

Consolidation of High-Modulus PET Laminates and the Role of Chemical Healing

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Synopsis

In this work, a process for making high-modulus (8 GPa) laminates of poly(ethylene terephthalate) (PET) has been developed. Oriented films of the polymer were produced by a technique utilizing a very high extension rate, and these films were crossplied and consolidated to form the product laminates. The procedures for drawing the original film lamina and consolidating the laminates were optimized with respect to the material properties. Further, the possibility of chemical healing—bonding of the lamina together by chemical reaction, not diffusion—was investigated for these materials. It was found that laminates could be formed with both high moduli and strong interply bonding and that the moduli actually increase due to crystallization during pressing. Long-range diffusion during bond formation was ruled out, since crosslinked polyesters were found to bond as readily as uncrosslinked. Chemical reactions between contacted surfaces appear to be a likely mechanism of bonding.

INTRODUCTION

This work stems from three recent studies on polymer engineering. The first of these, a method for producing highly oriented films of thermoplastic polymers,¹ provides high-modulus lamina as the building blocks of laminates. The second, a study on bonding polypropylene laminates,² yields a goal of finding a new method for consolidation. The third, finally, is the key to our new method—the development of chemical reactions as a mechanism for mechanical bonding.³⁻⁶

Oriented Films

It is well known that desirable mechanical properties such as high stiffness may be imparted to a polymer by certain processing techniques. What a process must do to the film to give it good strength and stiffness is orient it, that is, cause the individual polymer molecules to be stretched in some preferred direction or directions.⁷ The most highly oriented forms of polymers are oriented in extensional flow, as opposed to shearing flow.⁸

One way of getting extra high extensional flow in polymers is high-speed spinning. This is based on the concept that the extension rate of the flow field directly affects the degree of orientation imparted. The extension rate, $\dot{\epsilon}$, is defined as

$$\dot{\epsilon} = v/l$$

where v is the spinning take-up speed and l is the flow length, or length over which the material flows before solidification. This relationship suggests a simple means of increasing the extension rate, and hence the orientation and modulus: an increase of the spinning speed. The technique of high-speed spinning of polyester fibers has been used with quite impressive results in attaining high moduli.⁹

The extension rate relationship suggests another way of increasing orientation, however. Rather than increasing the value of the take-up speed, which may require difficult adaptation of spinning machinery or delicate stability problems, the same change in the extension rate can be effected by decreasing the flow length. Petermann and Gohil have demonstrated a novel laboratory technique for film casting that does just that, producing remarkably high extension rates for polyethylene with only a few cm/s of take-up speed.¹ This method is diagrammed in Figure 1. A dilute (0.1–1%) solution of the polymer is prepared in an appropriate solvent, a portion is poured onto a glass plate heated to a specific temperature, and the solvent is allowed to evaporate. The polymer film is then peeled from the plate. The film stretches and solidifies almost immediately as it comes off the glass. The flow length as measured by a gold sputtering technique proves to be only a few thousand angströms, thus yielding extension rates as high as 40,000/s! Moduli of a number of polymer films produced by this method show high values. Further, the films may be cast thin enough ($\sim 1000 \text{ \AA}$) for direct study by transmission electron microscopy.

Such oriented films, of course, have the drawback of possessing poor mechanical properties in the in-plane direction perpendicular to the orientation direction. In fact, the higher the orientation, modulus, and strength in the extension direction, the worse this drawback becomes in the transverse direction. It would be useful to create a planar structural solid polymer which takes advantage of high orientation, but does not have such a vulnerable direction as a detriment. In the next section, a method to do so is suggested.

Laminates from Oriented Films

To obtain a planar structural material from highly oriented films which are strong and stiff in only one direction, a stack of these films could be bonded

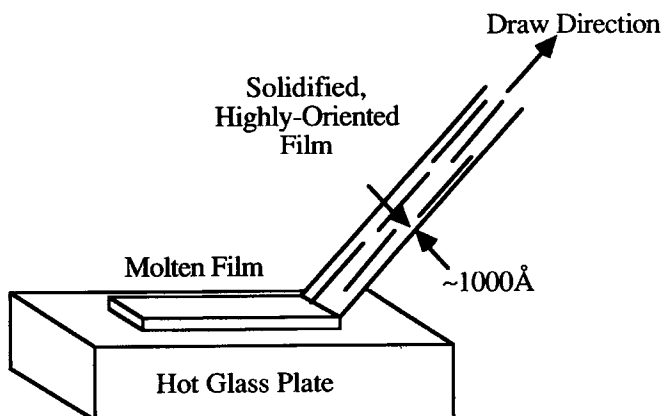


Fig. 1. Film-drawing technique.

with the layers oriented in different directions. In the simplest case, this means a stacking sequence of 0° , 90° , 0° , 90° , etc., as depicted in Figure 2. In this sequence, the weak direction of each layer is supported or reinforced by the strong direction of the adjacent layers, forming a laminate with no weak direction.

