# Metallization of Photosensitive Epoxy

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**ABSTRACT:** The adhesion strength of various photosensitive epoxies with copper or FR4 substrate was measured by the stud pull testing method. The adhesion strength was around 35–60 kg/cm$^2$ for photosensitive epoxy/copper laminate and 60–105 kg/cm$^2$ for photosensitive epoxy/FR-4 laminate. A high adhesion strength of metal/photosensitive epoxy can be obtained when the surface of photosensitive epoxy is subjected to 1 minute of microetching in the processes of metallization. Under such a processing condition, the adhesion strength of copper/photosensitive epoxy for Taiyo PVI-500/SA-50 can be as high as 145 kg/cm$^2$, and the adhesion strength remained higher than 145 kg/cm$^2$ after the solder float test. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1639–1645, 1998

**Key words:** adhesion strength; microetching; surface morphology; stud pull test; solder float test

## INTRODUCTION

In recent years, high-density, low-cost electronic packaging technologies are required to meet the down-sizing trend of both small computers and high-performance workstations.[1–7] To connect those high-density components, high-density surface wiring on printed circuit board with reduced through hole size and reduced copper and dielectric planes thickness was developed, as was the application of flip chip on board technology. Printed circuit board with a film redistribution layer (FRL)[8–13] is a component carrier technology capable of achieving wiring densities on the order of 500–1000 in/square inch[14,15] by allowing bare chips directly attached on the FRL through flip chip bonding. These FRL boards are fabricated with traditional fiberglass-reinforced epoxy copper clad as substrate, and photosensitive epoxy (solder mask) as film redistribution dielectric layers and wiring planes are sequentially built up on top by electroless and electrocopper plating. The main feature is a photosensitive dielectric layer used to produce small blind via holes instead of plating through holes for signal line connection. Also, FRL remains low cost because it can be manufactured with the materials and equipments that exist for the printed circuit board industry.

For successful manufacturing of FRL, the formation of a small photo via holes and reliable adhesion between wiring metal and photosensitive epoxy dielectric are necessary. In this study, the adhesions of photosensitive epoxy dielectric to the copper metal substrate or fiberglass-reinforced epoxy substrate and metallized conducting layer (electroless nickel or electroless copper layer) to the photosensitive epoxy dielectric layer were studied in order to find the optimal processing conditions for the metallization of photosensitive epoxy from Taiyo, Nan Ya, and Utek.

## EXPERIMENTAL

The photosensitive epoxy resins Taiyo PSR-4000/CA-40, Taiyo PVI-500/SA-50, Nan Ya LP-1G L/

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HP-10, and Utek UPC-9000/H-300 are commercially available solder masks used in the manufacturing of printed circuit board. According to the physical properties reported, such as coefficient of thermal expansion, glass transition temperature ($T_g$), Young's modulus, % water uptake, and dielectric constant, these photosensitive epoxies have great potential to be used as a dielectric in the manufacture of FRL. In this experiment, the adhesion strength of these photosensitive epoxy dielectrics to various substrates and to the wiring metal layer was studied to see whether they are suitable for the fabrication of FRL.

The main agent and hardener of photosensitive epoxy resins were stored separately in a refrigerator. The main agent and the hardener were mixed

