced by its melting point (about 167 °C) and by the SAXS data collected in Fig. 1. Also the cooling rate is similar since processing conditions are consistent. Therefore, it can be supposed that epitaxial growth arises from retarded crystallization of HDPE, resulting in thinner lamellae, which has been demonstrated by the reduction of melting point of HDPE with increasing of iPP content in iPP-rich compositions. We suggest that epitaxial growth at interfaces occurs only when the bulk crystallization is depressed. In other

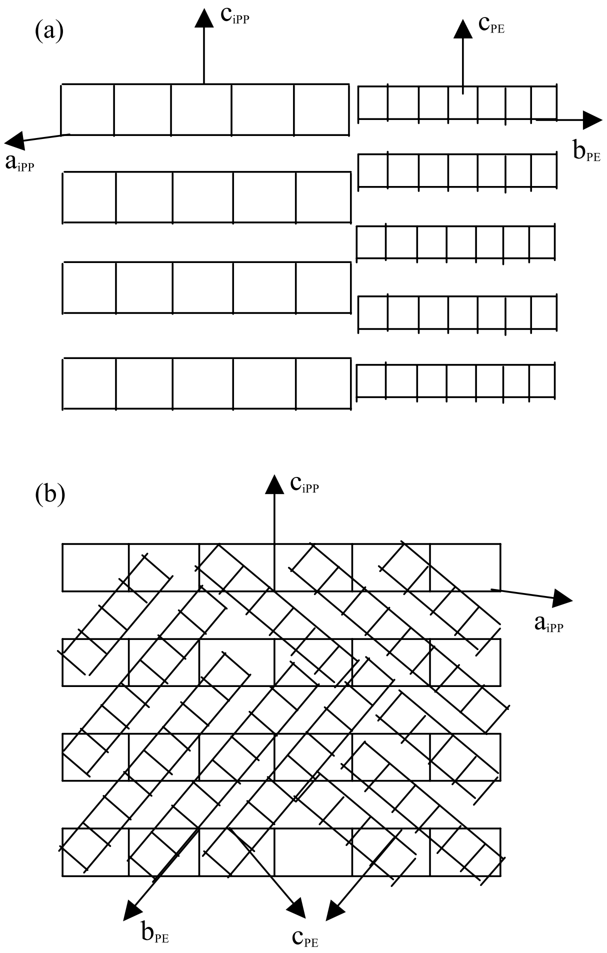

Fig. 4. Schematic diagram of orientation relation of lamellae and molecular chains between HDPE and iPP, (a) lamellae of both HDPE and iPP are oriented perpendicular to shear direction, and (b) lamellae of iPP are oriented perpendicular to shear direction while that of HDPE are about ± 40° apart from shear direction. Shear direction is vertical. Note that the long spacing and lamellar thickness are arbitrary.

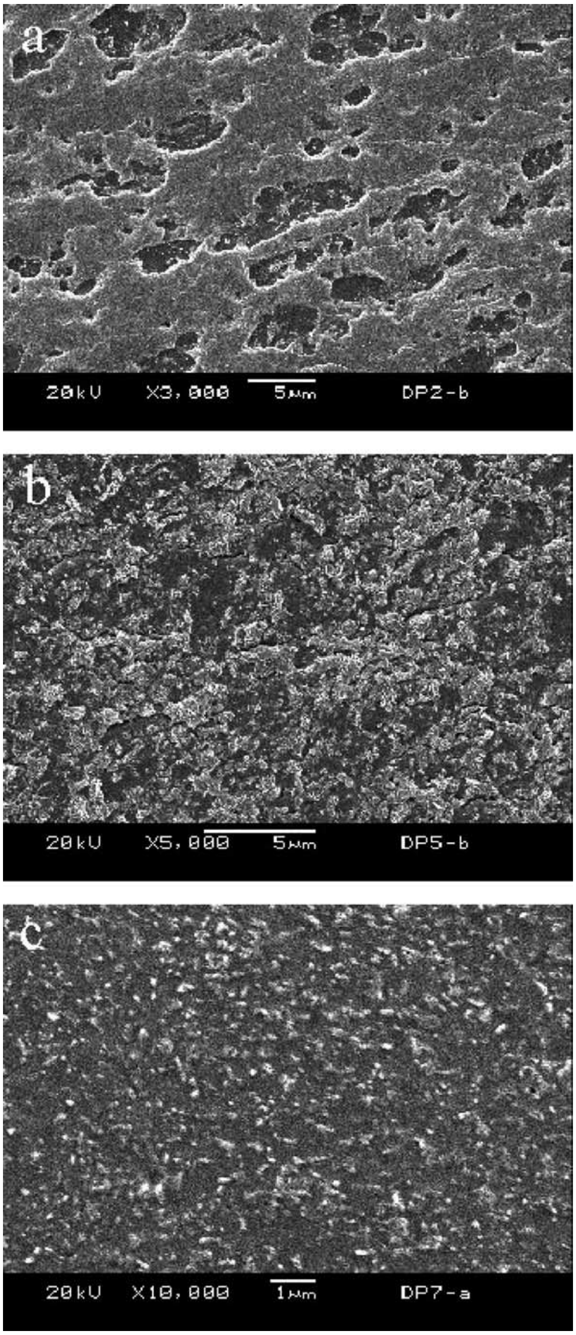

Fig. 5. SEM pictures of 20PP (a), 50PP (b) and 80PP (c) after etching.

