

# Epitaxial crystallization of high-density polyethylene on polypropylene in solution-cast films

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Epitaxial crystallization of high-density polyethylene (HDPE) on isotactic polypropylene (iPP) in solution-cast films has been investigated by electron microscopy. The specimen-tilt technique of electron microscopy has been used to study the structural relationship between HDPE and iPP crystals. HDPE exhibits different crystalline morphologies in the two basic types of iPP spherulite textures, cross-hatched and lathlike regions. In the former, the crystallographic  $c$  axis of HDPE lamellae is in the film plane, while in the latter, the  $c$  axis of HDPE crystallites is at an angle of about  $50^\circ$  with the normal of the film. In both structural regions of iPP, however, the contact planes of epitaxial growth are (010) for iPP and (100) for HDPE.

## 1. Introduction

Very recently, there has been considerable interest in epitaxial crystallization of crystalline polymers, among which the blends or complex films of isotactic polypropylene (iPP) with linear polyethylene (PE) have been of particular interest because of both the unusual crystalline morphologies and the synergism of the mechanical properties of the blends. Vapour deposition and recrystallization of low molecular weight PE on the surface of specially prepared iPP quadrates resulted in an epitaxial relationship between the two polymers [1, 2]. Sandwiched layers of oriented films of PE and iPP after heat treatment above the melting point of PE exhibited a cross-hatched lamellar morphology; the chain axes of the two kinds of lamellae were at an angle of  $45^\circ$ – $50^\circ$  to each other, showing an epitaxial growth of PE on oriented iPP [3–5]. As to the crystalline relationship of PE with iPP, however, there are other opinions which do not focus on epitaxial growth of PE on iPP [6–8].

The purpose of this work is to study the epitaxial relationship of high-density polyethylene (HDPE) on iPP in solution-cast films by means of electron microscopy.

## 2. Experimental details

The polymers used in this work were commercial products produced in China. The molecular weights of iPP (2401) and HDPE (Z1) are  $3 \times 10^5$  and  $3.5 \times 10^5$ , respectively.

Thin films of iPP/HDPE blends were prepared by casting 0.1–0.4 wt % xylene solution on the surface of glycerol at  $100^\circ\text{C}$ . These films were carbon coated to increase thermal conductivity and mechanical stability and then directly analysed by transmission

electron microscopy (TEM). A Hitachi 600 microscope operating at 100 kV was used in this study. Bright field (BF) electron micrographs were obtained by defocus of the objective lens [9, 10]. In order to minimize radiation damage by the electron beam, focusing was carried out on an area, then the film specimen was translated to its adjacent undamaged area and the image recorded immediately.

## 3. Results and discussion

### 3.1. Basic structure of iPP

Solution-cast films of iPP homopolymer consist of two types of basic structures, cross-hatched and lathlike lamellae [11], which coexist side by side in the same spherulite (Fig. 1). For the cross-hatched structure (left-hand side of Fig. 1), the tangential direction lamellae (daughter lamellae) epitaxially grew on the radial direction lamellae (parent lamellae) with their  $c$  and  $a$  axes in the film plane [11–13]. The intercrossing angle between the two kinds of lamellae is about  $80^\circ$ , while the contact planes for both the parent and the daughter branches are (010).

As to lathlike lamellae, sometimes called a single crystal-like structure, the crystallites join each other side by side within the amorphous region (right-hand side of Fig. 1). The crystallographic  $c$  axes are vertical to the film plane. The above results are confirmed by the electron diffraction patterns of the cross-hatched region (Fig. 2a) and lathlike area (Fig. 2b) of iPP.