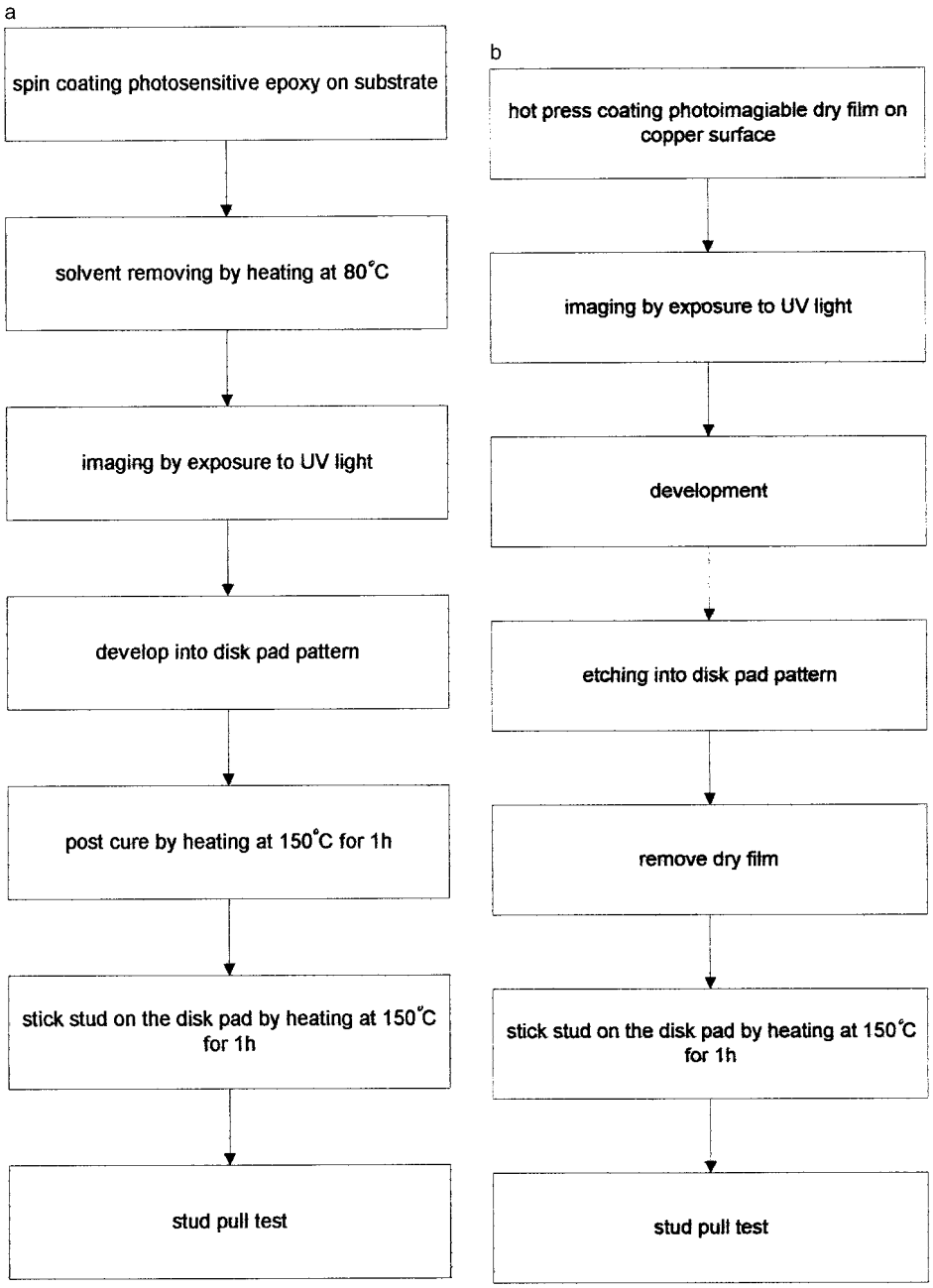


**Figure 1** Flowchart of sample preparation for stud pull test. (a) Upper layer is photosensitive epoxy, (b) Upper layer is electroplated copper.

