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Properties of layered structured PE/PP and PB-1/PP films having ultra-thin layers

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Highly oriented polymer films containing ultra-thin layers of polyethylene/polypropylene (PE/PP) or polybutene-1/polypropylene (PB-1/PP) were investigated with transmission electron microscopy, differential scanning calorimetry, optical birefringence methods and mechanical testing. The determination of the microstructures of the above systems before and after melting and recrystallization of the low-melting component revealed the existence of epitaxially crystallized PE lamellae in the PE/PP system, whereas no epitaxy was observed in the PB-1/PP system. However, if PB-1 was sandwiched between two layers of the polypropylene, a non-isotropic arrangement of the recrystallized PB-1 crystals was detected. The mechanical properties, as well as thermal behaviour and optical birefringence of these systems, were determined and the results were related to the specific morphologies present in the different samples. Reinforcement mechanisms resulting from epitaxially crystallized PE lamellae are discussed.

1. Introduction

Thin layered films have been widely investigated in the past decades and knowledge of their specific properties has made them very useful in a broad field of technical applications. Depending on the preparation method, such as solution casting or sublimation in a high vacuum [1, 2] the resulting morphologies are quite different and range from amorphous or polycrystalline to the precipitation of single crystals.

In some cases and under certain conditions epitaxial crystallization of a layer on top of a crystalline substrate occurs [3, 4] and this fact is widely very useful for applications in semiconductor technology where these epitaxial layers reveal well-defined electrical properties [5]. Epitaxial crystallization in thin layers of polymeric materials is also well known and numerous publications in the past few years revealed some interesting orientation relationships between the substrate and the recrystallizing layers [6–9]. Additionally, due to the specific arrangement of crystallites after epitaxial crystallization, improvements in mechanical as well as thermal properties can be achieved [10].

It is the aim of this study to present some results regarding the morphologies and physical properties of films, consisting of ultra-thin layers of two different polymers. The influence of epitaxial crystallization of one of the components on the mechanical behaviour of the composite is discussed.

2. Experimental details

2.1. Sample preparation

Polymers used in the present work were polyethylene, type Lupolen 6021 DX (HDPE) from BASF AG, polypropylene, type PPN from Hoechst AG and polybutene-1, type Vestolen BT from Chemische Werke Hüls.

Thin highly oriented films consisting of alternating layers of two different polymers were prepared by the following method [11]. Small amounts of two different 0.4% solutions of polymer in xylene were poured on

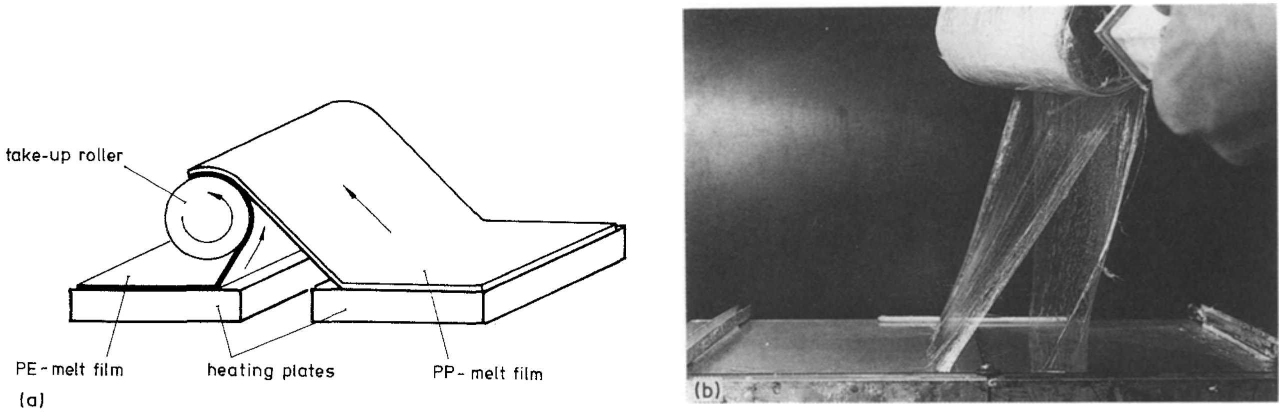

Figure 1 Representation of layered structured film formation: (a) schematical drawing; (b) photograph of the actual process.

