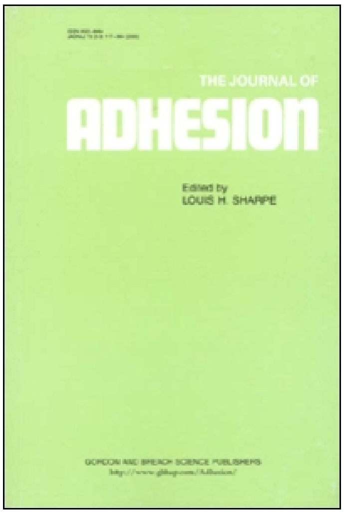

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The Application of Inelastic Electron Tunnelling Spectroscopy to Epoxide Adhesives

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The Application of Inelastic Electron Tunnelling Spectroscopy to Epoxide Adhesives

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The theory of inelastic electron tunnelling spectroscopy (IETS) and the suitability of this technique for examining adhesive-aluminium oxide interfaces are discussed. IET spectra are presented of an epoxide resin (the diglycidyl ether of bisphenol A), two aliphatic amine hardeners (di-[1-aminopropyl-3-ethoxy] ether and triethylene tetramine), and mixtures of resin and hardener before and after subjection to the usual heat curing schedules. These show that the curing reaction does not take place within an IETS junction; a possible reason for this is the epoxide resin is physically adsorbed on to the aluminium oxide surface whilst the hardeners may be chemically adsorbed through the amine groups.

1. INTRODUCTION

Epoxide adhesives are being increasingly used and one of their most important applications is in the aircraft industry where they are used in airframe construction. Aircraft are required to function in many diverse natural environments ranging from low temperature, arctic and high altitude conditions to tropical high humidity climates, and current commercial jets have anticipated lifetimes of up to 30 years. Thus the bonded components must be structurally reliable for a considerable period of time. However, epoxide adhesive-bonded structures suffer a reduction in strength with prolonged exposure to high humidity environments.[1–5] It has been demonstrated that such bond strength deterioration is due to the adverse effect of water on the adhesive-metal oxide interface, rather than on the bulk adhesive.[6,7]

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A recently developed technique which is suitable for studying the way in which organic materials are adsorbed onto metal oxide surfaces is inelastic electron tunnelling spectroscopy (IETS). This technique measures the vibrational spectrum of adsorbed molecules and allows changes in the spectrum to be correlated with changes in the chemical state of the molecule-oxide interface. Thus IETS is a convenient way of examining adhesive-metal oxide interfaces and has the potential to provide valuable information on the mechanism of bond strength deterioration in humid environments. White, Godwin and Wolfram[8] have already demonstrated the possible applications of IETS to adhesion.

IETS was discovered in 1966 by Jaklevic and Lambe,[9] and it records the vibrational spectrum of organic materials adsorbed on the insulator of a metal-insulator-metal junction. These junctions are most frequently of the form of aluminium-aluminium oxide-organic material-lead. Such a junction is represented in Figure 1a.

When a bias, V, is applied across a junction, the Fermi levels become separated in energy as shown in Figure 1b. Electrons may now tunnel elastically from the filled conduction states in metal 1 to adjacent empty states in metal 2. This elastic current increases linearly to a first approximation with applied bias.

When a monolayer of organic material is adsorbed on the insulator, a tunnelling electron may excite a vibrational mode of the adsorbate and lose energy in the process. Such an inelastic process, shown in Figure 1c, will require a minimum bias, V_{min}, given by

$$eV_{min} = h\nu \tag{1}$$

where e is the electronic charge, h is Planck's constant and ν is the vibrational frequency of the excited mode. Inelastic processes are relatively weak; typically less than 1% of the electrons tunnel inelastically. However, they may be distinguished from the elastic background by examining the associated steps in the conductance dI/dV, or more commonly the peaks in the second derivative d^2I/dV^2. The current-voltage characteristics are shown in Figure 2. The second derivative is usually measured by superimposing small modulation voltages on a slowly increasing junction bias and measuring the level of the second harmonic generated by the junction non-linearity.

A comprehensive review of IETS has been published by Hansma.[10]

2. EXPERIMENTAL PROCEDURE AND RESULTS

A description of the spectrometer and the experimental details of tunnel junction fabrication have been published elsewhere.[11] Briefly junctions were

