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Synergisms of mechanical properties in blends of semi-crystalline polymers

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The structure–property relationship of highly oriented polypropylene (PP) blends were investigated. The as prepared blends consist of very thin sandwiched layers of both the components. After annealing the blends above the melting point of polyethylene (PE) and cooling them to room temperature, an increase in mechanical properties (Young's modulus, fracture stress) is observed. The synergisms of the mechanical properties are explained by a structural model based on transmission electron micrographs.

1. Introduction

Numerous publications have appeared on the transport properties, thermal behaviour, morphology and mechanical properties of blends of polyethylene and polypropylene [1–7]. In general, compatible systems exhibit tensile strength as a function of blend composition, that follow at least a linear dependence on the concentration of one component or even a small maximum in tensile strength over composition [8–10]. In contrast, blends of incompatible polymers have been reported to exhibit a broad minimum in tensile strength over composition [11–13]. Only in a few systems, a synergism in tensile strength has been reported [14, 15].

In incompatible systems, such as polyethylene–polypropylene, the mechanical properties strongly depend on preparation conditions and morphology. Recently, a new technique of strain-induced oriented polymer blending was introduced [14–16], giving fine dispersions of both the components. The method involves the formation of very thin films ($\approx 0.1\,\mu$m), thin enough to enable direct investigation of the morphology of the blends by transmission electron microscopy. In the blends, a strong synergism of Young's modulus E as a function of composition is obtained. It is the purpose of this paper to correlate the morphology of the blends to their mechanical properties, and on the basis of the structure property relationship to suggest a model which predicts a synergetic strengthening of semi-crystalline polymer blends.

2. Experimental part

The high density polyethylene (Lupolen 6021 DX, melt index 0.1 to 0.25 g/10 min) was kindly supplied by BASF. Mechanical measurements were carried out using a standard Instron machine. The strain rate $\dot{\epsilon}$ was kept constant for all measurements ($\dot{\epsilon} = 0.004\,\text{min}^{-1}$) and the deformation temperature was 20° C. Thermal measurements were carried out on a Heraeus, DSC 500 Differential Scanning Calorimeter (DSC) with a heating rate of $10\,\text{K}\,\text{min}^{-1}$. Morphological investigations were performed with transmission electron microscopy (TEM), electron- and X-ray diffraction. The TEM used was a Jeol JEM 200 CX operated at 100 kV, X-ray investigations were carried out with a pinhole camera using Cu$K\alpha$ radiation.

Samples were prepared by dissolving the homopolymers in a common solvent (*o*-xylene), casting a thin film ($\approx 1\,\mu$m) on a pre-heated (130° C) glass plate and, subsequently, drawing the thin molten film vertically from the glass plate with the help of a polymer-coated glass rod. The resulting films were about $0.2\,\mu$m thick and had a highly molecular orientation. Single films were used for TEM investigations. For mechanical, thermal and X-ray measurements about 500 films were sandwiched,

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and sintered at room temperature under a pressure of about 1 MPa.

3. Results and discussion

Figs. 1a to d show electron micrographs of the pure polymers and the blends, all in the as-drawn state. The molecular direction (as indicated by inserted parts) is horizontal. The pure polymers have a lamellar morphology. The material of the films of 30% and 50% PP has segregated into separate layers of PP and PE. At 70% PP the PE appears as a ribbon in the PP film and at 85% PP the PE forms individual islands. Annealing below the melting point of the PE does not change the mor-