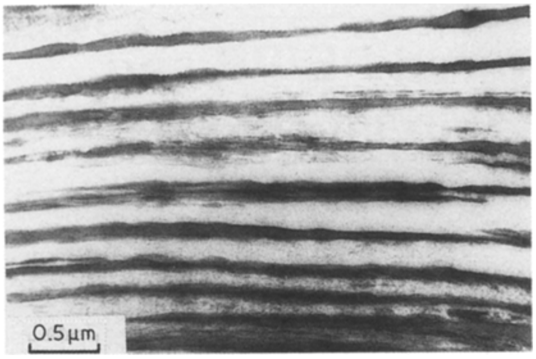

Figure 2 Transmission electron micrograph of a cross-sectional cut of a polybutadiene/polybutene-1 film, showing alternating layers.

two separately heated glass plates ($T = 140°$ C) where the solvent evaporated within seconds. The remaining films of different polymers on each of the glass plates were picked up simultaneously with a motor-driven take-up roll, see Figs 1a and b. In this manner films were obtained which exhibit a layer structure, one single layer having a thickness of about 50 nm. Two or even three layers could be used directly for TEM investigations while 1000 or more layers resulted in samples thick enough for macroscopical testing. The layer structure of a thick sample cut with an ultramicrotome is visible in the transmission electron micrograph in Fig. 2. In order to achieve a strong contrast between the layers, polybutadiene and polybutene-1, were used as alternating layers. The polybutadien layers were stained with OsO_4.

2.2. Characterization technique

Transmission electron microscopy was carried out with a Philips EM 400 T, operated at 100 kV using bright-field and diffraction techniques.

X-ray diffraction of thick samples was performed with a Philips PW1720 flatcamera (camera length = 35 mm) operated at 40 mA and 25 kV, using Cu$K\alpha$ radiation. The optical birefringence as a function of sample temperature was determined in an *in situ* experiment always from the same position of the sample. A Polyvar (Reichert-Jung) polarizing microscope with a compensator combined with a Kofler hot stage was used for this experiment. The thermal behaviour was recorded using a Heraeus DTA 500S DSC, sample weight about 6 mg and a heating rate of $10° \mathrm{C\,min^{-1}}$. Mechanical testing was carried out with a Zwick 1445 tensile testing machine, the deformation velocity being $5\,\mathrm{mm\,min^{-1}}$, gauge length 35 mm. Heat treatments of the samples took place in a thermostatically controlled oven for an annealing time of 10 min.

3. Results and discussion

3.2. Microstructural characterization

The morphologies of a sample consisting of a PP substrate and a PE layer on top before and after annealing are shown in the transmission electron micrographs of Figs 3a and b, respectively. In the as-drawn state, Fig. 3a, both materials exhibit a lamellar morphology with a highly crystalline fibre texture, both *c*-axes being parallel to each other. After annealing at 155° C (above T_m^{PE} but below T_m^{PP}) polyethylene recrystallizes epitaxially [6] with the PE lamellae now being inclined ± 40° with respect to the PP chain direction, see Fig. 3b. This particular morphology is maintained only if the single layer thickness is below 100 nm. In thicker layers the orientation changes as the lamellae begin to twist around their b-axis as they grow perpendicular to the substrate, indicating the importance of the structure transfer from the interface to the entire layer [12]. X-ray investigations performed on multi-layer samples showed the same results.

No epitaxial crystallization took place whenever PB-1 was melted at 155° C and recrystallized on a PP substrate [6], see Fig. 4b. The initially needle crystalline morphology of highly oriented PB-1 (Fig. 4a) changed to spherulitic after annealing and recrystallization. However, a difference in morphology was observed when a PB-1 layer was sandwiched between two PP layers, as shown in Fig. 4c. From the inserted diffraction pattern, a certain degree of preferred orientation of the PB-1 after recrystallization can be deduced. This fact is caused by the recrystallization in the tetragonal phase of the PB-1, with the lamellae-forming molecules being aligned in the orientation direction [13].

