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Epitaxial crystallization of linear low-density polyethylene on high-density polyethylene

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The oriented crystallization of linear low-density polyethylene (LLDPE) on high-density polyethylene (HDPE) has been investigated by transmission electron microscopy. From morphology and electron diffraction, it is confirmed that epitactic growth of LLDPE lamellae on the HDPE crystals takes place with an adoption of the HDPE crystal thickness at the interface and a continuous thinning of the LLDPE lamellae in the interface.

1. Introduction

The morphology and crystallization of binary blends of high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene have received considerable attention in recent years. Phase separation in the liquid state [1–4] and conditions of co-crystallization or segregation during isothermal crystallization have been studied by a wide range of techniques [5–9], and also the mechanical properties of blends of HDPE and LLDPE have been investigated [10, 11]. Some improvements in mechanical properties can be achieved as an effect of epitaxial interaction in blends of different polymers [12–15]. The epitaxial interface bonded by van der Waals forces results in good adhesion between the components of the polymer blends. The affinity between chemical identical polyethylenes should yield an influenced or especially epitaxial interaction between both components.

The present study involved a transmission electron microscopic investigation of melt-crystallized LLDPE on highly oriented HDPE. Different investigation and preparation techniques are used: electron diffraction and bright-field observation of the morphology of LLDPE/HDPE double-layered films and bright-field investigations of the cross-sectional morphology of multi-layered LLDPE/HDPE samples.

2. Experimental procedure

The HDPE used in the experiment was Lupolene 6021D and the LLDPE was a non-commercial charge, both from BASF Ludwigshafen, Germany. Uniaxially oriented thin films of polyethylene were prepared according to the technique reported by Petermann and Gohil [16]. A small amount of a 0.5 wt % solution of the polymer in xylene was poured and spread on a preheated glass side at a temperature of 130 °C. After evaporating the solvent, the remaining polymer film was picked up with drawing speed of $\sim 20\,\mathrm{cm\,s^{-1}}$. The resulting polyethylene films were 50–100 nm thick.

Non-oriented thin films of LLDPE were solution-cast from a 0.1 wt % solution in xylene on the surface of glycerine at a temperature of $\sim 120\,^{\circ}\mathrm{C}$ and layered on to the oriented HDPE films. Heat treatment of these double-layered films were carried out at temperature above the melting temperature of LLDPE (126 °C) and below the melting temperature of HDPE (136 °C). Afterwards the samples were directly used for TEM investigations.

To confirm the epitaxial crystallization behaviour of LLDPE on HDPE, multilayered samples were prepared. LLDPE layers with a thickness of several micrometres were alternately stacked with co-oriented thin HDPE films, pressed in a hot press at a temperature above the melting temperature of LLDPE and below the melting temperature of HDPE, and subsequently quenched to room temperature. Thin cross-sectional ultra-microtome cuts of these 1 mm thick samples were used for TEM investigations after the staining preparation described by Kanig [17].

TEM on single-, double- and multi-layered samples were performed using a Philips CM200 operated at 200 kV.

3. Results and discussion

Fig. 1 shows TEM bright-field micrographs of HDPE and LLDPE with corresponding diffraction patterns prepared as a uniaxially oriented film. 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 crystallographic *c*-axes are oriented along the drawing direction, indicated by the arrow. Compared to HDPE, the higher content of branching hinders the crystallization of LLDPE and

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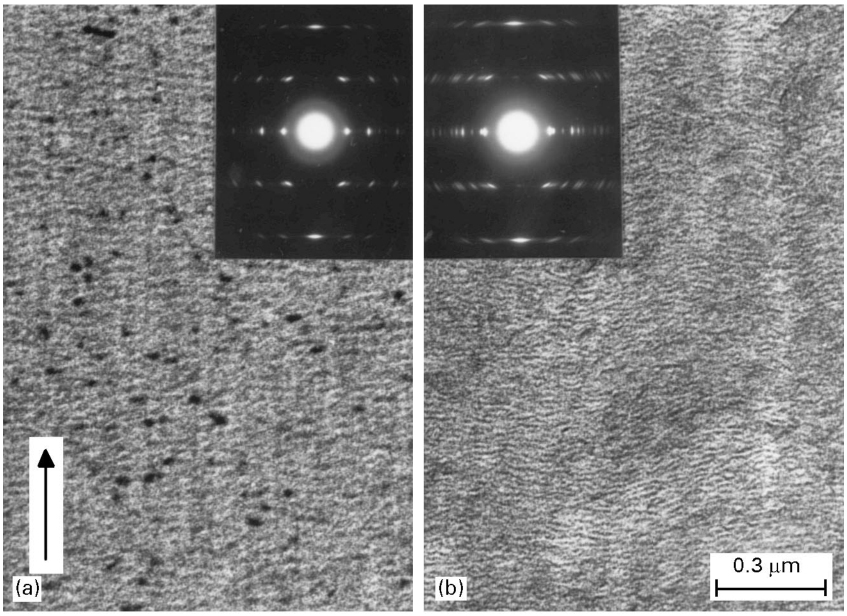

