

# DSC Analysis of Epoxy Molding Compound with Plasma Polymer-Coated Silica Fillers

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**ABSTRACT:** Silica fillers were modified by plasma-polymerization coating of 1,3-diaminopropane, allylamine, pyrrole, 1,2-epoxy-5-hexene, allylmercaptan, and allylalcohol using RF plasma (13.56 MHz). Modified fillers were then mixed with biphenyl epoxy resin, phenol novolac (curing agent), and optionally triphenylphosphine (catalyst) to prepare samples for DSC analyses. Some samples were also prepared from uncoated silica fillers and monomers used in plasma polymerization coating, instead of plasma polymer-coated silica fillers. Plasma polymer-coated silica fillers were characterized by FTIR, XPS, and water contact angle measurements. In DSC analyses, all samples with plasma polymer-coated silica fillers showed a large peak and an

additional one or two small exothermic peaks when catalyst was added, compared to only one large peak with as-received silica fillers. The large peak could be from epoxy-phenol novolac reaction in the presence of catalyst, whereas small reaction peaks were attributed to the chemical reaction between epoxy resin and functional moieties in the plasma polymer coating, such as amine, OH, and/or SH groups, as evidenced by FTIR and XPS analysis and contact angle measurements. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2508–2516, 2003

**Key words:** epoxy molding compounds (EMC); coatings; adhesion; differential scanning calorimetry (DSC); FTIR

## INTRODUCTION

Epoxy molding compounds (EMCs), which are generally prepared from epoxy resins and silica fillers,<sup>1–3</sup> are designed to provide good thermal and mechanical properties, coefficient of thermal expansion (CTE) matched to that of the die-pad, and low water absorption to protect microelectronic devices from harsh environments. Currently, more than 90% of semiconductors use EMCs because of their advantages in performance, cost, weight, size, and availability. However, semiconductor chips with EMC encapsulation are not free from functional failure, which occurs primarily because of delamination in the encapsulation and becomes worse if moisture is present.<sup>4</sup> Delamination can be initiated by a number of factors, one of which is a CTE mismatch between EMC and the die-pad.<sup>5–7</sup> Therefore, considerable research efforts have been devoted to the reduction of CTE mismatch by new resin synthesis,<sup>8–10</sup> high filler loading,<sup>11,12</sup> or surface modification of fillers for enhanced adhesion to the base resin.<sup>13–15</sup>

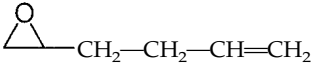

Among these approaches, the surface modification of silica fillers with silane coupling agents has been

extensively investigated because silane coupling agents are known to promote chemical bonds between silica fillers and epoxy resin, thus providing excellent adhesion between them.<sup>16–18</sup> In fact, use of silane coupling agents has been quite successful in enhancing the adhesion of silica fillers to epoxy resin, with the result that three methods have been introduced.<sup>14,15</sup> The best adhesion is rendered by the solution method despite the coagulation problem of silica fillers, which require a powdering process, whereas internal pretreatment and integral addition methods provide inferior adhesion compared to the solution method but without the coagulation problem.

Recently, increasing environmental concerns and a demand for a better surface modification method than use of silane coupling agents have led to studies of plasma polymerization techniques, which are known to be environmentally clean processes. Moreover, these techniques can provide excellent adhesion to various substrates attributed to *in situ* polymerization coating, as well as good solvent resistant coatings because of their crosslinked nature.<sup>19,20</sup> In fact, they have been used for the deposition of thin-film materials in microelectronic industries<sup>21</sup> and adopted in such adhesion fields as carbon fibers,<sup>22–25</sup> tire cords,<sup>26</sup> and corrosion-protective coatings.<sup>27</sup> Recently, the plasma polymerization coating technique was used in our laboratory to modify silica fillers for EMC. The results showed greatly enhanced flexural

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TABLE I  
Characteristics of Monomers for Plasma Polymerization Coating

Monomer	Structure	B.P. (°C)	Purity (%)	Supplier
1,3-Diaminopropane	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	140	99	Aldrich
Allylamine	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{NH}_2$	53	99	Aldrich
1,2-Epoxy-5-hexene		120	97	Aldrich
Pyrrrole		131	98	Aldrich
Allylmercaptan	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{SH}$	68	80	Aldrich
Allylalcohol	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{OH}$	97	99	Kanto Chemical

strength of EMC with 1,3-diaminopropane and allylamine.<sup>28</sup>

The enhanced adhesion was, in general, attributed to functional groups in the plasma polymerization coating, which could promote interactions with functional groups in matrix resins. The interactions could be hydrogen bonding,<sup>23</sup> acid–base interactions,<sup>24</sup> or possibly covalent bonds.<sup>23,25</sup> Our previous study with plasma polymer-coated silica fillers<sup>28</sup> also demonstrated possible chemical reactions between epoxy groups and functional moieties such as amine groups in the plasma polymer coating, which resulted in highly enhanced flexural strength of EMCs. Although enhanced adhesion by plasma polymerization coating is strongly believed to be attributed to chemical bond formation, the adhesion mechanism has not yet been clearly understood.

