

# Synthesis and Characterization of Water-Soluble Polymeric Adhesion Promoter for Epoxy Resin/Copper Joints

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**ABSTRACT:** Nobel polymeric adhesion promoter soluble in water was synthesized to improve the adhesion strength of copper lead frame/epoxy molding compound (EMC) joints. N-(4-phenolyl)-(benzotriazole-5-carboxylic)amide (PBCA) was synthesized by reacting benzotriazole-5-carboxylic acid (CBTA) with 4-aminophenol. Poly[acrylic-co-4-(5-benzotriazole)amido phenyl acrylate] (PAB) was synthesized by reacting poly acryloyl chloride with PBCA. The adhesion strength of PAB-treated copper lead frame/epoxy resin joints increased with the increase of PBCA content in PAB by forming more Cu–triazole complex. The adhesion strength of PAB-treated copper lead frame/epoxy resin joints having high PBCA content in PAB (more than 0.3 of mole ratio) is comparable to that of polybenzimidazole (PBI)-treated copper lead frame/epoxy resin joints. However, the adhesion strength of PAB-treated copper/epoxy resin joints decreased with the increase of PAB treatment time since Cu–triazole complex particles were formed on PAB-treated copper surface and acted as defects. The initial adhesion strength was maintained by suppressing the formation of Cu–triazole complex particles using PAB having low PBCA contents (0.003 mole ratio of PBCA). The solubility of PAB in water was dependent on the mole ratio of carboxylic acid to PBCA in PAB. The increase of carboxylic acid content in PAB improved the solubility of PAB in water but decreased the adhesion strength with copper. PAB containing 0.03 mole ratio of PBCA was soluble in water. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2202–2210, 2002

**Key words:** adhesion strength; water-soluble polymers; metal–polymer complexes; interfaces; thermosets

## INTRODUCTION

In chip packaging, proper adhesion between epoxy molding compound (EMC) and lead frame is

important for device reliability. But the adhesion strength between EMC and copper lead frame is not good because the mechanical strength of copper oxide layer naturally formed on the copper surface is very weak and the copper oxide degrades the epoxy resin at high temperature.<sup>1–6</sup> Especially, in the chip packaging process, since a copper lead frame is frequently exposed to high temperature through the processes of die attachment, gold wire bonding, and solder reflow, weak

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copper oxide is formed on the surface of copper lead frame. Moreover, it has been reported that the mechanical strength of copper oxide formed at high temperature is weaker than that formed at room temperature.<sup>7</sup>

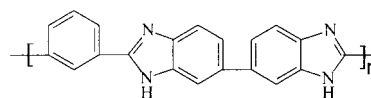
Therefore, adhesion promoters are required to improve the adhesion strength between EMC and copper lead frame. Azole compounds such as benzotriazole can be used as adhesion promoter for improving the adhesion strength of copper/epoxy resin joints since the azole moiety can react with copper to form the Cu-azole complex,<sup>8-11</sup> which acts as a passivation layer for copper. Song et al.<sup>6</sup> reported that polymeric adhesion promoter, polybenzimidazole (PBI), showed better adhesion strength than low molecular weight azole compounds because complete surface coverage of PBI prevented the surface of copper from oxidation and the mechanical strength of PBI was better than low molecular weight azole compounds. But PBI is not environmentally friendly since it is only soluble in amide solvent like dimethyl acetamide. Therefore, new polymeric adhesion promoter soluble in water is necessary.

In this study, water-soluble polymeric adhesion promoter for copper/epoxy resin joints has been synthesized by introducing triazole moiety to polyacryloyl chloride, and the adhesion strength of copper/epoxy resin joints was investigated.

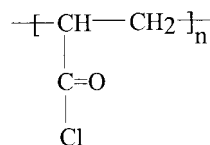
## EXPERIMENTAL

### Materials

Polyacryloyl chloride (Polymer Science, 25 wt % in dioxane), benzotriazole-5-carboxylic acid (Aldrich, 99%), 4-amino phenol (Aldrich, 98+%), dimethyl formamide (DMF, Aldrich, 98%), and triphenyl phosphite (Aldrich, 97%) were used as received. 1-Methyl-2-pyrrolidinone (NMP, Aldrich, 99.8%) was dried with CaH<sub>2</sub> and distilled under vacuum. Pyridine (Aldrich, 99%) was dried with KOH and distilled. For molding of epoxy resin, *o*-cresol novolac epoxy resin (LER N-673, epoxy equivalent weight = 210–230 g/eq; Lucky Epoxy Co., Korea), nadic methyl anhydride (NMA, Aldrich), and benzyl dimethylamine (BDMA, Aldrich) were used as received. Polybenzimidazole (PBI, Aldrich) was used as a polymeric azole compound. Figure 1 shows the chemical structures of PBI and polyacryloyl chloride.



