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Epitaxial interfaces in semi-crystalline polymers and their applications

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The epitaxial crystallization of polyethylene (PE) on uniaxially oriented polypropylene is investigated. Mechanical tests indicate that the epitaxial interfaces have strong adherence.

1. Introduction

Recently, it was reported that a number of polymers crystallize epitaxially on to polymeric substrates [1–6]. The work of Lotz and Wittmann [4], in particular, demonstrated that the side groups of helical polyolefins (polypropylene, polybutene-1) possess crystallographic interfaces in which the side groups form straight rows along which linear zig-zag chains can well align, and leading to distinct orientation relationships between the lattices of the helical and zig-zag molecules.

In the present work further detailed experiments on the epitaxial crystallization of polyethylene (PE) on to uniaxially oriented polypropylene (PP) were carried out. The influence of epitaxial interfaces on the adhesion of polymer laminates and the mechanical properties of sandwiched layers containing epitaxial interfaces are also reported.

2. Experimental procedure

The materials used for the experiments were polypropylene, type PPN from Höchst AG, polyethylene, type Lupolen 6021 DX (HDPE) and 1810 D (LDPE) from BASF AG and paraffin (n-$C_{28}H_{58}$) from Merck. Thin oriented substrate films were prepared according to the method of Petermann and Gohil [7]: a small amount of a 0.5% solution of the polymer (PP or PE) in xylene was poured on a hot glass slide where the solvent was allowed to evaporate. The remaining thin polymer film was then picked up on a motor driven cylinder, at a wind-up speed of $20\,\mathrm{cm\,sec^{-1}}$. The resulting thin polymer films were about 50 nm thick and highly oriented in the drawing direction. Oriented PP films containing the β-modification where crystallized in a strong temperature gradient ($200^\circ\,\mathrm{C\,mm^{-1}}$) by zone solidification with a solidification rate of $5\,\mu\mathrm{m\,min^{-1}}$ [8, 9]. The films were cut into $3 \times 3\,\mathrm{mm^2}$ pieces, floated on to distilled water and mounted on TEM grids. The materials were investigated using a Philips EM-400 T electron microscope operated at 100 kV.

Fig. 1 shows a transmission electron micrograph of a PP-substrate film prepared as described above. The films had a lamellar morphology and a high crystalline fibre texture, as can be estimated from the electron diffraction patterns, inserted into the micrograph. The polymer films used for the layers were solution cast on to hot orthophosphoric acid [10]. In Fig. 2 a layer-film from HDPE is shown. Again, the films were cut into pieces and put on top of the substrate films. Substrate and layers were heated subsequently to 155° C (above T_m of PE but below T_m of PP) and cooled at varying rates to room temperature. The films containing paraffin as the layers were heated to 80° C and subsequently cooled.

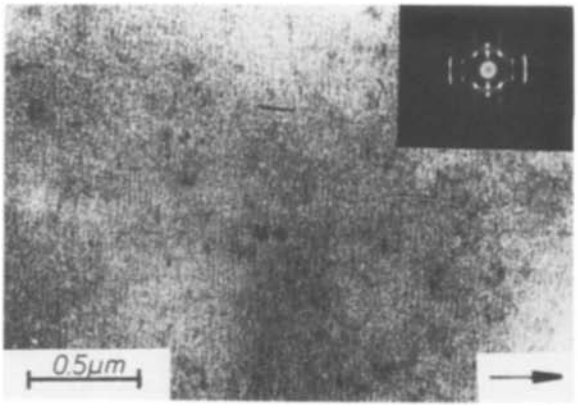

Figure 1 Transmission electron micrograph of a lamellar PP substrate film. The molecular direction is indicated by an arrow and the electron diffraction pattern is inserted.

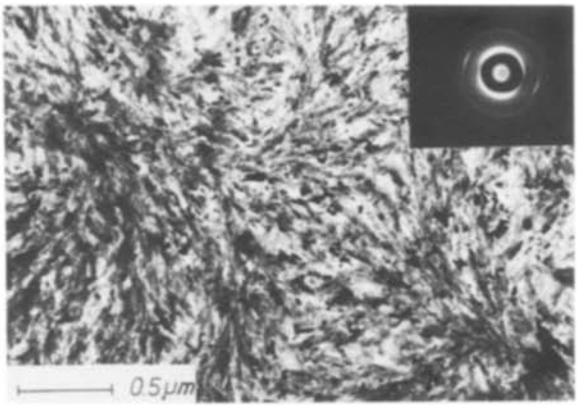

Figure 2 Transmission electron micrograph of a spherulitic PE film, as used for the layered film. Inserted is the electron diffraction pattern.

