Adhesion in laminates of highly oriented polypropylene sheets*

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The underlying causes of adhesion in highly oriented PP and PP-copolymer films have been investigated. The parallel-plied laminate was found to differ in behaviour from the cross-plied laminate. Relative to the cross-plies, the parallel-plies showed greater blocking force, but smaller birefringence, more disoriented WAXS patterns, and lower tensile strength and modulus. Annealing of the laminate before moulding affected blocking of the parallel-plies, but not the cross-plies. Microstructural differences were also noted in the TEM. The experimental observations lead to the conclusion that, for the parallel-plies, adhesion arises from retraction of the highly oriented amorphous region, followed by entanglement across the interface. Cross-plying hinders the elastic retractive forces from operating. Adhesion, in this case, comes about only after local melting of the more defective lamellae.

(Keywords: adhesion; orientation; polypropylene laminates; microstructure)

INTRODUCTION

Highly oriented polypropylene (PP), in film or fibre form, has been the subject of much interest in recent years[1-8]. This interest has come about as a result of the high moduli attained in the stretch direction with increasing draw ratios. However, in the uniaxially oriented film, the high strength and stiffness in the draw direction is nullified by extreme weakness in the transverse direction. Two approaches have been made towards solving this problem: biaxial stretching or orthogonal laminating of uniaxial films. Current methods of biaxial stretching have yielded PP films that are only moderately stiff in comparison to uniaxially oriented films[9]. Biaxial strength may also be achieved by cross-plying uniaxially oriented films perpendicular to each other. A major problem with this latter method has been that of developing adhesion between the plies so as to maintain the integrity of the laminate as a single unit, without simultaneously destroying the original strength and other physical properties of the films.

In this work, we have investigated adhesion in laminates made up of highly oriented PP and PP-copolymer films in an attempt to gain a better understanding of the molecular mechanisms underlying the process of adhesion in high modulus laminates.

EXPERIMENTAL

Characterization of as-supplied film

The PP and PP-copolymer films used in this investigation were supplied by the Army and Mechanics Research Center in Watertown, MA. The films were made by drawing extruded blown tubes to draw ratios of 14:1 by stretching in a radiant heat oven 170°C. The thickness of the drawn films was 0.0038 cm (0.0015 inches). The PP-

copolymer film contained 11% by volume of an ethene–propene block copolymer.

The films have been characterized by us, as shown in the following table:

Property	PP	PP-copolymer
Melting point	173°C	172°C
Density	0.9145 g/cm^3	0.9074 g/cm^3
Birefringence	0.0341	0.0307
Elastic modulus	12 GPa	7 GPa

The microstructure of the as-supplied films were characterized by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The SAXS patterns (*Figure 1*) show elongated meridional peaks and streaks in the transverse direction, indicating a fibrillar habit. TEM micrographs of replicas of the surface show this as well (*Figure 2a*) over much of the surface. Some lamellar structure is also observed (*Figure 2b*), though this is by no means dominant.

Sample preparation and characterization

Laminated samples were fabricated by stacking film plies orthogonally or parallel to each other. The laminates were then compression moulded at 2000 psi for 25 min over a range of temperatures. Pressure was found to have a significant effect on laminate properties as indicated in *Figure 3*. The operating pressure was maintained at 2000 psi throughout the remainder of this work, since adhesion was found to be at a maximum at that pressure. The observed maximum reflects the effect of two competitive factors: as pressure is increased, the likelihood of interaction across the interfaces is improved at the same time that immobilization of the chain segments occur.

In the annealing experiments, the film plies were separately annealed between aluminium foil at 160°C and

Densities were determined by a density gradient column using a carbon tetrachloride–toluene mixture.

Static mechanical tests were performed to determine the tensile modulus and the fracture stress. The specimen geometries used were specifically those for thin plastic sheet, as described in ASTM D 882-81.

Surface replicas for electron microscopy were prepared using platinum–carbon shadowing, and were removed from the substrate with poly(acrylic acid) solution.
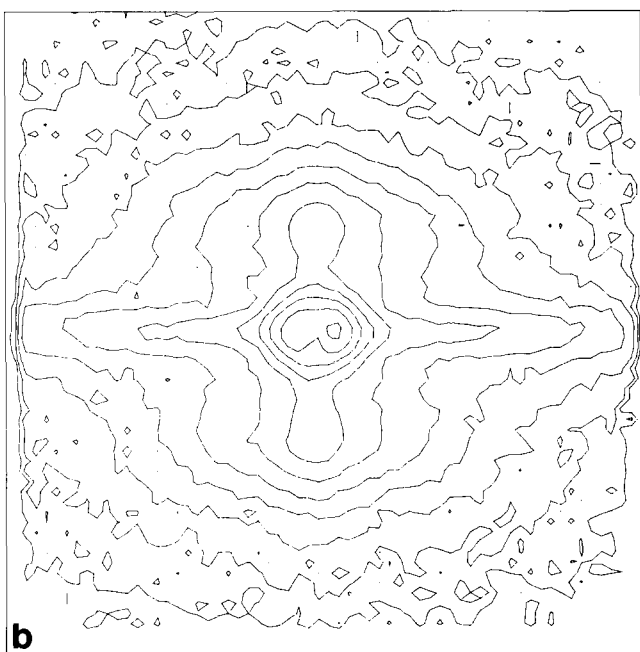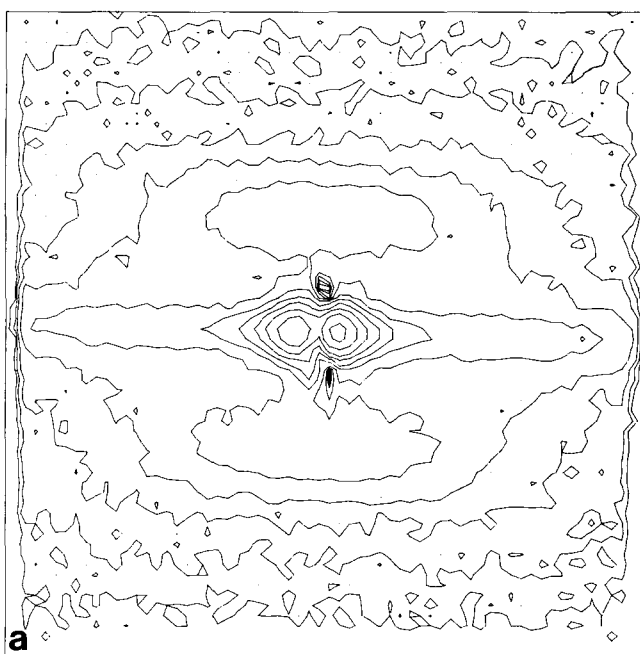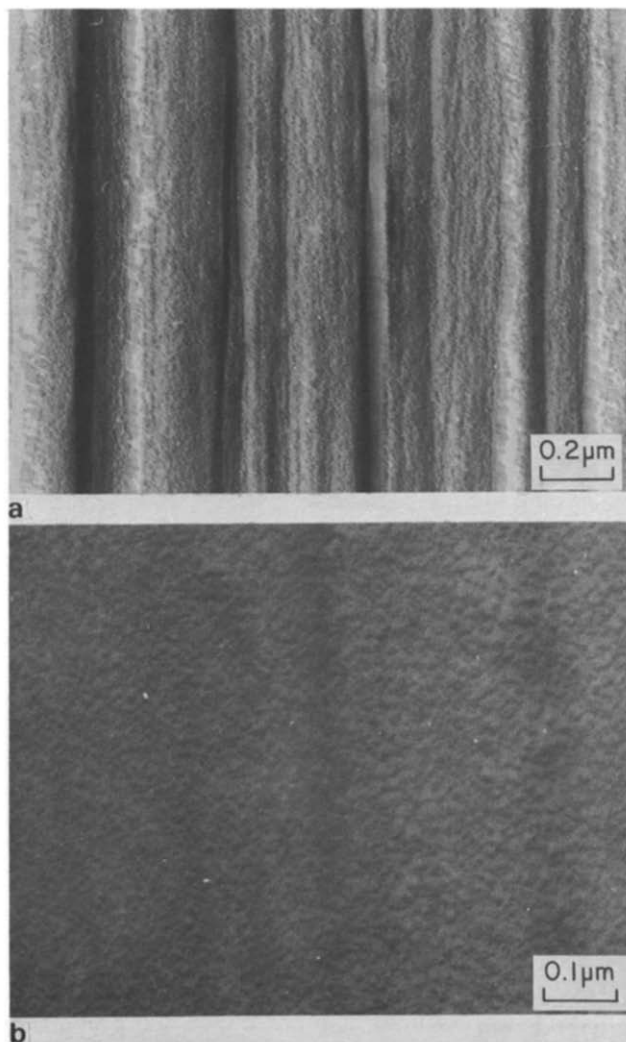

