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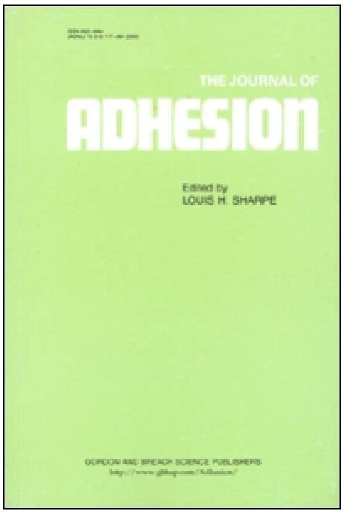

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Aging Effects of Epoxy Resin on Joining of Aluminum Plates

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Aluminum plates (type 2024) were subjected to various surface pretreatments and then joined by epoxy resin. The joints were tested for shear strength close to the time of joining, and after various storage periods at 25 ± 5°C and 40% relative humidity. Surfaces of the aluminum plates were examined using X-ray photoelectron spectroscopy, and scanning electron and optical microscopies. Specimens examined shortly after being joined showed a trend of cohesive failure, but those which were stored for some time showed a trend of adhesive failure. It was found that the mean shear strength (MSS) of the specimens treated by a chromic acid solution was lower than that of specimens treated by a phosphoric acid solution. Hardness (Shore type D-2) and structure (by X-ray diffraction) of epoxy control samples were also examined. It was observed that the hardness increases with longer aging time, while changes in the structure were observed after long-term storage (63 months). The failure development with time is discussed and correlated with the MSS and the failure mode.

KEY WORDS aging; epoxy resin; aluminum; surface pretreatment; joint strength; X-ray photoelectron spectroscopy; XPS.

1 INTRODUCTION

Investigations of failure in structural adhesive joints have progressed along two lines: (a) mechanical properties of the joints,[1,2] and (b) relationships between fracture behavior and adhesive chemical composition.[3] These investigations shed light on the expected service life and on the durability of the joint components in various applications. Epoxy adhesives have been particularly attractive for electronics, aerospace, and other industrial and construction applications.[4] For example, advantages of adhesive bonding are used to produce stronger and stiffer aluminum aircraft structures, wooden building components and even concrete railroad trestles.

The study of adherend surfaces and their effects on the performance and durability of adhesive joints has encouraged new developments in the area of surface preparation, namely, to improve the durability under stress and the strength of bonded joints. The strength of the joined system (adherends/epoxy resin) is determined by the weakest link. Failure of such a system can occur either at the adherend/

epoxy interface or in the bulk of the cured adhesive resin. The overall strength depends upon several parameters such as the cured resin properties, surface pretreatments of the adherends, curing time, processing temperature and pressure.[5-7] Environmental factors such as temperature, humidity and loading conditions are important, and joints have to be considered for specific applications, for example, geometry of the joining area, thickness of the cured adhesive resin and the duration of service.[8]

A controlled oxide layer can improve the adhesion between the metal and the cured epoxy resin.[9] It has been suggested[10] that the most important factor for strong adhesive joints is the presence of a microscopically rough oxide surface, to permit effective mechanical interlocking between the adhesive and the substrate. It is also known that chemical composition of the interface region can strongly affect the strength and durability of the adhesive joint. For example, chemical conversion of the surface in a process such as anodization[11,12] can prevent or retard the corrosion of a metallic substrate during exposure to a service environment which generally includes humidity.

This study presents a comparison of surface pretreatments using two types of solutions designed to produce an anodic layer: (a) a chromic acid solution (type A) and (b) a mixture of phosphoric acid and oxalic acid (type B). These pretreatments are especially suitable for long-term resistance against corrosive environments.[13-14] This study has permitted us to analyze the weakest link and to identify the quality of the joints by geometrical factor, chemical and mechanical effects. The weakest joints can be improved by surface pretreatment (for example type A or B) as demonstrated for systems of aluminum plates.

2 EXPERIMENTAL

Specimens of aluminum plates (type 2024) were pretreated by chromic acid (type A) or by phosphoric acid and oxalic acid (type B) to produce anodized layers. These layers were prepared without sealing, in accordance with MIL-B-8625. The layer thickness,* measured by a TC-1600 beta backscatter gauge (Twin City), was found to be 3 ± 0.5 μm. The plate size for lap shear strength evaluation was chosen according to ASTM-1002-64,[15] and the specimens were cleaned ultrasonically using Freon-TF before joining. Fresh 3M Scotchcast epoxy resins, Electrical Resin No. 9 (XR-5240) produced by 3M Company, Dielectric Materials and System Division, were used. The two components of the epoxy resin were mixed together under vacuum (5 Torr). After the resin was applied to the clean plate surfaces, these were joined under pressure (by a torque of 2000 g·cm). The resin was cured by heating at 45–50°C for 20 h. Some specimens were examined close to the time of joining, while the others were tested after various storage periods, up to 72 months. The evaluation procedure includes a shear strength test according to ASTM D-1002-64; scanning electron microscopy (SEM), using a Philips-505 instrument, and optical

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*Since the major commercial application of anodizing has been for protection against weathering of exposed aluminum parts, the use of quite thick oxide layers has been common.

microscopy [Bausch & Lomb stereoscope, up to × 150, and Reichert MeF-3, up to × 1500] were used to determine the failure mode. The lap shear bond strength at 25°C was measured using an Instron Mechanical Tester (crosshead speed of 2 mm/min).