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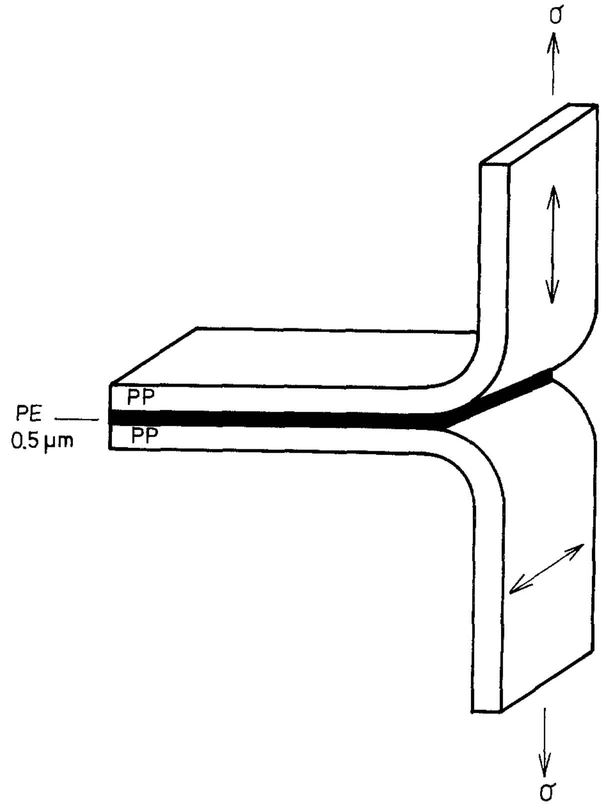

Figure 3 Schematic sketch of the peeling experiment. The arrows within the PP films denote the molecular directions.

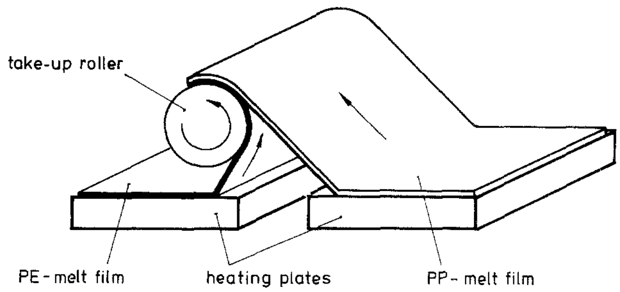

Figure 4 Schematic sketch for the preparation of the layered films.

The samples for the mechanical tests were prepared as follows: uniaxially oriented films of hot-drawn PP were cross-piled with a 200 nm thin PE film in between, heated in a hot press for 5 min at 155° C and cooled to room temperature. The adherence of the cross-piled films was tested in a 180° peel-test using a Zwick 1445 tensile testing machine. Fig. 3 shows the experimental arrangement for the test.

The sandwiched layered structures were produced as indicated in Fig. 4. The solutions of 0.5% PP and PE in xylene were poured on to two separately heated glass slides. After evaporation of the solvent, a motor driven cylinder was touched on to both glass slides, lifted up and was able to wind up very thin PP and PE-films simultaneously. Again, the films were 50 nm thick and highly oriented. After about 1000 turns of