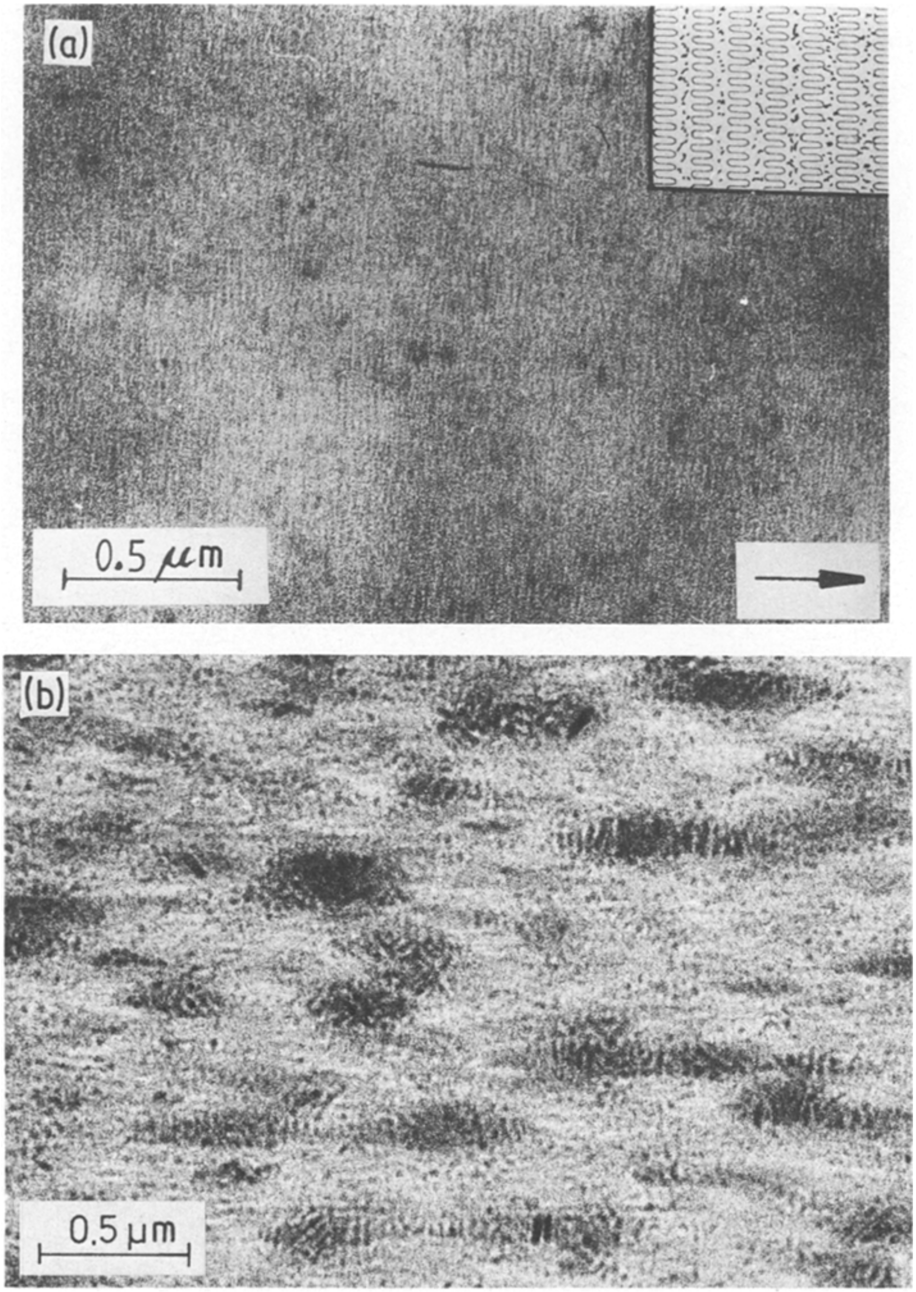

Figure 1 Phase contrast electron micrographs of the pure components (PP, PE) and some blends. The molecular direction is horizontal. (a) Pure PP. Inserted is a sketch of the morphology. (b) 85% PP/15% PE. The dark islands consist out of the PE lamellae. (c) 70% PP/30% PE. The ribbons consist of PE lamellae. (d) Pure PE.

