JOURNAL OF MATERIALS SCIENCE 24 (1989) 2183–2190

The mechanical behaviour of polyimide–copper laminates

Part 1 *Locus of failure studies*

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The peel energies of flexible laminates consisting of polyimide films bonded to copper foil with a polymeric adhesive have been measured and the peel mechanisms investigated by conducting peel tests inside a scanning electron microscope. These laminates were prepared from polyimide films that had been subjected to either a "high-thermal history" or "low-thermal history" treatment during the production of the film. The laminates prepared from the "high-thermal history" polyimide films had higher recorded peel energies and the locus of failure during the peel test was mainly by cohesive fracture through the adhesive layer. The laminates prepared from the "low-thermal history" polyimide films tended to fail in a weak boundary layer of the polyimide film. The peel energies were lower and displayed a greater scatter. The *in situ* peel tests have also identified various failure mechanisms which account for the different features observed on the peeled surfaces and the various types of peel energy traces which were recorded.

1. Introduction

Flexible printed electronic circuit boards may be manufactured by bonding a thin film of polyimide to a copper foil using a polymeric adhesive interlayer [1]. The bonded laminate must withstand further processing stages, such as photolithographic etching of the copper using various chemicals, ultraviolet light, and finally immersion in a molten solder bath [2]. The bonded laminate must also perform satisfactorily throughout its service-life where it may be exposed to a wide range of temperatures and high relative humidities. One of the major requirements for the flexible laminate to withstand these various processing and in-service conditions is that the laminate possesses an adequate resistance to delamination.

The present work concerns polyimide films which were especially selected for this research programme to investigate problems which may be experienced during the use of flexible circuit boards. The films are produced by casting a polyamic acid solution onto a surface and taking the partially imidized film through a series of heated chambers. It has been known for some time that a polyimide film that has been subjected to a low thermal history may produce a laminate with an inferior resistance to delamination, as assessed by peel test measurements, compared to one where the polyimide film had been subjected to a high thermal history. The reasons for this have been thought to be associated with different surface properties of the "low" and "high" thermal history polyimide films.

Our work has been directed towards investigating this and other explanations of these observations of the different delamination resistances of bonded laminates made from "low thermal history" and "high thermal history" polyimide films. This paper reports results from part of our research programme in which peel tests have been carried out inside a scanning electron microscope. The aims were to identify the loci of failure of these laminates and the failure mechanisms, and hence to ascertain the reasons for the inferior peel behaviour shown by laminates prepared from the "low-thermal history" polyimide films.

2. Experimental details

2.1. Materials

The polyimide films, Kapton, were supplied by the E.I. Du Pont De Nemours & Co, Ohio, USA. The films were made from pyromellitic dianhydride and 4,4′-diaminodiphenyl ether and the "high thermal history" film was commercially available which met the specifications for use in making copper laminates. The "low-thermal history" film was specially made for this study. All the films used in this study had a thickness of 51 μm. The copper foils used to prepare the laminates were 75 μm thick. One side of the foil had been chemically treated (Oak Materials Group Inc, N.J. USA) to produce a roughened surface of copper nodules of about 2 to 3 μm in diameter. The adhesive was a commercial material, Pyralux WA/A sheet adhesive supplied by E.I. Du Pont De Nemours & Co. The adhesive is a modified acrylic and the thickness used was about 23 μm.

The laminates were prepared by E.I. Du Pont De Nemours & Co. and consisted of stacked layers of copper–adhesive–polyimide–adhesive–copper which

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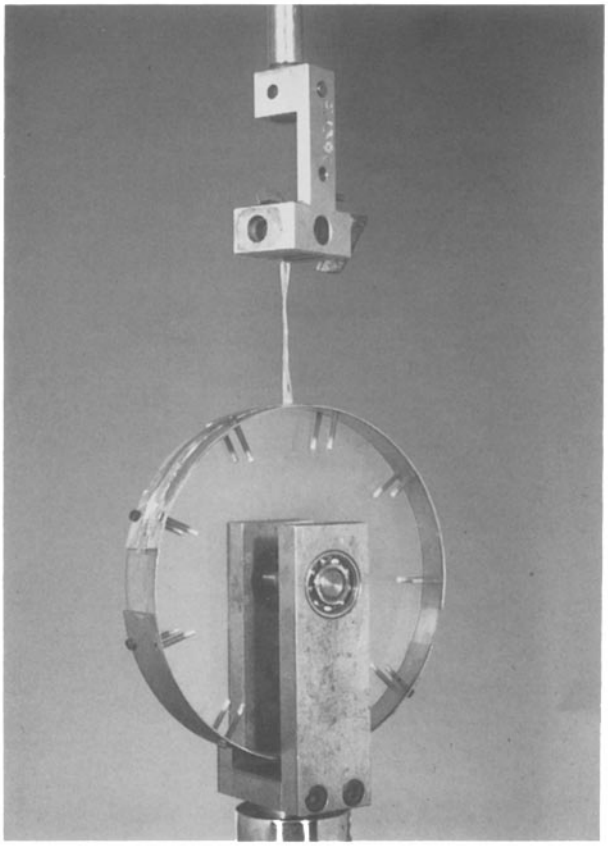

Figure 1 Photograph of modified "German Wheel" peel test.

were then hot-pressed at 180° C under a pressure of $1.4\,\mathrm{MN\,m^{-2}}$ for 30 min. Laminate strips for the peel tests were cut to a width of 6 mm on a precision cutter.

