

Surface Interaction Between Aluminum and Epoxy Resin

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Synopsis

Titration and infrared analysis found no primary chemical bonds between etched or unetched aluminum and an amine-cured epoxy resin. Titration of a very small amount of resin in contact with the large surface area of aluminum dust revealed no drop in epoxy content when oxygen was excluded. The spectra of a bulk-cured epoxy resin were essentially superimposable on the spectra obtained by attenuated total reflectance and specular reflectance of a very thin layer of the cured epoxy resin bonded to aluminum plate. Analysis of uncured epoxy resin in contact with aluminum plate and powder, subjected to the cure cycle in air, indicated that the epoxy ring is oxidized to a carboxylic acid. When air is excluded, no loss of epoxy groups is observed.

INTRODUCTION

The nature of the bond between cured epoxy resin and aluminum greatly influences the strength of a joint made of these materials. Preliminary indications of chemical bonding were present in earlier work,¹ but the data were very limited. Chemical bonding could occur by a number of mechanisms; e.g., it has been suggested² that interactions between hydroxyl groups of the resin and the aluminum surface account for the bonding. According to DeBruyne,³ the epoxy group itself can be involved in bonding. According to Rutzler,⁴ coordination complexes can form between transition metal ions in the surface of the adherend and the amine curing agents that are frequently employed. Barenholtz⁵ and co-workers postulate that certain epoxy resins, upon curing and heating, undergo thermal degradation. They propose that this degradation can create reactive free radicals that can chemically bond to the surface of aluminum and steel. However, the epoxy resin used in the present work is more thermally stable than that used by Barenholtz. The curing temperature was neither excessively high nor prolonged, yet excellent bonds were effected.

The purpose of this work was to ascertain whether or not there is a direct chemical reaction forming primary chemical bonds between a typical epoxy resin and an aluminum substrate. Since earlier workers⁶ have found that aluminum etched in chromic acid solutions exhibits a stronger attraction to amine-crosslinked epoxy resins, both etched and unetched aluminum plate and powder were examined.

EXPERIMENTAL

Epoxide Titration Procedure

The method used to determine the epoxide content consisted of mixing approximately 1 g of the epoxy resin with 50 ml isopropyl alcohol, 25 ml distilled water, and 50 ml of 0.2*N* pyridinium hydrochloride.⁷ The solution was refluxed for 1/2 hr, allowed to cool, and transferred to a 250-ml beaker. The excess pyridinium hydrochloride was then titrated with 0.5*N* sodium hydroxide. It was found that the aluminum dust interfered with the titration, owing to its amphoteric nature. It was therefore necessary to dissolve the resin in acetone, filter out the aluminum dust, and then remove the acetone with a rotary evaporator. The weight of resin found after the evaporation corresponded closely to the weight of resin in the aluminum-epoxy mixture before filtration; a negligible amount of resin remained with the aluminum. Further, the total epoxide content after the filtration was in agreement with the total epoxide content of the amount of resin added to the aluminum.

Preparation of Aluminum Plates

Polished sheet aluminum (Alcoa 6061-T651) was cut into 50 × 20-mm rectangles and degreased in refluxing trichloroethylene for 1/2 hr. The plates were allowed to cool and then placed in a desiccator until use. Etched joints were prepared by immersing the degreased plates in a 30:10:1 by weight solution of distilled water, sulfuric acid, and sodium dichromate at 60° to 65°C for 10 min. The plates were then washed in cold tap water and allowed to air dry for 1 hr before resin was applied. The etched plates were used immediately after preparation.

Cured epoxy-aluminum specimens were prepared by separately heating stoichiometric amounts of methylene dianiline and Epon 828 (registered trade mark of Shell Chemical Co.) in an oven at 120°C until the amine melted. The epoxy and crosslinking agent were mixed together thoroughly and used to bond two prepared aluminum plates together. The thickness of the epoxy laminate was varied by the amount of pressure applied to the aluminum plates. It was found that once the desired thickness of resin was attained, the cure could be effected without changing this thickness. Once the laminate was formed, the specimen was placed horizontally in an oven and cured at room temperature for 30 min, 80°C for 1 hr, and finally 150°C for 2 1/2 hr. The specimens were allowed to cool slowly and were split apart prior to analysis.

In the case of attenuated total reflectance (ATR), the two plates were mounted on two sides of a 50 × 20 × 2-mm-thick KRS-5 internal reflector plate with a 45° angle of incidence in a Wilkes Model 9 internal reflection attachment. Aluminum plates were also cut to 55 × 20 mm and 44 × 20 mm for use in a Wilkes MIR-18 multiple reflection cell at a fixed incident angle of approximately 45°. The plates were prepared as described above.

Both of the above methods were also used for the analysis of unreacted epoxy resin in contact with aluminum plate.

Preparation of Aluminum Powder

J. T. Baker reagent-grade aluminum powder was treated in much the same manner as the plates. The powder was degreased for $\frac{1}{2}$ hr and allowed to cool and air dry. It was then placed in sealed bottles until use. Chemically etched powder was made by mixing 2 g of the aluminum powder with the etching solution. However, the powder was etched for 5 min at 45° to 50°C , as the reaction at 60°C becomes violent. The powder was washed with 5000 ml cold tap water to remove traces of acid, allowed to air dry, and packed in sealed bottles.