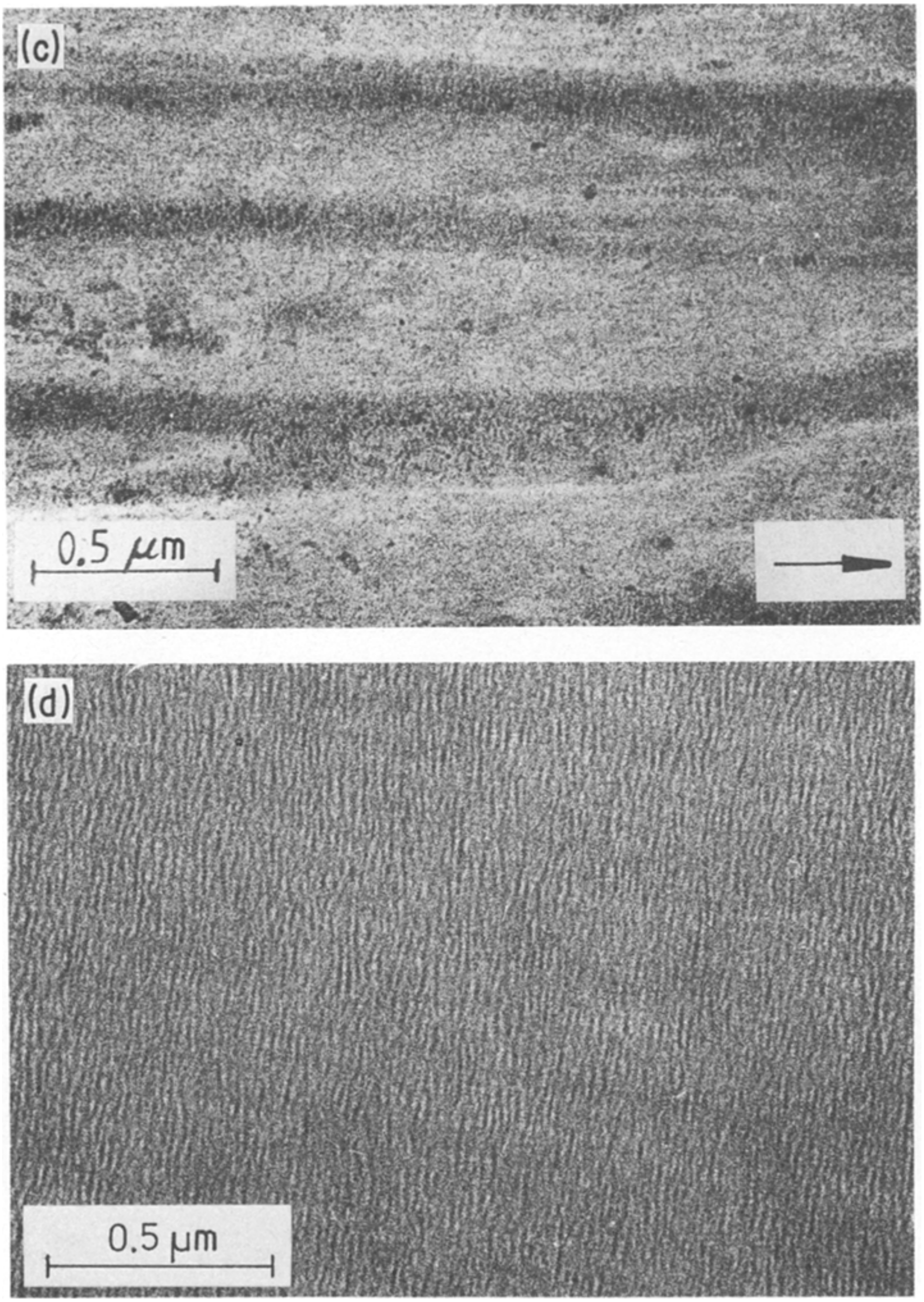

Figure 1 Continued.

phology of the blends. When heating the samples above the melting point of PE (140° C $< T_a <$ 160° C) and, subsequently, cooling to room temperature, the morphology of the PE changes in an unexpected manner. While pure PE recrystallizes in a spherulitic structure, the blends appear as a cross-hatch structure of PE lamellae (Figs. 2a and b) with the lamellae being about 45° inclined to the molecular direction of the PP. From the electron diffraction patterns (Figs. 3a to d), the crystal orientation of the PE lamellae was determined and a strong double texture resulting from epitaxial crystallization of the PE on the fibre texture of the PP film is observed [17] (Fig. 3d). In Fig. 4, the orientation relationship is depicted. The [001] directions of the PE lamellae is rotated 45° about an axis normal to the film surface and the [1 1 0] direction lies in the film plane.

