

Tensile behaviour of multilayer thermoplastic composites

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Multilayer thermoplastic composite sheets consisting of alternating layers of two materials mainly differing in their ductility were laminated. The mechanical behaviour, irreversible deformation mechanism and fracture of two systems made up of (I) polystyrene (PS)/Noryl and (II) rigid PVC/PVC-EVA blend were studied. In System I the tensile properties change with composition up to 40 to 60 vol% PS while at higher PS content the latter dictates the behaviour of the system. Upon stretching, crazes and cracks were formed in the PS layer. Their propagation was retarded by the Noryl Layers. Subsequently the PS was deformed to rather high strains, otherwise not attainable, and shear bands, which were initiated at the crack tips, developed in the Noryl layers. The interaction between cracks and shear zones resulted in delocalized deformation and fracture delay. In System II the low strain properties linearly change with composition, identical to the behaviour of blends of similar compositions. However the ultimate elongation of three layers sheets and PVC/EVA blends attain maximum values which are higher than those of the components themselves, while that of five layer sheets changes gradually with composition. The good interlayer adhesion in all the systems studied enables cooperative irreversible deformation processes reflected by the mechanical behaviour and the fracture surface morphology of the composite sheets.

1. Introduction

Multilayer polymeric composites are already being used for many years, especially in packaging and industrial applications. In such systems each layer is usually chosen to provide a specific end use property to the product such as chemical resistance, barrier, heat sealability, strength and appearance. Simultaneously, polymer blends were developed to close technical and economical gaps which could not be provided by any single polymer. A unique blend system having a continuous layered morphology can be produced by such methods as coating, lamination and coextrusion, the latter being probably the neatest and most economical method, especially for the production of many-layered sheets [1-4]. The physical properties of a multilayer polymer sheet mainly depend on the properties of the individual components, the system composition, the characteristics of the interfaces and the mechanical interaction between phases.

Laminar composites made of a brittle material are expected to exhibit higher tensile strength than individual sheets due to the reduced effect of "bad" flaws. Scop and Argon [5] have shown that the strength enhancement may be as high as 50% for a laminate with as few as five layers. Moreover, for a very large number of layers the strength of a laminate tends to approach that of a homogeneous material, namely its theoretical strength. Shrenk and Alfrey [1, 6] and Bhateja and Alfrey [7] have suggested two types of multilayer composite sheets which exhibit "mutual interlayer reinforcement" and "mutual interlayer des-

truction" depending on the systems composition, interlayer adhesion and the skin layer ductility. The toughening effect is expected in a laminar composite containing a layer of high modulus brittle polymer sandwiched between layers of a ductile polymer providing a good interlayer bonding. Such a behaviour is exhibited by a Mylar/adhesive/aluminium composite sheet [7]. The destructive effect has been demonstrated in the latter system when thin Mylar layers or poor interlayer adhesion were used as well as in polystyrene (skin)/high impact polystyrene (core) composite sheets [6] and in elastomeric substrates coated with thin paint film [8]. Hiltner *et al.* [9, 10] have recently studied the deformation behaviour of coextruded multilayer composites containing alternating layers of polycarbonate (PC) and poly(styrene-acrylonitrile). They have observed three modes of failure including a brittle, semi-ductile and ductile fracture depending on the system composition, the deformation strain rate and the extent of deformation the PC layers are able to undergo. In addition, interesting interaction of crazes and shear bands was observed, which produced an extended damage zone ahead of cracks, retarding crack propagation.

In the present work three and five layer composite sheets composed of alternating layers of brittle or semi-ductile and ductile thermoplastic polymers were studied. The components were chosen to yield systems with good interlayer adhesion to allow transfer of stresses. The aim of the investigation was to study the tensile behaviour, possible cooperative irreversible

deformation processes and potential synergistic effects in such unique thermoplastic composite systems.

2. Experimental procedures

Two couples of thermoplastics were selected to represent multilayer composite sheets comprising two materials exhibiting mainly different ductility and good adhesion. The first includes Noryl (a General Electric modified Poly(phenylene oxide) exhibiting a heat distortion temperature (HDT) of 125°C) and a general purpose polystyrene (PS-Israel Petrochemical Industries-HF55). The second couple includes a rigid poly(vinyl chloride) (PVC-Electrochemical Industries, Frutarom, Israel - 37I) and a blend consisting of PVC and 60 PHR ethylene vinyl acetate/vinyl chloride copolymer (EVA-VC, Huls, West Germany - Vestolit HIS 7587 containing 50% EVA; the latter contains 45% vinyl acetate). The blend and the PVC also contain 1% stabilizer (Ciba Geigy Irgastab 17M).

Three and five layer symmetric composite sheets were prepared with the more ductile material in the outer layer. Various compositions for each system were obtained by changing the relative thickness of each component (the thickness of identical layers was kept equal, in the range of 0.25 to 1.5 mm. Compression moulding was used first to prepare sheets of desired thicknesses and then for lamination (no adhesive was used). The moulding temperature for the composites was selected to attain good interlayer adhesion; Noryl/PS sheets were moulded at 175°C and EVA-VC + PVC/PVC sheets were moulded at 165°C. The sheets were moulded for 5 min at these temperatures, followed by quenching while still under pressure. The final thickness of the layers was determined using a calibrated optical microscope.