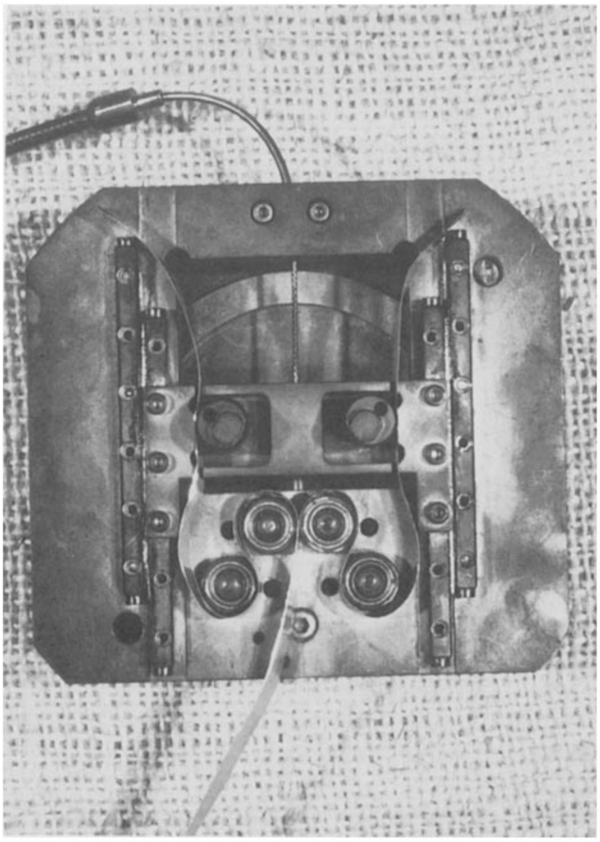

Figure 2 Photograph of *in situ* peel test stage.

2.2. Mechanical peel behaviour

The delamination resistance of the laminates are usually assessed by determining the peel energy and type of peel trace using a standard "German Wheel" test method [3]. (It should be noted that the commonly used term "peel strength" is somewhat of a misnomer, since a force per unit width or an energy per unit area is actually measured by such tests; so the term "peel energy" is in fact more appropriate.)

The "German Wheel" test method is shown in Fig. 1 and the equipment is designed to maintain the angle of peel to approximately 90°. However, this test method was slightly modified to prevent the laminate from becoming detached from the wheel during testing, since this will change the peeling angle appreciably and so could produce misleading results. In the present work, laminate strips were bonded onto a half steel ring using a rubber-toughened epoxy resin (Epoxy "E38", Permabond Ltd) and cured at 60° C for 1 h. The steel rings could then be fixed onto a conventional "German Wheel" of the same curvature. The peel tests were measured using a screw-driven tensile testing machine and conducted at room temperature and at displacement rates of 8.33×10^{-5} and $8.33 \times 10^{-4}\,\mathrm{m\,sec^{-1}}$. (The detailed mechanical peel behaviour of these laminates has been studied over a very wide range of test temperatures and displacement rates and will be the subject of another paper [4].)

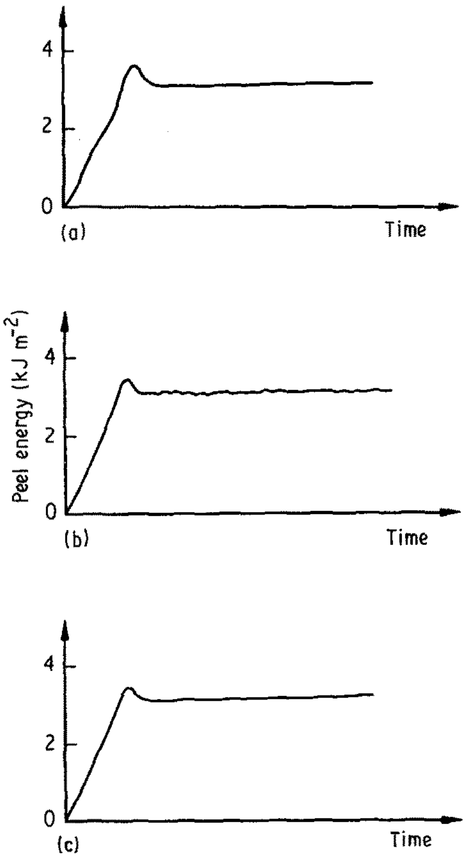

Figure 3 Schematic diagrams of the different peel traces for "high-thermal history" laminates. (a) Continuous crack growth in the adhesive. (b) "Micro-slip-stick" crack growth. (c) Continuous crack growth near the adhesive–copper interface.

