Localization of the curing agent at an epoxy resin/oxidized aluminium interface

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An epoxy resin/4,4'-diaminodiphenylmethane (DDM) curing agent system was selected and cured on oxidized aluminium to investigate the structure and interactions at the cured epoxy resin/oxidized aluminium interface. Epoxy resin cured on oxidized aluminium was immersed in 0.1 N HCl solution to dissolve the oxidized aluminium film and the interface was prepared. Surface and interface structure and surface free energy were measured by X-ray photoelectron spectroscopy and contact angle measurement, respectively. Competitive adsorption of epoxy resin and DDM on Al_2O_3 particles was measured by Fourier transform infra-red spectroscopy. DDM was adsorbed preferentially on Al_2O_3 particles and epoxy resin was adsorbed on Al_2O_3 particles whose surface was covered with DDM. Nitrogen content and surface free energy of the cured epoxy resin/oxidized aluminium interface were higher than those of the epoxy resin/air surface. It is suggested that DDM localized in the cured epoxy resin/oxidized aluminium interface. The interactions at the cured epoxy resin/oxidized aluminium interface were acid–base interactions formed between amino groups in DDM and acidic sites on the oxidized aluminium.

INTRODUCTION

High-performance materials are currently required in many important fields, and the various demands in each field cannot always be fulfilled by materials consisting of only one substance. As a result, multi-component materials consisting of two or more substances exist. However, composite materials also bring about some problems at the same time. For example, because of differences between the mechanical properties of each component, residual stress exists in the interface of composite materials.

Epoxy resin and epoxy/substrate composites are widely used in many important fields, such as the electronics and aerospace industries, owing to their excellent electronic and mechanical properties. For example, epoxy resin has been used as a protective for metals and semiconductors in the electronics industry and as a thermosetting adhesive in the aerospace industry. When epoxy resin is cured against a substrate at a high temperature and cooled down to room temperature, residual stress is known to arise because of the difference in thermal expansion coefficients of the resin and adherend[1-5]. The residual stress reduces adhesion strength and induces cracking in the materials. Furthermore, the residual stress might cause electronic insulating properties and weatherability to deteriorate, resulting in shorter lifetimes of integrated circuits and large-scale integrated circuits.

We have measured the residual stress at a cured epoxy resin/oxidized aluminium interface by means of X-ray diffraction and determined that a residual stress of 29 MPa exists[6]. Many researchers have tried to reduce the stress by modifying the epoxy resin, for instance, with rubbery components[7] and plasticizers[8], or by incorporating rubbery[9] or inorganic particles[2]. But such methods bring about deterioration of the electronic and mechanical properties of epoxy resin. On the other hand, only a few researchers have studied the characterization and control of the epoxy resin/substrate interface[10]. To reduce the residual stress without spoiling the properties of the epoxy resin, it is important to characterize the epoxy resin/substrate interface and form a well-ordered interface. We think that we can reduce the residual stress to design the interface. In this study, the structure and interactions at a cured epoxy resin/oxidized aluminium interface were investigated using X-ray photoelectron spectroscopy (X.p.s.), Fourier transform infra-red spectroscopy (*FT*i.r.), and contact angle and interfacial tension measurements.

EXPERIMENTAL

Materials

A liquid diglycidyl ether of bisphenol A type epoxy resin (Epikote 828, Shell Chemical Co; $M_n = 380$,

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H2N —⟨◯⟩—CH2 —⟨◯⟩—NH2

DDM

CH2-CH-CH2-O+⟨◯⟩-C⟨◯⟩-O-CH2-CH-CH2+O-⟨◯⟩-C-⟨◯⟩-O-CH2-CH-CH2
with CH3 groups and OH, CH3 labels

epoxy resin

Figure 1 Structural formulae of epoxy resin and DDM

epoxy equivalent $= 190 \pm 5$ g/equiv) and 4,4'-diamino-diphenylmethane (DDM), an aromatic diamine curing agent, were chosen as the resin system in this study. DDM was purified by recrystallization from methanol solution. The stoichiometric ratio of epoxy resin to DDM was 2:1. The molecular formulae of the curing agent and resin are given in *Figure 1*.