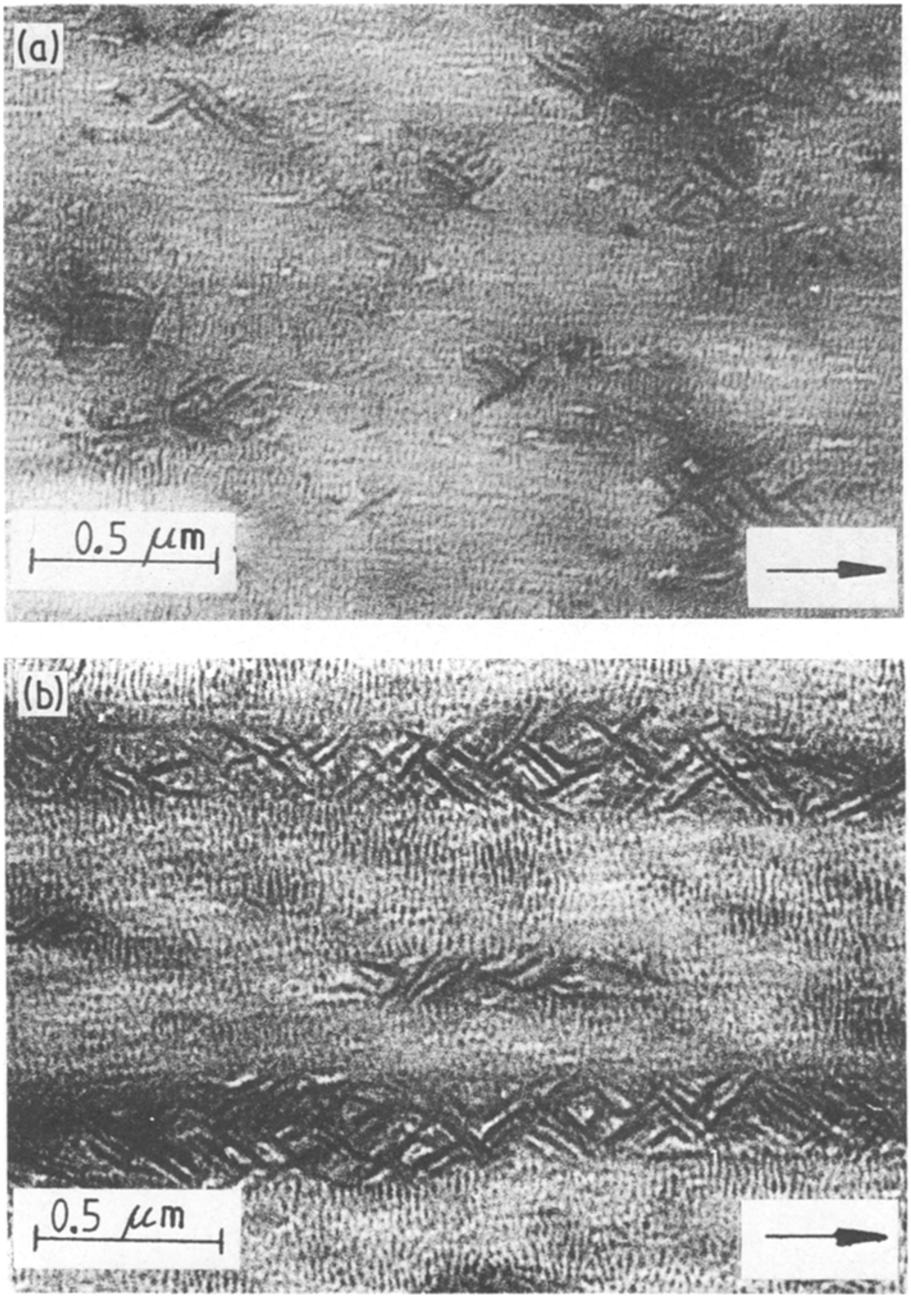

Figure 2 Blends, annealed at 150° C. The molecular direction of the PP is indicated by the arrow. (a) 85% PP/15% PE. (b) 70% PP/30% PE.

