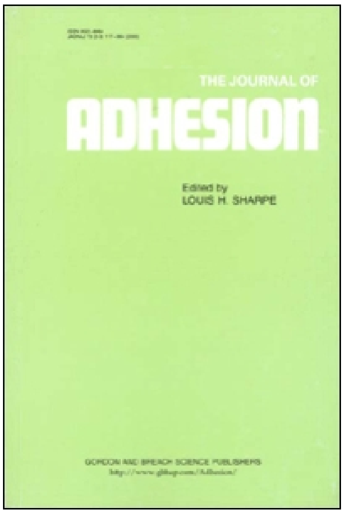

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Interlaminar Bond Strength and Failure Mechanisms in Commercial Flexible Polymer-Metal Laminates*

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An alternative to the 180° 'T' peel test (called simply the "T-peel test" in the USA) was developed by Cropper and Young for the measurement of interlaminar bonding in three-ply polypropylene-aluminium-polyester laminates used in food packaging applications. The effect of temperature on the interlaminar bond strength of three laminate systems has since been studied. In particular, the effect of temperature on both the failure mode and on the adhesive's appearance after testing has been determined. It is shown that as the temperature is raised about 23°C, the laminating adhesive begins to soften and the failure mode changes from almost exclusively adhesive failure at the polyurethane adhesive-aluminium interface to cohesive failure of the polyurethane adhesive itself. The change in the failure mode is accompanied by the appearance of a meniscus instability. The temperature at which the meniscus instability patterns become more prominent correspond to the temperature at which the maximum interlaminar bond strength is attained.

It is thought that this new test can be used to characterise the behaviour of laminating adhesives more fully, both in their change in appearance with temperature, and in their effectiveness in bonding layers together as temperatures are increased above ambient conditions.

KEY WORDS polymer-metal; polypropylene; laminate; polyurethanes; adhesive bonding; interlaminar bonding; bond energy.

1. INTRODUCTION

A test has recently been developed by Cropper and Young[1] to measure the interlaminar bond strength of flexible polymer-metal laminates. The test is similar to the cracked lap shear test (CLS) used by Johnson, Mangalgiri and Mall,[2,3] except that the CLS test is only related to rigid substrates. The new test has the advantage over conventional tests such as the T-peel test[4,5] of eliminating problems due to substrate bending. It also overcomes difficulties associated with high strength bonds where the substrate arms yield and/or fracture in preference to failure of the adhesive bond.

The test piece developed by Cropper and Young[1] is similar to a tensile test piece

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*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

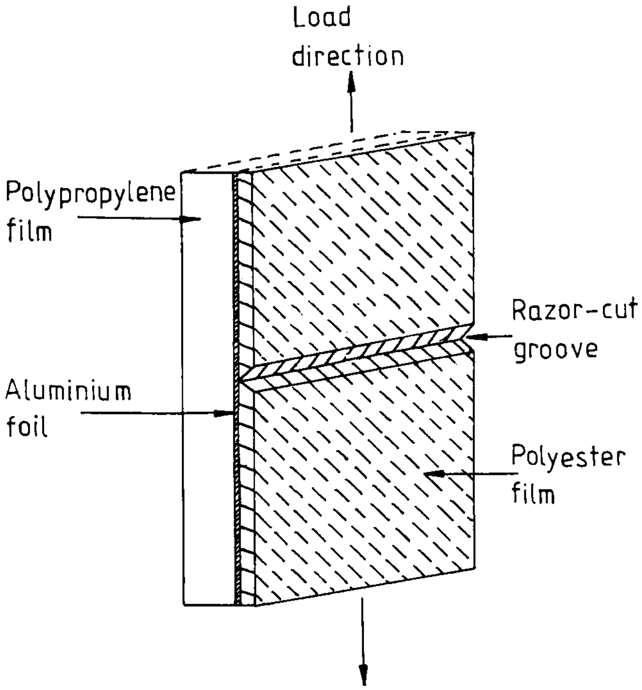

FIGURE 1 Bond test piece showing groove through polyester/aluminium layers of the laminate.

except that the laminate has a groove cut through the aluminium/polyester layers (Figure 1). Experiments were carried out in order to determine the effect of both test piece geometry and test conditions on the measured bond energy. Cropper and Young concluded that:[1]

(a) Above 15 mm, there was no significant effect of the specimen width on the measured bond energy
(b) The test piece gauge length was found to have no significant effect on the measured bond energy
(c) The bond energy was found to be independent of the final elongation of the test pieces
(d) The test speed had no effect on the measured bond energy in the range 20–200 mm/min
(e) Temperature had a significant effect on the measured bond energy. For the laminate systems studied, the bond energy was found to decrease in the range 18–40°C, then increase slightly as the temperature was raised above 40°C.

As a result of these studies standard text conditions were defined such that:

(i) All bond test pieces are of 50 mm gauge length
(ii) All bond test pieces are 25 mm wide
(iii) All bond test pieces are tested at a crosshead speed of 50 mm/min
(iv) All samples are tested to a final elongation of approximately 80 mm

Cropper and Young concluded[1] that the new test method appeared to be useful for comparing the bonding in polypropylene/aluminium laminates, particularly for high strength bonds which are difficult to measure by other methods. The test was found to be capable of highlighting differences in bond energy between laminates, while taking into account differences in geometry and film thickness which can affect peel test measurements.

The initial study by Cropper and Young[1] showed that the measured bond energy was significantly dependent on temperature. However, the temperature dependence on the bond strength of the laminates was not fully investigated. The object of this paper is to outline the bond strength *versus* temperature relationship of three commercial laminates, referred to here as "A," "B" and "C," and to determine the failure mechanisms of the adhesive in the laminates.

2. EXPERIMENTAL

2.1 Materials

The laminates used for the experimental work were three-ply polypropylene (PP)/aluminium (Al)/polyester (PET) laminates with the individual layers having nominal thicknesses of 50 μm, 9 μm and 12 μm, respectively. The layers of the laminate were bonded using a high-performance, polyurethane-based retort adhesive. This term refers to adhesives for laminates which are required to withstand sterilization treatments at temperatures above 100°C.[6] It is known that laminate manufacturers "B" and "C" use the same adhesive system, while laminate manufacturer "A" employs a different system. This paper is concerned principally with the test method and mechanisms of failure in the laminates. It is, therefore, not essential to know the full details of the chemistry or bulk properties of the adhesives employed at this stage. It is known that the curing behaviour and properties of these polyurethane adhesives are quite different in the bulk and when employed in laminates and this will be the subject of a future publication.[7]

2.2 Tensile Testing of PP Layer Samples

Sections of laminates were cut into 25 mm wide strips and dipped in THF solvent for 72 hours in order to separate the PP layer from the Al/PET layers. The separated PP layer samples were then washed, dried and mounted on window cards for tensile testing (the window cards ensured that the samples were of the desired gauge length and prevented sample slippage from the jaws during testing). It was found that once the films were dried the solvent had no effect on their properties. The samples were deformed on an Instron 1122 tensile testing machine (fitted with a 0.5 kN load cell and an Instron 3111 furnace) at a rate of 50 mm/min over a range of temperatures ($T = 23$°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C and 100°C). At each temperature tests were carried out on samples of different gauge lengths (G.L. = 20 mm, 30 mm, 40 mm and 50 mm) until five specimens had failed in the required manner at each gauge length, *i.e.* by yielding of the polypropylene followed by propagation of the yielded zone. From the data obtained graphs of plateau load *versus* gauge length were plotted in order to determine P_{0pp} at that temperature (P_{0pp} = Plateau load for PP film of zero gauge length).[1]

2.3 Bond Testing of Laminates

Bond test pieces were prepared by the standard method.[1] Testing of the samples was carried out on the same tensile testing machine (fitted with a 0.5 kN load cell and the same furnace), at a rate of 50 mm/min over a range of temperatures, until five test pieces had failed in the required manner at each temperature; *i.e.* by rapid failure of the Al/PET layers followed by yielding of the PP layer, accompanied by yielding of the PP/Al interface. Tearing or fracture of the PP layer was considered an invalid result as was yielding of the "bonding laminate" or re-adhesion of the Al to the freed PP adhesive. These failure modes invalidated the assumptions used to calculate the bond strength.

