

# High-Performance Printed Circuit Board Materials Based on Benzoxazine and Epoxy Blend System

Seon Ho Lee<sup>1</sup>  
Ki Seok Kim<sup>2</sup>  
Ji Hye Shim<sup>2</sup>  
Cheol-Hee Ahn<sup>\*1</sup>

<sup>1</sup> Research Institute of Advanced Materials (RIAM), Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea  
<sup>2</sup> ACI Process & Structure Group, Samsung Electro-Mechanics Co., Ltd, 150, Maeyoungro, Youngtong-gu, Suwon, Gyeonggi 16674, Korea

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**Abstract:** Epoxy resin has been used as an industrial printed circuit board (PCB) material based on its excellent mechanical strength and adhesion property to metal. Silica nanoparticle is employed as a component of hybrid matrix material with epoxy resin due to its superior electrical insulating properties. In this study, benzoxazine, which has attracted attention as a new generation of electrically insulating material and displays extraordinary thermal stability, was investigated as a candidate for PCB material. Benzoxazine and epoxy/silica nanoparticle hybrid films were prepared to achieve low dissipation factor and improved mechanical stability. Two types of benzoxazines, monobenzoxazine, and linear polybenzoxazine were investigated; for monobenzoxazine-based film, the blend with epoxy resin was required to improve physical property because monobenzoxazine film showed brittle nature which limited the application as a film with proper mechanical strength. Films with higher content of monobenzoxazine over epoxy resin resulted in lower dissipation factor around 0.005 frequency/10 GHz, however, the mechanical property of the film did not meet the condition as a PCB material. On the contrary, the linear polybenzoxazine-based film demonstrated enhanced mechanical stability but showed limitations in adhesion to the copper layer probably due to the lack of polar functional groups. To overcome the drawbacks, linear polybenzoxazine and epoxy blend systems were prepared to produce films with good adhesion and excellent electrical insulation property with the dissipation factor around 0.006 frequency/10 GHz.

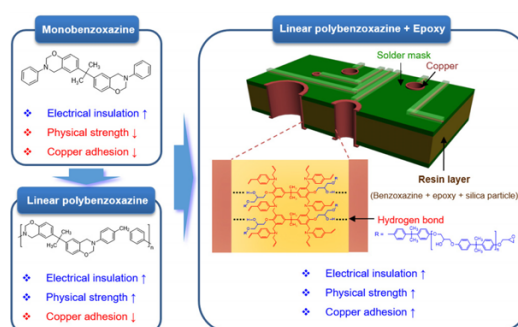
**Keywords:** printed circuit board (PCB), Benzoxazine, epoxy, hybrid film, dissipation factor.

## 1. Introduction

A printed circuit board (PCB) is a substrate to enable connection between electric components using multiple layers composed of copper and insulator sheets. The PCB materials require thermal stability and mechanical strength as well as electrical insulating performance. Even though dissipation factor and dielectric constant are commonly used standards for evaluation of insulation, the dissipation factor is regarded as the more important factor in PCB application since electric field in electronic devices keeps increasing to a higher frequency.<sup>1</sup> Epoxy resin is most widely used as a PCB material due to its flexibility, outstanding mechanical properties and excellent adhesiveness to copper.<sup>2,3</sup> However, the epoxy resin has crucial drawbacks in insulating performance to meet currently required needs because hydroxyl groups formed during curing process have been reported to contribute to the decrease in the insulating property. For improved insulation, resins such as polycyanate<sup>4-7</sup> and dicyclopentadiene<sup>8</sup> have been applied to PCB materials, but they have the disadvantage in their brittle nature. Inherently insulating

inorganic particles such as silica nanoparticles were used with thermoset resins as hybrid materials, which were reported to exhibit excellent electrical insulation as well as mechanical and thermal stability.<sup>9-11</sup>