The prepared powder was mixed with the epoxy resin in varying amounts and subjected to varying time and temperature treatments. It was not possible to analyze the powder-epoxy mixture by ATR or spectral reflectance, as the powder particles scattered too much radiation, so that the transmitted beam was of almost zero intensity. The aluminum powder was also mixed with stoichiometric amounts of resin and amine curing agent and crosslinked. It was not possible to analyze the cured system by infrared analysis for the reason mentioned above.

RESULTS AND DISCUSSION

Epoxide Content of Epoxy Resin in Contact with Etched and Unetched Aluminum Powder as Determined by Titration

Tables I and II show the experimental data for epoxy resin mixed with etched or unetched aluminum powder and heated through the prescribed cure cycle. The meq/g of epoxide in the unreacted epoxy resin was determined to be 5.20 ± 0.01 meq/g.

The epoxy resin did not undergo thermal degradation when heated alone through the prescribed cure cycle. When mixed with varying amounts of etched and unetched aluminum powder, the resin was air oxidized to a carboxylic acid as determined by an infrared analysis of the resin extracted from the aluminum. The same effect was observed for both etched and unetched aluminum. Samples consisting of etched or unetched aluminum

TABLE I
Epoxide Content of Resin Heated with Etched Aluminum Powder

Al, wt-%	Epoxide content, meq/g
$49.9 \pm .5$	$4.98 \pm .04$
$66.0 \pm .7$	$4.82 \pm .01$
$75.6 \pm .6$	$4.56 \pm .01$
78.5	4.33
50.2*	5.21

* Heated under argon.

TABLE II
Epoxide Content of Resin Heated with Unetched Aluminum Powder

Al, wt-%	Epoxide content, meq/g
50.8 ± 2.0	5.00 ± .04
67.3 ± 1.0	4.80 ± .04
71.6 ± 1.0	4.62 ± .04
80.7 ± .6	4.42 ± .04
50.0 ^a	5.21

^a Heated under argon.

mixed with the resin and heated under argon showed no apparent decrease in epoxide content. This would seem to indicate that no extensive primary bond formation occurs between the aluminum surface and the unreacted epoxide group.⁵ Even if the primary bond formation was not extensive, the large amounts of aluminum surface used would have resulted in a detectable drop in total epoxide content of the resin as compared with the total epoxide content of the same resin before addition to the aluminum.

Surface Interaction of Epoxy Resin with Aluminum Plate as Determined by IR Analysis

The spectra obtained by ATR and specular reflectance of amine-cured epoxy resin bonded to aluminum plate, both open to air and laminated between two plates, were essentially superimposable on the spectrum of a bulk-cured sample. There was no evidence of primary bond formation with the aluminum surface.

ATR and specular reflectance analysis of very thin layers of epoxy resin coated on etched and unetched aluminum plates showed no drop in epoxide content or rise in hydroxyl content at room temperature or 80°C for up to 22 hr. The epoxide content was determined as the infrared absorbance ratio of $A_{910\text{cm}^{-1}}$ to $A_{830\text{cm}^{-1}}$, the hydroxyl by the ratio of $A_{3500\text{cm}^{-1}}$ to $A_{2960\text{cm}^{-1}}$. Open-faced laminates of the uncured resin and aluminum plate heated at 150°C show a drop in epoxy content, an increase in hydroxyl content, and the appearance of carbonyl groups. These are an indication that the epoxide ring is being air oxidized to an α -hydroxyl aldehyde, which is further oxidized to a carboxylic acid. However, when a closed laminate is formed, the epoxy and hydroxyl content does not change, regardless of the surface treatment of the aluminum. The discrepancy between the open and closed laminates of etched and unetched aluminum plate is due to the amount of surface area presented to air that will undergo oxidation. On the etched aluminum, the resin tends to remain as a fairly uniform film. On the other hand, resin on the unetched aluminum draws up into droplets, decreasing the surface area. When the surface coverage is uniform, and oxygen is not allowed to come into contact with the resin, there is no apparent reaction of epoxide or hydroxyl groups with etched or unetched aluminum at the time and temperatures employed to crosslink the resin.

References

1. C. J. Lin and J. P. Bell, *J. Appl. Polym. Sci.*, **16**, 1721 (1972).
2. J. Glazer, *J. Polym. Sci.*, **13**, 355 (1954).
3. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1957; p. 213.
4. J. E. Rutzler, Jr., *Adhes. Age*, **2**, 29 (1959).
5. G. J. Barenholtz, I. C. Chu, and J. E. Rutzler, Div. of Paint, Plastics, and Printing Ink Chem., *ACS Preprints*, 177 (April 1960).
6. R. F. Wegman, *Adhes. Age*, **10**, 20 (1967).
7. J. P. Bell, *J. Polym. Sci. A-2*, **6**, 417 (1970).

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