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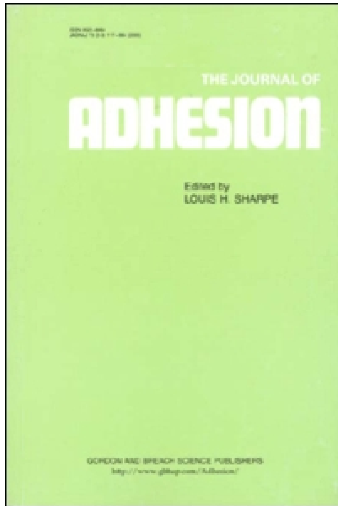

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The Mechanical Behaviour of Polyimide/Copper Laminates Part 2: Peel Energy Measurements

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The Mechanical Behaviour of Polyimide/ Copper Laminates Part 2: Peel Energy Measurements

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The mechanical peel behaviour of laminates consisting of polyimide films adhered to copper foil using a modified acrylic adhesive has been studied over a wide range of test rates and temperatures. The laminates were prepared from polyimide films which had been subjected to either a "high-thermal history" or a "low-thermal history" treatment during the production of the film. The measured peel energies of the laminates could be superimposed to give a master curve of peel energy *versus* the reduced rate of peel test, Ra_T, where R is the rate of peel test and a_T is the time-temperature shift factor. The appropriate shift factors were a function of the test temperature and were mainly deduced from tensile tests conducted on the bulk adhesive. The "high-thermal history" laminates gave higher peel energies and the locus of failure of the laminates was mainly by cohesive fracture through the adhesive layer. At low values of $\log_{10} Ra_T$, i.e. Low rates of peel and high test temperatures, the "low-thermal history" laminates also failed in the adhesive layer and possessed similar peel energies to those measured for the "high-thermal history" laminates. However, at high $\log_{10} Ra_T$ values, the peel energies measured for the "low-thermal history" laminates were lower and showed a wider scatter. These arose from a different locus of failure occurring in these "low-thermal history" laminates when tested under these conditions. Namely, it was found that most of these laminates failed in a weak boundary layer in the outer regions of the "low-thermal history" polyimide film.

KEY WORDS Laminates; master curves; peel tests; polyimides; thermal history; weak boundary layers.

INTRODUCTION

Flexible-printed electronic-circuit boards are typically manufactured from laminates made by bonding a thin film of polyimide to a copper foil using an adhesive interlayer.[1] The laminates must have adequate adhesion strength to withstand both the aggressive processing stages and in-service conditions that the circuit board experiences.

The polyimide films used in this study were especially selected to investigate problems which may occur in these laminates, and they have been described in a previous paper.[2] It is known that a polyimide film that has been subjected to a "high-thermal history" treatment may produce a laminate with better resistance

to delamination compared with one where the polyimide film has had a "low-thermal history" treatment. The reason for this was thought to be associated with different surface properties of the polyimide films. Our previous work has been concerned with investigating this, and other explanations, for the different delamination resistances of bonded laminates prepared from these polyimide films. Part 1[2] reported results from peel tests conducted using a tensile testing machine and inside a scanning electron microscope. It was found that laminates prepared from the "high-thermal history" polyimide films possessed higher recorded peel energies than those made with the "low-thermal history" polyimide films. Further, the "high-thermal history" laminates failed mainly by cohesive fracture through the adhesive layer, whilst laminates prepared from the "low-thermal history" polyimide films tended to fail in a weak boundary layer of the polyimide film. The peel tests conducted inside the scanning electron microscope also identified failure mechanisms which accounted for the different types of peel energy traces and for the fractographic features observed on the surfaces of the failed laminates.

The present paper reports the detailed peel behaviour of these laminates studied over a wide range of test temperatures and rates of peel. In order readily to compare the peel behaviour over a complete range of test conditions, peel data are expressed in the form of master curves. To establish the time-temperature shift factors, a_T, necessary to construct such master curves, the mechanical properties of the bulk adhesive have also been studied as a function of test temperature and rate of peel.

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EXPERIMENTAL

Materials

The Kapton® polyimide films used in this work were the same as those employed for the previous studies[2] and were supplied by the E.I. Du Pont De Nemours & Co. (registered trademark 'Kapton®'). The films were polymerized from pyromellitic dianhydride and 4,4′-diaminodiphenyl ether and were made by casting a polyamic acid solution onto a casting surface and then taking the film so produced through a series of heated chambers. During this process some films were subjected to a "high-thermal" treatment, whilst others were subjected to a "low-thermal" treatment. The "high-thermal history" films are commercially available, and met the specifications for use in making copper laminates. The "low-thermal history" films were especially made for this study.

Further, due to the way in which the polyimide films are produced, another distinction may be made between the surfaces of a given polyimide film. As mentioned above, the polyamic acid solution is cast onto a surface. Hence, the term casting side refers to the side of the polyimide film in contact with the casting surface during initial processing and the term air side is the opposite surface of the polyimide film, which was exposed to the air during initial film

forming in the manufacturing process. All the polyimide films used in the present work possessed a thickness of 51 μm.

The 2 oz copper foils used in the laminates were 71 μm thick. One side of the foil had been chemically treated (Oak Materials Group Inc.) to produce a roughened surface of copper nodules of about 2–3 μm in diameter. The adhesive employed was Pyralux WA/A® which is a modified-acrylic film adhesive and was supplied by E. I. Du Pont De Nemours & Co. The adhesive films used in the laminates were 23 μm thick, while thicker sheets of 0·5 mm were also prepared for obtaining the bulk mechanical properties of the adhesive.

The laminates were prepared by E. I. Du Pont De Neumours & Co. and consisted of stacked layers of copper/adhesive/polyimide/adhesive/copper which were then hot-pressed at 180°C under a pressure of 1.4 MPa for 30 minutes. Laminate strips for the peel tests were cut to a width of 6 mm on a precision cutter.

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Bulk properties of the adhesive

Dynamic mechanical analysis The moduli of cured adhesive were measured using a dynamic mechanical thermal analyser manufactured by Polymer Laboratories Ltd. A specimen, 30.0 × 15.0 × 0.5 mm, was rigidly clamped on both ends, a sinusoidal displacement was applied to the centre and the load was measured. From the measured loads and displacements a computer data system calculated values of storage modulus, E', the loss modulus, E'', and the loss factor tan δ_r, (where $\tan \delta_r = E''/E'$). The specimens were tested over a frequency range of 0.01 Hz to 90 Hz at a scan rate of 3–4°C/min from −80°C to 140°C.