### 3.2. Morphology of iPP/HDPE film in the cross-hatched region of iPP

As in iPP homopolymer, the iPP in the solution-cast films of iPP/HDPE blends consists of cross-hatched

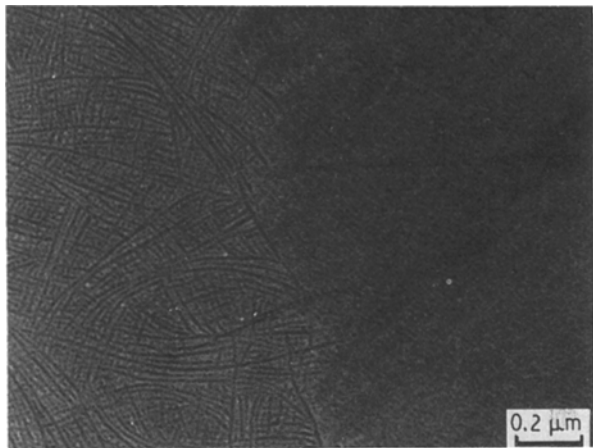


Figure 1 BF electron micrograph of iPP homopolymer cast on glycerol at 100 °C.

and lathlike structures. However, the crystalline morphology of HDPE existing in the cross-hatched region is different from that existing in the lathlike area of iPP. Fig. 3 shows BF defocus electron micrographs of

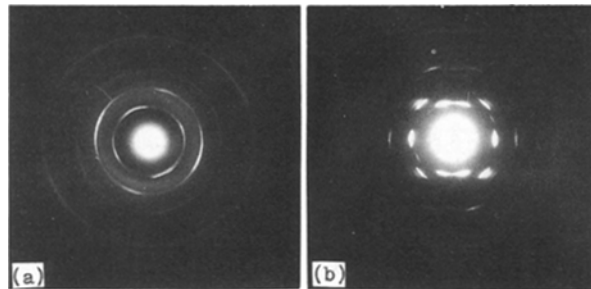


Figure 2 Electron diffraction patterns of (a) cross-hatched structure and (b) lathlike structure of iPP.

the cross-hatched regions of iPP in solution-cast films of iPP/HDPE blends with various compositions. The short, thick and dark lines in the micrographs are crystalline lamellae of HDPE, which disperse on the long, thin lamellae of iPP (including parent and daughter lamellae), while the various black patches among them represent lamellar regions of HDPE which are Bragg oriented with respect to the incident