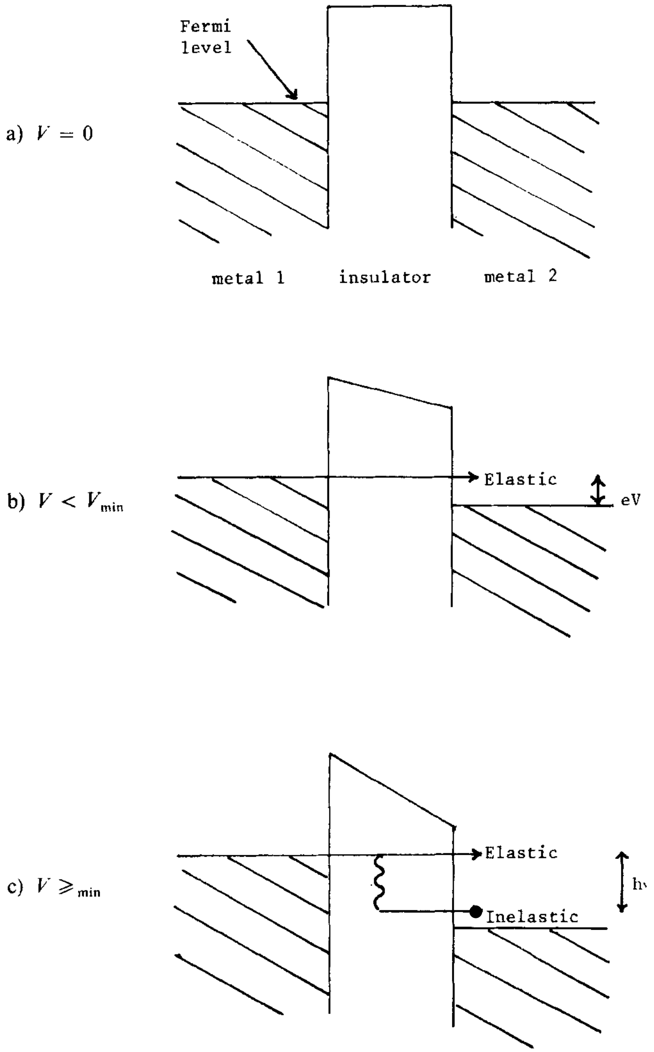


FIGURE 1 Elastic and inelastic tunnelling at absolute zero for non-superconducting metals.

prepared on glass microscope slides as shown in Figure 3. The metal electrodes were deposited by vacuum evaporation, their geometry being controlled by masks. Evaporation of the aluminium electrodes was followed by a glow discharge oxidation which produced an oxide layer approximately 3 nm thick. The slide was then covered with a dilute solution of the organic material and the excess spun off. The junctions were completed by evaporation of the lead electrodes. The completed glass slide was inserted into a specimen holder

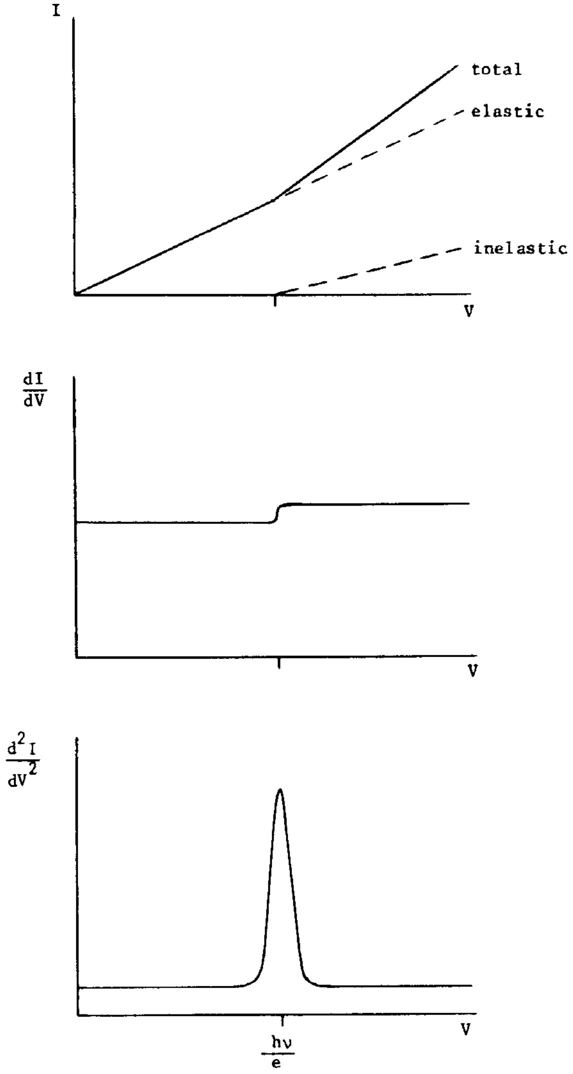


FIGURE 2 The detection of inelastic electron tunnelling.

which could be lowered into a liquid helium dewar and connected to the spectrometer.

The spectrometer is housed in a room totally screened with aluminium sheets and containing a filtered mains supply. This substantially eliminates both radiated and mains-borne noise so that a high signal to noise ratio is achieved. A block diagram of the spectrometer is shown in Figure 4.

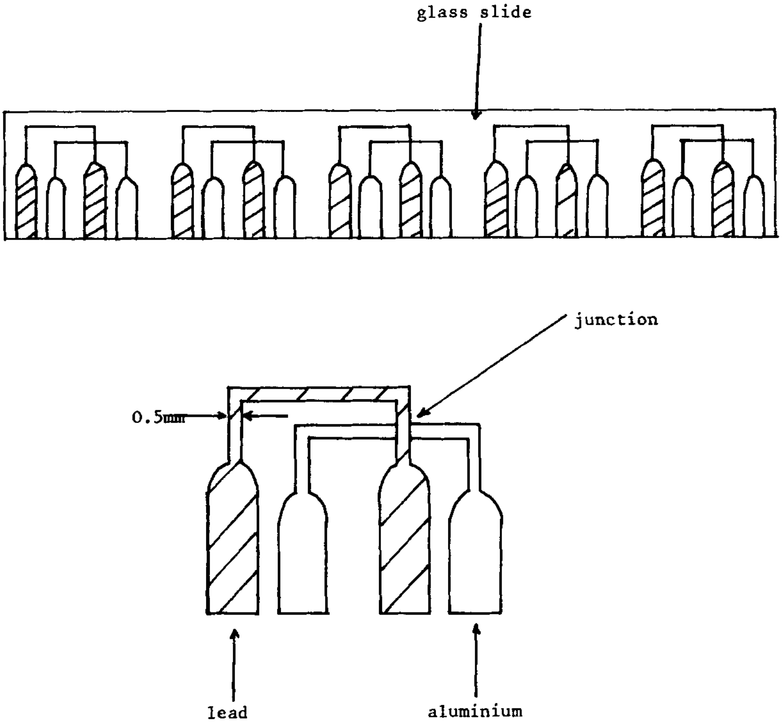


FIGURE 3 A completed device consisting of five tunnel junctions and a single junction shown in more detail.

