

CHARACTERISTICS OF CYANATE ESTER AND FLUORENYL EPOXY-BASED POLYMER-CERAMIC COMPOSITES

S. D. Park^{1,2,*}, D. S. Seo¹, M. J. Yoo¹, W. S. Lee¹, and D. K. Kim²

¹Korea Electronics Technology Institute, Seongnam 463-816, Korea

²Dept. of Chemistry & Applied Chemistry, Hanyang University, Ansan 426-791, Korea

* Corresponding author (sdpark@keti.re.kr)

Keywords: Cyanate ester, Fluorenyl epoxy, Silica, Prepreg, Composite

1 Introduction

In the field of high density printed circuit board for semiconductor package, needs of lead-free solder and low CTE (coefficient of thermal expansion) substrate increased recently so that the substrate materials with high glass transition temperature (T_g) became very important factor. Cyanate ester resin is generally used for high heat resistant substrate, but because it has poor moisture absorption property, it is used by mixing with other resins such as epoxy, bismaleimide, *etc.*. However, in this case, the heat resistance of mixed resin is degraded.

Introduction of fluorenyl "Cardo" structure into polymers results in excellent heat resistance and excellent solubility[1-5]. As it has rigid structure having many of aromatic rings, it shows high refractive index and high heat resistance. The solubility improvement resulted from the introduction of bulky "Cardo" structure in the repeating unit which decreases interchain interaction and increases the free volume between polymer main chains[1]. Moreover, it also has the properties such as low cure shrinkage, high chemical resistance, low thermal expansion, and nonflammability.

In this research, an epoxy with fluorenyl "Cardo" structure was used for the improvement of moisture absorption of cyanate ester. Several reports showed the excellent heat resistance of the bisphenol fluorene epoxy resin[6-9]. The glass transition temperature of cured bisphenol fluorene epoxy was about 250~260°C, which was higher value than that of conventional bisphenol A epoxy. But the effect of its partial replacement of cyanate ester has not been reported so far. We expected that we could get the resin composition for the high functional substrate material of printed circuit board(PCB) with low moisture absorption and high T_g simultaneously by mixing the fluorenyl "Cardo" epoxy with cyanate

ester. In addition, spherical silica powders were added into the mixed resin as fillers and the formed varnish was pre-impregnated into glass fabric. The fabricated prepregs were laminated, cured, and characterized.

2 Experimental

2.1 Materials

Fluorenyl "Cardo" epoxy was supplied by Osaka Gas Chemical, Japan under the trade name OGSOL PG-100. Novolac cyanate ester was supplied with the commercial name PT-30 by Lonza. Silica powder (SFP-30M by Denka, Japan, 0.6μm) as an inorganic filler was used with a dispersant. As curing agents[CA], methyl nadic anhydride (MNA) and 4,4'-diaminodiphenylsulfone(DDS) were tested, which were reagents supplied from Aldrich. They were selected among 10 candidates by pre-experiment for the selection of proper curing agent. TPP (triphenylphosphine supplied by TCI) was used as a catalyst, and to prepare varnish, 1,4-dioxane was used as a solvent.

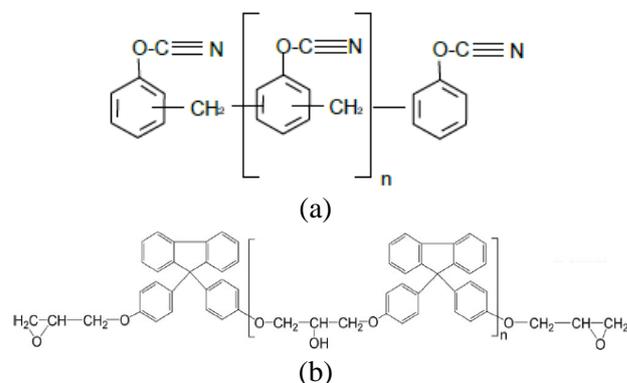


Fig. 1. Chemical structures of (a) cyanate ester [CE] and (b) fluorenyl "Cardo" epoxy [FE].