Adhesive/cohesive failure areas were determined by photographing the fracture surfaces and by microscopic observations, as descibed elsewhere.[16] Auger electron spectroscopy and X-ray photoelectron spectroscopy, (AES/XPS, Vacuum Generators ESCALAB 3MkII) with MgKα radiation was used for identifying the type of fracture and for studying the development of the fracture mechanism.

XPS high resolution spectra were analyzed using computer curve-fitting and graphics routines available in the data system. The hardness and structure of the epoxy bulk of control samples were measured by Shore (type D-2) and by X-ray-diffraction (XRD); Shore hardness is suitable for evaluating plastics, rubber and polymeric bulk materials.[17] XRD was performed using a Bragg-Brentano Philips diffractometer with a fixed beam divergence of 1° and Cu-Kα radiation. The data, obtained by stepscanned measurements with a step size of 0.03° and 3 sec time step, were analyzed using a computer program.

After joining, the specimens were stored at 25–30°C and 40% relative humidity (RH). At each stage of the experiment, 30 specimens were examined.

3 RESULTS AND DISCUSSION

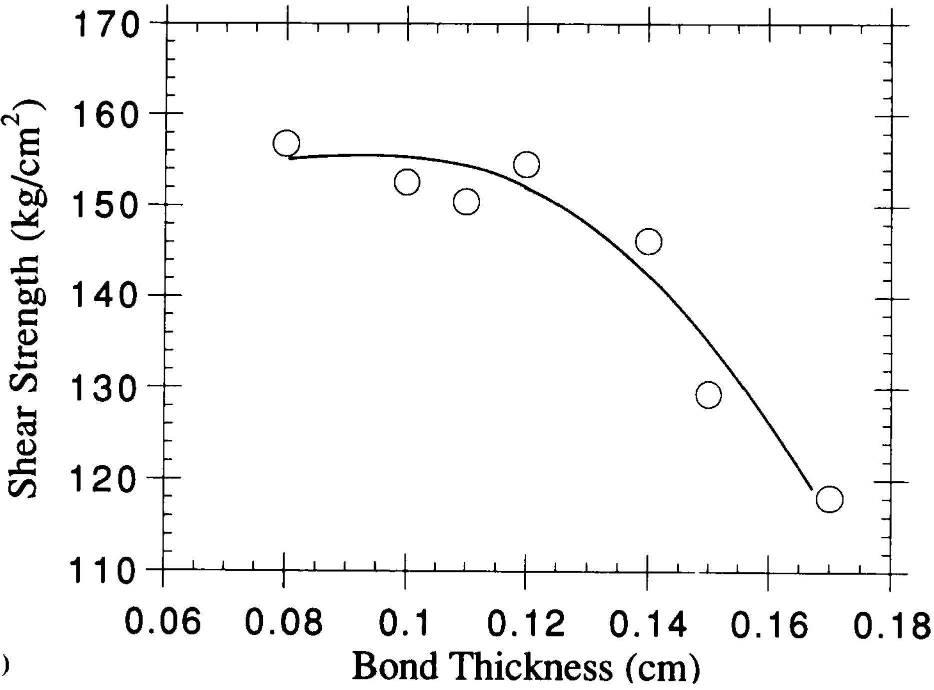
3.1 Joining Conditions

Figures 1(a) and (b) show plots of shear strength τ of the joints as a function of the bond thickness, and of the correction factor K, respectively. K is the ratio of the area covered by epoxy outside the joining surface (A_1) to the total joining area (A_2), $K = A_1/A_2$. These results indicate that too large an amount of epoxy resin decreases the strength per unit area of the joints on the one hand, and increases the required load resulting from increased K, on the other hand. To account for the amount of epoxy resin outside the joining surface, K was used to determine the samples' normalized shear strength τ_n according to the expression

