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A cross-sectional preparation method for TEM and AFM investigations on layered poylmer interfaces

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Summary

The epitaxial crystallization of polyethylene (PE) on uniaxially oriented isotactic polypropylene (iPP) has been investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The cross-sectional morphology of the epitaxial interfaces of multi-layered samples prepared by a new preparation method has been observed with view direction parallel to the epitaxial interfaces. It is found that fairly oriented PE lamellae grow perpendicular to the iPP layers with nucleation initiation on the iPP surfaces.

Introduction

In recent years many investigations have been devoted to epitaxial crystallization of polymers. Most of the investigations are applied to epitaxy between iPP and some zig-zag chain polymers, in which the molecule chains incline ±50° to the iPP chain direction (1-5). Especially, the epitaxial relationship between iPP and PE has been explained in terms of the alignment of the zig-zag chains along methyl group rows of iPP with 0.5nm intermolecular distances for a chain-row matching (6). The epitaxial interfaces bonded by van der Waals forces result in a very good adhesion between the components of a non miscible polymer blend, like PE-iPP. Some improvements in mechanical properties can be achieved as an effect of such epitaxial interaction (7-10). For epitaxial relationships studied by TEM, thin film sample preparation techniques usually are used. These films can easily be imaged directly by TEM in a view mode perpendicular to the film plane by mounting them onto the conventionally used copper grids. But particularly for research of epitaxial or non-epitaxial interfaces and their relation to mechanical properties as for the overall bulk properties without influence of the surfaces, cross-sectional investigations are important (11, 12). Thin film specimens prepared for cross-sectional microtom cuts by embedding in epoxies or other embedding materials can show changes of the structure or even dissolution of the film. Also properties of thin samples with epitaxial interfaces are strongly influenced by the high surface to volume ratio and could be different to the bulk properties. In this paper we report an improved investigation method based on an easy preparation technique that allows TEM morphology images parallel to the interfaces. This cross-sectional technique and the orientation relationship found may help for the further understanding of the mechanisms of interfacial crystallization in polymers.

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Experimental

The high density PE used in these experiments was Lupolene 6021D and the iPP was Novolen, both from BASF AG Ludwigshafen, Germany. According to the melt draw technique reported by Petermann and Gohil (13) a small amount of 0.3wt.-% iPP and 0.7wt.-% PE solution in xylene was spread on the surface of a hot glass slide (130°C). After evaporating the solvent, the remaining polymer blend film was picked up with a drawing speed of ~0.2ms^{-1}. The resulting films were about 100nm thick and about 10000 films were stacked on each other, pressed in a hot press at 155°C, above the melting temperature of the PE and below the melting temperature of the iPP, and subsequently quenched to room temperature. Thin ultra microtom cuts of these 1mm thick samples were used for TEM and AFM investigations after chlorsulfone acid preparation described by Kanig (14). TEM samples were stained with uranylacetate for improving the contrast in brightfield mode. Electron microscopy on the multi-layered samples were performed using a Philips CM200 operated at 200kV. A Digital Instruments Inc. Nanoscope III was used for AFM investigations of the morphology of the samples in contact and tapping mode.

Results and Discussion

Figure 1 presents a sketch of the sample morphology and the geometry of the cross-sectional cut as well as the viewing direction of the electron micrographs and the AFM images in Figures 2, 3 and 4.

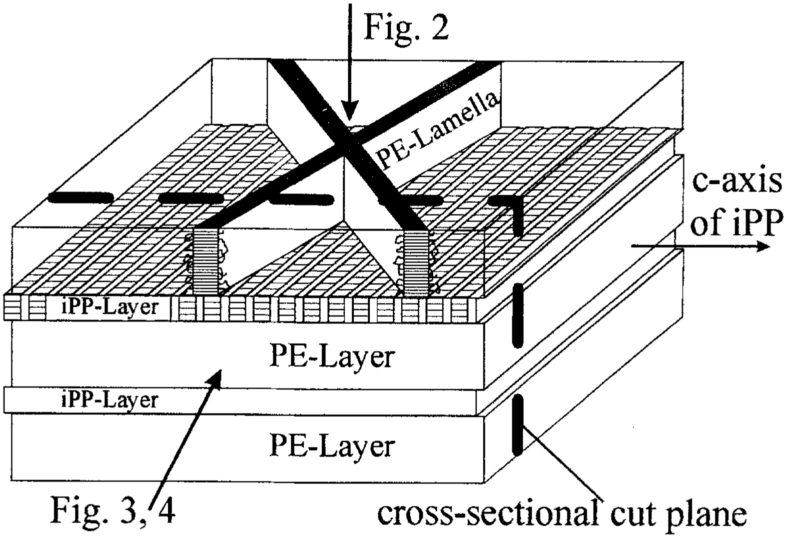

Figure 1. Sketch of the PE-iPP multi layered sample morphology and geometry. The arrows indicate the view directions in Fig. 2, 3 and 4 and the dotted plane the cross-sectional cut.