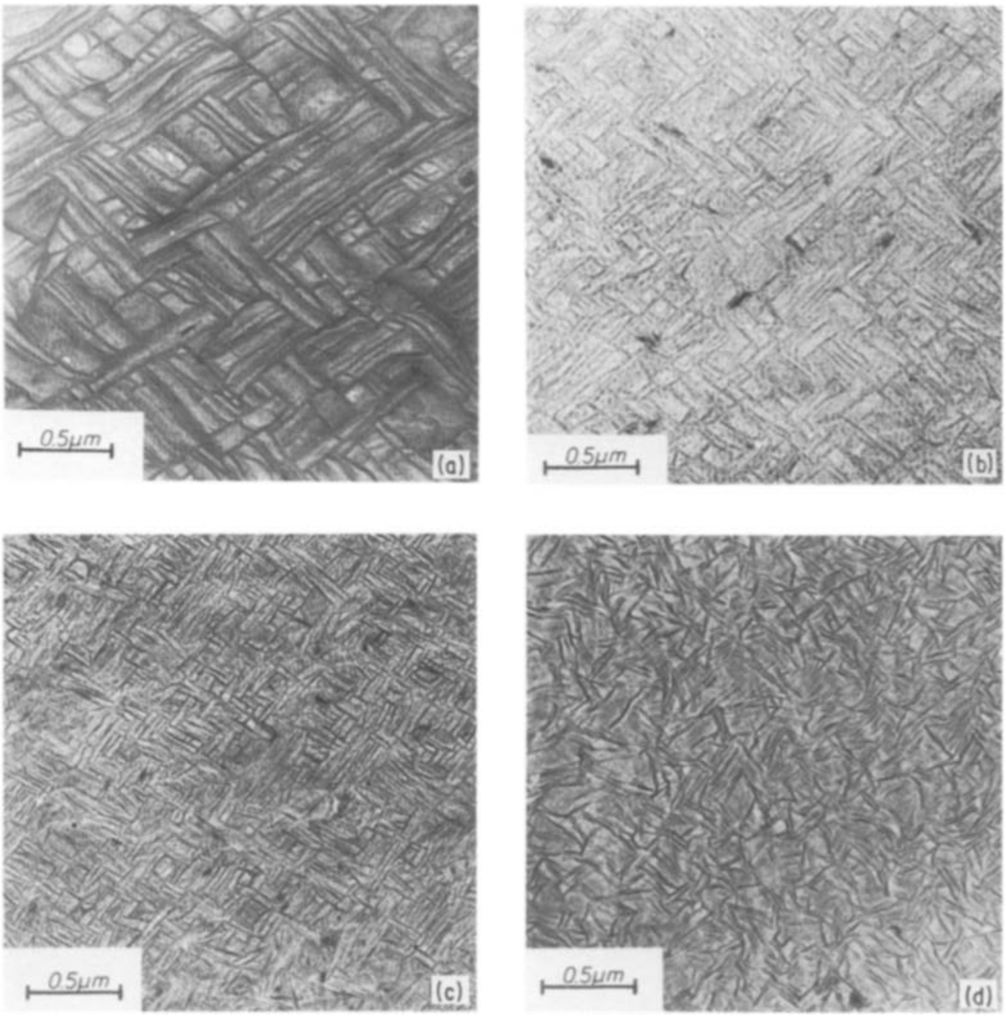

Figure 5 Transmission electron micrographs of epitaxially crystallized HDPE. The molecular directions of the PP-substrates are horizontal. (a) Cooling rate 1° C $\min^{-1}$, (b) cooling rate 10° C $\min^{-1}$, (c) cooling rate 100° C $\min^{-1}$, (d) rapid quenching into ice–water.

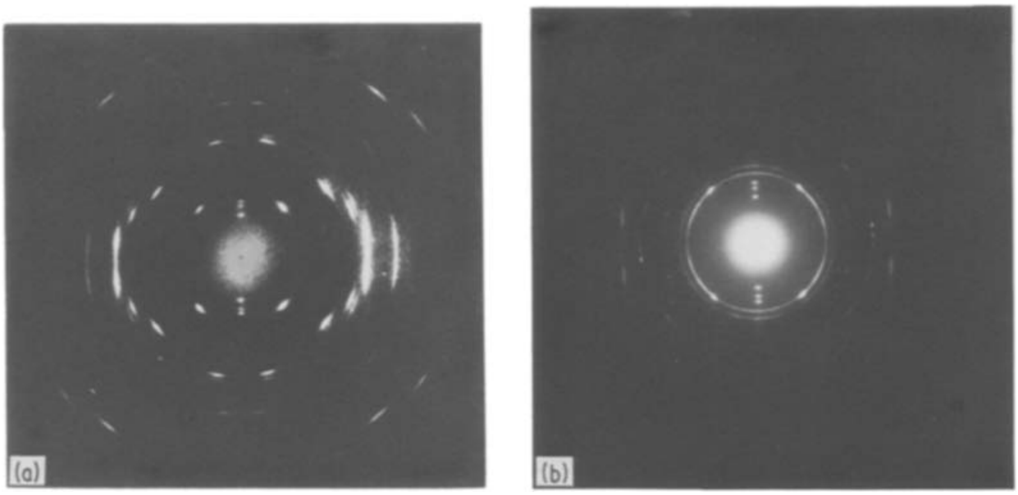

Figure 6 Electron diffraction patterns from (a) the epitaxial morphologies, and (b) the rapidly quenched samples.

