Hydrothermal Stability of Aluminum/Epoxy Adhesive Bonds

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The effect of silane primers on the failure properties of aluminum/epoxy tapered double cantilever beam (TDCB) specimens was determined. TDCB specimens that were tested in air using increasing loads always failed by propagation of cracks along the center of the bondline at G_{Ic} values between 1.58 and 1.80×10^5 mJ/m^2 whether primers were used or not. However, γ-aminopropyltriethoxysilane (γ-APS) primers had a significant effect on the time to failure of TDCB specimens subjected to static loads in water at 60°C. The time to failure was always increased when the beams were pretreated with dilute aqueous solutions of γ-APS. The pH at which the primers were applied did not affect the failure characteritics of the beams but heat treating the primer films before bonding did. The longest times to failure were always obtained when the primer films were dried in air at 100°C for about ten minutes. Shorter or longer drying times always resulted in lower times to failure. Increases in time to failure obtained using primed adherends were related to the ability of the primer films to inhibit hydration of the oxide.

KEY WORDS Aluminum/epoxy adhesive bonds; durability; hydrothermal stability; primers; silanes; tapered double cantilever beam (TDCB).

I INTRODUCTION

The use of silane coupling agents in primers to improve the hydrothermal stability of adhesive bonds to metals has been

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† Presented at the Ninth Annual Meeting of The Adhesion Society, Inc., Hilton Head Island, SC, U.S.A., February 9–12, 1986.

described previously. Boerio and Williams[1] showed that thin films of γ-aminopropyltriethoxysilane (γ-APS) applied to iron adherends from dilute aqueous solutions were effective primers for improving the hydrothermal stability of iron/epoxy lap joints. They also showed that the pH of the aqueous solutions from which the silane was applied had an important effect on the hydrothermal stability of the joints. γ-APS films applied to the adherends at pH 8.0 were more effective as primers than films applied at pH 10.4. Boerio and Dillingham[2] obtained somewhat different results for titanium/epoxy lap joints. γ-APS films were effective primers for titanium/epoxy lap joints but the pH at which the primers were applied was not significant.

The investigations described above were carried out by immersing lap joints in water at an elevated temperature for long periods of time and then determining the residual breaking strength of the joints using a mechanical testing instrument. The results were expressed as breaking strength *versus* immersion time and were used to compare the effects of different adherend pretreatment processes. In the case of iron/epoxy lap joints it was found that joints prepared from unprimed adherends retained only about 25% of their initial strength after 60 days in water at 60°C but joints prepared from adherends that were pretreated in dilute aqueous solutions of γ-APS at pH values of 10.4 and 8.0 retained about 50% and 75% of their initial strength, respectively. Titanium/epoxy lap joints prepared from unprimed adherends decreased about 20% in breaking strength after immersion in water at 60°C for 60 days but joints prepared from primed adherends changed very little in breaking strength regardless of the pH at which the primer was applied.

The breaking strength of lap joints is very dependent on the geometry of the joints and it is difficult to compare the results obtained from lap joints with the results obtained using other test specimens. As a result, it is more useful to discuss the failure of adhesive joints in terms of fracture energy than in terms of breaking stress.

The tapered double catilever beam (TDCB) specimens described by Mostovoy and Ripling[3] provide a convenient method for determing the failure characteristics of adhesive joints. Beams are fabricated from the adherend material of interest and bonded together. The critical strain energy release rate required to propa-

gate a crack along the bondline is then determined or, alternatively, a fixed (static) load is applied to the specimen during exposure to an aggressive environment and the time required for a crack to propagate the length of the beams is determined. The beams are contoured so that the applied strain energy release rate is a constant that is independent of crack length.

Several papers have described the use of TDCB specimens to determine the effect of silane primers on the durability of adhesive bonds to aluminum during exposure to humid atmospheres to to water. Patrick[4,5] showed that TDCB specimens that were statically loaded with the bondline exposed to water at room temperature failed near the interface. γ-APS primers inhibited such interfacial failure as long as the concentration of the solution from which the silane was deposited was closed to 0.01%. At higher or lower concentrations, failure near the interface was still obtained.