Tensile tests Tensile-test specimens of the bulk acrylic adhesive were stamped from cured adhesive sheets and were tested using a screw-driven tensile testing machine in displacement control and equipped with a temperature chamber. Tests were conducted over a temperature range of −40°C to 40°C and a range of displacement rates of 8.33×10^{-8} m/s to 8.33×10^{-3} m/s. The initial maximum load was determined and used to construct a time-temperature master curve and evaluate the necessary shift factors, a_T.

Studies on the laminates

Peel tests As mentioned[2] in Part 1, the 90° German-wheel test is the standard test[3] method used by the flexible circuit-board industry, but during the earlier work it was found necessary to modify the test method to prevent the laminate from becoming detached from the wheel during testing since this leads to a change in the nominal peel angle which could produce misleading results. In the present work, the copper foil of the laminate strips were bonded onto a half steel ring using an epoxy resin ("E38," Permabond Ltd.). The ring was then fixed to the wheel (see Figure 1). Some of the specimens were bonded with the casting

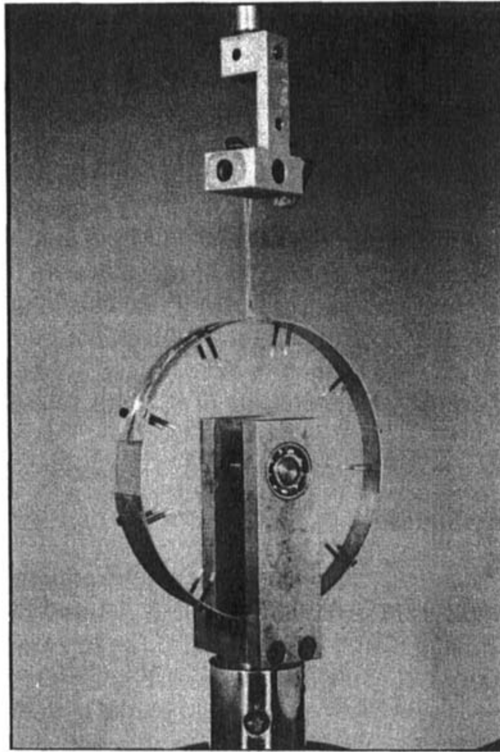

FIGURE 1 Photograph of the modified German-wheel peel test.

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side of the polyimide away from the steel ring. Thus, when the top copper strip was peeled away the peel behaviour would be characteristic of the side of the polyimide which had been adjacent to the casting surface during the preparation of the polyimide film. Similarly, other laminates were bonded so that the "air" side of the polyimide could be studied.

Therefore, the four material variables which were investigated are;

(i) HC for the "high-thermal history" polyimide laminate peeled on the casting side.

(ii) HA for the "high-thermal history" polyimide laminate peeled on the air side.

(iii) LC for the "low-thermal history" polyimide laminate peeled on the casting side.

(iv) LA for the "low-thermal history" polyimide laminate peeled on the air side.

The peel tests were conducted using a screw-driven tensile-testing machine operated in displacement control, and equipped with an environmental chamber. The effects of test temperature and rate of peel on the peel behaviour were studied over a temperature range of −40°C to 80°C and at a range of

displacement rates from 8.33×10^{-8} m/s to 8.33×10^{-3} m/s. The peel traces, i.e. peel load *versus* time curves, were recorded.

Fractographic studies Fracture surfaces from the peel tests were sputter-coated with gold and then examined using a scanning electron microscope.

RESULTS AND DISCUSSION

Dynamic mechanical behaviour of the bulk adhesive

When a load is applied to a polymer, the molecules take a finite time to rearrange. Hence, the resultant deformation is out-of-phase with the stress, where the phase angle or phase lag is denoted by δ_r. This phenomenon can be characterised by measuring the storage modulus, E', which is determined from the components of the in-phase stress and strain, and the loss modulus, E'', which is determined from the components of stress and strain 90° out-of-phase with each other.[4–6] The values of these parameters will obviously be dependent upon the rate, or frequency, of the test. Now the mobility of molecules is fast at high temperatures and sluggish at low temperatures[6,7] and this results in the observed rate and temperature dependence of the mechanical properties of polymers.

A typical plot of the loss factor, tan δ_r, *versus* the test temperature at a frequency of 10 Hz is shown for the modified-acrylic adhesive in Figure 2. The only viscoelastic transition which may be seen is that at 53°C associated with the glass-transition temperature of the adhesive. The maximum in the loss factor may be taken as a definition of the glass-transition temperature, T_g, of the adhesive and, as expected, the value of T_g is a function of the test frequency. The dependence of the value of the T_g upon frequency is shown in Figure 3.

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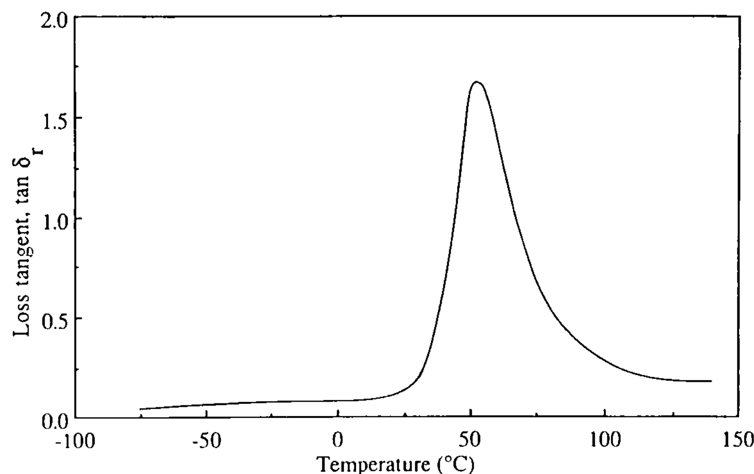

FIGURE 2 Loss tangent, tan δ_r, *versus* test temperature at 10 Hz for the bulk adhesive.