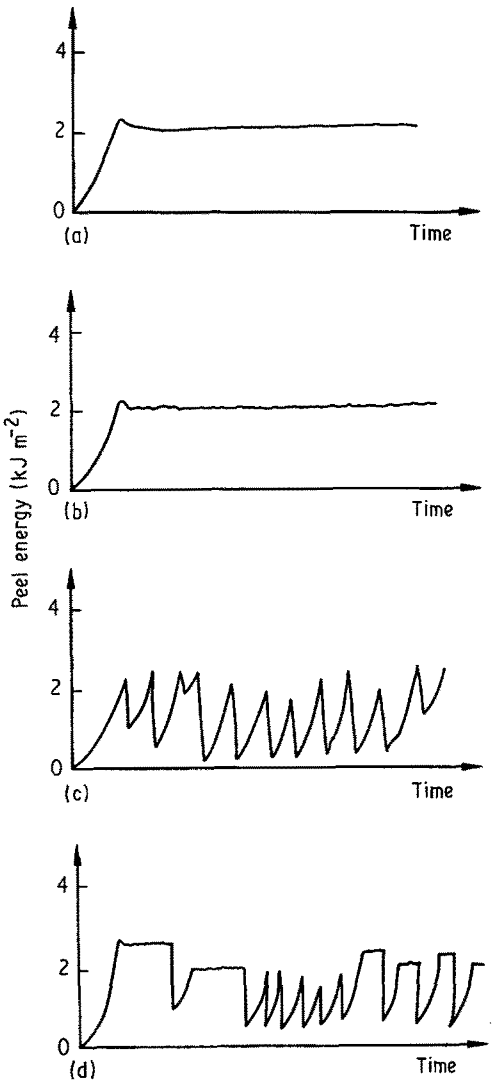

Figure 4 Schematic diagrams of the different peel traces for the "low-thermal history" laminates. (a) Continuous crack growth through a boundary layer of the polyimide. (b) "Micro-slip–stick" crack growth. (c) "Macro-slip–stick" crack growth. (d) Multiple fracture path failure.

2.3. *In situ* peel tests

A special peel stage was designed to carry out 180° T-peel tests in a Jeol T200 scanning electron microscope. The peel stage is shown in Fig. 2. A 6 mm strip, gold coated on the edges, was placed on the frictionless bearings on the peel stage. One of the copper foils on either side of the polyimide, was detached from the rest of the laminate to produce two "peel arms" of suitable lengths. The peel arms were pulled by a drive connected to a small electric motor outside the microscope. The specimen was peeled at a rate of about 8.33×10^{-5} to $8.33 \times 10^{-4}\,\mathrm{m\,sec^{-1}}$; i.e. at a rate comparable to that used for the "German Wheel" peel tests. An important feature of the test rig is that the arrangement of the bearings allows the point of peel to be maintained at the same position throughout the operation. This was essential when the peel process was examined at high magnifications of up to 500 to 10 000 times. The peel process was recorded on video tapes and still frame photographs.

2.4. Loci of failure studies

The fracture surfaces of the failed laminates were gold coated and examined in the scanning electron microscope. In some cases, the polyimide film was removed from the copper substrate before examination. This allowed energy dispersive for X-ray analysis to be conducted on the fractured polyimide without the added complication of detecting the underlying copper.

TABLE I Peel behaviour of the laminates

Polyimide used in the laminate	Peel energy (kJ m^{-2})	
	Rate $8.33 \times 10^{5}\,\mathrm{m\,sec^{-1}}$	Rate $8.33 \times 10^{4}\,\mathrm{m\,sec^{-1}}$
"High-thermal history"	3.43 ± 0.14	3.31 ± 0.13
"Low-thermal history"	2.17 ± 0.55	2.22 ± 0.54

3. Results and discussion

3.1. Mechanical peel behaviour

Laminates made from the "low-thermal history" polyimide films gave relatively low values of peel energy and exhibited a larger degree of scatter on the measured peel energy than those of the "high-thermal history" laminate, as may be clearly seen from the data shown in Table I. The laminates also exhibited different types of peel traces, i.e., the plots of peel energy against time as the peel front propagates through the laminate. The types of peel traces are shown in Figs 3 and 4 for the "high-thermal history" and "low-thermal history" laminates respectively, but this aspect is complex and is more conveniently discussed below when the results from the *in situ* peel studies are considered. However, one important point that should be noted is that for the "high-thermal history" laminates all the different types of peel behaviour shown in Fig. 3 occur at approximately the same relatively high value of peel energy. Whilst for the "low-thermal history" laminates (Fig. 4) not only is the mean value of the peel energy always significantly lower but the variation in the peel energy values is relatively large.

3.2. *In situ* peel tests

3.2.1. *Laminates prepared using the "high-thermal history" polyimide films*

The *in situ* peel test conducted in the scanning electron microscopy revealed that the laminates prepared using

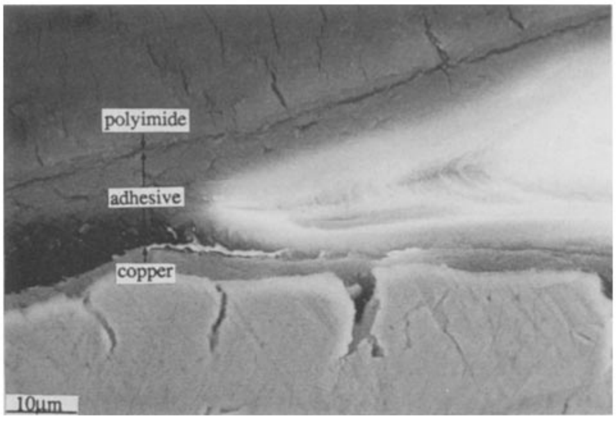

Figure 5 Scanning electron micrograph from the *in situ* peel test of a "high-thermal history" laminate showing continuous crack growth in the adhesive layer.

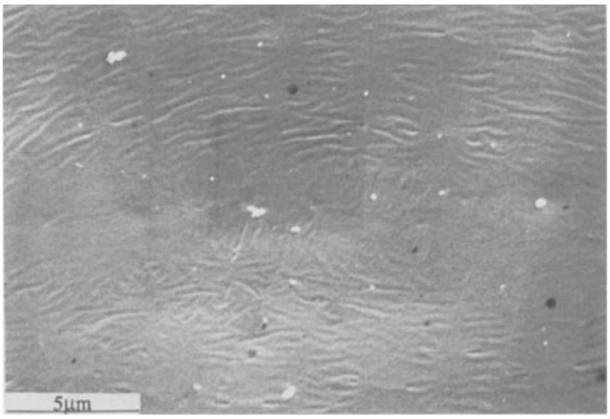

Figure 6 Scanning electron micrograph of the fracture surface from the test shown in Fig. 5.