Tensile specimens (dumb-bell of 39 mm gauge length and 6.6 mm nominal width) were milled from the moulded composite sheets and tested in a standard Instron machine at a strain rate of 1.3 and 0.05 min⁻¹ for the PVC/blend and PS/Noryl systems, respectively. Each test was repeated six times and the average values are reported.

Specimens for optical microscopy were polished edge on with alumina powder down to 0.05 μm. The specimens were either deformed in the Instron machine and immediately observed, or by using a stretching jig in the microscope. Either transmission or reflection modes were used depending on the transparency of the specimens. Scanning electron microscopy was used to study the fracture surface of the composite specimens.

3. Results and discussion

The two composite systems consisting of Noryl/PS and EVA-VC + PVC/PVC will be discussed separately.

3.1. Noryl/polystyrene

Five three layer composite sheets of different Noryl/PS ratio (the nominal thickness of the Noryl layers was kept constant at 1 mm and that of PS was changed in the range of 0.25 to 1.5 mm) were studied. The stress-strain curves of the composite sheets (stress applied parallel to the layers) change quite gradually between those of the brittle PS and the ductile Noryl; neither

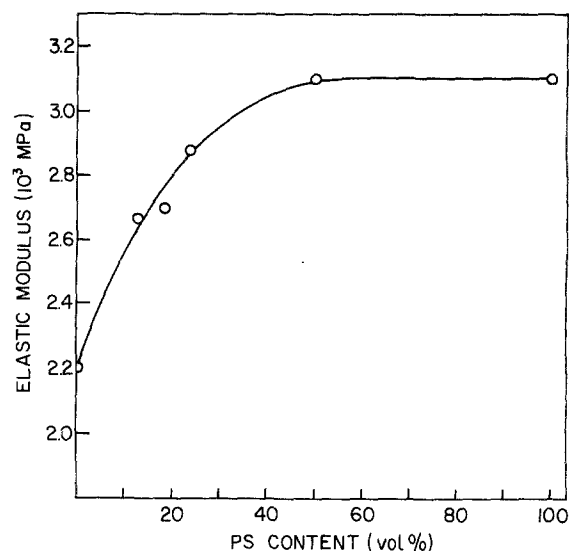


Figure 1 Elastic modulus of three layer Noryl/PS/Noryl composite sheets.

exhibits a clear yield point. The moduli of the composites and the controls are shown in Fig. 1. The average values for the Noryl and PS controls, 2.2×10^3 and 3.1×10^3 MPa, respectively, are in good agreement with values quoted by the materials producers. The elastic modulus of the composite sheets at first gradually increases with PS content, attaining its maximum value (that of PS) at a 40 vol % PS content. Surprisingly, this system does not follow any of the expected mixing rules. The modulus does not change linearly with composition as would be expected, especially for systems in which both components form continuous phases in the direction of the applied stress. The observed behaviour is similar to that of blends consisting of a glassy matrix and dispersed rubbery particles [11], which is not the case here. This unique modulus-composition relation may indicate the formation of a new PS rich phase at the interlayer region of the composite sheets. The formation of such an interlayer is possible during the quite long lamination process which takes place at a high temperature. Since this phase thickness depends solely on the moulding conditions and duration, it is expected to be similar in all the compositions studied and thus becomes predominant, together with the PS layer, on decreasing the thickness of the Noryl layers.

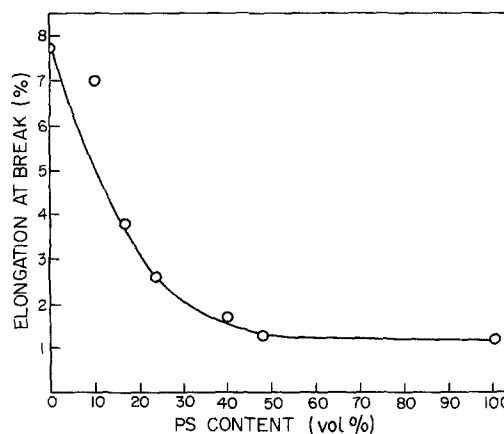


Figure 2 Ultimate elongation of three layer Noryl/PS/Noryl composite sheets.

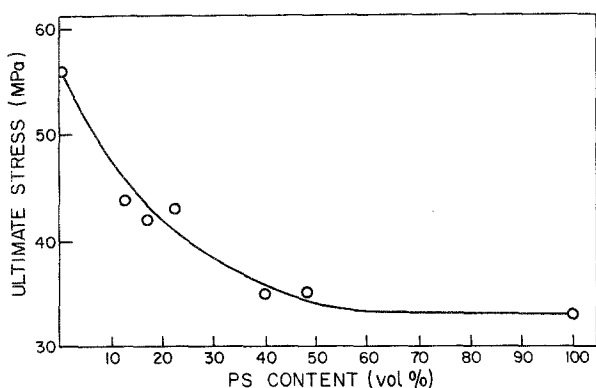


Figure 3 Tensile strength of three layer Noryl/PS/Noryl composite sheets.