Polybenzimidazole(PBI)



Polyacryloyl chloride

**Figure 1** Chemical structure of PBI and polyacryloyl chloride.

### Analysis of Synthetic Products

Synthesized polymeric azole compounds were analyzed using Bio-Rad FTS 370C FTIR (Fourier transform infrared) spectrometer and FT-300 Bruker ASPECT 3000 (nuclear magnetic resonance) spectrometer. The melting point was measured with Hakke buchler melting point apparatus.

### Treatment of Copper Lead Frame with Azole Compounds

The copper coupons (C19400, Poongsan Co., Korea) were degreased with dichloromethane and rinsed with acetone. Then, the copper coupons were immersed in 5 wt % sulfuric acid solution for 5 min to remove the weak, naturally formed copper oxide and rinsed with distilled water, and then the copper coupons were immersed in the adhesion promoter solutions such as poly(acrylic acid-co-4-(5-benzotriazole)amido phenyl acrylate) (PAB) and PBI. The amounts of 0.1 and 0.5 wt % of PAB solutions were made in DMF, ethanol/water mixture, and water with decreasing the amount of azole moiety in PAB (Table I). Immersion time of copper coupons in PAB solution was varied from 15 s to 10 min at the reaction temperature of 80°C. The treated copper coupons were then taken out, mildly blown with air, and dried at 150°C for 30 min.

In order to study the thermal stability of PAB-treated copper, PAB-treated copper coupons were baked at 200°C in a convection oven for 30 min before molding of epoxy resin, and then the adhe-

**Table I** Three Different PABs Having Different Mole Ratio of PBCA

Product	Mole Ratio of Reactants, PBCA/Acryloyl Chloride	Measured Mole Ratio of PBCA in PAB	Solvent
PAB0.3	0.02/1	0.003/1	Water
PAB1	0.05/1	0.01/1	Water/ethanol = 7/3(v/v)
PAB33	0.30/1	0.33/1	DMF

sion strength of PAB-treated copper/epoxy resin joints was examined depending on the baked time.

#### Preparation of Peel Test Samples of Copper/Epoxy Resin Joints

*O*-cresol novolac epoxy resin (100 parts) and nadic methyl anhydride (80 parts) as a curing agent were mixed in an 100°C oil bath, and benzyl dimethylamine (0.3 part) as a catalyst was added to the epoxy resin mixture. The epoxy resin mixture was poured onto copper coupons treated with adhesion promoter, and then cured at 90°C for 2 h and at 150°C for 4 h to make the copper/epoxy resin joints.

#### Peel Strength Measurements of Copper/Epoxy Resin Joints

After curing copper/epoxy resin joints, the copper coupons were cut with the dimensions of 5 × 70 mm for a 90° peel test. The adhesion strength of copper/epoxy resin joints was measured by a 90° peel test at a peel rate of 5 mm/min using an Instron (Model 4206) and the peeled length was 20 mm. The number of tested specimens was more than 12 for each experimental condition.

#### Wettability Measurements

The wettability of PAB-treated copper was monitored by measuring the equilibrium contact angle of water on PAB-treated copper using a contact angle goniometer (CA-A, Kyowa Surface Science Co., Tokyo, Japan). The contact angle was measured 20 times for each specimen.

#### Surface Defect Test and Morphology of the PAB-Treated Copper

The PAB-treated copper was immersed in 0.001M aqueous silver nitrate solution for 10 min and rinsed with water and acetone.<sup>5</sup> The copper area unreacted with PAB in the surface of PAB-treated copper reacted with silver nitrate to form a silver

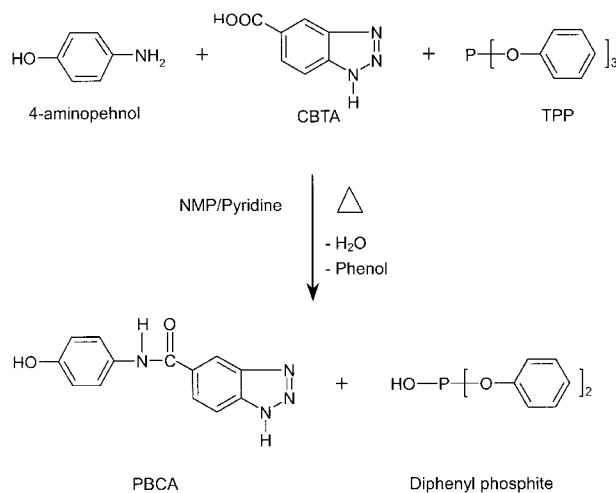
spot, which was observed using optical microscope (Carl Zeiss, German) in the reflection mode. The surface morphology of the PAB-treated copper was also investigated using a scanning electron microscope (Hitachi S-570).