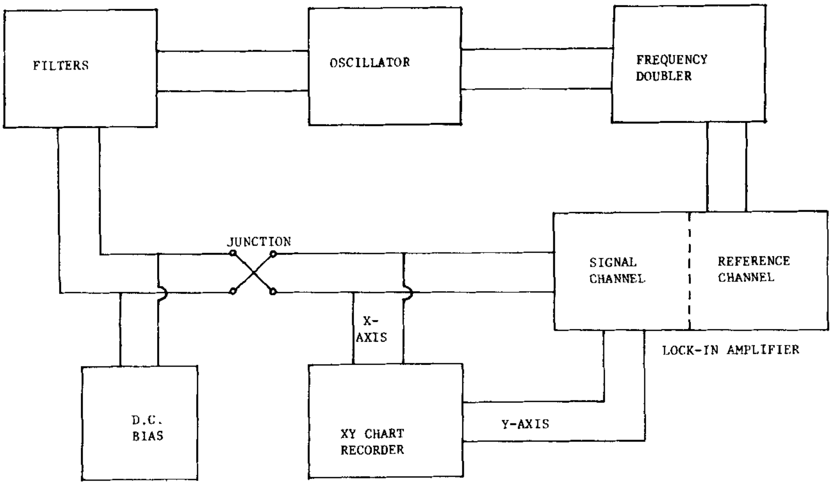


FIGURE 4 Block diagram of IET spectrometer.

The small non-linearities in the junction current-voltage characteristics are measured by superimposing a 50 kHz A.C. modulation voltage (usually $\leqslant 4$ mV peak-to-peak) on a slowly increasing junction bias voltage. The modulation current produces a second harmonic voltage across the junction which is proportional to the second derivative, d^2V/dI^2. This small second harmonic voltage is recovered by a lock-in amplifier and plotted as a d.c. signal on the y-axis of an x-y recorder. The bias voltage is recorded on the x-axis.

The adhesive components studied were the diglycidyl ether of bisphenol A (DGEBA) and two aliphatic amine hardeners, namely di(l-aminopropyl-3-ethoxy) ether (DAPEE) and triethylene tetramine (TETA). All were soluble in benzene (spectroscopy grade) which did not leave a detectable residue in the junction after doping. The IET spectra shown in Figures 5, 6 and 7 were obtained from solutions containing 0.05 mg cm^{-3} DGEBA, 0.5 mg cm^{-3} DAPEE and 0.5 mg cm^{-3} TETA respectively. IET spectra of a simple epoxide, styrene oxide (50 mg cm^{-3} in spectroscopy grade ethanol), and a simple amine, 1,6-diaminohexane (0.5 mg cm^{-3} in deionised water) were also studied to aid in peak assignments.

In Tables I and II the IET spectra of DGEBA and DAPEE are compared with the corresponding IR and Raman spectra and some vibrational mode assignments[12] are given. IR spectra were obtained from smears on KBr discs using a Beckman AccuLab 1 spectrometer. Raman spectra were measured using a Cary 83 spectrometer.

IET spectra, shown in Figures 8 and 9, were obtained from benzene solutions of the uncured adhesive mixtures DGEBA/DAPEE (0.033 mg cm^{-3} DGEBA and 0.011 mg cm^{-3} DAPEE) and DGEBA/TETA (0.1 mg cm^{-3} DGEBA and 0.011 mg cm^{-3} TETA). The solutions were prepared using the recommended resin to hardener ratios.[13, 14]

Three curing schedules were investigated for the DGEBA/DAPEE adhesive. These were room temperature curing for up to 70 hours, 80°C for 3 hours, and 120°C for 3 hours. To prevent contamination room temperature curing was carried out on completed tunnel junctions in a sealed glass vessel which had been evacuated using a sorption pump containing type 4A molecular sieves. Curing at elevated temperatures was carried out in the evaporator, prior to the deposition of the lead electrodes. Vacuum was $\leqslant 10^{-4}\tau$ and heating was by means of a coil (200 W) attached to the masks holding the glass slide in position. Curing at 80°C for 3 hours was also investigated for junctions doped with a benzene solution containing twice the recommended concentration of DAPEE (0.033 mg cm^{-3} DGEBA and 0.022 mg cm^{-3} DAPEE). Only one curing schedule, 3 hours at 60°C, was studied in the case of the DGEBA/TETA adhesive.