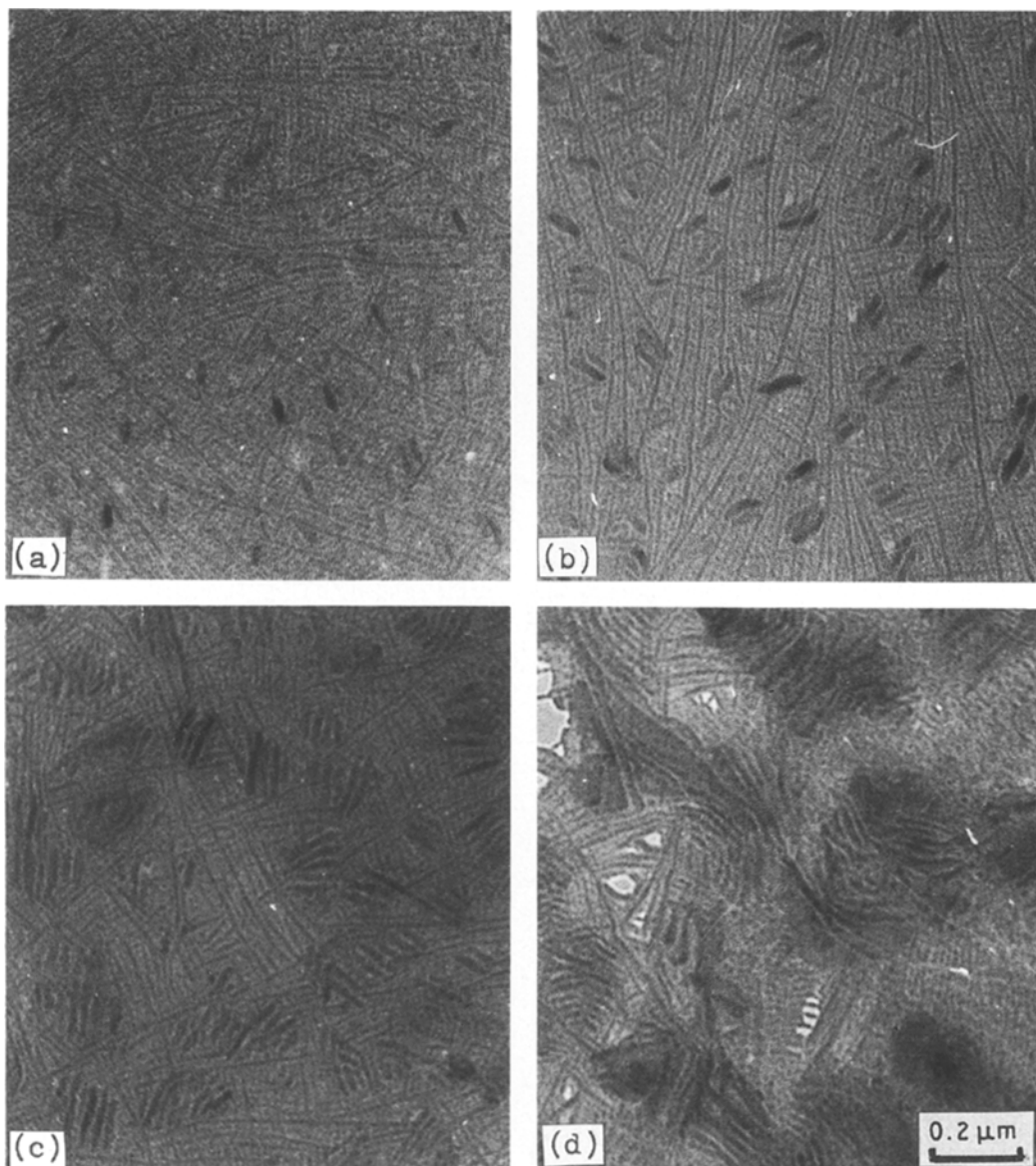


Figure 3 BF electron micrographs of cross-hatched regions of iPP of solution-cast films of iPP/HDPE blends with various compositions: (a) 90/10; (b) 80/20; (c) 70/30; (d) 50/50.

electron beam. When the content of HDPE in the blends is low, for example, 10 wt %, the dispersed domains of the HDPE phase consist of single or double lamellae (Fig. 3a). The number and the width of HDPE lamellae of the dispersed domains, i.e., the size of the HDPE phase, increase with the increase in HDPE content of the blends (Fig. 3b and c). The HDPE lamellae are parallel to each other in the same domain of HDPE and seem to have a definite orientation between different HDPE domains. The average thickness of HDPE lamellae is about 25 nm, which does not change with the increase in HDPE content of the blends. Careful examination showed that the long lamellae of iPP, both parent and daughter lamellae, overlapped the domains of the HDPE phase. This means the domains of HDPE as a dispersed phase in the blends are not independent, but grow on the parent or daughter lamellae of iPP. It is particularly interesting that there is a definite intercrossing angle of about  $45^{\circ}$ – $50^{\circ}$  between the two kinds of lamellae. This result is consistent with those of vapour deposition [1, 2] or complex films [3–5] of PE with iPP. When HDPE in the blend is over 50 wt %, the HDPE becomes a continuous phase. There is no definite

orientation relationship between HDPE lamellae and iPP lamellae (Fig. 3d).