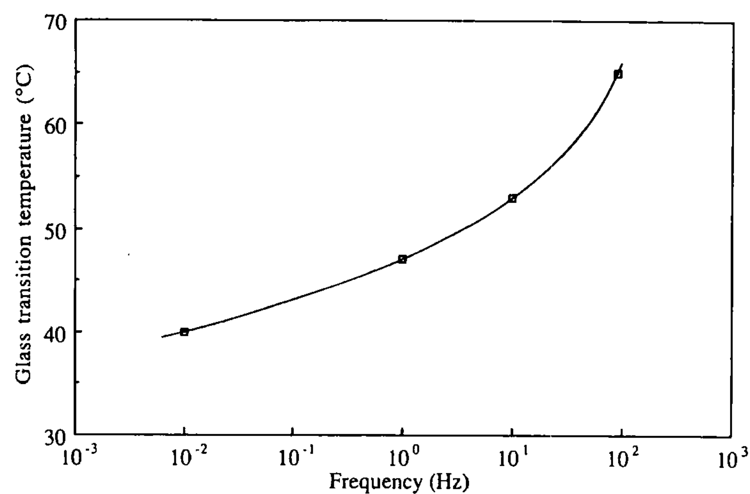

FIGURE 3 Glass-transition temperature, T_g, *versus* test frequency for the bulk adhesive.

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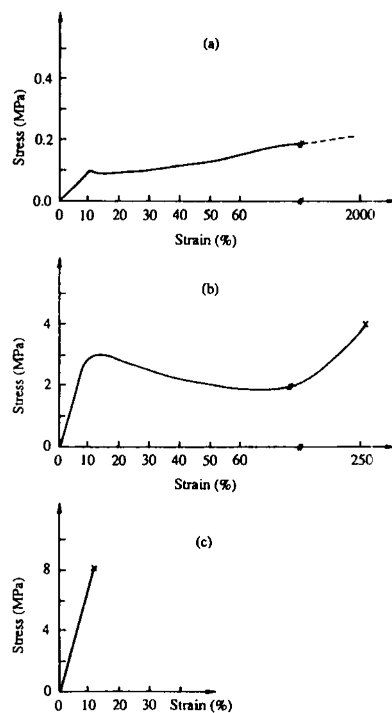

FIGURE 4 Tensile stress, σ, *versus* strain relations for the adhesive; tests rate, R, 8.33×10^{-4} m/s. a Test temperature 40°C. b Test rate temperature 22°C. c Test rate temperature −40°C.

Tensile properties of the bulk adhesive

Figures 4a, b and c show the typical stress *versus* strain behaviour of the bulk adhesive at an elevated, an intermediate and a low test-temperature, respectively. In Figure 4a the stress *versus* strain curve typically observed at high temperatures, or slow rates, is shown. Most marked is the very high strain capability of the adhesive under these test conditions. The adhesive behaves in a liquid-like manner and undergoes extensive plastic deformation. Indeed, the strain at rupture is greater than several thousand percent; at this point the extension of the specimen went beyond the range that could be measured. The stress goes through a small inflection, taken as the yield stress, σ_y, and then increases steadily, but the stress-bearing capability of the adhesive under these conditions is very limited. At room temperature and moderate rates of strain, Figure 4b, the stress *versus* strain behaviour shows the presence of a clearly defined upper and lower yield point; the yield stress, σ_y, was taken to be the value of the upper yield stress. The adhesive still shows extensive plasticity, but the strain at rupture is now about 250%. At the very lowest test temperatures employed the adhesive was well below its glass transition temperature. The adhesive behaves in a glassy manner and possesses an almost linear stress *versus* strain curve, as may clearly be seen from the typical stress *versus* strain curve shown in Figure 4c. There is no indication of bulk plastic deformation of the adhesive and the maximum stress that may be measured corresponds to the brittle fracture stress, σ_f.

Figure 5 shows the measured yield stress, σ_y, or the brittle fracture stress, σ_f, of the bulk adhesive plotted against the displacement rate, R, as a function of the test temperature. At high temperatures or slow rates, the stress taken is, of course, the yield stress, σ_y, and the values of this parameter are typically 0.2 MPa

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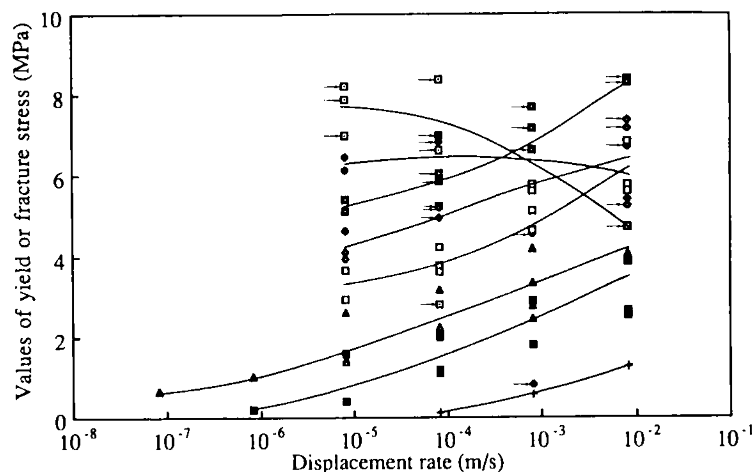

FIGURE 5 Yield stress, σ_y, or brittle fracture stress, σ_f, of the bulk adhesive *versus* test displacement rate, R, as a function of test temperature. ⊡ −40°C; ◆ −25°C; ■ −10°C; ◈ 0°C; □ 10°C; ▲ 22°C; ■ 30°C; + 40°C. Arrows represent brittle fracture stress and those without arrows are yield stress values.

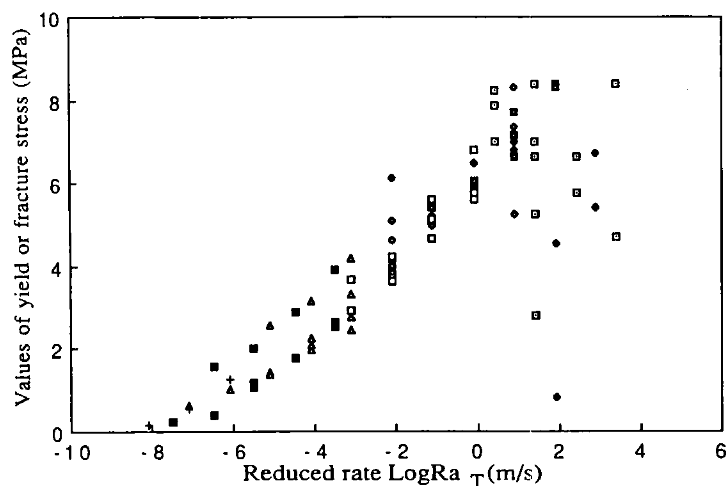

FIGURE 6 Master curve of yield stress, σ_y, or brittle fracture stress, σ_f, of the bulk adhesive *versus* the reduced rate of test, $\log_{10} Ra_T$; reference temperature of 22°C. ◘ −40°C; ◆ −25°C; ■ −10°C; ◆0°C; □10°C; ▲22°C; ■30°C; + 40°C.