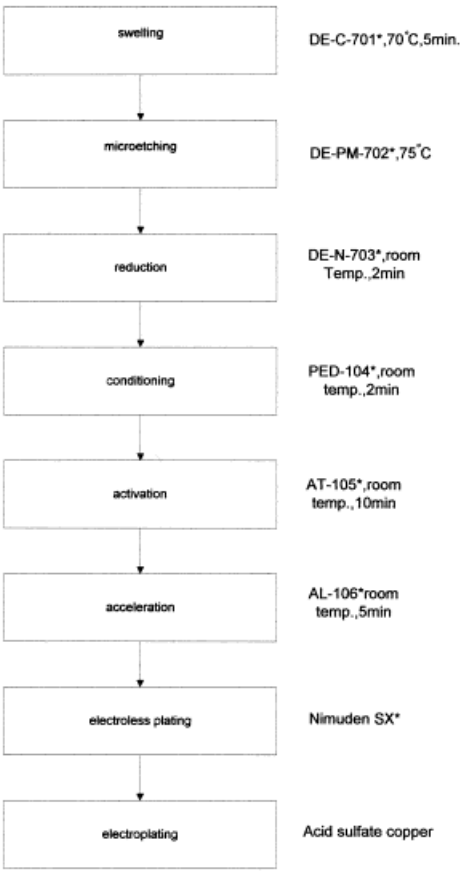


**Figure 2** Processes of metallization. *All chemicals are from Taiwan Uyemura Co. Ltd.

at room temperature before use. The mixing ratios of main agent to hardener were 75 to 25% for Taiyo PSR-4000/CA-40, 70 to 30% for Taiyo PVI-500/SA-50, 65 to 35% for NanYa LP-1G L/HP-10, and 75 to 25% for Utek UPC-9000/H-300. The viscosities of the mixture were around 130, 2–20, 150–250, and 100 ps in the above order. After mixing, mixture was coated on 5.75 × 5.75 cm copper foil, FR4, or ceramic at a thickness of 160 $\mu$m. The solvent was removed by heating at 80°C for 60 minutes, except for PVI-500, which was heated at 80°C for 100 minutes. The samples were then exposed to 800 milli joule/cm$^2$ ultraviolet (UV) light, except those made of PVI-500, which were exposed to 120 mJ/cm$^2$. The UV exposure was from ORC model UV-330. If formation of via is required, the samples were then etched with 1% sodium carbonate solution to develop via holes. After light exposure, the epoxy resin was then postcured at 150°C for another 60 minutes. The thickness of the postcured epoxy dielectric was kept around 45 $\mu$m. The adhesion strengths of the photosensitive epoxy to the substrate were investigated following the process shown in Figure 1. The adhesion strength of electroless copper or electroless nickel to the photosensitive epoxy was rather high. Therefore, theoretically, one should coat photosensitive epoxy resin on a substrate which has a stronger adhesion with photosensitive epoxy. In this experiment, all samples were prepared by coating photosensitive epoxy resins on ceramic. After various curing processes, as described in the previous paragraph, the cured epoxy was metallized. The processes of metallization are shown in Figure 2. In this experiment, the period of microetching (desmear) was varied to obtain an optimal adhesion strength of the metal (electroless copper or electroless nickel)/photosensitive epoxy dielectric interface. The surface of the epoxy after microetching was examined by a scanning electron microscope made by Olympus. The thickness of electroless nickel or copper was around 0.1–0.3 $\mu$m and that of electroplated copper was around 35 $\mu$m. The adhesion strength of electroless copper/photosensitive epoxy dielectric and electroless nickel/photosensitive epoxy dielectric was also studied.

The adhesion strength of various interfaces was measured following the processes shown in Figure 1. The adhesion strength testing process involves etching the upper layer of testing samples into a small disk pad, and the diameter of the disk of the negative film was matched with the head size of the study pull testing stud. The adhesion strength was tested by Sabastian five from Quad Group. After solder float at 260°C for 10 seconds, the adhesion strength was measured again. Each adhesion strength was measured

**Table I Average Adhesion Strength of Photosensitive Epoxy with Substrate**

| | Epoxy | | | |
|---|---|---|---|---|
| Substrate | PSR-4000 | PVI-500 | Utek | Nan-Ya |
| Cu[a] | 62/44 | 51/48 | 51/20 | 37/21 |
| FR-4[a] | 105/114 | 93/112 | 81/90 | 63/54 |
| Ceramic[a] | 148/161 | 161/179 | 146/153 | 147/116 |
| Cu[b] | 113 | 111 | 74 | 64 |
| FR-4[b] | 101 | 102 | 89 | 73 |
| Ceramic[b] | 151 | 227 | 194 | 172 |

[a] Before solder float/after solder float (kg/cm$^2$).
[b] Before solder float (kg/cm$^2$).

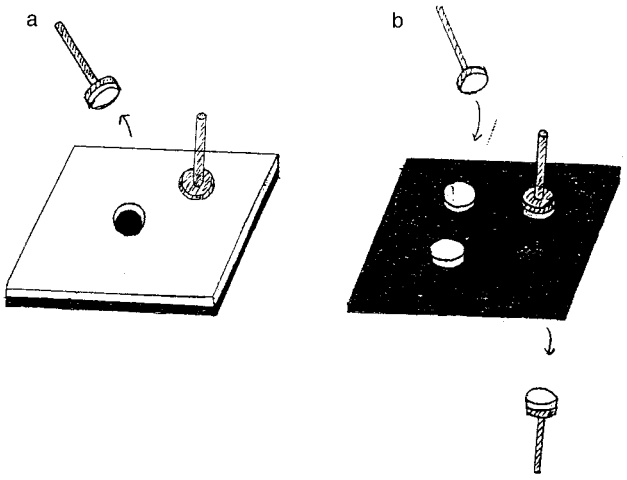


**Figure 3** Stud pull test.

three to five times, and the average value was reported.