3.2. Optical birefringence

As mentioned in Section 2.2, the optical birefringence was measured *in situ* as a function of temperature, using one fixed sample location. The data obtained were normalized to the initial value obtained at room temperature and plots of this relative birefringence

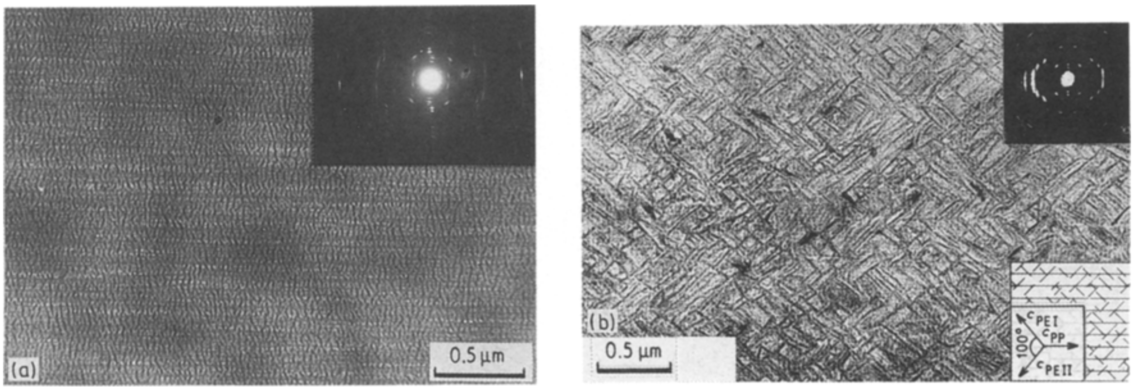

Figure 3 TEM bright-field micrographs of PE/PP double-layer films: (a) as-spun; (b) after annealing at 155° C and recrystallization.