2.2 Characterization of mixed resin composition

At first, the curing characteristic of fluorenyl epoxy [FE] was investigated. It was solved in 1,4-dioxane so that 60wt% FE solution was made up. It was mixed with equivalent amount of MNA or DDS and 1 phr TPP. Sample of this solution was poured into aluminum dish, dried at 100°C during 3 hours, and then cured at 250°C during 5 hours (rate: 10°C/min) in convection oven. Small sample of cured FE was analyzed by DSC for T_g measurement. Next, cyanate ester was mixed with FE epoxy composition. Mixing ratio [CE/(FE+CA)] was changed from 40/60 to 70/30. Through similar test method, the properties of mixed resin composition were measured. Besides DSC T_g, DMA T_g, storage modulus, and moisture absorption were measured.

2.3 Preparation of composite film and prepreg

Silica powder was ball milled with a dispersant in 1,4-dioxane for 24 hours to remove agglomerates and achieve homogeneity. Amount of added silica was 40 wt% in all of non-volatile ingredients. The SiO₂ slurry was mixed with CE, FE, MNA, and TPP by additional ball milling at ambient temperature for 24 hours using zirconia ball media. The obtained varnish was defoamed and then cast to film by comma coater or pre-impregnated into glass fabric (#2116) to make prepregs.

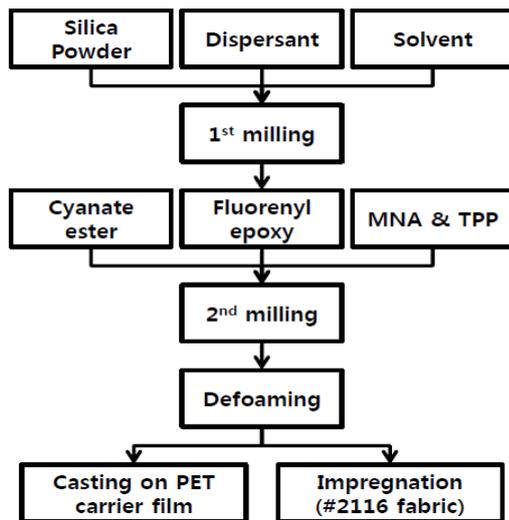


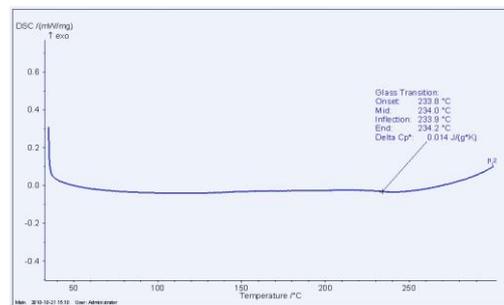
Fig. 2. Fabrication procedure for composite films & prepregs.

2.4 Preparation of composite laminates and characterization

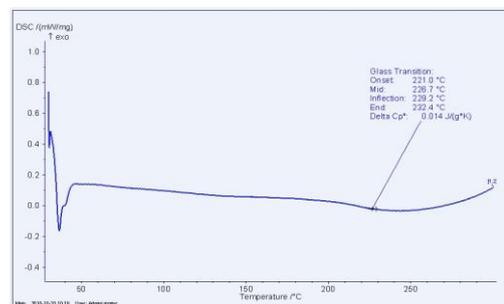
Two films or prepregs (10 cm x 10 cm) were attached together by hot roll laminator and then the attached laminates were cured at 250°C during 5 hours (rate: 10°C/min) in convection oven. Test samples for DMA and moisture absorption were made by laser drilling machine. The glass transition temperature of cured sample was measured by Q800 DMA of TA Instruments and the moisture absorption was measured by JIS C 6481 standard method. The measured data were compared with the values of mixed resin without filler or glass fabric.

3 Result and discussion

DSC results of cured fluorenyl Cardo epoxy with two curing agents were showed in Figure 3. The baseline change was observed at 234°C in MNA-used composition and at 226°C in DDS-used composition, which were concluded as the DSC T_g's of two cured compositions.