A chromel-alumel thermocouple junction in thermal contact with the

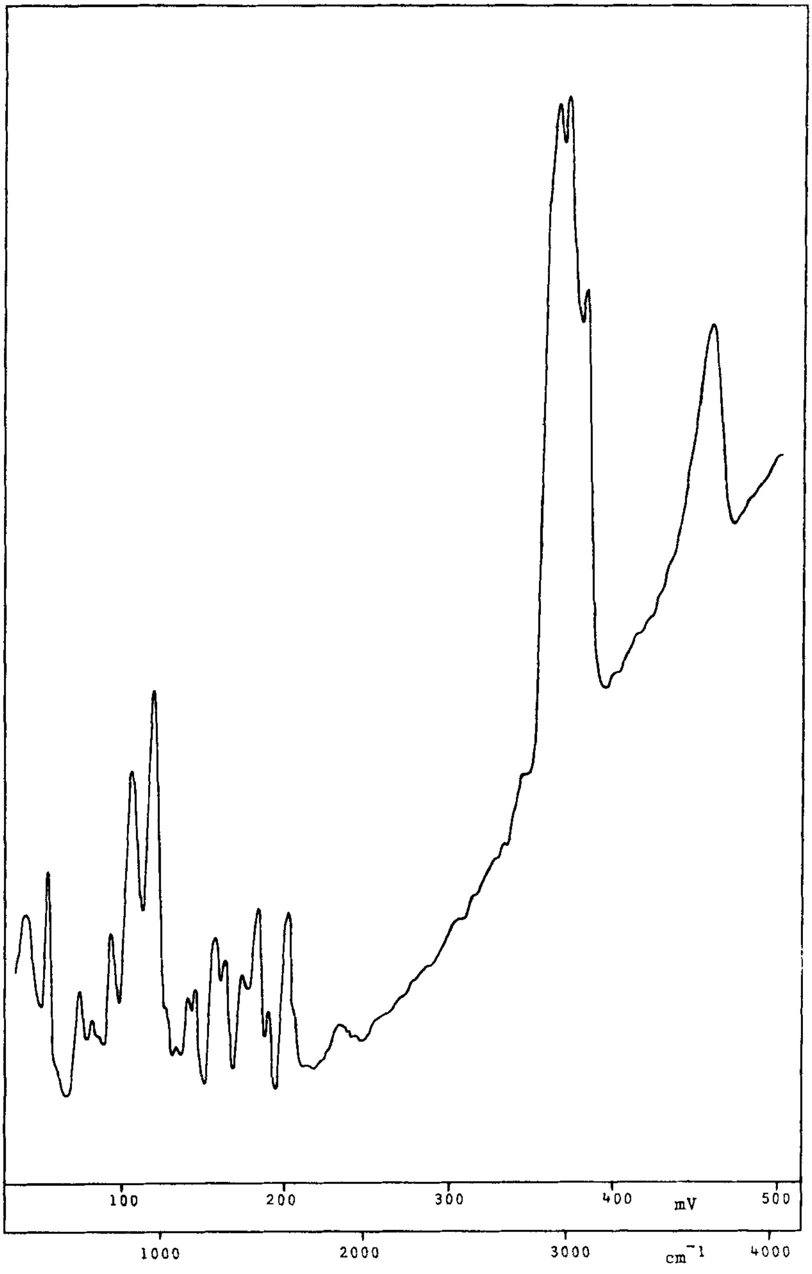


FIGURE 5 IET spectrum of DGEBA.

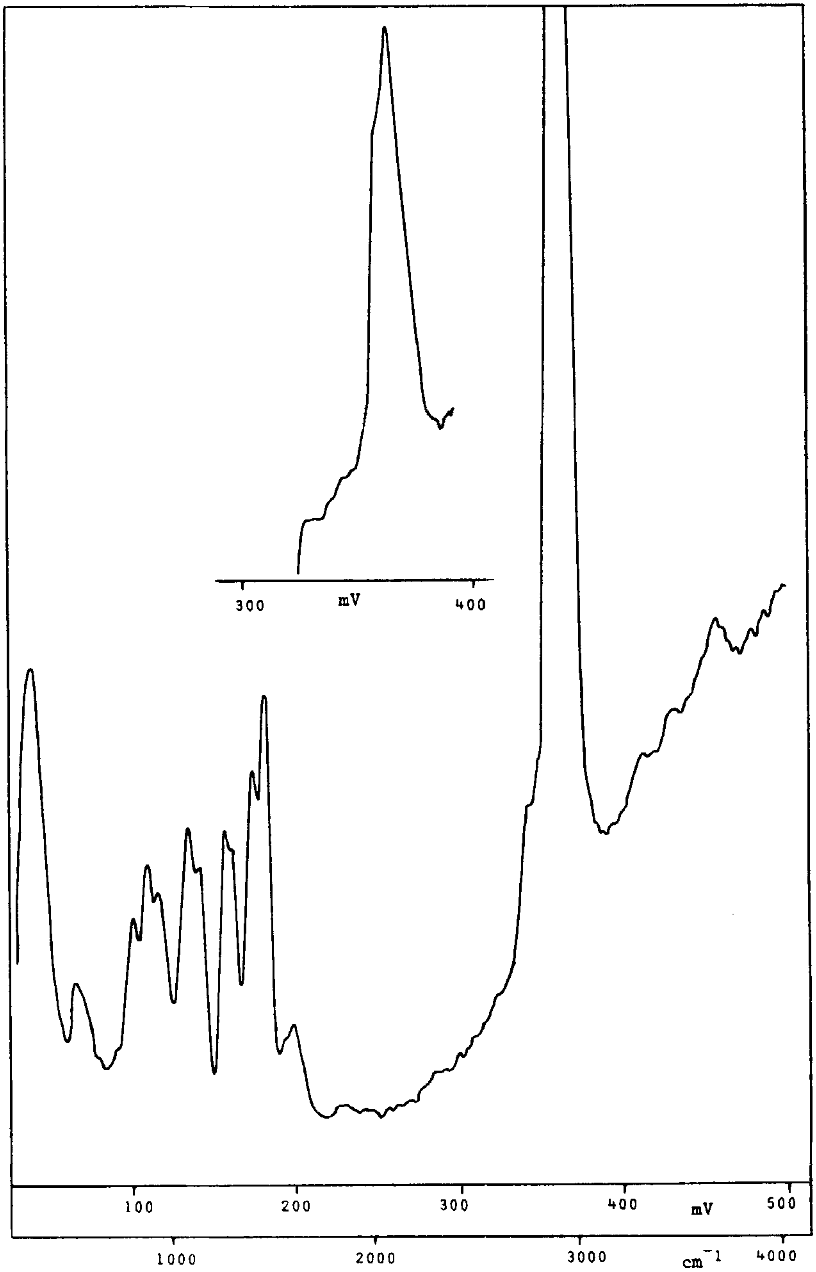


FIGURE 6 IET spectrum of DAPEE.