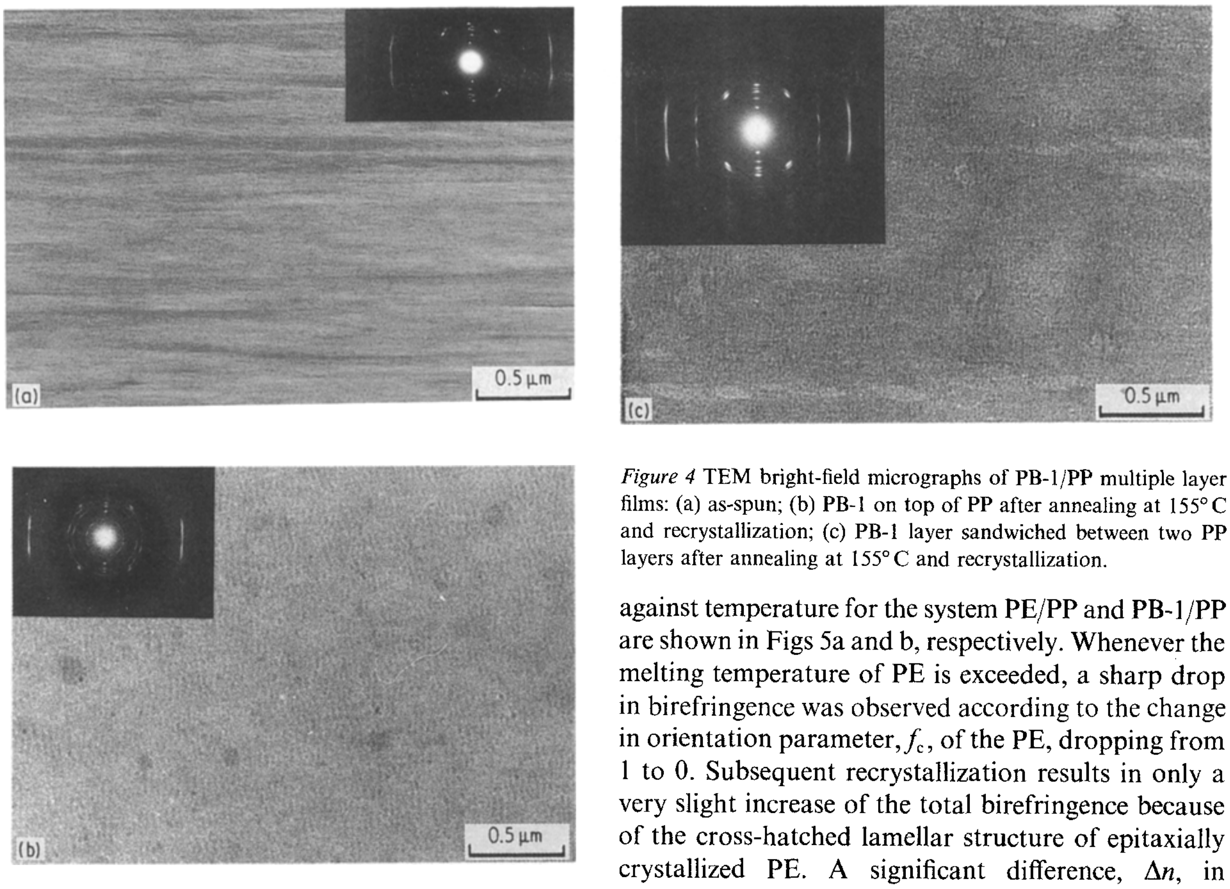

Figure 4 TEM bright-field micrographs of PB-1/PP multiple layer films: (a) as-spun; (b) PB-1 on top of PP after annealing at 155° C and recrystallization; (c) PB-1 layer sandwiched between two PP layers after annealing at 155° C and recrystallization.

against temperature for the system PE/PP and PB-1/PP are shown in Figs 5a and b, respectively. Whenever the melting temperature of PE is exceeded, a sharp drop in birefringence was observed according to the change in orientation parameter, f_c, of the PE, dropping from 1 to 0. Subsequent recrystallization results in only a very slight increase of the total birefringence because of the cross-hatched lamellar structure of epitaxially crystallized PE. A significant difference, Δn, in

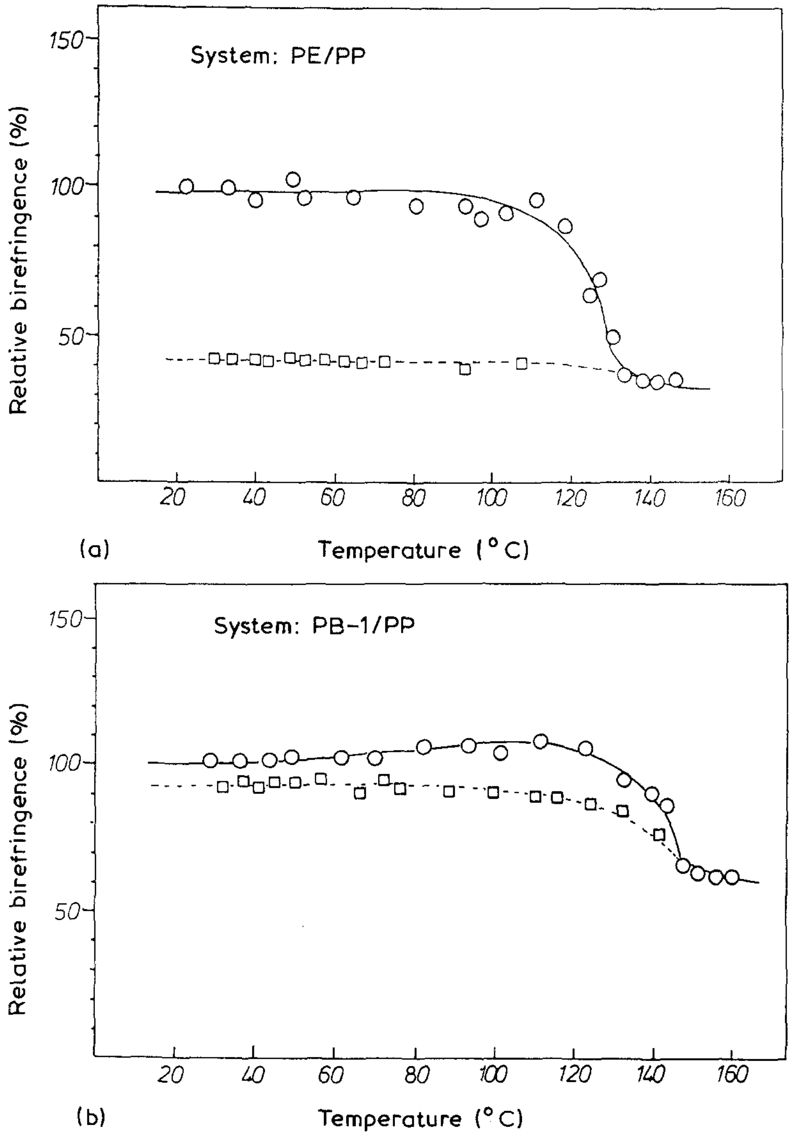

Figure 5 Relative birefringence of layered structured films plotted against temperature. (a) PE/PP film; (b) PB-1/PP film. (○) Heating, (□) cooling.