2.4 SEM Analysis of Failed Specimens

A selection of failed bond test pieces was prepared for SEM analysis by folding back the debonded Al/PET layers and inserting the samples on SEM stubs. The samples were then given a thin coating of gold using an Edwards S150B sputter coating unit. Once coated, the samples were viewed using Philips 505 or 525 scanning electron microscopes set at a voltage of 10 kV with a spot size of 50 nm and micrographs were obtained from features of interest.

3. RESULTS AND DISCUSSION

The results obtained from bond testing of the three laminates are given in Tables I–III and the variation of E_B with temperature is illustrated graphically in Figures 2–4. In this section the results will be discussed with respect to laminate "A," with laminates "B" and "C" being compared later.

TABLE I
Results obtained from bond testing of laminate "A"

Temp (°C)	P_B (N)	P_{0pp} (N)	ΔP (N)	X_f/A (m^{-1})	E_B (J/m^2)
23	56.1 (0.7)	38.7	17.4	167.0 (2.7)	2906 (127)
30	48.4 (1.0)	35.0	13.4	179.8 (5.2)	2412 (254)
40	40.6 (0.8)	29.9	10.7	177.3 (2.5)	1896 (152)
50	35.2 (0.5)	25.3	9.9	186.3 (2.2)	1843 (98)
60	34.8 (0.7)	21.0	13.8	195.8 (11.0)	2697 (153)
70	35.0 (0.7)	17.4	17.6	223.0 (17.3)	3814 (222)
80	26.2 (0.4)	14.3	11.9	184.8 (3.8)	2201 (124)
90	21.3 (0.5)	11.8	9.5	185.1 (4.0)	1758 (114)
100	18.5 (1.1)	9.6	8.9	171.3 (5.3)	1527 (213)

Figures in parentheses are 1 standard deviation, calculated from a minimum of five results.

TABLE II
Results obtained from bond testing of laminate "B"

Temp (°C)	P_B (N)	P_{0pp} (N)	ΔP (N)	X_f/A (m^{-1})	E_B (J/m^2)
23	48.1 (0.3)	37.1	11.7	163.2 (5.2)	1899 (17)
30	44.6 (0.4)	33.8	10.8	168.0 (4.3)	1827 (99)
40	39.3 (0.3)	29.5	10.0	165.0 (4.4)	1618 (41)
50	34.4 (0.5)	25.3	9.1	172.8 (3.9)	1574 (142)
60	31.5 (0.4)	21.5	10.0	167.9 (6.4)	1678 (73)
70	27.7 (0.4)	17.7	10.0	175.7 (4.5)	1756 (83)
80	24.7 (0.6)	14.4	10.3	177.2 (4.6)	1824 (89)
90	20.5 (0.5)	11.3	9.2	181.2 (11.8)	1671 (196)
100	17.9 (0.6)	8.7	9.2	169.7 (4.2)	1568 (109)

Figures in parentheses are 1 standard deviation, calculated from a minimum of five results.

TABLE III
Results obtained from bond testing of laminate "C"

Temp (°C)	P_B (N)	P_{0pp} (N)	ΔP (N)	X_f/A (m^{-1})	E_B (J/m^2)
23	45.3 (0.3)	35.9	9.4	177.3 (15.3)	1656 (126)
30	42.2 (0.8)	32.4	9.8	179.7 (8.4)	1765 (226)
40	37.8 (0.4)	27.9	9.9	183.6 (4.4)	1781 (120)
50	32.0 (0)	23.6	8.4	188.0 (4.7)	1579 (40)
60	27.9 (0.4)	19.8	8.1	186.9 (8.2)	1512 (57)
70	24.8 (0.3)	16.0	8.8	185.6 (3.9)	1633 (53)
80	21.3 (0.4)	12.7	8.6	196.3 (11.5)	1690 (162)
90	19.0 (0.5)	9.7	9.3	188.3 (14.0)	1753 (205)
100	16.6 (0.4)	7.1	9.5	177.3 (15.3)	1656 (126)

Figures in parentheses are 1 standard deviation, calculated from a minimum of five results.

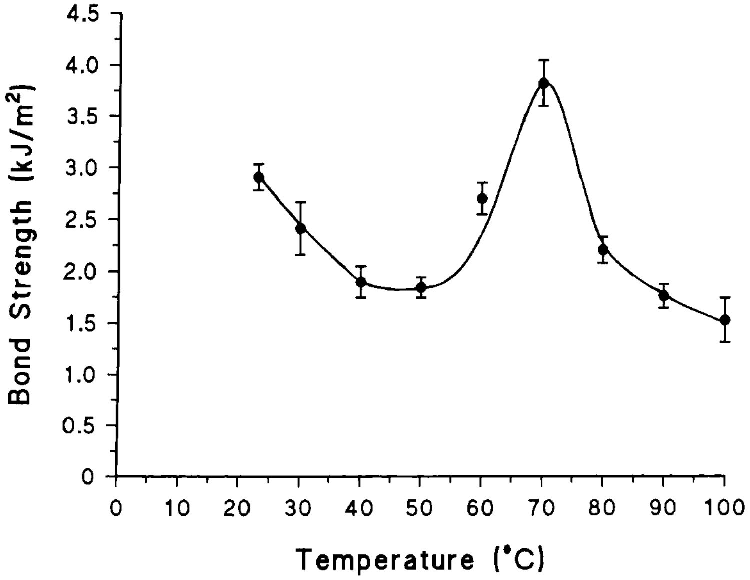

FIGURE 2 Plot of bond strength *versus* temperature for laminate "A."

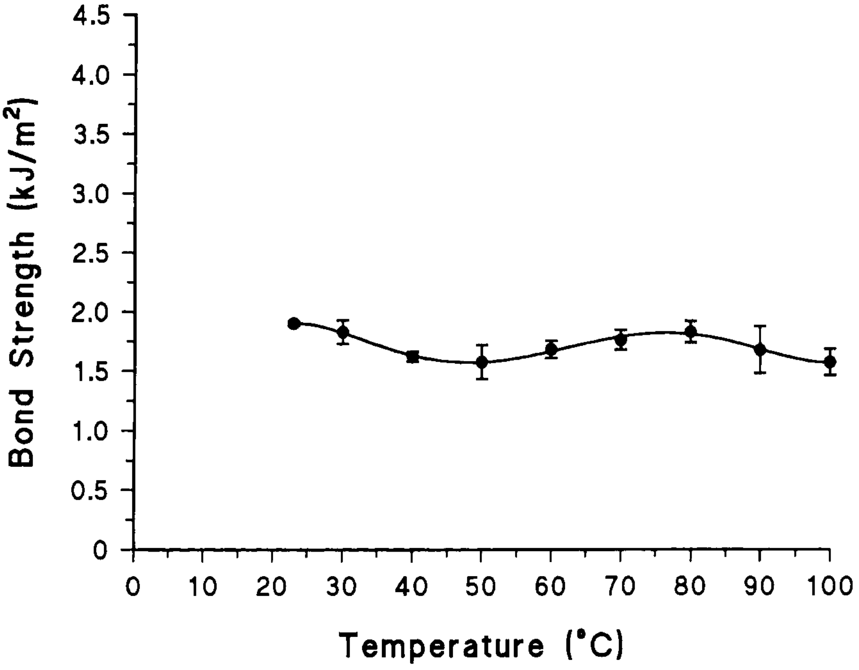

FIGURE 3 Plot of bond strength *versus* temperature for laminate "B."