Structural laminates generally are designed to have desirable mechanical properties in all the directions in the plane without much concern for the properties in the through direction. One property that is crucial in this direction, however, is the toughness of the interlaminar bond or connection, since this is needed to transfer load from one layer to the next. If the individual layers have a preferential direction for their mechanical properties, this is especially important, since load in any direction must be borne by only some of the layers, not all of them.

However, there is a kinetic resistance to bonding of polymer interfaces. To join two pieces of polymeric material without chemical reaction, the molecules of one piece may be induced to diffuse into the other piece to a significant depth. Macromolecules, as compared to small molecules, interdiffuse at very slow rates, since they are intimately entangled with neighboring molecules and may undergo long-range motion only by *reptation*, the process of diffusing as though confined within a twisted tube.^{10,11} This microscopic situation is reflected in the macroscopic picture: the mutual diffusion coefficients for polymers are more than 10 orders of magnitude smaller than those of small molecules.¹² The problem is further complicated in the case of semicrystalline polymers (above the glass transition temperature), where crystallinity forms effective crosslinks which further preclude diffusion.¹³

Chemical transitions are a plausible means to this end. If a chemical reaction can be used to bond molecules in one ply with those in adjacent plies, interlaminar bonding could conceivably be formed without significant loss of orientation. Such situations have been found to exist; chemical interactions appear to play a major role in fiber/matrix adhesion in glass-reinforced composites,¹⁴ for example. For this work with polyesters, several reactions are available to potentially form bonds between molecules on opposite sides of an interface.

Chemical Healing

Several common chemical reactions may take place in condensation polymers, and some of these reactions may form covalent bonds between contacted pieces of these polymers in the solid state. This process, *chemical healing*,³⁻⁶ leads to

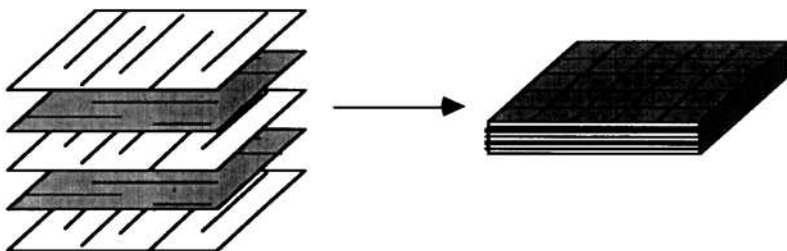


Fig. 2. Stacking and consolidation of laminate.

the development of mechanical bonding between the two pieces, as diagrammed in Figure 3.

Two basic classes of chemical reactions are of particular interest in the study of this phenomenon in polyesters: polycondensation and ester-interchange reactions. It has been reported that the most common mechanisms of both these reactions involve the attack of an ester linkage by a hydroxy end group, and that the rates, activation energies, and catalyst effects are therefore similar in magnitude for the two reactions.¹⁵ A number of detailed studies and reviews of these chemical processes have been reported previously.^{3,16-36}

These chemical reactions can be of use to consolidation of polymer laminates only if they can take place in the solid state. For the reactions of interest, solid-state rates are quite low compared with those at higher temperatures in the melt,^{24,26-29} though they may be raised significantly by the addition of transesterification catalysts (which are used in the commercial polymerization processes and are therefore present in most commercial polyesters). Also, it is reasonable that a small extent of reaction across an interface between two films can contribute greatly to the mechanical bond, since the connections thus formed are fully covalent bonds as opposed to simply partial entanglements. For example, it has been shown that a fairly strong bond can be formed between films of poly(ethylene terephthalate) (PET) consolidated at relatively low temperatures.³ Even in crosslinked polyamides, where diffusion is greatly suppressed, significant bonding has been obtained in the solid state.⁶ Thus, chemical reactions are a potential mechanism for the consolidation of high-modulus polymer laminates at mild conditions, thus avoiding deterioration of in-plane mechanical properties.

The goal of the present work is to combine several developments—the film-drawing method, the crossplying for in-plane strength, and the chemical healing phenomenon—to form a high-modulus laminate through use of chemical reactions to consolidate the system.