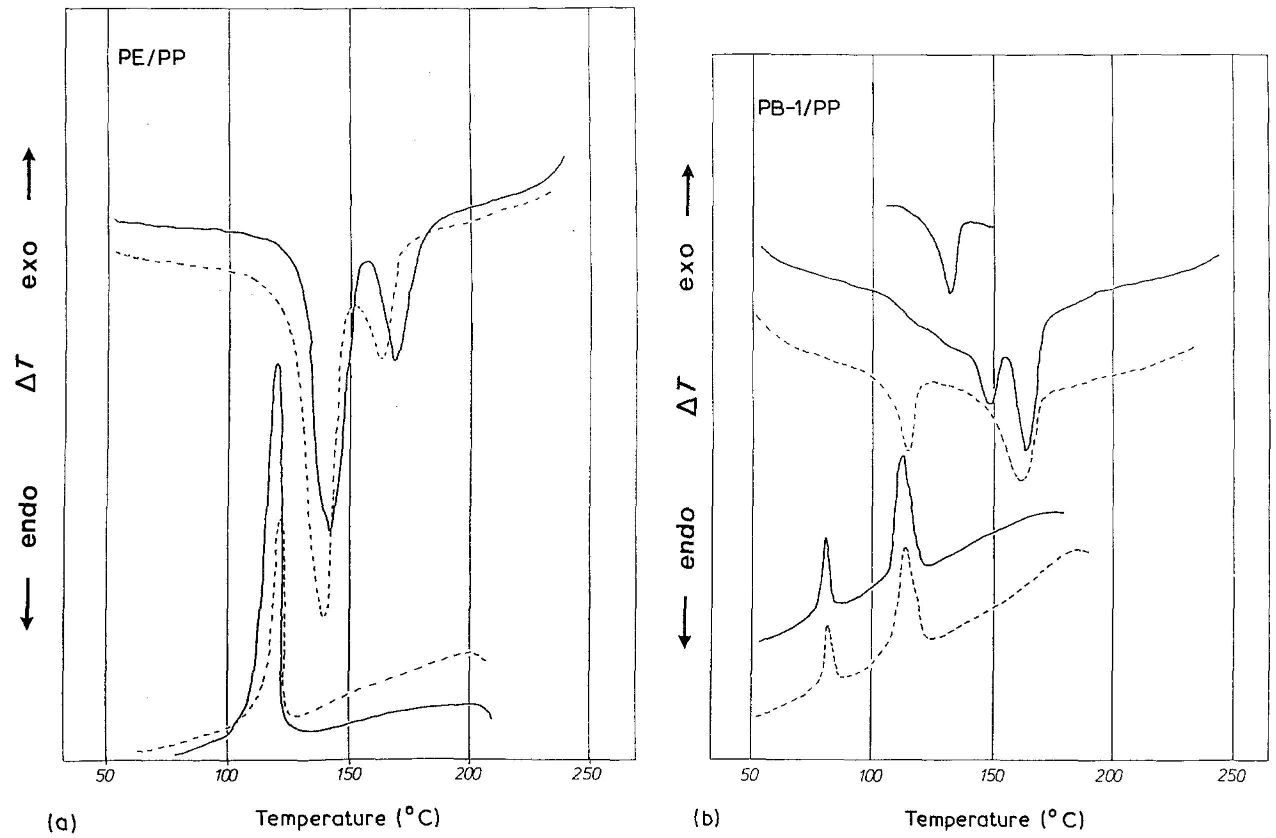

Figure 6 DSC curves of layered structured films, heating rate 10° C min^{-1}: (a) PE/PP film; (b) PB-1/PP film. (——) 1st run, (- - -) 2nd run.

the course of birefringence is observed in the case of PB-1/PP, see Fig. 5b. Here Δn nearly reaches the initial value after recrystallization of the PB-1 layer. This fact confirms the assumption that constrained PB-1 layers again achieve some preferred alignment in the former orientation direction as already observed from the diffraction pattern in Fig. 4c.