the cylinder, the procedure was stopped and the material was taken off the cylinder. Samples for tensile testing were 50 mm long, and 7 mm wide. They were heated to 155° C and subsequently cooled to room temperature. The tensile tests were performed in a Zwick 1445, deformation velocity 5 mm min^{-1} and gauge length 35 mm.

3. Results and discussion

3.1. Microscopic investigations

Figs. 5a to d show transmission electron micrographs of epitaxially crystallized HDPE on PP-substrates. The cooling rates were 1, 10 and 100° C min^{-1} and rapid quenching into ice–water, respectively. The corresponding electron diffraction patterns are seen in Figs 6a and b. The same morphologies were observed in the layered structures for each layer as well as in the cross-piled arrangement of the PP/PE/PP. On the electron micrographs, the PE lamellae are inclined $\pm 40°$ to the horizontal direction which is also the molecular direction in the PP films. The vertical fine striations represent the lamellar structure of the PP films. Comparing slow and high cooling rates (Figs 5a to c), a decrease in the thickness and length of the PE lamellae can be recognized, but only splat cooling suppresses the epitaxy (Figs 5d and 6b). The peculiar arrangement of the PE lamellae was explained by Wittmann and Lotz with an epitaxy of (1 0 0) PE lattice planes parallel to the (0 1 0) lattice plane of the PP [4].

In Fig. 7, a sketch of the (0 1 0) lattice planes in the monoclinic PP crystals is presented. The methyl side groups of the PP chains, which stick out of the plane are shaded. In those planes, inclined 50° to the PP chain direction, rows of the methyl groups can be seen. The inter-row distance is 0.505 nm. The orientation of the PE chains is along the rows, and in the (1 0 0) plane of the PE, the chains are 0.495 nm apart. The lattice orientation relationship fits the observed diffraction patterns (Fig. 6a) [4]. Only a few crystallites of the lamellar packing in the PP substrate have the required (0 1 0) surface (each ($h\,k\,0$) plane can be a surface plane as revealed from the fibre texture, insert in Fig. 1) and if these planes act as the nucleation sides for the PE lamellae the numbers of lamellae per unit area should be constant. As seen from Figs 5a to c, this is not the case. Furthermore, supposing the packing arguments from Fig. 7 are right, a similar texture of the PE on the hexagonal PP would be expected (Fig. 8). A structural analysis predicts the PE chains inclined $\pm 45°$ on the ($1\,0\,\bar{1}\,0$) planes of the PP parallel to the (1 1 0) planes of the PE. As seen from Fig. 9, a random orientation of the PE is obtained when cooling it on a substrate of uniaxially oriented β-PP. Finally, if atomic or

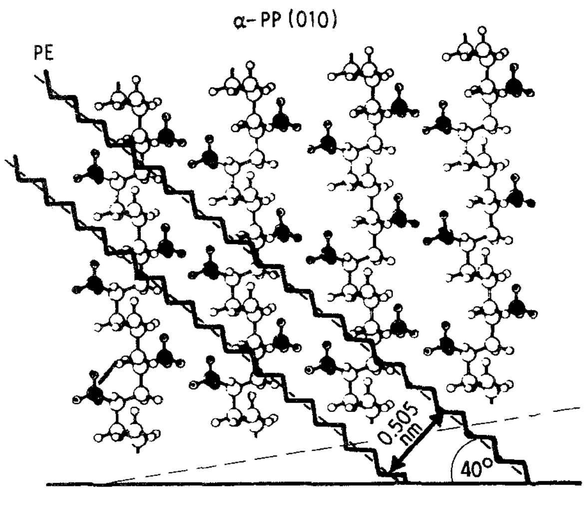

Figure 7 Sketch of the (0 1 0) plane of the α-PP. The dark methyl groups are sticking out of the plane.