The adherends used were commercial Al plate and film (99.9% purity). The Al plate and film were polished with an abrasive and cleaned ultrasonically in acetone for 5 min. They were washed in deionized water, treated with chromic acid and washed in deionized water again. Then they were treated at 300°C for 3 h under N_2 to remove water. The Al surface was observed by scanning electron microscopy; representative micrographs are shown in *Figure 2*. For the most part, the Al surfaces were flat and no noticeable roughness was found. Surface roughness was also measured using a surface roughness meter, the results showing that the roughness was < 0.2 μm. The initial surface chemistry of the Al plate was studied by X.p.s. The Al 2p spectra consisted of a doublet, the main peak at higher binding energy (~ 75 eV) corresponding to the oxidized aluminium, $-Al-O-$, and the lower binding energy peak (~ 73 eV) corresponding to pure Al. Only a small amount of C 1s peak was also detected, due to contamination.

Epoxy resin was mixed with various amounts of DDM at 100°C. The mixture was poured on Al and precured at 80°C for 2 h, then cured at 180°C for 6 h. After curing, the specimen was cooled down gradually to room temperature and preserved in desiccator for > 24 h. To observe the cured epoxy resin/oxidized aluminium interface, the specimen was immersed in 0.1 N HCl solution to dissolve the Al.

Figure 2 Scanning electron micrographs of polished oxidized aluminium surfaces

Measurements

X.p.s. measurements were performed using a Kratos XSAM800 instrument with an X-ray source of Mg Kα radiation. The binding energy scales for the sample were referenced by setting the C–H peak maxima in the C 1s spectra to 285.0 eV. The take-off angle was 0 or 60°. The pressure in the X.p.s. chamber was $\sim 5 \times 10^{-8}$ Pa, the power output of the X-ray tube was 150 W.

Infra-red spectra were taken using a Shimadzu FTIR-4200 spectrophotometer. The spectral resolution was 2 cm^{-2} and 500–1000 scans were recorded to improve the signal-to-noise ratio. Adsorbance of epoxy resin and DDM on Al_2O_3 was determined from the peak height of the i.r. spectra.

Contact angle measurements were carried out using a liquid drop technique; the experimental procedure used here has been described in an earlier publication[11]. Equation (1) was used to determine the contact angle θ from the advancing contact angle θ_a and the receding contact angle θ_r:

$$\cos \theta = (\cos \theta_a + \cos \theta_r)/2 \qquad (1)$$

Surface free energy was determined by Owens' equation[12] with contact angles of water and methylene iodide.

Interfacial tension measurements were performed with a du Nouy type Shimadzu interfacial tension-meter.

RESULTS AND DISCUSSION

Competitive adsorption

Competitive adsorption of epoxy resin and DDM on Al_2O_3 particles was carried out from xylene solution, xylene being a good solvent for epoxy resin and DDM. Epoxy resin and DDM were mixed stoichiometrically. The xylene solution was prepared by dissolving 1 g of the mixture in 100 ml of xylene. Al_2O_3 particles were added to the solution. The adsorbance of each component on the Al_2O_3 particles was determined from the i.r. spectra of the supernatant solution by monitoring the absorbance peaks at wavenumbers that did not overlap one another, i.e. the C–N peak at 1620 cm^{-1} of DDM and the ether peak at 1040 cm^{-1} of epoxy resin.

The spectra of the supernatant solution in these regions are shown as a function of time in *Figure 3*. Because reaction of epoxy resin and DDM might cause changes in intensity in the i.r. spectra, we also measured the i.r. spectra of epoxy resin and DDM in xylene solution that did not include Al_2O_3 particles, as a blank. As also shown in *Figure 3*, the intensity of the i.r. spectrum of the blank remained constant. This indicates either that the reaction of epoxy resin and DDM did not occur in the xylene solution or that the reaction had no effect on the intensity. The spectrum of the epoxy resin hardly changed after 3 h, while that of DDM changed significantly during the same time.