According to the structural relationship mentioned above and the nucleation action of iPP on HDPE [1–5], we propose that for epitaxial growth of HDPE on iPP in solution-cast films of HDPE/iPP blends with low HDPE contents ( $\leq 30\%$ ), the crystallographic  $b$  and  $c$  axes of HDPE crystals should be in the film plane. The specimen-tilt technique of electron microscopy was used to study the structural relationship between HDPE and iPP crystals of the films. Fig. 4 shows the electron diffraction patterns of iPP/HDPE = 80/20 blend in the cross-hatched region of iPP before and after tilting  $\pm 34^{\circ}$  about the  $c$  axis of HDPE crystals. It is seen that under normal conditions, in addition to (001) and (101) reflections of iPP (compare with Fig. 2a), there exist weak (110), (200) and strong (020), (011) reflections of HDPE (Fig. 4a). After tilting  $\pm 34^{\circ}$  about the  $c$  axis of HDPE, the intensities of (020) and (011) reflections of HDPE decreased considerably, while the intensities of (110) and (200) reflections increased, with the (110) reflection attaining a maximum (Fig. 4b). The above results indicate that the crystallographic  $a$  axis of HDPE crystals is normal to the film plane, while the  $b$  and  $c$  axes are in the plane of the film.

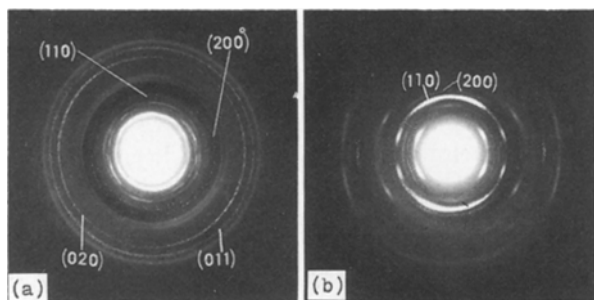


Figure 4 Electron diffraction patterns of iPP/HDPE = 80/20 blend in cross-hatched region of iPP at tilt angles of (a)  $0^{\circ}$  and (b)  $34^{\circ}$ , respectively.

Fig. 5a and b are HDPE (110) dark-field (DF) electron micrographs of the cross-hatched region of iPP of the specimen of iPP/HDPE = 80/20 blend with tilt angles of  $0^{\circ}$  and  $34^{\circ}$ , respectively. The number of the bright regions (due to Bragg diffraction from the (110) planes of HDPE) attains a maximum at tilt angles of  $\pm 34^{\circ}$ . This result is consistent with the electron diffraction patterns (Fig. 4). Fig. 6 shows the corresponding BF electron micrograph recorded at a tilt angle of  $34^{\circ}$ . It is obvious, by comparing it with Fig. 3b, that the number of black patches, which represent the strongly diffracting (110) regions, attains a maximum. The texture of the HDPE lamellae