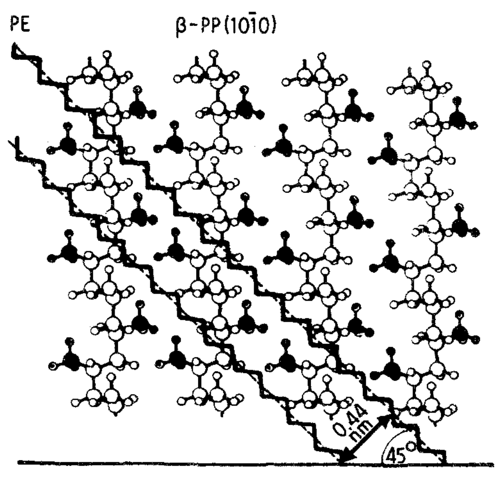

Figure 8 Sketch of the ($1\,0\,\bar{1}\,0$) plane of the β-PP. The dark methyl groups are sticking out of the plane.

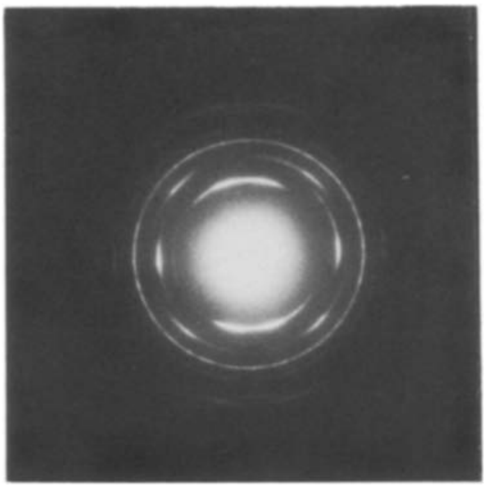

Figure 9 Electron diffraction patterns of PE, crystallized on to β-PP.

molecular matching in the interface is the main reason for the epitaxial behaviour, the deposition of linear paraffin on to a uniaxially oriented PE substrate should result in parallel interfaces of the equivalent lattice planes, as the crystal lattice and the chain configurations of paraffin and PE are nearly identical. Fig. 10 shows the electron diffraction pattern of the uniaxially oriented PE substrate, on which a thin film of paraffin was crystallized. The paraffin molecules are perpendicular to the PE molecules. A molecular matching exists with $[1\,1\,0]_{\mathrm{PE}} \parallel [1\,1\,0]_{\mathrm{paraffin}}$ or $[2\,0\,0]_{\mathrm{PE}} \parallel [2\,0\,0]_{\mathrm{paraffin}}$ and $(h\,k\,0)_{\mathrm{PE}} \parallel (0\,0\,1)_{\mathrm{paraffin}}$, but a perfect matching of identical planes and directions is not observed. Chain configurations and lattice geometry may, however, play a major role in the epitaxial behaviour but the atomic nature of the interaction must be explored further.

LDPE was also used as the layered material, instead of HDPE. No specific orientation relationship between the PP substrate and the LDPE has been detected. This is an indication that even small irregularities in the chain conformation disturbs the interaction between the chemically different molecules. Crosslinking the substrate also suppresses the epitaxy [6]. A qualitative measure of the strength of the interaction of the molecules in the interface can be obtained from mechanical tests.

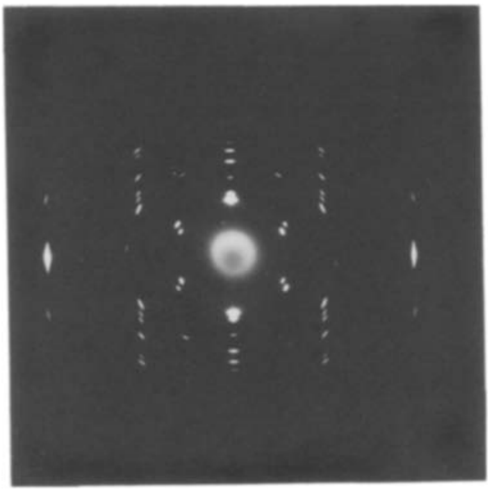

Figure 10 Electron diffraction patterns of paraffin crystallized on oriented HDPE.