## RESULTS AND DISCUSSION

### Adhesion Strength of Photosensitive Epoxy with Substrate

The average adhesion strengths of various photosensitive epoxies with copper foil, FR4, or ceramic substrates were listed in Table I. Figure 3b shows the adhesion strength of epoxy/substrate when the upper layer of epoxy was etched into a small disk of stud size; this was the true adhesion strength of the epoxy/substrate. Figure 3a also shows the adhesion strength of epoxy/substrate when the upper layer epoxy was not etched into the pattern. The adhesion strength of Figure 3a actually included the peel-off strength of the upper layer epoxy of disk's ring size. Therefore, in general, the adhesion strength of the samples with disk pattern was lower than those without pattern for the same epoxy.

Figure 3b showed that, in general, the adhesion strength was highest for all four kinds of epoxy with ceramic, and all were around 145–160 kg/cm$^2$. It was possible that the surface of ceramic was the most porous one among the three substrates. After the solder float test at 260°C for 10 seconds, the adhesion strength of all samples remained higher than 115 kg/cm$^2$.

The adhesion strength was around 35–60 kg/cm$^2$ for all four kinds of photosensitive epoxy/copper laminate. Even with very careful pretreatment of copper surface, such as polishing with aluminium oxide or cleaning with CD-102 microetching solution, the adhesion strength was still the lowest of the three kinds of interfaces. It was speculated that the smooth copper surface attributed to such a behavior. After the solder float test at 260°C for 10 seconds, the adhesion strength was reduced somewhat, except for that of the samples from Yaiyo PVI-500, which remained as high as 48 kg/cm$^2$.

The adhesion strength of all kinds of photosensitive epoxies with FR-4 substrate was around 60–105 kg/cm$^2$. After the solder float test, the adhesion strength did not change much for all four kinds of epoxy/FR-4 interfaces. For the same interface, the standard deviation of each measurement of adhesion strength was around $\pm$15 kg/cm$^2$, probably because in the process of testing, some part of the epoxy was peeled off instead of the interface failing for some samples.

### Surface Morphology of Epoxy

The adhesion strength of conducting metal with photosensitive epoxy substrate would be affected by the morphology of the epoxy substrate. The surface morphology of various kinds of epoxy was examined with a reflective microscope (Fig. 4). It showed that without microetching, the surface of epoxy was very smooth and hydrophobic, making it hard to be electroless plated. If the microetching period was from 5 seconds to 1 minute, the surface became more rough and hydrophilic, rending it more susceptible to the subsequent electroless plating. If the microetching period was from 1–5 minutes, it would be etched into the epoxy structure, and the epoxy surface depth profile would be even more rough. If the microetching period was longer than 10 minutes, because the epoxy was exposed to the etching solution for too long a period, the epoxy (except for Nan-Ya epoxy) inside structure was etched and the surface of the epoxy became spongy. Delamination of the epoxy/ceramic interface might take place after prolonged exposure to the etching solution. Surface morphology by scanning electron microscopy showed that no matter how long the microetching period was, the epoxy from Nan-Ya LP-1G L/HP-10 (unlike the other epoxy) was unable to be etched very deep into the epoxy structure; however, its surface part was etched away gradually, and the epoxy became thinner or delamination occurred for the epoxy/ceramic interface. This