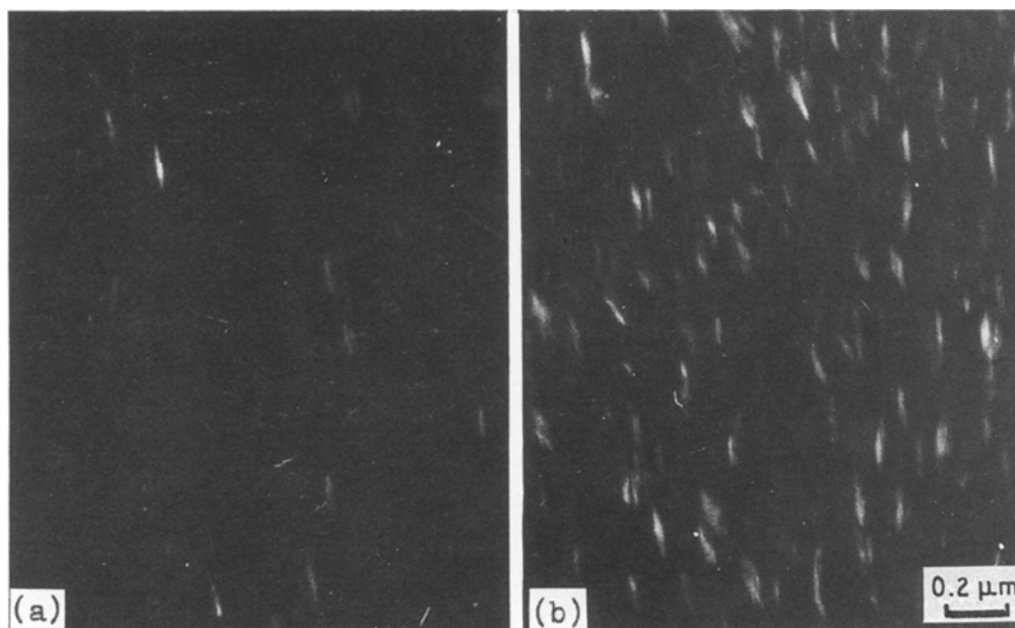


Figure 5 HDPE (110) DF images of cross-hatched region of iPP of iPP/HDPE = 80/20 blend at tilt angles of (a)  $0^{\circ}$  and (b)  $34^{\circ}$ , respectively.

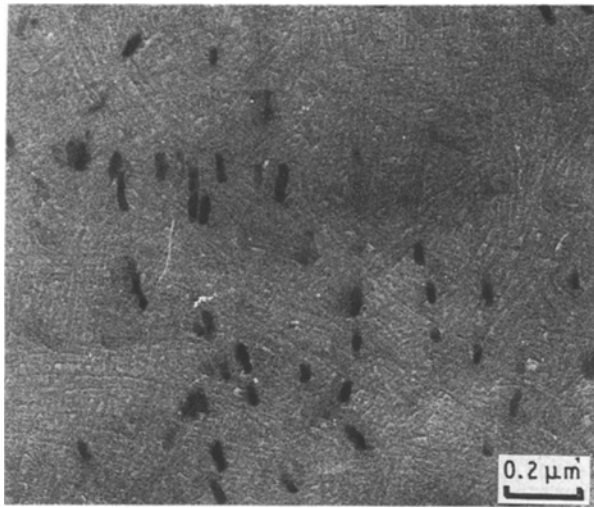


Figure 6 Corresponding BF electron micrograph at a tilt angle of 34°.

in the cross-hatched region of iPP is thus approximately a (200) surface. All of the above results verified the hypothesis we proposed for epitaxial growth of HDPE on iPP in the blends. The crystallographic  $a$  axis of HDPE is normal to the film plane. The  $c$  axes of both HDPE and iPP are in the film plane with an intercrossing angle of 45°–50°, while the contact planes are (010) for iPP and (100) for HDPE. The epitaxial relationship is depicted in Fig. 7.

The existence of the above epitaxial growth of HDPE on iPP implies that the crystallization of iPP takes place prior to that of HDPE during the film specimen preparation from the blends by the solution-casting method. It should be pointed out that no epitaxial relationship has been observed for the blends with a high content of HDPE ( $\geq 50\%$ ) (Fig. 3d). In this case, the iPP, even crystallized prior to HDPE,

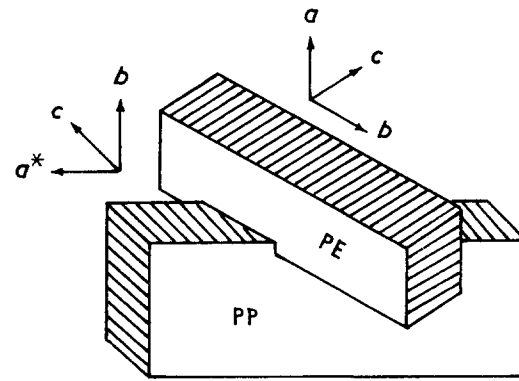


Figure 7 Orientation relationship between iPP and HDPE lamellae in cross-hatched region of iPP.

could not play the role of substrate for crystalline growth of HDPE because of the formation of a continuous phase of HDPE.

