

The Effect of Soluble Cations on the Bonding of Epoxy Resins to Aluminum

W. T. McCARVILL and J. P. BELL, *Institute of Materials Science and Chemical Engineering Department, University of Connecticut, Storrs, Connecticut 06268*

Synopsis

The bond strength of an amine-cured epoxy resin to etched aluminum washed with, or washed with and immersed in, 10°C tap water was found to be greater than joints similarly pretreated in 10°C distilled water. The higher bond strength was found to be induced by soluble cations of less than 0.8 Å radius; larger cations had no effect. When aluminum is etched in a solution of chromic acid at 65°C, the aluminum surface is oxidized to $\gamma\text{-Al}_2\text{O}_3$. It is possible that the small, soluble cations can occupy the cationic vacancies in the defect spinel structure of the $\gamma\text{-Al}_2\text{O}_3$ and reduce the negative charge on the surface of the aluminum joints. Joints pretreated in 60°C tap water exhibited higher bond strengths than those pretreated in 60°C distilled water, as the growth of a thick, weak layer of bayerite was inhibited by large anions present in the tap water.

INTRODUCTION

The nature of the aluminum surface greatly influences the strength of a bond formed between it and an amine-cured epoxy resin. An oxide layer is formed very rapidly when aluminum is exposed to air. The types of oxides, and hydrated oxides, of aluminum have been reviewed.¹ The most important of these, in that they are likely to be formed under conditions used in industry to prepare aluminum for bonding, are $\gamma\text{-Al}_2\text{O}_3$, and the hydrated oxides, bayerite ($\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite ($\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Bayerite formation is favored by immersion of aluminum in water below 75°C, while boehmite forms more readily above this temperature. Gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) is formed by dehydration of a hydrated oxide by heat or chemical oxidation and has a defect spinel structure, possibly possessing both cationic and anionic vacancies.

Past experimenters^{2,3} have observed that aluminum etched in a solution of chromic acid, a strong oxidizing agent, bonded more strongly to an amine-cured epoxy resin than unetched aluminum. It was also noted that washing the freshly etched aluminum joints in tap or distilled water at or above 60°C gave different results. It was postulated⁴ that an anion in the tap water protected the aluminum surface and a significant thickness of a cohesively weak hydrated film was not formed. In the case of 60°C distilled water, the aluminum hydrated rapidly and formed a thick, iridescent film of the bayerite, yielding poor bond strengths.

Early in this investigation, it was found that immersion of etched aluminum in 10°C tap and distilled water resulted in similar bond strengths to cured epoxy resin, although consistent small differences remained.

In this work, the differences in bond strengths caused by varying the aluminum surface pretreatment were evaluated. The torsional test method of Lin and Bell³ was used, as this method utilizes a modified tubular butt joint in torsion and gives excellent reproducibility.

EXPERIMENTAL

The details of the adhesive joint and test procedure have been described.³ The joints, prior to each use, were machined on a lathe to the proper specifications. After turning, they were buffed on a polishing wheel with 5.0 μ , then 0.3 μ alumina suspended in distilled water and then washed with distilled water and acetone. The joints were allowed to air dry, followed by degreasing in refluxing trichloroethylene for 1/2 hr. When the hot joints were removed from the degreaser and had cooled to 60° to 65°C, they were immersed in a bath of chromic acid at 60° to 65°C for 10 min. The chromic acid was generated by mixing 1 part by weight sodium dichromate with 30 parts distilled water and 10 parts sulfuric acid. After etching, the joints were either rinsed with, or rinsed with and immersed in, tap or distilled water at varying temperatures or distilled water at 10°C with added soluble cations. The joints were air dried for 1 hr at about 55% relative humidity and at room temperature before resin was applied. The resin was applied and cured as described by Lin and Bell,³ except that the curing schedule was modified to 30 min at room temperature, 80°C for 1 hr, then 150°C for 2 1/2 hr. The cured specimens were broken at 0.005 in./min cross-head speed (0.4%/min strain rate), with the force to break recorded in pounds. Average bond strengths are reported, with each average being based on seven to nine individual joint breaks. Joints which were found to have gaps in the annular ring of resin are not included in the data. The Wilcoxon-Mann-Whitney⁵ test was applied to the data; the test is a simple rank correlational analysis for a small population of data. The null hypothesis (H_0) states that the data from different series may be treated as if they belonged to the same population. The method attempts to prove or disprove this hypothesis by comparing a series of joint strengths designated as x -values and another series designated as y -values. A significance is obtained for the truth of the hypothesis; a very low significance indicates that the hypothesis is false. A more detailed application of the test has been given.⁶