These results are summarized in *Figure 4*, from which it is clear that first DDM adsorbed preferentially on the Al_2O_3 particles and that the epoxy resin adsorbed on Al_2O_3 particles whose surface was covered with DDM.

Spectra were also obtained from separate adsorption experiments of each component, and the absorbance ratios after 8 h are also shown in *Figure 4* as dotted lines. After 3 h, the adsorbance of DDM from the combined epoxy/DDM system was almost equal to that of the separately adsorbed DDM, i.e. the adsorbance of DDM reached saturation after 3 h. However, the adsorbance of epoxy resin after 8 h from
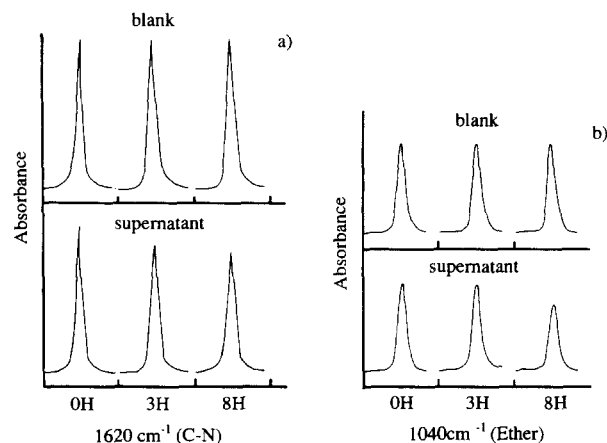

Figure 3 I.r. spectra of the supernatant solution, revealing the adsorption of DDM (a) and epoxy resin (b) on Al_2O_3 as a function of adsorption time
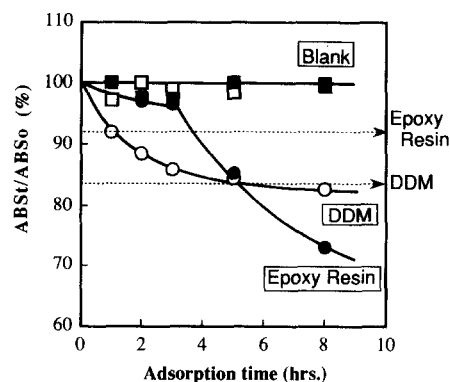

Figure 4 Absorbance ratio (from i.r. spectra) of the supernatant solution, revealing the competitive adsorption of epoxy resin and DDM from xylene solution on Al_2O_3 particles as a function of adsorption time: ●, epoxy resin; ○, DDM; ■, epoxy resin blank; □, DDM blank. Dotted lines indicate absorbance ratio obtained from separate adsorption experiments of each component

the combined system was three times greater than that from the separately adsorbed system.

This result suggested that epoxy resin is not adsorbed on the surface of Al_2O_3 particles directly but on the surface of particles covered with DDM. Epoxy resin and DDM are of equal mobility in xylene solution. Thus preferential adsorption of DDM may be caused by a difference in interaction between the components and Al_2O_3. DDM may have a stronger interaction with Al_2O_3 than epoxy resin.

X.p.s. measurements

Figure 5 shows the nitrogen content at the interface, calculated from N 1s X.p.s. spectra, *versus* DDM/epoxy resin ratio for cured epoxy resin/air and cured epoxy resin/oxidized aluminium interfaces. Before proceeding with this experiment, we confirmed that the nitrogen content of the cured epoxy resin/air interface did not change when the cured epoxy resin was immersed in HCl solution. As shown in *Figure 5*, the nitrogen content at each interface was approximately constant at the various DDM/epoxy resin ratios;
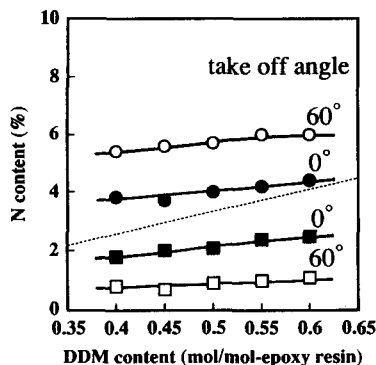
Figure 5 Nitrogen content, as obtained from N 1s X.p.s. peak, as a function of DDM/epoxy resin ratio for: ●, ○, epoxy resin/oxidized aluminium interface; ■, □, epoxy resin/air interface. Dotted line indicates nitrogen content in the bulk
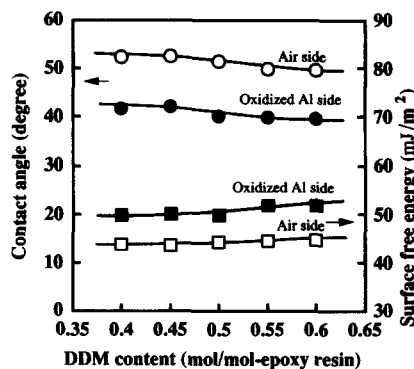