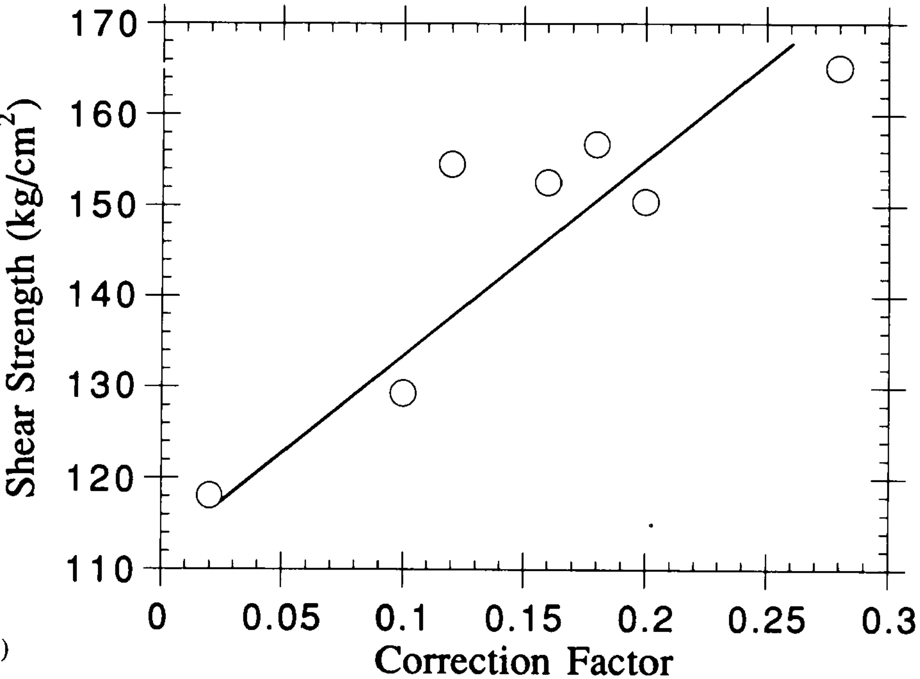
$$\tau_n = \tau_m(1 - K),$$

where τ_m is the measured shear strength. The adhesive bond thickness t_b of all specimens was found to be 0.08–0.10 cm, and τ_n values are constant for specimens joined and tested under nominally identical conditions.

The τ values are seen to decrease for $t_b > 0.12$ cm (Fig. 1a). According to results of Kinloch and Shaw,[18] the maximum adhesive fracture energy ϵ_f occurs in the range $0.105 \leq t_b \geq 0.6$ cm. We feel that in our case ϵ_f occurs for $t_b \sim 0.08$–0.12 cm. However, ϵ_f is known to depend upon strain rate, temperature and specimen width.[18,19] Bascom and co-workers[8,19] used an elastic-plastic model for the deformation zone to study the variation of ϵ_f with t_b. According to them, and to Kinloch and Shaw,[18] ϵ_f is reduced by decreasing t_b. The ϵ_f value is also affected by the presence of a plastic deformation zone and by the amount of stored elastic energy in the sample.



(a)



(b)

FIGURE 1 Shear Strength of the joints (aluminum/epoxy/aluminum) as a function of: (a) the bond thickness t_b; (b) the correction factor K.

TABLE I
Strength of specimens as measured (τ_m), and its correlation with normalized shear strength (τ_n) and with shear strength of samples devoid of epoxy outside the joining area (τ_m^*)

Sample no.	τ (kg/cm^2)	K	τ_n (kg/cm^2)	τ_m^* (kg/cm^2)
1	189.4	0.13	164.8	—
2	187.0	0.11	166.4	—
3	150.6	0.09	137.0	—
4	168.7	0.08	155.2	—
5	—	—	—	153.1
6	—	—	—	161.8
7	—	—	—	163.6
8	—	—	—	148.6
MSS*	173.9	—	155.8	156.8

*mean shear strength.
(—) no treatment was applied.

This implies that the amount of epoxy in bonded joints must be recognized as a factor which can affect the strength and durability of joints. However, other factors such as crack propagation behavior of the adhesive and its thickness dependence are also very important to the bond life.[20]

3.2 Shear Strength

In order to examine the effect of K on shear strength τ, two sets of joints were tested. τ values of the first group (Table I, samples No. 1–4) were calculated taking K into account, while in the second group the epoxy outside the joining surface was removed shortly after joining (Table I, samples No. 5–8). The results in Table I show that the mean shear strength (MSS) values are very similar for both groups.

Table II presents the results of MSS corresponding to type A and B pretreatments, as a function of storage duration (aging time). MSS values of the pretreated

TABLE II
Normalized MSS of type A and B treatments and hardness of control samples of bulk adhesive resin, as a function of aging time

Aging time (months)	Shore hardness[+] (type D-2)	Normalized MSS* (kg/cm^2) Type A	Type B
0	66	123.7	147.6
1	66	125.1	150.4
12	70	128.2	154.0
24	73	128.5	155.8
36	74	133.1	162.3
52	76	134.6	164.5
63	81	125.4	162.0
72	82	124.6	158.9

[+] mean error ± 2.
*mean value of 15 samples.