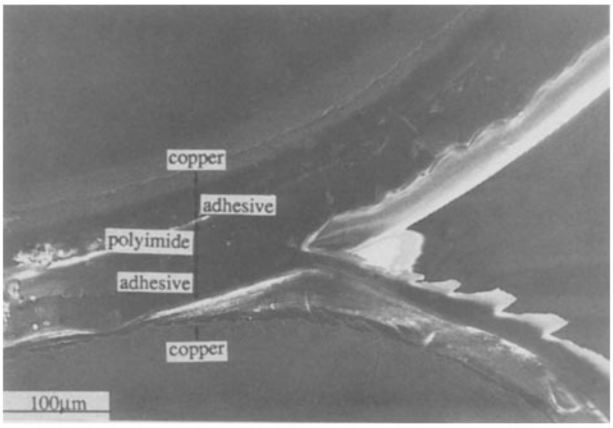

Figure 7 Scanning electron micrograph from the *in situ* peel test of a "high-thermal history" laminate showing "micro-slip–stick" crack growth in the adhesive layer.

the "high-thermal history" polyimide film tended to fail via a crack propagating through the polymeric adhesive layer. However, three different failure modes could be identified, which could be related to the different types of peel behaviour shown in Fig. 3.

Firstly, some cracks advanced steadily, in a completely continuous or steady manner, approximately through the centre of the adhesive layer. This was associated with the peel behaviour shown schematically in Fig. 3a. The scanning electron micrograph of the advancing peel front is shown in Fig. 5 and a typical micrograph of the corresponding fracture surface of the adhesive is shown in Fig. 6. There are signs of fibrils being drawn out behind the advancing crack tip and these probably give rise to the lines seen on the fracture surfaces (Fig. 6).

Secondly, the crack still travelled approximately through the centre of the adhesive layer but did so via a "micro-slip–stick" mechanism. Fig. 7 is a scanning electron micrograph of the peel front and clearly reveals the formation of a serrated fracture path through the adhesive. The spacing between the serrations is approximately 20 to 100 μm. The mechanism by which the serrations in the adhesive layer are formed was clearly visible in the video pictures of this type of failure and is shown schematically in Fig. 8. The peel propagated firstly by reaching a state of high stress at the crack tip indicated by apparent formation of dense microcracks (as discussed later in Section 3.3). A new crack then initiated ahead of the peel front in the adhesive layer, and propagated back towards the

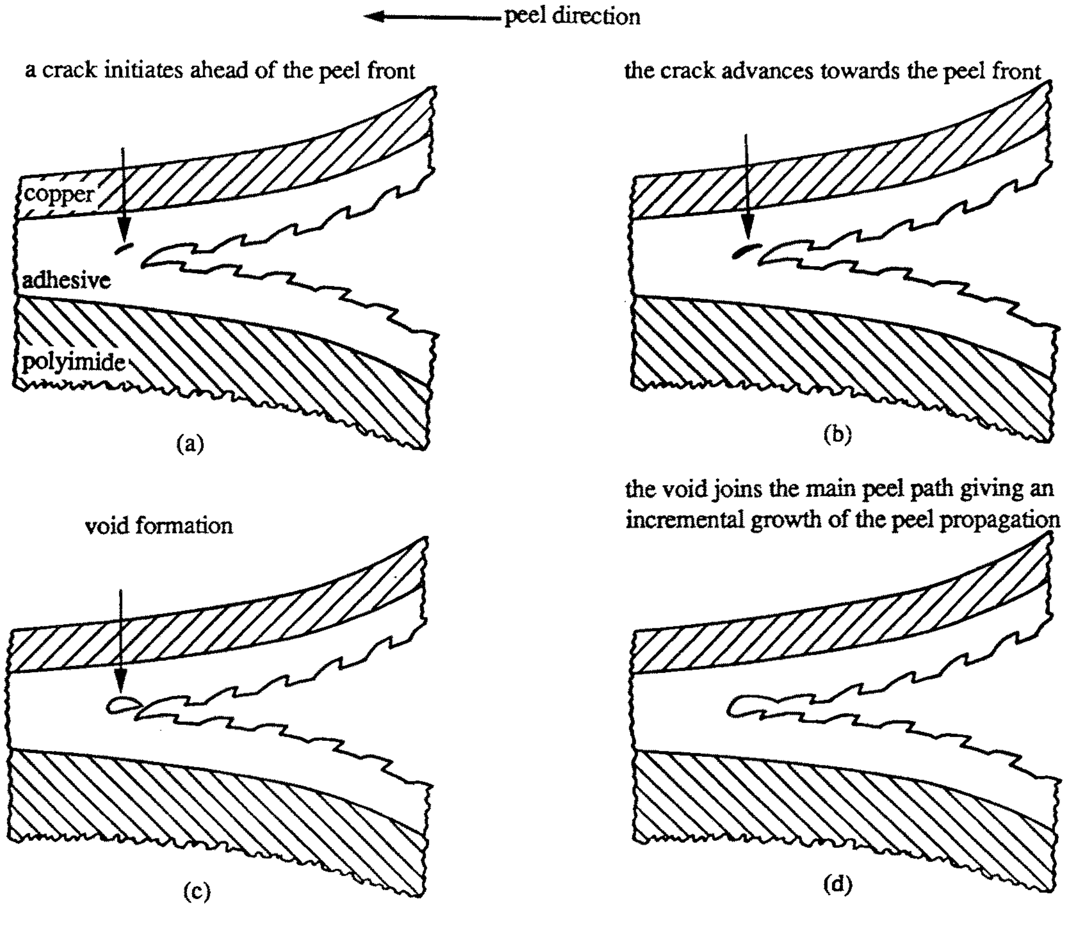

Figure 8 Sketch showing how micro-slip–stick crack growth in the adhesive layer occurs in the "high-thermal history" laminate.