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to 3 MPa. At low test temperatures and faster rates the appropriate stress is the brittle fracture stress, σ_f, and the values of this parameter are typically about 3 MPa to 8 MPa. Using 22°C as the reference temperature, the results were shifted on a reduced rate axis, $\log Ra_T$ (m/s), to give a master curve as demonstrated in Figure 6. The concepts of using a rate-temperature equivalence for viscoelastic materials are well established[6,8] and this approach has been applied by many workers, e.g. Refs. 9–11, when studying the mechanical behaviour of adhesives and adhesive joints. It is of interest to note that the maximum in the master curve is associated with the transition from ductile to brittle behaviour of the adhesive. The scatter in the high $\log Ra_T$ range is probably due to increased sensitivity to inherent defects when the adhesive is very brittle in nature. The values of the shift factor, $\log a_T$, needed to form the master curve for the bulk tensile data of the adhesive (Figure 6) are plotted as a function of the test temperature in Figure 7.

Peel behaviour of the laminates

Peel traces The different peel mechanisms and the resultant peel traces have been described in detail previously[2] and are summarized schematically in Figure 8. Figure 8a shows a smooth peel trace, typical of the results obtained when a crack propagated steadily through the laminate. Figure 8b shows a "micro-slip/stick" peel where a crack advanced by a rapid, small increment of growth followed by crack arrest, with this process being repeated along the specimen. Thirdly, Figure 8c illustrates where the peel front propagated in a classic slip/stick manner. The crack would suddenly grow through the laminate in an unstable

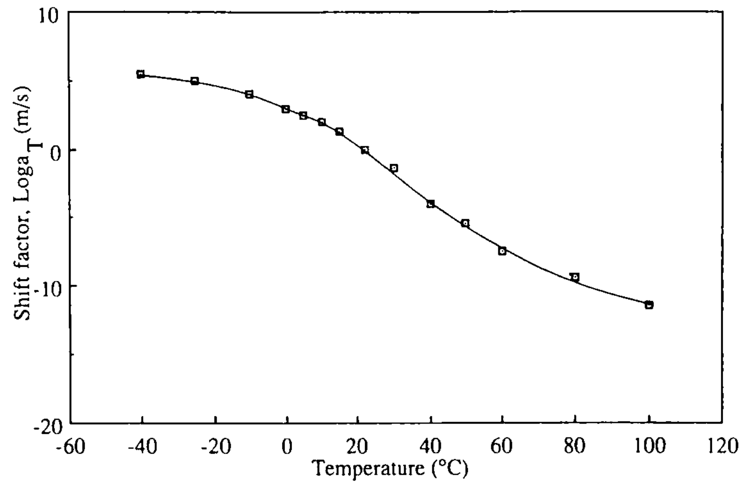

FIGURE 7 Shift factor, $\log_{10} a_T$, *versus* test temperature, deduced from the tensile tests conducted on the bulk adhesive, see Figure 5.

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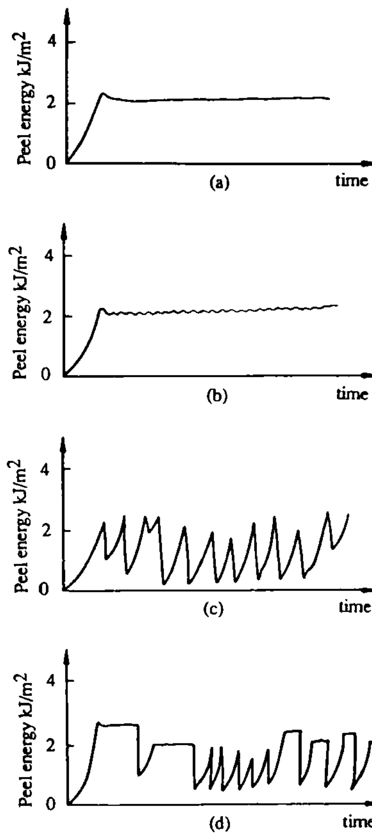

FIGURE 8 Typical traces of peel energy *versus* time for the laminates. a Stable crack growth. b Micro-slip/stick. c Macro-slip/stick. d Multiple fracture path failure.

fashion for a relatively long distance and, when the stored elastic-energy was insufficient to sustain further growth, it would arrest. This process was repeated and gave rise to the saw-tooth shaped peel trace. Fourthly, some laminates failed by a combination of all three types of crack growth described above and the typical resultant peel trace is shown in Figure 8d. When 'slip/stick crack growth occurred the peel force was taken as the average of the maxima, i.e. of the peak values.

Master curves Master curves of the peel energy *versus* the reduced rate of peel test, Ra_T, were largely constructed using the shift factors, a_T, which were ascertained from the tensile tests conducted on the bulk adhesive. However, at the highest test temperatures the yield stress of the adhesive, σ_y, could not be determined from the tensile stress *versus* strain curves for the bulk adhesive due to the very low modulus and the very large extent of plastic flow. Hence, for this range of test temperatures the values of the shift factors, a_T, were determined directly from the peel data.

These master curves of the peel energy *versus* reduced rate of peel test, Ra_T, for the different laminates are shown in Figures 9 to 12, and are compared in Figure 13. They have a common shape, but the "high-thermal history" laminates have generally higher peel energies. The master curves may be divided into three regions according to the peel traces and results from the fractographic examination of the peel surfaces. These regions partly overlap each other and the transitions between the types of behaviour occur at somewhat different values of the reduced rate axis for the "high" and "low" thermal history laminates. These aspects will now be discussed in detail.