Figure 1 SAXS patterns of the as-supplied film: (a) PP; (b) PP-copolymer

Figure 2 Surface replica of the as-supplied PP film: (a) fibrillar; (b) lamellar

2000 psi for various annealing times prior to stacking and compression-moulding the laminates.

The compression-moulded laminates were characterized using birefringence, wide-angle X-ray scattering (WAXS), density measurements, mechanical testing and electron microscopy.

Birefringence measurements were made with a Zeiss polarizing microscope set up with an Eringhaus compensator. Specimens were prepared by peeling single lamina from the compression-moulded samples. Each measurement was an average of 7 to 13 such specimens.

WAXS patterns were taken with a pinhole camera. Nickel-filtered CuKα radiation of 1.54 ångstroms was used. Specimens from the parallel-plied samples were used as they were, while those from the cross-plied samples were prepared in the same manner as in the birefringence measurements.
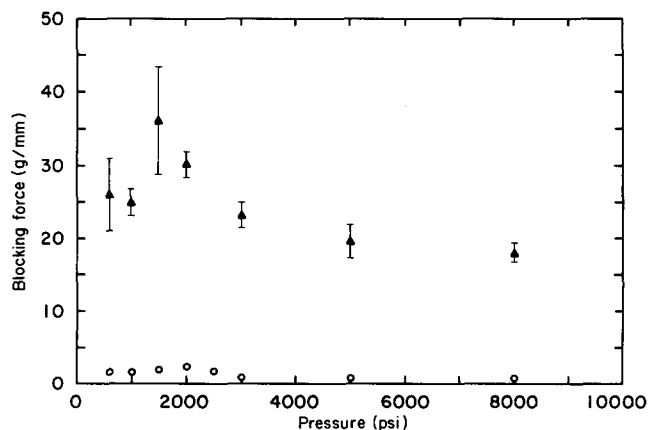

Figure 3 Blocking force as a function of moulding pressure in the cross-plied laminate. Moulding conditions: 173°C, 25 min: (O) PP; (▲) PP–copolymer

Adhesion measurements

Adhesion in the laminate was measured by a peel test, ASTM D 1893-67. *Figure 4* shows the test set-up. The fixture consists of a cylindrical bar supported on a frame. The force required to draw the bar through two adjacent plies at a constant speed of 5 inches per min (12.7 cm/min) was measured. The blocking force is defined as the recorded force per unit width. Five to eight specimens were tested for each sample.

RESULTS

Blocking force measurements

The blocking force was determined for both PP and PP-copolymer as a function of the moulding temperature, mode of stacking and annealing time. As expected, the adhesion in the laminate increases with moulding temperature (*Figure 5*). An interesting feature is observed
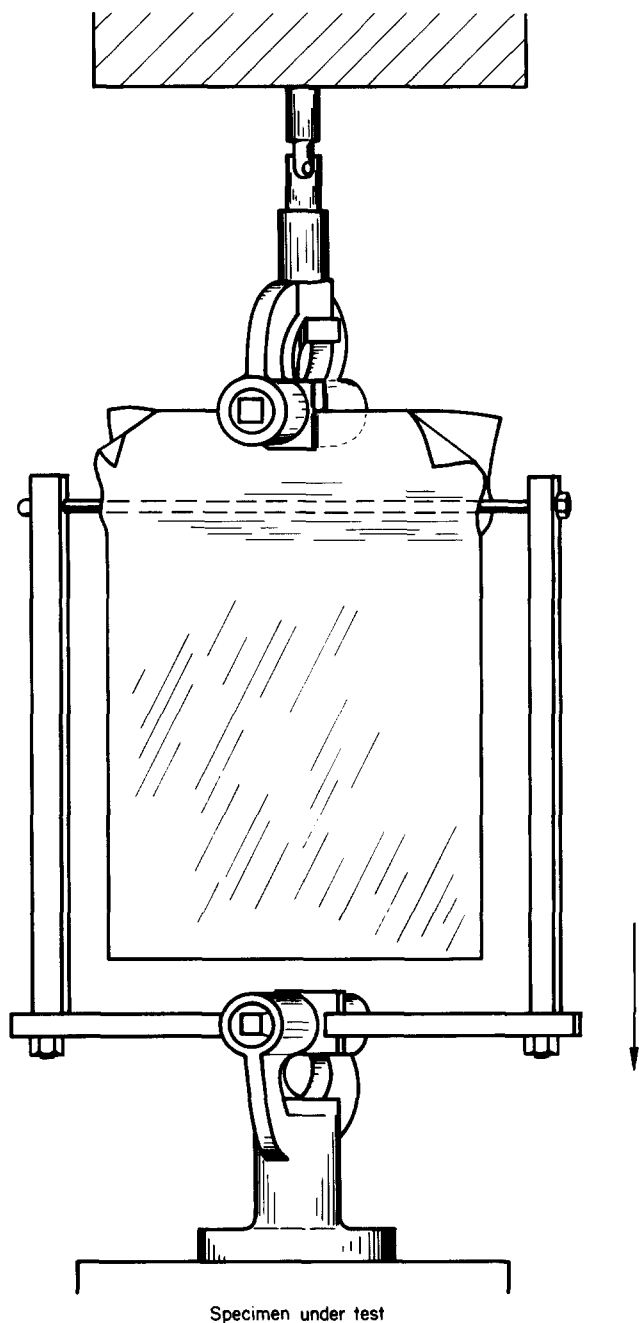
during peel testing of laminates made of parallel plies. At 167°C and above, the adhesive strength in the parallel-plied laminates grows strikingly higher with temperature, compared with that in the cross-plied laminate. For instance, blocking in parallel-plied PP-copolymer laminate at 174°C is 4 times higher than in the cross-plied laminate; in the PP laminate it is 8 times higher.