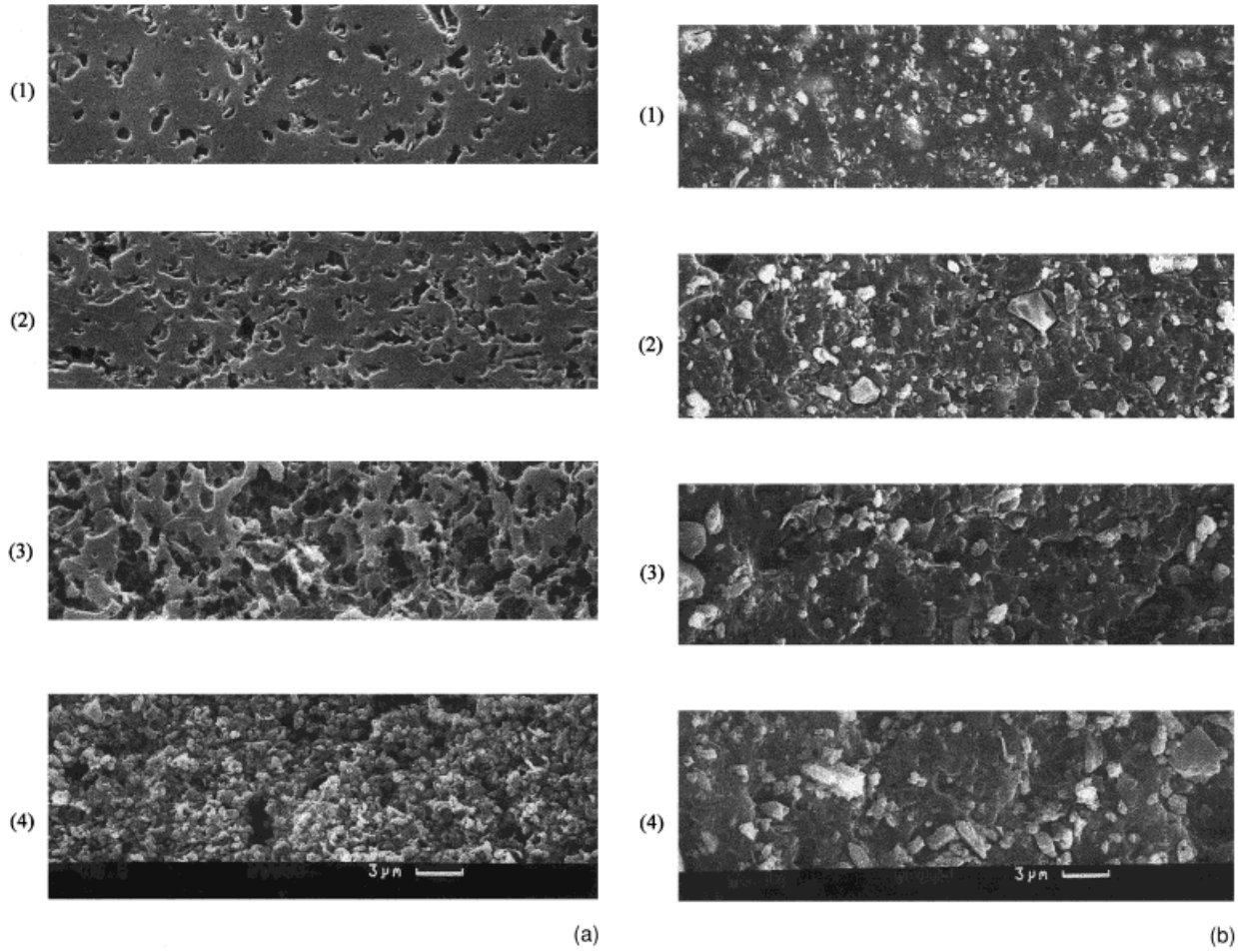


**Figure 4** (a) Surface morphology of Taiyo PVI-500 epoxy. Etching period: (1) 15 seconds, (2) 1 minute, (3) 5 minutes, and (4) 15 minutes. (b) Surface morphology of Nan-Ya epoxy. Etching period: (1) 15 seconds, (2) 1 minute, (3) 5 minutes, and (4) 15 minutes.

observation indicated that the optimal microetching period of surface pretreatment for electroless plating was 1 minute for all four kinds of epoxy. Therefore, in this experiment, the adhesion strength was studied with a microetching period of around 1 minute.

### Adhesion Strength of Electroless Nickel/ Photosensitive Epoxy

The average adhesion strength of electroless nickel/ photosensitive epoxy laminate with the epoxy surface subjected to different microetching periods is shown in Table II. Without microetching, the epoxy surface was very difficult to be electroless nickel plated and the adhesion strength of electroless nickel with such an epoxy surface approached zero. The adhesion strength was around 125 kg/cm$^2$ or higher if the microetching period was from 5 seconds to 5 minutes for electroless nickel/Taiyo PVI-500 epoxy. After the solder float test at 260°C for 10 seconds, the adhesion strength remained high. The adhesion strength of electroless nickel with the other epoxy was around 85–180 kg/cm$^2$. However, after the solder float test at 260°C for 10 seconds, the adhesion strength was reduced a lot; some were even lower than 10 kg/cm$^2$.