Benzoxazine has been developed as a new series of phenolic resin and displays a great potential to prepare thermosetting polymers with various molecular structures.<sup>12</sup> Benzoxazine has characteristics in near-zero expansion and shrinkage during the thermal curing process and exhibits a wide range of mechanical properties based on a variety of monomeric units which can be prepared in a well-established method. Mannich reaction is used in the preparation of monomeric benzoxazines using hydroxyl- and amine-functionalized compounds with paraformaldehyde in bulk or solution condition in a short reaction time.<sup>13</sup> The polymerization of benzoxazine proceeds through simple catalyst-free thermal treatment, and no by-product formation is observed in the curing process. The hydroxyl and tertiary amine groups generated during the thermosetting process were reported to form inter- and intramolecular hydrogen bonding, which led to high  $T_g$ , low water absorption, and excellent electrical insulation performance.<sup>14,15</sup> However, film formation based on single monobenzoxazine was limited due to their brittle nature.<sup>16</sup> Various studies have been carried out to overcome the brittle property of benzoxazine-based films. One approach



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**\*Corresponding Author:** Cheol-Hee Ahn (chahn@snu.ac.kr)

is a blend system with a polymer displaying better film-forming property, flexibility, and toughness such as epoxy or polyurethane.<sup>17-19</sup> Another approach is to employ higher molecular weight polybenzoxazine precursors which can be prepared by condensation polymerization of dihydroxy and diamine-based monomers.<sup>20</sup> These researches reported the successful production of physically stable benzoxazine-based films.

Here, hybrid materials consisting of benzoxazine, epoxy and silica nanoparticles were prepared to develop a PCB material with enhanced electrical insulation and mechanical properties. Blend system with epoxy resin was employed to improve the brittle nature of benzoxazine-based film and to provide adhesiveness to a copper layer since the phenol groups generated from the thermal curing of benzoxazine did not provide sufficient adhesion property.<sup>21</sup> The optimized hybrid system was suggested based on low dissipation factor, high mechanical strength and enhanced adhesion to a copper layer.

## 2. Experimental

### 2.1. Materials

Bisphenol A (99%), 1,4-dioxane and chloroform were purchased from Daejung Chem. Paraformaldehyde (95%, degree of polymerization: 8 to 100), 4,4'-diaminodiphenylmethane (97%), 4-dimethylamino pyridine (DMAP, 99%) and cyclohexanone (99%) were obtained from Sigma-Aldrich. Monobenzoxazine (BA-a, bisphenol A-based benzoxazine) was kindly supplied by Huntsman. Epoxy with the trade name of YD-128 (epoxy equivalent weight, EEW: 184~190 g/eq) and phenoxy thermoplastic were received from Kukdo. PS-6313 (equivalent weight : 148 g/eq), epoxy curing agent, was purchased from Gun Ei Chemical Industry. Leveller, whose name is BYK 337 (0.14 g), was used as received from BYK. Active-ester catalyst with the trade name of HPC-8000-65T (equivalent weight : 223 g/eq) was acquired by DIC., and silica nanoparticle slurry coated by epoxy was obtained from Admatechs.

### 2.2. Synthesis of linear polybenzoxazine

Linear polybenzoxazine was synthesized using reported method.<sup>20</sup> 260 mL chloroform dissolving bisphenol A (20.0 g, 87.6 mmol), diaminodiphenylmethane (17.4 g, 87.6 mmol), and paraformaldehyde (10.5 g, 350.4 mmol) were charged to a 1 neck round-bottomed flask equipped with a condenser. The mixture was refluxed with vigorous stirring for 5, 12, 36, and 72 h, respectively. After cooled to room temperature, the solution was filtered and washed with 1 N NaHCO<sub>3</sub>, water and dried with magnesium sulfate. Finally, the organic layer was dropped into diethyl ether to take a precipitated sample and the filtered sample was dried at 25 °C in a vacuum oven for overnight.