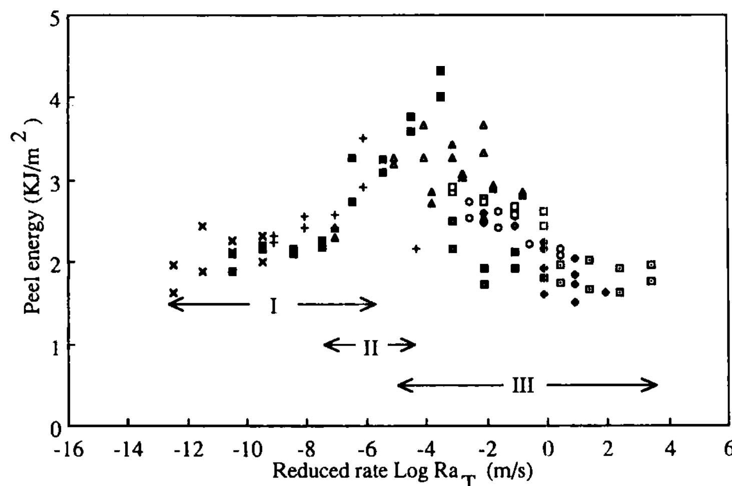

FIGURE 9 Master curve of peel energy *versus* the reduced rate of test, Ra_T, (reference temperature 22°C) for the high-thermal history/casting side (HC) laminates. ⊡ −40°C; ◆ −25°C; ■ −10°C; ◆0°C; ○5°C; □ 10°C; ▲ 15°c; ▲22°C; ■ 30°C; + 40°C; ⊞50°C; × 60°C.

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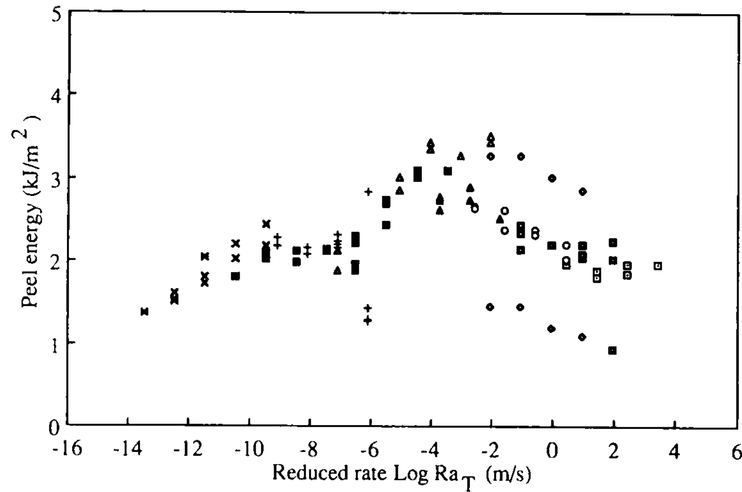

FIGURE 10 Master curve of peel energy *versus* the reduced rate of test, Ra_T, (reference temperature 22°C) for the high-thermal history/air side (HA) laminates. ⊡ −40°C; ■ −10°C; ◆ 0°C; ○ 5°C; ▲ 15°C; ▲ 22°C; ■ 30°C; + 40°C; ⊞ 50°C; × 60°C; × 80°C.

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"High-thermal history" laminates The master curves for the high-thermal history laminates where the copper foil was peeled away from the casting side (HC) and from the air side (HA) of the polyimide are shown in Figures 9 and 10 respectively. The three regions which may be identified are:

Region I—this occurs at elevated test temperatures and/or slow displacement rates of peel; *i.e.* at Ra_T values from about 10^{-13} m/s to 10^{-6} m/s. In this region

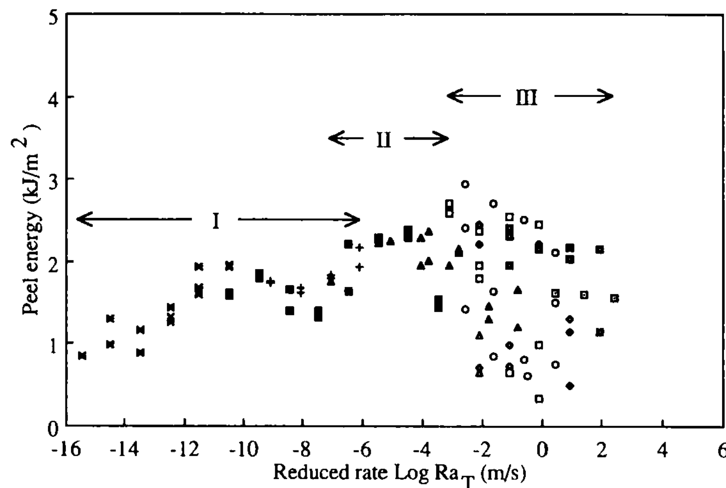

FIGURE 11 Master curve of peel energy *versus* the reduced rate of test, Ra_T, (reference temperature 22°C) for the low-thermal history/casting side (LC) laminates. ⊡ −40°C; ■ −10°C; ◆ 0°C; ○ 5°C; □ 10°C; ▲ 15°C; ▲ 22°C; ■ 30°C; + 40°C; ⊞ 50°C; × 60°C; × 80°C.

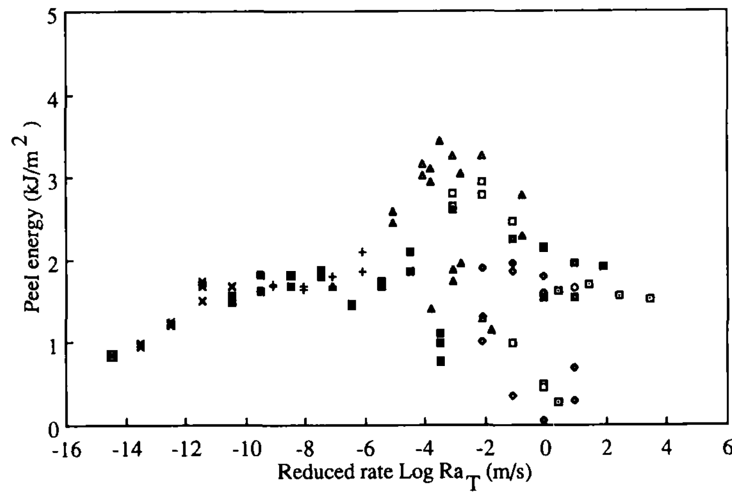

FIGURE 12 Master curve of peel energy *versus* the reduced rate of test, Ra_T, (reference temperature 22°C) for the low-thermal history/air side (LA) laminates. ⊡ −40°C; ■ −10°C; ◆0°C; ○ 5°C; □ 10°C; ▲ 15°C; ▲22°C; ■ 30°C; + 40°C; ⊞50°C; × 60°C; × 80°C.