The ultimate tensile properties of the composite sheets change gradually with composition from the higher values of Noryl to the lower values of PS, as depicted in Figs 2 and 3. These properties attain their lowest values (those of PS) in sheets containing 50–60 vol % PS. Approximation of the stresses acting on the Noryl layers following the failure of the PS layer indicates that in systems containing > 50% PS, the stresses are higher than the Noryl tensile strength. Thus the failure of the PS layer also results in the immediate failure of the Noryl layers, which is not the case in systems containing < 50% PS. This effect, combined with the formation of a PS rich interlayer, may be responsible for the low ultimate elongations attained by the composite sheets. Nevertheless, the rather high elongations attained by the brittle PS when sandwiched between two ductile Noryl layers are noteworthy, and will be further discussed below.

Optical microscopy of specimens which were tensile

tested up to failure shows the formation of crazes, oriented perpendicular to the stress direction, throughout the thickness of the PS layer (some crazes have healed upon the stress release). In specimens which failed at low elongation (high PS content) all observed crazes were initiated at the PS/Noryl interface (see Fig. 4a, in which the dark area is the Noryl layer). However, in specimens of low PS content, which failed at rather high elongations, profused crazing was observed throughout the PS layer (see Fig. 4b). The only irreversible deformation event in the Noryl layer was observed in the fracture region. As is seen in Fig. 4c, a triangular shear deformation zone was formed, which has been initiated at the Noryl/PS interface, ahead of a crack in the PS, and propagated through the Noryl layer. All oblique striations observed in the micrographs are the result of polishing prior to stretching. Complimentary observations were made by optical microscopy of deforming specimens. Fig. 5 includes a series of micrographs of a multilayer sheet containing 16 vol % PS which has undergone various extents of deformation (PS is the darker layer). At low deformation (Fig. 5a) crazes are observed in the PS layer, most of which are initiated at the PS/Noryl interface; no deformation marks are yet observed in the Noryl layer. Upon further stretching, additional crazes were formed (sporadically initiated in the PS layer) while those already existing have propagated through the layer thickness. Since further crack propagation is retarded by the Noryl layers, the cracks grow in width turning in part into cracks (see Fig. 5b). At even higher deformations, prior to fracture, as wide cracks are formed in the PS layer the development of shear deformation zones in the Noryl layers is observed (see Fig. 5c). These zones were initiated at the very sharp crack tips, which crossed into the Noryl layers. The shear zones have propagated across the Noryl layers forming triangular deformation zones, in agreement with observations made in Fig. 4c. At higher magnification (not shown) dense crazing is simultaneously observed in the PS layer. It should also be noted that those crazes which turned first into cracks are approximately equidistant. Thus, equisize PS blocks were formed which

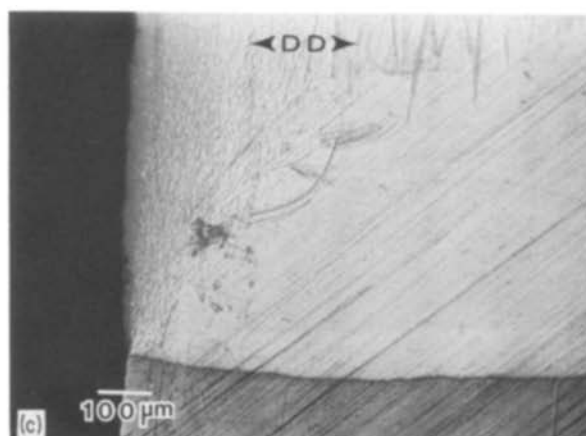
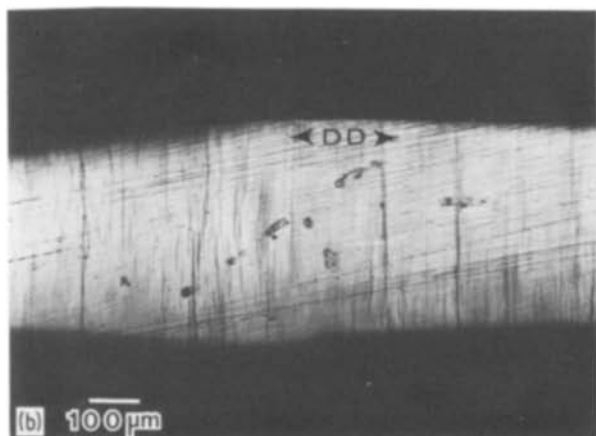
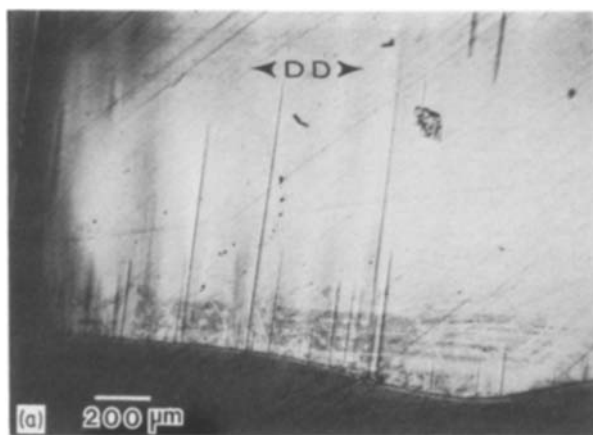


