

# 플라즈마 코팅된 실리카와 에폭시 수지간의 반응성 연구

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## Study of Heat of Reaction Between Plasma Polymer Coated Silica Fillers and Biphenyl Epoxy Resin

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### Abstract

Silica fillers were coated by plasma polymer coatings of 1,3-diaminopropane, allylamine, pyrrole, 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol using RF plasma (13.56 MHz). The coated fillers were then mixed with biphenyl epoxy, phenol novolac (curing agent) and/or triphenylphosphine (catalyst), and subjected to DSC analyses in order to elucidate the chemical reaction between functional moieties in the plasma polymer coatings and the epoxy resin. Only the samples with 1,3-diaminopropane and allylamine plasma polymer coated silica fillers showed heat of reaction peaks when they were mixed with biphenyl epoxy resin only, while these samples as well as the samples with 1,3-diaminopropane, allylamine and pyrrole plasma polymer coated silica fillers exhibited heat of reaction peaks when mixed with both biphenyl epoxy and phenol novolac (curing agent).

**Key Words:** silica filler, plasma polymer coating.

### 1. INTRODUCTION

Epoxy Molding Compounds (EMCs) have found wide usage as encapsulants for semiconductor devices. Their cost, size, weight, performance, availability and reliability makes these materials quite suitable in protecting semiconductor devices from harsh environments such as moisture, dust, vibration and mechanical/thermal shock [1-3]. However, an EMC failure occurs at times mainly due to the coefficient of thermal expansion (CTE) mismatch between the EMC and the chip or leadframe [4]. This has led to a number of studies to reduce the CTE of EMC, which can be achieved by increasing the inorganic filler

content such as silica [5-6]. As the loading of silica fillers increases, however, the adhesion between the silica filler and the epoxy resin becomes a critical factor in determining EMC performance.

Therefore, in order to enhance the adhesion of inorganic fillers to epoxy resin, surface modification with silane coupling agents has been extensively utilized, as they are believed to generate covalent bonds between silica filler and epoxy resin [7-8].

However, in view of the drawbacks of silane coupling agents, plasma polymerization was introduced to modify silica fillers for EMCs in our laboratory [9-10] since it is known to provide functional moieties on the filler surface for the formation of chemical bonds and thus

good adhesion, as well as it is a dry and environmentally clean process [11-13].

In this study, it was attempted to investigate the chemical reaction between plasma polymer coated silica fillers and epoxy resin by DSC. The samples were prepared from plasma polymer coated silica fillers, epoxy resin, phenol novolac (hardener) and/or triphenylphosphine (catalyst). All samples were analyzed by DSC and plasma polymer coatings were also analyzed by FT-IR.

## 2. EXPERIMENTAL

### 2.1. Materials

Biphenyl epoxy resin (YX-4000, Yuka-Shell Co., Japan), phenol novolac (HF-1, Kolon Chemical, Korea) and triphenylphosphine (TPP) (Hokko Chemical, Japan) were utilized as base resin, hardener and catalyst, respectively. Fused spherical silica (S-COL, Micron Co., Japan) with a mean diameter of 29  $\mu\text{m}$  was used as the inorganic filler. 1,3-Diaminopropane, allylamine, pyrrole, 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol were used as monomers for plasma polymer coatings of silica fillers, as previously reported [9].

### 2.2. Plasma polymer coatings

Plasma polymerization on silica fillers was carried out in an RF (13.56 MHz) electrodeless plasma generator (HPPS-300, Hanatek Co., Korea) with a tubular type reactor [9]. During plasma polymerization, the Pyrex reactor was designed to rotate in direction opposite to the mixing blade in the reactor so as to provide good mixing. Silicon wafers were also coated with plasma polymers and analyzed by FT-IR (IR 2000, Perkin Elmer) and 32 scans were recorded at a resolution of 4  $\text{cm}^{-1}$ .

### 2.3. Sample preparation

Plasma polymerization was carried out at

optimum conditions with 1,3-diaminopropane, allylamine, pyrrole, 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol, as reported previously [9]. The samples for DSC analyses were prepared and mixed at 130°C for 3-5 min and then rapidly cooled to RT, followed by differential scanning calorimetry (DSC, TA-2010) analyses at 10°C/min. For comparison, the samples for DSC analyses were also prepared with as-received silica fillers.

## 3. RESULTS AND DISCUSSION

### 3.1. Samples with plasma polymer coated silica and biphenyl epoxy

In the DSC analyses, the samples from Group 1P (biphenyl epoxy + plasma polymer coated silica) exhibited one large heat of reaction peak with 1,3-diaminopropane and only a weak one with allylamine coated silica fillers, compared to no peak with pyrrole, 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol coated silica fillers, besides an endothermic peak at around 100°C due to melting of epoxy resin. The samples with 1,3-diaminopropane and allylamine coated silica fillers exhibited exothermic peaks around 270°C and 290°C, respectively, but these temperatures are rather high to be attributed to the chemical reaction between epoxide groups and amine moieties in the plasma polymer coatings.