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the peel crack propagated through the laminates in a continuous manner, as indicated by the observation of smooth peel traces (Figure 8a), and the peel energy increased steadily as the reduced rate, Ra_T, of test increased. Scanning electron micrographs of the fracture surface of the peeled copper strip revealed the presence of star shaped tears which were surrounded by fine striations radiating from the tear, as may be seen in Figure 14a. On the opposite fracture surface, the electron micrograph in Figure 14b revealed the presence of

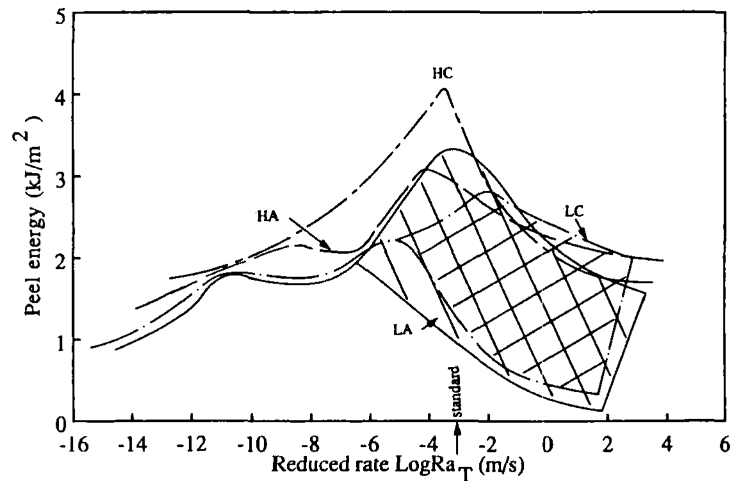

FIGURE 13 Comparison of the master peel cuves for the four different laminates. (Industrial standard test is conducted at Ra_T of 10^{-3} m/s). ——— HC; --- HA; ////////// LC; \\\\\\\\\\ LA.

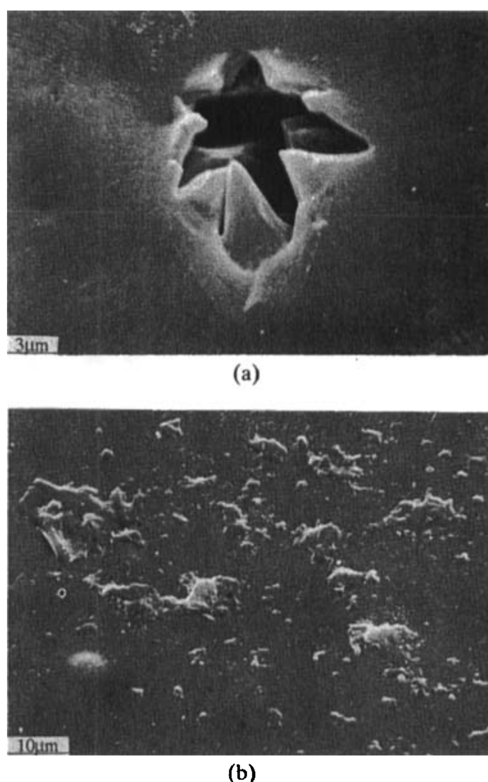

FIGURE 14 Scanning electron micographs of fracture surfaces of the high-thermal history laminates in Region I of the master curve showing cohesive failure in the adhesive. a. copper side. b. polymide side.

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corresponding hillocks. Under these test conditions the adhesive is extremely weak (see Figure 5) and the locus of failure appears to be inside the adhesive layer. The features observed probably arise from local inhomogenities in the adhesive causing secondary cracks or tears to form in the adhesive layer ahead of the main peel crack.

Region II—this occurs at intermediate test temperatures and rates of peel; i.e. at Ra_T values greater than about 10^{-7} m/s but less than about $10^{-4.5}$ m/s. In this region most of the peel traces were smooth, but some revealed indications of a limited amount of micro-slip/stick crack growth, see Figure 8b. The fracture surfaces of the laminates had a relatively rough appearance, as shown in the scanning electron micrograph in Figure 15a and, in some instances striations were also visible, as shown in Figure 15b. The striations arise from the slip/stick crack growth process and are formed when the peel front arrests and then re-initiates. These fracture surfaces are similar to those observed[2] previously from the *in-situ* peel tests on the high-thermal history laminates at a comparable reduced rate of peel test. In the peel studies conducted inside the scanning electron microscope it was clearly established that the peel crack propagated steadily through the centre

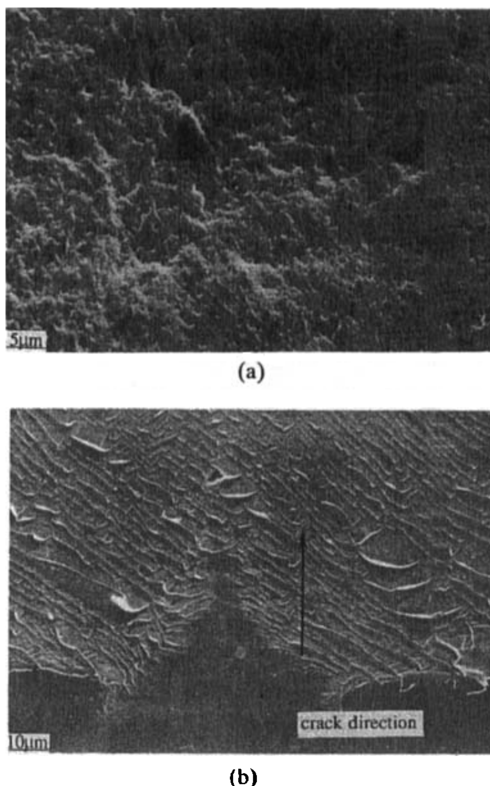

FIGURE 15 Scanning electron micrographs of fracture surfaces of the high-thermal history laminates in Region II of the master curve showing cohesive failure in the adhesive. a. rough appearance. b. striations.

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of the adhesive layer.[2] Therefore, it is suggested that these HC and HA laminates also failed cohesively in the adhesive layer.