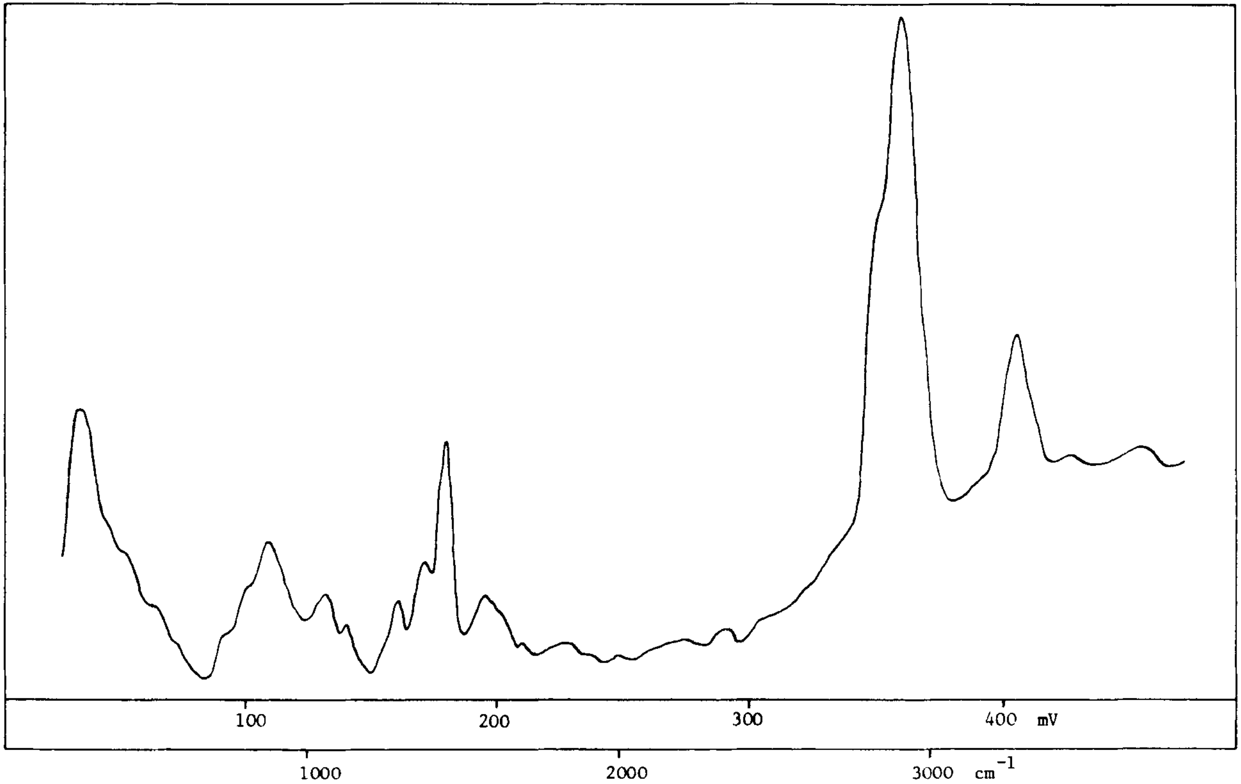


FIGURE 7 IET spectrum of TETA.

TABLE I

Comparison of IET, IR and Raman spectra of DGEBA

IET (mV)	IET (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	Peak Assignment
40	311m			aluminium oxide phonon
			385w	
53	423s			aromatic C-C bend out of plane
59	*466w			
73	582w			
81	648w	650w	630m	
84	*671w		660m	
93	741m		730w	
		770m	750w	
			800s	aromatic C-H bend out of plane
			820s	
104	829s	840s	830s	
			910m	
117	939s	925m	930w	asymmetric epoxide ring vibration
126	*1007w	980w		
133	1063w	1045s		aromatic C-H bend in plane
			1090w	
140	1117w	1115w	1110s	aliphatic ether C-O stretch
		1140w	1130w	
144	1157w	1165w	1150w	Aliphatic C-C stretch
		1195s	1180m	
			1225m	
156	1250m	1260s	1245m	aromatic ether C-O stretch
			1280w	
162	1300m	1310s		
		1355m		
		1370m		
173	1386w	1395		aliphatic C-H bend
		1425m		
		1440m		
181	1453m	1465m		
188	1509w	1520s		
		1560w		
200	1601m	1590m	1605m	aromatic C-C stretch
204	*1640w	1620s		
		1780w		
234	1877w			
		1900w		overtone and combination bands
		2090w		
342	2750w	2785w		
			2880w	
362	2913s	2900m		aliphatic C-H stretch
368	2962s	2955s	2940w	
		2995s		
381	3061s	3090m	3080w	aromatic C-H stretch
		3540m		
456	3670s			O-H stretch

* shoulder w weak m medium s strong

TABLE II

Comparison of IET, IR and Raman spectra of DAPEE

IET (mV)	IET (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	Peak Assignment
38	299s			aluminium oxide phonon
65	519w			
70	*555w		550w	
80	*637w			
92	*732w			CH_2 rock
102	815w			NH_3^+ rock
		865m	850w	
111	884m			
116	929m	935m		
			1030w	
135	1077m			C-N stretch
141	1127m	1110s	1125s	C-O stretch
157	1261m	1250w	1240w	CH_2 wag
160	*1285m	1300w	1280m	NH_3^+ deformation; CH_2 wag
		1350m		
174	1392s			
181	1453s	1465m	1460w	C-H bend
		1480m		
			1525m	
199	1597w	1600m		N-H bend; NH_3^+ deformation
327	*2625w		2650w	
341	*2740w			
357	*2873s	2875s	2880m	C-H stretch
361	2907s	2940s	2920m	
411	3307w	3310m		NH_3^+ stretch; N-H stretch
		3375m		N-H stretch
429	3454w			
456	3666w			O-H stretch

supporting microscope slide was used to measure and control curing temperatures.