In this study, therefore, DSC analyses were performed to elucidate the adhesion mechanism between plasma polymer-modified silica fillers and epoxy resin by demonstrating chemical bond formation. Fused silica fillers were coated by plasma polymer coating of 1,3-diaminopropane, allylamine, pyrrole,

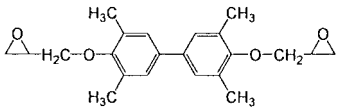
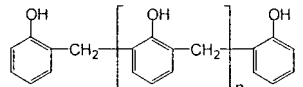
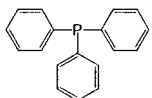
2-epoxy-5-hexene, allylmercaptan, or allylalcohol. The silica fillers were then mixed with biphenyl epoxy and phenol novolac, with triphenylphosphine (TPP) added to only selected samples, to prepare samples for DSC analyses. Samples were also prepared with as-received silica fillers and monomers for plasma polymer coatings. Plasma polymer-coated silica fillers were analyzed by FTIR, XPS, and water contact angle measurements.

## EXPERIMENTAL

### Materials

Monomers such as 1,3-diaminopropane, allylamine, pyrrole, 1,2-epoxy-5-hexene, allylmercaptan, and allylalcohol were used for the plasma polymerization coating of silica fillers. The characteristics of these monomers are summarized in Table I. Biphenyl epoxy resin (YX-4000, Yuka-Shell, Japan) was used as base resin with phenol novolac (HF-1, Kolon Chemical, Korea) and TPP (Hokko Chemical, Japan) used as hardener and catalyst, respectively (Table II). Fused

TABLE II  
Materials for EMC Preparation

Compound	Type	Structure	$T_m^a$ (°C)	EEW <sup>b</sup> (eq/g)	Wt %	Supplier
Epoxy	Biphenyl epoxy		105	185	25.47	Yuka-Shell
Hardener	Phenol novolac		75	105	14.45	Kolon
Catalyst	Triphenyl phosphine		80	—	0.08	Hokko
Silica	Fused, spherical (29 μm)	—	—	—	60	Micron

<sup>a</sup>  $T_m$ , melting temperature.

<sup>b</sup> EEW, epoxy equivalent weight.

spherical silica (S-COL, Micron Co., Japan) with a mean diameter of 29  $\mu\text{m}$  was used as filler.

### Plasma polymerization coating

Silica fillers were subjected to plasma polymerization coating by radio frequency (13.56 MHz) electroless plasma generator (HPPS-300, Hanatek Co., Korea) with a Pyrex tubular-type reactor. The reactor was designed to rotate in the opposite direction to the mixing blade to induce good mixing and thus uniform coating of silica fillers. Plasma polymerization coatings were carried out at optimum conditions reported previously,<sup>28</sup> and characterized by FTIR, XPS, and contact angle measurements.

### DSC analysis

The samples for DSC analyses were prepared from plasma polymer-coated silica fillers, biphenyl epoxy resin, phenol novolac, and optionally TPP (catalyst). The components were mixed at 110°C for a short time and rapidly cooled to room temperature. The mixing time was made as short as possible to minimize the chemical reaction of epoxy resin with functional groups in plasma polymer coatings. The analysis was performed with a DSC-2010 apparatus (TA Instruments, New Castle, DE) at a heating rate of 10°C/min.

### Characterization of plasma polymer coating

#### FTIR analysis

Plasma polymer coatings were characterized by FTIR (Perkin-Elmer IR 2000 Series; Perkin Elmer Cetus Instruments, Norwalk, CT) with KBr powder instead of silica filler. The KBr powder was dried at 100°C for 12 h before plasma polymerization coating. Plasma polymerization coating was carried out at optimized conditions previously reported<sup>28</sup> and 32 scans were recorded at 4  $\text{cm}^{-1}$  FTIR resolution.