All of the locus of failure interfaces were observed to be epoxy/ceramic, indicating that the actual adhesion strength between electroless nickel and photosensitive epoxy should be higher than those reported in Table II. Before the solder float test, the adhesion strength of the photosensitive epoxy with ceramic, as reported in the previ-

**Table II Average Adhesion Strength of Electroless Nickel with Photosensitive Epoxy (Before Solder Float/After Solder Float, kg/cm$^2$)**

| | Epoxy | | | |
|---|---|---|---|---|
| Microetching Period | PSR-4000 | PVI-500 | Utek | Nan-Ya |
| 5 seconds | 170/135 | 126/44 | 198/35 | 115/13 |
| 15 seconds | — | 188/104 | — | — |
| 30 seconds | 101/149 | 106/114 | 175/47 | 90/3 |
| 45 seconds | — | 130/117 | — | — |
| 1 minute | 142/38 | 129/111 | 157/42 | 141/3 |
| 5 minutes | 94/36 | 135/156 | 164/15 | 85/5 |

*Note.* —data not available.

ous section (145–160 kg/cm$^2$), was more or less higher than the data reported in this section (125 kg/cm$^2$, the failure interface was also epoxy/ceramic) and seemed to indicate that further metallization of photosensitive epoxy and subsequent electroplating processes did not affect the adhesion of epoxy with ceramic substrate. However, after the solder float test at 260°C for 10 seconds, all of the adhesion strength of the Nan-Ya laminate studied in this section became lower than 25 kg/cm$^2$, although most of the samples made from Taiyo PVI-500 remained higher than 110 kg/cm$^2$, while the adhesion strength of the other samples studied in this section were also reduced a lot. For the same interface, the standard deviation of each measurement of adhesion strength was around $\pm$15 kg/cm$^2$ for the same reason as discussed in the first section.

### Adhesion Strength of Electroless Copper/ Photosensitive Epoxy

The average adhesion strength data of electroless copper with various kinds of photosensitive epoxy are shown in Table III. Without microetching, the adhesion strength approached zero for all kinds of epoxy. The adhesion strength for samples made of Taiyo PVI-500 and Utek UPC-9000/H-300 was around 135–160 kg/cm$^2$ when the microetching period was from 5 seconds to 5 minutes. However, if the microetching period was shorter than 1 minute, probably because the surface was not rough enough, it was not easy for the activation agent to be strongly adhered to the surface of epoxy. Therefore, the rinse process after activation must be very gentle; otherwise, part of the activation agent would be carried away by rinse water and it would not be able to be effectively electroless copper plated. Hence, the adhesion strength for samples with a microetching period of less than 1 minute depended on the rinse process, which was very difficult to control.

It was very difficult to electroless copper plate epoxy from Taiyo PSR-4000 if the microetching period was shorter than 10 minutes, and the adhesion strength became lower if the microetching period was from 10 to 20 minutes. No matter how long the microetching period was, it was very difficult for epoxy from Nan-Ya to be electroless copper plated and the subsequent processes were unable to be carried out.

After the solder float test at 260°C for 10 seconds, the adhesion strength of the sample made of Utek was reduced a lot, but samples made of Taiyo PVI-500 remained high. All of these adhe-

**Table III Average Adhesion Strength of Electroless Copper with Photosensitive Epoxy (Before Solder float/After Solder Float, kg/cm$^2$)**

| | Epoxy | | |
|---|---|---|---|
| Microetching Period | PV500 | Utek | PSR-4000 |
| 5 seconds | 103/100 | 119/67 | — |
| 15 seconds | 140/111 | — | — |
| 30 seconds | 149/146 | 172/91 | — |
| 45 seconds | 139/157 | — | — |
| 1 minute | 146/154 | 178/162 | — |
| 5 minutes | 164/140 | 167/19 | x |
| 7 minutes | — | — | x |
| 10 minutes | — | — | 135/159 |
| 15 minutes | — | — | 118/132 |
| 17 minutes | — | — | 79/45 |
| 20 minutes | — | — | 18/3 |

sion strength measurements indicate that Taiyo PVI-500 photosensitive epoxy is most suitable for the application of the fabrication of FRL.

Similar to electroless nickel, the failure interface was photosensitive epoxy/ceramic instead of electroless copper/photosensitive epoxy, indicating that the actual adhesion strength between electroless copper and photosensitive epoxy should be higher than those reported in Table III. For the same reason as discussed in the previous sections, the standard deviation of the adhesion strength data was around $\pm 15$ kg/cm$^2$.

## CONCLUSION

The adhesion strength of photosensitive epoxy with copper substrate was around 35–60 kg/cm$^2$, and the adhesion strength of photosensitive epoxy with FR-4 substrate was around 60–105 kg/cm$^2$. The results of this experiment showed that if one followed the processes of metallization shown in Figure 2 with a 1-minute microetching period, a high adhesion of electroless copper/photosensitive epoxy laminate from Taiyo PVI-500/SA-50 can be obtained. The adhesion strength remained higher than 150 kg/cm$^2$ after solder float at 260°C for 10 seconds.

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