Annealing of the film plies prior to stacking and compression-moulding also has a differing effect on the adhesive strength of the two kinds of laminates. The films were annealed at 160°C and 2000 psi. The laminates were then compression-moulded at 174°C for 25 min at 2000 psi. *Figure 6* shows the peel test results. The parallel-
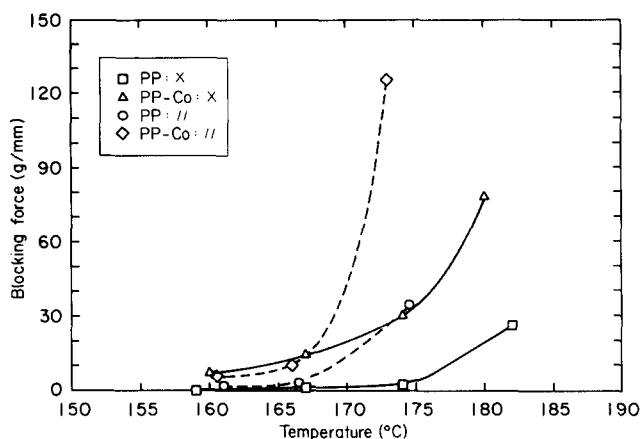

Figure 5 Blocking force against moulding temperature for cross- and parallel-plied laminates. Moulding conditions: 25 min, 2000 psi

Specimen under test

Figure 4 Fixture used in peel testing of the laminates (from ASTM D 1893-67)
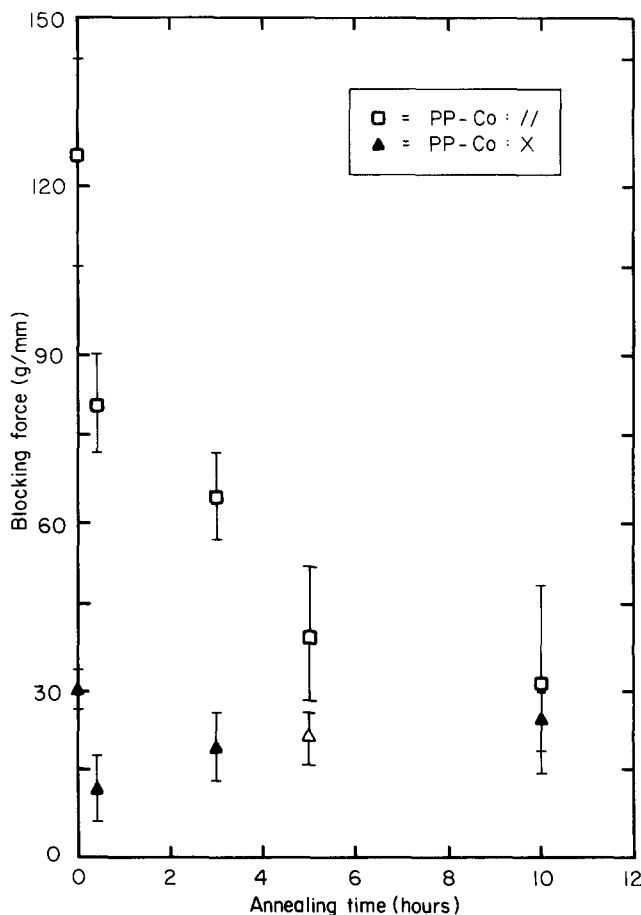

Figure 6 Blocking force against annealing time for cross- and parallel-plied PP-copolymer laminate. The films were annealed singly at 160°C and 2000 psi. The annealed films were then laminated and moulded at 174°C for 25 min and 2000 psi

plied laminate shows a sharp drop in blocking force with annealing time, whereas there is hardly any change for the cross-plied laminate.

Orientation measurements

The overall orientation of a polymer can be determined from its birefringence[10]. Assuming a two-phase system, the birefringence may be expressed as follows:

$$\Delta T = \beta \Delta_c^\circ f_c + (1 - \beta)\Delta_{am}^\circ f_{am}$$

where β is the crystalline volume fraction, Δ° is the intrinsic birefringence of the perfectly oriented phase and f is the orientation function. *Figure 7* shows that the birefringence in the cross-plied laminate decreases very slowly until about 183°C, when large-scale melting begins, after which it drops sharply. The parallel-plied laminate exhibits a greater decrease in its birefringence throughout the range 165°C and 190°C, indicating a larger degree of disorientation compared to the cross-plied laminate.

Annealing of the films at 160°C has no effect on the overall orientation (*Figure 8*).

The crystalline orientation function, f, is revealed in the WAXS diffraction patterns. WAXS pictures taken of cross- and parallel-plied laminates are shown in *Figure 9*. For the cross-plied laminate, the diffraction pattern remains relatively unchanged, compared to the as-supplied film, after moulding at 159°C, 167°C and 174°C. After treatment at 186°C some disorientation of the crystalline phase is inferred from the increase in the arc length of the reflections. In addition, the (110) a'-axis oriented reflections appear for the first time. The (110) and
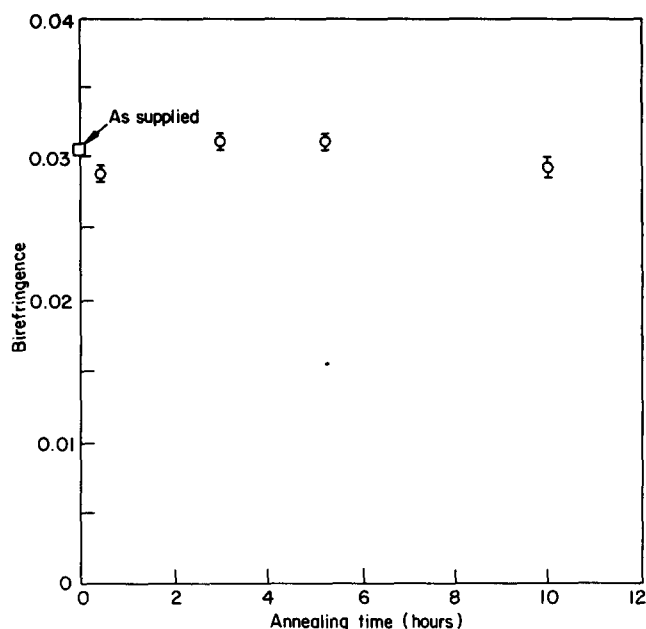

Figure 8 Birefringence against annealing time for PP-copolymer. Annealing conditions: 160°C, 2000 psi

(130) a'-axis oriented reflections have been observed in oriented isotactic PP fibres after annealing or melt-spinning at temperatures close to the melting point and are characteristic of high temperature treatment[10]. By 201°C, complete melting has occurred; the crystalline orientation is now entirely random, as indicated by the Debye rings.