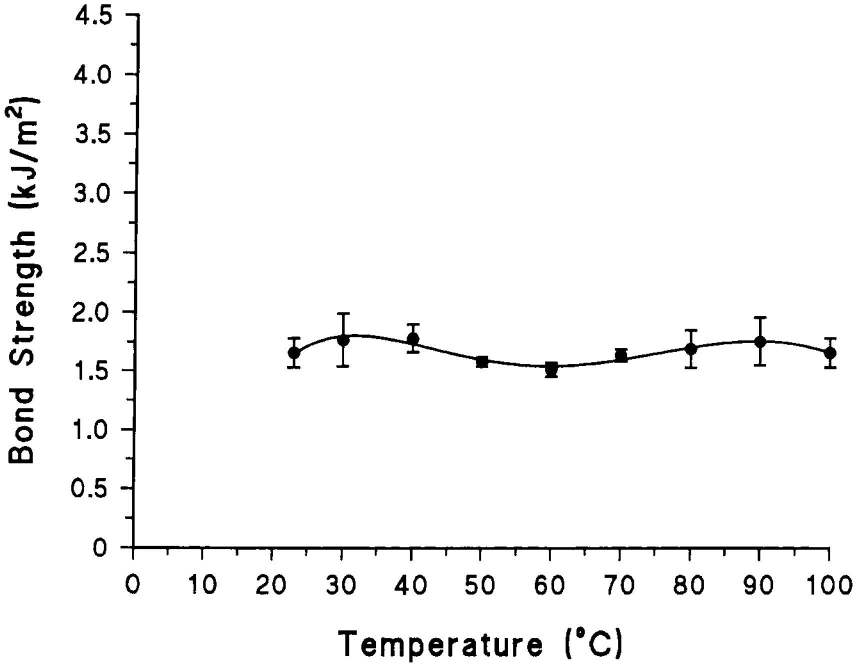

FIGURE 4 Plot of bond strength *versus* temperature for laminate "C."

3.1 Laminate "A"

3.1.1 Bond strength measurements The interlaminar bond strength is given by the following equation:[1]

$$E_B = \frac{X_f \Delta P}{A} \tag{1}$$

where X_f is the final elongation of the samples, A is the area of separated laminate, and ΔP is the difference between the plateau loads for the bond test piece and for testing of zero gauge length polypropylene.

From Table I it can be seen that for laminate "A," there is a close correspondence between the variation of bond strength with temperature and that of ΔP. The bond strength *versus* temperature curve in Figure 2 can be divided into three main regions:

(1) 23°C–50°C: In this region the bond strength decreases due to the value of P_B falling more rapidly than the value of P_{0pp}. As the overall dependence of P_{0pp} with temperature follows a smooth curve it can be assumed that the change in bond strength is not due to changes within the polypropylene film. Indeed, the bond strength analysis has been developed to account for the contribution of the polypropylene film.

Hence, it is thought that the decrease in temperature in this range is due to a weakening of the adhesive as reported elsewhere.[8] Although the bond strength decreases in this range, the mechanism by which the adhesive weakens is not fully understood.

(2) 50°C–70°C: In this range the bond strength increases until it reaches a maximum value at 70°C. Previous studies on polyurethanes[8] have shown that although most properties such as modulus, elongation to failure and tensile strength decrease with temperature, the tear strength did not decrease although no explanation could be found for this behaviour. However, it is known that polyurethanes can be cured in the range 23°C–150°C.[9] More recently cure temperatures in the range 60°C–80°C[10] have been suggested, presumably because the adhesives attain their maximum strength at this temperature. The curing step acts to cross-link the polyurethane and it is possible that the adhesive used in the laminate was not fully cured.

(3) 70°C–100°C: In this region the bond strength falls rapidly with temperature. It is known that polyurethanes exhibit very low bond strengths above 80°C.[11] The mechanisms by which the adhesive weakens are not fully known but the adhesive is thought to soften. The softening of the adhesive is dependent on several factors, these including:

   (i) Polyurethanes mixed using aliphatic acids are softer and more flexible than those synthesised using aromatic acids,[11] and

   (ii) Two part polyurethane adhesives are manufactured by the reaction of polyfunctional isocyanates with certain polyesters. The resultant polymer is then cross-linked with a polyol or hindered aromatic amine. Often the polyfunctional isocyanate can be retarded from reacting completely to improve the heat resistance of the resultant polymer.[11] It is thought that this results on further curing when the adhesive is exposed to elevated temperatures rather than the adhesive simply degrading. The polyurethanes which form consist of flexible chains of low glass transition temperature and highly polar, relatively rigid blocks. The polyester component makes up the soft blocks and the hard blocks are formed by the reaction of isocyanate with a low molecular weight glycol or diamine. As the urethanes are heated above 70°C the properties diminish rapidly such that they generally cannot be used in load bearing applications above 95°C. The rapid fall off in properties is due to an irreversible destructive change in chemical structure. Analysis of similar polyurethanes by differential scanning calorimetry (DSC) has shown endotherms which relate to the dissociation of the urethane soft block hydrogen bonds.[11] The polyurethane adhesive used to bond the laminate is a high performance adhesive system which can be used up to 121°C providing it is not subjected to stresses at these temperatures. Hence the adhesive would have been expected to retain its high temperature properties better than it actually did.

Hence in this region the adhesive used in laminate "A" weakens considerably. This is probably due to the high temperatures affecting the polyurethane's structure by the mechanism mentioned previously.

3.1.2 Failure mechanisms SEM analysis of a selection of failed specimens of laminate "A" tested at different temperatures also yielded information which could be related to the bond strength versus temperature data (Figure 2). It should be noted that the SEM was employed to determine the macroscopic characteristics of failure at the polypropylene-aluminium interface rather than the microscopic mode of failure.

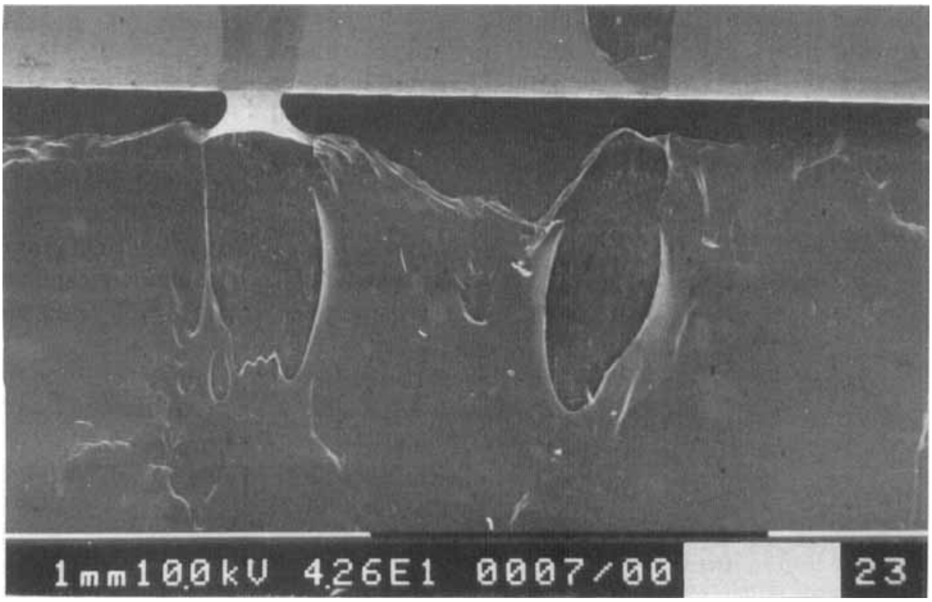

FIGURE 5 PP surface of laminate "A," bond tested at 23°C.

At 23°C the adhesive layer between the debonded polypropylene and aluminium surfaces appeared quite smooth and sheet-like (Figure 5). Failure at the polypropylene-aluminium interface was found to occur almost exclusively at this temperature by adhesive failure of the aluminium-adhesive interfacial bonds with a small amount of polypropylene-adhesive interfacial failure occurring. Hence, at this temperature it is clear that the adhesive itself remains intact and the bond strength of the polypropylene-aluminium interface is limited by the strength of the aluminium-adhesive interfacial bonds. This was found to be true for all temperatures up to 50°C.

