

The Effect of Time and Type of Water Pretreatment on the Bond Strength of Epoxy-Aluminum Joints

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Synopsis

The bond strength of unetched aluminum-epoxy joints induced by tap and distilled water pretreatment at 10°C increased to a maximum, then decreased as a function of immersion time. In distilled water, the maximum bond strength occurs after an immersion time of about 1 hr, after which the bond strength decreases. In the case of tap water pretreatment, the maximum bond strength occurred at about 12 hr of immersion time. The bond strengths at the maxima found for the tap water-pretreated samples were greater than those found at the maxima for the joints pretreated in distilled water. Growth of the hydrated oxide bayerite is proposed as the controlling factor; the bayerite grows more rapidly and less perfectly in distilled water than in tap water. Thick layers of bayerite are structurally weak, while thin layers seem to promote adhesion. A slight surface roughness effect was also observed.

INTRODUCTION

The strength of epoxy-aluminum bonds is dependent on the nature of the aluminum surface. Previous workers have noted that aluminum washed with room temperature tap water before application of the adhesive yielded better bonds to a typical amine-cured epoxy resin than if washed in distilled water and that subjecting aluminum to hot tap and distilled water gave similar results.^{1,2}

Since aluminum exposed to air is covered with the metal oxide and this oxide is associated with adsorbed water, the preparation of the aluminum surface is of vital importance in order to achieve maximum bond strength. The oxide film can be removed from aluminum by mechanical abrasion or by chemical reaction, such as by suitable acid or alkaline solutions. A new oxide film forms almost immediately upon washing and drying; however, the new film may or may not possess different properties from the original oxide film. It is possible, under controlled conditions, to strip off the original oxide layer and induce the formation of one which is a more suitable substrate to achieve maximum bond strength.

The different oxides and hydrated forms of aluminum have been reviewed.³ The most important of these, in that they are formed at conditions most often found in industrial preparation of aluminum for bonding,

are bayerite ($\beta\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$), boehmite ($\alpha\text{-Al}_2\text{O}_3\cdot \text{H}_2\text{O}$), and $\gamma\text{-Al}_2\text{O}_3$. Dehydration of a hydroxide or hydrated oxide will produce $\gamma\text{-Al}_2\text{O}_3$, a defect spinel structure with both cationic and anionic vacancies. Aluminum immersed in water below 75°C forms a film of bayerite; above this temperature, the monohydrate, boehmite, dominates. Whereas the bayerite forms a stronger, more cohesive film that strongly adsorbs epoxy resins,⁴ boehmite is a loose, weak film. The growth of the bayerite layer becomes slower at temperatures below 75°C .⁴ The formation of the hydrates is also greatly retarded by the presence of divalent anionic species such as found in tap water.^{4,5}

The purpose of this work was to subject aluminum to tap and distilled water at 10°C , such that the growth of the trihydrate was controlled. The preexisting oxide film on the aluminum was stripped off by mechanical abrasion, and the new film was allowed to form under varying conditions. The torsional test method developed by Lin and Bell² was used to determine the strength of the bond between an amine-cured epoxy resin and aluminum joints with varying surface pretreatments.

EXPERIMENTAL

Aluminum Surface Preparation

The type of modified tubular butt joints used has been previously described, as have the adhesive preparation and cure.² Prior to each use, the aluminum joint was machined on a lathe to the proper specifications. Depending on the roughness of the surface desired, the joints were degreased after machining or after having been buffed on a polishing wheel with $5\ \mu$ alumina suspended in distilled water. After the joints were degreased and had cooled to room temperature, they were immersed in tap or distilled water at 10°C for varying times. The joints were allowed to air dry at about 55% relative humidity for 1 hr before the adhesive mixture was applied. The adhesive joint was then cured, allowed to cool, and broken in a torsional test apparatus, with the force to break being recorded in pounds. The tap and distilled water used were both slightly acidic (pH about 6.4). The proper immersion temperature was maintained by a cooling jacket of cold water.

The Wilcoxon-Mann-Whitney test⁶ was applied to the data; the test is a simple rank correlational analysis for a small population of data. A more complete discussion of application of the test to epoxy-aluminum joints is given elsewhere.⁷ The results are shown in Appendices A and B, where H_0 , the null hypothesis, states that data from different samples may be treated as if they are all identical. The significance level is given for either a one-sided test, where one set of joint strengths appears lower than one another, or a two-sided test to determine if two sets are equivalent to one another. "Accept" H_0 means that the two series can be treated as one. "Reject" H_0 means that the two series are significantly different; the

smaller the significance level, the smaller the probability that the two series are similar.