### 2.3. Preparation of hybrid film

#### 2.3.1. Benzoxazine hybrid film

BA-a (2.00 g, 4.33 mmol) was dissolved in 6 mL 1,4-dioxane in a 70 mL vial. To the solution, phenoxy thermoplastic (0.57 g,

10.00 phr), leveller (0.24 g, 1.50 phr) and epoxy functionalized silica nanoparticle slurry (7.27 g, 70 wt% of the total reagent mixture) were added and well mixed. After casting the solution onto a copper foil with the size of 100 mm×100 mm×0.125 mm, the solvent was removed at 80 °C for 10 min in an oven to form pre-cured film. The film-coated copper foil was cut into a size of 100 mm×3 mm×0.125 mm and sequentially cured at 180 °C for 2 h and 200 °C for 2 h. After curing, the copper foil on the produced hybrid film was removed using 50 wt% nitric acid aqueous solution. The obtained hybrid film was rinsed with distilled water 3 times and dried at 90 °C for 3 h in an oven. Hybrid film based on linear polybenzoxazine was also prepared by adding epoxy, silica nanoparticle slurry, solvent and other reagents in the same proportions as in the case of BA-a.

#### 2.3.2. Benzoxazine blend hybrid film

BA-a (0.60 g, 1.30 mmol), epoxy (0.60 g), epoxy curing agent (0.10 g, 11.68 phr), active-ester catalyst (0.76 g, 81.90 phr), phenoxy thermoplastic (0.50 g, 10.00 phr), DMAP (6.03 mg, 0.05 mmol), leveller (0.15 g, 1.50 phr) and epoxy functionalized silica nanoparticle slurry (6.40 g, 70 wt% of the total reagent mixture) were well mixed in 0.77 mL cyclohexanone in a 70 mL vial and cast on a copper foil with the size of 100 mm×100 mm×0.125 mm. The solvent drying method of the cast solution on the copper foil, the cutting size of film-coated copper foil, the curing condition and the work-up process followed the same method mentioned above.

The linear polybenzoxazine-based hybrid film was fabricated in the same method as above after dissolving 0.6 g linear polybenzoxazine in 1.8 mL 1,4-dioxane. Weight ratios of the other reagents were the same as described above.

BA-a and polybenzoxazine hybrid films with a different weight ratio of benzoxazine and epoxy were prepared using the same method mentioned above. The following abbreviation was coined: BA-a 1 stands for the blend composed of 1:1 weight ratio of BA-a: epoxy, and BA-a 2 for the 2:1 weight ratio of BA-a: epoxy. Linear polybenzoxazine 1 and 2 stand for the same weight ratio of the blend system.

### 2.4. Characterization

<sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) were performed on an Avance-300 (Bruker) at 300 MHz frequency with deuterium chloroform as a solvent. Gel permeation chromatography (GPC) was taken with CTO-10A (Shimadzu) at 40 °C using tetrahydrofuran as an eluent at the rate of 1.0 mL/min and the molecular weight was calculated with polystyrene standards. Differential scanning calorimetry (DSC) was performed with Q10 (TA instrument) at the heating rate of 10 °C/min under N<sub>2</sub> atmosphere.

The dissipation factor was analyzed with resonant cavity type microwave dielectrometer (AET, INC) on the frequency of 10 GHz at 25 °C. The film was prepared as described in the previous section.

For peeling test, benzoxazine hybrid mixtures in 1,4-dioxane were cast on PET films and pre-cured at 80 °C for 10 min. A copper clad laminate (CCL) was placed on the pre-cured film, and lamination process was performed to remove the PET film

after compression at 90 °C for 60 s with a pressure of 8 kgf/cm<sup>2</sup>. After curing at 180 °C for 2 h and 200 °C for 2 h, desmear process was conducted on the film surface. A copper seed was introduced through an electroless plating process then a copper plating was carried out through an electroplating process. Finally, the copper crystal growth was completed by heating at 170 °C for 1 h. The peeling test was performed using CCL with average surface roughness of 0.5 μm in 10 mm×30 mm size. The rate of crosshead movement was 10 mm/min and the analyzing temperature was 25 °C with the universal testing machine (TA instrument).