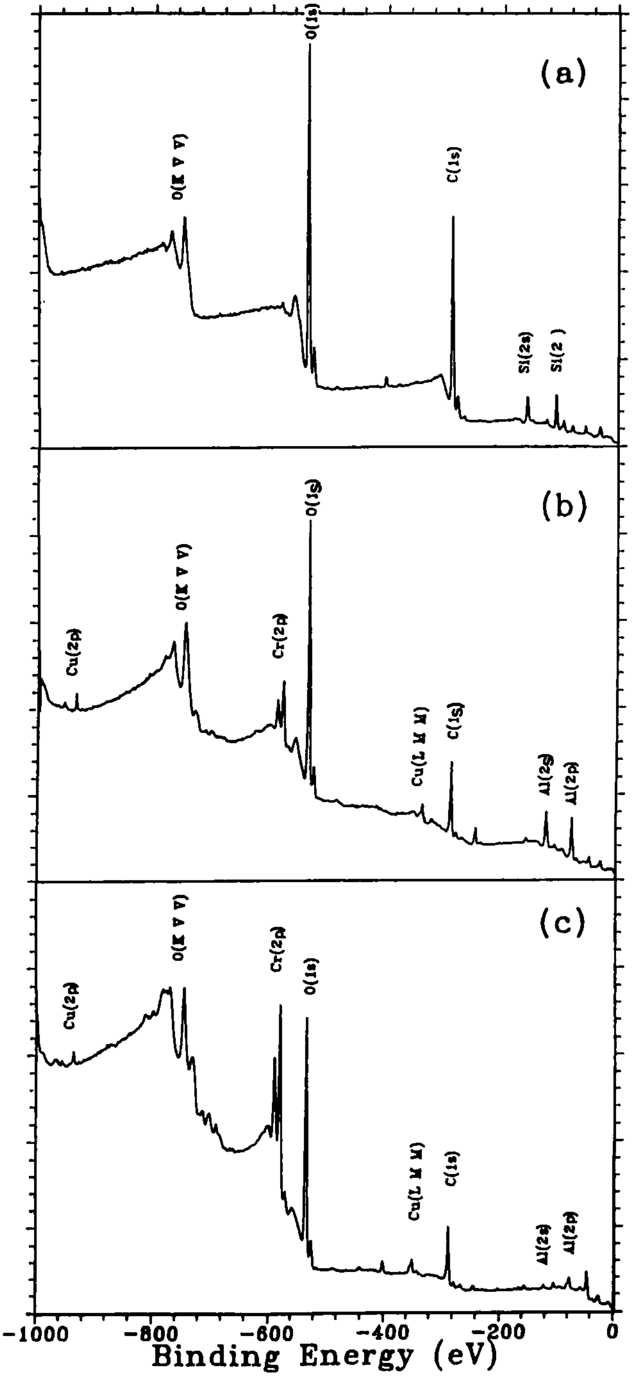


FIGURE 2 XPS Spectra of a fracture surface after aging of joint for 63 months. (a) epoxy interface; (b) aluminum surface; (c) oxide reference.

samples tend to increase with aging time up to 52 months, but decrease thereafter. The differences in the joint strengths are probably related to adhesion of the epoxy to the anodic oxide layers and to the oxide morphology, rather than to aging of the epoxy itself.

We conclude from Table II that the MSS reaches a maximum after 52 months, whereas the hardness of the epoxy steadily increases with aging time. We believe the increase in joint strength with time is due to the rise in hardness of the epoxy, from 66 ± 2 to 76 ± 2. It may, however, also result from some degree of residual post cure and/or stress relief at the oxide/adhesive interface. The MSS drop after 52 months may result from weakening of the epoxy/oxide interface, as observed for type A and B pretreated samples. Figure 2 shows XPS spectra on the epoxy side of the fracture surface (Fig. 2a), and on the aluminum side (Fig. 2b), compared with the fresh chromic acid prepared oxide layer (Fig. 2c). We note that the amount of the chromic-oxide on the epoxy side is much less than that on the aluminum side (see Fig. 2 and Table III). This suggests that after 63 months of aging the fracture occurs predominantly in the epoxy/oxide interface rather than at the aluminum/oxide interface.

The observed increase in hardness of the epoxy can also be due to post curing during the aging period, as indicated by experiments using accelerated curing at 100 and 150°C. Curing at elevated temperatures shows that the epoxy hardness of control samples increases to 80 Shore (type D-2) whereas normalized MSS of lap shear specimens, after type A pretreatment, increases to 170 and 230 kg/cm^2 after heating at 100°C and 150°C, respectively.

The structure and morphology of the treated adherend surfaces can appreciably affect the shear strength of joints. SEM examinations of the surface morphology of samples exposed to type A or B pretreatments show porous surfaces. The average pore size was 50 nm for type A and 100 nm for type B. Adhesive bond strengths to aluminum have been found to depend very strongly on oxide morphology,[18] particularly on the presence of a microscopically rough oxide surface.[10] Venables *et al.*[21] used high-resolution transmission electron microscopy to show that oxide can mechanically interlock with the adhesive to enhance bond strength, which can account for the strength of the phosphoric anodized surface-treated joints.

TABLE III
Elemental analysis of adhesive failure area of epoxy/aluminum interface

Spectrum	Interface location	Composition (at.%)									
		C	O	Cr	Al	Si	Cu	Fe	Mn	Mg	Zn
a	epoxy/epoxy	55.5	35.5	—	—	9.0	—	—	—	—	—
b	epoxy/Al	27.6	40.3	4.0	24.7	0.4	—	—	—	—	—
c	epoxy/oxide	29.1	44.5	14.5	—	11.5	0.4	—	—	—	—
Al-2024	untreated	—	—	0.1 max	Rem	0.5 max	3.8–4.9	0.5	0.3–0.9	1.2–1.8	0.25 max

—not observed.
Rem-Remainder

3.3 Failure Mode

SEM and AES/XPS studies show three types of failures: adhesive, cohesive, and combinations of the two. Failures are characterized by the fracture location, and by the amount of epoxy which remains on each part of the fractured surface. Adhesive failure is defined as a situation where at least 90% of the total adhesion area of the aluminum plate is uncovered. In a cohesive failure, 90% or more of the two plates remain covered by epoxy in the adhesion area. Mixed failure is defined as an intermediate situation between these two. We have found a correlation between the type of failure and the aging time of the joined samples: Specimens which were tested for shear strength soon after joining show cohesive failure; after a storage period of 12 months the failure mode is mixed, and then it tends toward adhesive failure. These results tend to confirm the concept that increased epoxy strength (through additional crosslinking) during aging is responsible, rather than stress relief at the oxide/adhesive interface. This is especially clear after long aging (52 months), and it agrees with the accelerated curing results at temperatures up to 150°C. This is also discussed elsewhere.[22]