words, whether epitaxial growth occurs or not depends on the competition of nucleation of HDPE in its bulk and at the interface (i.e. surface of iPP crystal). Note that in their blends only if HDPE nucleates on the iPP crystal at their interface can epitaxy grow. Retarded crystallization can take place by crystallization in the confined space due to lack of heterogeneous nuclei, which has been demonstrated in many systems [25]. In our case, it is evident that HDPE droplets with sub-micron size are dispersed in the iPP matrix (i.e. 50 and 80PP) by examination of phase morphology, as shown in Fig. 5. Note that, due to its weaker resistant to the etchant, iPP was extracted from the samples, represented by the dark area in the pictures. While HDPE droplets dispersed in the iPP matrix are very small (i.e. 80PP), we are dealing with a situation of crystallization of a dispersed medium as performed e.g. by Koutsky and Waltow for PE dispersed in silicone oil[26]. The fact that do not contain any active heterogeneity (nuclei) will nucleate via epitaxial crystallization of PE on the well made of crystalline iPP, and generate the peculiar 50° orientation showed in both 50 and 80PP. For the 20PP sample (and to some extant the 50PP sample) shearing is able to induce fiber orientation of the PE component. These fiber are more effective nucleation for the molten PE, and take precedence (are active at higher temperature) than the PE/iPP epitaxy and thus give rise to the SAXS reflection on the meridian characteristic of a fiber pattern. In the 20PP sample, continuity of the PE component allows this lamellar growth throughout the PE component. In the 50PP sample, the higher density of iPP wells limits spread of PE growth and allow for both mechanisms to take place. WAXS patterns indicate that substantial amount of iPP chains are either parallel or perpendicular to the fiber axis (i.e. lamellar parallel and perpendicular to the fiber). However, SAXS displays only peaks on the meridian, it does not give any clue on lamellar oriented parallel to the fiber axis (find generation of daughter lamellar, i.e. the so called *c* axis orientation). These observations make sense when considering the possible orientation of the lamellar relative to the fiber axis.

For lamellar perpendicular to the fiber axis, all the lamellar contribute to the SAXS diffraction peaks on the meridian, since the geometry is adequate. The WAXS pattern is, however, that of a fiber, since the *a* and *b* axis can take all azimuthal orientation: only a small fraction of the hk0 diffracting planes contribute to the WAXS pattern.

For lamellar parallel to the fiber axis, the situation is in some ways (but only partly) opposite. The lamellar planes can take any azimuthal orientation, and the SAXS pattern is therefore analogous to a 'fiber' pattern. Only a small fraction of these lamellar are oriented parallel to the X-ray beam, and the associated diffraction peak (that should appear on, or near the equator) is expected to be weak in any case. Moreover, the very nature of the nucleation process (by homoepitaxy) does not have a regular stretching of the lamellar, which may contribute to the fact that no SAXS reflections are observed in our experiments. The WAXS pattern associated with this lamellar orientation (the so-called *a* axis orientation) combine two patterns. Since a* is parallel to the fiber axis, the (110) planes that make only a small angle with a* are virtually all in diffracting position (near perpendicular to the fiber axis). The *b* axis, and therefore the (040) planes that diffract on the equator in spread over all azimuthal angles, and only a small fraction is in diffracting orientation.

5. Conclusion

Orientation of lamellae and molecular chains has been characterized with the aid of 2D SAXS and 2D WAXS. Parent lamellar orientation of iPP is perpendicular to the shear direction, irrespective of compositions. Various lamellar orientation of HDPE are observed for different compositions of the blends, either perpendicular to the shear direction when PE is the matrix, or ±40° away from the shear direction when PE is dispersed in droplet. In the latter case, HDPE crystallizes epitaxially crystallizes onto iPP with $(100)_{\mathrm{HDPE}}//(010)_{\mathrm{iPP}}$. The dominant factor seems to be competition between bulk crystallization and epitaxial growth. No epitaxy occurs in HDPE matrix since shear induces HDPE to crystallize at low supercooling. When the bulk crystallization is depressed due to lack of heterogeneous nuclei in finely dispersed HDPE droplets, the epitaxial crystallization of HDPE onto iPP lamellae becomes the dominant nucleation process.

Acknowledgements

We would like to express our sincere thanks to National Natural Science Foundation of China (20274028, 50373030 and 20490220) for Financial Support. This work was subsidized by the Special Funds for Major State Basic Research Projects of China (2003CB615600). Our thanks are also due to the very helpful comments and suggestions from Prof B. Lotz at Strasbourg, France.

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