Micro-roughening of Epoxy and Cyanate Ester Laminates as a Precursor to Electroless Plating

By Dr. Gregory L. Young*

The feasibility of copper plating an epoxy and a cyanate ester laminate was studied. A sufficiently microroughened surface is critical to film adhesion. An alkaline permanganate etchant was selected to microroughen the surface. The etchant was applied by three methods: immersion, ultrasonic immersion and spray etching. Initial screening experiments indicated that the cyanate ester resin system was more susceptible than the epoxy resin system to micro-roughening by the permanganate etchant. Micro-roughened laminated samples were subsequently copper plated using an electroless process. The adhesion of the copper film was measured using a peel tape test. The relationship between micro-roughened surfaces and film adhesion was analyzed. Etching unidirectional cyanate ester resin laminates produced a surface topography that was successfully plated with a copper film through an electroless deposition process. The use of ultrasonic immersion and spray etching improved the film adhesion strength. The adhesion strength of the copper film on the cyanate ester laminate was at least 1.4 MPa (200 lb/in.²).

Over the past decade, there has been an increase in composite materials applications. Advances in composite materials research have made it feasible to replace metal with lightweight composites of equal strength and stiffness. While metals offer a high degree of ductility, strength and electrical conductivity, they are generally much heavier than graphite/resin laminates. In applica-

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Loosely put, this work involves another area of plated plastics. It deals with plating on non-metallic laminates and composites that offer strengths and other properties that are superior to metals at considerably less weight. The problem lies in achieving reliable adhesion. The key is in obtaining the proper etch, or micro-roughening. The author has studied the details of getting the right etch conditions to reliably copper plate epoxy and cyanate ester laminates. tions where electrical conductivity is of importance, the deposition of a thin metal layer via electroless plating onto a graphite resin laminate makes it possible to utilize the electrical conductivity of metals and structural properties of graphite composites.

Although plating of plastics was introduced in the 1960s,¹ plating on undoped graphite/epoxy and graphite/ cyanate ester laminates is still a current issue in applications where the resin is designed to resist to swelling, corrosion or absorption of water.

Due to the smooth surface finish of most plastics and composites, the adhesion strength of metal films on untreated surfaces is poor. A surface roughening step is essential to obtain good adhesion between metal and the plastic substrate. A micro-roughened surface provides anchoring sites for the metal film. Chemical etching, plasma etching and mechanical abrasion are the major processes used to micro-roughen a plastic substrate.

There are two major types of chemical etching: acid and alkaline. Chromic acid etching was the predominant acid etching method used in the past. However, hexavalent chromium is an environmentally regulated heavy metal and ultimate disposal is problematic. Concentrated sulfuric acid, an alternative to chromic acid, is not regenerable. Because it is not regenerable, sulfuric acid is not feasible for production processes. Alkaline etching overcomes most of these problems. Alkaline permanganate etching has been shown to achieve uniform and controlled etching rates. Additionally, alkaline permanganate systems are regenerable and are more environmentally friendly. The manganese dioxide (MnO₂) produced during the etching reaction can be electrolytically reoxidized back to permanganate (MnO_4^{-}) to be used for subsequent etching.² The regeneration of the manganese dioxide helps to reduce the amount of waste produced from the etching process.

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Etching mechanism of the resin system

Thorn and Walsh³ studied the etching mechanism for alkaline permanganate (MnO_4^-) etching of glass fiber/epoxy composites. It was proposed that the permanganate solution etched the epoxy by oxidizing the covalent bonds within the polymer network by first cleaving the crosslink sites, then breaking down the monomers into soluble components which were further degraded to carbon dioxide. A similar mechanism is assumed to apply for cyanate ester laminates. In both mechanisms, the resin is attacked by the etchant. The carbon-based fiber is impervious to the chemical etchant.

Thorn and Walsh suggested a three-step process to etch the resin of the laminates. The three steps are: conditioning, etching, and neutralization. In the conditioning step, an organic solvent, such N-methylpyrrolidone, is allowed to diffuse into the resin matrix of the laminate. The conditioner swells the resin matrix and replaces polymer-polymer bonds with polymer-solvent bonds. The etching step attacks the strained polymer-polymer and polymer-solvent bonds, cleaving the crossed-linked sites. The neutralization step removes the oxide film that builds up on the laminate surface as a result of the etching.