#### XPS analysis

Plasma polymer-coated silica fillers were analyzed by XPS (Perkin-Elmer PHI-5400), equipped with a monochromatic Mg-K $\alpha$  X-ray source (1253.6 eV) at 14 kV and 300 W with an emission current of 25 mA and take-off angle of 90° with a hemispherical analyzer. Silicon wafers were used and subjected to XPS analyses at a 15° take-off angle, followed by deconvolution of C1s, N1s, and S2p. Wide scans were first obtained, followed by narrow scans under vacuum conditions of  $5 \times 10^{-7}$  mTorr or lower. C1s electron binding energy was referenced to 285.0 eV and a Gaussian function was used for deconvolution of C1s and N1s peaks with full and half maximum algorithm.

#### Water contact angle measurements

Water contact angles of plasma polymer coatings were evaluated with a glass slide using a goniometer (Kyowa Interface Science, CA-S150). The glass slides were washed with acetone in an ultrasonic bath for 3 min and dried at 100°C under vacuum for 30 min before the plasma polymerization coating. Deionized water was used to form a droplet on the surface of plasma polymer-coated glass slide. Three measurements were made and the results averaged.

## RESULTS AND DISCUSSION

### Characterization of plasma polymer-coated silica fillers

#### FTIR analysis

The plasma polymer coatings of 1,3-diaminopropane, allylamine, and pyrrole exhibited peaks around 1100, 1600, 1660, 2980, and 3340  $\text{cm}^{-1}$ , as shown in Figure 1. These peaks were similar to results previously reported.<sup>29,30</sup> As expected, the peaks around 3340 and 1660  $\text{cm}^{-1}$  were assigned to stretching of primary/secondary amine moieties and bending of primary amine groups and/or stretching of imine groups, respectively. The peaks at 3400, 2980, and 1600/1100  $\text{cm}^{-1}$  were assigned to O—H, CH $_x$ , and C—O groups, respectively, all of which are typical peaks in plasma polymer coatings.<sup>19</sup> As expected, these results clearly showed the presence of amine functional moieties in the plasma polymer coating of monomers containing amine groups, such as 1,3-diaminopropane, allylamine, and pyrrole. This could be valuable information for explaining any possible chemical reaction with epoxy resins.

The plasma polymer coatings of 1,2-epoxy-5-hexene, allylmercaptan, and allyl alcohol showed peaks around 1100, 1600, 2900, and 3400  $\text{cm}^{-1}$ , which can be assigned to C—O, C=C, CH $_x$ , and O—H, respectively.<sup>31,32</sup> As shown in Figure 1, strong O—H and CH $_x$  peaks were observed from the 1,2-epoxy-5-hexene coating, which can be attributed to oxidation and/or plasma polymerization of 1,2-epoxy-5-hexene monomer, but the presence of epoxy groups (1250  $\text{cm}^{-1}$ ) is not clear, whereas allyl alcohol plasma polymer coatings also exhibited strong O—H groups. However, the mercapto (S—H) moiety whose peak was supposed to appear at 2550–2600  $\text{cm}^{-1}$  was not detected from the plasma polymer coating of allylmercaptan, although the presence of sulfonic acid type moieties (SO $_3$ H) could not be ruled out, given that S—H moieties may have undergone oxidation during the plasma polymerization process.

#### XPS analysis

All plasma polymer-coated silica fillers exhibited very similar wide scans in XPS analysis, showing C1s, O1s,