Figure 2a shows an electron brightfield micrograph with corresponding electron diffraction pattern of a PE-iPP double layer film in the usual viewing direction perpendicular to the film plane (sample preparation described in (7)). Using phase contrast in underfocus conditions, the darker contrast correlates to the higher density or crystalline areas and the brighter contrast to the lower density or amorphous areas. The film consists out of a highly oriented crystalline lamellar morphology of the iPP substrate with the crystallographic c-axis oriented along the drawing direction, indicated by the arrow. All the PE grows epitaxially onto the iPP substrate and forms a cross-hatched structure with

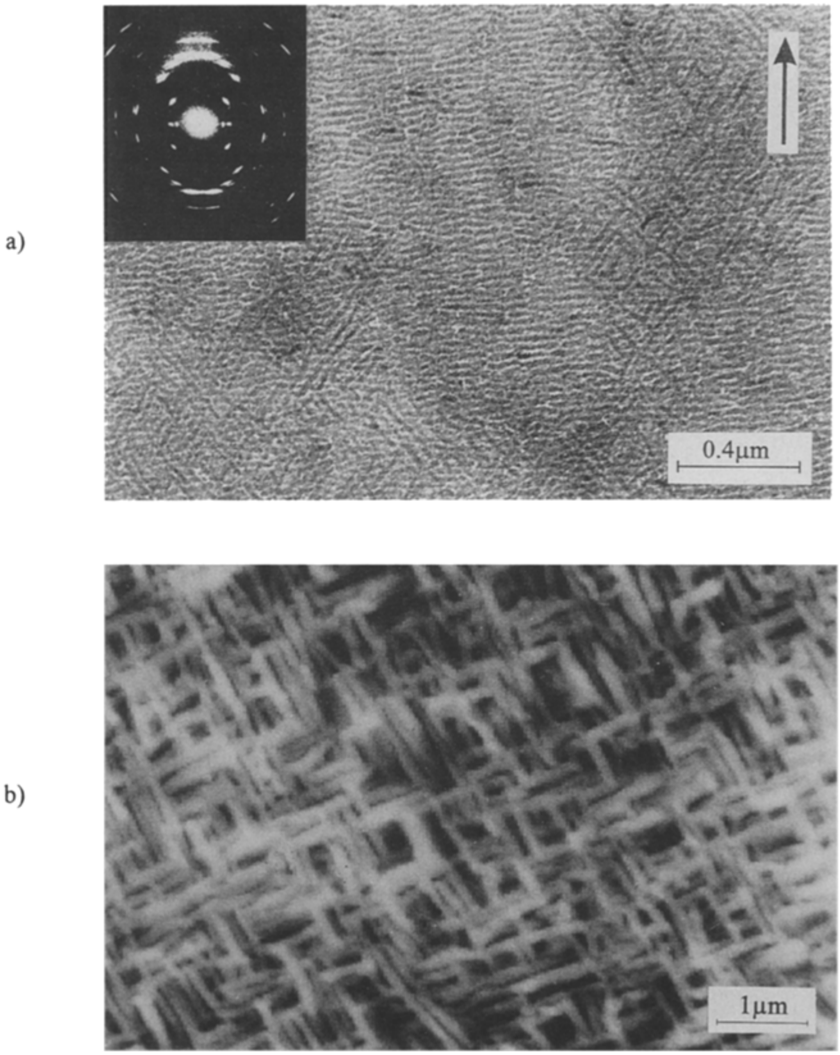

Figure 2. Transmission electron micrograph with corresponding diffraction pattern of layered PE-iPP films (a) and the equivalent AFM image in contact mode with cross-hatched PE lamellae (b). The molecular direction of iPP is indicated by an arrow.

the PE molecules being about ±50° inclined to the molecular direction of iPP. The thickness of the PE lamellae is averaged to about 20nm and the long period to 40nm, respectively. An AFM overview in contact mode of the arrangement of the PE lamellae on top of the iPP substrate film is shown in Figure 2b. Single lamellae are not resolved and the contrast results from domains of equivalently oriented lamellae.