Electroless plating

Electroless copper plating is used in industry to deposit metal onto composite materials. The nonconductive nature of carbon fiber composites limits the deposition to either a chemical (electroless) or a physical (sputtering) technique. After electroless copper plating, the composite substrate is rendered conductive. Once the surface becomes electrically conductive, an electrolytic copper plating process can be used if necessary. Literature has shown that adequate etching is critical to achieve sufficient metal to substrate adhesion for successful electroless plating.³

There are four major steps in electroless plating: sensitization, activation, acceleration and electroless copper deposition.⁴ An acidic stannous chloride (SnCl₂) solution sensitizes the substrate. This increases the wetting of SnCl₂ on the substrate. The substrate is then activated in a solution of acid palladium chloride. Nucleation of palladium (Pd) occurs through the reaction between Pd⁺² and Sn⁺² as shown in Equation 1. This reaction produces a metallic alloy colloid of Pd and Sn surrounded by stabilizing layers of SnCl₂ and Sn(OH)₂. Palladium has been proven to provide the catalytic surface required for electroless copper deposition. Accelerators such as NaOH and EDTA are effective in removing the tin from the palladium/tin colloid to increase the initial rate of copper deposition. Electroless copper deposition is achieved in an electroless copper plating bath. Copper sulfate (CuSO₄) is used as a copper source and formaldehyde (HCHO) is used as a reducing agent. Two major reactions taking place in this bath are shown in Equations 2 and 3, respectively. The overall reaction is shown in Equation 4.

Nucleation of Palladium:

$$Pd^{+2} + Sn^{+2} \rightarrow Pd + Sn^{+4}$$
 (1)

Anodic reaction:

$$CH_2O + 2OH^- \xrightarrow{catalytic surface} CHO_2^- + \frac{1}{2}H_2 + H_2O + e^-$$
 (2)

Cathodic reaction:

$$Cu^{+2} + 2e^{-} \xrightarrow{\text{catalytic surface}} Cu$$
 (3)

Overall reaction: $Cu^{+2} + 2CH_{2}O + 4OH^{-} \xrightarrow{\text{catalytic surface}} Cu + 2CHO_{2}^{-} + 2H_{2}O + H_{2}$ (4)

Experimental design

The feasibility of micro-roughening and electroless copper plating carbon fiber laminates was investigated in two parts. Initially, the feasibility of utilizing the etchant on the selected epoxy and cyanate ester resin was investigated. The resins selected for this study were aerospace qualified resins. Neat resin samples of approximately 6.0 cm² (0.93 in.²) were immersion etched. The permanganate etchant concentration was held constant at 90.0 g/L (12.0 oz/gal). The samples were etched for times of 4 and 12 min. The thickness of the resin samples was approximately 0.3 cm (0.12 in.). The tool side of the resin samples was studied. The topography of the etched neat resins and laminate samples were qualitatively analyzed by optical microscopy.

Based upon the initial resin etching results, laminate coupons were etched under different times and application method, and subsequently copper plated. The adhesion strength of the copper plated film was quantified. Fabricated laminate coupons were approximately 6.0 to 7.0 cm² (0.93 to 1.09 in.²) in size. Five plys of unidirectional pan-based carbon fiber tape were used to make the laminate samples. The average resin thickness at the surface of the laminate was approximately 2.0 μ m (79 μ -in.). The effect of etchant time and application methods on the adhesion strength of the copper film was investigated. The three application methods studied were immersion, ultrasonic immersion and spray etching. Increasing the anisotropy of the etching process by using ultrasonic energy or a spray system has been shown to improve the microroughening of the surface.5 The spray etching system consisted of a large reservoir of etchant solution and a fixture to hold the substrate stationary in front of a nozzle. Etchant was pumped from the reservoir through the nozzle and directed at the substrate. The excess etchant was allowed to drain back into the reservoir.

An ultrasonic tank^{**} was used to ultrasonically etch the samples. The tank was filled with deionized water and a small amount of surfactant. A beaker of the permanganate etchant was placed in the ultrasonic tank. The ultrasonic energy generated by the tank was transferred into the etchant beaker.

Sample etching was performed using a five-step surface preparation process: alkaline cleaning, acid cleaning, resin conditioning, permanganate etching and neutralization. A 12M NaOH alkaline solution and a 3% H_2SO_4 acid solution were used to remove any gross contamination of organics and salts from the laminates. The conditioning, etching and neutralization steps were described in the etching mechanisms section of this paper.