### 3. Results and discussion

Two different benzoxazines were employed in this study: bisphenol A based monobenzoxazine (BA-a) and linear polybenzoxazine. The chemical structures of BA-a and epoxy used in the preparation of a blend system as well as a synthetic scheme of linear polybenzoxazine are respectively illustrated in Scheme 1 and Scheme 2. Linear polybenzoxazine was prepared with 1 mole of bisphenol A, 1 mole of diaminodiphenylmethane and 4 moles of paraformaldehyde in refluxing chloroform. The molar ratio of bisphenol A to diaminodiphenylmethane was carefully controlled to be an equimolar ratio in order to obtain a high molecular weight of linear polybenzoxazine. After pre-determined polymerization time at 5, 12, 36, and 72 h, the reaction mixture was washed with 1 N NaHCO<sub>3</sub> and water, then precipitated into diethyl ether to obtain white powder product. The overall isolation yield was about 92% and the higher molecular weight polymer was obtained with longer polymerization time. The polymerization results are summarized in Table 1. Preparation of linear polybenzoxazine-based film and measurement of the mechanical

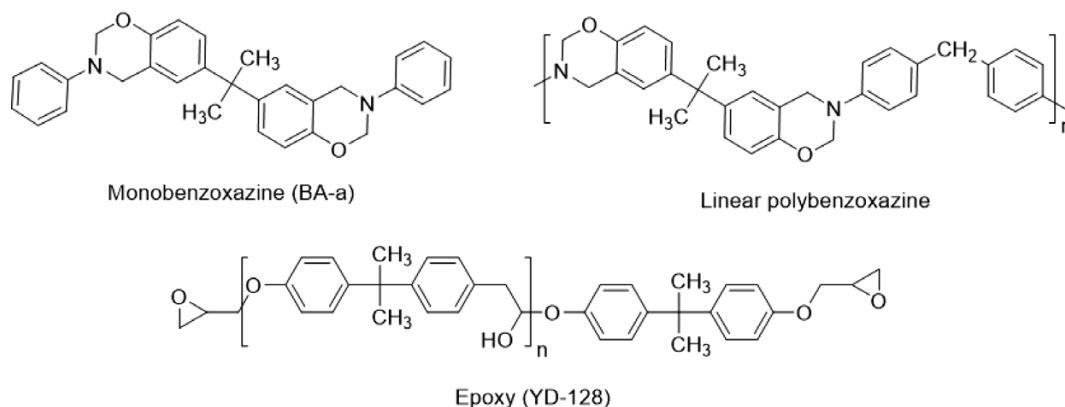
**Table 1.** Molecular weight of linear polybenzoxazines

Polymerization time (h)	<i>M<sub>n</sub></i>	<i>M<sub>w</sub>/M<sub>n</sub></i>
5	1,550	2.07
12	2,550	2.48
36	3,550	2.47
72	9,300	4.79

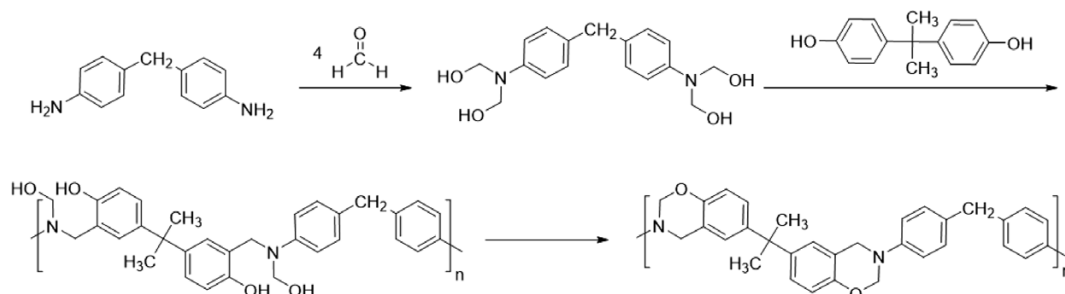
properties were performed using the polymers with the highest number average molecular weight of 9,300.