In the parallel-plied laminate, the diffraction patterns also remain relatively unchanged after moulding at 160°C and 167°C. By 174°C, two things may be observed: (1) the arc lengths of the (130), (040), (110) and (111) reflections are increased compared to the corresponding arcs of the cross-plied sample, and (2) the (110) a'-axis oriented reflections can be clearly seen in the parallel-plied laminate but are absent in the cross-plied laminate. At 184°C, the degree of disorientation in the parallel-plied laminate compared to the cross-plied laminate is very noticeable; the arc lengths are much increased. In addition, the (110) a'-axis reflection shows up more strongly and the (130) a'- axis reflection appears for the first time.

Mechanical properties

Tensile modulus and fracture stress data are shown in *Figures 10* and *11*. In both PP and PP-copolymer laminates, a larger drop in the tensile modulus and fracture stress with moulding temperature for the parallel-plied laminate is observed, compared to the cross-plied laminate, causing a crossover in the two curves.

Shrinkage of the parallel plies in the draw direction was noted after moulding at 167°C and 174°C. At higher temperatures expansion induced by melt flow occurred. The cross plies remained dimensionally stable at 167°C and 174°C.

Transmission electron microscopy

TEM micrographs of surface replicas taken from debonded cross- and parallel-plied PP laminates moulded at 159, 174 and 183°C are shown in *Figures 12* and *13*. Replicas taken of compresssion-moulded single films at the same temperatures are shown in *Figure 14*.
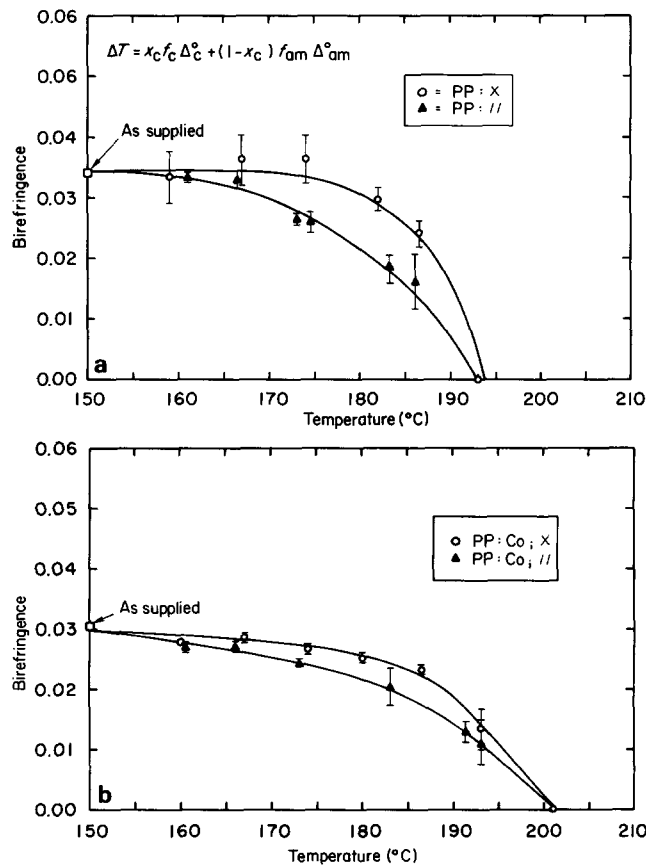

Figure 7 Birefringence against moulding temperature for cross- and parallel-plied laminates. Moulding conditions: (a) PP; (b) PP-copolymer
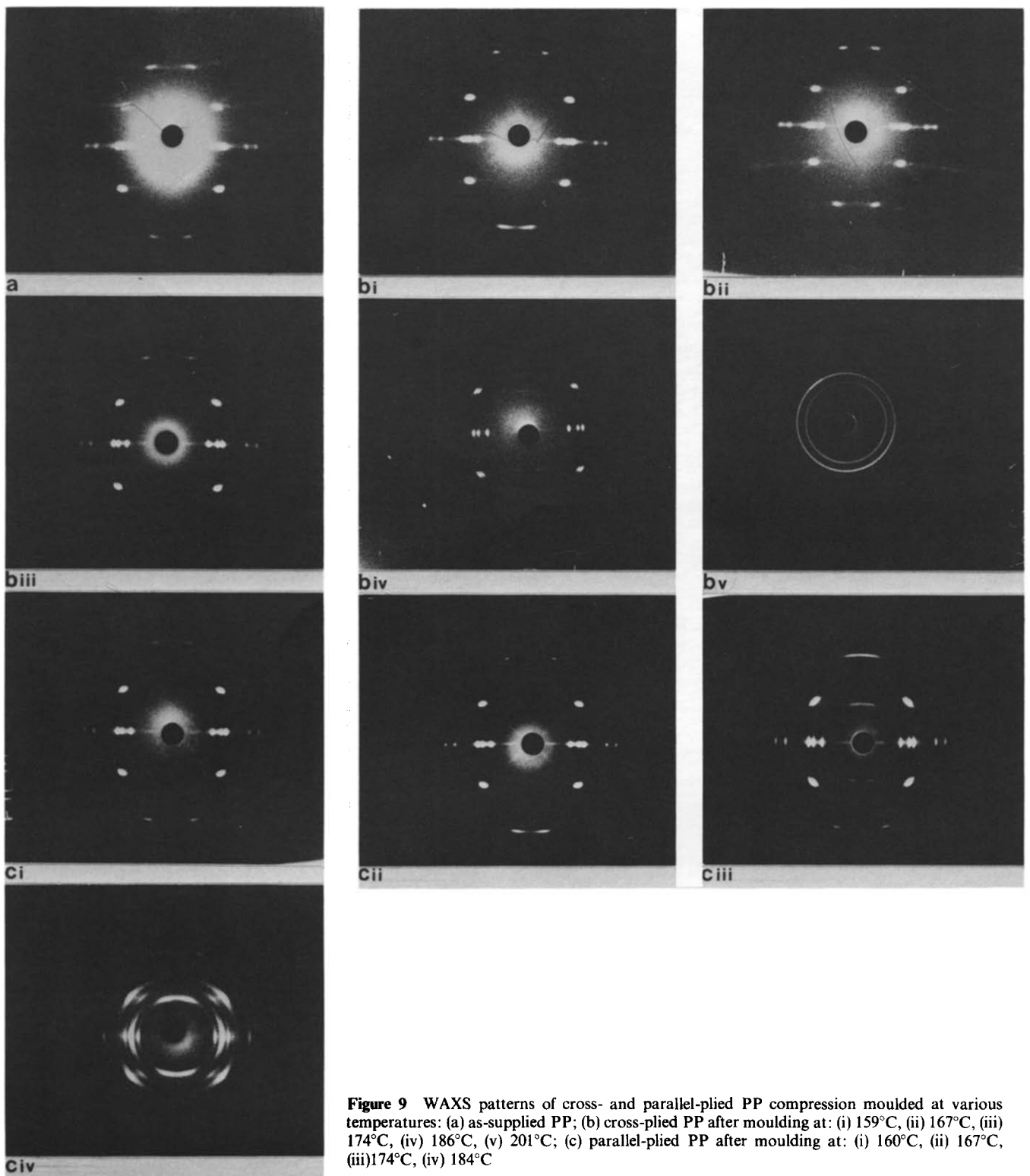
Figure 9 WAXS patterns of cross- and parallel-plied PP compression moulded at various temperatures: (a) as-supplied PP; (b) cross-plied PP after moulding at: (i) 159°C, (ii) 167°C, (iii) 174°C, (iv) 186°C, (v) 201°C; (c) parallel-plied PP after moulding at: (i) 160°C, (ii) 167°C, (iii)174°C, (iv) 184°C