Figure 3a is a transmission electron micrograph of an ultra microtomed PE-iPP multi layer sample prepared by the technique as described above. Using the absorption contrast in the stained samples, the darker contrast correlates to the amorphous phase, destroyed by chlorosulfonic acid and enriched with high density uranium, and the brighter contrast to

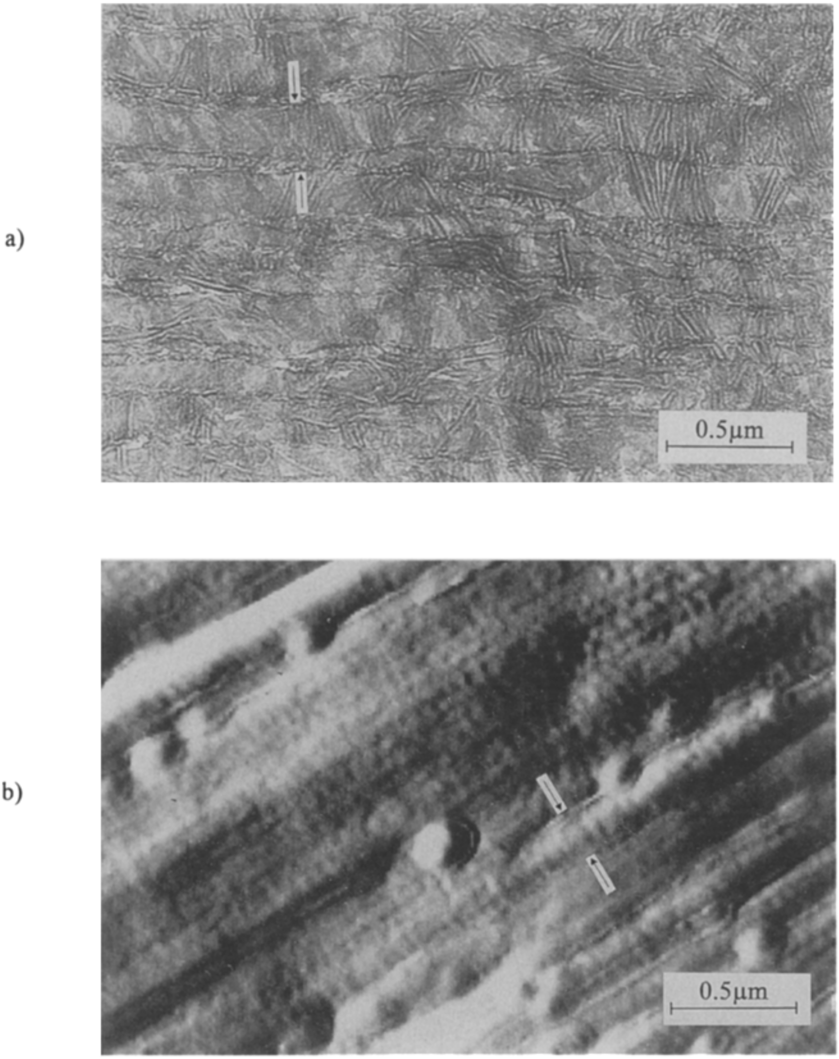

Figure 3. Transmission electron micrograph of a microtomed PE-iPP multi layer sample (a) and the corresponding AFM image in tapping mode (b). The thickness of a single layer is indicated by arrows.

the less enriched crystalline areas of the polymer. During the melt drawing preparation of the single layers, the iPP crystallized faster than the PE and built a continuous film with a thickness depending on its volume fraction, on which subsequently the PE crystallizes. While pressing and annealing the layered film, only the PE is molten and due to the high viscosity of the polymer melt, the not molten iPP layers are a stable arrangement with a repetition width corresponding to the thickness of a single layer. The layered structure of the sample is clearly visible with an averaged thickness of 100nm. The parallel darker contrast areas in Figure 3a are identical to the 30% volume fraction of iPP and the brighter contrast areas to the 70% volume fraction of PE. At this magnification the lamellar sub-structure is not clearly visible. The same result is found in the AFM image

(Fig. 3b). Using tapping mode, lower areas yield to a darker and higher areas to a brighter contrast. The layered structure of the sample is obvious, with the same repetition width of 100nm as in the electron micrograph.