Figure 1 Transmission electron micrographs of (a) uniaxially oriented HDPE and (b) LLDPE for the comparison of their lamellar crystal thicknesses and orientation.

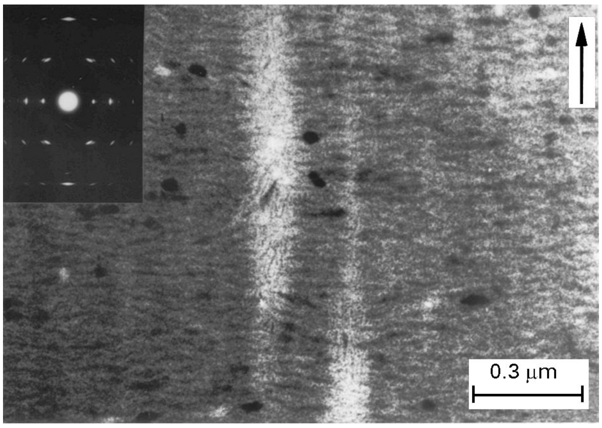

Figure 2 Transmission electron micrograph of a double-layered LLDPE/HDPE sample after heat treatment. In the middle of the micrograph, a hole in the HDPE film is visible, on to which the non-oriented LLDPE crystallizes.

results in lower density or crystallinity and a smaller crystal thickness.

Fig. 2 shows a bright-field electron micrograph of a LLDPE/HDPE double-layered sample annealed at 130 °C for 10 min and subsequently cooled to room temperature. After the heat treatment, only thick lamellae are visible, assigned to the HDPE. The configurational similarity of HDPE and LLDPE results in the oriented crystallization of the LLDPE crystals parallel to the HDPE lamellae. The TEM bright-field principle causes a two-dimensional imaging of the three-dimensional investigated sample so that, with the viewing direction perpendicular to the film plane of the sample, only large structures like the thick HDPE lamellae dominate the image, without consideration of the thin LLDPE crystals. However, presence of the LLDPE is recognizable at an HDPE substrate hole in the centre of the picture. Without the influence of the HDPE, unoriented growth of LLDPE lamellae with a similar crystal thickness as shown in Fig. 1, can be seen.

More evidence for oriented crystallization of LLDPE on HDPE results from electron diffraction investigations. Fig. 3 shows an electron diffraction pattern of an annealed LLDPE/HDPE double-layered sample with a corresponding sketch. The HDPE oriented film was prepared having a double texture with the crystallographic *b*-axis being preferentially in the plane of the film (Fig. 1), almost resulting in the absence of the (2 0 0) reflection in the diffraction patterns [18]. The LLDPE was a non-oriented film. After heat treatment (10 min at 130 °C), the LLDPE adopted not only the *c*-axis orientation of the HDPE film, but also the double texture. From this observation it can be concluded that the LLDPE not only exhibits oriented crystallization (*c*-axis orientation), but also adopts the complete crystallographic information from the substrate (epitaxial crystallization). More information about the crystallization behaviour of the LLDPE on HDPE can be obtained from the cross-sectional preparation technique [19–21].