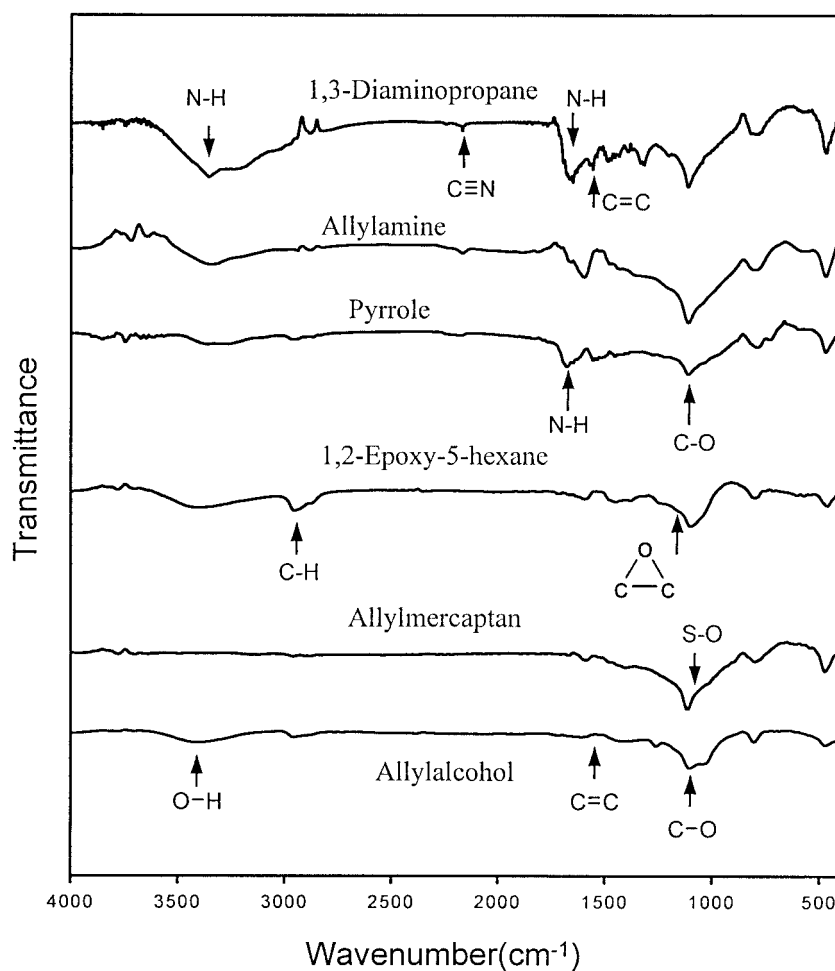


Figure 1 FTIR of plasma polymer coatings.

Si2p, N1s, and/or S2p. However, as expected, the N1s peak was observed only from 1,3-diaminopropane-, allylamine-, and pyrrole-coated silica, whereas the S2p peak was detected from allylmercaptan-coated silica. In narrow scans, the atomic concentrations of C1s, O1s, and Si2p were around 20, 55, and 25%, respec-

tively, whereas those of N1s and S2p were in the order of 1%, as summarized in Table III. Relatively high Si concentration and very low N1s and S2p concentration can be attributed to the very thin plasma polymer coating. In fact, these results correlated well with the coating thickness of 60–80 nm, as reported previ-

TABLE III  
Atomic Concentration of Elements from XPS Analysis with Silica

Plasma polymer	C1s	O1s	N1s	Si2p	S2p
1,3-Diaminopropane	23.6 285.0	49.4 532.8	1.4 400.1	25.6 103.4	—
Allylamine	20.3 285.0	51.3 532.8	1.5 399.9	26.9 103.4	—
Pyrrole	18.9 285.0	53.6 532.9	1.2 400.2	26.8 103.5	—
1,2-Epoxy-5-hexene	17.3 285.0	55.4 533.0	—	27.2 103.6	—
Allylmercaptan	16.5 285.0	55.1 533.0	—	27.4 103.6	1.0 164.1
Allyl alcohol	18.3 285.0	54.6 532.8	—	26.7 103.4	—
As-received	34.5 285.0	44.7 533.7	—	20.8 104.3	—

**TABLE IV**  
Atomic Concentration of Elements from XPS Analysis with Si Wafer

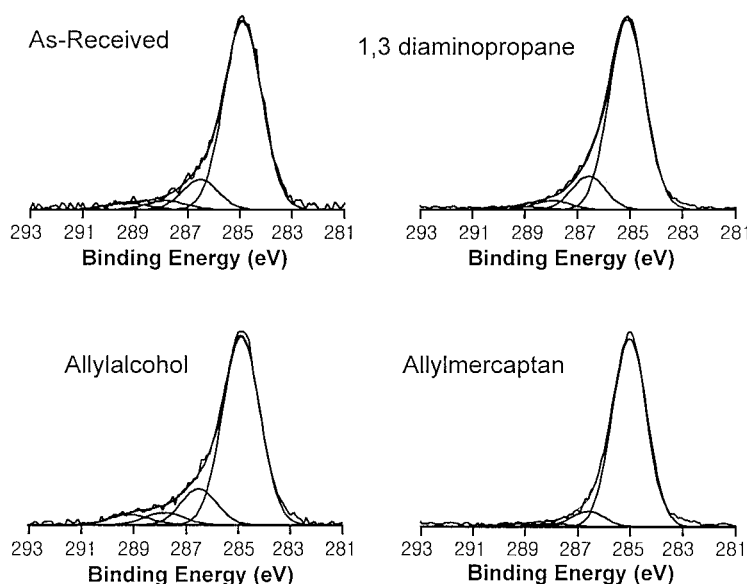
Plasma polymer coating	C1s	O1s	N1s	Si2p	S2p
1,3-Diaminopropane	60.59	18.86 532.5	5.89 399.6	14.66 102.4	—
Allylamine	60.81 285.0	19.19 532.3	5.75 399.4	14.24 102.0	—
Pyrrole	59.5 285.0	20.17 532.6	5.69 400.3	14.64 102.4	—
1,2-Epoxy-5-hexene	67.88 285.0	18.82 532.6	—	13.30 102.4	—
Allylmercaptan	62.69 285.0	18.10 532.4	—	14.99 102.4	4.22 163.9
Allylalcohol	69.78 285.0	23.23 532.6	—	7.00 102.2	—
As-received	21.61 285.0	47.0 532.7	—	30.61 103.2, 99.2	—

ously.<sup>28</sup> Compared to the plasma polymer-coated silica fillers, as-received silica fillers also exhibited high C1s concentration, indicating contamination from handling and possibly from the carbon tape used for holding silica fillers on the sample stage.