Figure 6 Contact angle of water on cured epoxy resin and surface free energy as a function of DDM/epoxy resin ratio for: ●, ○, epoxy resin/oxidized aluminium interface; ■, □, epoxy resin/air interface.

however, there was a great tendency that the nitrogen content of the cured epoxy resin/oxidized aluminium interface was higher than that of the cured epoxy resin/air interface and of the bulk (dotted line). The results of angle-dependent X.p.s. analysis showed the same trend. The sampling depth is about 60 and 30 Å for take-off angles of 0 and 60°, respectively[13]. Nitrogen content increased near the cured epoxy resin/oxidized aluminium interface.

This result suggests that the structure near the interface is not homogeneous. Epoxy resin units are localized at the cured epoxy resin/air interface, while DDM units are localized at the cured epoxy resin/oxidized aluminium interface in spite of the DDM/epoxy resin ratio. The surface and interface structure did not reflect the bulk structure linearly.

Contact angle measurements

The results of contact angle and surface free energy measurements for various DDM/epoxy resin ratios are presented in *Figure 6*. Before the measurements, we also confirmed that θ_a and θ_r of the cured epoxy resin/air interface remained unchanged after immersion of the cured epoxy resin in HCl solution. The contact angle of water and surface free energy were also approximately constant with DDM/epoxy resin ratio. The results show that the surface and interface structure did not reflect the bulk structure linearly. It was clear that the contact angle of the cured epoxy resin/oxidized aluminium interface was smaller than that of the cured epoxy resin/air interface and that the surface free energy of the cured epoxy resin/oxidized aluminium interface was larger than that of the cured epoxy resin/air interface. This result agrees with X.p.s. measurements and the tendency that DDM units adsorb preferentially on the oxidized aluminium surface, confirming once again that epoxy resin units localize at the interface of cured epoxy resin/air and that DDM units localize at the interface of cured epoxy resin/oxidized aluminium. Thus *FT* i.r., X.p.s. and contact angle measurements indicate that DDM interacts with the surface of the oxidized aluminium.
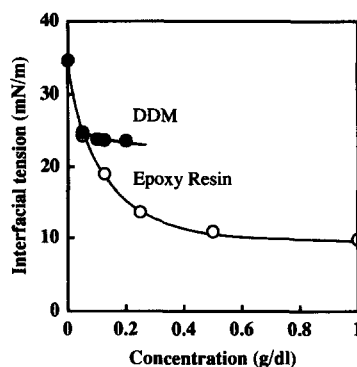
Figure 7 Interfacial tension measurements between water and xylene solutions of epoxy resin (○) and DDM (●)

Interactions in the interface

To investigate further the interactions between cured epoxy resin and oxidized aluminium, interfacial tension measurements and X.p.s. studies of DDM thin films cast or adsorbed on oxidized aluminium were carried out.

Figure 7 shows the results of interfacial tension measurements between water and epoxy/xylene and DDM/xylene solutions of varying concentration. The interfacial tension between water and xylene solution of epoxy resin was remarkably lower than that between water and xylene solution of DDM. This tendency depended not on an effect arising from the difference in molecular weights, but on the difference between the hydrophile–lipophile balance of epoxy resin and DDM.