Table IV illustrates the relationship between failure mode and aging time. Macroscopic examinations did not show any clear difference between the types of treatments. However, the microscopic and AES/XPS examinations indicated that the failure occurred in two regions, namely at the aluminum/treated layer interface, and at the treated layer/epoxy resin interface. The results indicate that the weakest link of type B samples is the treated layer/aluminum interface, while for type A samples it is the treated layer/epoxy resin interface. The differences between type A and B is attributable to the structure and morphology of the oxide layers, and to the stronger adhesion at the epoxy/treated layer interface compared with that between the treated layer and the Al plate. The shear strength results indicate that the adhesion between epoxy joint/layer "A" is smaller than that between layer "B" and the aluminum plate, as seen from Table II and from the AES/XPS studies.

The above results agree with the "attachment sites" model,[23] which is based on the assumption that the strength of the boundary layer depends directly on the number of mechanically effective "attachment sites." Weak boundary layers are characterized by the existence of few or no operative attachment sites, which results in a low joint strength and an adhesive failure mode. As the number of effective

TABLE IV
Relative distribution of specimens by different failure modes

Aging time (months)	% of Samples		
	Cohesive	Mixed	Adhesive
1	95	5	0
12	40	30	30
24	0	55	45
36	5	45	50
48	0	45	55
72	0	30	70

attachment sites increases by chemical and/or physical modification of the participating surfaces, the joint strength also increases, accompanied by a change to the mixed mode of joint failure.

3.4 Epoxy Aging

Figure 3 shows X-ray diffractograms of the epoxy resin after different aging periods. The XRD spectra were examined with regard to peak position, broadening (full width at half maximum, FWHM), and intensity. The results are summarized in

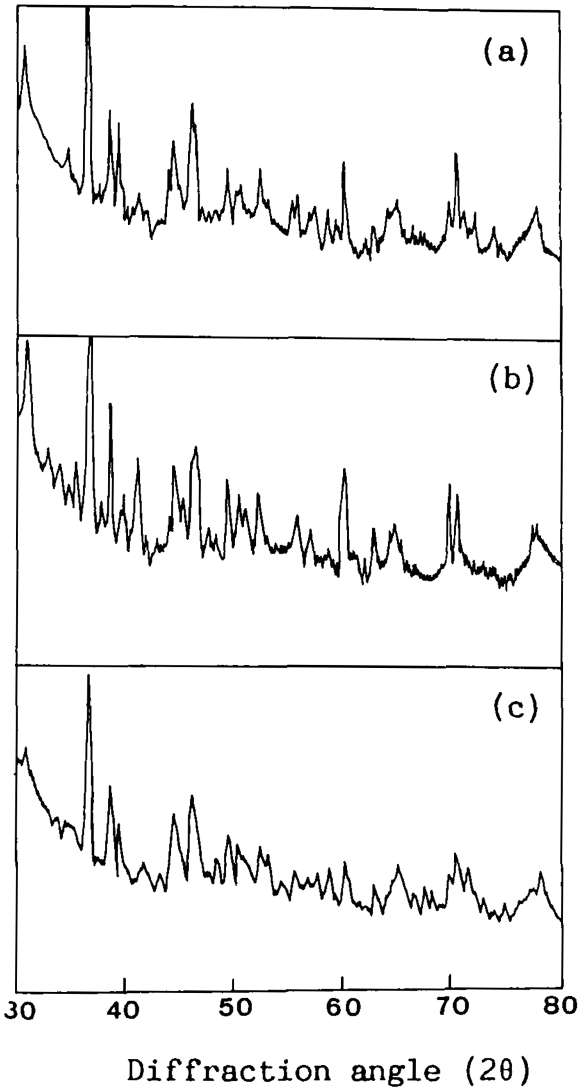


FIGURE 3 X-ray diffractograms of the epoxy resin close to the joining time (a) and after aging for 36 months (b) and 63 months (c).

Table V. Figure 3 and Table V show a decrease of the peak intensities and a shift to higher diffraction angles, indicating an expansion of the lattice parameters. This effect can be explained by slow chemical changes taking place during aging, namely hydrolysis and oxidation of epoxide groups.[24]

The AES/XPS results show that exposure to humid environment has a greater effect on the anodic layer/epoxy interface than on the bulk of the epoxy, the interface regions being found to be richer in oxygen than the bulk, Table III. Similar results were observed by Dickie[25] for organic coating/steel interfaces. The observed adhesion loss may therefore presumably be linked with the long term aging of the interfacial region at 40% RH.

Figure 4 represents high resolution C_{1s} XPS spectra of the 40% RH exposed interfacial surfaces (Fig. 4b) and of a reference sample (Fig. 4a). Deconvolutions of the spectra according to the method of Clark and Thomas[26] show three sub-peaks, namely C—C and C—H (C1), ether or alcohol (C2), and carboxyl or double ether (C3), for the reference sample, Fig. 4a. After 63 months of aging at 40% RH, four sub-peaks are observed, namely C1, C2, C3 and carboxylate (C4), Fig. 4b. After fracture and immersing the sample in distilled water for 5 hours, yet another peak, carbonate (C5), was observed. The assignments and concentrations of the bonded carbon species are given in Table VI. It is clear from Fig. 4b that carboxylate was formed in the interfacial region after 63 months of exposure to humid environment before fracture, attributable to the additional presence of atmospheric carbon dioxide at the interface. The high humidity leads to the formation of carbonate species, in addition to carboxylate, as shown in Table VI. This indicates that aging in humid environment can affect the hydrolysis and oxidation of epoxide groups near the interface of the adherends, and this can explain the adhesion loss at the oxidized region of the epoxy/aluminum interface.