After treatment at 159°C, the debonded surfaces of the cross- and parallel-plied laminates are relatively undistorted (*Figures 12a* and *13a*). This is consistent with the poor bonding strengths measured at that temperature. Note that the surface structure is now distinctly lamellar for the parallel-plied surface, whereas both lamellar and fibrillar habits are apparent in the cross-plied surface. The single film surface shows a lamellar microstructure as well. After moulding at 173°C, the debonded cross-plied surface shows some degree of distortion, but both lamellar and fibrillar structures are still recognizable (*Figure 12b*). It may be further noted that the fibrillar population has been reduced. In contrast, the parallel-plied surface shows a great deal of plastic deformation, with regions of highly drawn fibrils, as seen in *Figure 13b*. This is consistent with the large difference observed in bonding strength between the cross- and parallel-plied laminates after moulding at this temperature. Somewhat surprisingly, the cross-plied surface still exhibits small regions of fibrillar morphology after compression moulding at 184°C (*Figure 12c*).
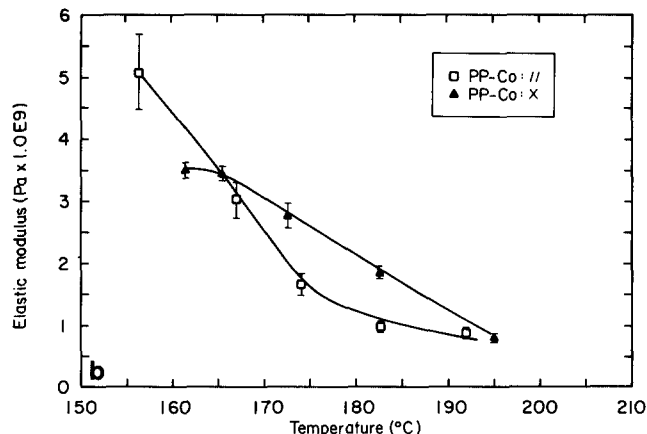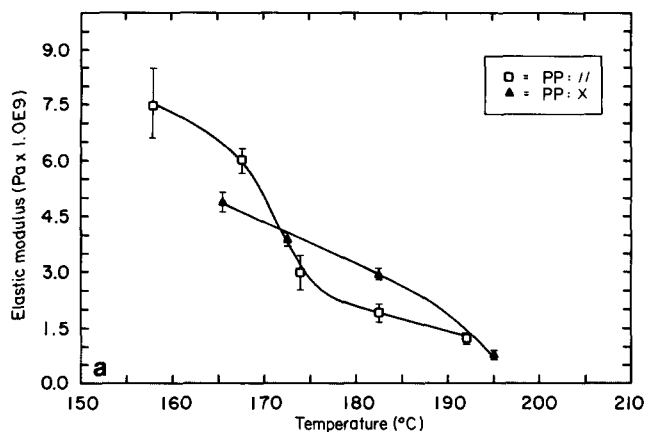
Figure 10 Tensile modulus as a function of moulding temperature for cross- and parallel-plied laminates: (a) PP; (b) PP-copolymer
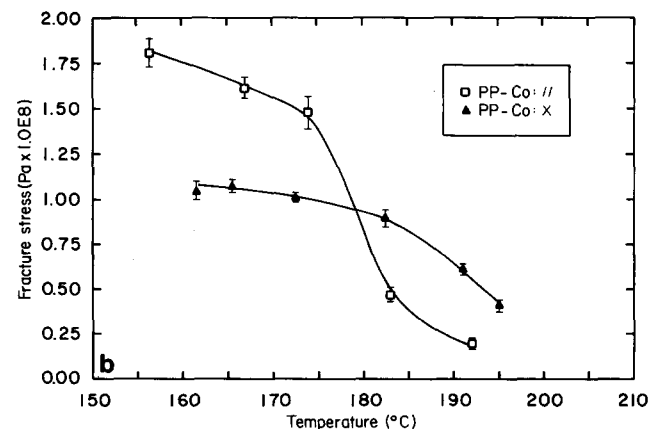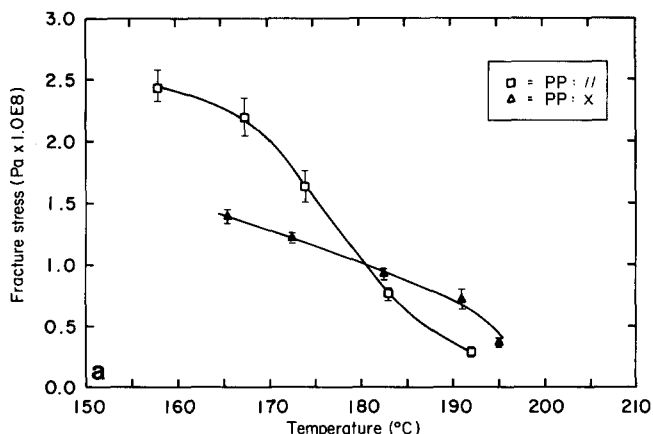