3.3. Thermal behaviour

DSC traces of PE/PP and PB-1/PP samples are shown in Figs 6a and b, respectively. Heating and cooling curves of the PE/PP system show the expected behaviour, the melting peaks being in the range of the pure materials (see Fig. 6a). In the case of PB-1/PP, however, a drastic increase in melting temperature of the PB-1 was observed, see Fig. 6b, reaching a value of 150° C. Similar results were obtained when highly oriented pure PB-1 samples were tested with fixed ends [14]. Accordingly, the assumption is justified that in the present system the PP layers act as clamps for the PB-1, preventing the oriented amorphous regions from complete relaxation during melting.

3.4. Mechanical properties

The mechanical properties reflect the corresponding morphologies of the different systems. Young's

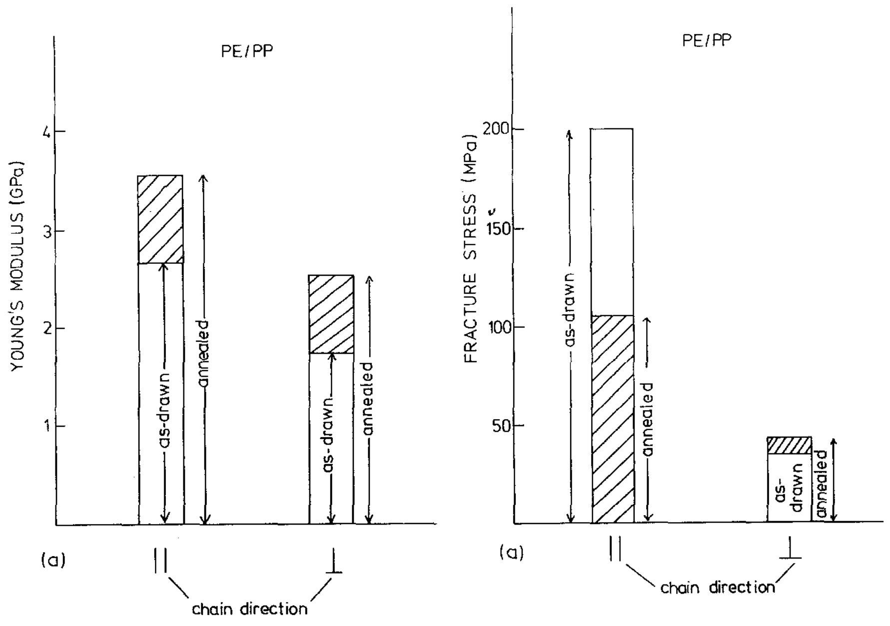

Figure 7 Young's modulus, E, and fracture stress, σ_f, of PE/PP films before and after epitaxial crystallization ||, testing in orientation direction; ⊥, testing in transverse direction. (a) Young's modulus; (b) fracture stress.

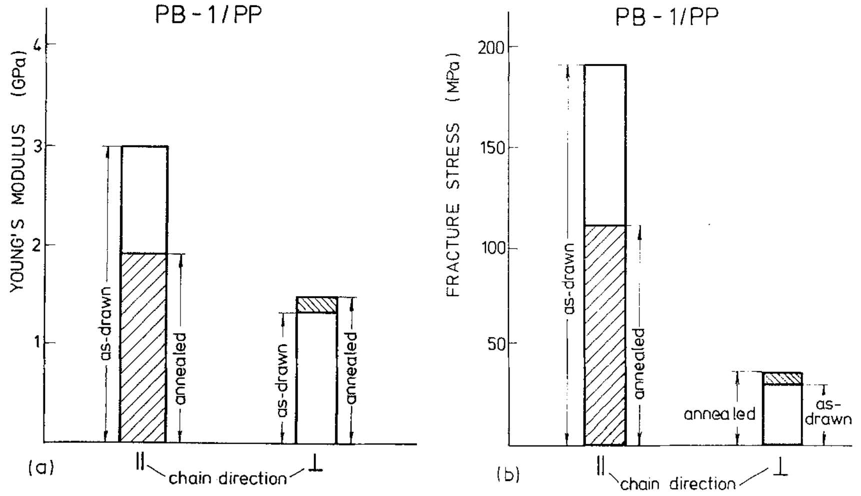

Figure 8 Young's modulus, E, and fracture stress, σ_f, of PB-1/PP films before and after recrystallization. ∥, testing in orientation direction; ⊥, testing in transverse direction. (a) Young's modulus; (b) fracture stress.