Because of unusually low N1s and S2p concentrations with silica fillers, deconvolution of these peaks was attempted with plasma polymer-coated Si wafers and analyzed at 15° take-off angle. As expected, much higher N1s (5%) and S2p (5%) concentrations were observed with Si wafer, as shown in Table IV. This difference could be attributed to the 15° take-off angle, which was much lower than the 90° used for silica fillers. As expected, the as-received Si wafer also showed high carbon concentration (22%), possibly because of contamination. In the curve fitting of C1s peaks, the deconvolution of C—O and C—N was not

attempted because they had small binding energy differences. Thus, all C1s peaks were deconvoluted into C—C (285 eV), C—O/C—N (286.5 eV), C=O (288 eV), and O—C=O (289 eV), as shown in Figure 2. All samples with plasma polymer-coated Si wafers exhibited similar concentrations, except allyl alcohol plasma-coated Si wafer, which showed a slightly higher C—O, C=O, and O—C=O concentration, as summarized in Table V.

In the curve fitting of the N1s peak from 1,3-diaminopropane plasma polymer coating, the peak was deconvoluted to three peaks at 398.7, 399.6, and 400.8 eV (Fig. 3), which can be assigned to NH<sub>2</sub>, NH, and NH<sub>3</sub><sup>+</sup>. The intensity of these peaks was approximately 38, 46, and 16%, indicating high NH<sub>2</sub> moiety, although the accuracy of atomic concentration is debatable. Deconvolution of the N1s peak from allylamine and pyrrole



**Figure 2** Deconvoluted C1s peaks from plasma polymer coatings with silica fillers.

TABLE V  
Atomic Concentration of Deconvoluted C1s Peaks of Si Wafer

Plasma polymer	C—C 285 eV	C—O/C—N 286.5 eV	C=O 288 eV	O—C=O 289 eV
1,3-Diaminopropane	81.57	13.26	3.69	1.48
Allylamine	80.76	13.67	4.34	1.62
Pyrrole	79.89	12.92	5.51	1.68
1,2-Epoxy-5-hexene	85.31	10.25	3.45	0.99
Allylmercaptan	89.70	7.17	1.62	1.51
Allyl alcohol	71.25	19.2	6.28	3.27
As-received	81.04	12.09	3.84	3.03

plasma polymer coatings exhibited similar behavior, but slightly lower  $\text{NH}_2$  concentration. On the other hand, the S2p peak from allylmercaptan plasma polymer coating was composed of two peaks, 2p<sub>3/2</sub> (163.8 eV) and 2p<sub>1/2</sub> (165.2 eV), indicating the presence of only S—H-type moieties, which was somewhat different from the FTIR data. The difference can be explained by very shallow XPS sampling depth compared to FTIR, which suggests the presence of the S—H moiety on the surface layer only.

#### Water contact angle

The plasma polymer coating of 1,2-epoxy-5-hexene provided the lowest water contact angle (2°) followed by 1,3-diaminopropane (7°), allylamine (8°), allyl alcohol (12°), pyrrole (58°), and allylmercaptan (72°) compared to 34° with a glass slide. As expected, the plasma polymer coatings of 1,3-diaminopropane (7°) and allylamine (8°) provided very low water contact angles, possibly because of the amine functional moieties, as evidenced by XPS and FTIR analysis. The unusually low water contact angle from 1,2-epoxy-5-hexene (2°) plasma polymer coatings can be explained by O—H groups and possibly by epoxy moieties, whereas the low contact angle with allyl alcohol (12°) can be attributed to O—H functional groups. Consequently, relatively high water contact angles with pyrrole and allylmercaptan coatings are likely attributable to low amine and OH concentration, respectively,

as evidenced in FTIR. Therefore, it can be said that some functional groups such as amine moieties can lower the water contact angle, while enhancing the flexural strength of EMC samples by forming covalent bonds with epoxy resins. However, others like the O—H moiety can lower the water contact angle only because they are much less reactive than amine groups to epoxy resins.