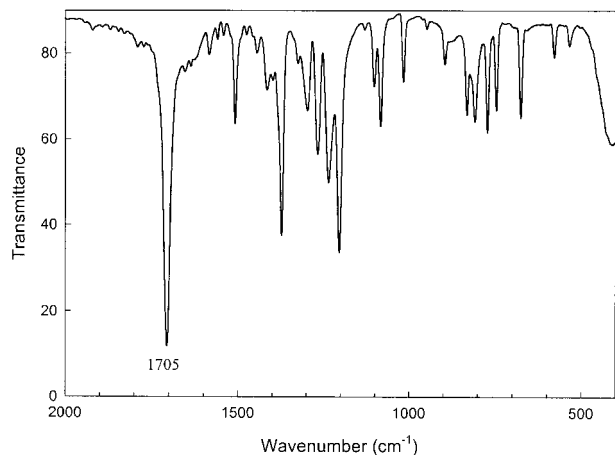
## RESULTS AND DISCUSSION

#### Synthesis of N-(4-phenolyl)-(benzotriazole-5-carboxylic)amide

Hydroxy functionality was introduced to benzotriazole-5-carboxylic acid (CBTA) by reacting CBTA with 4-amino phenol to synthesize the azole compound which can easily react with polyacryloyl chloride. Synthesis of N-(4-phenolyl)-(benzotriazole-5-carboxylic)amide (PBCA) could be accomplished by using triphenyl phosphite (TPP) and pyridine as catalysts, proposed by N. Yamazaki.<sup>13–15</sup> The synthetic scheme of PBCA is shown in Figure 2.

A dry 250 mL four-neck, round-bottom flask was fitted with a reflux condenser, three dropping funnels, magnetic stirrer, and a nitrogen inlet. 4-Aminophenol (4.07 g, 0.037 mol) and NMP (20

**Figure 2** Synthetic scheme of PBCA.



**Figure 3** FTIR spectrum of CBTA.

g) were placed in the reaction vessel and stirred in a 120°C oil bath. TPP (11.62 g, 0.037 mol)/NMP (10 g), CBTA (6.08 g, 0.037 mol)/NMP (33 g), and pyridine (13.42 g, 0.17 mol)/NMP (7 g) were placed in dropping funnels, respectively. Pyridine and TPP were added into the vessel, and then CBTA was added dropwise over a period of 30 min with stirring. The reaction proceeded for 12 h at 120°C and then the reaction mixture was cooled down to room temperature.

The reaction mixture was added dropwise to 350 mL distilled water with stirring and then fine PBCA particles were formed. The solution was filtered with filter paper to get rid of oily and black diphenyl phosphite floating on the surface of the solution. The oily and black diphenyl phosphite was adsorbed on the filter paper and the fine PBCA particles passed the filter paper. And the solution was kept in a refrigerator for 24 h. Pale-brown particles were precipitated in the cold solution and filtered by filter paper. The particles were dissolved in 140 mL ethanol at 60°C and recrystallized by dropping 350 mL of water. The reaction product was filtered and dried in a vacuum oven at 50°C for overnight. It was pale-brown particle and the yield of the product was over 47%.