Thus in the range 23°C–50°C the interlaminar bond strength is dependent on the strength of the aluminium-adhesive interfacial bonds. The strength of these aluminium-adhesive bonds therefore decreases in the range 23°C–50°C, resulting in the bond strength falling off with temperature. The strength of the adhesive itself and of the polypropylene-adhesive interfacial bonds may also fall but in this temperature range they are not important since the behaviour is controlled by the strength of the aluminium-adhesive bonds.

At 60°C there is a change in the appearance of the adhesive which may explain the increase in bond strength. As can be seen in Figure 6 the adhesive appears to have become more "tacky" and to undergo more deformation before debonding occurs. This could be due to the adhesive curing at the elevated temperatures but it is more likely that the adhesive has softened. As a result the polypropylene-aluminium interface does not fail by the same mechanism as was found at lower temperatures. At 60°C the adhesive appeared to have undergone more deformation under loading before debonding occurred. At 60°C failure was found to occur by a combination of adhesive failure of the aluminium-adhesive bonds and deformation and cohesive failure of the adhesive itself.

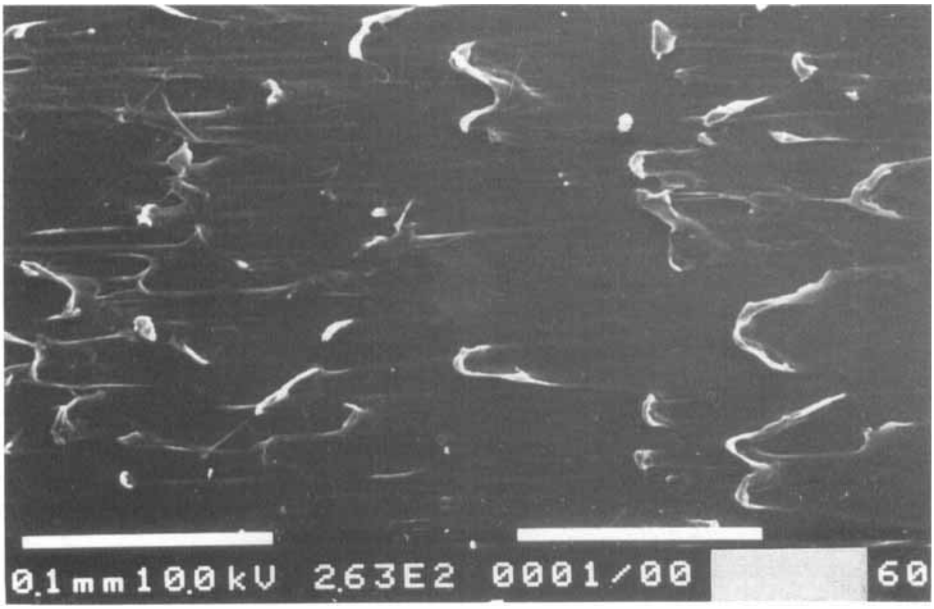

FIGURE 6 PP surface of laminate "A," bond tested at 60°C.

At 70°C the measured bond energy reaches its maximum value. This was found to coincide with a change in the appearance of the debonded polypropylene and aluminium surfaces. As Figure 7 shows, the adhesive appears as long strands indicating that considerable deformation has taken place before failure at the polypropylene-aluminium interface has occurred. The mode of debonding was also found to be completely different from that found at lower temperatures. At 70°C the adhesive appears to be behaving as a viscous liquid.

Earlier work by Taylor[12,13] and more recently by Fields and Ashby[14] was concerned with the effect of liquid viscosity and debonding speed on meniscus instability patterns when voids or cracks propagated along an interface by fluid flow (see Appendix A for details). Fields and Ashby found that an initial sinusoidal instability developed into large finger-like crack growth as the velocity of a roller applying a liquid onto a glass plate was increased. They proposed that the spacing of these fingers, λ, is given by:[14]

$$\lambda = \sqrt{\frac{\Gamma h^2}{6\alpha\eta\nu}} \tag{2}$$

where h = thickness of the fluid film,
ν = velocity of the roller,
α = constant,
η = viscosity of the fluid, and
Γ = surface tension.

This equation predicts that a steady state spacing is achieved which is rather smaller than the fastest growing perturbation. It can be clearly seen that the spacing of the

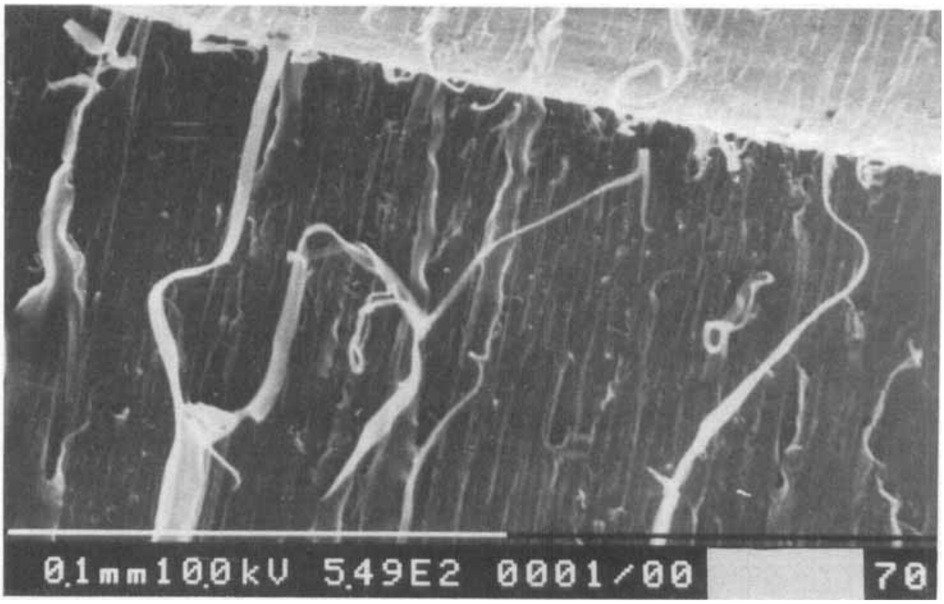

FIGURE 7 PP/Al interface of laminate "A," bond tested at 70°C.

fingers is proportional to $\nu^{-1/2}$ and to $\eta^{-1/2}$. Hence, as the velocity of the roller is increased at constant temperature, the spacing between the fingers decreases and the sinusoidal instability develops into finger-like adhesive failure.

For the specimens tested, the adhesive was found to exhibit finger-like crack growth with the fingers exhibiting a regular spacing (Figure 8). As the spacing is regular it can be assumed that steady state adhesive failure occurred. The only important variable at constant temperature will be the test speed since the viscosity of the adhesive is then controlled only by test speed at a given temperature.

The observation of these meniscus instability patterns corresponds to a difference in the mode of failure compared with samples tested at lower temperatures. As mentioned earlier, debonding occurred at lower temperatures mainly by adhesive failure at the aluminium-adhesive interface. However, at 70°C failure was found to occur by cohesive failure of the adhesive itself. This may be due to the state of the adhesive at this temperature. The high viscosity of the adhesive at this temperature means that rather than debonding occurring along a small region at any one time, as was found in the temperature range 23°C–60°C, the adhesive exhibits meniscus instability such that a larger area of sample is being debonded at any one interval during the test. This means that a larger load is required to carry out the debonding process which should result in the value of P_B appearing high compared with P_{0pp}. This was found to be true as shown in Table I. Also, as Table I shows, the value of X_f/A is larger than for other temperatures indicating that for a given elongation of polypropylene film, much less of the Al/PET layers become debonded. Hence, the adhesive behaving as a viscous liquid results in the debonding process being more difficult and, as a result, the measured bond energy is higher.