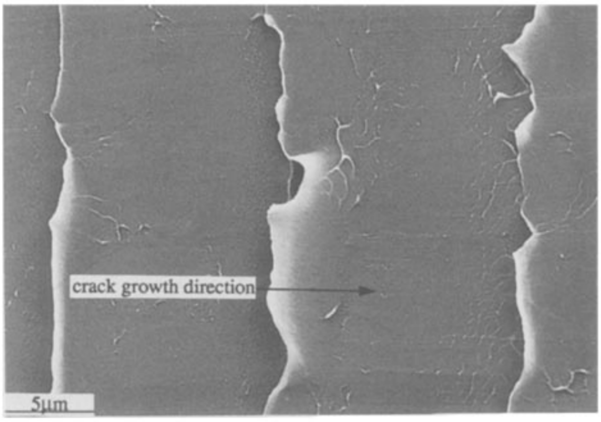

Figure 9 Scanning electron micrograph of the fracture surfaces from the test shown in Fig. 8.

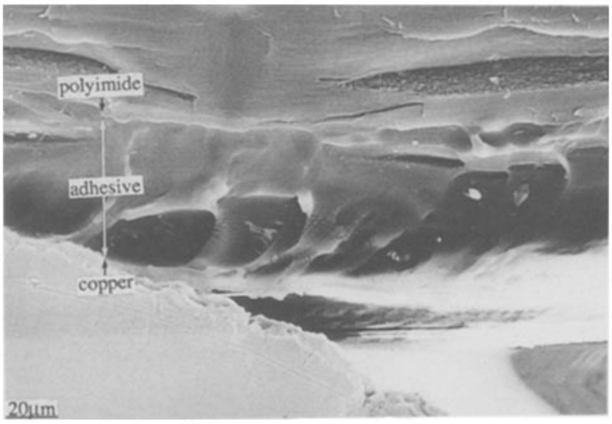

Figure 10 Scanning electron micrograph from the *in situ* peel test of a "high-thermal history" laminate showing continuous crack growth in the adhesive layer but near the adhesive–copper interface.

front, giving rise to the formation of the serrated, tooth-like, appearance of the fracture path. At this point the stress concentration at the peel front is relaxed and the measured peel load decreases a little. The peel load then gradually builds up as the peel front advances until the above process is repeated. This is therefore the mechanism responsible for what we have termed the "micro slip–stick" mechanism and obviously also explains the behaviour of the peel energy plotted against time trace shown in Fig. 3b. Furthermore, the fracture surfaces of the laminate are very distinctive when this mechanism is occurring. As may be seen from Fig. 9, striations of about 10 to 20 μm apart are clearly visible on the fracture surface of the adhesive.

Thirdly, in some instances the peel front propagated in a steady continuous manner, mainly in the adhesive, but very close to the adhesive–copper interface. This results in a form of peel trace identical to that for continuous crack growth through the adhesive, as may be seen by comparing Figs 3a and c. A typical micrograph from the *in situ* peel experiments of such a failure mode is shown in Fig. 10. A layer of retained adhesive on the copper substrate of the once-bonded laminate is apparent on the fracture surface of the failed laminate, see Fig. 11a. Fig. 11b shows the facing side (i.e. the adhesive side of the fracture) on which impressions of the nodular surface of the copper can be seen. By using energy-dispersive X-ray analysis (Fig. 12) it was found that some nodules of copper had fractured from the copper surface and are present on the adhesive side of the failed laminate.

It would be of interest to understand fully why these three different modes of failure are observed. The reason appears to be due to the manner in which the laminate is peeled apart by hand to initiate the peel front prior to starting the peel test. It was observed that the type of failure mode occurred randomly from one test specimen to the next but rarely changed during the course of a peel test on a given specimen. Hence, the tentative conclusion that the uncontrolled method of starting the peel front by hand prior to undertaking the peel test leads to the peel crack being located in the adhesive, but at different locations within the adhesive layer. When the peel test is undertaken the initial location of the crack governs the type of failure mode, and hence the peel behaviour, which is observed.