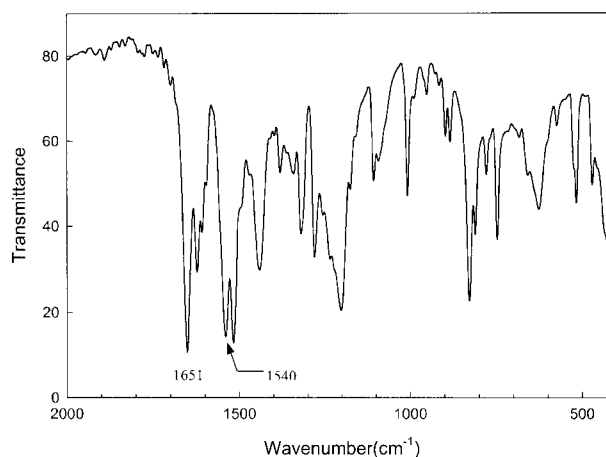
FTIR analysis shows the formation of amide bonds (amide I: 1651  $\text{cm}^{-1}$ , C=O stretching; amide II: 1540  $\text{cm}^{-1}$ , NH bending) in PBCA and the disappearance of carbonyl peak (1705  $\text{cm}^{-1}$ ) in CBTA (Fig. 3 and Fig. 4). Proton NMR analysis was conducted with the solvent of deuterated dimethylsulfoxide (DMSO-d) to confirm the chemical structure of the synthesized PBCA. The detail identification of each proton peaks is shown in

Figure 5. The single melting temperature of PBCA was shown at 294–296°C. As the results of FTIR, NMR, and melting point analysis, it was confirmed that PBCA was synthesized successfully.

### Synthesis of PAB

To synthesize a new polymeric azole compound, PBCA was reacted with polyacryloyl chloride to make polyacrylic acid having azole moiety, PAB. It is well known that acryloyl chloride easily reacts with alcohol at room temperature.<sup>16</sup> The synthetic scheme of PAB is shown in Figure 6.

The reaction procedure to synthesize PAB having 0.3 mol ratio of PBCA to carboxylic acid was as follows: In a glove box, polyacryloyl chloride (9.60 g, acryloyl chloride 0.013 mol equivalents)/NMP (60 g), pyridine (3.16 g, 0.040 mol)/NMP (10 g), and PBCA (2.20 g, 0.0080 mol)/NMP (24 g) were placed in three dropping funnels, respectively. A dry 250 mL four-neck, round-bottom flask was fitted with three dropping funnels and nitrogen inlet with magnetic stirrer. Polyacryloyl chloride was placed in the reaction vessel and then PBCA was added with stirring. Pyridine was added dropwise for 30 min. The reaction proceeded for 2 h at room temperature. Distilled water (1 mL) was added to the reaction mixture to hydrolyze the remaining acryloyl chloride. After 2 h, the reaction mixture was added dropwise to distilled water (440 mL) with stirring and then stored in refrigerator for 12 h. Then, the reaction mixture was filtered and dried in a vacuum oven at 50°C.