3. DISCUSSION

The IET spectrum of DGEBA agrees well with IR and Raman data; most of the peak positions are within ±10 cm^{-1} of the corresponding IR peaks and ±20 cm^{-1} of the corresponding Raman peaks. The asymmetric epoxide ring vibration occurs as a strong peak at 939 cm^{-1} (117 mV) in the IET spectrum, compared with a medium intensity peak at 925 cm^{-1} in the IR spectrum and a weak peak at 930 cm^{-1} in the Raman spectrum. There is no evidence from the IET spectrum to suggest that DGEBA is chemisorbed onto the aluminium oxide surface, therefore it is assumed that the molecule is attached by physical adsorption.

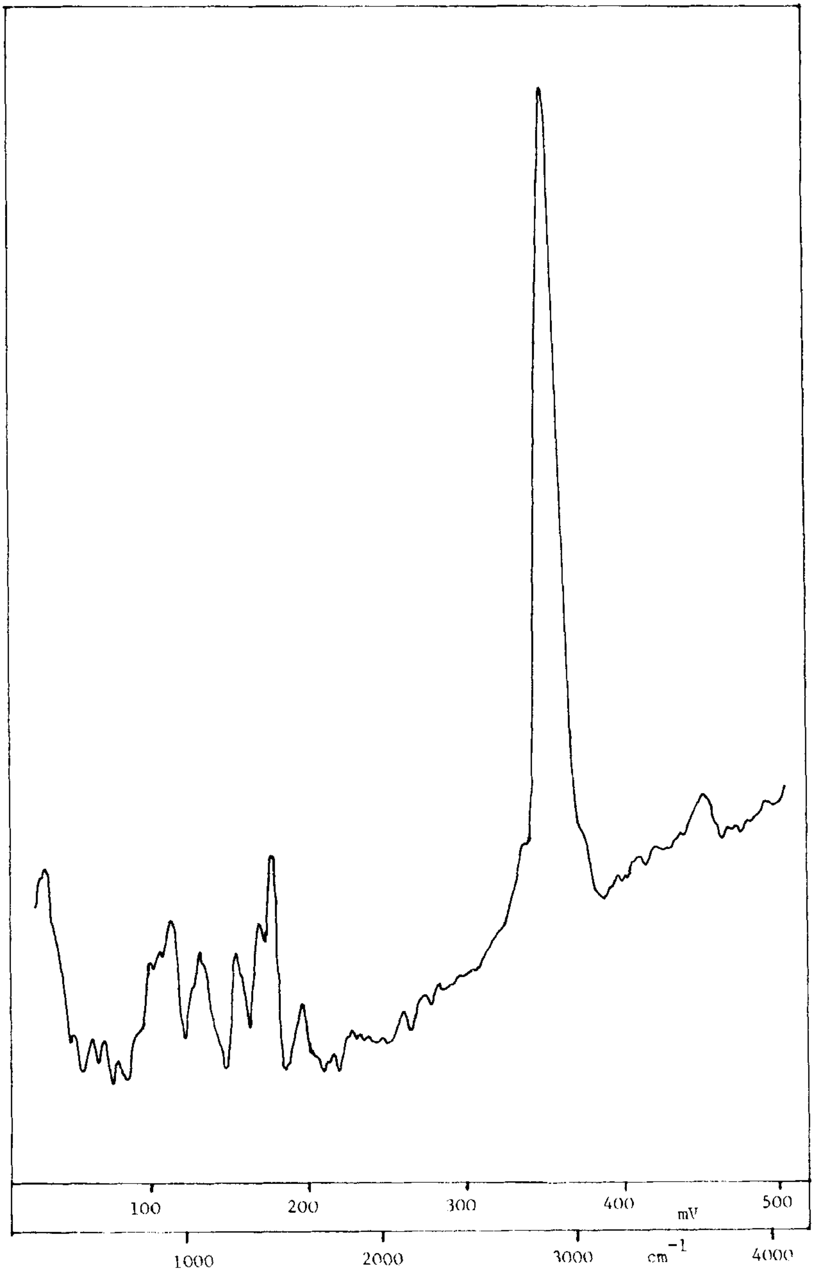


FIGURE 8 IET spectrum of an uncured mixture of DGEBA and DAPEE.