The electroless copper plating of the laminates was done according to the process discussed above in the electroless plating section. Samples were plated with $2.5 \times 10^{-2} \mu m (1.0 \ \mu\text{-in.})$ of copper.

A tape test^{***} was used to quantify the adhesion strength of metal films.⁶ Adhesion strength is classified on a scale of zero to five. A tape test classification of five indicates that the adhesion is at least 1.4 MPa (200 lb/in.²). A tape test classification of zero indicates that there is no adhesion strength for the deposited film.

Resin study

Figures 1(a) and (b) show the tray side topography of the epoxy and cyanate ester resin prior to etching. There was an initial roughness to both surfaces. The epoxy resin sample had a smoother initial unetched finish. Maintaining a constant etchant concentration of 90 g/L (12 oz/gal) permanganate, the surface finish of both resins was compared for immersion times of 4 and 12 min. Figures 2(a)

^{**} Branson Model 5210, Branson Precision Processing, Danbury, CT.
*** GARDCO Paint Adhesion Test Kit, Paul N. Gardner Company, Inc., Pompano Beach, FL.



Figure 1-(a) Unetched epoxy resin (500X); (b) Unetched cyanate resin (500X).



Figure 2-(a) Epoxy resin etched for 4 min (500X); (b) Epoxy resin etched for 12 min (500X).



Figure 3-(a) Cyanate resin etched for 4 min (500X); (b) Cyanate resin etched for 12 min (500X).

and (b) show the results of etching the epoxy resin. Figures 3(a) and (b) show the results of etching the cyanate ester resin.

Etching the epoxy resin for 4 min [Fig. 2(a)] resulted in an increase in surface roughness. There were more peaks and valleys in etched coupon, when compared to the unetched coupon. However, increasing the etching time to 12 min for the epoxy resin did not increase the roughness. The epoxy coupon etched for 12 min [Fig. 2(b)] had a smoother finish than the epoxy coupon that was etched for 4 min [Fig. 2(a)]. The surface of the sample etched for 12 min looked similar to the unetched epoxy sample [Fig. 1(a)]. Prolonged exposure to the etchant appeared to result in a bulk etching effect that leveled the surface of the resin [Fig. 2(b)].

The cyanate ester system did not behave in the same manner as the epoxy system. Examining the cyanate ester resin, the surface topography became increasingly rougher as the etchant immersion time was increased. After 4 min of etching [Fig. 3(a)], the surface had a slight increase in roughness over the unetched coupon [Fig. 1(b)]. After 12 min of etching, raised islands were observed on the surface of the resin [Fig. 3(b)]. The slight peaks and depressions of the unetched cyanate ester resin [Fig. 1(b)] have been magnified after 12 min of etching.

Laminate study

Based upon the etching results of the epoxy and cyanate ester resins, unidirectional carbon fiber laminates were made with both resins systems. Preliminary experiments determined that an etchant concentration of 90 g/L 12 oz/gal) overetched the laminates, stripping away all the resin from the surface of the laminate in less than 1 min.⁶ Bare fiber was exposed along the surface. Figure 4 is an example of overetched laminate coupon.

The light lines in Fig. 4 represent carbon fibers on the surface. The resin has been completely removed from the top layer of the laminate leaving exposed rows of fiber. While copper can be plated onto the fibers, there is very little tensile strength of the fiber. Previous screening experiments indicated that a MnO_4^- concentration of 40 g/L (5.3 oz/gal) would not overetch the laminate coupons for etch times ranging from 2 to 12 min.⁶

Immersion etching uniformly removed the resin from around the carbon fiber bundles. Figure 5 shows the surface of the epoxy laminate after immersion etching. The resin has been etched around the fiber bundles leaving uniform trenches along the surface. Some of the surface fiber bundles were completely exposed. Several etch pits, indicated by dark spots in Fig. 5, can be seen on the surface of the laminate.

The ultrasonic immersion and spray etching methods etched the laminate surfaces in a more anisotropic manner. Small etch pits were created on the surface of all laminates. Figures 6 and 7 show the surface topographies of ultrasonic and





Figure 4–Overetched epoxy laminate (500X).

Figure 5-Epoxy laminate - 4 min immersion etch (500X).

sprayed etched cyanate ester laminates respectively. The circled areas in each figure highlight the etch pits.