This orientation relationship was confirmed on bulk samples by wide-angle X-ray diffraction (WAXS) using the pinhole technique. The Young's modulus E and the failure stress σ_u, as a function of the concentrations are shown in Figs. 5a and b. The solid line presents the data of the as-prepared samples; the dashed curves of the annealed samples. Most significant in the as-prepared samples is the maximum at about 85% PP. In a previous investigation on the system polyethylene–polybutene-1, a similar pattern was observed [14] and explained by a percolation behaviour of the component with the higher crystallization temperature. As long as this component consists of

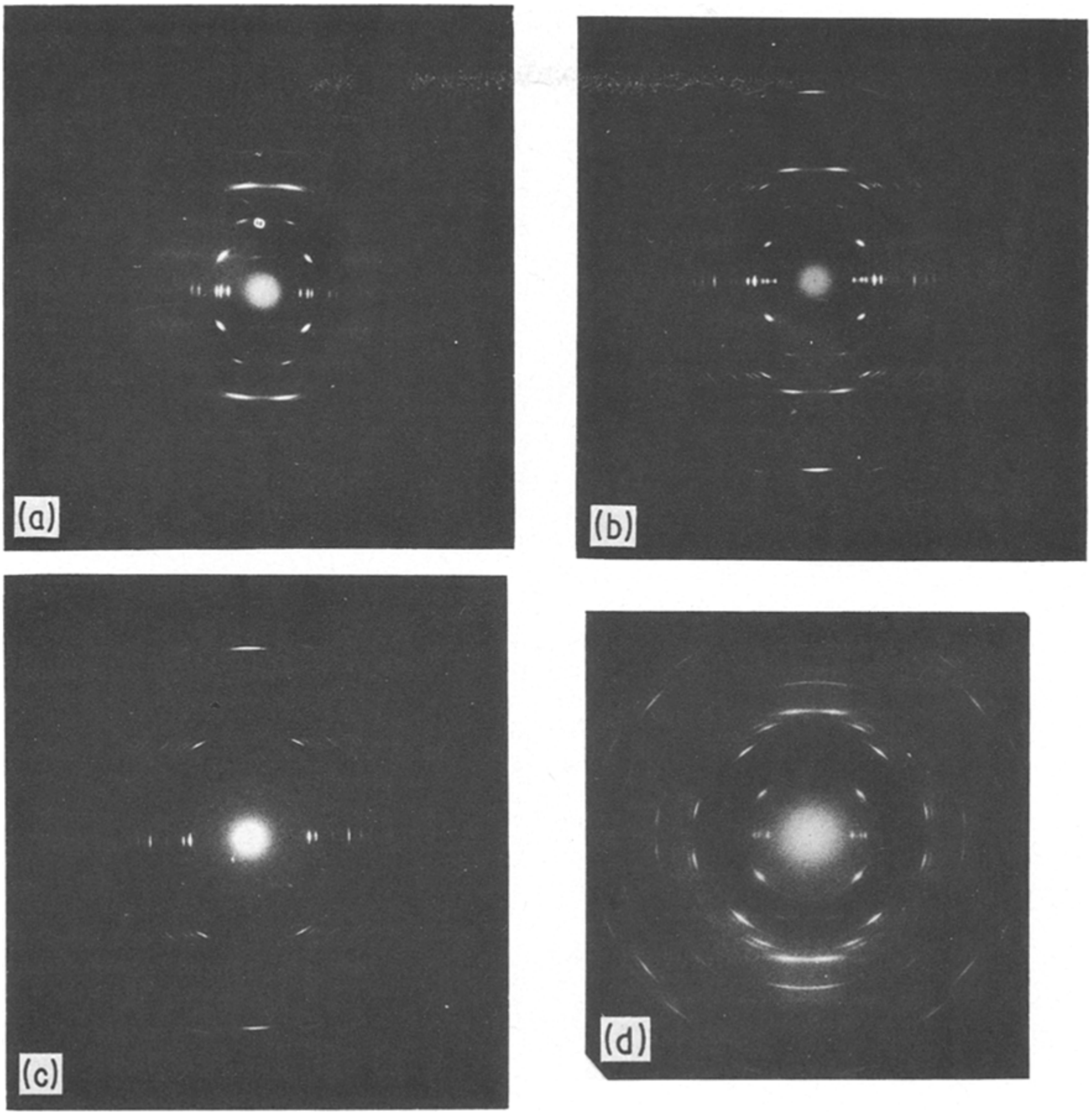

Figure 3 Electron diffraction patterns of (a) pure PP, (b) 50% PP/50% PE, and (c) pure PE. The molecular directions are vertical. (d) 50% PP/50% PE, annealed at 150°C. The molecular direction of the PP is vertical.

isolated clusters within the liquid matrix of the second component, the flow stress of the liquid matrix is increased (constant stress model) giving rise to higher orientation of the second component. When the first crystallizing component forms an interconnected network, the liquid component may relax in the cavities of the network and loses orientation. Theoretically, the percolation limit (transition from isolated clusters to interconnected networks) is supposed to be about at a concentration of 15% [18], in accordance with the experimental observation of the maximum in the mechanical properties. However, it is not easy to predict or to measure, which component is crystallizing first, keeping in mind that the flow field has a longitudinal dimension of 1 μm only [14, 19].