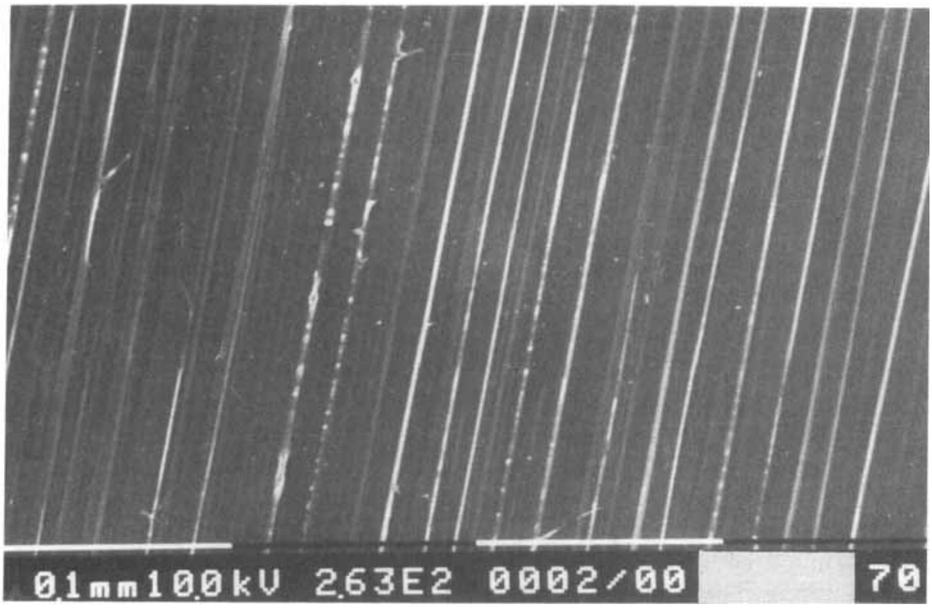

FIGURE 8 Al surface of laminate "A," bond tested at 70°C.

At 80°C the debonded surfaces indicate that failure at the polypropylene-aluminium interface is still occurring by cohesive failure of the adhesive itself with the adhesive remaining on both the debonded polypropylene and aluminium surfaces (Figure 9). Although there is some evidence of a meniscus instability at this temperature the adhesive does not appear to have undergone as much deformation as was found at 70°C. This is reflected in the X_f/A values which are similar to those obtained at lower temperatures.

At 90°C the measured bond energy dropped dramatically (Figure 2). Failure at this temperature was found to occur by two mechanisms, these being either by cohesive failure of the adhesive itself or by adhesive failure of the polypropylene-adhesive and aluminium-adhesive bonds. The adhesive appeared very tacky, indicating that at this temperature it had degraded such that it was offering very little resistance to the debonding process and behaved essentially like a low viscosity liquid (Figure 10).

At 100°C the samples appeared similar to the samples tested at 90°C. The adhesive seemed to have degraded completely such that during bond testing the adhesive had very little strength, the tackiness of the adhesive being the only factors influencing the bond strength. This is reflected in the value of the bond energy at 100°C. The measured bond energy was found to be approximately 1500 J/m^2, less than half of the value obtained at room temperature and one third of the peak value at 70°C.

3.1.3 Effect of test speed on the observed meniscus instability As a result of the meniscus instability patterns that were observed at 70°C, bond testing was carried out over a range of cross-head speeds (10 mm/min, 20 mm/min, 50 mm/min and 100 mm/min) in order to determine the effect of test speed on the spacing of the

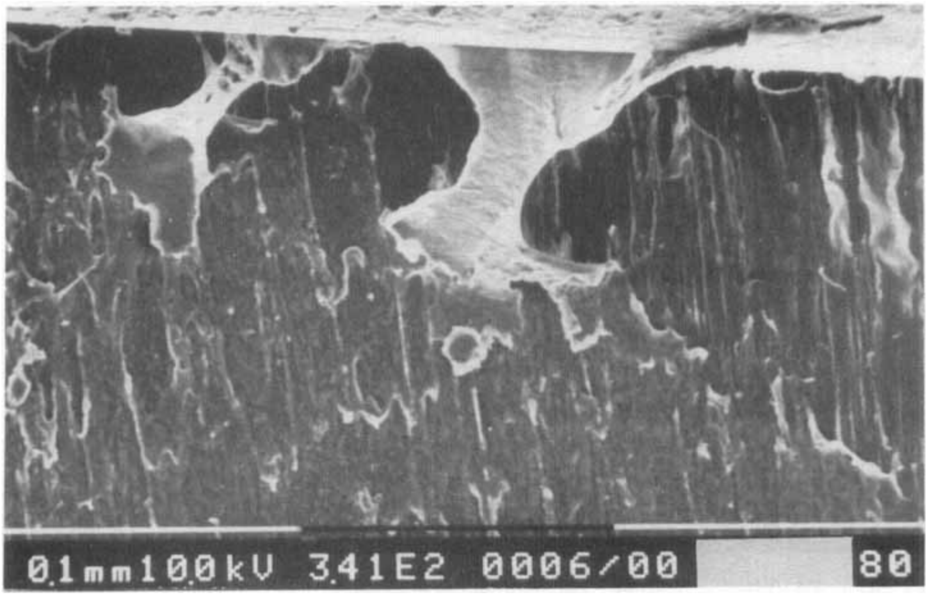

FIGURE 9 PP/Al interface of laminate "A," bond tested at 80°C.

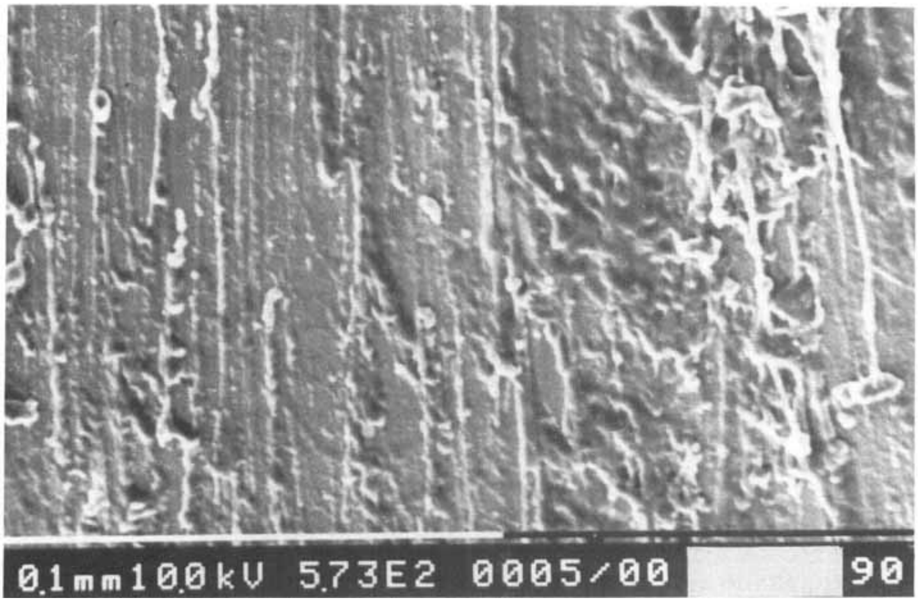

FIGURE 10 PP surface of laminate "A," bond tested at 90°C.

fingers and to deduce if the equation developed by Fields and Ashby[14] was valid for the systems being studied.

Testing was carried out at the speeds described above at 70°C using bond test pieces prepared by the standard method. The results obtained from bond testing of the laminate over the range of speeds are provided in Table IV, and illustrated graphically in Figure 11.