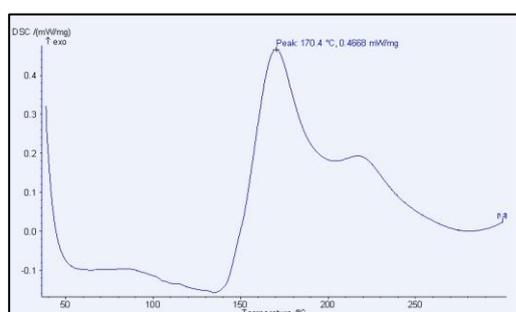
(a) FE+MNA



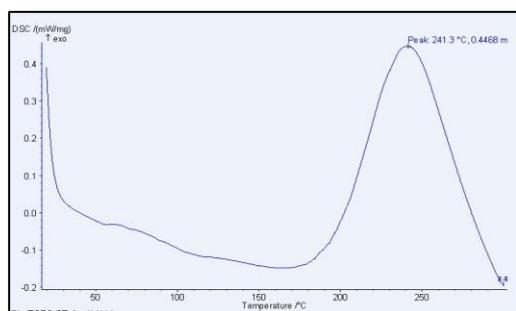
(b) FE+DDS

Fig. 3. DSC results of two fluorenyl epoxy / curing agent compositions.

MNA-used composition showed higher T_g. When MNA was used as a curing agent, the curing peak appeared at 170°C. Fully cured epoxy body was expected to obtain in curing at 250°C. In case of DDS, however, the curing peak appeared at 241°C. So, when DDS was used as a curing agent, the curing reaction maybe didn't finish at 250°C curing. Figure 4 showed the difference of DSC result according to the two curing agents. Therefore, we deduced the T_g of MNA-used composition could show higher value and fixed MNA as the curing agent of fluorenyl epoxy in next experiment for mixing with cyanate ester.



(a) FE+MNA



(b) FE+DDS

Fig. 4. Comparison of curing peaks according to curing agent by DSC analysis (rate: 10°C/min up to 300°C).

Table 1 shows the properties of CE/FE-mixed cured compositions. The glass transition temperature was increased with increasing amount of cyanate ester, but the moisture absorption was increased together. When only cyanate ester was cured at the same curing condition, the value of moisture absorption

was 2.6%. On the contrary, this result meant that the addition of fluorenyl Cardo epoxy into cyanate ester could improve the moisture absorption. DMA T_g's were over 300°C in all the mixed compositions. We could deduce that fluorenyl Cardo epoxy had an important role to reduce the moisture absorption with keeping high glass transition temperature over 300°C in cyanate-epoxy mixed composition because FE was a high T_g epoxy.

Table 1. Properties of cured CE/(FE+MNA)-mixed resin composition.

Item	Unit	Amount of CE (wt%)				
		40	50	60	70	
T _g	DMA	°C	301	308	315	328
	DSC	°C	253	270	264	270
S.M.*	25°C	GPa	2.2	3.3	3.0	3.2
	250°C	GPa	1.2	1.9	1.7	1.9
M. A.**	%		1.97	2.03	2.09	2.35

* Storage modulus by DMA

** Moisture absorption (after immersion 23°C/24hrs)

From the above results, two compositions with low moisture absorption (CE40 & 50 wt%) were selected and mixed with silica powders as inorganic filler. At first, the silica-added compositions were formed into film shape on PET carrier film and evaluated after lamination curing. Figure 5 showed the fabricated film on PET carrier. We couldn't get films from the compositions without silica addition.

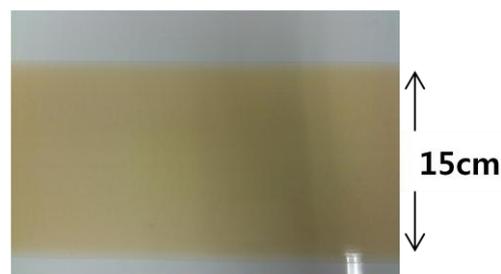


Fig. 5. Composite film cast on PET carrier film.