In order to understand the changes in mechanical properties of the annealed blends, a brief description of morphologies and mechanisms which would increase the strength of lamellar semi-crystalline polymers will be outlined. Having a stack of lamellar crystals interconnected in series by the amorphous phase, and applying a uniaxial tensile test with the force normal to the lamellae

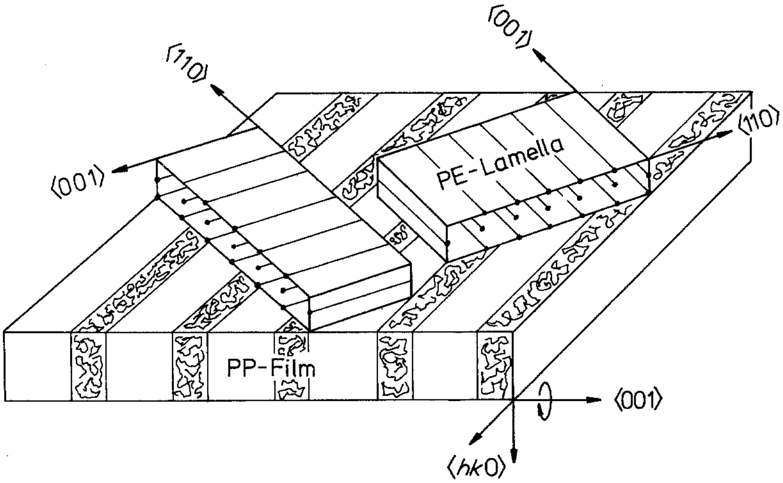

Figure 4 Orientation relationship between PP and PE lamellae after annealing at 150° C.

surfaces, the mechanically weaker parts (amorphous phase) will control the Young's modulus, and fracture stress, as predicted by the isostress model [20]. The amorphous parts can be stiffened either by incorporating strained tie molecules or by blending stiffer molecules. An alternative approach is the bridging of the amorphous layers by short fibrils [21] or by inclined crystalline lamellae (Fig. 6). As seen from the electron micrographs (Figs. 2a and b), the mechanism of the inclined bridging, crystalline lamellae may act as the reinforcing mechanism in our case, after the annealing treatment. The effectiveness of the stiffening depends on the adhesion of the PE lamellae to the PP lamellae and on the thickness of the PE lamellae. Similarly to the fibre-reinforcing mechanism [22], the load between the lamellae is transferred by shear stresses. The thinner the lamellae, the higher the shear stress, and the more the load can be transferred. A good adhesion between the lamellae of the two components is necessary in order to avoid slipping. The occurrence of the epitaxy is an indication of good adhesion.

From the morphological point of view, the mechanical properties of the PE–PP blends can be explained for the non-annealed samples by an iso-