TABLE V

XRD peak characteristics of epoxy control samples after various aging times

d_{hkl} (Å)	Normalized peak intensity (%)				FWHM (degrees)			
	a	b	c	d	a	b	c	d
4.24	63.10	61.00	46.00	25.19	0.06	0.05	0.07	0.06
3.86	27.11	26.35	24.70	6.11	0.14	0.17	0.26	0.24
3.33	100.00	100.00	100.00	100.00	0.12	0.12	0.17	0.16
3.11	44.7	41.10	41.10	23.71	0.06	0.07	0.09	0.06
2.98	26.35	25.91	25.45	5.05	0.11	0.14	0.16	0.14
2.62	24.70	23.40	22.25	4.40	0.17	0.19	0.22	0.20
2.49	46.00	40.80	39.72	12.13	0.06	0.11	0.14	0.12
2.45	19.50	18.60	16.65	14.88	0.07	0.07	0.09	0.08
1.82	17.25	17.12	15.15	16.67	0.08	0.08	0.09	0.06
1.67	18.55	18.10	14.90	4.72	0.16	0.21	0.26	0.24

a, reference sample;
b, after 36 months;
c, after 63 months;
d, after accelerated curing for 20 h at 100°C.

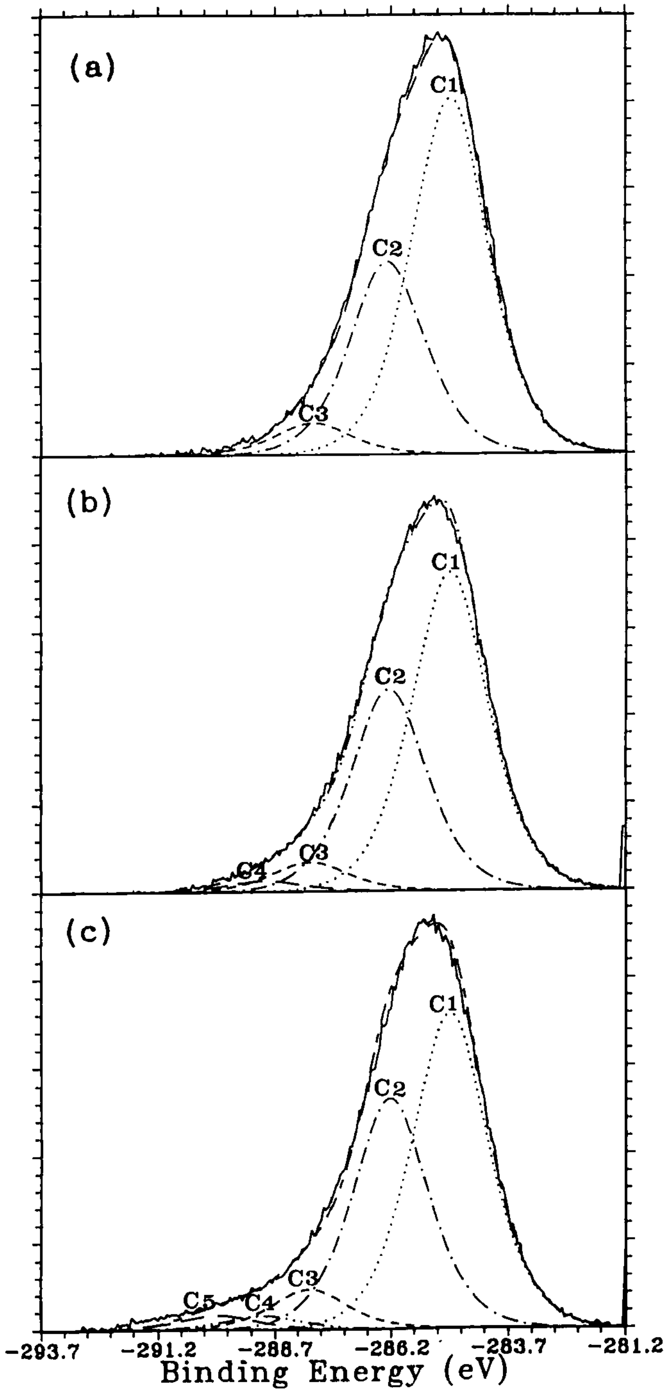


FIGURE 4 XPS of C_{1s} spectra. (a) epoxy reference; (b) epoxy surface of adhesive fracture after 63 months at 40% humidity; (c) epoxy surface of adhesive fracture after immersion in boiling distilled water for 5 h.

TABLE VI
Types of bonded carbon species deduced from XPS analysis

Carbon Species Binding Energy (eV)	C1 285.0	C2 286.6	C3 288.0	C4 289.0	C5 290.0
Identification	C—C C—H	C—O—C C—OH	C=O O—C—O	O=C—O	O O=C O
	Relative area of C_{1s} peak (%)				
epoxy untreated	61.5	33.0	5.5	—	—
low humidity (40%)	57.0	36.0	5.0	2.0	—
high humidity (immerse in water)	51.0	38.0	6.5	2.0	2.5

—not observed.