Figure 11 Fracture stress as a function of moulding temperature for cross- and parallel-plied laminates: (a) PP; (b) PP-copolymer
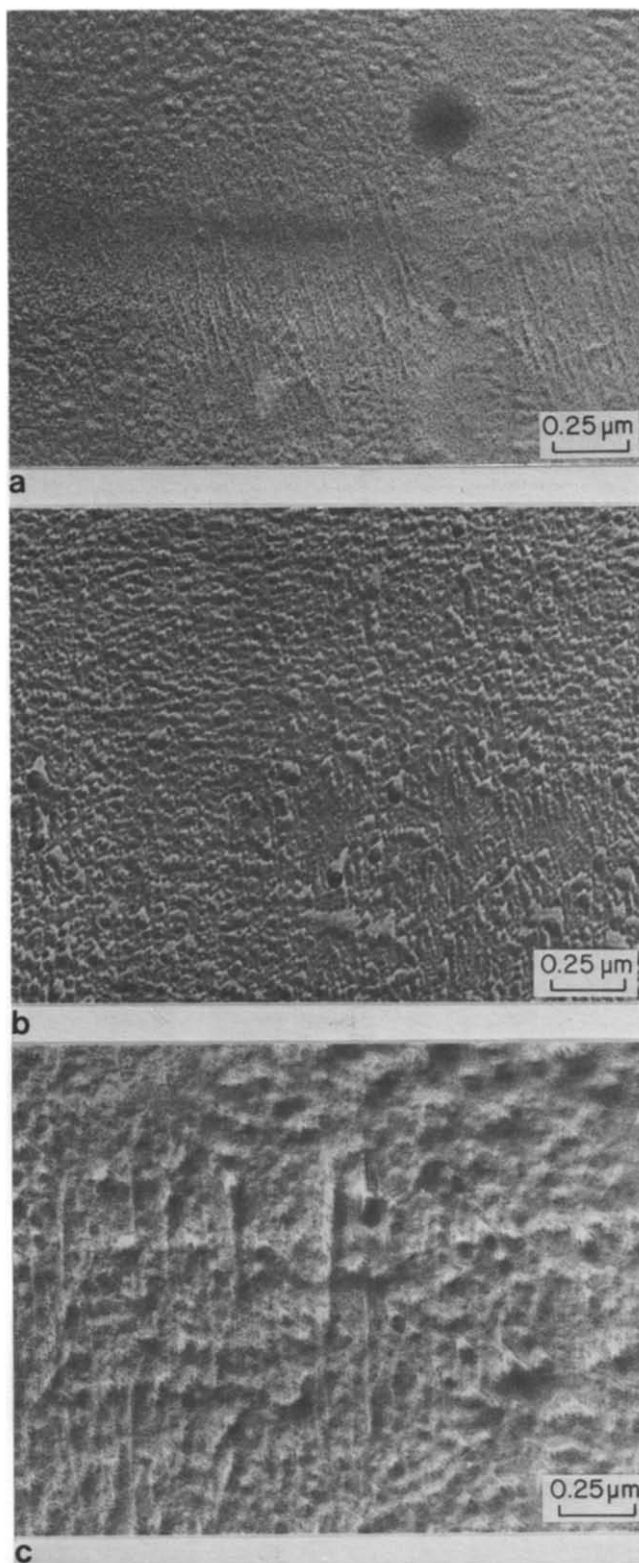

Figure 12 Transmission electron micrographs of replicas of debonded cross-plied surfaces compression-moulded at 2000 psi for 25 min and (a) 159°C; (b) 173°C; (c) 183°C

Surface replicas of the PP-copolymer films after annealing (but before plying and compression moulding) are shown in *Figure 15*. The lamellar thickness is observed to increase in thickness with annealing, from 210 ångstroms after 25 min to 331 ångstroms after 10 h. The crystallinity, determined through density measurements, shows an increase of approximately 3% over this time period (*Figure 16*).
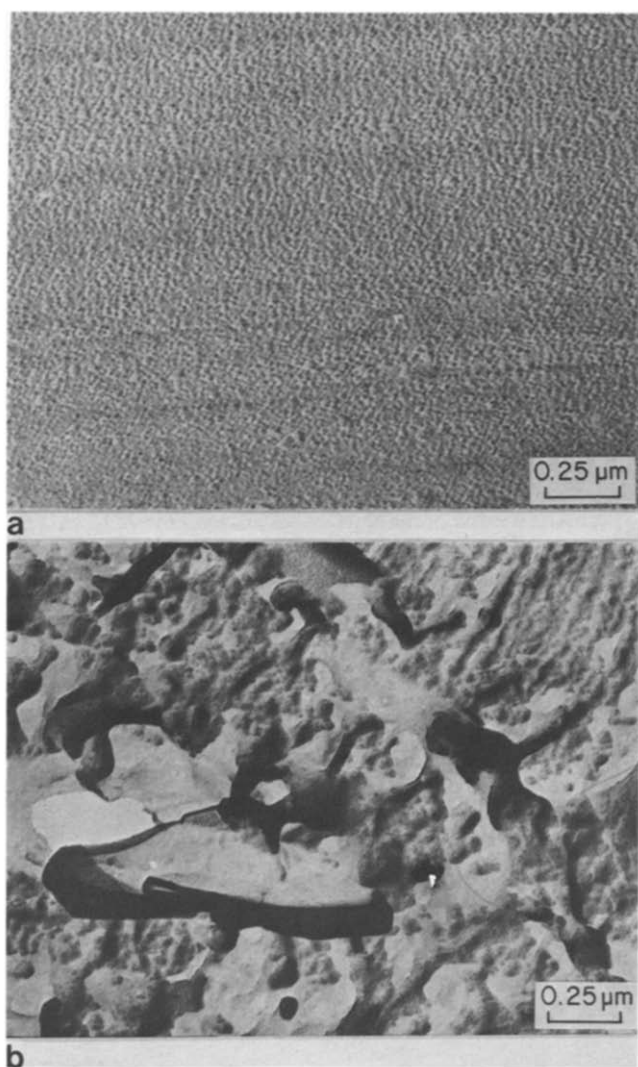
Figure 13 Transmission electron micrographs of replicas of debonded parallel-plied surfaces compression-moulded at 2000 psi for 25 min and (a) 157°C; (b) 174°C

DISCUSSION

A central result of the present work is the difference in the behaviour of parallel-plied and cross-plied laminates following bonding treatment. Relative to cross-plied laminates, parallel-plied materials exhibit much larger shrinkage and blocking force, but show steeper drops in birefringence and modulus with increasing bonding temperature. This difference in behaviour is a result of the interpenetration of molecules required for the physical healing process to occur[11-13], as sketched in *Figure 17*. The explanation follows.

Birefringence results show that the drawn films contain highly oriented tie molecules. Shrinkage and modulus decrement occur by the recoiling of such taut-tie molecules. The healing process occurs through the interpenetration of these same non-crystalline chain segments across the interlaminar interface. Thus, the difference in the behaviour of the cross- and parallel-plied laminates must originate in the re-coiling and/or interpenetration processes.

In *Figure 18(a)* two parallel-plied laminates are depicted. Here the amorphous region ABCD of sheet 1 can intertangle fully with the amorphous region A'B'C'D'

of sheet 2. These chains are free, given sufficient thermal motion for chains to re-coil and contract and for crystalline blocks to align with each other[14]. The chain re-coiling is responsible for the lowering of the modulus. For the cross-plied case shown in *Figure 18(b)*, amorphous chains in the zone ABCF of sheet 1 face the crystalline 'wall' A'B'C'F' in sheet 2. The chains in ABCF, unable to intertangle with the crystalline zone A'B'C'F', may contract only by raising their own density, an energetically costly process. The zone FCDE can intertangle with F'C'D'E', but a contraction of FCDE while ABCF is stationary would cause an energy-expensive elastic bending of the crystallites adjoining these regions in sheet 1. Consequently, adhesion in the cross-plied case can occur only after local melting of the crystalline 'walls', i.e. when the temperature is sufficiently high to melt the most defective or smallest crystallites.