Fig. 4 presents a sketch of the sample morphology prepared by the technique described above and the geometry of the cross-sectional cut as well as the cross-sectional viewing direction. Fig. 5 shows an electron micrograph of the LLDPE/HDPE interface. Using absorption contrast in a stained sample, the darker contrast correlates to the amorphous phase destroyed by chlorosulphonic acid and enriched with uranium, and the brighter contrast correlates to the less-enriched crystalline areas of the polymers. After the heat treatment, the thin HDPE film remains oriented, an oriented transcrystalline layer of the LLDPE forms at the interface, and finally, non-oriented LLDPE lamellae connect to the transcrystalline layer.

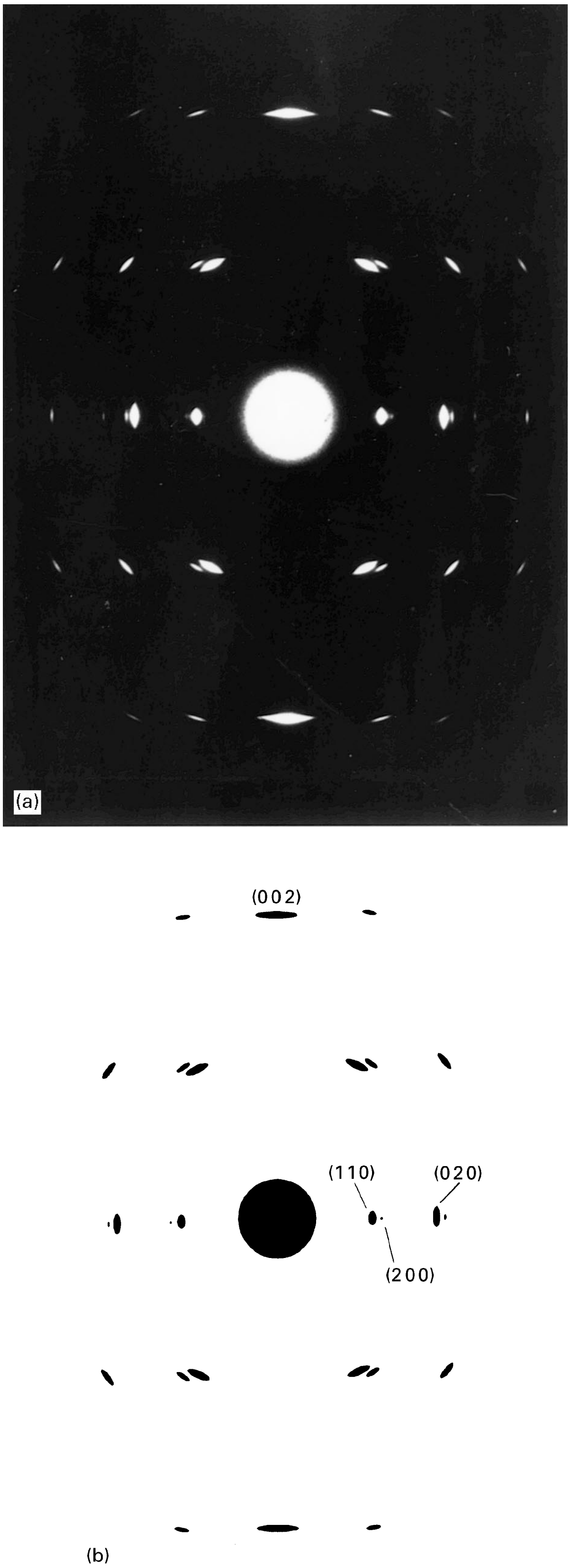

Figure 3 (a) Electron diffraction pattern of a double-layered LLDPE/HDPE sample after heat treatment; (b) the corresponding sketch.

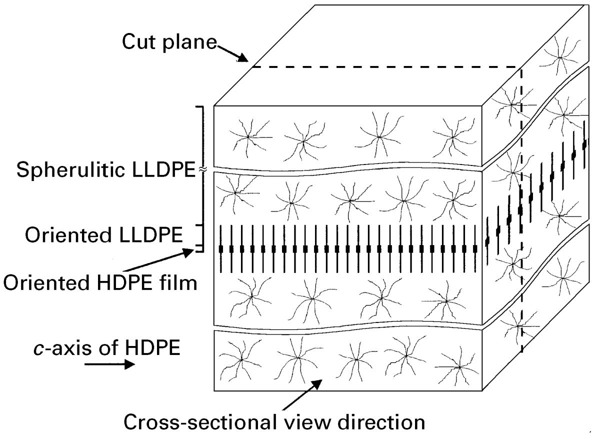

Figure 4 Sketch of the LLDPE/HDPE multi-layered sample morphology and geometry.