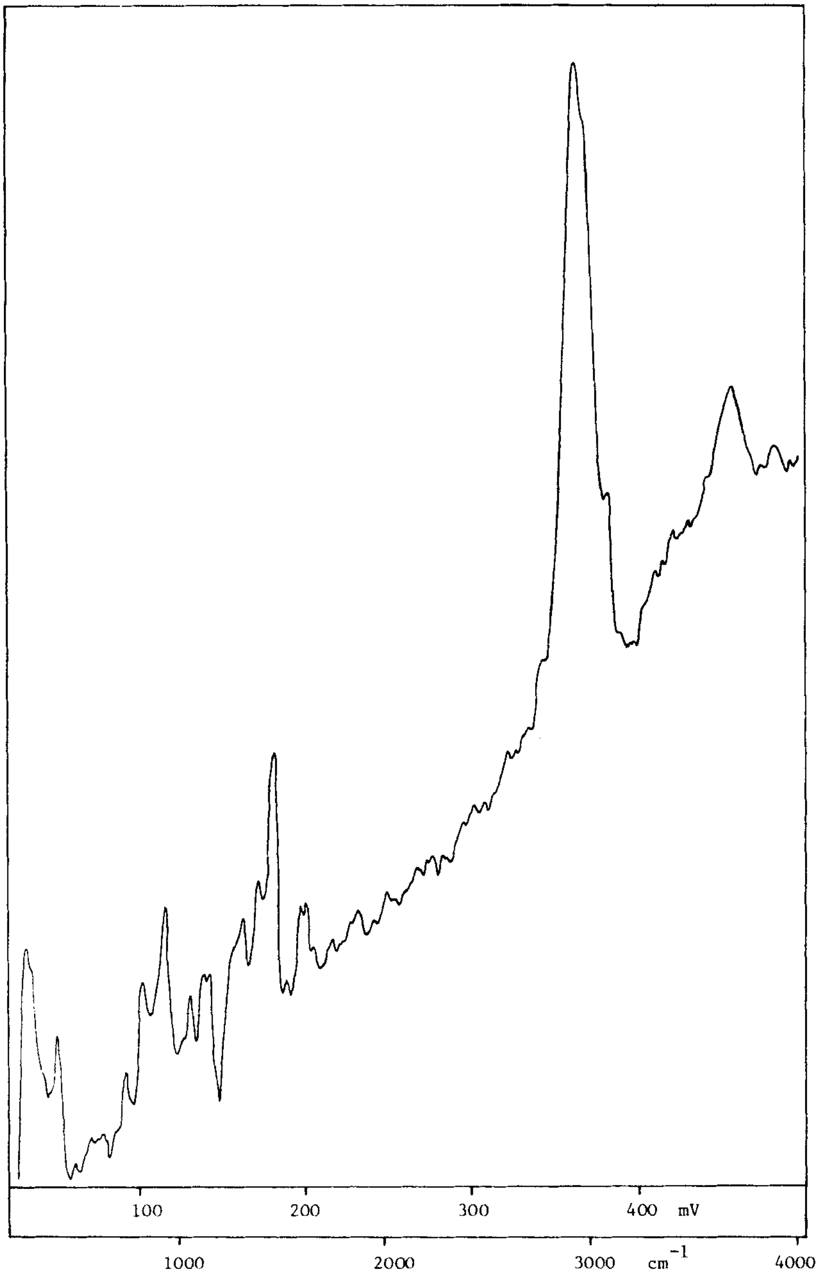
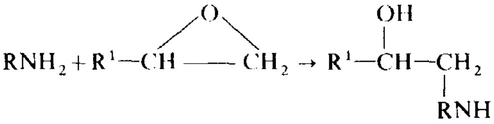


FIGURE 9 IET spectrum of an uncured mixture of DGEBA and TETA.

The IET spectrum of DAPEE is also in close agreement with the IR and Raman spectra. The IET spectrum however, in common with that of TETA, shows only weak N-H bending and stretching modes. This suggests that some form of chemisorption of amine groups on the aluminium oxide surface may be occurring.

The IET spectra of the uncured adhesive mixtures show features of the corresponding component spectra. In the spectrum of the DGEBA/DAPEE mixture, the epoxide peak occurs at 932 cm^{-1} (116.5 mV) and an N-H stretching mode is present at 3320 cm^{-1} (413.4 mV); in the DGEBA/TETA spectrum, the epoxide ring absorbs at 930 cm^{-1} (116.3 mV).

For both the adhesives and all the curing schedules investigated, the spectra obtained after curing were essentially the same as the spectra of the uncured adhesive mixtures. Also, no significant changes could be detected after curing for the DGEBA/DAPEE adhesive containing excess hardener. The main difference to be expected between the uncured and cured spectra is the disappearance of the epoxide ring due to its reaction with amine, thus

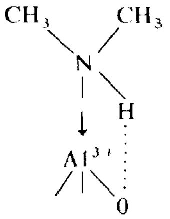


$$RNH_2 + R^1\text{—}\overbrace{CH\text{——}CH_2}^{O} \rightarrow R^1\text{—}\overset{\displaystyle OH}{\overset{|}{CH}}\text{—}\underset{\underset{\displaystyle RNH}{|}}{CH_2}$$

This reaction can easily be followed using IR spectroscopy and by using the technique[15] it has been shown that the curing schedules used are more than normally adequate to bring about the chemical cure of epoxides based on DGEBA and alipatic amines.

The persistence of the epoxide peak throughout the curing treatments leads to the conclusion that the epoxide ring in DGEBA does not react with amine hardeners within a tunnel junction. This could be due to the epoxide and/or amine groups being adsorbed at the aluminium oxide surface and so prevented from reacting with each other. There is some evidence in the literature to suggest that this may be the case.

Cook and Ross[16] postulated that at low surface coverages methylamines are chemisorbed on γ-alumina in the following manner



and at higher coverages, adsorbate-adsorbate interactions such as van der Waals forces occur. From a study of a series of aliphatic amines on alumina, Koubek *et al.*,[17] suggested that at low surface coverages very strong adsorption occurs on aluminium ions, whereas at higher coverages, hydroxyl groups and then oxide ions become the active adsorption sites. Baldwin *et al.*,[18] compared IR spectra of octadecylamine alone and adsorbed on alumina. A broad band at 2,500 cm^{-1} in the later spectrum was attributed to the formation of an amine salt, $RNH_3^+ \ {}^-O—Al—$. Evidence suggesting the protonation of amines on alumina surfaces has also been found by IETS,[19,20] where peaks have been assigned to NH_3^+ rocking, deformation and stretching modes. However, a study[21] of the adsorption of amines on alumina by NMR showed no evidence of large chemical shifts such as occur on protonation of the amines in aqueous acids.