There were several reports that benzoxazine ring was not intact during the reaction at high temperature and closed-ring structures co-existed with opened-ring structures in the reaction mixture.<sup>20,22</sup> Figure 1 shows a representative <sup>1</sup>H NMR spectrum of linear polybenzoxazine. The protons of oxazine ring appeared at 4.6 and 5.4 ppm, which respectively corresponds to -O-CH<sub>2</sub>-N- and -Ar-CH<sub>2</sub>-N-. The methyl proton of -Ar-C(CH<sub>3</sub>)<sub>2</sub>-Ar- and methylene proton of -Ar-CH<sub>2</sub>-Ar- were detected at 1.5 and 3.8 ppm, respectively. A new peak from ring-opened structure of benzoxazine ring was reported to appear around 3.8 ppm and it was difficult to separate the peak from that from methylene proton of bisphenol A. However, the obtained linear polybenzoxazine was clearly soluble in chloroform, THF and 1,4-dioxane at room temperature without any noticeable precipitates, which led to a conclusion that the formation of network structure stemmed from ring-opening of oxazine was limited during the polymerization condition.

Previous works reported that curing process of benzoxazine should be performed at the temperature above the exothermic curing peaks, usually above 230 °C, which was obtained in DSC analysis with a fixed heating rate.<sup>23</sup> Since a curing temperature below 200 °C was required in this study due to the device con-



**Scheme 1.** The chemical structures of benzoxazine and epoxy resin.



**Scheme 2.** Synthetic scheme for the preparation of linear polybenzoxazine.<sup>24</sup>

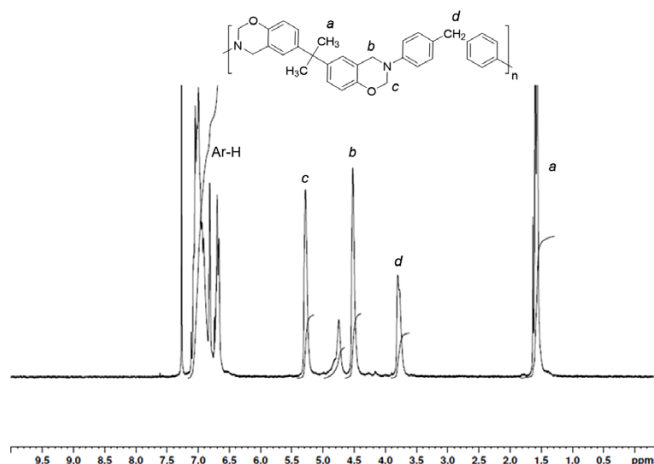


Figure 1.  $^1\text{H}$  NMR spectrum of linear polybenzoxazine.