By another way, two silica-added compositions was formed into prepreg shape through pre-impregnation into glass fabric and evaluated after lamination.

Table 2 shows the properties of cured laminates which were composed of mixed resin and silica fillers. From the comparison with Table 1, we could find that silica addition reduced the moisture absorption and increased the storage modulus. Moreover, glass transition temperature (T_g), storage modulus (S.M.) and moisture absorption (M.A.) were more improved by pre-impregnation of varnish into glass fabric. When the inorganic material such as silica powder and glass fabric was mixed with resin composition, the resin portion was reduced so that the improvement of physical properties was a matter of course. Finally, the T_g of composite laminate reached up to 317°C and the moisture absorption was reduced to 0.57%.

Table 2. Properties of CE/(FE+MNA)-mixed silica-filled (40wt%) laminates.

Item		Unit	Film laminate		Prepreg laminate	
			CE 40	CE 50	CE 40	CE 50
T _g	DMA	°C	307	307	317	315
S.M.	25°C	GPa	7.9	4.6	18.6	19.6
	250°C	GPa	6.2	2.8	16.0	16.1
M. A.		%	1.76	1.78	0.57	0.91

4 Conclusions

Cyanate ester and fluorenyl “Cardo” epoxy-based composition mixed with silica powder was investigated for the substrate material with high glass transition temperature and low moisture absorption. MNA was selected for the optimum curing agent of the fluorenyl epoxy. The partial replacement of CE with FE could reduce the moisture absorption with keeping high glass transition temperature over 300°C. In addition, silica powder addition and pre-impregnation into glass fabric could more improve the moisture absorption and the storage modulus of composite with keeping high T_g. Finally, CE/(FE+MNA)-mixed, silica-filled (40wt%), and pre-impregnated laminate showed high T_g of 317°C and low moisture absorption of 0.57%.

Acknowledgement

This work was supported by the Technology Innovation Program funded by the Ministry of Knowledge Economy (MKE, Korea).

References

1. G.-S. Liou *et al.*, “Synthesis and Properties of Wholly Aromatic Polymers Bearing Cardo Fluorene Moieties”, *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 45, 4352–4363 (2007)
2. Kazuhiko Mizuuchi *et al.*, “High Resolution Cardo Polymer Dielectric VPA-series”, *2002 ECTC Proceedings*, 924-930 (2002)
3. Zhiqiang Hu *et al.*, “Synthesis and Properties of Polyamide-imides Containing Fluorenyl Cardo Structure”, *Journal of Applied Polymer Science*, Vol. 106, 2494–2501 (2007)
4. A. D. Sagar *et al.*, “Polyamides containing s-triazine rings and fluorene “cardo” groups: synthesis and characterization”, *European Polymer Journal*, Vol. 37, 1493-1498 (2001)
5. Katsuhisa Tokumitsu *et al.*, “Viscoelastic Properties of Bis(phenyl)fluorene-Based Cardo Polymers with Different Chemical Structure”, *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 43, 2259–2268 (2005)
6. Zhen Dai *et al.*, “Kinetics and thermal properties of epoxy resins based on bisphenol fluorine structure”, *European Polymer Journal*, Vol. 45, 1941–1948 (2009)
7. Zhen Dai *et al.*, “Preparation, Curing Kinetics, and Thermal Properties of Bisphenol Fluorene Epoxy Resin”, *Journal of Applied Polymer Science*, Vol. 106, 1476–1481 (2007)
8. Wenbin Liu *et al.*, “Preparation and Properties of One Epoxy System Bearing Fluorene Moieties”, *Journal of Applied Polymer Science*, Vol. 113, 1289–1297 (2009)
9. Yuanqin Xiong *et al.*, “Crystal Structure, Curing Kinetics, and Thermal Properties of Bisphenol Fluorene Epoxy Resin”, *Journal of Applied Polymer Science*, Vol. 118, 827–833 (2010)