EXPERIMENTAL

The material chosen for this study was a polyester, owing to its relatively well-known chemical and physical properties and its utility to industry at present. The specific polyester, poly(ethylene terephthalate), was used due to its high stability and good mechanical properties.

Before considering the consolidation process, the film-drawing step was studied in detail. To make highly oriented films of PET, the procedure of Petermann and Rieck³⁷ was used. The best procedure found was as follows. High-

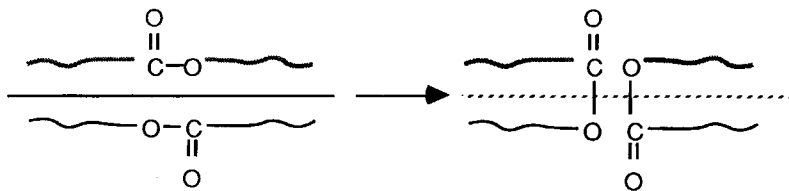


Fig. 3. An example of a bond-forming reaction across an interface.

molecular-weight PET ($M_w \approx 60,000$ g/mol), the grade commonly used in tire cords and injection molding, was used for this work. This was either Celanese 0.94 I.V. or Goodyear Cleartuf 1002A. The pellets were dissolved in trifluoroacetic acid at room temperature by magnetically stirring for several hours. The minimum polymer mass concentration, determined by that at which the drawn film does not readily tear, was found to be about 0.125% for the drawing temperatures of interest. A few milliliters of the dilute solution was poured on a thin (ca. 0.3 mm), level glass plate heated upon a temperature-controlled hot plate, and the solvent was allowed to evaporate. This left a PET film with uniform thickness on the plate. A bit of the edge was then picked up with tweezers and the film was wound around a glass plate or cylinder. Multiple layers, either parallel- or crossplied, could be built up for subsequent cutting into test specimens. After a batch of specimens was made in this manner, they were placed into a vacuum oven at approximately 50°C for at least 15 h to remove any residual trifluoroacetic acid and stored in a vacuum desiccator to prevent moisture uptake—a cause of hydrolysis at high temperatures.³⁸ The conditions of polymer mass concentration in solution and temperature of the glass plate were varied and the axial moduli of the films were measured. These data were then used to determine the optimum preparation conditions for the film lamina.

To measure the moduli of the films, parallel-ply stacks of 10–50 layers were cut axially into strips 0.5 cm wide and 5–8 cm long. These specimens were weighed on an analytical balance to determine their cross-sectional areas (using an assumed density of 1.385 g/cm³). The strips were tested in tension at a crosshead speed of 0.5 cm/min in an Instron Corporation Model TTCM universal testing machine. Their moduli were then calculated using the steepest tangent to the stress/strain curve before the yield point.

For consolidation of a laminate, it was necessary to have the stack in vacuum prior to heating and pressing to prevent hydrolysis by airborne moisture and to remove air bubbles from between the plies. It was therefore placed into the device shown in Figure 4. For specimens to be tensile-tested, the laminate was itself sandwiched between two sheets of Teflon film; for those to be peel-tested, the laminate was laid up as shown in Figure 5 with a nylon 6,6 backing layer.

For each consolidation, vacuum was drawn on the press device and it was slid into the preheated press, which was quickly closed to the desired force

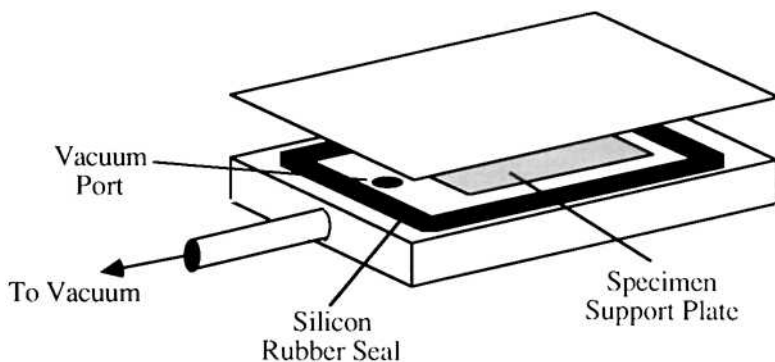


Fig. 4. Vacuum device used for pressing laminates.