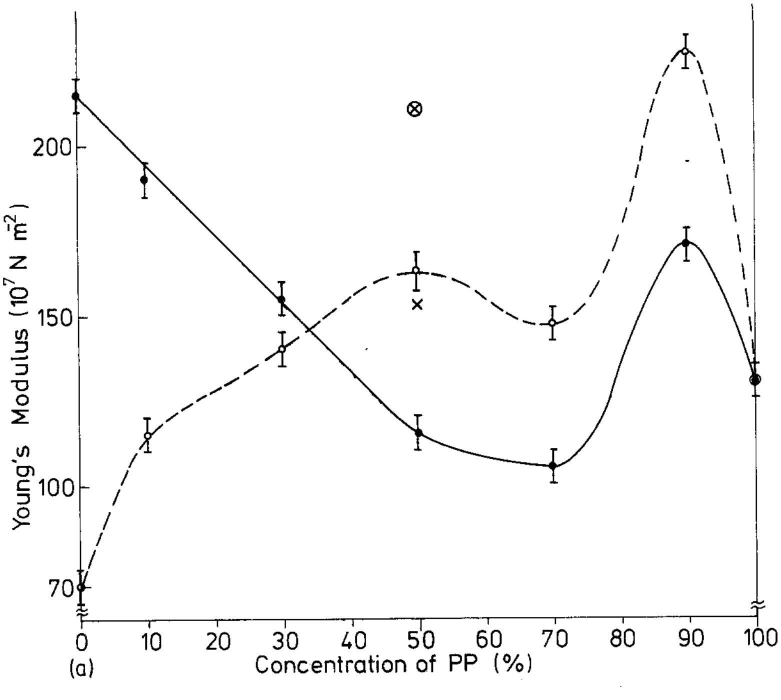

Figure 5 Mechanical properties of the blends (a) Young's modulus versus concentration ——— as prepared; ------- after annealing at 150° C. The cross x corresponds to the sample of alternating layers of PP and PE, and the cross ⊗ corresponds to the same sample, but annealed at 150° C. (b) Failure stress against concentration. ——— as prepared; ------- after annealing at 150° C.

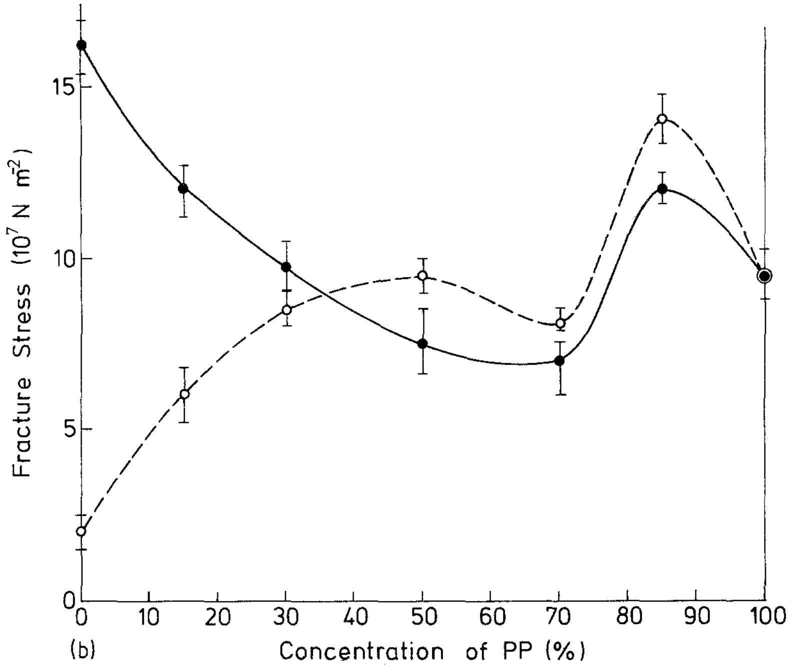

Figure 5 Continued.

stress model. The stiff crystalline parts and the soft amorphous layers are loaded in series. After the annealing treatment, the isostress model does not apply anymore, as the crystalline parts of the PP are now interlinked by PE lamellae. The interlinking is responsible for the increase in mechanical properties of the blends. In order to test this hypothesis, alternating thin (approximately 100 nm) layers of lamellar PE and PP were prepared. Samples consisting of about a thousand alternating layers were strained in a tensile test. The Young's modulus of this sample appears to be the arithmetic average of the pure components (the cross x in Fig. 5a). After annealing the sample above the melting point of the PE component (5 min at 150° C) and quenching to room temperature, the Young's modulus increases considerably above the arithmetic average (cross ⊗ in Fig. 5a). The morphology of the annealed sample is shown in Fig. 7. As in the case of the blends, the cross-hatched structure of the PE lamellae is apparent.