3.2.2. Laminates prepared using the "low-thermal history" polyimide films

The most striking aspect of the video and still micrographs obtained from the *in situ* tests on the laminates prepared from the "low-thermal history" polyimide films was that the locus of failure was frequently through a boundary layer near the surface of the film. This may be clearly seen in Figs 13, 15 and 17. Four different failure modes were identified, and again these

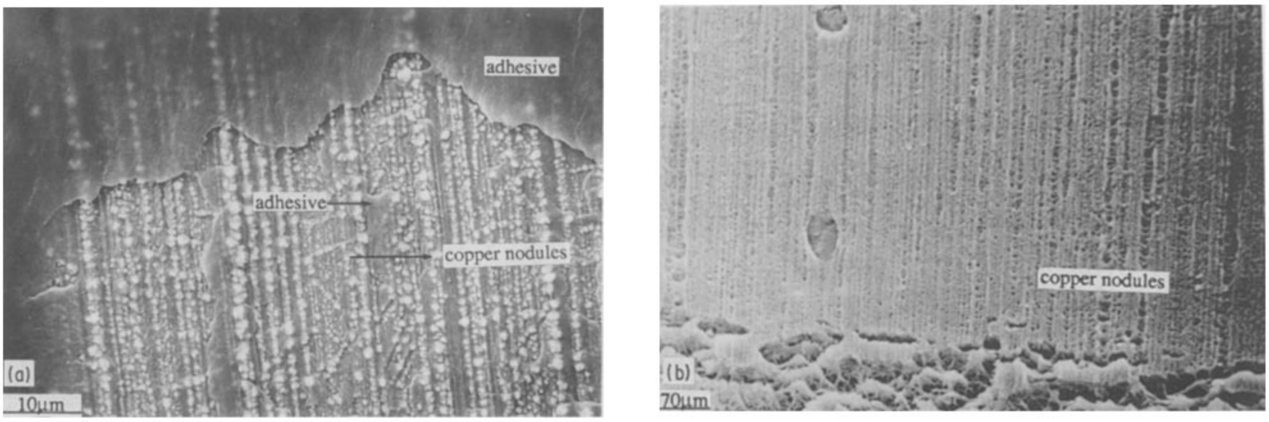

Figure 11 Scanning electron micrograph of the fracture surface of the copper (a) and (b) adhesive side of the failed laminate from the test shown in Fig. 10.

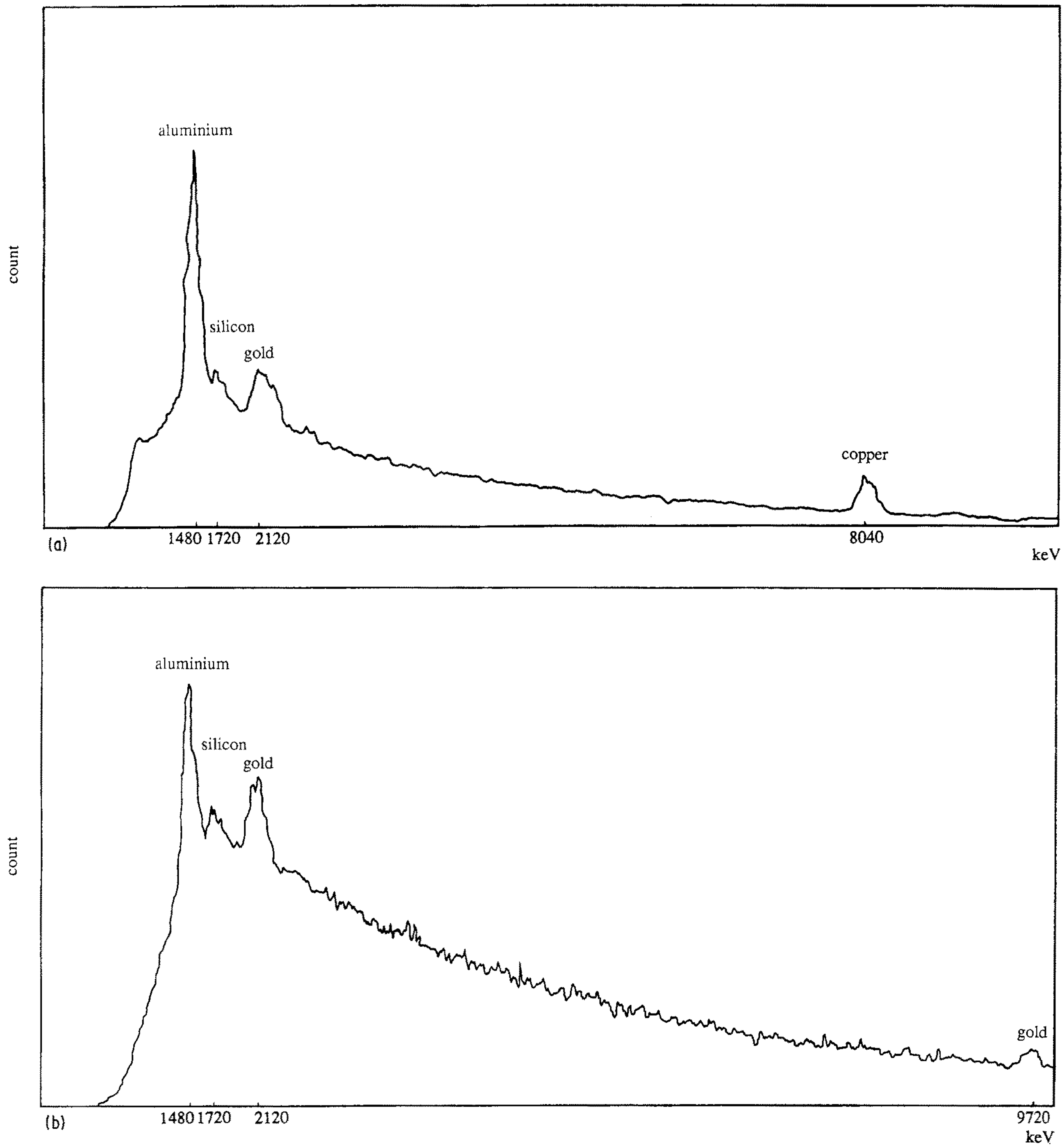

Figure 12 Spectra from energy dispersive for X-ray analysis studies. (a) On a copper particle present on an "adhesive" fracture surface. (b) On an area adjacent to (a) but containing no particles (notice absence of copper signal).

were associated with different types of peel behaviour which are shown schematically in Fig. 4.