Figure 4 Optical micrographs of tensile tested Noryl/PS/Noryl sheets (edge on): (a) sheet containing 48 vol % PS (transmission mode); (b) sheet containing 16 vol % PS (transmission mode); (c) sheet containing 16 vol % PS (reflection mode).

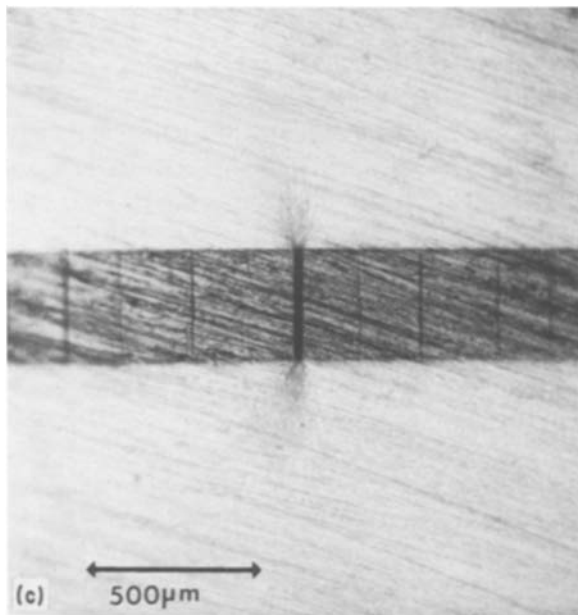
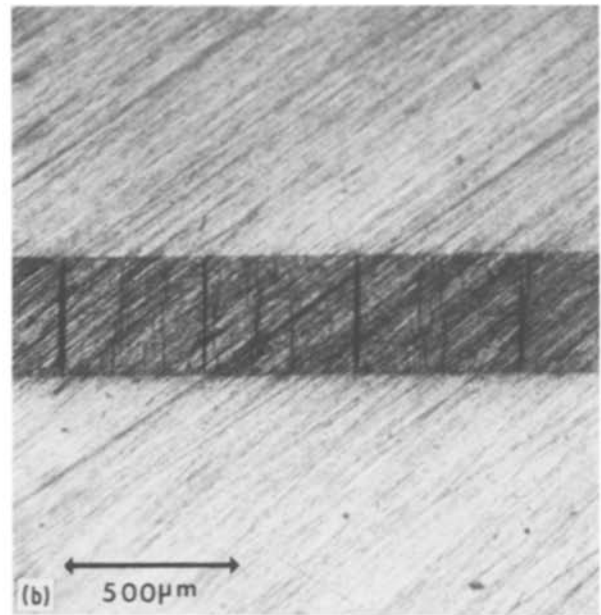
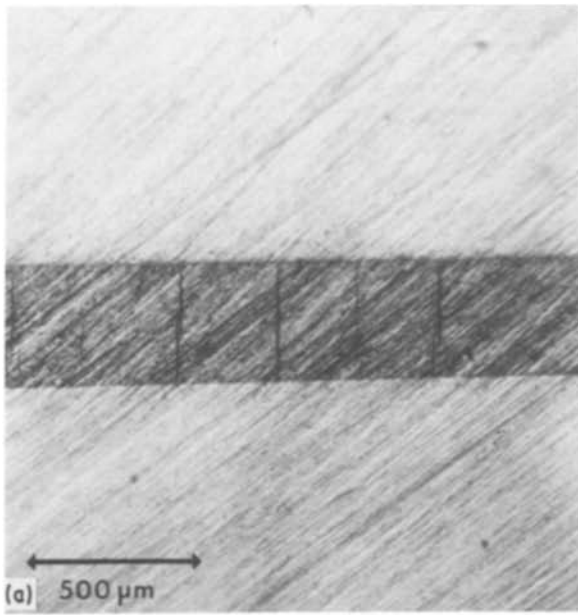


Figure 5 Optical micrographs of a Noryl/PS/Noryl sheet containing 16 vol % PS (edge on) deformed under the microscope.

are held together by the Noryl layers. A similar phenomenon was recently observed in PC/SAN composite sheets [10].

Scanning electron microscopy of fracture surfaces confirms the very different morphological characteris-

tics for the brittle PS [12–14] and semi-ductile Noryl [15] (see Fig. 6). Morphological gradual variations are observed in the fracture surface of the Noryl layer. The structural units become larger and rougher with increasing distance from the Noryl/PS interface, probably due to the changing crack propagation velocity which is slower close to the boundary. The good adhesion between the layers is demonstrated in Fig. 6; the interface can only be distinguished by the different fracture surface morphology of the layers. However, in most specimens a crack parallel to the layer interface has developed in the PS layer at a distance from the interface. This crack is probably a result of shear stresses developed between layers of different elastic moduli. The location of the crack in the PS layer rather than in the interface also indicates a good interlayer adhesion.