**Figure 4** FTIR spectrum of PBCA.

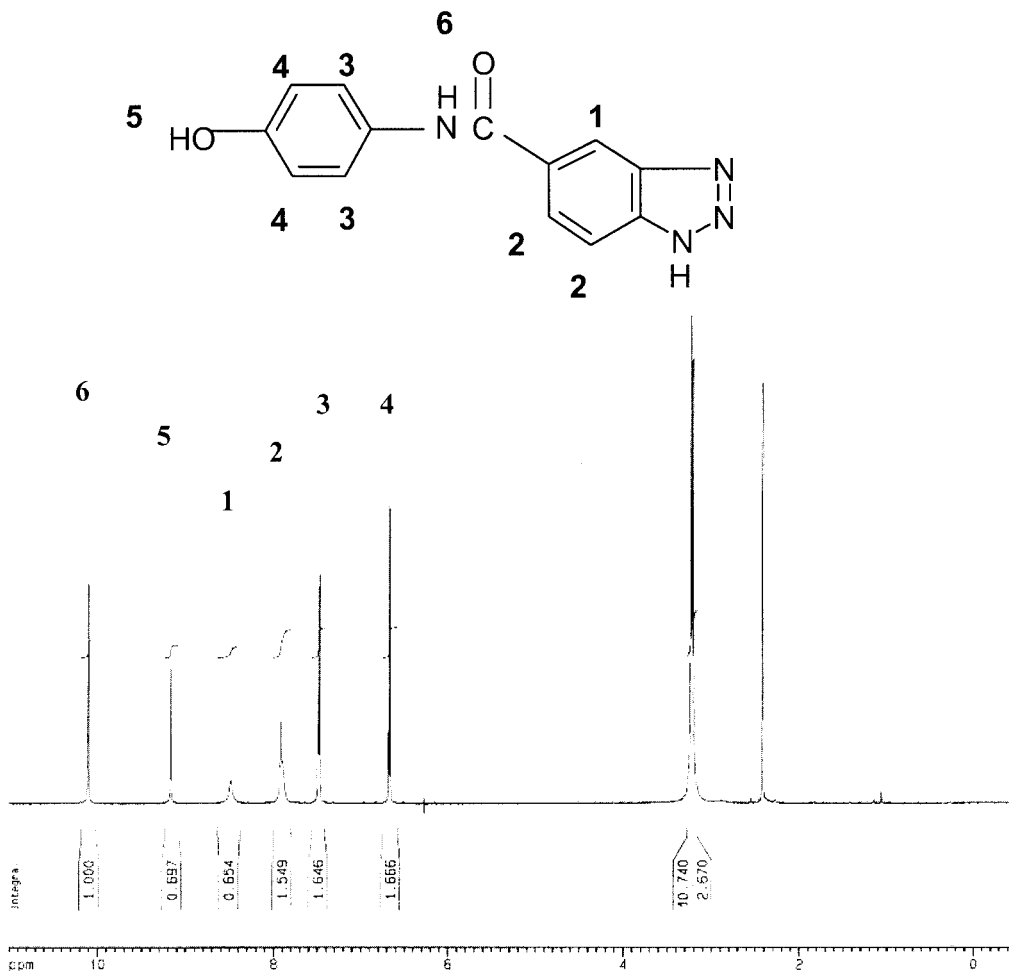


Figure 5 NMR spectrum of PBCA.

The synthesis of PAB was confirmed by FTIR analysis shown in Figure 7. Carbonyl peak of ester ( $1734\text{ cm}^{-1}$ , C=O stretching) was formed by

reacting hydroxyl group in PBCA with acryloyl chloride in polyacryloyl chloride and carbonyl peak ( $1718\text{ cm}^{-1}$ , C=O stretching) of carboxylic

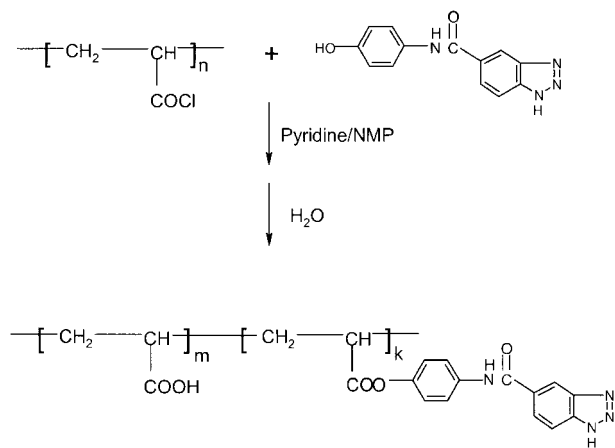


Figure 6 Synthetic scheme of PAB.

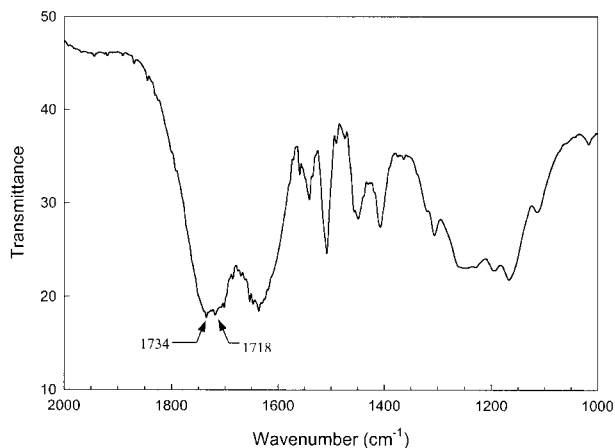
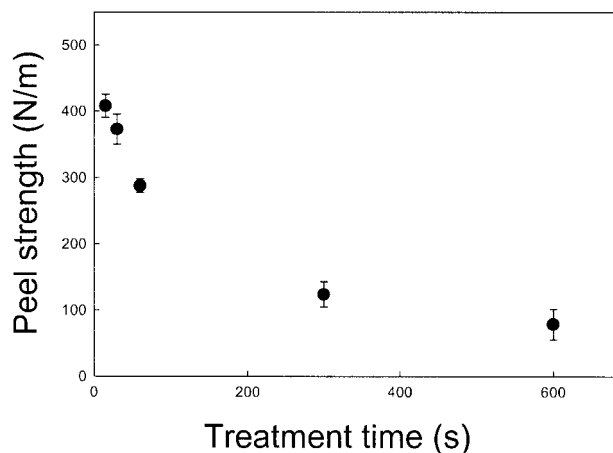


Figure 7 FTIR spectrum of PAB33.