Kinloch[6] determined the time to failure for statically loaded aluminum/epoxy tapered double cantilever beams during exposure to 56% relative humidity or to water at room temperature. Beams exposed to water failed near the interface but those exposed to 56% relative humidity failed cohesively at times to failure that were greater by a factor of about two orders of magnitude for all strain energy release rates that were considered. The characteristics of TDCB specimens prepared from adherends primed with thin films of γ-glycidoxypropyltrimethoxysilane (γ-GPS) and immersed in water were similar to those of specmens exposed to 56% humidity. That is, failure was cohesive and the time to failure was increased by a factor of about two orders of magnitude.

The primary objective of this research was to use the tapered double cantilever beam configuration to determine the effects of thin films of γ-aminopropyltriethoxysilane (γ-APS) on the failure characteristics of aluminum/epoxy adhesive joints immersed in water at elevated temperatures. An additional objective was to determine the effects of variables such as the pH at which the primers were applied and the extent to which the primers were dried before bonding.

II EXPERIMENTAL

Tapered double cantilever beams were machined from half-inch 2024–T23 aluminum bars. The surfaces of the beams were prepared
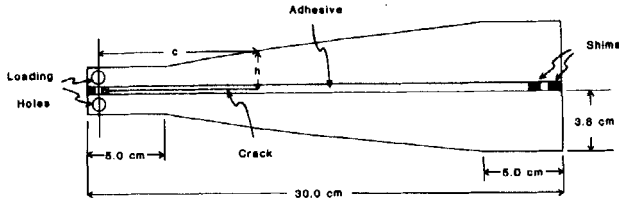
FIGURE 1   Tapered double cantilever beam (TDCB) specimen for determining durability characteristics of aluminum/epoxy adhesive joints.

by mechanical polishing first with aluminum oxide and then with magnesium oxide. After polishing, the beams were rinsed with distilled water and dried in nitrogen. In some cases primer films were applied to the polished beams by flooding the surfaces with 1% aqueous solutions of γ-APS at the natural pH of 10.4 or after the pH had been adjusted to 8.0 by the addition of HCl. After 10 minutes the solution was blown from the surface using a stream of nitrogen. In a few cases the primer films were dried by heating the beams in an oven at 100°C. The beams were then bonded together as shown in Figure 1 using an adhesive consisting of an epoxy resin (Epon 828, Shell Chemical Company) and a tertiary amine curing agent (K-61B, Pacific Anchor Chemical Company). The thickness of the bondline was 0.5 mm and was determined by placing shims near each end of the beams. The adhesive was cured by heating the specimens in an oven at 135°C. After 2.5 hours the oven was turned off and the beams were allowed to cool slowly to room temperature.

After the adhesive was cured, all of the specimens were pre-cracked in a mechanical testing instrument using a strain rate of 0.127 cm/min. Most of the beams were then immersed in distilled water at 60°C and statically loaded and the time to failure (the time required for the precrack to propagate the entire length of the beams) was measured. A few beams were tested without immersion in water to determine the critical strain energy release rate (G_{Ic}) for crack propagation in the absence of environmental effects and to serve as a control.

The applied strain energy release rate was calculated from the relation[3]

$$G_I = 4P^2M/Eb^2 \qquad (1)$$

where P is the applied load, E is the elastic modulus of the substrate, and b is the width of the specimen. M is a geometrical factor given by

$$M = 3c^2/h^3 + 1/h \qquad (2)$$

where h is the height of the beam for a crack length c (see Figure 1). The beams used here were contoured so that $M = 40/\text{cm}$.