It is possible to correlate the microdeformation processes in the multilayer composite sheets with the bulk behaviour. With increasing the Noryl/PS ratio the composite systems turn more ductile as a result of the stronger interaction between crazing and shearing processes in the PS and Noryl layers, respectively. This

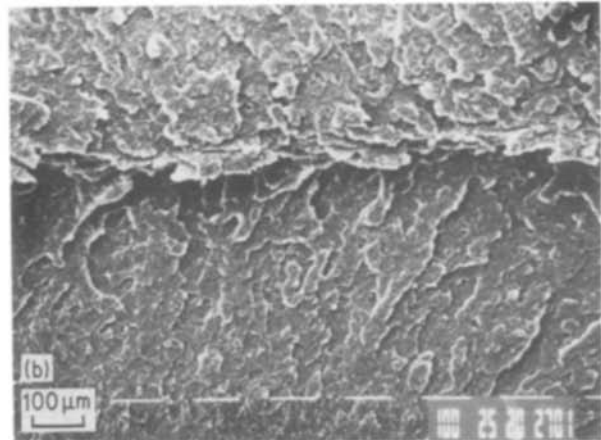
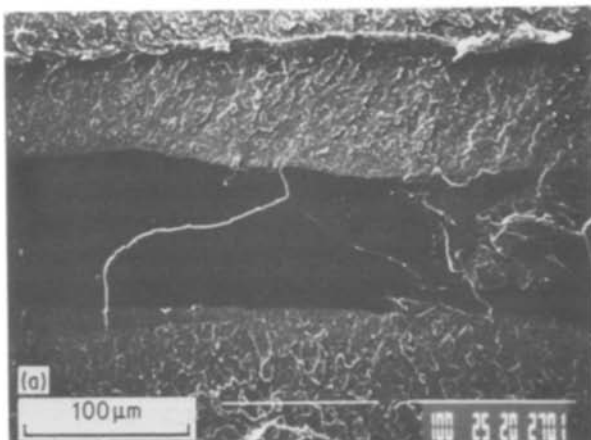


Figure 6 Scanning electron micrographs of fracture surfaces of a Noryl/PS/Noryl sheet containing 25 vol % PS. (a) General view, (b) higher magnification of the Noryl layer (bottom being closer to the PS layer).

interaction can only occur when good interlayer adhesion is provided. Combining all optical and electron microscopy studies the following deformation mechanism can be suggested: upon straining the composite system, isolated crazes develop in the PS layer, the number of which increases with extent of deformation [16]. At this point no irreversible deformation events can be observed in the Noryl layer. At higher strain some of the crazes turn into cracks, which are first blunted by the ductile Noryl layer thus, postponing failure. This crack arrest mechanism enables further deformation and so denser crazing in the PS layer. Simultaneously, the stress concentration at the crack tips, which have crossed into the Noryl, initiates the formation of shear zones, consisting of shear bands [17], in the Noryl layer [10]. Similar shear zone formation ahead of cracks propagating in ductile polymers has been observed in polymers such as polycarbonate [18], polysulphone [19] and poly(2, 6-simethyl 1, 4-phenylene oxide [20–22]. At higher strains more crazes and cracks are formed in the PS layer resulting in the breaking down of this layer into small blocks which are held together by the ductile Noryl layer, in which more deformation zones are developed. Finally, the system fails when a crack in the PS layer propagates across a deformation zone in the Noryl layer, as shown in Fig. 4c. Additional cracks are formed in the PS layer in a plane parallel to the layers, stemming from the different elastic moduli of the two materials. The end effect of these processes is the delocalization of stresses, the expansion of the damage zone and thus delayed fracture.

3.2. PVC and PVC/EVA–VC

Three and five layers composite sheets consisting of alternating layers of rigid PVC and a 10/6 blend of PVC and EVA–VC were studied and compared with PVC/EVA–VC blends having comparable compositions. The tensile behaviour of the latter was recently reported [23].

Rigid PVC deforms in tensile inhomogeneously through the formation of a neck which propagates to a limited extent prior to failure [24]. However, the PVC/EVA–VC blend deforms more uniformly; a neck is formed which propagates through the whole specimen length [23]. The composite sheets deform, as visually observed, similarly to the blends. It is interesting to note that no delamination was observed in composite sheets containing up to 45 vol % rigid PVC, while in sheets containing thicker PVC layers delamination occurred in the region close to the fracture zone. Moreover, in the same regions surface cracks in the blend layers are observed (see Fig. 7). This surface phenomenon in the otherwise ductile material may indicate the formation of a PVC rich interface layer during the laminate moulding, the cracks in which are only observable upon delamination. The formation of such a layer was also suggested in the Noryl/PS composite sheets.