In addition, such intertangling of adjacent cross-plied amorphous layers is inhibited by the shrinkage forces acting. The chains in FCDE re-coil in response to a contractile force acting to move the two lamellar surfaces toward each other. Many chain segments which had lain approximately perpendicular to the lamellar surfaces of sheet 1 now lay more nearly parallel to those surfaces and
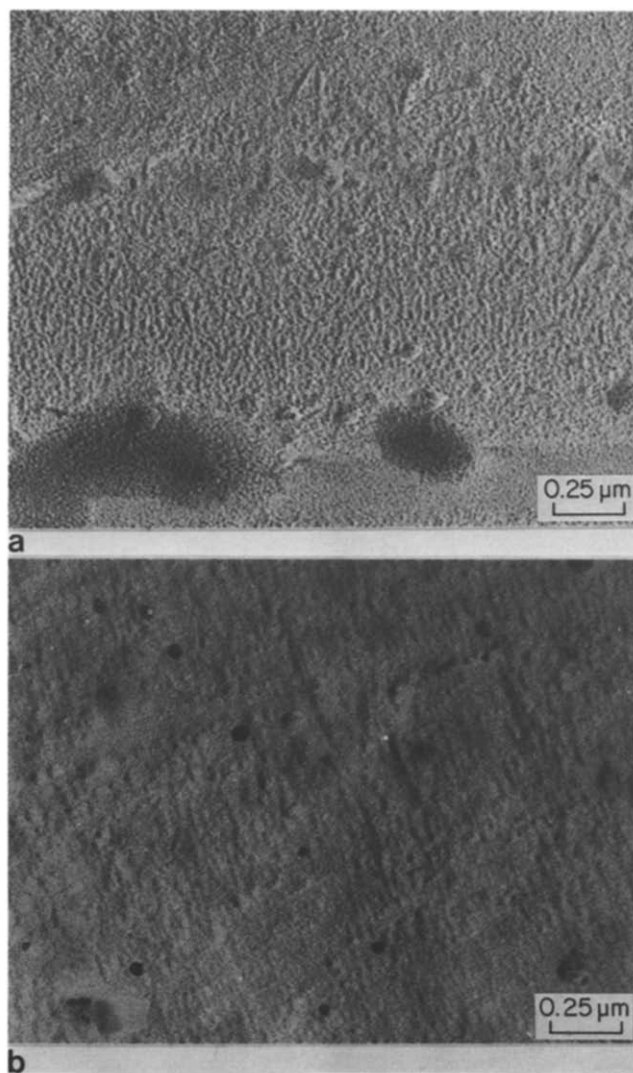

Figure 14 Transmission electron micrographs of replicas of single film surfaces compression-moulded at 2000 psi for 25 min and (a) 160°C; (b) 173°C
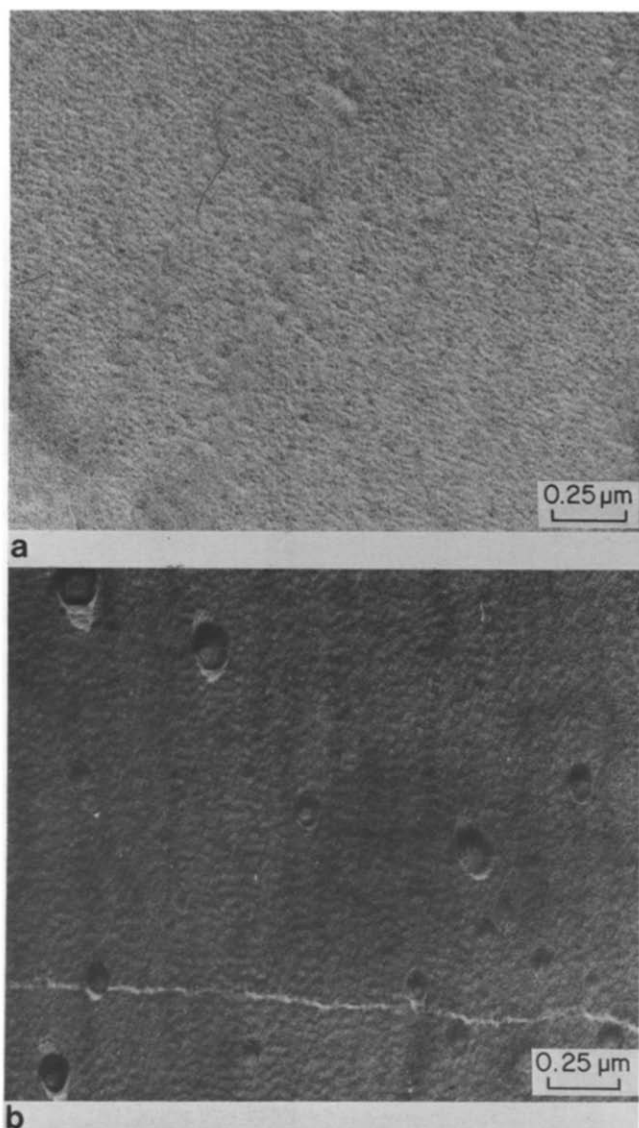
Figure 15 Transmission electron micrographs of replicas of annealed film surfaces. Annealing conditions: 160°C, 2000 psi (a) 25 min; (b) 10 h

174°C (*Figure 9*), whereas the amorphous disalignment and increase in the bonding strength had already been observed by 167°C (*Figures 5* and *7*).

The effect of amorphous relaxation is also carried over into the mechanical properties of the laminate. Initially, the tensile modulus in the parallel-plied laminate is higher than that of the cross-plied laminate, because the parallel plies contain approximately twice the number of extended chain molecules per unit cross sectional area in the testing direction. During heat treatment, contraction of the extended chains occurs in the parallel-plied laminate, resulting in a large drop in the tensile modulus (*Figure 10*). When the moulding temperature is sufficiently high, enough energy is imparted to the cross plies to allow shrinking and melting, so that both cross and parallel-plied tensile modulus approach the isotropic state. A similar argument may be applied to the fracture stress, which shows the same sort of trend (*Figure 11*).

A further implication arising from this model is the continued persistence of the fibrillar habit in the cross plies. The inability of the amorphous chains to penetrate the crystalline 'walls' acts to immobilize the tie chains, and thereby prevents the fibrillar-to-lamellar transition. This is borne out by the TEM micrographs in *Figures 12–14*. Notice the presence of fibrils even after treatment at 184°C in the debonded cross-plied surface and their absence in both the single ply and debonded parallel-plied surfaces. Studies of the fibrillar to lamellar transition[14,17] have noted that, for PP, the transformation occurs within minutes at 159°C under vacuum when no constraints are present.

constitute an expansive (tensile) force parallel to the lamellar surfaces. At the same time, the amorphous layer chains of sheet 2 exert a contractile force perpendicular to the lamellar surfaces in that sheet. These contractile forces are opposed by the expansive lateral forces in sheet 1. Similarly, the contractile forces in sheet 1 are opposed by the expansive lateral forces of sheet 2. The net effect is to inhibit chain re-coil in all sheets.