#### DSC analysis

##### Samples without catalyst

The first group of samples for DSC analyses was prepared from epoxy resin, phenol novolac, and plasma polymer-coated silica fillers, but no TPP (catalyst), to detect reactions other than the epoxy-phenol novolac reaction [e.g., the epoxy-amine, epoxy-mercapto, or epoxy-OH (—COOH) reaction]. As shown in Figure 4, the samples from 1,3-diaminopropane-coated silica fillers exhibited two distinct reaction peaks at around 190 and 260°C, whereas the samples from allylamine-coated fillers showed one clear (at 200°C) and one vague (at 270°C) peak. In comparison, only one peak was detected with pyrrole plasma polymer coating (at 260°C). The exothermic reaction peaks can be correlated to the number and/or type of amine groups in the plasma polymer coating and thus to the monomer structure. As noted, 1,3-diaminopropane and allylamine have two or one primary amine groups, re-

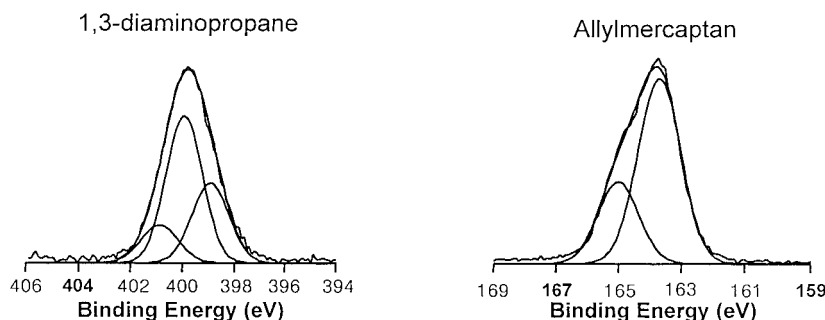
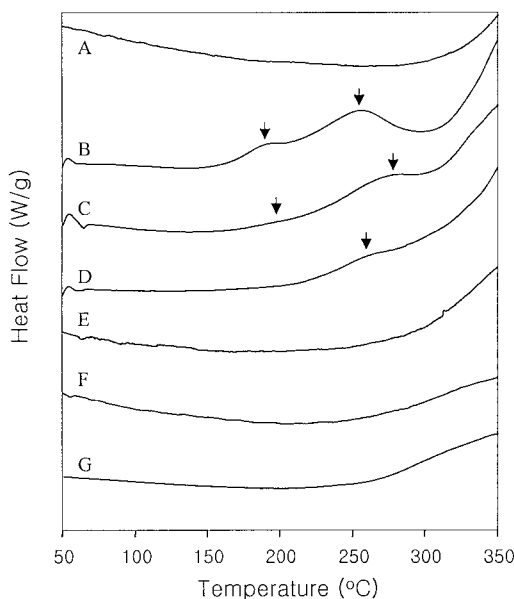


Figure 3 Deconvoluted N1s and S2p peak from plasma polymer coatings of 1,3-diaminopropane and allylmercaptan, respectively.



**Figure 4** DSC thermograms of plasma polymer-coated silica fillers with no catalyst: (A) as-received silica, (B) 1,3-diaminopropane, (C) allylamine, (D) pyrrole, (E) 1,2-epoxy-5-hexene, (F) allylmercaptan, (G) allylalcohol.

spectively, whereas pyrrole has one secondary amine group. Therefore, it is highly likely that the exothermic peak at around 200°C resulted from the primary amine-epoxy reaction, whereas one at around 270°C is from the secondary amine-epoxy reaction. FTIR and XPS results support such conclusions, by indicating the presence of amine functional groups in the plasma polymer coatings of 1,3-diaminopropane, allylamine, and pyrrole.