### 3.3. Morphology of HDPE/iPP film in the lathlike area of iPP

In the lathlike area of iPP, however, the HDPE in the blends exhibits a completely different texture from that existing in the cross-hatched region of iPP. Fig. 8a shows the BF defocus electron micrograph of the film of iPP/HDPE = 80/20 blend. The dark patches represent dispersed crystallites of HDPE, which are oriented for Bragg reflection with respect to the incident electron beam. The lateral length of these crystallites is much larger than the thickness of HDPE lamellae (compare with Fig. 3). It is noticed that the crystals of HDPE which are not in Bragg orientation could hardly be seen. These dispersed crystallites of HDPE, however, could be recorded much more clearly from metal-shadowed film of the blends

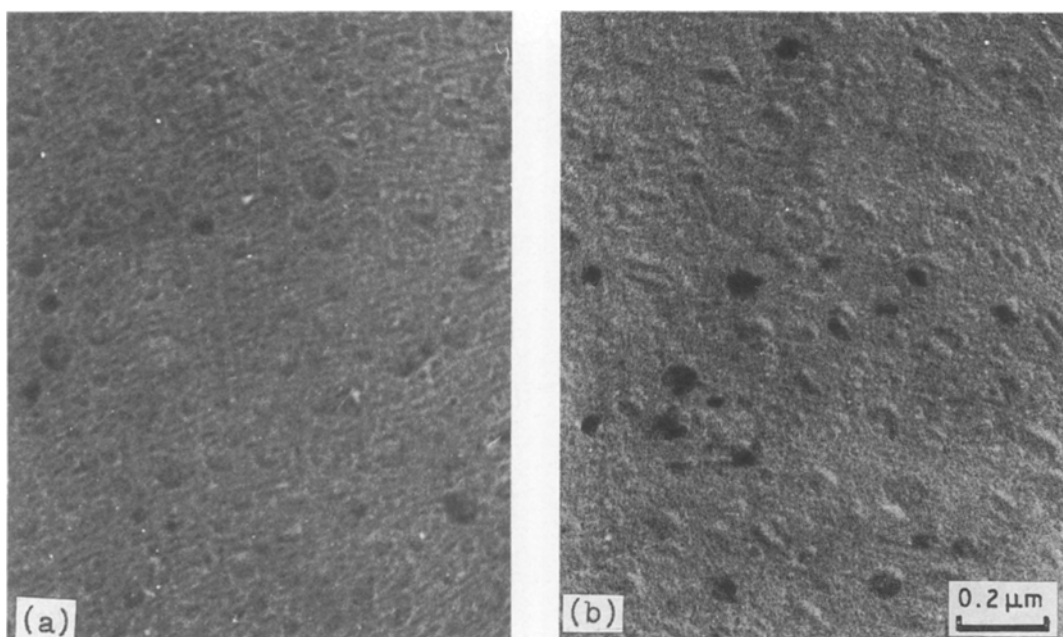


Figure 8 (a) BF electron micrograph of lathlike area of iPP of the film of iPP/HDPE = 80/20 blend. (b) BF image of metal-shadowed specimen.

(Fig. 8b). The shadowing also indicates that the crystallites of HDPE grow out of the film plane.