The results are all consistent with this basic model. Peel test results show that adhesion in the parallel-plied laminate is dramatically higher than that in the cross-plied laminate. In addition, the re-coiling occurring in the parallel-plied laminate should result in greater overall disorientation, as was observed from the greater drop in birefringence. The WAXS patterns show a larger degree of crystalline disorientation in the parallel-plied laminate as well. This is in line with the birefringence results since amorphous re-coil will eventually disalign the crystalline units through the interconnecting tie molecules. Such behaviour has been documented previously for poly(ethylene terephthalate) and nylon-6,6 fibres[15,16]. It is noteworthy that the crystalline disalignment in the parallel-plied laminate was visible in the WAXS from
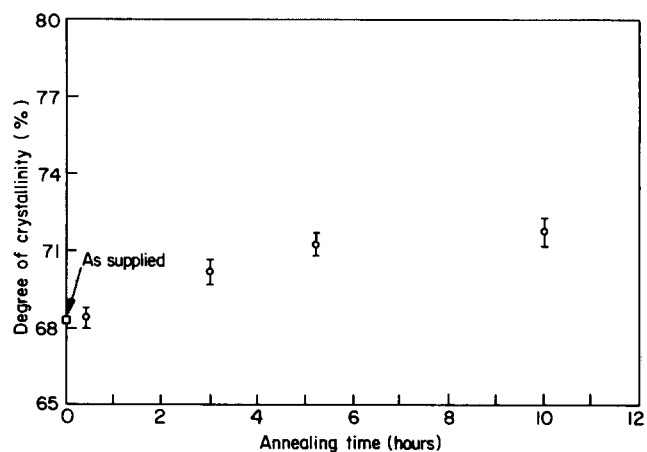

Figure 16 Degree of crystallinity as a function of annealing time: annealing conditions 160°C, 2000 psi
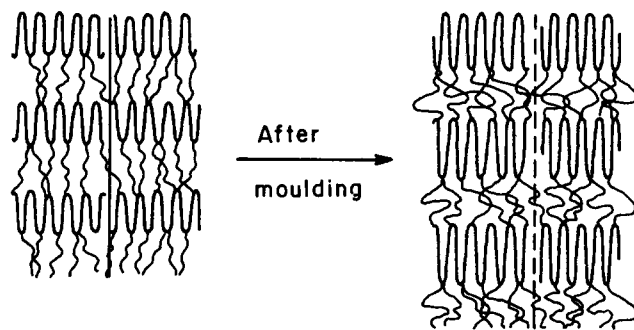

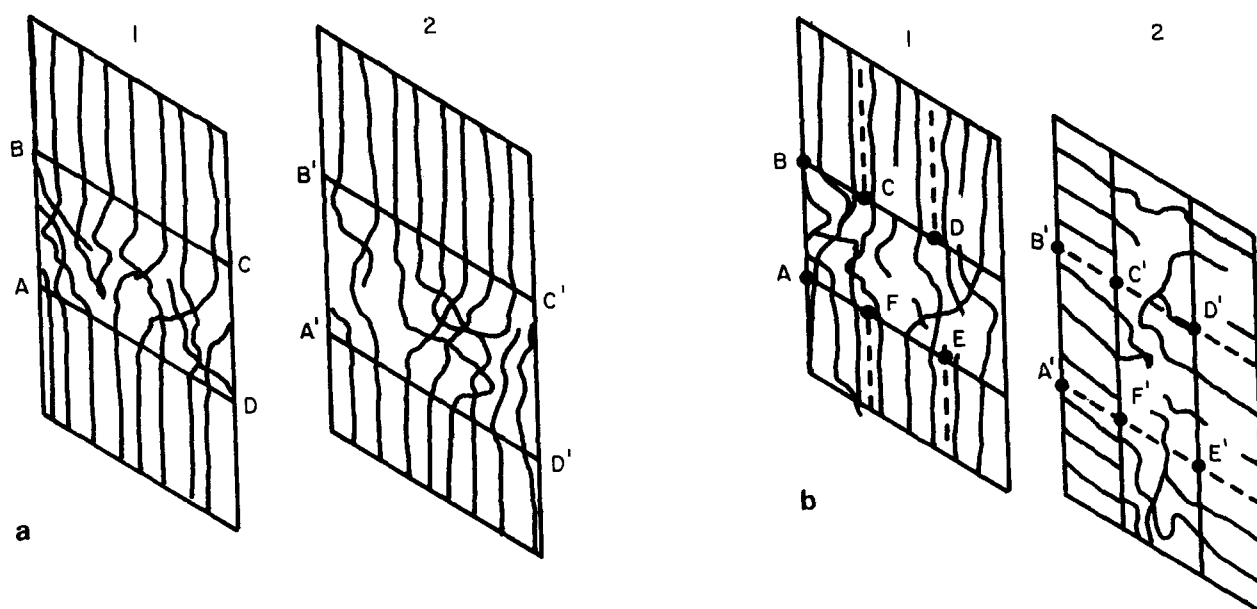Figure 17 Model for adhesion by interpenetration of amorphous regions

Figure 18 Parallel-ply (a) and cross-ply (b) laminate microstructures. In (a) non-crystalline chains in ABCD of sheet 1 can freely intertangle with chains in A'B'C'D of sheet 2. In (b), the crystalline region A'B'C'F' blocks the penetration of chains from ABCF into sheet 2

Annealing of the films at 160°C resulted in both an increase in the lamellar thickness, as seen from the TEM micrographs in *Figure 15*, and in the degree of crystallinity, as seen in *Figure 16*. The two factors serve to reduce the number of amorphous zones in the crystalline–amorphous assembly. For the parallel-plies, a result of this reduction is that the chances of having two amorphous zones from adjacent amorphous regions across the interface is lowered, and a drop in the bonding force in the parallel-plies should be observed with annealing time. Such a drop is seen in *Figure 6*. In addition, since adhesion in the cross-plied laminate is not largely due to amorphous re-coiling and subsequent entanglement, the reduction in the number of amorphous zones should have little effect. This has also been observed (*Figure 6*).

CONCLUSIONS

Adhesion in highly oriented PP laminates is strongly influenced by the mode of stacking and by annealing conditions.

In the case of parallel plies, adhesion arises primarily because re-coiling of the taut amorphous region causes entanglement of the chains across the interface between adjacent plies. Such a mechanism is prevented from occurring in the cross-plies at temperatures below melting because of the blockage by the crystalline 'walls'. Instead, bonding arises mainly through crystalline bridging across the interface after small-scale melting of the lamellae.

Annealing decreases the thickness of the amorphous zones, resulting in a reduction in the chances for entanglement across the interface. This has an effect on the parallel-plies but not on the cross-plies.

ACKNOWLEDGEMENTS

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