The adsorption of epoxides on aluminium oxide has been less widely studied. Baldwin *et al.*,[18] investigated the adsorption of an epoxide resin and diethylenetriamine on alumina. They found that while both compounds were physically adsorbed on the surface, diethylenetriamine was adsorbed more strongly, resulting in the amine being preferentially adsorbed from a 5% chloroform solution of a mixture of the two components (94 parts epoxide resin :6 parts amine). Similar results have been obtained by Freidin *et al.*,[22,23] who found that octadecylamine was adsorbed more strongly on γ-alumina than ED-5 epoxide resin and the former could not be displaced by the latter. Yakoulev *et al.*,[24] studies the interaction of an epoxide resin with aluminium powder in the absence of amines and found that on heating, the formation of metal-polymer covalent bonds was accompanied by a decrease in the epoxide group content and an increase in the OH group content of the original polymer. The formation of an epoxide resin-aluminium bond was confirmed by attenuated total reflectance IR spectroscopy.

Thus it appears that for an epoxide/amine mixture within an IETS junction, the amine may be preferentially adsorbed on the aluminium oxide surface and the strong interaction, which may be chemical in nature, cannot be disrupted by the epoxide resin. Hence the curing reaction is prevented from taking place.

However, it may be possible to induce cure within an IETS junction by choosing an amine which will adsorb less strongly on aluminium oxide. Kozlov *et al.*,[25] found that aliphatic normal amine molecules adsorb vertically on alumina and the amount of adsorption decreases with increasing branching of the aliphatic radical, for example, n-$BuNH_2$ > sec-$BuNH_2$ > tert-$BuNH_2$. From an investigation of ethyl-, diethyl-, and triethylamine adsorbed on alumina, Koubek *et al.*,[17] showed that the amount of adsorption decreased in the order primary amine > secondary > tertiary due to the effects of steric hindrance. These results indicate that a tertiary amine with branched aliphatic groups will adsorb relatively weakly, and may therefore be suitable for curing an epoxide on an aluminium oxide surface.

If cure of epoxide-amine adhesives does not take place at interfaces with aluminium oxide, due to preferential adsorption of amine groups at the interface, two possible structures for the interfacial region in adhesive joints can be put forward. In the first of these a layer of amine containing molecules is completely adsorbed on the oxide, so separating the bulk of the cured adhesive, which is a cross linked network, from the oxide layer. The integrity of the adhesive bond will thus depend on the forces between the various layers at the interface any one of which might be weak and so constitute a potential focus of joint failure.

The forces between the bulk of the adhesive and the amine layer, which would consist of polar and dispersion forces and possibly hydrogen bonds might constitute a weak layer.

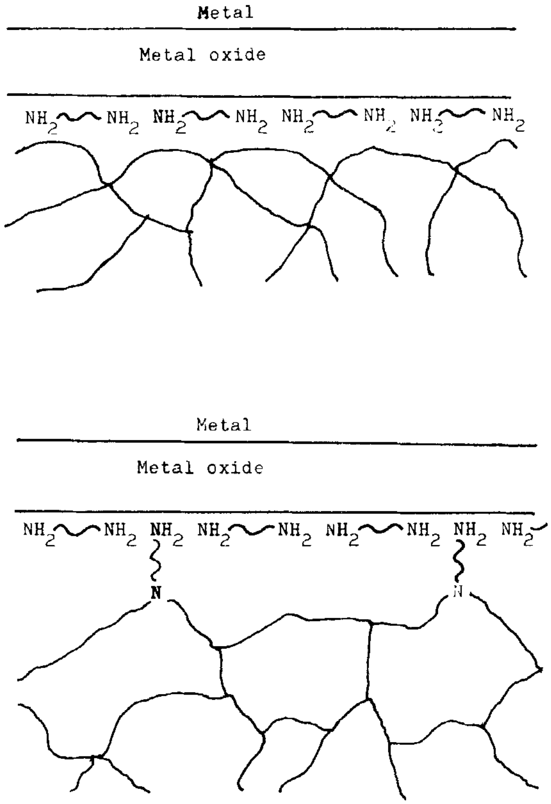


FIGURE 10 Models for the interface in epoxide to metal joints.

What seems a more plausible model is for some of the amine containing molecules to be partially adsorbed on the oxide. That is for some amine groups to be free whilst others are adsorbed to the oxide. Whilst the first model may be possible for amines applied to the surface from dilute solution (the case in making IETS junctions) when a bulk mixture of components is applied, the lower state of order implied by partial adsorption is more likely. The free amines are now free to participate in reaction with epoxides in the curing process and so form covalent bonds, removing the potential weak layer.

These two models are illustrated for the case of a simple diamine in figure 10.

4. CONCLUSIONS

(a) IETS spectra can be obtained for the resin and amines used in epoxide adhesives. These spectra are quite similar to their IR and Raman spectra.

(b) The peak assigned to the epoxide group is not removed when an IETS junction containing an epoxide-amine mixture is heated to temperatures at which such a mixture would normally be expected to cure. It is concluded that cure of the epoxide does not take place in the junction, a possible reason for this is the adsorption of amine groups on the aluminium oxide surface.

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