The crack opening δ was determined as a function of time by using a personal computer to monitor the output of a linear variable differential transfromer (LVDT) that was attached to the beams near the loading holes. The crack length c was determined from δ using the expression

$$c = (Eb)8P_cM)\delta \qquad (3)$$

given by Mostovoy.[3]

III RESULTS AND DISCUSSION

When TDCB specimens were tested in air by applying increasing loads, the precrack always extended along the center of the bondline at a load of about 75 or 80 lbs, corresponding to C_{lc} between 1.58 and $1.80 \times 10^5 \text{ mJ/m}^2$, whether a primer was used or not. However, when curing conditions other than those described above were used, the precrack usually propagated along the interface for specimens prepared without the silane primer.

A plot of applied strain energy release rate (G_I) *versus* time to failure is shown in Figure 2 for specimens aged in water at 60°C. Beams prepared from primed substrates always failed at much longer times than beams prepared from unprimed substrates. Data for unprimed beams always fell on a straight line but there was considerable variation in the data for beams prepared from primed adherends. The time to failure for the primed beams always fell within the region defined by the lines labelled "B" and "C" in Figure 2. The pH of the aqueous solutions from which the primers were applied had little effect on the time to failure. However, drying the primer films before adhesive bonding did have a strong effect. When the drying time was about ten minutes, the longest times to failure, near the line labelled "C" in Figure 2, were
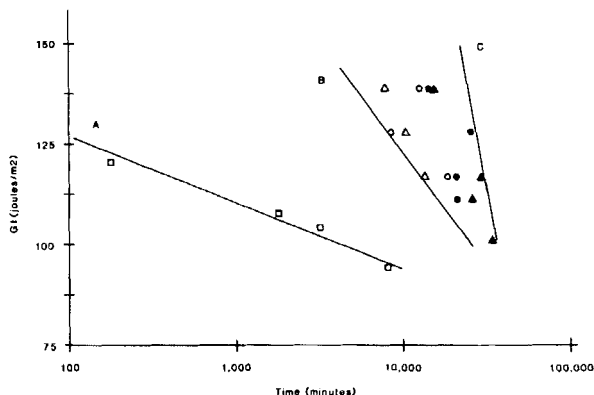
FIGURE 2   Time to failure versus applied fracture energy for aluminum/epoxy TDCB specimens immersed in water at 60°C: (□)-no primer, (○)-γ-APS primer at pH 10.4, (△)-γ-APS primer at pH 8.0, (▲)-γ-APS primer at pH 10.4 heat treated at 100°C for 6 minutes, and (●)-γ-APS primer at pH 10.4 heat treated at 100°C for 10 minutes.

obtained. When shorter or longer drying times were used, the time to failure was closer to line "B".

The use of γ-APS primers did not affect the mechanism of failure. The precrack was always near the center of the bondline but during lengthy immersion in water a new crack developed near the interface above or below the tip of the precrack. Failure of the joints always involved the propagation of this secondary crack near the interface.

In a few cases, the secondary crack began to grow in an almost steady manner shortly after the TDCB specimen was immersed in the water (see Figure 3A). This usually occurred when rather large strain energy release rates were applied to specimens prepared from unprimed adherends. In most cases the secondary crack grew very slowly but then suddenly propagated very rapidly, resulting in the failure of the specimen. TDCB specimens prepared from primed adherends usually showed such behaviour, regardless of the applied strain energy release rate. A plot of crack length *versus* time for a sample behaving in this was is shown in Figure 3B. In some cases, particularly when the adhrends were pretreated with γ-APS primers, the secondary crack would alternately remain stationary for a
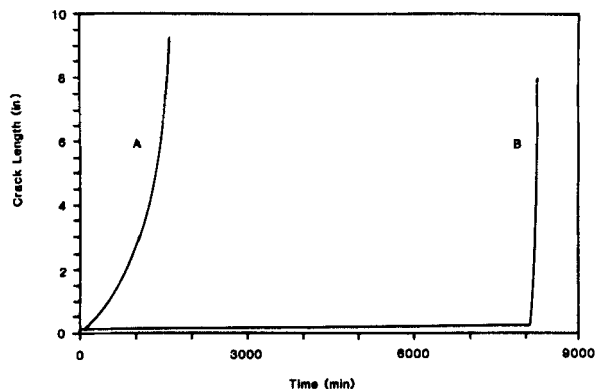
FIGURE 3   Crack length as a function of time for unprimed aluminum/epoxy TDCB specimens that were loaded in water at 60°C. The applied fracture energies were (A)-1.10 × 10⁵ and (B)-0.95 × 10⁵ mj/m².

time and then jump forward. This behaviour was associated with primer films that were not iniform in thickness.