Firstly, a steady advance of the peel front running about 2 to 10 μm inside the polyimide film, close to the polyimide–adhesive interface was observed. This is illustrated in Fig. 13 and gives rise to a continuous type of peel behaviour, but at a relatively low value of peel energy, compared to the values for the "high-thermal history" laminate, as shown in Fig. 4a. Fig. 14 is a micrograph of the resulting fracture surfaces of the polyimide. The fracture surfaces appears to be relatively flat, similar to the fracture of adhesive as may be seen from Fig. 6.

Secondly, the crack propagated through the polyimide, in a boundary layer close to the polyimide–adhesive interface but a "micro-slip-stick" peel mechanism was observed. The *in situ* scanning electron micrograph of this type of failure mode is shown in Fig. 15. (Note that at the crack tip in Fig. 15 some "smearing" of the adhesive over the adhesive–polyimide interface has occurred, creating the illusion of the crack being in the adhesive. However, the video pictures and the micrographs from the region just behind the crack tip show clearly that the fracture is in a boundary layer of the polyimide.) As might be expected from the previous discussions, this mechanism leads to the resulting fracture surfaces showing striations which in this case are about 10 to 20 μm apart, as may be seen in Fig. 16. This failure mode arises from a mechanism similar to that described in Section 3.2.1 and shown schematically in Fig. 8 and results in the peel behaviour shown in Fig. 4b. It is noteworthy

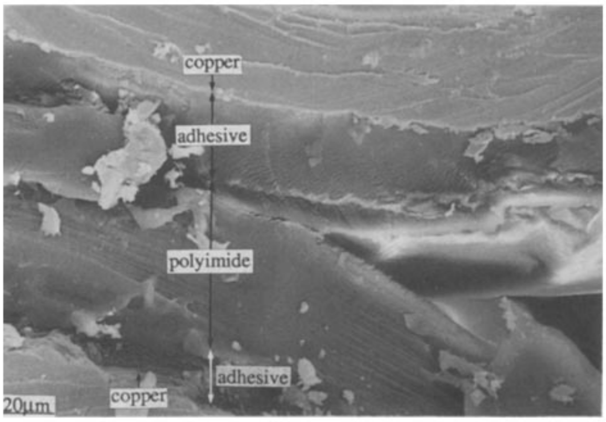

Figure 13 Scanning electron micrograph from the *in situ* peel test of a "low-thermal history" laminate showing continuous crack growth in a boundary layer of the polyimide.

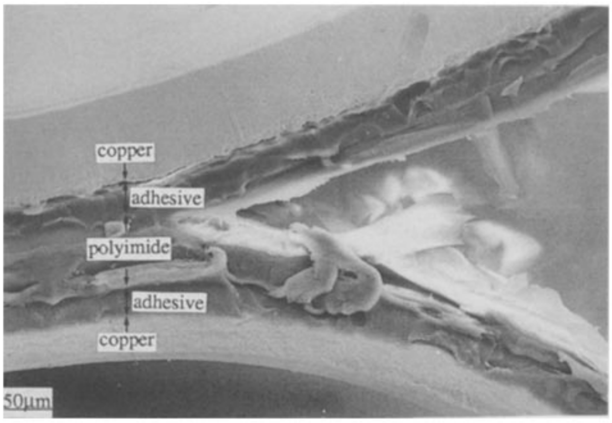

Figure 15 Scanning electron micrograph from the *in situ* peel test of a "low-thermal history" laminate showing "micro-slip–stick" crack growth in a boundary layer of the polyimide.

that the peel behaviour shown in Fig. 4b is identical to that shown in Fig. 3b for the "high-thermal history" laminate except that in the latter case the crack grows through the adhesive layer at a much greater peel energy.

Thirdly, the crack propagated again through a boundary layer of the polyimide but in a "macro-slip–stick" manner at 2 to 8 mm per crack growth increment. A relatively smooth fracture surface appearance, indistinguishable from that of the continuous fracture (Fig. 14), was observed. The peel behaviour shown in Fig. 4c reveals a classic slip–stick pattern showing the distinctive saw-tooth appearance [5]. *In situ* peel studies showed that a crack propagated through a weak boundary zone at a rate faster than the displacement rate of the peel arms. The peel arms became slack and the crack arrested. This corresponded to a sudden drop of peel load, i.e., the "slip" process. As the peel test was conducted at a constant displacement rate, elastic energy would build up: the "stick" part of the peel curve. When enough elastic energy was available, the crack would re-initiate. The process was repeated giving rise to the saw-tooth shape peel trace observed in the mechanical peel tests.

Fourthly, some laminates failed by a combination of all the three mechanisms described above. The video sequences revealed how this complex failure mode would give rise to the "macro-slip–stick" peeling behaviour, as depicted in Fig. 4d. This observation also emphasises the inhomogeneous nature of the boundary layer region of the "low-thermal history" polyimide film.