Figure 4a shows a higher magnification electron micrograph and a corresponding AFM image in the tapping mode (Fig. 4b) of the same sample. After melting and recrystallization, high density PE forms highly oriented lamellar crystals with growth direction perpendicular to the iPP substrate (see Fig. 1). With a specimen thickness of about 60nm, the PE cross-hatched morphology visible at usual view direction result in parallel lamellae for cross-sectional investigations. The thickness of the PE crystals grown on the layered iPP substrates is about 20nm with a long period of 40nm corresponding to Figure 2. The dark iPP layers show the usual lamellar morphology of melt drawn iPP.

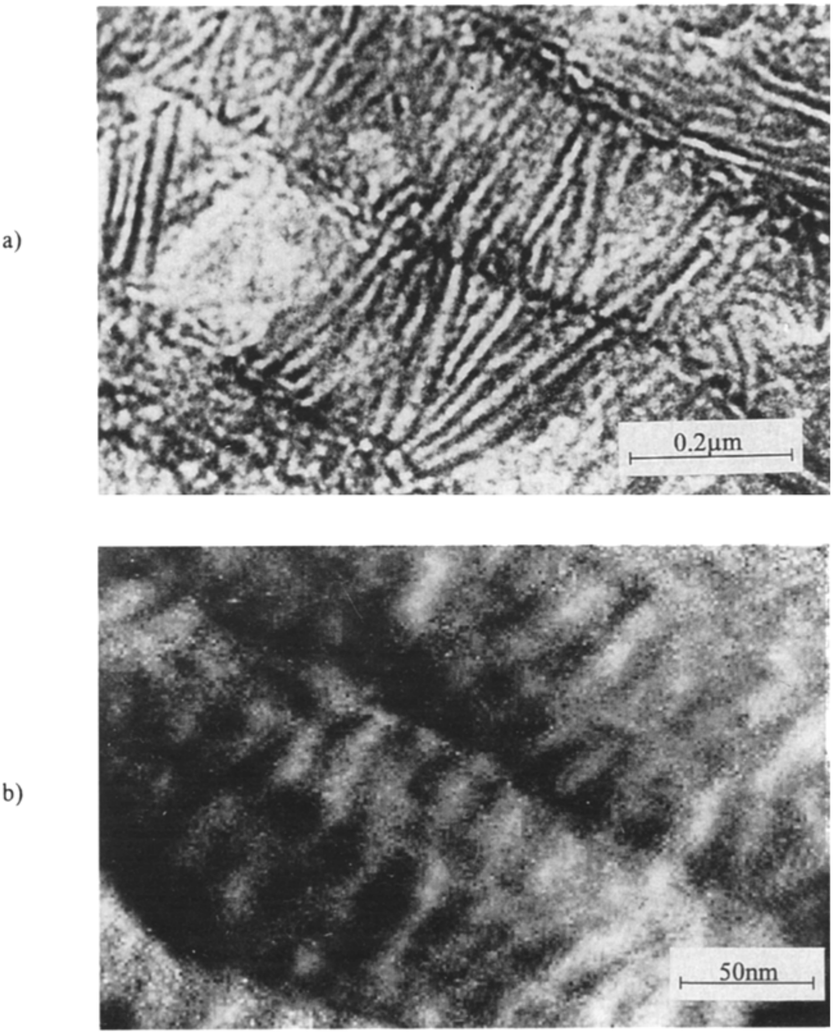

Figure 4. High magnification transmission electron micrograph of the identical sample shown in Fig. 3 (a) and the corresponding AFM image in tapping mode (b).

From Figure 2 it can be visualized, that the epitaxially crystallized PE lamellae are nucleated at the iPP layers and grow with an inclination of 40° to this interface. In the TEM contrast of the cross-sectional cuts, only the projected density variation through the cut film in viewing direction causes the absorption contrast. Due to the ±40° inclination of the PE lamellae and a possible not perfect cut along the molecular direction (see Fig. 1), some areas may appear having the lamellar contrast others not. The AFM picture images only the surface of the sample and all PE lamellae are perpendicular to the iPP layers. While in the "conventional" imaging modes (Fig 2), either the surfaces (AFM) or projected morphologies are seen, the cross-sectional cuts give the possibility to image the interface in high resolution directly. More detailed information about the crystallization at interfaces may be obtained by this method. Further experiments on epitaxial crystallization using cross-sectional cutting are under progress.

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