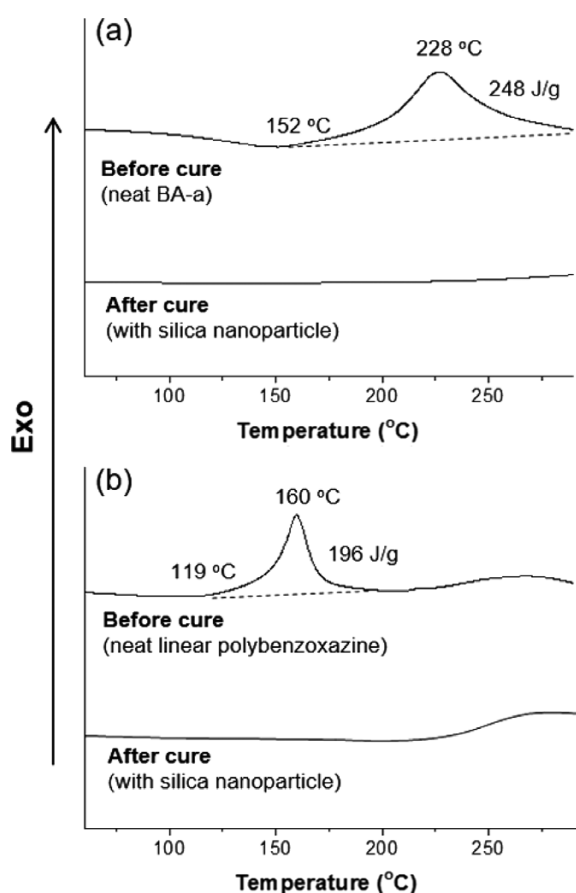


Figure 2. DSC traces of (a) BA-a, (b) linear polybenzoxazine precursors.

ditions at Samsung Electro-Mechanics Co., optimized curing temperature was investigated with the mixtures of benzoxazine and epoxy-coated silica nanoparticles. Figure 2 shows DSC traces of neat benzoxazines and benzoxazine/silica nanoparticles (7/3 weight ratio) before and after sequential curing at 180 °C for 2 h and 200 °C for 2 h. The thermograms of neat BA-a with the heating rate of 10 °C/min displayed a curing exotherm of benzoxazine units into the 3-dimensional structure at 228 °C. Benzoxazine/silica nanoparticle mixtures, experienced the sequential curing conditions, were fully cured and the exotherm peaks completely disappeared, which proved that the applied thermal

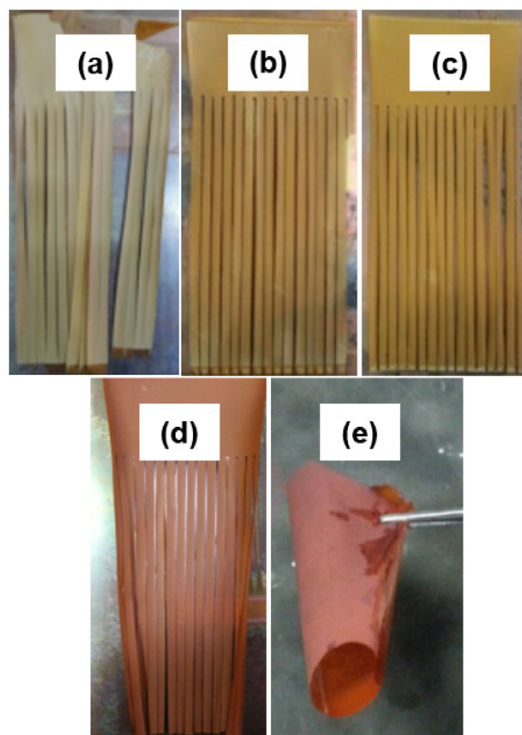


Figure 3. Photograph images of (a) BA-a H, (b) BA-a 2 blend H, (c) BA-a 1 blend H, (d) linear polybenzoxazine H, and (e) neat linear polybenzoxazine film.

conditions led to a complete curing of the benzoxazine rings even at the temperature far below its peak temperature of curing exotherm. The curing condition at 180 °C for 2 h and 200 °C for 2 h was set up in preparing for all the films in this study. Neat linear polybenzoxazine showed the exotherm peak at 160 °C, but the same curing profile was applied to endow the final films with the equivalent thermal history.

The films of benzoxazines and hybrids were prepared as described in the experimental section and the pictures are illustrated in Figure 3. As shown in Figure 3(a), the film composed of BA-a only was so brittle that it was difficult to maintain the cast form of a film, but good enough to measure the dissipation factor with reliable reproducibility. As the amount of epoxy resin increased from BA-a 2 to BA-a 1, the prepared films displayed enhanced mechanical properties. In case of linear polybenzoxazine, flexible films with the excellent mechanical property were prepared and the film of neat linear polybenzoxazine was strong enough to be fully bent without any breakage.