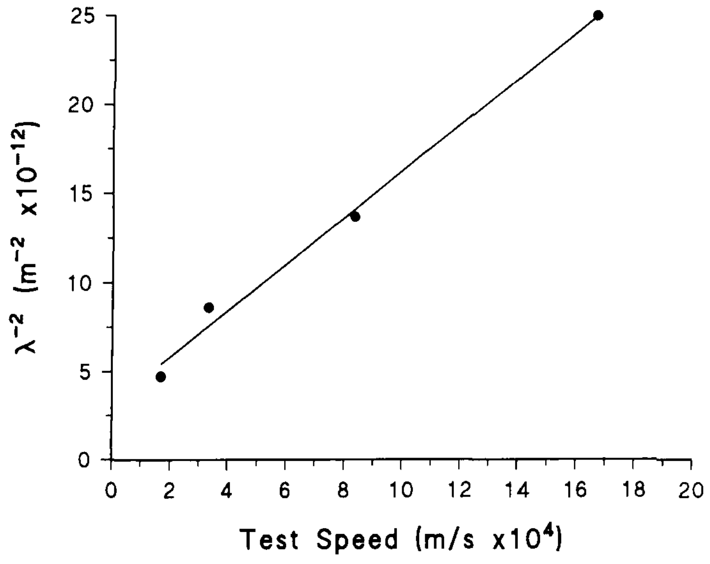

FIGURE 11 Plot of ν vs λ^{-2}. The slope of line is $7.3 \times 10^{-17} m^3/s$.

TABLE IV
Results obtained from bond testing of laminate "A" over a range of speeds at 70°C

ν (m/s × 10^4)	λ (m × 10^6)	λ^{-2} (m^{-2} × 10^{-12})
1.667	0.46	4.73
3.333	0.34	8.65
8.333	0.27	13.7
16.67	0.20	25.0

From equation (2) developed by Fields and Ashby[14] it can be seen that the steady state spacing is proportional to $\nu^{-1/2}$. Hence if a graph of velocity *versus* λ^{-2} is plotted, a straight line of slope $\Gamma h^2/6\alpha\eta$ should be obtained. From Figure 11 it can be seen that a straight line has been obtained for the data for four different test speeds. Assuming that the thickness of the adhesive layer is 2 μm, $\alpha = 1/4$ and $\Gamma = 0.04$ J/m^2 (Ref. 15), then it should be possible to determine the viscosity of the adhesive. Inserting the values into the equation yielded a value of 2200 Ns/m^2 (22000 Poise) for the viscosity of the adhesive. In practice it is found that the viscosity of a molten polymer can vary from 100 Ns/m^2 for nylon at 270°C to 40000 Ns/m^2 for PVC at 190°C,[15] so the value obtained for the polyurethane laminating adhesive is well within expected limits. Hence it can be concluded that the equation developed by Fields and Ashby[14] is of the correct form to describe the behaviour of the adhesive system being studied and that it can be used to determine the adhesive's viscosity at 70°C to a first approximation. It was believed that this analysis was valid because at 70°C the adhesive was behaving like a viscous liquid rather than a viscoelastic solid.

3.1.4 Overall failure behaviour for laminate A The bond strength *versus* temperature curve can, therefore, be seen to have three distinct sectors, a schematic interpretation being given in Figure 12:

(i) 23°C–50°C where the bond strength decreases with increasing temperature. SEM analysis could not detect any visible change in the adhesive although it was thought that the change in measured bond energy was due to a general softening within the adhesive. Failure of the polypropylene-aluminium layers was found to occur primarily by adhesive failure at the aluminium-adhesive interface.

(ii) 50°C–70°C where the measured bond energy increased. SEM analysis revealed that there was evidence of meniscus instability indicating that the adhesive was behaving as a viscous liquid. The properties of the adhesive at this temperature meant that instead of a small region undergoing debonding, a larger area had to be debonded at any one time. This resulted in the debonding process being more difficult and hence a larger load (with respect to temperature) was required to carry out the process. As a result of this a much smaller area of the Al/PET layers was debonded for a given cross-head displacement during the test.

(iii) 70°C–100°C where the bond strength fell rapidly with temperature. This was thought to be due to flow of the adhesive, possibly by some of the chemical bonds of the polyurethane becoming dissociated (most likely the soft block

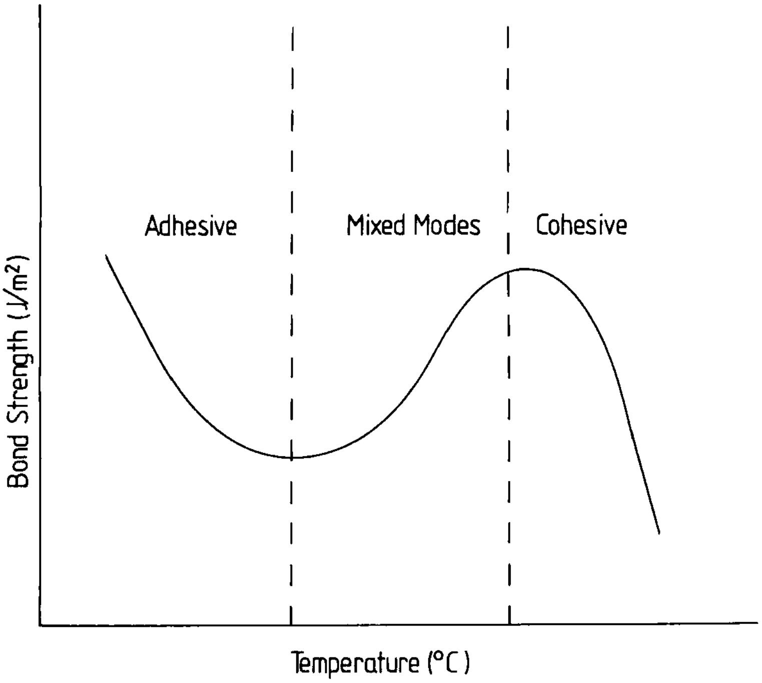

FIGURE 12 Schematic representation of the change in mode of failure of the PP-Al interface with temperature.

hydrogen bonds[11]). SEM analysis revealed that the adhesive had undergone very little deformation before debonding occurred. The adhesive actually appeared to have sagged under the influence of gravity. In this temperature range the polypropylene-aluminium interface failed by a mixture of cohesive failure of the adhesive itself and adhesive failure at the polypropylene-adhesive and aluminium-adhesive interfaces indicating that at this temperature all the bonds were very weak. Hence the performance of the adhesive appeared to have deteriorated significantly as the temperature was increased above 70°C.

3.2 Laminate "B"

3.2.1 Bond strength measurements The results obtained from bond testing of laminate "B" are shown in Table II and illustrated graphically in Figure 3. Laminate "B" was found to behave in essentially the same way as laminate "A." The bond strength fell in the range 23°C–50°C, increased in the range 50°C–80°C and finally dropped off above 80°C. However, the magnitude of the changes was not the same as was found for laminate "A." The bond strength of laminate "B" was highest at 23°C, and when it peaked again at 80°C it still had a lower bond strength than was found for laminate "A" at the same temperature. The overall temperature dependence of the measured bond energy of laminate "B" also appeared less critical than was found for laminate "A."

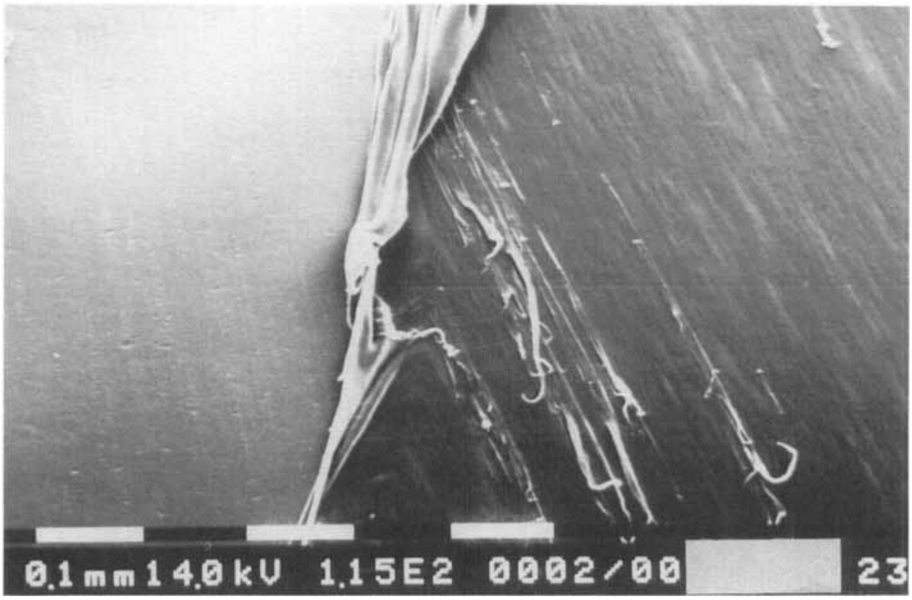

FIGURE 13 PP surface of laminate "B," bond tested at 23°C.