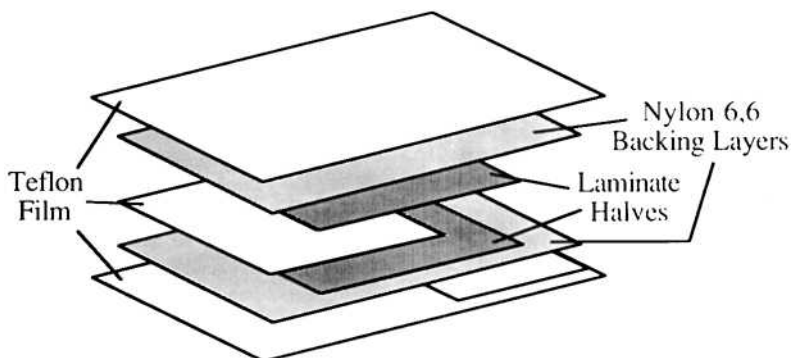


Fig. 5. Laminate lay-up for peel-test specimen.

level. After soaking at the desired temperature for the desired time duration, the pressure and vacuum were released and the film sandwich was removed and quenched between cold steel plates. The specimen was subsequently cut into strips for mechanical testing.

As with the film-drawing step, the consolidation step was optimized with respect to the final laminate properties. The process conditions varied were the temperature, time duration, and pressure; the final properties measured were the 0° modulus and the bond energy of the laminate.

The moduli of the laminates were measured in the same manner as those of the axially plied films, though the specimen lengths were generally 4–6 cm and their widths were approximately 0.4 cm.

Peel-test specimens were prepared as follows. The Teflon films were removed from the pressed stack which was then cut into 0.4-cm-wide strips. The free ends of each specimen were aligned into light plastic grips, used due to the low loads (< 10 g force) needed to peel. The gripped specimens were then mounted into the test machine and peeled at a crosshead speed of 0.5 cm/min (Fig. 6). The specimens were peeled completely apart and the load value to propagate peel was used to calculate the bond energy by the relationship

$$G_a = 2F/w$$

where G_a is the adhesion energy per unit area, F is the force to peel, and w is the width of the specimen. The factor of 2 appears because the actual length of the peeled area is half that of the crosshead travel.

It was also a goal of this research to determine whether the mechanism of consolidation of these laminates was likely to be chemical instead of physical. To test this, the fact that diffusion is severely hampered by crosslinking in polymers was used. Crosslinked polyester specimens were bonded and peel-tested, and the behavior of bond energy with respect to degree of crosslinking (measured by gel fraction) was examined.

Since PET requires prohibitively high radiation doses (> 1000 Mrad) for crosslinking,^{39–41} poly(butylene terephthalate) (PBT) was used for this part of the work; PBT presumably follows the same healing mechanism as the chemically and physically similar PET. PBT films were prepared by the same

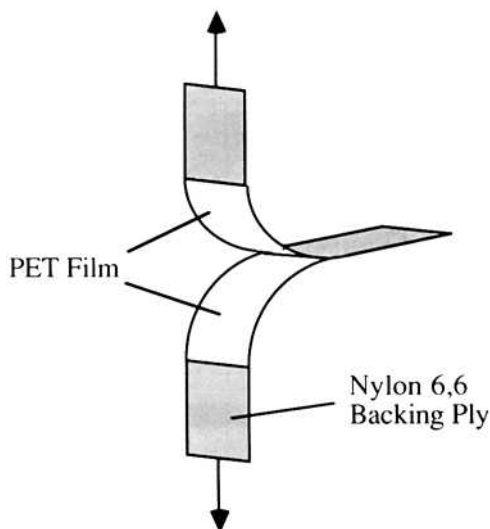


Fig. 6. Peel test for bond energy.

technique as the PET, except at higher draw temperatures (170–200°C) and solution mass fraction (0.5%). These were consolidated by the same technique described above, but with only one film on each side of the interface. To make PBT films of moderate gel fraction, 55%, a technique similar to that of Ref. 42 was used. Each film was placed in a test tube with powdered dicumyl peroxide (Hercules Di-Cup R) and the test tube immersed in a hot water bath carefully controlled between 45 and 60°C. This melted the peroxide which was allowed to be absorbed into the film for at least 20 h. The film was next removed from the peroxide melt, laid on a warmed ($\sim 55^\circ\text{C}$) glass plate, and spread out flat. The excess peroxide was then rinsed off with acetone. The material was cured immediately on a Teflon-covered glass plate under a nitrogen blanket at 0.7 atm and 170°C for 90 min. The oven was then evacuated and the film allowed to remain there for 90 min more for removal of the peroxide residue, which could also be further washed off with acetone.