This result could not explain the previous findings that DDM adsorbed preferentially on the Al_2O_3 particles and that DDM units localized at the cured epoxy resin/oxidized aluminium interface. Generally, an oxidized aluminium surface has hydrophilic character. In the case that the interaction between oxidized aluminium and the resin components is a hydrophilic interaction, epoxy resin will localize in the interface. Accordingly, we suggest that the interaction between DDM and oxidized aluminium is not a hydrophilic–hydrophobic effect.

Next, the interfacial tension between water and epoxy or DDM solution was measured as a function of

pH. At high pH (in the alkaline region) the interfacial tension did not change remarkably. On the other hand, at low pH (in the acidic region), while the interfacial tension between water and epoxy solution hardly changed, that between water and DDM solution could not be measured because DDM dissolved in the water phase. This phenomenon is interpreted as indicating that ionization of DDM occurred under acidic conditions and ionized DDM had a strong interaction with acidic substances.

The X.p.s. Al 2p and N 1s spectra of DDM thin films cast (A) and adsorbed (B) on oxidized aluminium from xylene solution are shown in *Figures 8* and *9*, respectively. Film A was prepared by casting of DDM on oxidized aluminium from 0.1 wt% xylene solution while film B was prepared by adsorption of DDM on oxidized aluminium from 0.01 wt% xylene solution. After adsorption, the oxidized aluminium surface on which DDM had been adsorbed was rinsed with pure xylene. In the case of the cast film Al 2p spectra could not be detected, indicating that the film thickness was greater than the sampling depth of X.p.s. In this case, the N 1s spectra were assigned on the bulk information. On the contrary, for the adsorbed film a clear Al 2p peak was obtained; i.e. the adsorbed film was thinner than the sampling depth of X.p.s. In this case, N 1s spectra included information from the DDM/oxidized aluminium interface. The N 1s spectrum of the adsorbed film shifted to higher binding energy.

This result indicates ionization of the DDM that adsorbed on the oxidized aluminium surface. Generally, the isoelectric point (*IEPS*) of an Al_2O_3 surface is in the range 7.5–9.1, showing that Al_2O_3 has both acidic and basic character. DDM has a strongly basic character, while the acid–base character of epoxy resin is not clear but could be weaker than that of DDM. The oxidized aluminium surface has many anionic charges and few cationic charges in the presence of a basic substance like DDM. Accordingly, electron exchange between the oxidized aluminium surface and DDM can easily occur, and acid–base interactions of the type $N^+H_3 \cdots O^-$–Al form between the amino groups of DDM and acidic sites on the oxidized aluminium. We also measured the X.p.s. N 1s spectrum of sample B after heat treatment at 180°C for 6 h. No noticeable change was observed in the spectrum. Thus it was not clear whether the form of bonds between DDM and oxidized aluminium change after curing.

Figure 10 is a schematic representation of the cured epoxy resin/oxidized aluminium interface. When the epoxy resin is cured with DDM under the application of heat, molecules of both DDM and epoxy resin are able to move freely in the system. As a result, DDM molecules can be adsorbed on the oxidized aluminium surface and form acid–base interactions between the amino groups in DDM and the acidic sites on the surface.
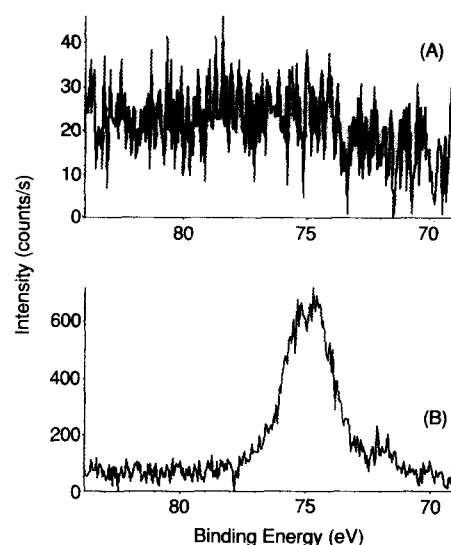