**Figure 8** Peel strength of PAB33-treated Cu/epoxy resin joints depending on the treatment time with 0.1 wt % of PAB33.

acid was formed from the hydrolysis of acryloyl chloride.

The solubility of PAB was dependent on the relative ratio of PBCA and carboxylic acid in PAB. The increase of carboxylic acid content improved the solubility of PAB to water and the increase of PBCA content enhanced the capability of PAB as adhesion promoter by increasing the reaction site in PAB to copper. Therefore, three different PABs were synthesized with the different mole ratio of PBCA to acryloyl chloride as shown in Table I.

There is some difference between the amount of PBCA added as a reactant and that of PBCA introduced to PAB. The amount of PBCA introduced to PAB was measured by proton NMR and calculated from the relative ratio of proton in aromatic ring of PBCA and proton in ethylene of PAB backbone. In the case of PAB33, the content of PBCA in PAB was higher than that of PBCA added as a reactant since PAB having low content of PBCA was soluble in water and lost in the workup procedure. On the other hand, for the case of PAB0.3 and PAB1, the solubility of PAB0.3 and PAB1 in water was so good that water could not be used to precipitate PAB0.3 and PAB1 in the reaction mixture. Therefore, PAB0.3 and PAB1 was extracted from the reaction mixture using ethyl acetate. The amount of ethyl acetate used was 15 times of the NMP used for synthesis of PAB0.3 and PAB1. Ethyl acetate was evaporated in a rotary evaporator and the resulting PAB0.3 and PAB1 were dried in a vacuum oven at 50°C. In the cases of PAB0.3 and PAB1, the content of PBCA in PAB0.3 and PAB1 was

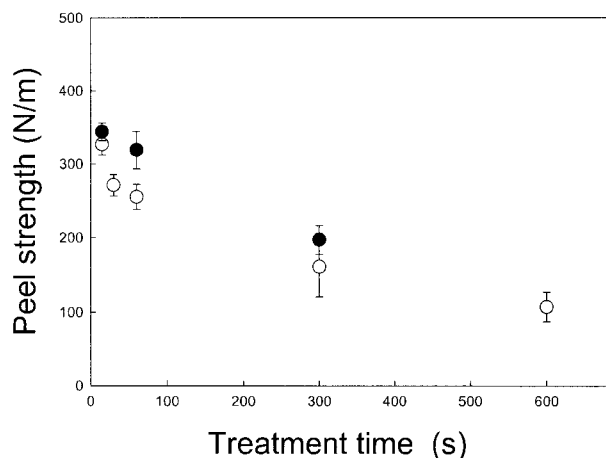
lower than that of PBCA added as a reactant. Since PBCA was more soluble in water than ethyl acetate, PAB having high content of PBCA was soluble in water and lost in the workup procedure.

#### Adhesion Strength Between PAB -Treated Copper and Epoxy Resin

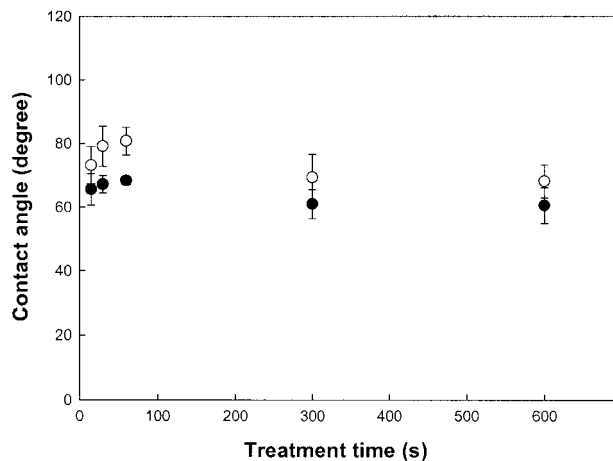
The adhesion strength between PAB-treated copper and epoxy resin is shown in Figure 8 (PAB33) and Figure 9 (PAB1) depending on the PAB treatment time and concentration. The concentration of PAB did not affect the adhesion strength of PAB-treated copper/epoxy resin joints. It appeared that 0.1 wt % of PAB solution was enough to form the Cu-triazole complex on copper surface.

The adhesion strength of PAB-treated copper/epoxy resin joints decreased with the increase of PAB treatment time. This behavior was very similar to those of CBTA and 8-azaadenine -treated copper/epoxy resin joints. Song et al.<sup>6</sup> reported that the decrease of adhesion strength of CBTA and 8-azaadenine -treated copper/epoxy resin joints came from the growth of the thick, porous Cu-azole complex having weak mechanical strength with increasing azole treatment time.