RESULTS AND DISCUSSION

Effect of Time and Type of Water Immersion Pretreatment on Bond Strength

The experimental data for freshly etched joints immersed in tap or distilled water at 10°C for varying times are shown in Table I. The bond

TABLE I
Bond Strengths of Etched Aluminum-Epoxy Joints Pretreated in
10°C Tap and Distilled Water

	Average bond strength, lb to break	
	Tap	Distilled
Quick wash	319 (series 1)	297 (series 4)
1/2-hr Immersion	339 (series 2)	322 (series 5)
6-hr Immersion	341 (series 3)	322 (series 6)

strength for both distilled and tap water immersion pretreatments rapidly rises to a limiting value. The tap water-pretreated joints exhibited consistently higher bond strengths. However, the initial rise in bond strength is probably due to limited formation of a hydrated oxide. The growth of the hydrate at 10°C is slow and the bond strength does not change, even after 6 hr of immersion time; one would expect the bond strength to drop after very long immersion times.⁷ It is proposed that the difference between the two sets of bond strengths is likely due to small, soluble cations that can either occupy cationic vacancies in the γ -Al₂O₃ or can reduce the negative charge on the aluminum surface. The reduced negative charge would more strongly attract electronegative species such as oxygen or nitrogen, both of which are found in the cured epoxy resin.

The results of applying the Wilcoxon-Mann-Whitney test to the experimental data in Table I show that the bond strength for both sets rises to a limiting value. The test also indicates that there is a significant difference between joint strength induced by cold tap and distilled water up to 6 hr of immersion time.

Effect of Soluble Cation Size and Concentration on Bond Strength

Various cations were dissolved in 2 to 3 liters distilled water at room temperature, and these solutions were cooled to 10°C. Freshly etched joints were washed with, or washed with and immersed in, these solutions.

Table II shows the effect of washing etched joints with 10°C distilled water containing about 10 ppm dissolved cations of varying size, charge, and associated anion. Cations having an ionic radius⁸ larger than about 0.8 Å do not seem to affect bond strengths. Those that are smaller than this ionic radius, however, induce bond strengths that are the same as for joints washed in tap water. The statistical analysis of the experimental data contained in Table II shows that the bond strengths induced by soluble cations below 0.8 Å in ionic radius may be treated as if they belong to one population and that those induced by cations larger than 0.8 Å may be considered as coming from another. Pooling the mean bond strengths from each population shows that there is a significant difference between the two populations.

Table III shows the experimental data for joints washed with distilled water containing approximately 1 ppm dissolved cations. The results are

TABLE II
Bond Strength for Etched Joints Washed with 100 ppm Cation Solution

Series	Cation	Cation solution, g/l.	Ionic radius, Å	Ave. bond strength, lb to break
7	Fe ³⁺	0.04 Fe ₂ (SO ₄) ₃	0.64	315
8	Ca ²⁺	0.03 CaCl ₂	0.99	300
9	Na ⁺	0.02 NaCl	0.97	297
10	Fe ³⁺	0.05 FeCl ₃ ·6H ₂ O	0.64	314
11	Cu ²⁺	0.03 CuCl ₂	0.72	313
12	Hg ²⁺	0.014 HgCl ₂	1.10	296
13	K ⁺	0.02 KCl	1.33	300
14	Ba ²⁺	0.02 BaCl ₂	1.34	298

TABLE III
Bond Strengths for Etched Joints Washed with 1 ppm Cation Solution

Series	Cation	Cation solution, g/l.	Ionic radius, Å	Ave. bond strength, lb to break
15	Fe ³⁺	0.005 FeCl ₃ ·6H ₂ O	0.64	319
16	K ⁺	0.002 KCl	1.33	301
17	Li ⁺	0.006 LiCl	0.68	318

the same as for joints washed with distilled water containing 10 ppm dissolved cations. There is a significant difference between joint strengths induced by soluble cations above 0.8 Å radius and those induced by cations below this size.