If epitaxial crystallization between HDPE and iPP lamellae in the lathlike area takes place the contact planes should be (0 1 0) for iPP and (1 0 0) for HDPE, while the  $c$  axis of HDPE should be at an angle of about  $45^\circ$ – $50^\circ$  with the normal to the film plane (the direction of  $c$  axis of iPP crystals). Studies using the specimen-tilt technique of electron microscopy were carried out to prove the inference. Fig. 9 shows electron diffraction patterns of the film specimen of iPP/HDPE = 80/20 blend in the lathlike area of iPP at tilt angles of  $0^\circ$  and  $45^\circ$ , respectively. The (1 1 0) reflection intensity of HDPE crystals attained a maximum at  $\pm (45^\circ$ – $50^\circ)$  angles about the  $a$  axis of HDPE crystals (Fig. 9b), while the (2 0 0) reflection intensity was almost the same as that at  $0^\circ$  (Fig. 9a). Figs 10 and 11 show the corresponding DF ((1 1 0) reflection) and BF electron micrographs of iPP/HDPE = 80/20 blend in the lathlike area of iPP at tilt angles of  $0^\circ$  and  $45^\circ$ , respectively. The number of the strong (1 1 0) diffracting regions (the bright regions in DF images and the black patches in BF images) attained a maximum at tilt angles of about  $45^\circ$  (Figs 10b and 11).

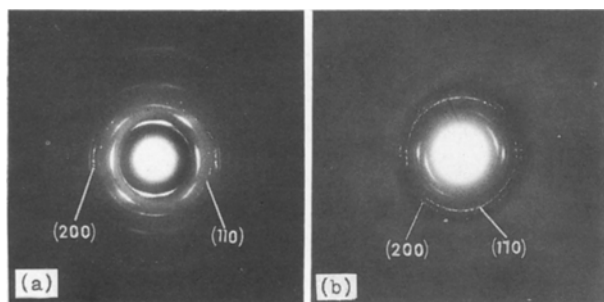


Figure 9 Electron diffraction patterns of the specimen of iPP/HDPE = 80/20 blend in lathlike area of iPP at tilt angles of (a)  $0^\circ$  and (b)  $45^\circ$ , respectively.

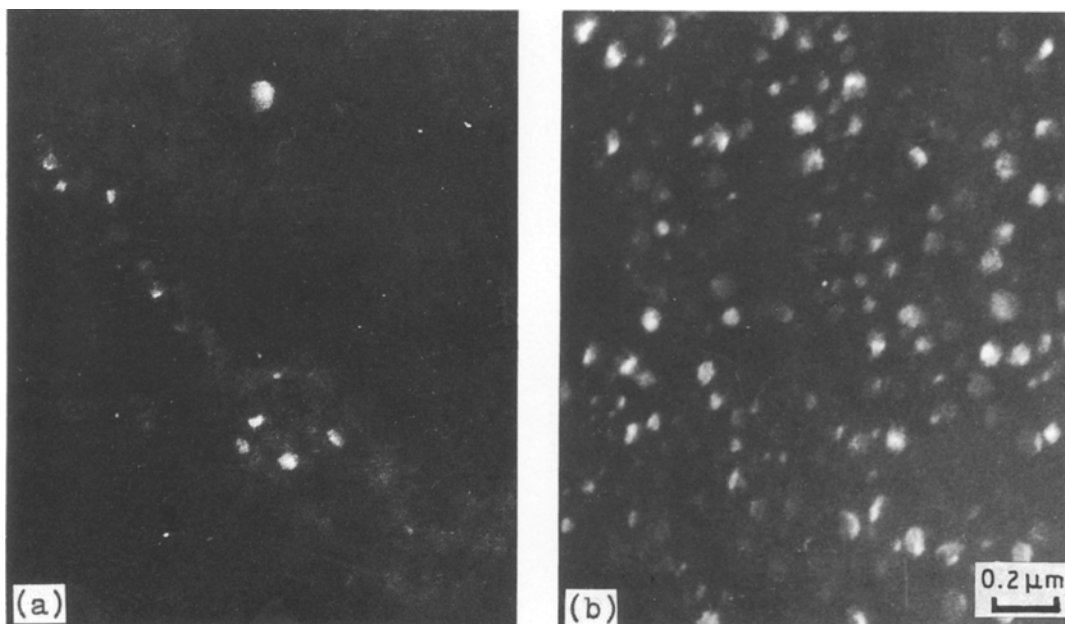


Figure 10 Corresponding HDPE (1 1 0) DF images at tilt angles of (a)  $0^\circ$  and (b)  $45^\circ$ , respectively.