RESULTS

The Effect of Distilled Water Pretreatment on Bond Strength

Table I shows the bond strengths of modified tubular butts and a typical amine-cured epoxy resin as a function of time in distilled water pretreatment. The joints were prepared as described above, and the surface roughness varied by either buffing the joints with $5\ \mu$ alumina suspended in distilled water, or by using freshly machined joints showing concentric rings made by the cutting tool. The time required to buff an aluminum joint in the distilled water was less than 1 min. As shown graphed in Figure 1, the bond strength rises rapidly and goes through a maximum after about 30 min immersion pretreatment in 10°C distilled water. The bond strength then drops off less rapidly. The turned surface shows higher bond strengths than corresponding $5\ \mu$ alumina polished joints.

The statistical analysis shown in Appendix A indicates that series 1 is lower in bond strength than series 2, and that series 2 is statistically equiv-

TABLE I
Bond Strength of Epoxy-Aluminum Joints as a Function of
Pretreatment Time in 10°C Distilled Water

Force to break, lb			
Polished			
Series 1 (quick wash)	Series 2 ($1/2$ hr)	Series 3 (2 hr)	Series 4 (6 hr)
250	308	295	266
256	303	306	264
246	295	307	279
268	300	302	280
269	298	300	279
235	297	293	282
240	305	290	288
252 ave.	309	308	277 ave.
	302 ave.	300 ave.	
Machined			
Series 5 (quick wash)	Series 6 ($1/2$ hr)	Series 7 (2 hr)	Series 8 (6 hr)
253	316	305	293
251	320	294	284
230	307	316	303
267	322	300	285
252	308	297	300
252	300	314	306
251 ave.	300	314	287
	310 ave.	308	294 ave.
		306 ave.	

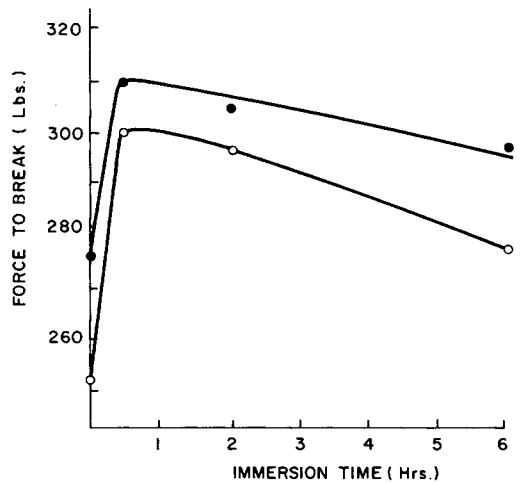


Fig. 1. Effect of immersion time in 10°C distilled water pretreatment on bond strength: (○) polished joints; (●) machined joints.

alent to series 3. The bond strengths in series 4 were found to be lower than those in series 3. In the case of machined joints immersed in distilled water, the result of applying the Wilcoxon-Mann-Whitney test is as follows: series 5 is lower than series 6, series 6 is equivalent to series 7, and series 8 is lower than series 7.

Effect of Tap Water Pretreatment on Bond Strength

Table II shows the experimental data for joints pretreated for varying times in 10°C tap water. The surface roughness was varied in the same

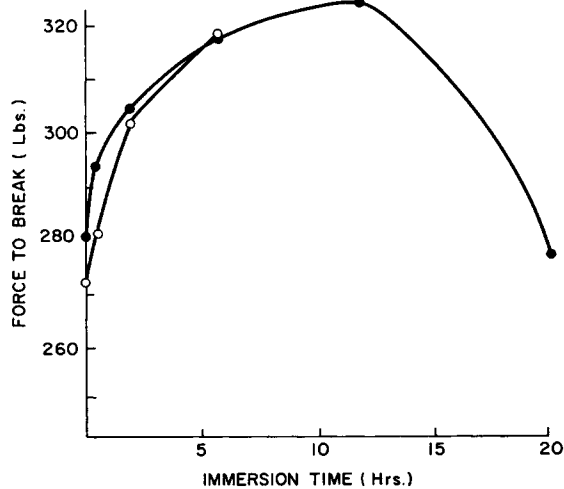


Fig. 2. Effect of immersion time in 10°C tap water pretreatment on bond strength: (○) polished points; (●) machined joints.