3.3. Other observations from the *in situ* peel studies

For the "high-thermal history" and "low-thermal history" polyimide laminates some other observations are noteworthy. Firstly, secondary cracks were sometimes found to develop in the laminate above and below the primary peel front. For example, Fig. 7 shows such a secondary crack in the adhesive, near the adhesive–copper interface, below the primary peel front which is propagating through the centre of the adhesive layer via the "micro-slip–stick" mechanism. Another example is shown in Fig. 17 which reveals the primary peel front in the polyimide, but with a secondary crack having initiated and grown near the polyimide–adhesive interface. Secondly, fine cracks were observed on the faces of the laminate specimens. The larger ones (see Fig. 5) are defects introduced when the specimens were cut into strips using the precision cutter. The multitude of much finer cracks (see Figs 5 and 13) are thought to be artefacts arising from the cracking of the gold coating which was sputtered onto the sides of the specimens to reduce charging effects [6].

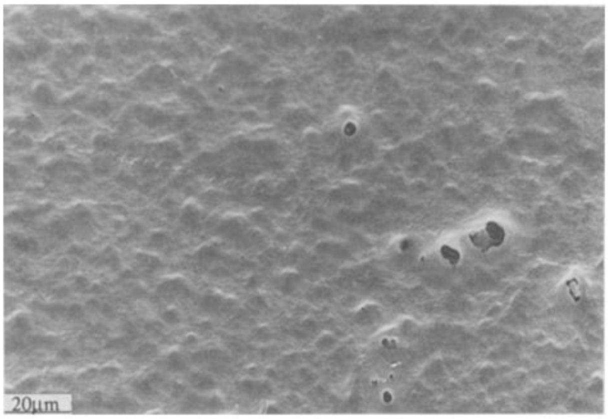

Figure 14 Scanning electron micrograph of the fracture surface from the test shown in Fig. 13.

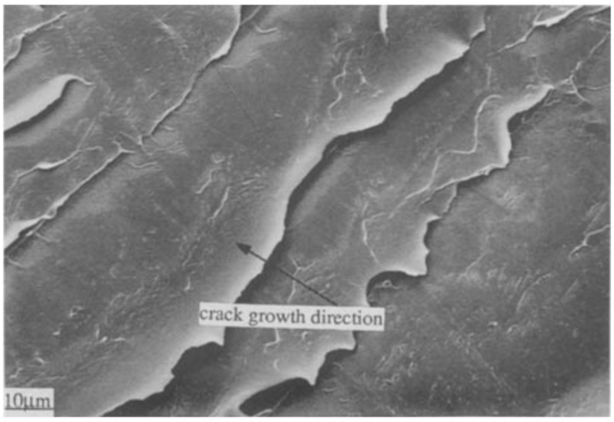

Figure 16 Scanning electron micrograph of the fracture surface from the test shown in Fig. 15.

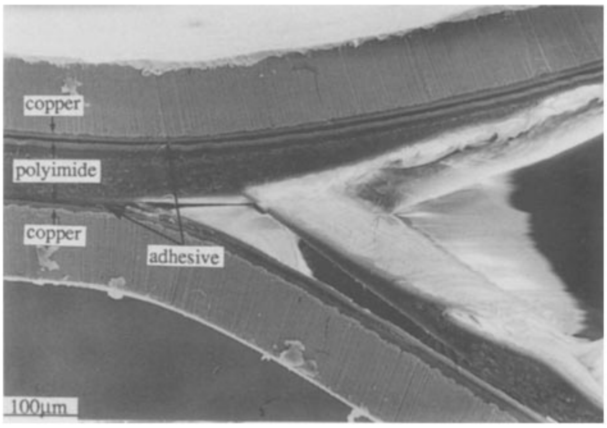

Figure 17 Scanning electron micrograph from the *in situ* peel test of a "low-thermal history" laminate showing the primary crack propagating in the polyimide film but with a secondary crack having developed near the polyimide–adhesive interface.

3.4. Role of the polyimide–adhesive interface

It was noteworthy that there was no evidence of true interfacial failure between the polyimide and adhesive layer in any of these laminates. Hence, any effect that the thermal history might have on the surface properties of the polyimide would appear to be irrelevant. Indeed, other studies have found no significant differences in the surface chemistries of the "low-thermal history" and "high-thermal history" treated polyimide films, even when using the most sensitive surface analytical techniques such as X-ray photoelectron and fast atom bombardment spectroscopy [4]. What appears to be of primary importance is that the "low-thermal history" film possesses a relatively weak boundary layer close to its surface which acts as an inherently low energy fracture path during a peel test. On the other hand, the polyimide film subjected to the "high-thermal history" does not possess such a weak boundary layer and the laminates fracture mainly by cohesive fracture through the adhesive layer.

4. Conclusions

The peel tests conducted inside the scanning electron microscope on polyimide–copper laminates have identified the various failure modes which may be observed and these have been employed to successfully explain the various types of peel behaviour which have been recorded in the standard peel test for such laminates. Further, the *in situ* peel tests have conclusively demonstrated that the superior peel energies of the laminates made using "high-thermal history" polyimide films, compared to those using "low-thermal history" films, is associated with the relative strengths of a boundary region of these polyimide films. The "low-thermal history" polyimide films possess a relatively weak boundary region close to the surface through which a peel crack may propagate comparatively readily. Current work is concentrated on identifying the nature of the weak boundary layer present on the "low-thermal history" treated polyimide films.

Acknowledgements

The authors would like to thank E.I. Du Pont De Nemours & Co. for financial support for this research programme and, in particular, Dr J. R. Edman for his support and encouragement in so many ways.

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Received 12 July
and accepted 15 September 1988