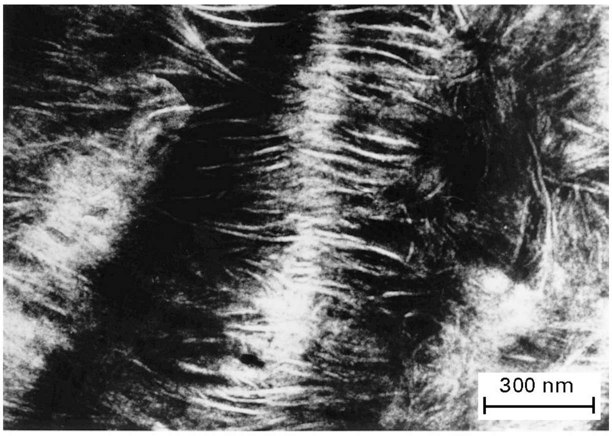

Figure 5 Transmission electron micrograph of the epitactic LLDPE/HDPE interface.

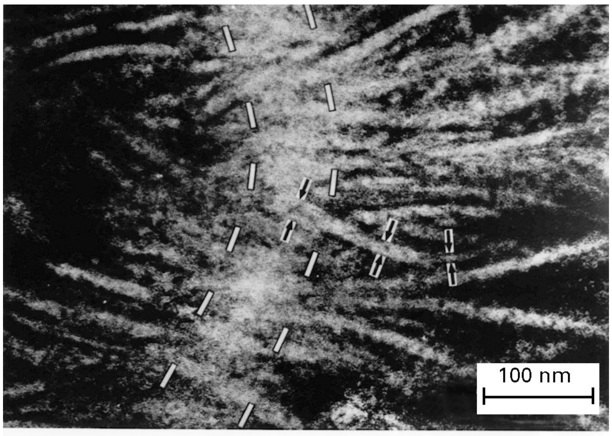

Figure 6 High-magnification transmission electronmicrograph of the epitactic LLDPE/HDPE interface. The decrease in the thickness of a LLDPE lamella is indicated by arrows and the assumed thickness of the HDPE film is marked.

A higher magnified electron micrograph of the interface is shown in Fig. 6. Vertically centred in the image, the oriented HDPE film is visible, with a crystal thickness of about 17 nm. The cross-sectional preparation of the sample results in an HDPE lamellar length corresponding to the film thickness (50–100 nm), and the lamellar crystals with length more than 100–300 nm shown in Fig. 6 are oriented LLDPE crystals, epitaxially grown on the HDPE crystals without any distinct transition. The thickness of these crystals decreases with increasing distance from the HDPE film from the original HDPE lamellar thickness (17 nm) to the lamellar thickness of pure and uninfluenced bulk LLDPE (10 nm, see Fig. 5).

The configurational similarity of HDPE and LLDPE results in the epitaxial crystallization of LLDPE on the HDPE substrate. During crystallization, the LLDPE adopts the crystal structure and the orientation of the HDPE and it adopts additionally the crystal thickness of the HDPE lamellae at the interface. A gradual decrease of the crystal thickness within a transitional zone was also observed in the interfaces of shish–kebab crystals in ultra-high molecular weight polyethylene [22], but may result for different reasons. While in the transitional zone of shish–kebab crystals, the number of strained tie molecules was responsible for the gradual decrease of crystal thickness, in the epitaxial layered zone between HDPE and LLDPE, the critical nucleus size of the LLDPE may cause the decrease in crystal thickness. Epitaxial crystallization enhances the nucleation and consequently, crystallization can occur at higher temperature with larger crystal sizes.

4. Conclusion

The crystallization of LLDPE on uniaxially oriented HDPE was studied by TEM and electron diffraction experiments. From the electron diffraction experiments of the crystallization of LLDPE on to a double-texture oriented HDPE film it was concluded that epitaxy (and not only oriented crystallization) occurs. TEM investigations on cross-sectionally prepared samples showed that the crystallite thickness of the LLDPE lamellae adopts the thickness of the HDPE crystals at the interface, even under different crystallization conditions.

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