TABLE II
Bond Strength of Epoxy-Aluminum Joints as a Function of
Pretreatment Time in 10° Tap Water

Force to Break, lb					
Polished					
Series 9 (quick wash)	Series 10 (1/2 hr)	Series 11 (2 hr)	Series 12 (6 hr)		
273	273	309	312		
274	286	301	323		
278	283	312	325		
278	290	307	319		
275	280	292	315		
274	280	300	319		
268	282 ave.	300	307		
267		303 ave.	317 ave.		
273 ave.					
Machined					
Series 13 (quick wash)	Series 14 (1/2 hr)	Series 15 (2 hr)	Series 16 (6 hr)	Series 17 (12 hr)	Series 18 (20 hr)
279	308	310	306	316	273
285	300	302	330	327	269
290	294	306	326	318	288
281	293	311	316	316	271
279	290	310	313	326	267
292	290	317	315	334	261
271	286	314	308	320	280
282 ave.	294 ave.	301	316 ave.	316	274 ave.
		308 ave.		322 ave.	

manner as for the joints pretreated in distilled water. Figure 2 shows the bond strength plotted as a function of pretreatment time in 10°C tap water. The bond strength gradually increases, then slowly decreases to about 274 lb after an immersion pretreatment time of 20 hr.

In general, the turned joints exhibit higher bond strengths than the 5 μ alumina polished joints, where the failure is primarily adhesive. When the bond failure begins to be more cohesive in nature, at around 320 lb, the effects due to the differing surface roughness disappear. The statistical analysis shown in Appendix B indicates that bond strength increases in the order series 9, 10, 11, 12 in the tap water immersion of 5 μ polished aluminum. For machined aluminum in tap water, the bond strength increases in the order series 13, 14, 15, 16, 17, then decreases for series 18.

Figures 3 and 4 show the effect of using tap or distilled water pretreatment while holding the surface roughness constant. The maximum bond strength induced by the distilled water pretreatment occurs after much shorter immersion times than that found for the tap water immersion, but is 10 to 20 lb lower.

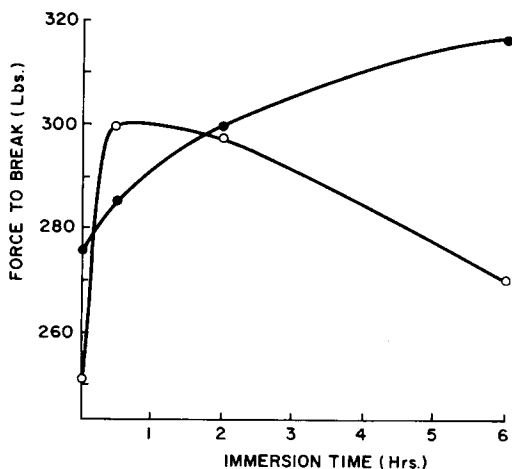


Fig. 3. Effect of immersion time in 10°C distilled and tap water on the bond strength between epoxy resin and polished aluminum: (O) distilled water; (●) tap water.

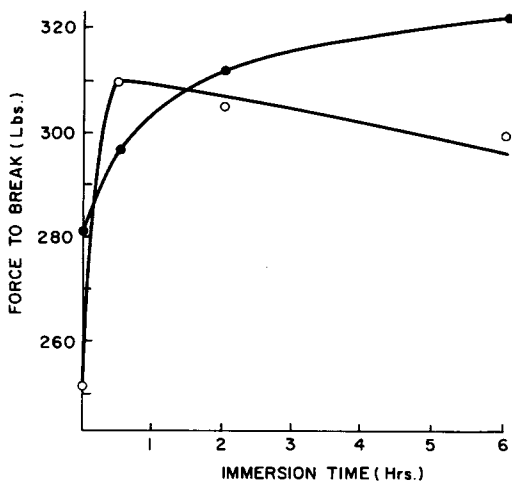


Fig. 4. Effect of immersion time in 10°C tap and distilled water on the bond strength between epoxy resin and machined aluminum: (O) distilled water; (●) tap water.

DISCUSSION

The presence of the trihydrate, bayerite, seems to be necessary for maximum bond strength in bonding a typical amine-cured epoxy resin to aluminum. However, past experimenters^{1,4} have found that covering the aluminum surface with a thick film of this hydrated oxide by immersion of aluminum in 60°C distilled water led to bond failures that were completely adhesive. At 10°C in water, the bayerite grows very slowly, and the thickness of this hydrated oxide can be controlled. In distilled water, after an immersion time of about 1 hr, there is a sufficient thickness of bayerite

present to yield the maximum bond strengths. After this time, the bayerite film becomes thicker,⁴ and although the cured resin is strongly attracted to the trihydrate, the bond fails at a lower strength owing to the weakness of this film.