To prepare PBT films of high gel fraction, 70%, two crosslinking steps were needed. At the start, the material was dissolved with 5 pph (parts per hundred) *N,N'*-*m*-phenylenedimaleimide (Du Pont HVA-2) as a crosslinking agent. Films made from this solution were next irradiated in a nitrogen-filled bag to a dose of 80 Mrad using a LINAC linear electron accelerator. (This radiation procedure is patented in Refs. 43 and 44.) Now starting from a gel fraction of 57%, the peroxide procedure above was followed to increase the gel fraction to its final value.

The PBT materials were bonded and peel-tested as above. To determine whether a significant change in crystallinity occurred in the crosslinking process, X-ray diffractometer scans were run on each type of unpressed specimen.

RESULTS AND DISCUSSION

Film Drawing

In the examination of the film-drawing process, it was found that only a certain range of polymer concentration in solution is practical. The lower limit

proved to be around 0.125%, below which the films readily tore during attempts to draw them. The highest value used was 0.5%; this value already showed a trend of decreasing modulus with increasing orientation, presumably due to decreasing stress on the flow region of the material during extension. Electron diffraction patterns made from the thinnest films showed very high orientation. The behavior of this orientation, as reflected in the axial moduli, is shown in Figure 7. There appears to be a maximum in modulus with respect to drawing temperature in the films made from 0.5% solution, with the highest value, about 7 GPa, occurring at 100°C. For films made from 0.25% solution, a maximum occurs at the same temperature, but has a considerably larger value—nearly 9 GPa. These moduli are quite high for a one-step process in drawing PET; they are comparable to those obtained commercially in fibers that are produced by the two-step process of spinning followed by cold-drawing.

Consolidation

For consolidation of the PET laminates, there were three process variables to consider—the temperature, time duration, and pressure of the pressing step. The temperature was varied from that which gave the first appreciable bonding, 150°C, to the melting peak temperature found for the films with fixed edges (Fig. 8), 250°C. The minimum time duration, about 2 min, was chosen to allow the press to reach isothermal conditions; the maximum was chosen to be 100 min, since embrittlement became a problem at longer times in the high-temperature range of most interest. The lowest pressure, 8 MPa, was determined by the minimum to still afford good wetting, and the highest pressure, about 45 MPa, was the maximum possible for the press used at its force limit (100 kN) and a reasonably large sample area of 23.7 cm².

The moduli of the laminates were found to actually increase with temperature over much of the pressing-time range studied (Figs. 9 and 10). This is in contrast with the behavior of oriented polypropylene laminates² studied by Lee and Schultz. Density measurements of selected specimens showed that this increase in moduli may be attributed to additional crystallization; the crystallinity of a

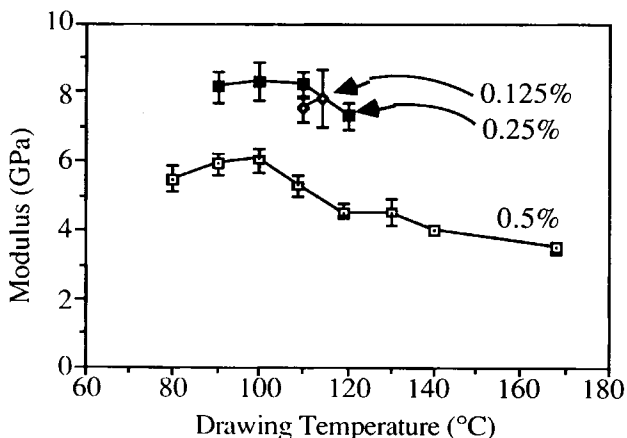


Fig. 7. Axial moduli of as-drawn PET films.

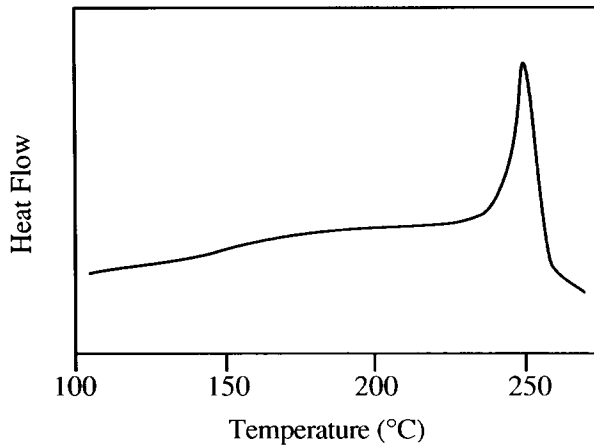


Fig. 8. Differential scanning calorimeter trace of as-drawn PET films with fixed edges. Heating rate = 20°C/min.

laminate of modulus 4.54 GPa (pressed at 150°C for 5 min) was 38%, while that of a laminate of modulus 8.07 GPa (pressed at 200°C for 100 min) was 56%. The optimum range (in terms of high modulus) in temperature and time duration appears to be from about 200 to 225°C and from 30 to 90 min, respectively. The modulus proved to be affected little or not at all by pressure (Fig. 11).