Representative stress–strain curves of PVC, PVC/EVA–VC and some of their composite sheets are depicted in Fig. 8. The curves change gradually in shape from that of the rigid PVC to that of the blend.

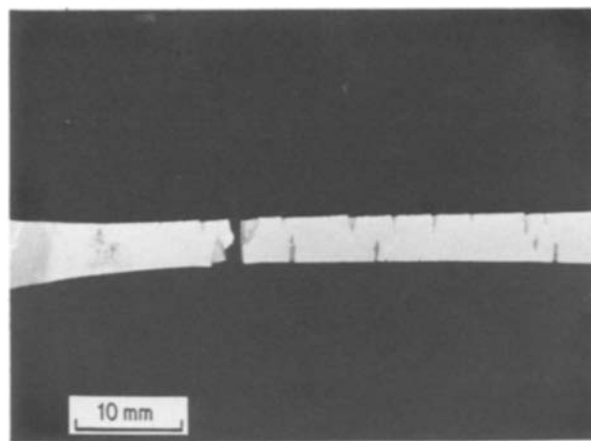


Figure 7 Optical micrograph of a blend layer in a five layer system composed of PVC and PVC/EVA–VC blend following fracture (62 vol % strain) and delamination.

As clearly seen, with a decrease in the volume fraction of rigid PVC the extent of instability as reflected in the yield region of the curves decreases, indicating more homogeneous, delocalized deformation, similar to the behaviour observed for impact modified PVC [23, 24]. The elastic modulus of the composite sheets linearly increases with an increase in the volume fraction of the rigid PVC layer. When a comparison is made between the three and five layer systems and blends on a common basis of EVA–VC content, all modulus values fall on a single line (see Fig. 9). Thus, the dependence of elastic modulus on composition is not affected by the arrangement of components. Thus, the elastic modulus of a system containing rigid PVC and rubbery EVA–VC copolymer whether in the form of a two phase blend or in multilayer systems consisting of alternating continuous layers of PVC and a blend only depend on the average composition. Furthermore, in all these systems the composition dependence of the elastic modulus follows the simple linear rule of mixing. Similarly, the yield stress of the three systems also changes linearly with the average composition (not shown). However, regarding the ultimate properties, an effect on the systems structure is observed. The stresses at break in all systems are equal to the flow stresses (there is hardly strain hardening); they are consistently highest for the blends and lowest for the five layer systems; however, the differences are rather small (< 20%). The composition dependence of the ultimate elongation in the various systems is interesting (see Fig. 10). The elongation of the composite sheets components, namely rigid PVC and the blend containing 42 vol % EVA–VC (10/6 PVC/EVA–VC) are 31 and 108%, respectively. The elongation of the blends attains a maximum value of 160% for a blend containing 25 vol % copolymer and that of the three layer sheets attains a maximum value of 112% for a composite system containing 15 vol % copolymer (equivalent to 65 vol % of rigid PVC layer). Both values, especially that for the blend, exceed the elongation of the rubbery copolymer when by itself. However, the ultimate elongation of the five layer sheets changes differently with composition; gradually increasing with EVA–VC content. The elongations of the three systems seem to coincide at the high end of

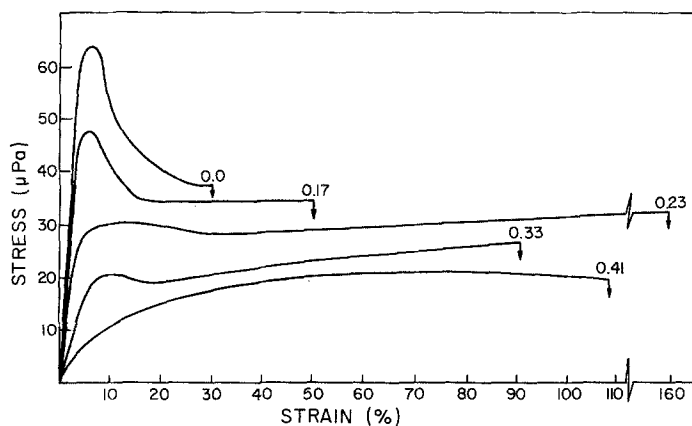


Figure 8 Stress-strain curves of five alternating layers systems composed of PVC and PVC/EVA-VC blend. The numbers denote the rigid PVC layers volume fraction.

the studied copolymer content. It should also be noted that the rigid PVC layer in the composite systems attains very high strains, which are not obtainable for the rigid PVC when by itself. The observation of the maximum elongation in the blends can possibly stem from changes in the blend multiphase structure, however that observed in three layer systems is presently unexplainable.