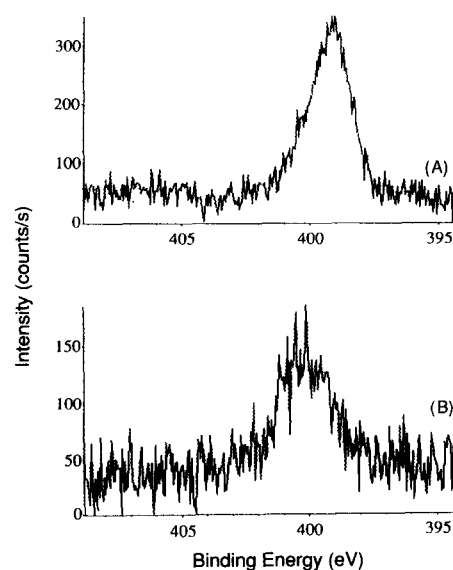**Figure 8** Al 2p spectra of DDM cast (A) and adsorbed (B) on oxidized aluminium surface

Figure 9 N 1s spectra of DDM cast (A) and adsorbed (B) on oxidized aluminium surface

Residual stress in epoxy resin/oxidized aluminium interface

This study has confirmed that DDM units are localized in the epoxy resin/oxidized aluminium interface. We then tried to control the interface structure, to reduce the residual stress there. First, DDM was adsorbed on an oxidized aluminium surface from xylene solution as a stress-relaxation layer. After a rinse and heat treatment, epoxy resin was cured on the modified surface.

The residual stress was measured by X-ray diffraction. In this method, the strain ε in the Al crystal at different angles of inclination Ψ of the incident X-ray beam was measured. When a uniaxial residual stress σ exists, the relationship between ε and Ψ can be expressed as:
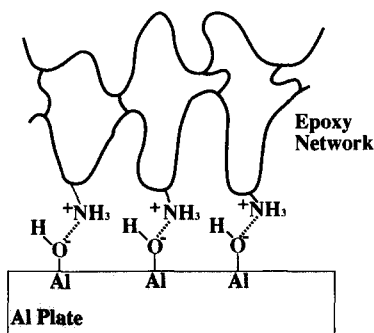
$$\varepsilon = \{(1 + v)\sigma/E\} \sin^2 \Psi \qquad (2)$$

Figure 10 Schematic representation of structure and interaction at cured epoxy resin/oxidized aluminium surface

Figure 11 Relationship between strain of the Al plate and $\sin^2 \Psi$: O, conventional system; ●, controlled system

where E and v are the elastic modulus (75.5 GPa) and the Poisson's ratio (0.33) of the Al crystal, respectively. Details are given in an earlier publication[6].

The relationship between σ and $\sin^2 \Psi$ is shown in *Figure 11*, along with the results of conventional curing of the epoxy resin system. Residual stress was almost the same in the conventional and controlled systems; we could find no apparent effect of the controlled system. However, future studies of surface modification using a stress-relaxation layer should allow us to achieve a decrease in the residual stress at the interface.

CONCLUSIONS

Structure and interactions at the interface between cured epoxy resin and oxidized aluminium have been studied. Results showed that units of the DDM curing agent are localized at the interface. This has been attributed to acid–base interactions formed between the amino groups in DDM and acidic sites on the oxidized aluminium surface. These findings are in agreement with a previous study of Affroman et al.[14].

While we believe that residual stress can be reduced to design the interface and interphase between cured epoxy resin and a substrate – for example, by introdu-
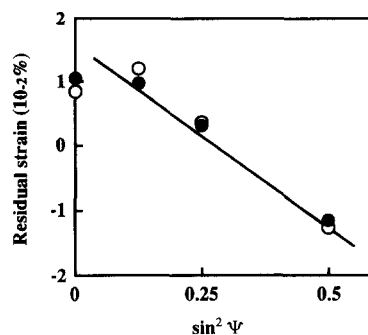
cing a highly oriented monolayer of diamine at the interface as a stress-relaxation phase – we could not achieve a sufficient effect in this study. Further experiments should be conducted towards this end.

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