For adhesion energy, the effects of temperature and time duration were as one might qualitatively expect (Figs. 12 and 13); bond energy showed a monotonic increase with both variables. The range of temperatures and pressing times that was optimum for modulus proved to be very good for adhesion as well. The bond energies in this range are substantially higher than those possible from simply breaking covalent bonds (Fig. 14), indicating that plastic defor-

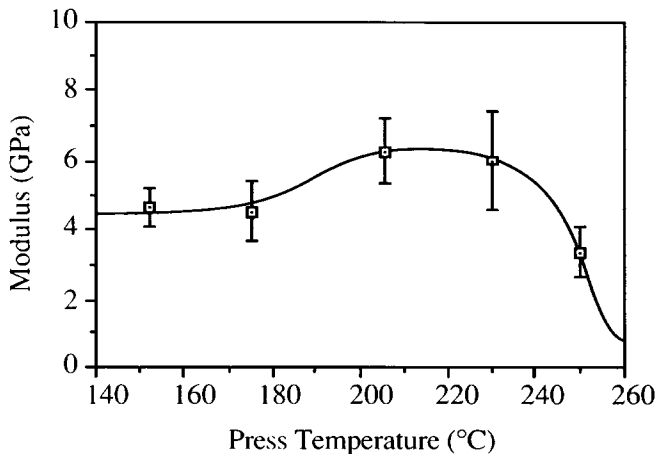


Fig. 9. Modulus of PET laminates as a function of press temperature. Pressing time = 5 min; pressing pressure = 29 MPa.

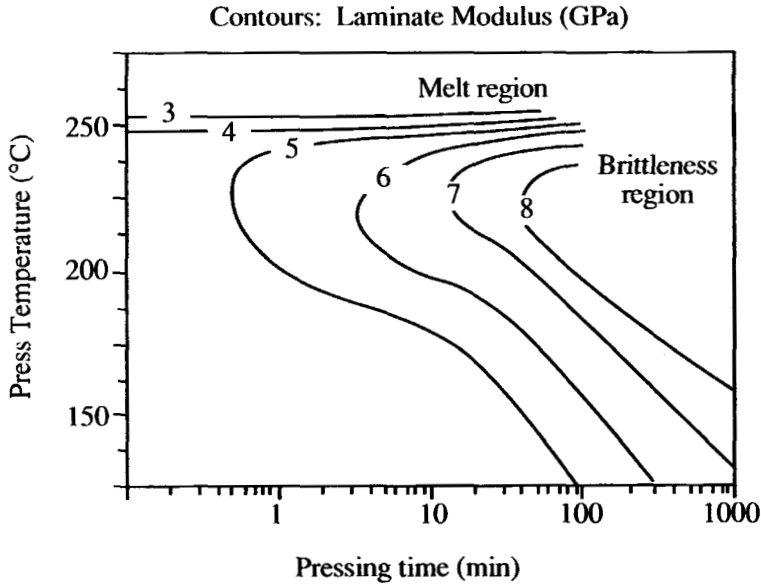


Fig. 10. Contour plot of modulus of PET laminates as a function of press temperature and pressing time. Pressing pressure = 29 MPa.

mation may be taking place in the vicinity of the interface. It appears, then, that the optimum-moduli laminates also are quite good in terms of bond toughness as well. Like the laminate modulus, the bond energy was largely unaffected by variation in pressing pressure (Fig. 15). Note that specimens pressed at room temperature, where no reaction or diffusion may be expected to occur, showed negligible adhesion (0.14 J/m^2).

Chemical Healing

In the study on the effect of chemical healing on bond energy, little effect of degree of crosslinking on bond energy was found (Fig. 16). The uncrosslinked

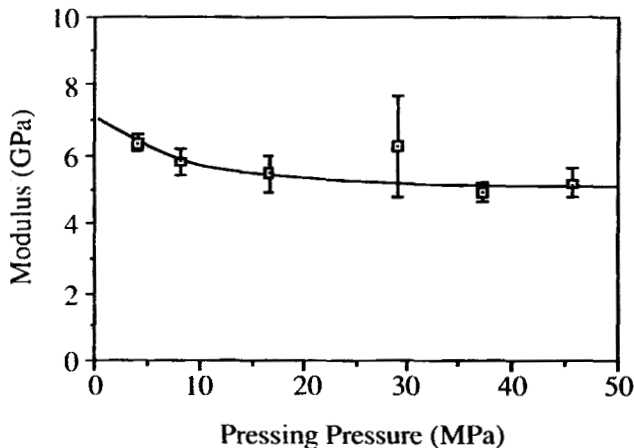


Fig. 11. Modulus of PET laminates as a function of pressing pressure. Press temperature = 200°C ; pressing time = 30 min.