3.2.2 Failure Mechanisms SEM analysis was again employed to determine the mode of failure of laminate "B" over the range of temperatures at which it was tested. At 23°C failure at the polypropylene-aluminium layer was found to occur by adhesive failure at the aluminium-polyurethane interface (Figure 13). This was found to be the case for all temperatures up to 50°C.

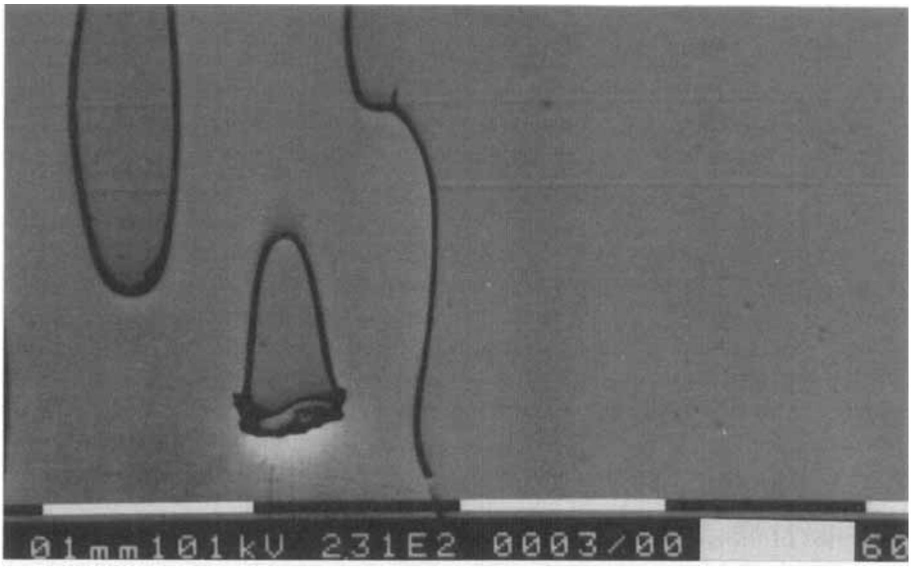

FIGURE 14 PP surface of laminate "B," bond tested at 60°C.

In the range 60°C–100°C failure was still found to occur by adhesive failure at the Al-polyurethane interface (*e.g.* Figure 14). Hence, although there was a variation in the measured bond energy with temperature, this could not be related to either any transitions within the adhesive itself or in the mode of failure of the polypropylene-aluminium layer. Laminate "B" did, however, exhibit some meniscus instability patterns at 70°C, as was found for laminate "A."

The bond strength of laminate "B" again shows a significant temperature dependence and changes in the mode of failure of the polypropylene-aluminium layer could be detected. It was found that the adhesive's appearance did not change significantly except to become slightly more "tacky" at higher temperatures.

3.3 Laminate "C"

3.3.1 Bond strength measurements The results for laminate "C" are shown in Table III and illustrated graphically in Figure 4. As can be seen, the results initially appear different from those found for laminates "A" and "B."

The bond strength *versus* temperature curve was found to increase up to 40°C, decrease between 40°C and 60°C, increase between 60°C and 90°C and fall off above 90°C.

3.3.2 Failure mechanisms SEM analysis yielded data on the modes of failure of the polypropylene-aluminium layer over the range of test temperatures. At 23°C debonding of the polypropylene-aluminium layer was found to occur by adhesive failure at the aluminium-polyurethane interface (Figure 15). At 30°C failure was found to occur by mixed modes. As well as adhesive failure occurring at the

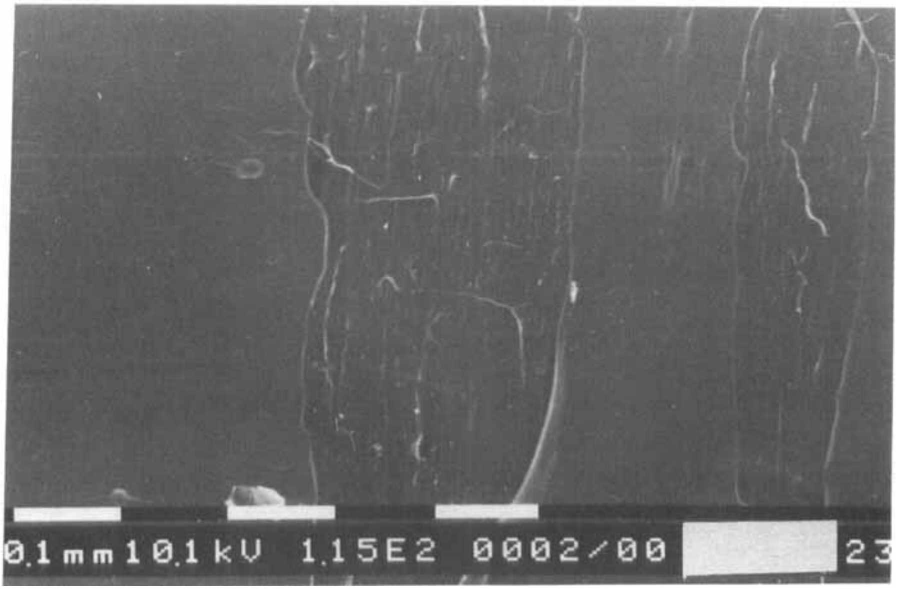

FIGURE 15 PP surface of laminate "B," bond tested at 23°C.

aluminium-polyurethane interface, failure also occurred by cohesive failure of the adhesive itself (Figure 16). The cohesive failure also resulted in the appearance of meniscus instability patterns. Again, the appearance of these meniscus instability patterns corresponded to an increase in the measured bond energy.

At 40°C the polypropylene-aluminium layer failed by adhesive failure at the polyurethane-aluminium interface. The surface of the polypropylene which retained the adhesive appeared slightly tacky (Figure 17) indicating that the adhesive may have undergone some deformation before debonding occurred. As the temperature was increased above 40°C the adhesive did not appear as tacky. At all subsequent temperatures failure at the polypropylene-aluminium layer was found to occur by adhesive failure at the aluminium-polyurethane interface.

Hence, although measured bond energy for laminate "C" exhibited a significant temperature dependence, only one transition could be detected within the adhesive and this occurred at 30°C–40°C. Above this temperature the adhesive's appearance and the mode of failure of the polypropylene-aluminium layer did not change dramatically.

3.4 Comparison of Laminates "B" and "C"

The bond strength *versus* temperature curves of laminates "B" and "C" are quite similar. The two laminates have essentially the same bond strength *versus* temperature curves albeit 10°C out of phase. It was known that the two laminate manufacturers had employed the same polyurethane adhesive system (different from laminate "A") indicating the repeatability of the bond strength test. The differences between the two bond strength curves may be due to a number of factors:

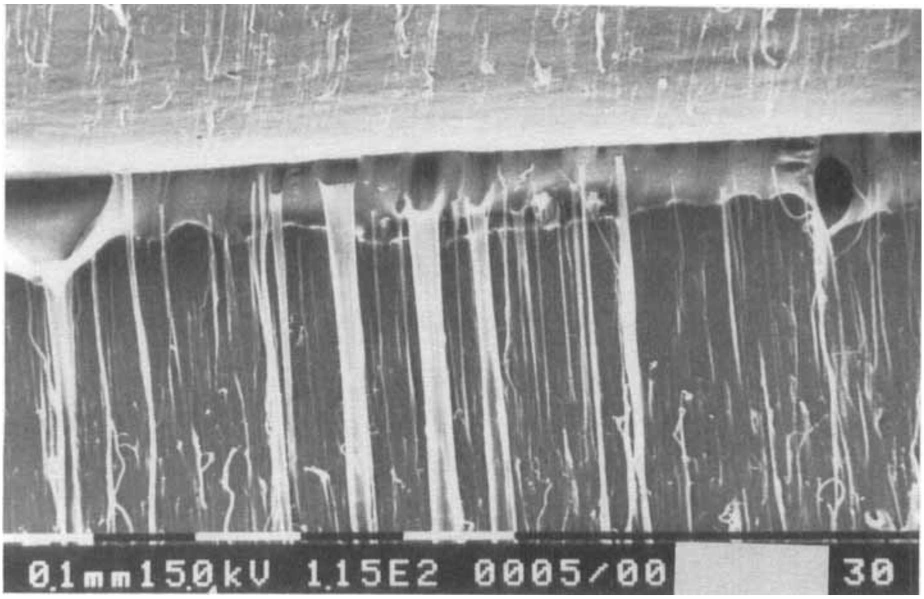

FIGURE 16 PP/Al interface of laminate "C," bond tested at 30°C.