The contact angle of water on CBTA- and 8-azaadenine-treated copper decreased to zero with increasing azole treatment time since water soaked into the thick, porous Cu-azole complex.<sup>6</sup> However, the contact angle of water on PAB33- and PAB1-treated copper did not change with



**Figure 9** Peel strength of PAB1-treated Cu/epoxy resin joints depending the treatment time and the concentration: ●, 0.5 wt % and ○, 0.1 wt %



**Figure 10** The contact angle of water on PAB-treated copper depending on PAB treatment time: ●, PAB1 and ○, PAB33.

PAB treatment time as shown in Figure 10. This represents that the porous Cu–triazole complex was not formed on PAB-treated copper.

To investigate the surface morphology of PAB-treated copper, PAB33-treated copper was examined by SEM. With the short treatment time of PAB, no particle was formed but Cu–triazole complex particles was observed with increasing PAB treatment time as shown in Figure 11. The formation of Cu–triazole complex particles acts as defects and decreases the adhesion strength of PAB-treated copper/epoxy resin joints (Figs. 8 and 9).

The initial adhesion strength of PAB-treated copper/epoxy resin joints increased with increasing PBCA content in PAB (Figs. 8, 9, and 13). It appeared that the increase of the reaction site to form the Cu–triazole complex could increase the initial adhesion strength of PAB-treated copper/epoxy resin joints.

Although the initial adhesion strength of PAB33-treated copper/epoxy resin joints was high enough (400 N/m), the initial adhesion strength of PBI-treated copper/epoxy resin joints was higher (485 N/m) than that of PAB33 and did not decrease with increasing PBI treatment time. S. M. Song et al.<sup>6</sup> reported that complete surface coverage of PBI on copper prevented the oxidation of copper and increased the adhesion strength of PBI-treated copper/epoxy resin joints.

The surface defect test showed that the surface coverage of PAB on copper was improved with the increase of PAB treatment time (Fig. 12). But the surface coverage was not complete. Since PBI has

a higher amount of azole moiety than that of PAB33, the number of reaction sites in PAB33 was less than that of PBI and the surface coverage of PAB33 was consequently not enough.

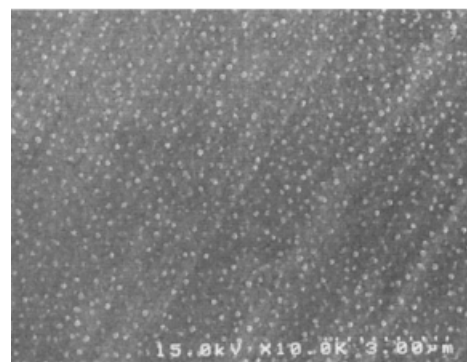
Although the initial adhesion strength of PAB0.3-treated copper/epoxy resin joints was lower than those of PAB33- and PAB1-treated copper/epoxy resin joints, the adhesion strength of PAB0.3-treated copper/epoxy resin joints did not decrease with the increase of PAB treatment time (Fig. 13). The lower initial adhesion strength came from the limited reaction sites between PAB0.3 and copper. However the initial adhesion strength was maintained since the formation of weak Cu–triazole complex particles was suppressed. PAB0.3 was completely soluble in water due to low content of PBCA in PAB0.3.

### Thermal Stability of PAB

Thermal stability of PAB as an adhesion promoter is important since the PAB-treated lead