However, these rather high heat of reaction temperatures can be explained by two hypotheses; 1) due to the low reactivity of amine-like moieties which were changed from amine groups by plasma energy, and 2) due to reactions between epoxy resin and OH moiety in the plasma polymer coating, which was catalyzed by amine moiety [14] since these samples are composed of only biphenyl epoxy and plasma polymer coated silica fillers containing OH and amine moieties. As noted, the peak obtained with 1,3-diaminopropane

coated silica fillers was much bigger than the one with allylamine, which can be attributed to higher reactivity of amine groups in 1,3-diaminopropane compared to those in allylamine. On the other hand, the samples with pyrrole plasma polymer coated silica fillers did not show any heat of reaction peaks, despite possible amine functional groups as evidenced in FT-IR analysis, which can be explained by very low reactivity of amine moieties in the pyrrole plasma polymer coatings due to the aromatic resonance effect. The same hypothesis can be used to explain the absence of heat of reaction peaks from the samples with 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol plasma polymer coated silica fillers.

### 3.2. Samples with plasma polymer coated silica, biphenyl epoxy and phenol novolac

Group 2P samples, containing biphenyl epoxy and phenol novolac, showed two, one or no heat of reaction peaks. The samples with 1,3-diaminopropane and allylamine coated silica fillers exhibited two peaks at around 200 and 260°C, and at 200 and 270°C, respectively, while those with pyrrole coated silica fillers showed only one peak at 260°C. However, the samples with 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol coated silica fillers showed no peaks. As noted, the heat of reaction peaks appeared at around 200 and 260-270°C, indicating two types of chemical reactions, and the peaks at 260-270°C are similar to those observed from the Group 1P samples with 1,3-diaminopropane and allylamine coated silica fillers, despite that those from Group 2P were much bigger. Thus, the peaks at 260-270°C from Group 2P with 1,3-diaminopropane and allylamine coated silica filler can be said to result from epoxy-amine reaction as well as epoxy-phenol novolac reaction, possibly catalyzed by amine moieties [14].

On the other hand, the peaks at around 200°C with 1,3-diaminopropane and allylamine coated silica fillers, which were not observed from Group 1P samples, can be explained by the amine catalyzed epoxy-phenol novolac reaction since these samples contained biphenyl epoxy and phenol novolac. On the contrary, the samples with pyrrole plasma coated silica fillers exhibited a peak at around 260°C, but not at 200°C. This can be attributed to the low catalytic effect of amine moiety in pyrrole plasma polymer coating, which was not able to catalyze epoxy-phenol novolac reaction at 200°C, but possible at 260°C. If this is true, the absence of peaks from 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol coated silica fillers can be clearly explained by the absence of amine groups, or the lack of catalytic effect of functional groups in the plasma polymer coatings. However, increased heat flow was observed from all samples at above 300°C, which can be attributed to the heat catalyzed epoxy-phenol novolac reaction and possibly degradation of biphenyl epoxy resin.

### 3.3. Samples with plasma polymer coated silica, biphenyl epoxy, phenol novolac and triphenylphosphine

The samples containing phenol novolac (curing agent) and triphenylphosphine(catalyst) (Group 3P) showed a large peak at around 170°C along with small peaks in the 250-330°C range and at around 80°C. This is comparable to the single peak at around 170°C observed from the control samples with as-received silica fillers, which is mainly due to the epoxy-phenol novolac reaction resulting from the presence of triphenylphosphine. It was noted that the peaks observed from plasma polymer coated silica fillers were much broader than the peak from as-received silica filler samples, indicating additional chemical reaction besides the epoxy-phenol novolac reaction, such as the reaction between epoxy and functional moieties

introduced by plasma polymerization, which were catalyzed by the added triphenylphosphine.

Among the samples, 1,3-diaminopropane sample provided the broadest peak, followed by those with allylamine, pyrrole, 1,2-epoxy-5-hexene, allyl mercaptan and allyl alcohol coated silica fillers, indicating that extra chemical reactions occurred with 1,3-diaminopropane coating than with others. This behavior can be correlated to much bigger heat of reaction peak obtained with 1,3-diaminopropane than that with Group 2P samples. The small peaks in the 250-330°C range can be attributed to the epoxy-phenol(secondary) reaction as well as to the reaction between epoxy and functional groups in the plasma polymer coatings, which were catalyzed by the added triphenylphosphine, while those at 80°C were attributed to melting of phenol novolac.

#### 4. CONCLUSIONS

1. The samples with biphenylepoxy + plasma polymer coated silica fillers showed heat of reaction peaks, demonstrating amine-epoxy and/or amine catalyzed epoxy-phenol reactions.
2. Additional chemical reactions due to the functional groups in plasma polymer coatings were also confirmed from the broadening of heat of reaction peaks in the samples with biphenyl epoxy, phenol novolac and triphenylphosphine (catalyst).

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