The tensile fracture surfaces of the rigid PVC and the PVC/EVA-VC blends are quite distinguishable (see Fig. 11); they are both characteristic of semi-ductile materials. The difference in the ductility of the two materials is reflected by the size of the morphological units observed in the fracture surfaces; large and elongated in PVC (Fig. 11a) and small and rounded in the blend (Fig. 11b). The fracture surface of a three layer system shows clearly the layered structure and the interlayer boundaries, which indicate strong interlayer adhesion. The surface morphology also indicates that the crack has propagated through the specimen crossing the interlayer boundaries in a continuous manner. The differences between the PVC fracture surface morphology observed in Figs 11 and 12 mainly stem from the strain at fracture being 30 and 100%, respectively. It is the first time that a fracture surface of such highly drawn rigid PVC is shown. When these two micrographs are compared (Figs 11 and 12) it is obvious that the latter is of a

more deformed material than that of the PVC by itself. The fracture surfaces of the other three layer composite sheets studied are similar, although the surface morphology of the PVC becomes smoother with a decrease in the strain fracture, depending on the composition of the sheets. In the five layer systems the tensile fracture surfaces are very similar to those observed in the three layer ones (see Fig. 13). Here also the crack propagates continuously through the whole specimen cross-section, leaving behind a layered fracture surface in which the different layers are only distinguishable due to their surface morphology, and the boundaries are clearly seen as sharp lines. In this composite system, as in the Noryl/PS sheets, the cooperative fracture process in all layers is rather pronounced, which also indicates interaction between irreversible deformation events in the different layers.

4. Conclusions

The tensile mechanical properties, the irreversible deformation processes and the fracture of thermoplastic laminates consisting of alternating layers made of two polymeric materials, differing in their ductility, were investigated.

In the PS/Noryl composites the tensile properties continuously changed with composition only as long as the Noryl content was larger than about 50%. In the laminates containing more than about 50% PS all tensile properties were predominated by those of PS. At low strains, crazes formed in the PS layer were

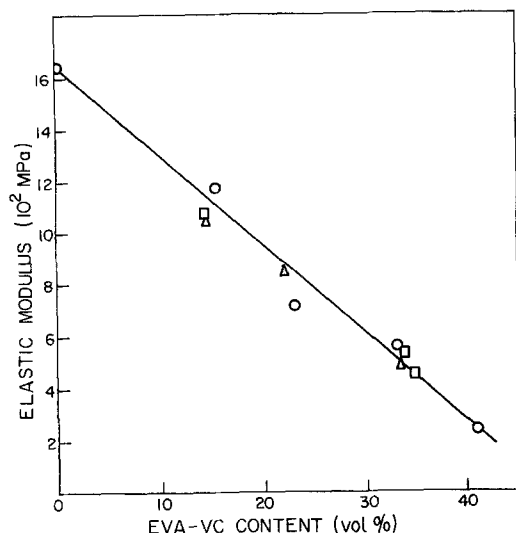


Figure 9 Elastic modulus of (○) PVC/EVA-VC blends and (□) three and (Δ) five layer composite sheets consisting of PVC and a 10/6 PVC/EVA-VC blend.

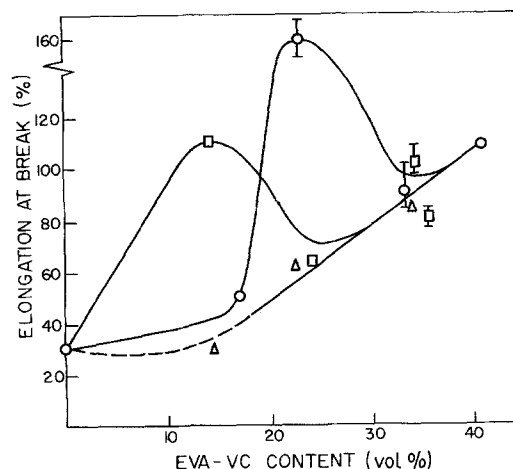


Figure 10 Ultimate elongation of (○) PVC/EVA-VC blends and (□) three and (Δ) five layer composite sheets containing of PVC and 10/6 PVC/EVA-VC blend.

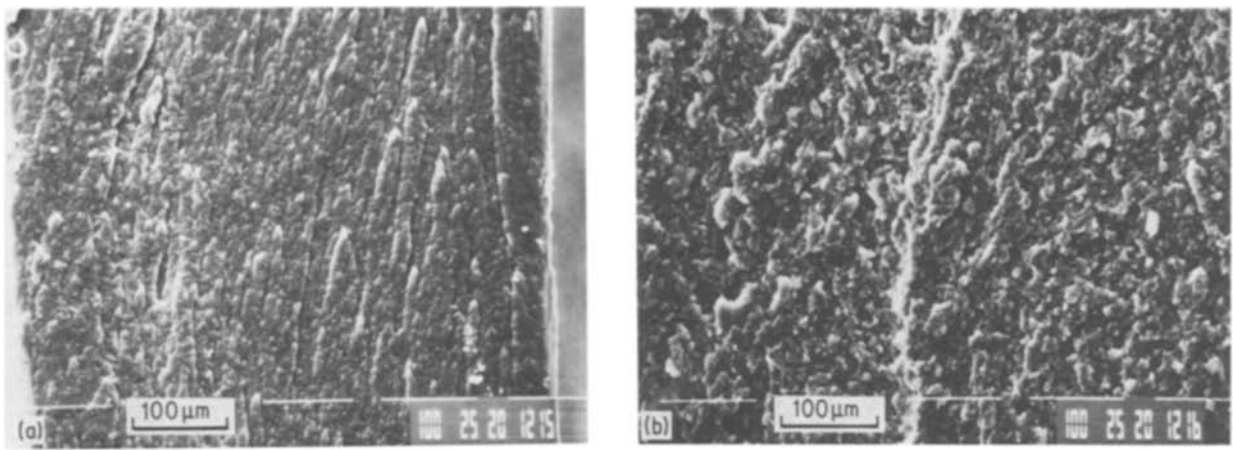


Figure 11 Scanning electron micrographs of (a) PVC and (b) PVC/EVA-VC blend tensile fracture surface.