Region III—this occurs at the lowest test temperatures and the highest peel rates; *i.e.* Ra_T values greater than about 10^{-5} m/s. In this region the value of the peel energy declines steadily from its maximum value of about 4.5 kJ/m^2 for the HC laminates and 3.8 kJ/m^2 for the HA laminates. Most of the laminates failed by the crack propagating through the adhesive in a steady manner (Figure 8a), but very occasionally the crack grew in a slip/stick manner (Figure 8c). In this region the crack propagates essentially in the adhesive layer, but close to the adhesive/copper interface, except that when it grew in a stick-slip manner it propagated in the boundary layer of the polyimide film close the polyimide/adhesive interface. The locus of failure close to the adhesive/copper interface is the feature which distinguishes this region from the previous two regions and is readily recognized from the scanning electron micrographs of the fracture surfaces. Figure 16a shows a thin layer of adhesive among the characteristic copper nodules on the "copper side" of the failed laminates and Figure 16b shows the impression of these nodules in the adhesive on the opposite

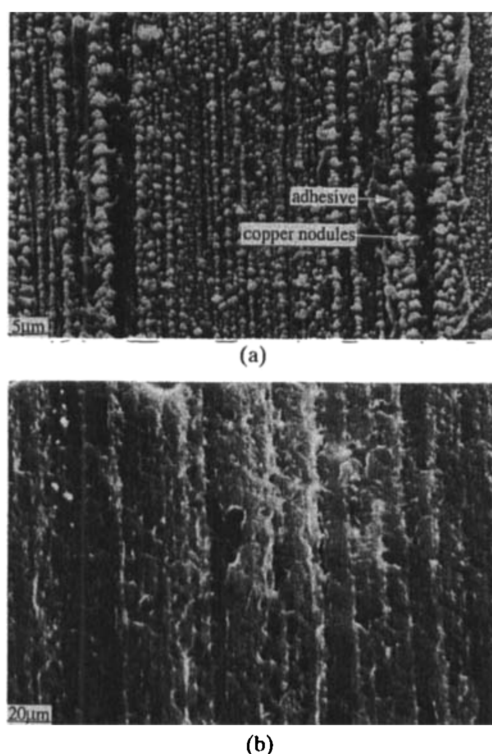

FIGURE 16 Scanning electron micrographs of fracture surfaces of the high-thermal history laminates in Region III of the master curve showing failure near the copper/adhesive interface. a. copper side. b. polyimide side.

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fracture surface. It appears that the lower test temperature/higher rate of peel leads to an increased modulus of the adhesive and this results in the stress concentration at the peel front being focused close to the adhesive/copper interface. Furthermore, the increasing glassy state of the adhesive means that there will be less viscoelastic and plastic energy dissipation around the tip of the propagating crack, hence the peel energy steadily decreases as the reduced rate of test, Ra_T, is increased.

"*Low-thermal history*" *laminates* The master curves of the low-thermal history laminates are shown in Figures 11 and 12 for the cases when the copper foil was peeled away from the casting side (LC) and from the air side (LA) of the polyimide. The master curves for the LC and LA are very similar and again three distinct regions may be identified according to the peel traces and fractography observed. These regions overlap each other and are similar to those recorded for the high-thermal history laminates, but at somewhat different reduced rate, Ra_T, values and, in some instances, there are important differences in the locus of joint failure.

Region I—at elevated test temperatures and/or slow displacement rates, i.e.

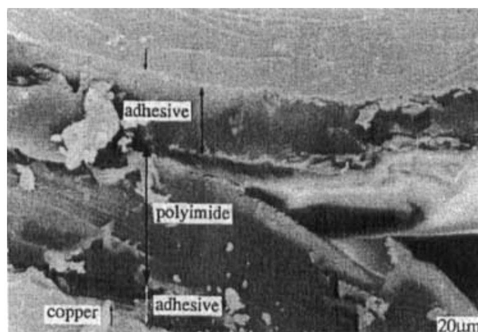

FIGURE 17 Scanning electron micrograph from an *in-situ* peel test of a low-thermal history laminate, showing a crack propagating through a weak boundary layer of the polyimide film.

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$\log_{10} Ra_T$ values less than about 10^{-6} m/s, the peel behaviour in this region was very similiar to that of the high-thermal history polyimide laminates. The peel energy increased with the value of Ra_T, although the absolute values were slightly lower than those for the HC and HA laminates. The peel crack propagated in the adhesive and the fracture surfaces appeared identical to those shown in Figure 14a and b.

Region II—at intermediate test temperatures and rates of peel, i.e. values Ra_T between about 10^{-7} and 10^{-3} m/s, the peel traces were generally smooth (Figure 8a) indicative of steady crack propagation but occasionally some micro-slip/stick crack growth (Figure 8b) was also recorded. However, from the previous *in-situ* peel tests[2] on these low-thermal history laminates the locus of failure is *via* cohesive fracture in a weak boundary layer in the polyimide. Indeed, Figure 17 shows a scanning electron micrograph of the crack propagating through this weak boundary layer in the polyimide film taken from the *in-situ* peel tests on these low-thermal history laminates. Hence, as discussed in more detail below, the measured peel energies are considerably lower for the LC and LA laminates compared to the HC and HA laminates.

Region III—at the lowest test temperatures and highest rates of peel, i.e. Ra_T values more than about 10^{-3} m/s, the peel energy declines from its maximum value of about 3 to 3.5 kJ/m^2. A few of the low-thermal history samples gave smooth peel traces (Figure 8a) but most peel traces were indicative of slip/stick (Figure 8c) or of a multiple fracture path (Figure 8d). Results from the *in-situ* peel tests of these low-thermal history polyimide laminates revealed peel mechanisms that may explain these observations. Firstly, the smooth peel traces (Figure 8a) were associated with steady peeling through the adhesive near the copper/adhesive interface. Secondly, the slip/stick trace (Figure 8c) appeared to result from intermittent castastrophic peel propagation in the weak boundary layer of the polyimide. Thirdly, the complex trace sketched in Figure 8d resulted from a combination of these peel mechanisms, and Figure 18 is a scanning electron micrograph from an *in-situ* peel test showing such a multiple fracture path.

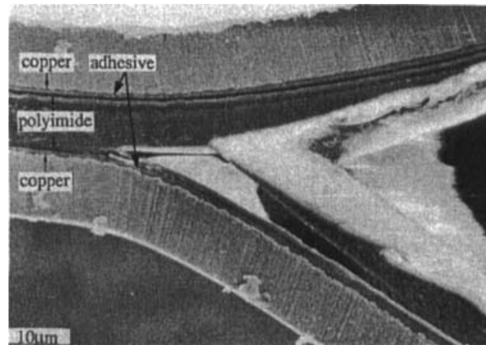

FIGURE 18 Scanning electron micrograph from an *in-situ* peel test of a low-thermal history laminate, showing a primary crack propagating in the polyimide film with a secondary crack having developed near the polyimide/adhesive interface (Region III from the master curves).

Comparison of the peel behaviour of the laminates

The master curves for the different laminates are compared in Figure 13 and they show several interesting points. Firstly, the use of the shift factors, a_T, ascertained from the bulk tensile properties of the adhesive to produce time-temperature master curves of the peel energies of the different laminates has been successful. This suggests that the rate-temperature dependence of the measured peel energies is largely influenced by the viscoelastic and plastic behaviour of the modified-acrylic adhesive. Indeed, the master curves for all the four laminates show the same general shape of the peel energy versus the reduced rate, Ra_T, of test curve.