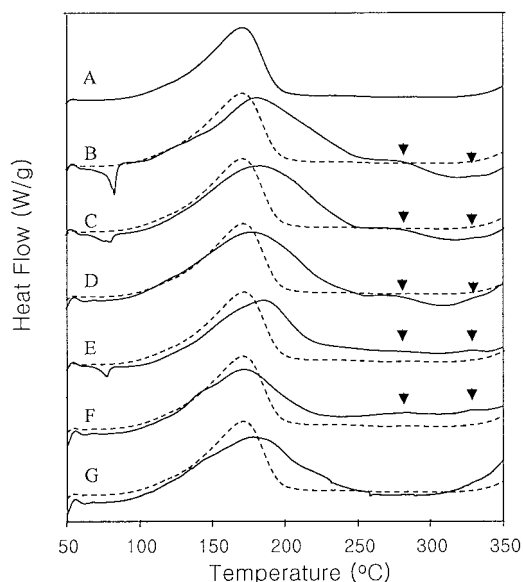
Compared to these samples, those from 1,2-epoxy-5-hexene, allylalcohol, and allylmercaptan plasma polymer-coated silica fillers as well as from as-received silica fillers did not show any exothermic reaction peaks because of their very low reactivity of OH and SH moieties in the absence of TPP. However, these samples exhibited increased heat flow in the 300–350°C range, which can be attributed to the chemical reaction of OH and SH moieties with epoxy resin because high temperature increased the reactivity of these moieties. Moreover, if such heat flow increases because of the chemical reaction, a small hump around 330°C in samples with allylalcohol and allylmercaptan plasma polymer-coated silica fillers can be said to be an exothermic reaction peak, as a result of epoxy-OH or epoxy-SH reaction in the absence of TPP. These results clearly demonstrate the occurrence of exothermic chemical reactions, indicating the presence of reactive functional moieties in the plasma polymer coatings.

#### Samples with catalyst

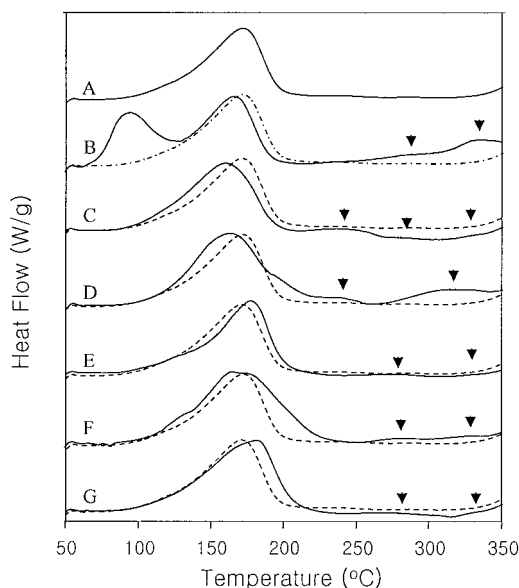
To determine the effect of catalyst, samples for DSC analysis were also prepared from TPP (catalyst), ep-

oxy resin, phenol novolac, and plasma polymer-coated silica fillers. As shown in Figure 5, the samples with as-received silica fillers showed a single large peak around 170°C, which is attributed to the epoxy-phenol novolac reaction in the presence of TPP. The samples with plasma polymer-coated silica fillers also showed a large peak around 180°C and additional small reaction peaks around 280 and 330°C in most samples. However, compared to the as-received silica filler samples, the large peak at 180°C was very broad (80–250°C) in 1,3-diaminopropane, allylamine, pyrrole, and allylalcohol plasma polymer-coated fillers, followed by a somewhat less broad peak for samples (80–220°C) with 1,2-epoxy-5-hexene and allylmercaptan plasma polymer-coated fillers.

The broadness of the peak width can be explained by the combined effect of at least two different exothermic reactions, one from the epoxy-phenol novolac reaction in the presence of catalyst and the other from epoxy-functional moieties in the plasma polymer coating of NH<sub>2</sub>, OH, and/or SH in the presence of catalyst. Therefore, the broad peak found in 1,3-diaminopropane, allylamine, and pyrrole samples can be attributed to the extra reaction from NH<sub>2</sub>, which was absent in 1,2-epoxy-5-hexene and allylmercaptan plasma polymer-coated fillers, both of which exhibited slightly narrower peaks. The small extra reaction peaks at 280 and 330°C can also be attributed to extra chemical reactions such as epoxy-amine, -OH, and/or -SH reactions resulting from functional groups introduced by plasma polymerization coating. Therefore, it can be said that the presence of TPP (catalyst) promoted the epoxy-phenol reaction, resulting in a large



**Figure 5** DSC thermograms of plasma polymer-coated silica fillers with catalyst: (A) as-received silica, (B) 1,3-diaminopropane, (C) allylamine, (D) pyrrole, (E) 1,2-epoxy-5-hexene, (F) allylmercaptan, (G) allylalcohol.



**Figure 6** DSC thermograms of as-received silica fillers and a monomer for plasma polymer coating: (A) as-received silica, (B) 1,3-diaminopropane, (C) allylamine, (D) pyrrole, (E) 1,2-epoxy-5-hexene, (F) allylmercaptan, (G) allylalcohol.

peak at 180°C, and also chemical reactions between epoxy resin and the functional groups in the plasma polymer coating, which led to the small peaks.