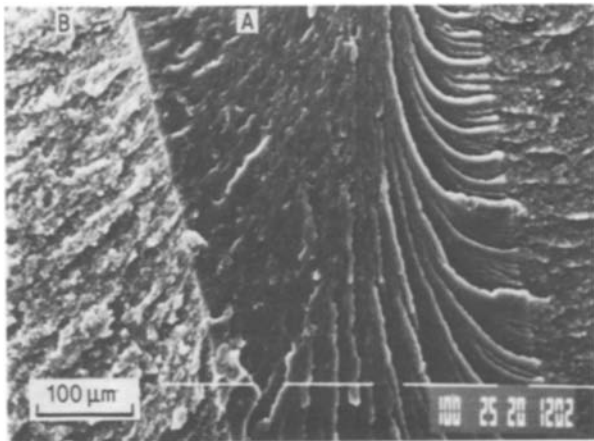


Figure 12 Scanning electron micrographs of tensile fracture surface of a three layer composite sheet containing (A) 16 vol % rigid PVC and (B) 84 vol % 10/6 PVC/EVA-VC blend; failure occurred at 100% strain.

blunted by the Noryl layers resulting in rather highly deformed and densely crazed PS layer. The high interlayer adhesion enabled stress transfer and further deformation. At higher strains shear zones were initiated in the Noryl layers ahead of the cracks previously formed in the PS. This interaction between cracks and shear bands, two energy absorbing deformation mechanisms, is responsible for retarding crack propagation and thus for postponing failure.

In the rigid PVC/PVC-EVA composites, both elastic modulus and yield stress change linearly with composition as is the case in the PVC-EVA blends of the same compositions. However, the three layer composites and the blends exhibit a maximum elongation (higher than that of the components by themselves) at some intermediate compositions, while the elongation of the five layer composites continuously changes with the composite system composition. Fracture surfaces of the composite sheets indicate good interlayer adhesion and a cooperative failure mechanism of all layers.

In both systems it has been demonstrated that the construction of a laminate in which a brittle polymer sheet is sandwiched between ductile layers, providing good interlayer adhesion, significantly postpones the failure of the brittle component to appreciable extents of deformation. Such laminar blends could possibly be advantageous relative to random blends of polymers exhibiting limited compatibility. Such an enhancement of properties should be even more pronounced in thin laminate layers, where interlayer adhesion should not play a dominating role.

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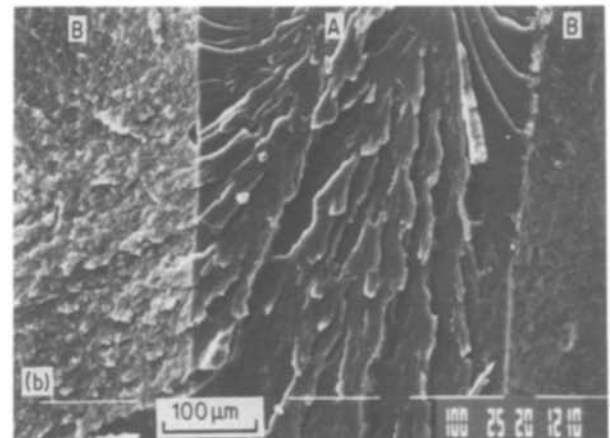
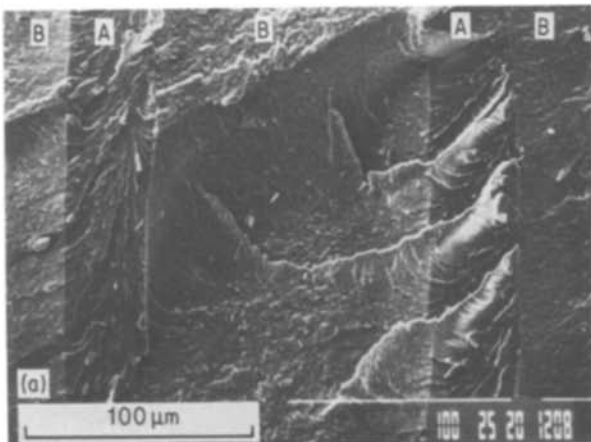


Figure 13 Scanning electron micrographs of tensile fracture surface of a five layer composite sheet containing (A) 20 vol % rigid PVC and (B) 80 vol % 10/6 PVC/EVA-VC blend; failure occurred at 80% strain. (a) General view; (b) higher magnification of a selected area.

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