These etch pits provide physical anchoring sites for the subsequently plated copper film. Resin was only partially removed from the fiber bundles in both Figs. 6 and 7. Note that the density of the etch pits is greater for the ultrasonic etched coupon. The spray etch produced more of a non-uniform bulk trench etch with etch pits randomly appearing on the surface. Figure 8 shows the surface topography of an ultrasonic etched epoxy sample. Compared to the cyanate ester laminate system, the epoxy laminate has a larger amount of exposed fiber.

Figures 9 and 10 show the tape test results for each copper plated laminate resin system. Overall, the cyanate ester resin laminates exhibited superior adhesion strength. The epoxy-based laminates demonstrated increasing adhesion strength with increasing time. Application of the etchant by ultrasonic immersion or spray etching resulted in an increase in adhesion strength of epoxy based laminates. There was no detectable difference in adhesion strength as the application technique and etchant contact time were varied for the cyanate ester laminates. All the cyanate ester resin laminates scored the maximum level on the tape test. Quantitatively, it can be said that all etched cyanate ester laminate samples have a film adhesion strength greater than 1.4 MPa (200 lb/in.²) (the adhesion strength of the tape).

The adhesion strength of the copper on the epoxy laminates was greatest for the spray etching technique and weakest for the immersion technique. The anisotropic application of the etchant to the epoxy improved the adhesion of the copper. Comparing an immersion etched sample and an ultrasonic sample; there is a dramatic difference in surface topography (Figs. 5 and 8). The immersion etched sample had almost no etch pits. The ultrasonic etched sample showed etch pits along the length of the surface fiber bundles. In addition to changes in topography due to application method, longer etchant contact time improved the adhesion of the copper film to the epoxy laminate.

Conclusions

Both epoxy and cyanate ester laminates can be successfully micro-roughened using an alkaline permanganate etchant. Based upon adhesion strength, the cyanate ester laminates produces a more desir-

able surface topography for electroless copper plating compared to epoxy systems under the same conditions.

Immersion, ultrasonic immersion and spray etching methods resulted in different surface topographies of the epoxy resin. Immersion etching generated relatively uniform surfaces and few etch pits were formed on the laminate surface. Ultrasonic and spray etching were two methods used to produce an anisotropic etching environment. Pits were formed on laminated surfaces etched by these two methods.

In general superior adhesion strength of copper was achieved using a cyanate ester laminates. Utilizing a MnO_4^- concentration of 40 g/L (5.3 oz/gal), the adhesion results for the cyanate ester laminates were independent of application technique and exposure time (2 to 4 min). All copper plated samples achieved the highest rating by the tape test. The adhesion of the copper film was at least 1.4 MPa (200 lb/in.²).

Etching depends not only on permanganate concentration and etching time, but also on the type of resin used to fabricate the laminate. Comparing Figs. 6 and 8, it is clear that the topography of these laminates etched by ultrasonic immersion method is very different. For the same etching time and application method, a larger number of etch pits were formed on the cyanate ester resin laminate. Additionally, the epoxy laminate had more exposed fiber bundles on the surface.

Continued on page 39



Figure 6-Cyanate laminate - 4 min ultrasonic etch (500X).



Figure 7–*Cyanate laminate - 4 min spray etch* (500X).



Figure 8–Epoxy Laminate - 4 min ultrasonic etch (500X).

- 2) The electroless nickel preplate is a more suitable primer layer for aluminum alloy wheels with large window depths.
- 3) The CASS test results show that the electroplated aluminum alloy wheels preplated with an electroless nickel layer can pass the 44-hr CASS test.

The electroless nickel technology we describe here provides extended product life and quality. We also recognize that there is a cost premium associated with electroless nickel. However, the benefits may well be worth the added expense to the customer.

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Micro-roughening of Epoxy and Cyanate Ester Laminates as a Precursor to Electroless Plating *Continued from page 29*



The process for each system still needs to be optimized for metal film adhesion strength. The tape test indicates that plated film has adhesion strength of at least 1.4 MPa (200 lb/in.²). A quantitative method to measure the exact adhesion strength of the film should be explored. In addition to optimizing the etching process, the laminate systems that were investigated could be improved to promote better micro-roughening conditions. A carbon fiber fabric, instead of a tape could be used to provide an initial surface that is more susceptible to micro-roughening. In addition, the resin content of the laminate could be increased to provide more bulk material to etch with out exposing fibers.

Acknowledgements

The author would like to thank Space Systems Loral for funding this research and fabricating the resin and laminate samples.

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