3.5 Characteristics of the Failure Development

Figure 5 shows an optical micrograph of a characteristic area representing the fracture surface after aging and shear testing. The light, "island"-like region is aluminum, documenting adhesive failure after long-term aging. Figure 6 depicts the development of the "islands" in two stages where the resin was cured for various

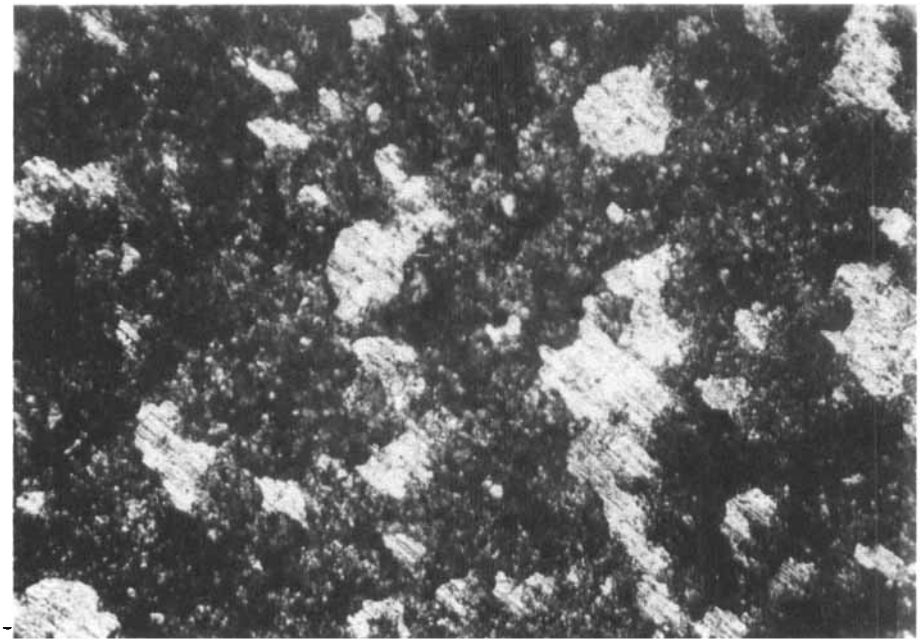


FIGURE 5 Typical optical micrograph of a fractured surface (×1200). curing time = 20 h; aging time = 36 months.