modulus, E, and fracture stress, σ_f, in orientation and transverse direction obtained from the PE/PP system in the as-drawn state, as well as after epitaxial recrystallization, are shown in Figs 7a and b. As is clearly visible, $E_{\parallel}$ increases after heat treatment of the sample. On first sight one would expect the opposite behaviour because the initial alignment of PE chain direction parallel to PP chain direction switches to a 40° angle with respect to the PP chain direction and this is expected to result in a decrease of $E_{\parallel}$ if chain orientation only was responsible for the stiffness of the layers. However, due to the cross-hatched lamellar morphology of PE, bridging of the soft amorphous parts of PP by the stiffer PE lamellae is now occurring, reinforcing the entire sample. The elastic deformation in a stacked lamellar structure as in the PP-substrate is mainly determined by the soft amorphous interlamellar parts of the sample so that strengthening of these parts can be achieved by bridging them with PE lamellae. Additionally, $E_{\perp}$ and σ_f also increase in the transverse direction due to the increase in chain orientation into this direction after annealing. However, the fracture stress in the orientation direction decreases significantly after annealing and epitaxial recrystallization. The loss of orientation is a more dominant factor than bridging of soft amorphous parts regarding the fracture behaviour of this sample [15].

In the case of PB-1/PP samples, Figs 8a and b, Young's modulus $E_{\parallel}$ decreases after recrystallization of the PB-1 layers, because a change in the PB-1 from a stiff needle-like structure to a stacked lamellar structure without bridging the amorphous parts of the PP substrate, takes place. Testing in the transverse direction reveals a slightly larger value for $E_{\perp}$ compared to the as-drawn sample. The same arguments as above apply here; the slight loss of molecular orientation into draw direction reflects in the increase of $E_{\perp}$. Fig. 9 shows schematically how the PE lamellae are arranged after epitaxial crystallization and how they contribute to sample reinforcement.

4. Conclusion

The present study shows some interesting properties of layered structures having ultra-thin two component films which are able to form epitaxially crystallized interfaces. At least in the case of PE/PP systems, very desirable mechanical properties in both orientation and transverse directions can be obtained after epitaxial arrangement of the PE lamellae. But in addition, a non-epitaxial system like PB-1/PP can achieve improved properties, as documented in its improved thermal behaviour. This study confirms that the properties of polymer laminates can synergetically change, if the thickness of the laminate components is reduced to near molecular dimension.

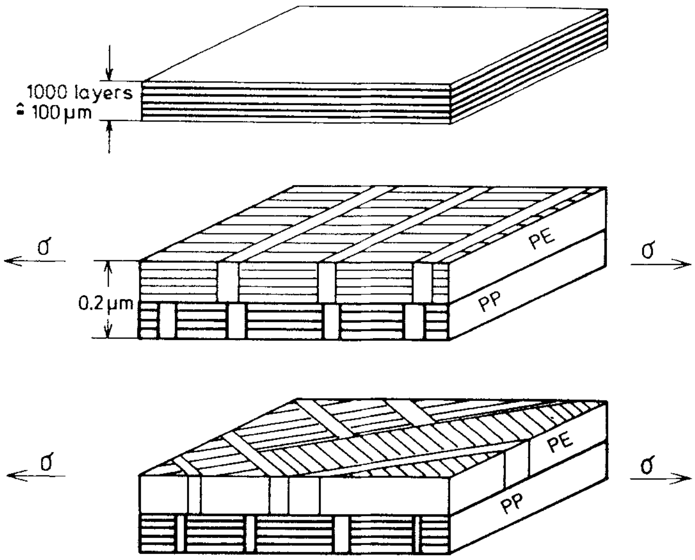

Figure 9 Schematic sketch of the reinforcement mechanism in epitaxially crystallized films. Cross-hatched lamellae are bridging soft amorphous parts.

Acknowledgements

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