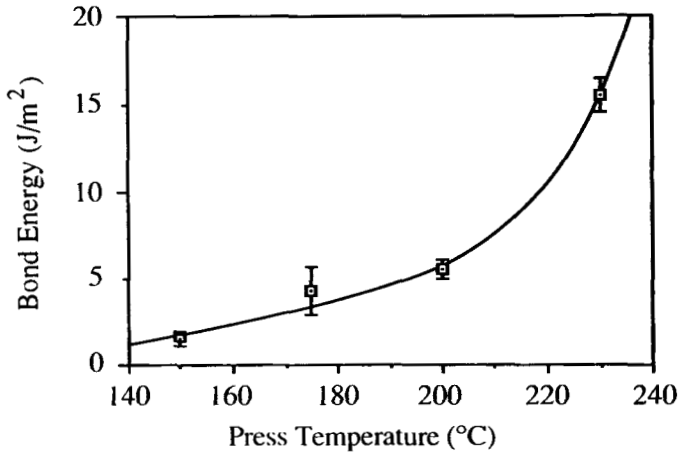


Fig. 12. Bond energy of PET laminates as a function of press temperature. Pressing time = 5 min; pressing pressure = 29 MPa.

(0% gel) specimens of PBT show the same type of press-temperature dependence as was seen for PET. The 55 and 70% gels, interestingly, show the same bond energies as the uncrosslinked at two different temperatures. Furthermore, X-ray diffractometer scans of the three PBT materials showed no significant difference in crystallinity, which could also affect diffusion. It appears, then, that the healing process for these polyester laminates does not depend on center-of-mass diffusion, since the diffusion required for physical healing is strongly

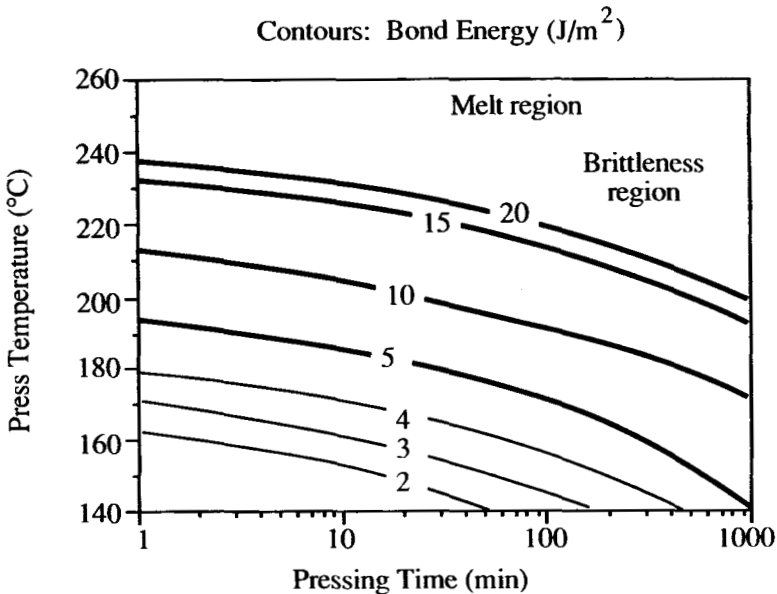


Fig. 13. Contour plot of bond energy of PET laminates as a function of press temperature and pressing time. Pressing pressure = 29 MPa.

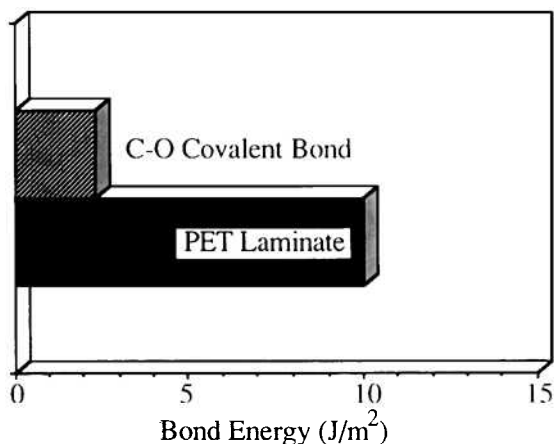


Fig. 14. Comparison of intrinsic bond energy of a carbon-oxygen covalent bond in a PET crystal to the adhesion energy in a typical PET laminate. The large value for the latter appears to be due to plastic deformation near the interface upon peel testing.

suppressed in the crosslinked material. Chemical reactions, which require only local motions, are therefore a likely mechanism for healing.