Epoxy resin is generally crosslinked with the presence of polyfunctional amine-based curing agents. If the same system is employed in the present study, non-reacted amino groups could produce a negative effect on dissipation factor probably due to its highly polar nature. It was investigated using isothermal DSC analysis whether the phenol groups generated during the curing of benzoxazine rings could play the role in curing epoxide rings. Figure 4 shows DSC traces of BA-a, epoxy and BA-a/epoxy blend with the isothermal heating at 180 °C for 2 h and then 200 °C for 2 h. The neat epoxy was hardly cross-linked during the heat treatment; on the contrary, the trace of BA-a showed the exotherm peak of curing at the beginning of the

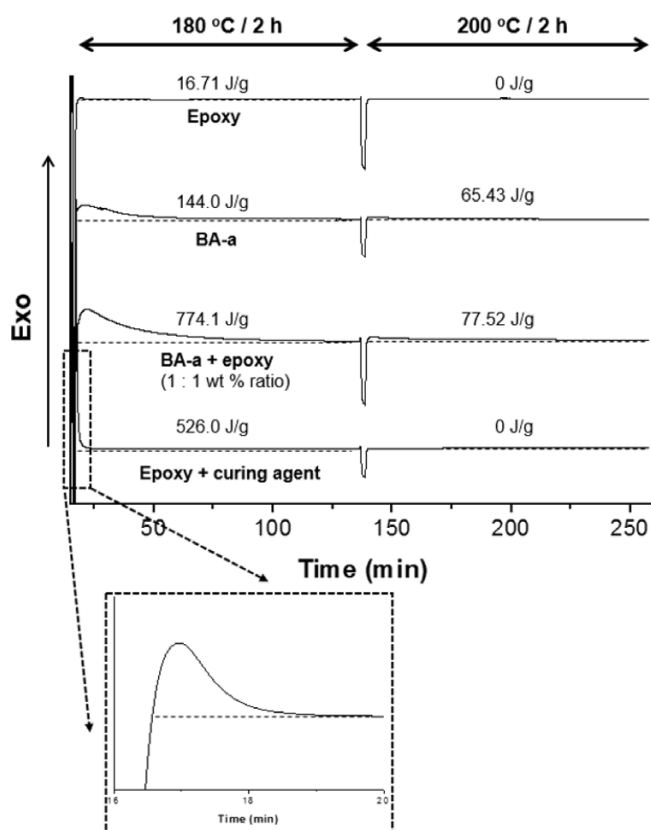


Figure 4. DSC trace of epoxy, BA-a and blend system.

first heating cycle with the enthalpy of transition of 144.0 J/g. Enthalpy of transition in the case of epoxy resin with curing agent was dramatically increased, which implied that the curing agent quickly crosslinked the epoxy rings at the beginning of the cure cycle. The DSC trace of BA-a/epoxy blend system followed the similar trend with that of BA-a and exhibited the exotherm transition of 774.1 J/g. Considering the fact that the enthalpy of curing in the epoxy with curing agent system was 536.0 J/g, the epoxide ring was believed to be fully crosslinked by the presence of the phenol groups in the cured polybenzoxazine. These results also indicated that epoxy resin and polybenzoxazine were not physically mixed but formed chemically conjugated blend systems.

In order to investigate the feasibility of the hybrid films consisting of benzoxazine, epoxy and silica nanoparticles as a PCB material, dissipation factors were measured and peeling test was conducted with CCL as described in the experimental section. The results are summarized in Table 2. Dissipation factors