The bond strengths of epoxy-aluminum joints pretreated for 1/2 hr or 6 hr in 10 ppm solutions of dissolved cations at 10°C are shown in Table IV. The smaller cations, regardless of valency, induce bond strengths identical to those found for tap water pretreated joints. The solutions containing larger cations induce bond strengths that do not differ from those found for distilled water pretreated joints. The result of the statistical analysis again shows that cations below 0.8 Å in radius induce significantly higher bond strengths than those above 0.8 Å.

The experimental data for etched aluminum washed with varying concentrations of ferric ions is shown in Table V. If the nominal concentration of the cation is increased from 1 ppm to 10 ppm, there is a slight drop in induced bond strength. Joints pretreated in a 100 nominal ppm solution exhibit slightly lower bond strengths. Aluminum joints which were pretreated by a 100 ppm solution of soluble cations and dried were found to be covered by a thin, dull film. This film may be due to the dissolved solids in the distilled water that are left on the aluminum surface when the water evaporates. As this film is only mechanically held on the surface of the aluminum, the resulting bond with epoxy resin is correspondingly weaker. At 1 ppm and 10 ppm, the amount of dissolved solids in the distilled water is

TABLE IV
Bond Strengths for Etched Joints Washed with and Immersed in
10 ppm Cation Solution

Series	Cation	Cation solution, g/l.	Ionic radius, Å	Ave. bond strength, l to break
1/2-Hr Immersion				
18	Fe ³⁺	0.05 FeCl ₃ ·6H ₂ O	0.64	338
19	Ba ²⁺	0.02 BaCl ₂	1.34	323
20	Na ⁺	0.02 NaCl	0.97	327
6-Hr Immersion				
21	Fe ³⁺	0.05 FeCl ₃ ·6H ₂ O	0.64	336
22	Ca ²⁺	0.033 CaCl ₂	0.99	317
23	Ba ²⁺	0.02 BaCl ₂	1.34	319

TABLE V
Bond Strengths for Etched Joints Washed with Varying Concentrations of Ferric Ions

Series	Ferric ion concentration, ppm	Average bond strength, lb to break
24	1	319
25	10	315
26	100	310

low enough so that the aluminum surface is not covered by a weak film deposited when the water evaporates. It is also possible that redox reactions can be occurring on the aluminum surface between aluminum and the dissolved cations and that these reactions are concentration dependent. Although statistically the bond strengths do not differ significantly among the three concentrations, there is a general trend toward lower bond strengths in the order series 25, 26, 27.

Effect of Water Pretreatment Temperature on Epoxy-Aluminum Bond Strength

Table VI shows the effect of pretreating etched aluminum with 60°C tap and distilled water on bond strength with epoxy resin. When exposed to distilled water at 60°C for 1/2 hr, aluminum becomes covered with a cohesively weak, iridescent film of the trihydrate. The bond strength of epoxy resin to aluminum covered with this film is very low. When the aluminum joints were pretreated in 60°C tap water for 1/2 hr, the bond strengths were equivalent to those found for joints pretreated in 10°C tap water. The aluminum surface is protected by divalent anions present in the tap water,⁴ whereas the aluminum in hot distilled water is readily hydrated. Upon the application of the Wilcoxon-Mann-Whitney test to the data in Table VI, it was noted that the bond strengths induced by hot or cold tap water may be

TABLE VI
Effect of Temperature of Wash Water Pretreatment on Bond Strength^a

Temp., °C	Average bond strength, lb to break	
	Tap water	Distilled water
10	339	322
60	339	93

^a Immersion time 1/2 hr.

treated as if they belonged to the same population. The bond strengths induced by hot and cold distilled water were found to be significantly different. The bond strengths induced by tap water were found to be significantly higher than those induced by distilled water.