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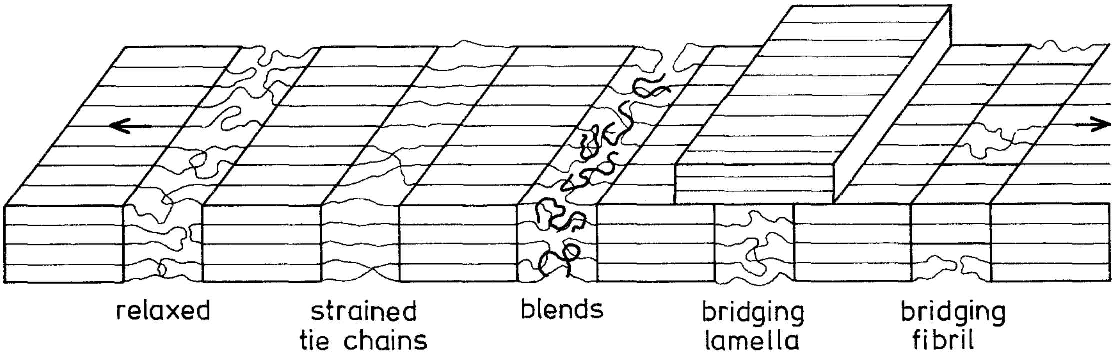

Figure 6 Model for hardening mechanisms in lamellar crystalline polymers.

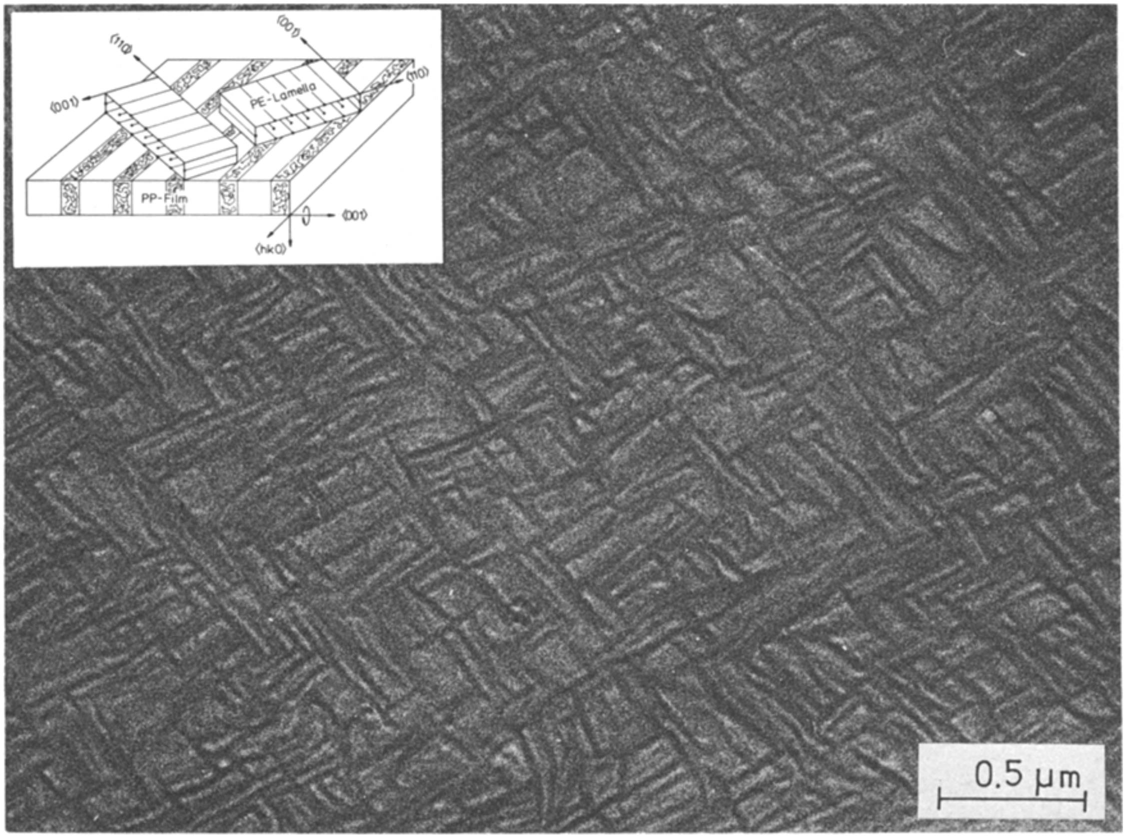

Figure 7 Morphology of two sandwiched layers of PP and PE, annealed at 150° C. Inserted is a sketch of the morphology.

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