Secondly, from Figure 13, for a given thermal history, it does appear that there is a significant difference between the master curves for the laminates where the peel test has been conducted on either the casting side or the air side of the polyimide film. The peel energies measured by peeling the copper foil away from the casting side of the polyimide film are somewhat higher in value compared with those obtained by peeling the copper foil away from the air side of the polyimide films. For the high-thermal history laminates this effect is most marked at Ra_T values of about 10^{-5} to 10^{-3} m/s, when the peel energies from both the casting and air sides of the polyimide are around their maximum value. This effect might, therefore, be ascribed to the peel crack propagating through a boundary layer of the air side polyimide under these conditions. That is, the surface layer of the air side of the polyimide being mechanically weaker than that of the casting side, so that the peel front propagates through this layer for the air side (i.e. HA) laminates tested under these conditions. Hence, a lower peel energy would be recorded when the bonded copper foil is peeled away from the air side of the polyimide. However, there is no conclusive evidence for this change in locus of failure; i.e. a change from the cohesive-in-adhesive failure which is usually observed with the high-thermal history laminates. Indeed, at Ra_T values below 10^{-6} m/s, the general trend of peel energies is HC > HA > LC > LA, and the locus of failure in all these cases is clearly in the adhesive layer. No

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satisfactory explanation can really be offered for those observations at the present, although it is possible that the air side of the polyimide films does possess a surface layer which exhibits inferior mechanical properties to that associated with the casting side of the polyimide film. Some indirect evidence for this suggestion will be discussed in Part 3 of this series of papers[12] and this effect may arise from the different thermal histories that the air and casting sides experience during manufacture of the polyimide film. If this is the case, then it should be noted that the locus of failure would not necessarily have to be actually through any weaker boundary layer of polyimide for the surface layer to have an influence. This is because the surface layer of the polyimide would be encompassed in the viscoelastic/plastic process zone at the advancing peel front. Hence, the mechanical properties of the surface regions of the polyimide would be reflected in the measured peel energy, even without the locus of failure of the laminate actually being through the weaker surface region of the air side laminates.

Thirdly, at Ra_T values lower than 10^{-7} m/s both high-thermal history and low-thermal history laminates clearly failed in the adhesive layer, but above Ra_T values of 10^{-7} m/s there are very significant differences between the master curves of the two laminates. In this range above Ra_T values of about 10^{-7} m/s the modulus and strength of the adhesive are increasing and these are at first accompanied by greater energy dissipation occuring in the adhesive layer. This leads to high peel energies being recorded for the high-thermal history laminates, where the locus of joint failure remains in the adhesive layer. However, in the low-thermal history laminates the increased tensile stresses which now occur in the vicinity of the peel front cause these laminates to fracture by a crack propagating through a weak boundary layer in the polyimide, close to the polyimide/adhesive interface. This mode of failure is accompanied by low peel energies and a greatly increased scatter in the measured peel energies being observed for the low-thermal history laminates under these test conditions.

Fourthly, when the test conditions are such that the adhesive is well below its effective glass transition temperature, T_g, (i.e. at Ra_T values greater than about 10^{-2} m/s), the extent of viscoelastic and plastic energy dissipation in the adhesive layer becomes far more limited and both laminates possess relatively low peel energies.

Fifthly, it is interesting to note that the industry standard test[3] calls for a peel test to be conducted at a Ra_T value of approximately 10^{-3} m/s. Under this test condition the peel energies of the laminates are close to their maximum value and the differences between the high-thermal history laminates and the low-thermal history laminates are most marked. If, for example, the industry standard test required a lower rate of peel then the differences between the two laminates would be far less marked.

Finally, it should be noted that since the peel energy of the laminate is so dependent upon the rate and temperature of test the performance of the laminate at low or high test temperatures cannot be predicted from simply conducting peeling experiments at a single, arbitrary, rate and temperature of testing.

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CONCLUSIONS

The mechanical peel behaviour of laminates consisting of polyimide films bonded to copper foil using a modified-acrylic adhesive has been studied over a wide range of test rates and temperatures. These laminates were prepared from polyimide films which had been subjected to either a "high-thermal history" or a "low-thermal history" treatment during the production of the film. A further variant in the production of the polyimide films was that they possessed a casting or an air side. The following conclusions were reached.

(i) The measured peel energies of the laminates could be superimposed to give a master curve of peel energy *versus* the reduced rate of test, Ra_T; where R is the rate of test and a_T is the time-temperature shift factor.

(ii) The appropriate shift factors were a function of the test temperature and were deduced from tensile tests conducted on the bulk adhesive. This suggests that the viscoelastic and plastic behaviour of the modified-acrylic adhesive is responsible for the observed rate and temperature dependence of the measured peel energies of the laminates.

(iii) The "high-thermal history" laminates gave higher peel energies and the locus of failure of the laminates was found to be mainly by cohesive fracture through the adhesive layer. At low values of $\log_{10} Ra_T$, i.e. low displacement rates and high test temperatures, the "low-thermal history" laminates also failed in the adhesive layer and, as would be expected, possessed similar peel energies to those measured for the "high-thermal history" laminates.

(iv) However, at high $\log_{10} Ra_T$ values; *i.e.* at relatively fast rates of peel and low temperatures, the peel energies of the "low-thermal history" laminates were lower and showed a wider scatter. This observation arises from a different locus of failure occurring in these "low-thermal history" laminates when tested under these conditions. Namely, it was found that most of these laminates failed in a weak boundary layer in the outer regions of the "low-thermal history" polyimide film.

(v) For a given thermal history it does appear that there is a difference between the master curves for the laminates where the peel test has been conducted on either the "casting" or the "air" sides of the polyimide film. The peel energies measured by peeling the copper foil from the "casting" side of the polyimide film, to which it had been bonded, are somewhat higher in value and this effect is particularly marked at higher Ra_T values.

(vi) Since the peel energy of the laminate is very dependent upon the rate and temperature of test, the performance of the laminate at low or high test temperatures cannot be predicted from simply conducting peeling experiments at a single, arbitrary, rate and temperature of testing. The use of master curves to depict the rate-temperature dependence of the peel behaviour of the laminates is an excellent technique for comparing different adhesive formulations and different processing methods and for predicting the performance of the laminate at low and high test temperatures.

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