#### Samples with as-received silica filler and monomer

DSC analyses were also performed with samples from monomers, as-received silica fillers, biphenyl epoxy resin, phenol novolac, and TPP. A monomer was simply added to the sample instead of being used to coat the silica filler to demonstrate the chemical reaction between epoxy resin and the monomer. As shown in Figure 6, DSC thermograms from these samples were similar to those from plasma polymer-coated silica fillers with catalyst (Fig. 5), showing a large peak around 170°C and small peaks in the 230–330°C range. However, the large peaks at 170°C were much narrower than those found in plasma polymer-coated silica fillers. It is also noted that a single large extra peak at 100°C was found only with 1,3-diaminopropane monomer, which can be attributed to the epoxy-amine reaction, possibly from the primary amine.

Comparing the peaks at 170°C in Figure 6, it is noted that the samples prepared from 1,3-diaminopropane, allylamine, and pyrrole monomers exhibited peak widening in the temperature range below 180°C, whereas the others from 1,2-epoxy-5-hexene, allylalcohol, and allylmercaptan monomers showed peak widening in the temperature range above 180°C, in contrast to the peaks from the as-received silica fillers. Therefore, peak widening below 180°C is attributed to the amine-epoxy reaction, whereas that above 180°C is attributed to the epoxy-OH (or -COOH) reaction

and possibly the epoxy-SH reaction depending on the monomers used.

Two or three peaks (230, 280, and 330°C) were found in the 230–330°C range, depending on the monomers used, whereas the as-received silica fillers showed no such peaks. Therefore, it can be concluded that those peaks are from epoxy-amine, -OH, and/or -SH reactions. In addition, these peaks appeared at certain temperatures such as 230, 280, and 330°C (shown in Figs. 4 and 5), but as shown in Figure 6, peaks appeared as a combination of those in Figures 4 and 5. Therefore, it can be said that the functional moieties in the monomers added led to much higher reactivity compared to the plasma polymer coatings, thereby generating exothermic chemical reactions in different temperature ranges. It can also be said that DSC analyses of samples with monomers and as-received silica fillers clearly demonstrated a chemical reaction between the monomer added and the epoxy resin in the presence of catalyst, which is another strong evidence of chemical reaction between epoxy resin and functional moieties in the plasma polymer coating of those monomers.

## CONCLUSIONS

Silica fillers, a major component of EMC, were subjected to plasma polymerization coating with 1,3-diaminopropane, allylamine, 1,2-epoxy-5-hexene, pyrrole, allylmercaptan, and allylalcohol. These samples were analyzed by DSC to elucidate the adhesion mechanism. Major findings are summarized below:

1. FTIR analysis revealed the presence of amine functional groups (primary and secondary amines) in 1,3-diaminopropane, allylamine, and pyrrole plasma coatings, and strong O—H moieties in allylalcohol plasma coating, although the presence of epoxy and S—H moieties in 1,2-epoxy-5-hexene and allylmercaptan plasma coatings were not clear.
2. Deconvolution of C1s and N1s peaks in the XPS analysis of plasma polymer-coated Si wafer revealed the presence of NH<sub>2</sub>, OH, COOH, and/or SH functional moieties, depending on the monomer used for plasma polymerization.
3. Plasma polymer coating of 1,2-epoxy-5-hexene, 1,3-diaminopropane, allylamine, allylalcohol, pyrrole, and allylmercaptan provided water contact angles of 2, 7, 8, 12, 58, and 72°, respectively, indicating that some polar groups introduced by plasma polymer coatings are responsible for low water contact angles.
4. DSC analysis of the samples prepared from plasma polymer-coated silica, epoxy resin, and catalyst showed heat of reaction peaks with 1,3-diaminopropane, allylamine, and pyrrole coat-



ings, compared to no reaction peak obtained from 1,2-epoxy-5-hexene, allyl alcohol, and allylmercaptan coatings, as well as from as-received silica fillers, demonstrating chemical reaction between epoxy resin and amine functional moieties in the plasma polymer coating in the absence of catalyst.

5. In the presence of the catalyst triphenylphosphine, as-received silica samples exhibited a single large peak around 180°C, whereas all other samples with plasma polymer-coated silica showed a much broader large peak at 180°C with additional smaller peaks at 280 and 330°C, again indicating extra chemical reactions from functional moieties in the plasma polymer coating.
6. When monomers were added, instead of being used to coat silica fillers, the samples exhibited a behavior very similar to that of samples from plasma polymer-coated silica fillers with catalyst, showing a large peak around 180°C and additional smaller peaks in the 230–330°C range, with the exception of a large peak at 100°C with 1,3-diaminopropane samples.

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