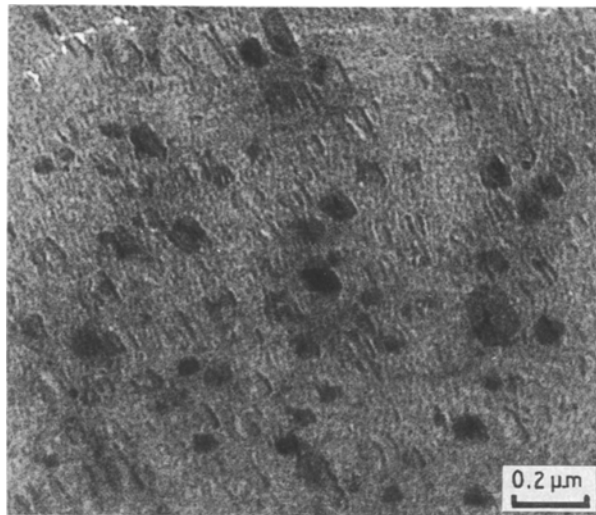


Figure 11 Corresponding BF image at a tilt angle of  $45^\circ$ .

indicate that the crystallographic  $c$  axis of HDPE crystals in the lathlike area of iPP is at an angle of  $45^\circ$ – $50^\circ$  with the normal to the film plane. There should be an epitaxial relationship between HDPE and iPP, as depicted by Fig. 12. As is the case of the cross-hatched region of iPP, when the content of HDPE in the blends is over 50 wt %, no epitaxial relationship has been observed because of the formation of an independent HDPE phase (Fig. 3d).

#### 4. Conclusion

1. In confirmation of findings by other authors, the spherulites of iPP in solution-cast films have two types of structures, cross-hatched and lathlike lamellae.
2. HDPE crystals grow epitaxially on both the cross-hatched and the lathlike lamellae of iPP in the blends of HDPE/iPP at low contents of HDPE ( $\leq 30$  wt %). No epitaxial relationship between

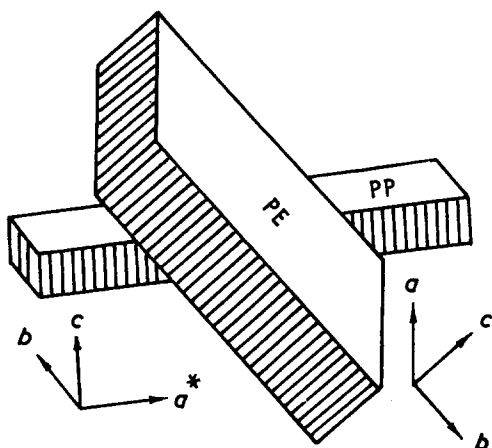


Figure 12 Orientation relationship between iPP and HDPE lamellae in lathlike area of iPP.

HDPE and iPP has been found when the HDPE content is over 50 wt %.

3. In the cross-hatched region of iPP in the blends the dispersed domains of HDPE consist of lamellae parallel to each other, which grow epitaxially on iPP lamellae (including parent and daughter lamellae). The crystallographic  $b$  and  $c$  axes of HDPE crystals are in the film plane. The intercrossing angle between the two kinds of lamellae is about  $45^{\circ}$ – $50^{\circ}$ , while the contact planes of the epitaxial growth are (010) for iPP and (100) for HDPE.

4. In the lathlike area of iPP in the films of the blends, the HDPE exists as dispersed crystallites, which grow out of the plane of the film. The crystallographic  $c$  axis of the HDPE crystallites is at an angle of  $45^{\circ}$ – $50^{\circ}$  to the normal of the film plane ( $c$  axis of iPP

crystals), while the  $b$  axis is in the film plane. The contact planes of the two kinds of epitaxial lamellae are the same as that in the cross-hatched region of iPP.

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