The results obtained were somewhat different from those reported by Kinloch.[6] As described above, Kinloch found that γ-GPS primers always increased the time to failure for aluminum/epoxy TDCB specimens exposed to water at 23°C by a factor of about two orders of magnitude regardless of the strain energy release rate. In this work it was found that γ-APS primers increased the time to failure for TDCB specimens immersed in water at 60°C by an amount that was additive. That is, the slopes of lines "B" and "C" in Figure 2 are greater than the slope of line "A". The difference between the results obtained by Kinloch and those obtained here is related to the difference in the temperature of the water in which the TDCB specimens were tested rather than to the difference in silanes.

The durability of adhesive bonds to aluminum in the presence of high humidity or water is related to the stability of the aluminum oxide.[7] Moisture transforms the oxide to boehmite, a hydroxide which adheres poorly to the aluminum substrate. Once boehmite forms, bond strength is greatly reduced.

The formation of boehmite on aluminum during immersion in distilled water is preceeded by an induction period that varies with

temperature.[8] At temperatures above about 50°C, the activation energy for the process responsible for the induction time is 18.7 kcal/mole. The induction time is about ten minutes at 50°C and about one minute at 80°C. At temperatures below 50°C, the activation energy is much greater, indicating a change in the mechanism by which water interacts with the oxidized surface of aluminum. The induction time is several hours at 40°C and is much greater at lower temperatures.

In this work, the time to failure for aluminum/epoxy TDCB specimens immersed in water at 60°C was always long compared to the induction time for the formation of boehmite. It was found that the time to failure was increased by an additive amount through the use of γ-APS primers and that the failure was very near the interface and associated with corrosion of the substrate. Therefore, it seems likely that the effect of the silane primer was to increase the induction time.

It is well known that certain inorganic ions inhibit the formation of boehmite on aluminum during immersion in water.[8] Silicates and phosphates are particularly effective and it has been suggested that small amounts of phosphates formed at the surface of the oxide are associated with the outstanding durability of adhesive bonds to aluminum anodized in phosphoric acid.[9] It seems also been shown that organic phosphonates, such as nitrilotrismethylene-triphosphonic acid, are effective inhibitors.[10] Not many investigations of the effects of silanes on the hydration of aluminum oxides have been reported. However, we have shown that primers based on γ-methacryloxypropyltrimethoxysilane (γ-MPS) inhibit formation of boehmite at the interface between ethylene/vinyl acetate copolymers and aluminum very effectively.[11]

Kinloch[6] found that the time to failure for aluminum/epoxy TDCB specimens immersed in water at 23°C was increased by a factor or about 10^2 through the use of γ-GPS primers and that the failure shifted from near the interface to near the center of the bond. The times to failure reported by Kinloch were mostly less than the induction time for formation of boehmite at 23°C. Failure in those experiments may have been within a thin layer of adhesive near the interface and the effect of the silane primer may have been to alter G_{IC} in that layer.

It is interesting to speculate on the times to failure that were

observed for TDCB specimens that were given different heat treatments prior to adhesive bonding. γ-APS primer films that were polymerized by heating at elevated temperatures for a few minutes probably inhibited hydration of the oxide more effectively than films that were less well polymerized. Similar results have been reported for γ-MPS.[12] However, excessive drying may have resulted in films that were brittle and had poor mechanical properties. At intermediate drying times the properties of the interphase were optimized and the time to failure was at a maximum.

Acknowledgements

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