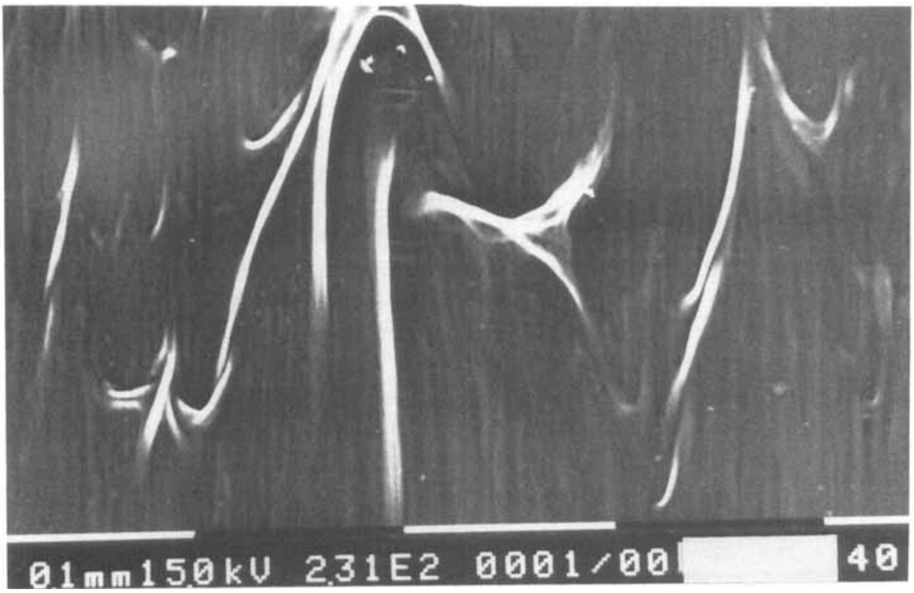

FIGURE 17 PP surface of laminate "C," bond tested at 40°C.

(1) The two laminate manufacturers may use different coating weights when applying the adhesive. As a result, the final thickness of the adhesive may be different. Indeed the thickness of the adhesive layer on laminate "C" appears to be greater than for laminate "B." This could correspond to the observation that laminate "C" appeared to have slightly higher bond strength.
(2) The two laminate manufacturers may apply the adhesive differently which could result in the two laminates having different thicknesses of adhesive.
(3) The curing temperatures and times employed by the laminate manufacturers may be different. This would result in the properties of the two adhesive systems being slightly different. In addition, the residual solvent levels within the two adhesive systems may be different.

The effect of the above factors upon the failure of the laminate will be the subject of a future publication.[7]

3.5 General Discussion

From the results obtained from the bond testing of the three laminates it appears that laminates "B" and "C" use similar, if not identical, grades of adhesive to bond the polypropylene and aluminium layers together. The manufacturer of laminate "A" appears to use a completely different grade of adhesive. Although laminate "A" was found to exhibit the highest bond energy (3800 J/m^2 at 70°C) there were very small differences in the measured bond energies of the three laminates above 80°C. Thus, it can be assumed that the performance of the polypropylene-aluminium layer of these three laminates should be similar in the presence of hot water. It should be noted that the early problems encountered by Cropper and Young[1] due to sample crinkling at elevated temperatures were not found to be an obstacle during the testing of the three laminates mentioned above.

The bond strength test appears to be a useful means of comparing the bonding of polypropylene-aluminium laminates, particularly for high strength bonds, which are difficult to measure by other methods. The test has been shown to highlight differences between laminates. As shown by the results, temperature was found to have a significant effect on the measured bond energies and failure mechanisms. As the measured bond energy can be directly related to the performance of the adhesive, the bond strength test can be used to measure not only the bond strength at ambient temperature, but also to determine the elevated temperature performance of adhesive systems used in the manufacture of laminates. Coupled with SEM analysis, the mode of failure at the polypropylene-aluminium interface and the appearance of the adhesive at a particular temperature can be deduced, thus providing valuable information on its resistance to thermal degradation.

4. CONCLUSIONS

The new bond strength test appears to be a useful method for determining the effect of temperature on the effectiveness of laminating adhesives. Not only can the change in mode of failure with temperature be detected, but the change in the appearance of the adhesive itself can be determined and, hence, a temperature profile of the adhesive can be established. The test has highlighted that optimum bonding is attained when the adhesive softens sufficiently for cohesive failure to occur. Maximum bond strengths are attained when meniscus instability patterns are observed and this instability can be characterised using an analysis developed by Fields and Ashby. It is thought that this test could be used to determine which adhesives would be the best candidates for high temperature applications.

Acknowledgements

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APPENDIX A

Meniscus Instability

Work by Taylor in the early 1950's[12] showed that when two superposed fluids of different densities were accelerated in a direction perpendicular to their interface, the surface was either stable or unstable depending on whether the acceleration was directed from the heavier to the lighter fluid or vice versa. Taylor later found[13] that when a viscous fluid filling the voids in a porous medium was driven forward by the pressure of another driving fluid, the interface between them was liable to be unstable if the driving fluid was the less viscous of the two. Assuming that the two fluids remained completely separated along a defined interface, Taylor[13] showed that the instability developed into rounded fingers of less dense fluid penetrating into the more dense one.

The work of Taylor has more recently been adapted by Fields and Ashby[14] to derive conditions for the growth of cracks in stressed solids. From the knowledge that if a pressure gradient (dp/dx) was established along a crack in a fluid film of viscosity η and thickness h between two plates, then it was shown that the crack would advance at velocity v according to the following relationship:

$$v = -\frac{h^2}{12\eta}\frac{dp}{dx} \qquad \text{A1}$$

When the crack front was perturbed into a sinusoidal shape of wavelength λ, then for the fingers to grow, the pressure drop at the tips of the fingers (dp/dx), must exceed the restraining effect of the surface tension Γ. This means that:

$$\frac{dp}{dx} > -\frac{4\pi^2\Gamma}{\lambda^2} \qquad \text{A2a}$$

or

$$\lambda > \pi\sqrt{\frac{\Gamma h^2}{3\eta v}} \qquad \text{A2b}$$

Extending this theory to the steady state growth of finger-like cracks, Fields and Ashby showed that the steady state spacing of fingers in a fluid film, λ_{ss}, is given by:

$$\lambda_{ss} = \sqrt{\frac{\Gamma h^2}{6\alpha\eta\nu}} \qquad \text{A3}$$

where α = constant,
h = thickness of the fluid film,
η = viscosity of the fluid,
Γ = surface tension, and
ν = velocity of the roller.

This result has the same form as equation A2b. However, the experimental value of α was found to be approximately ¼, indicating that equation A3 predicts a steady state spacing which is rather smaller than the fastest growing perturbation.

Hence, although steady state finger growth occurs, it can only be analysed in an approximate way. Fields and Ashby's analysis shows that in both the solid and liquid state, the steady state finger spacing is almost equal to the wavelength of the initial instability.