In the case of tap water pretreatment, the formation of the trihydrate is greatly slowed by the presence of divalent anionic species.^{4,5} The maximum bond strength is attained after about 12 hr immersion time and then very slowly decreases. The ability of the divalent anions to retard the bayerite growth rate is shown by the fact that even after immersing aluminum in 60°C tap water, high bond strengths are achieved, whereas immersion in 60°C distilled water leads to a weak, thick, iridescent layer of the bayerite and poor bond strength.⁴ Upon long immersion times at 10°C, however, the bayerite film becomes thicker and the bond strength drops. Surface roughness seems to be a factor in the bond strength between the cured resin and the aluminum. The machined joints, having concentric rings, gave consistently higher bond strengths than found for 5 μ polished joints. The difference is not large and disappears when the bond failure becomes more cohesive in nature. This indicates that surface roughness plays a small part in adhesive bonding; there appears to be a benefit associated with the slightly greater surface area or mechanical interlocking with the resin in the case of the machined joint.

The bond strengths at the maxima found for the tap water-pretreated samples were greater in all cases than those found at the maxima for the joints pretreated in distilled water. This could be due to small cationic species in the tap water which can be adsorbed on the aluminum surface and reduce the negative charge on the surface which is due to the acidic nature of alumina in water. This reduced negative charge could induce a greater attraction for electronegative atoms such as oxygen in hydroxyl groups and free electrons on nitrogen found in the crosslinking agent. As an alternative explanation, the slower growth of the surface film in tap water could also lead to the formation of a more perfect, stronger surface overgrowth of the bayerite. In distilled water, the bayerite formed could be less perfect and cohesively weaker.

CONCLUSIONS

The best bond strengths between an amine-cured epoxy resin and unetched aluminum can be induced by the controlled formation of bayerite. Good bond strengths can be achieved in 10°C distilled water after an immersion of 1/2 hr. Slightly better bond strengths can be induced by immersion of aluminum in 10°C tap water for 12 hr. Further work is needed to determine if good bond strengths could be effected for shorter immersion times in tap and distilled water at temperatures higher than those used in this work. The determination of the optimal immersion temperature and time of immersion should lead to greater reproducibility of maximum bond strength in industrial preparation of epoxy-aluminum bonds.

Appendix A

Statistical Analysis of Bond Strengths for Machined and Polished Joints Immersed in 10°C Distilled Water⁷

Polished

Series 1 versus series 2: Reject H_0 at significance level 0.005 (one-sided test) where $U_1 < d = 7$, for $m = 7, n = 8$.

Series 2 versus series 3: Accept H_0 (two-sided test) where $U > d = 17$, for $m = n = 8$.

Series 3 versus series 4: Reject H_0 at significance level 0.005 (one-sided test) where $U_4 < d = 7, m = 7, n = 8$.

Machined

Series 5 versus series 6: Reject H_0 at significance level 0.004 (one-sided test) where $U_5 < d = 4$, for $m = 6, n = 7$.

Series 6 versus series 7: Accept H_0 (two-sided test) where $U > d = 15$, for $m = 7, n = 8$.

Series 7 versus series 8: Reject H_0 at significance level 0.020 (one-sided test) where $U_8 < d = 1$, for $m = 7, n = 8$.

Appendix B

Statistical Analysis of Bond Strengths for Machined and Polished Joints Immersed in 10°C Distilled Water⁷

Polished

Series 9 versus series 10: Reject H_0 at significance level 0.006 (one-sided test) where $U_9 < d = 6$, for $m = 6, n = 8$.

Series 10 versus series 11: Reject H_0 at significance level 0.004 (one-sided test) where $U_{10} < d = 4$, for $m = 6, n = 7$.

Series 11 versus series 12: Reject H_0 at significance level 0.004 (one-sided test) where $U_{11} < d = 5$, for $m = n = 7$.

Machined

Series 13 versus series 14: Reject H_0 at significance level 0.006 (one-sided test) where $U_{13} < d = 6$, for $m = n = 7$.

Series 14 versus series 15: Reject H_0 at significance level 0.005 (one-sided test) where $U_{14} < d = 7$, for $m = 7, n = 8$.

Series 15 versus series 16: Reject H_0 at significance level 0.060 (one-sided test) where $U_{15} < d = 15$, for $m = 7, n = 8$.

Series 16 versus series 17: Reject H_0 at significance level 0.060 (one-sided test) where $U_{16} < d = 15$, for $m = 7, n = 8$.

Series 17 versus series 18: Reject H_0 at significance level 0.005 (one-sided test) where $U_{18} < d = 7$, for $m = 7, n = 8$.

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