CONCLUSIONS

When aluminum is etched in a solution of chromic acid at 65°C, the aluminum surface is oxidized to γ -Al₂O₃. This oxide film may contain anionic and cationic vacancies which can affect the strength of an adhesive bond formed between aluminum and amine-cured epoxy resin. When freshly etched aluminum is washed with cold tap or distilled water, there is a difference in bond strength effected between the aluminum and the epoxy resin. This difference was duplicated if distilled water containing various soluble cations was used to wash the etched aluminum joints. It was found that cations having an ionic radius less than 0.8 Å, regardless of valency or associated anion, induced the higher bond strengths found for tap water washes and that above this radius, the bond strengths were identical to those found for distilled water-washed samples. This is consistent with the size of the vacancies in the oxide structure.

It is possible that the small, soluble cations can either occupy the cationic vacancies in the defect spinel structure of γ -Al₂O₃ or diffuse into the oxide film present on the surface of the aluminum. Both processes lead to the same effect, reduction of the negative charge on the surface of the aluminum joint. This could more strongly attract electronegative species such as oxygen and nitrogen, both of which are found in the cured epoxy resin. If diffusion were the mechanism by which this net positive charge was formed, then long immersion times would allow even the largest cation to penetrate the oxide film, and high bond strengths would be observed. This was not found, even for immersion times of 6 hr, as only the cations below 0.8 Å radius induced the higher bond strengths.

Other workers⁹ have found that upon the inductive postcure heating of epoxy-aluminum joints, maximum bond strengths were achieved when the maximum positive charge was induced on the aluminum surface. Upon the removal of the charge, the bond strength dropped. This would seem to indicate that the formation of a surface positive charge or reduction of a surface negative charge by either the absorption of cations or electrical

induction leads to stronger bonding between the aluminum surface and a typical amine-cured epoxy resin.

When freshly etched aluminum joints are immersed in cold tap or distilled water, a thin layer of hydrated oxide (bayerite) is formed that does not hinder the passage of the small cationic species. This thin layer appears to attract the cured resin more strongly than the γ - Al_2O_3 formed during the etching process due to hydrogen bonding. At 10°C , the hydrated oxide film grows very slowly, so that the bond strength remains at a high level, even after 6 hr of immersion time. At 60°C , however, the bayerite grows very rapidly in distilled water, yielding a thick, cohesively weak layer that results in poor bond strengths. In 60°C tap water, the hydration of the aluminum surface is probably prevented by the presence of large, divalent anionic species, as found by Wegman.⁴ The aluminum surface is protected, and the small cationic species can penetrate the thin bayerite layer and reduce the negative charge on the surface of the aluminum.

References

1. A. S. Russel et. al., *Aluminum Properties*, Technical Paper No. 10, Alum. Co. of Amer., 1956.
2. R. F. Wegman, *Adhes. Age*, **10**, 20 (1967).
3. C. J. Lin and J. P. Bell, *J. Appl. Polym. Sci. A-1*, **16**, 1721 (1972).
4. R. F. Wegman and M. J. Bodnar, "Energistic Materials," Soc. Aerospace Mater. Process Eng., 13th Nat. Symp. Exhibition, Western Periodical Co., North Hollywood, California, 1968, pp. 243-252.
5. G. Noether, *Introduction to Statistics*, Houghton-Mifflin, Boston, 1973, p. 133.
6. W. T. McCarvill and J. P. Bell, *J. Adhesion*, submitted.
7. W. T. McCarvill and J. P. Bell, *J. Appl. Polym. Sci.*, **18**, 343 (1974).
8. *Handbook of Chemistry and Physics*, 51st ed., R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1971, F 171.
9. R. A. Raff and A. M. Sharan, *J. Appl. Polym. Sci. A-1*, **13**, 1129 (1969).

Received July 2, 1973