of benzoxazine and hybrid films were lower than that of epoxy and silica nanoparticle film which was evaluated as  $0.0079 \pm 0.0001$ . The BA-a film showed the lowest dissipation factor around 0.0042, but it was so brittle and non-adhesive that peeling test could not proceed. The addition of epoxy resin had been reported to have a negative influence on the dissipation factor, however, it was considered indispensable in terms of improvement in mechanical properties and adhesion to CCL. As expected, the dissipation factor increased with increasing the amount of epoxy in BA-a hybrid while the films showed flexible properties to some extent, but the improved physical properties were still not good enough to produce reliable results in the peeling test. The dissipation factor of 0.0052 displayed by linear polybenzoxazine was slightly higher than that of BA-a and much lower than that of epoxy. The film made of linear polybenzoxazine showed excellent mechanical properties, but its adhesiveness was limited to be applied as a PCB material. Phenol group formation during the curing of benzoxazine was quite similar to hydroxyl group formation from epoxide ring opening, in terms of production of polar groups which was reported to play an important role in improving the adhesive property to CCL and, at the same time, producing negative effects on the dissipation factor. The observation that polybenzoxazine film exhibited lower dissipation factor and non-adhesiveness was in good agreement with the previous reports that the phenol groups formed during the benzoxazine ring opening process participated in the formation of hydrogen bonding inside the benzoxazine system. In order to endow the linear polybenzoxazine based films with adhesiveness, the epoxy hybrid system was prepared. The dissipation factors of the linear polybenzoxazine hybrids increased with the amount of blended epoxy resin, but the difference was not so large as the case of BA-a hybrids. Regardless of the blend ratio, linear polybenzoxazine hybrids displayed comparable values of dissipation factor and peel strength, which were improved than epoxy based hybrid systems.

#### 4. Conclusions

Hybrid films consisting of benzoxazine, epoxy, and epoxy-coated silica nanoparticles were prepared and their feasibility as a PCB material was investigated. Bisphenol A based monobenzoxazine, linear polybenzoxazine with the molecular weight of 9,300 and epoxy with the grade in industrial use were employed with different ratio of benzoxazine and epoxy resin. In contrast to the previous researches reporting that higher temperature was required for efficient curing of benzoxazine rings, the opti-

Table 2. Dissipation factor, brittleness, peel strength of BA-a or linear polybenzoxazine film

Film	Dissipation factor	Brittleness	Peel strength
BA-a H <sup>a</sup>	0.0042±0.0001 (n=2)	Very brittle	N/A <sup>c</sup>
BA-a 2 blend H <sup>b</sup>	0.0059±0.0001 (n=2)	Very brittle	N/A <sup>c</sup>
BA-a 1 blend H <sup>b</sup>	0.0066±0.0002 (n=2)	Moderately brittle	N/A <sup>c</sup>
Linear polybenzoxazine H <sup>a</sup>	0.0052±0.0001 (n=2)	Flexible	N/A <sup>d</sup>
Linear polybenzoxazine 2 blend H <sup>b</sup>	0.0058±0.0001 (n=2)	Flexible	0.59±0.05 (n=2)
Linear polybenzoxazine 1 blend H <sup>b</sup>	0.0064±0.0001 (n=2)	Flexible	0.65±0.04 (n=2)

<sup>a</sup>Benzoxazine/silica nanoparticle hybrid. <sup>b</sup>Benzoxazine/epoxy/silica nanoparticle hybrid. <sup>c</sup>Due to brittleness. <sup>d</sup>Due to the poor adhesion to copper. Dissipation factor of epoxy/silica hybrid film :  $0.0079 \pm 0.0001$  (n=2).

mized temperature for complete curing was determined at a lower temperature and the temperature was acceptable in the industrial process. Monobenzoxazine hybrid films showed a lower dissipation factor than that of epoxy based films and poor mechanical property, while polybenzoxazine hybrid films exhibited a lower dissipation factor and excellent mechanical property. Both films displayed non-adhesiveness to CCL and blending with epoxy resin was indispensable. Among various compositions of benzoxazine and epoxy blend system, hybrid films with higher content of monobenzoxazine exhibited a lower dissipation factor around 0.005 frequency/10 GHz. The Linear polybenzoxazine hybrid film showed excellent mechanical strength, an acceptable dissipation factor around 0.006 and adhesiveness to CCL, which implied that benzoxazine resin could be a new candidate in the preparation of films displaying excellent electrical insulation.

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