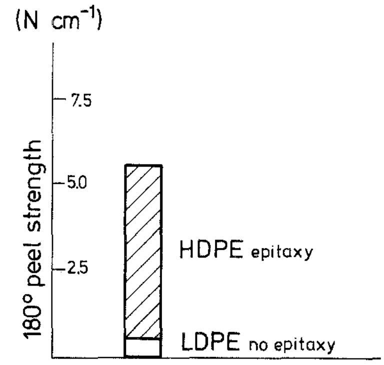

Figure 11 180° C peel strength of cross-piled highly oriented PP-films, having a very thin PE-layer ($\approx 0.5\,\mu$m) as an adhesive.

3.2. Mechanical investigations

The bonding of the epitaxial interface can be tested by using PE as an adhesive to cross-piled uniaxial-oriented PP films. Non-epitaxial interfaces were obtained with LDPE, but epitaxial interfaces with HDPE. In Fig. 11 the 180° peel strength of those films is shown. Using LDPE (no epitaxial interface) the peel strength is $0.4\,\mathrm{N\,cm^{-1}}$ and with HDPE as the contact layer the peel strength reaches $5.5\,\mathrm{N\,cm^{-1}}$. Whether the rupture occurred directly at the interface or within the contact layer was not investigated, thus the bonding of epitaxial interfaces could be more than ten times higher compared to nonepitaxial interfaces.

The Young's moduli of the layered structures are another indirect measure of the interfacial bonding. The material tested contained about $700\,\mathrm{cm^2}$ interfaces per sample, or $2 \times 10^4\,\mathrm{cm^2/cm^3}$. The high specific interfacial area is expected to influence the mechanical properties. Fig. 12 shows the Young's moduli of the material. The as-prepared material has a high molecular orientation of both PP and PE, parallel to the straining direction in the tensile test experiment but no epitactic interface contact between the layers. Generating epitactic interfaces by melting and cooling the PE layers increases the Young's modulus by a factor of three, whereas no change is observed when using LDPE layers, which do not form epitactic interfaces. The reason for the increase in the Young's modulus has already been proposed elsewhere [11]. The inclined PE lamellae bridge the amorphous intercrystalline regions in the stacked lamellar morphology

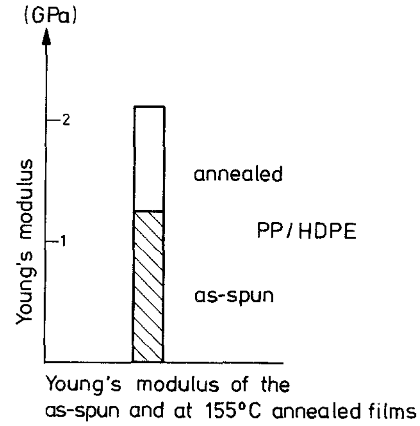

Figure 12 Young's moduli of layered structures, having non-epitaxial (as-spun) and epitaxial (annealed) interfaces.

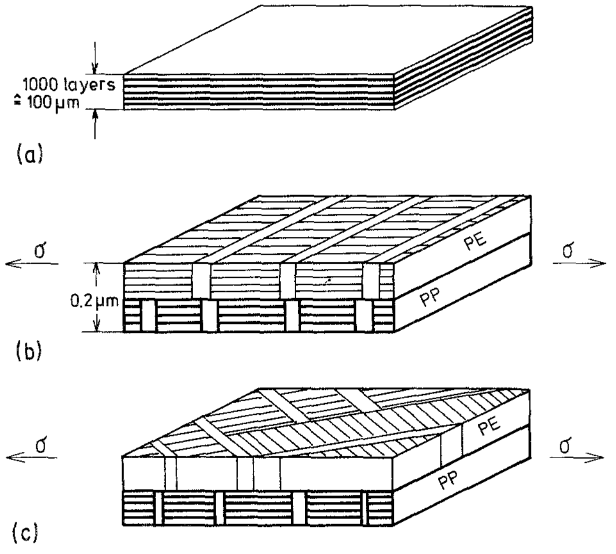

Figure 13 Schematic sketches of a layered structured sample (a), its morphology after preparation (b), and after annealing (c). The arrow denotes the deformation direction in the tensile test experiments.

of the PP layers (Fig. 13). This leads, when there is strong bonding between the PP and PE lamellae and sufficiently thin PE layers, to a reinforcement of the mechanically soft amorphous parts of the stacked lamellar arrangement of the PP.

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