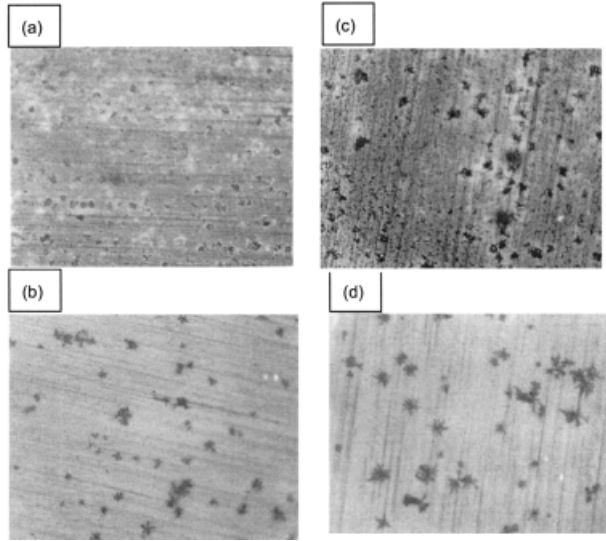


(a) PAB33 15s



(b) PAB33 5min

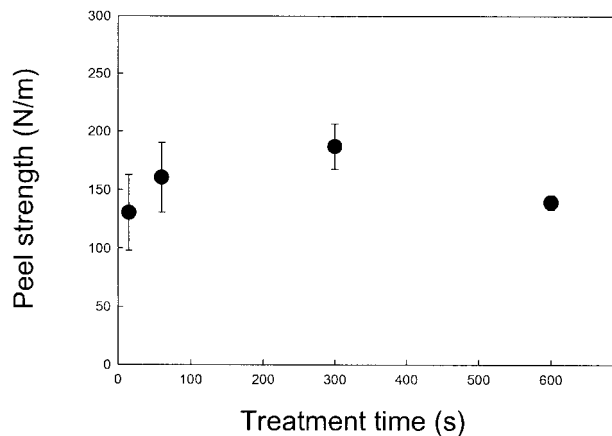
**Figure 11** SEM micrograph of PAB33-treated copper for (a) 15 s and (b) 5 min.



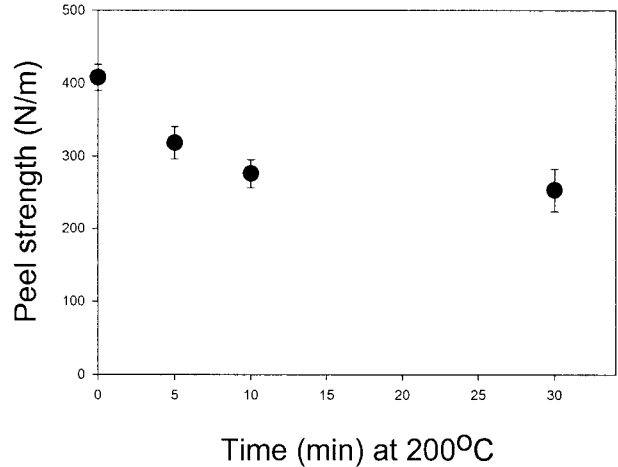
**Figure 12** Optical micrographs of surface defect test of PAB-treated copper depending on the azole treatment time: PAB1 for (a) 15 s and (b) 5 min; PAB33 for (c) 15 s and (d) 5 min.

frame experiences high temperature atmosphere during the packaging processes such as die attachment (above 200°C) and solder reflow (above 225°C).

When the PAB33-treated copper was exposed to 200°C in air atmosphere before molding epoxy resin onto copper coupon, the adhesion strength between PAB33-treated copper and epoxy resin decreased with the increase of exposure time (Fig. 14). But the adhesion strength of 250 N/m was maintained even with 30 min of stored time at 200°C.



**Figure 13** Peel strength of PAB0.3-treated copper/epoxy resin joints depending on PAB 0.3 treatment time.



**Figure 14** Peel strength of PAB33-treated copper/epoxy resin joints depending on the stored time at 200°C.

From the result of peel strength, it is confirmed that PAB can be used to improve the reliability of semiconductor devices by improving the adhesion strength between epoxy molding compound and copper lead frame even after the hostile packaging processes.

**CONCLUSIONS**

PBCA was synthesized and polyacryloyl chloride was modified with PBCA to make the water-soluble polymeric adhesion promoter PAB. The solubility of PAB depended on the relative ratio of carboxyl acid and PBCA in PAB. The solubility of PAB in water improved with the increase of carboxylic acid content in PAB. And the increase of PBCA content in PAB increased the adhesion strength of copper/epoxy resin joint by forming the Cu-triazole complex. When PAB33, PAB1, and PAB0.3 were used as adhesion promoters, the maximum adhesion strength was 408, 327, and 187 N/m, respectively. The adhesion strength of PAB33-treated copper/epoxy resin joints was 8 times that of untreated copper/epoxy resin joints. However, the adhesion strengths of PAB33- and PAB1-treated joints decreased with the increase of PAB treatment time because weak Cu-triazole complex particles were formed on PAB-treated copper surface and acted as defects. Although the adhesion strength of PAB33-treated copper/epoxy resin joints decreased at 200°C, the 250 N/m of adhesion strength was maintained even after storing PAB33-treated copper in air atmosphere



at 200°C for 30 min. In conclusion, the application of PAB to a copper lead frame can improve the adhesion strength of copper lead frame/EMC joints and the reliability of semiconductor devices even in the hostile environment.

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