The trend of both crosslinked materials to show actually *higher* bond energy than the uncrosslinked may be a real one. The same phenomenon has been found in bonding of crosslinked and uncrosslinked nylon films, and it was attributed to increased reactivity of the amide linkages in the vicinity of crosslinks.⁶ This could stem from extra stress at these chain contact points, which would be relieved through interchange reaction with a neighboring chain segment.

Subsequent studies on the extents of solid-state polycondensation and ester-interchange reactions in these laminates have already shown that both these

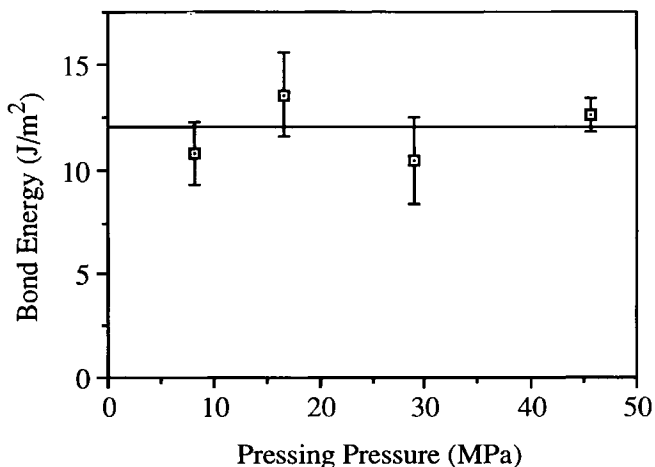


Fig. 15. Bond energy of PET laminates as a function of pressing pressure. Press temperature = 200°C; pressing time = 5 min.

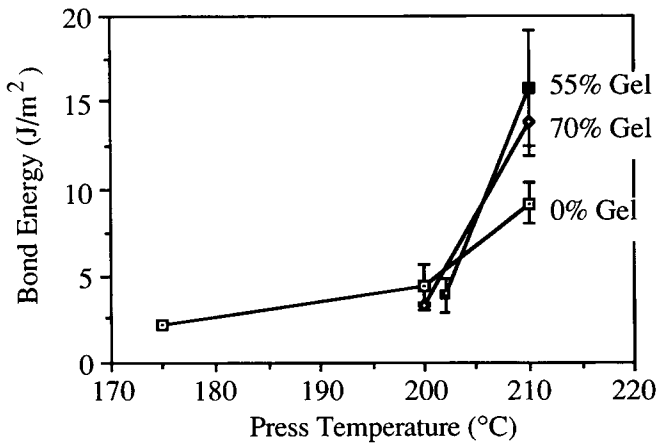


Fig. 16. Bond energy of crosslinked and uncrosslinked PBT laminates as a function of press temperature. The fact that crosslinking shows no negative effect on adhesion indicates that healing is by reaction, not diffusion. Pressing time = 5 min.

reactions proceed at significant rates in the bulk at the temperatures used for consolidation of these laminates. Further, it has been found that at least the polycondensation reaction occurs across the interface between two contacted plies. These findings, which will be forthcoming, serve as additional evidence that chemical reactions cause the bonding in these laminates.

CONCLUSIONS

This work showed that laminates of polyethylene terephthalate can be made with high in-plane moduli (8 GPa) and good interply bonding ($> 10 \text{ J/m}^2$) by preparing them from highly oriented films. It is also essential that the proper consolidation conditions are used to gain the optimum moduli. These conditions are:

$$200^\circ\text{C} < \text{press temperature} < 225^\circ\text{C}$$

$$30 \text{ min} < \text{pressing time} < 90 \text{ min}$$

pressure: high enough for complete wetting

The nondiffusive bonding formed in this consolidation process most probably arises from chemical reactions taking place across the interfaces in the film stack. This low-temperature adhesion is an advantage toward the goal of forming a high-modulus laminate, since the molecular motion needed for diffusional processes also leads to loss of orientation within the lamina themselves. A consolidation process such as this can form substantial bonding well below the melting temperature, and should be generally applicable to condensation polymer laminates.

Financial support from the National Science Foundation and the Plastics Institute of America is gratefully acknowledged.

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Received June 16, 1989

Accepted July 13, 1989