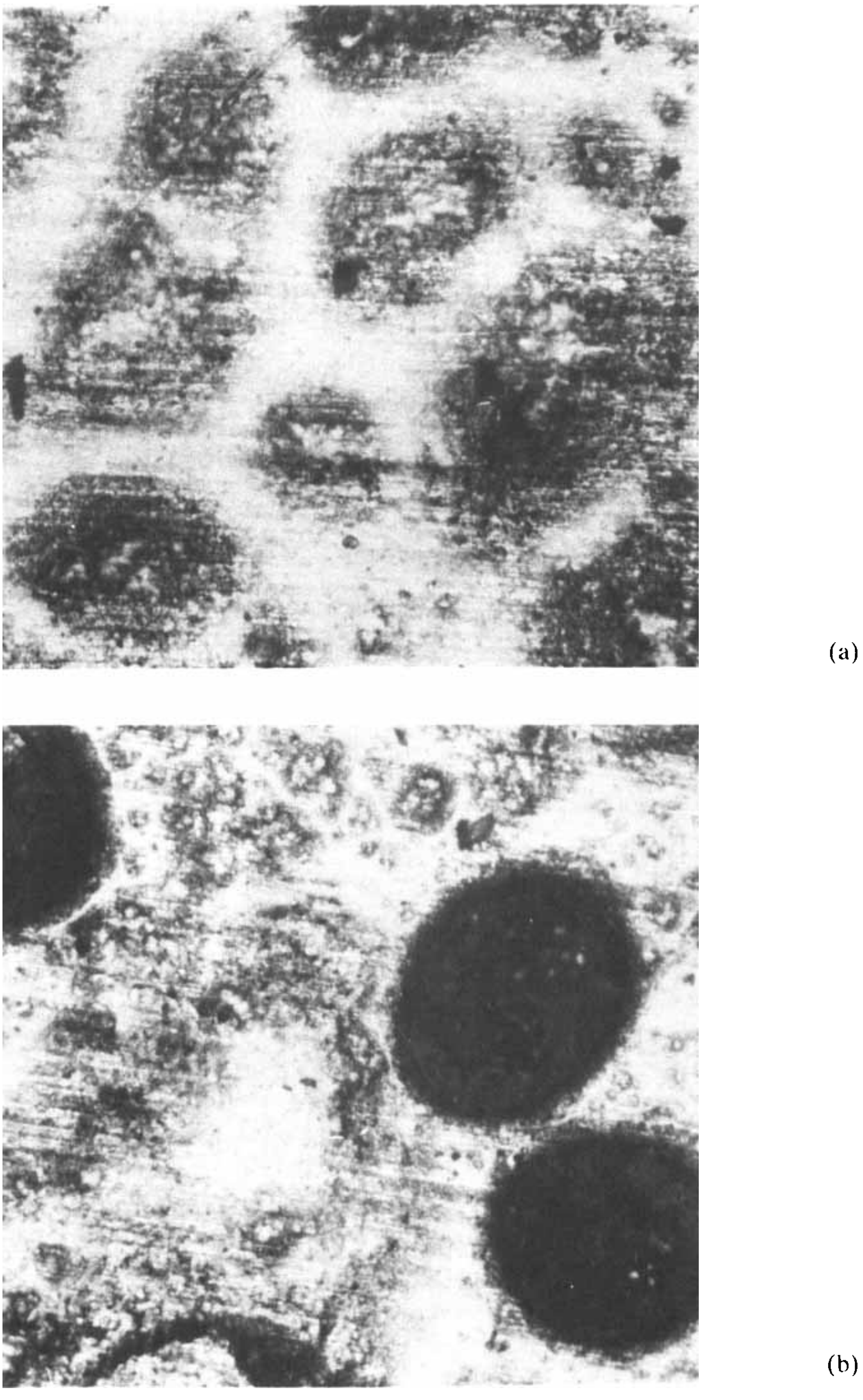


FIGURE 6 Optical micrographs showing two stages in the fracture development of specimen examined shortly after being joined (× 1440): (a) small area of polymerized epoxy after curing of 8 h; (b) microscropic adhesive failure after curing of 20 h.

durations: (a) after 8 hours of polymerization (Fig. 6a) a part of the epoxy remains bonded to one aluminum plate while the remainder of the epoxy separates; (b) after 20 hours of polymerization, when the shear strength increases, microscopic adhesive failure occurs (Fig. 6b), as indicated also by SEM and AES/XPS. The surface composition after fracture can be an indication of the failure location, *i.e.* in the epoxy bulk or at the epoxy/Al interface. Microscopic adhesive failure produces a surface consisting of the elements of chromic oxide, while these elements were not observed following cohesive failure.

3.6 Correlation between Shear Strength and Failure Mode

Figure 7 presents the corrected, normalized shear strength τ_n as a function of the bare aluminum surface for type "A" aluminum plates (treated by chromic acid), where τ_n is seen to decrease with increasing bare surface. After long duration of storage (63 months, curve c), the failure mode has changed from a cohesive to an adhesive mode, *via* a mixed failure mode. This shows that changes in bond strength correlate with changes in failure mode. Figure 7 also shows that the bond strength correlates with the bare surface area and/or with the aging time.

The fracture mode of specimens tested close to their time of joining (cohesive), and after aging (adhesive), indicate that the weakest link is transferred from the epoxy to the oxide/aluminum interface. This depends on the surface preparation and on the epoxy properties, as seen from the results. The effect of the oxide layer on the durability of the structural adhesive bond is discussed elsewhere.[9,27]

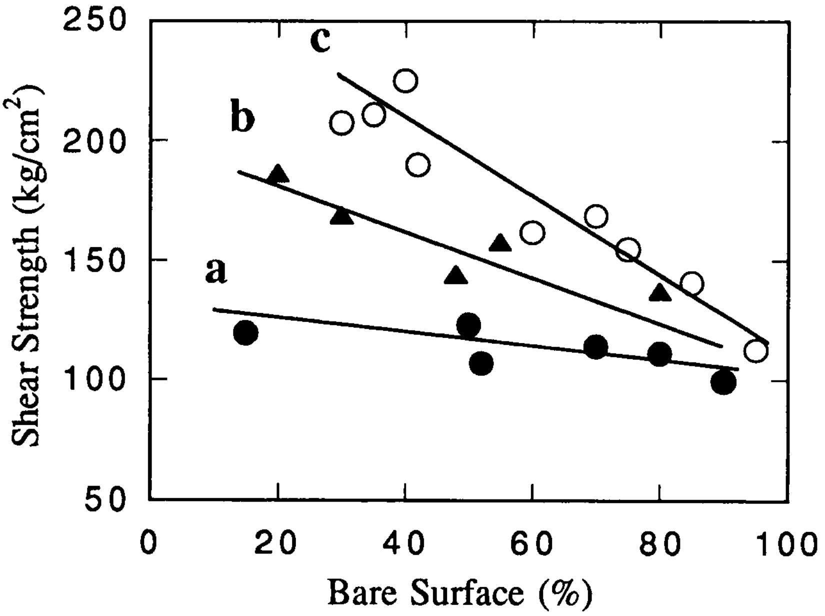


FIGURE 7 Normalized shear strength as a function of the epoxy surface after aging of 12 months (a), 36 months (b) and 63 months (c).

4 CONCLUSIONS

(a) The bond strength depends on competitive effects arising from increasing hardness of the epoxy during the aging period, and weakening of the epoxy/oxide interface.

(b) The durability of the joints and location of failure are affected by the epoxy and oxide layer properties. The weakest link of type A samples is the oxide layer/epoxy interface, while that of type B samples is the oxide layer/aluminum interface.

(c) Aging in humid environment can affect the oxidized region of the epoxy/aluminum interface, and it changes the failure mode.

(d) The durability of joints after pretreatment by phosphoric-acid and oxalic acid (type B) is better than that obtained by chromic-acid anodized surface pretreatment (type A).

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