Article

Copyright © 2016 American Scientific Publishers
All rights reserved
Printed in the United States of America

Journal of
Nanoscience and Nanotechnology
Vol. 16, 3009–3013, 2016
www.aspbs.com/jnn

The Electrical Properties for Phenolic Isocyanate-Modified Bisphenol-Based Epoxy Resins Comprising Benzoate Group

Eun Yong Lee[1,2,†], Il Seok Chae[3,†], Dongkyung Park[4], Hongsuk Suh[4], and Sang Wook Kang[1,*]

[1] Department of Chemistry, Sangmyung University, Seoul 110-743, Republic of Korea
[2] Shin-A T&C Company, Gasan-dong, Geumcheon-gu, Seoul 481-10, Republic of Korea
[3] Department of Energy Engineering, Hanyang University, Seoul 133-791, Republic of Korea
[4] Department of Chemistry and Chemistry Institute for Functional Materials,
Pusan National University, Busan 609-735, Republic of Korea

Epoxy resin has been required to have a low dielectric constant (D_k), low dissipation factor (Df), low coefficient of thermal expansion (CTE), low water absorption, high mechanical, and high adhesion properties for various applications. A series of novel phenolic isocyanate-modified bisphenol-based epoxy resins comprising benzoate group were prepared for practical electronic packaging applications. The developed epoxy resins showed highly reduced dielectric constants (D_k~3.00 at 1 GHz) and low dissipation values (Df~0.014 at 1 GHz) as well as enhanced thermal properties.

Delivered by Ingenta to: Chinese University of Hong Kong
IP: 37.0.40.66 On: Mon, 24 Oct 2016 16:42:46
Copyright: American Scientific Publishers

Keywords: Epoxy Resin, Dielectric Constant, Dissipation Factor, Coefficient of Thermal Expansion.

1. INTRODUCTION

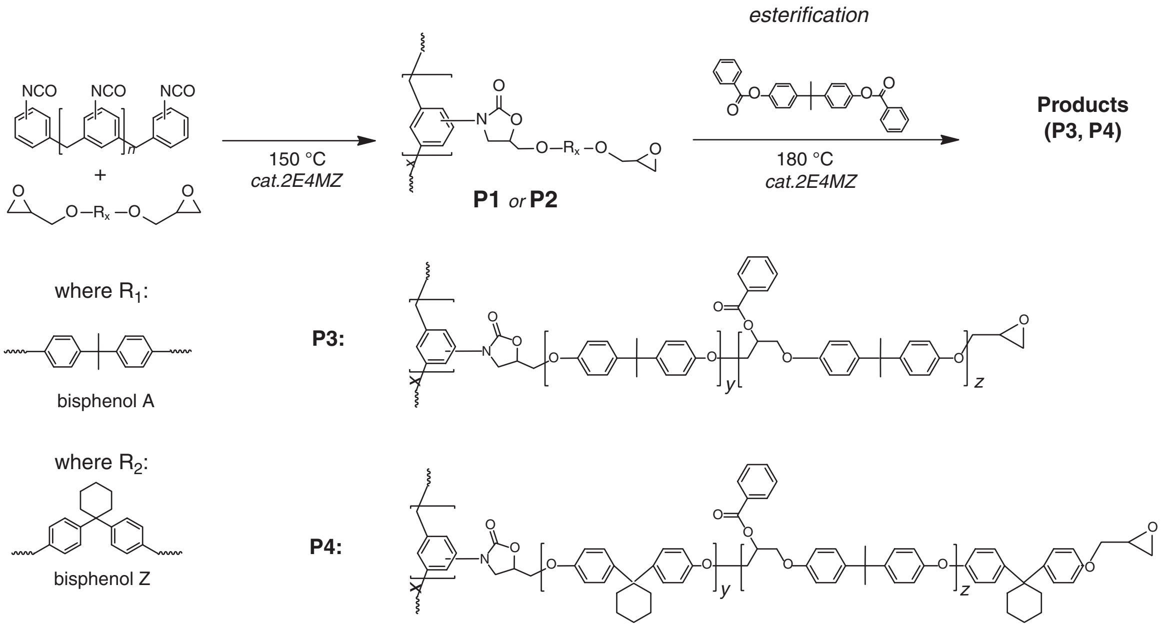
Epoxy resins are widely used as underfill materials in electrical/electronic devices due to its excellent electrical insulation properties, high thermal stability, easy conversion from liquid to non-melting solids and excellent mechanic characteristics.[1,2] Recently, with the growing demands for miniaturization and high power density in electronic devices, high electrical insulating epoxy resin systems with lower coefficients of thermal expansion should be required in electronic packaging applications.[3–5] Also, at inner layer of multilayer printed circuit board, the adhesion property of epoxy resin is very important for practical applications. This is strongly related to the kind of hardener, which governs the toughness character of cured resin. Since the prohibition of plumbum (Pb) compound by the law, the use of Tin/Silver (Sn/Ag) alloys requires the relatively higher temperatures in soldering process,[6,7] which have accelerated the change hardener from dicyandiamide (DICY) to phenolic compounds.[8] However, the cured matrix by phenolic compounds is too brittle; consequently, easily cracked by low stress.[9] To overcome such toughness characters, a lot of efforts were made through modification of the structure of the resin itself, in particular, reformation by isocyanate compound.[10–12] Although developed chemical structures can alter bulk properties of epoxy such as the elastic modulus and glass-transition temperature, they have the disadvantage in heat-resisting properties and electrical properties, such as the dielectric constant (D_k) and dissipation (D_f) values. To solve these problems, the adamantane-containing epoxy resin diglycidyl ether of bisphenol-adamantane (DGEBAda) was reported and their dielectric constant was 3.74.[13]

We have recently reported the benzoate-group-substituted epoxy resin with low dielectric constant (D_k), low dielectric loss (dissipation values, Df), low coefficient of thermal expansion (CTE), and high adhesion properties.[14] Our strategy is that the introduction of benzoate group to the main chain, instead of the hydroxyl group in the common bisphenol A diglycidyl ether epoxy resin, apparently gives rise to increasing hydrophobic nature. Note that the D_k value of water is 78.[15] In present study, through esterification using

---

[*] Author to whom correspondence should be addressed.
[†] These two authors contributed equally to this work as first authors.

1533-4880/2016/16/3009/005 doi:10.1166/jnn.2016.11117



Scheme 1. Preparation of phenolic isocyanate-modified bisphenol-based epoxy resins comprising benzoate group.

bisphenol A dibenzolate, we report the novel phenolic isocyanate-modified bisphenol-based epoxy resins comprising benzoate group (Scheme 1) for various practical electronic packaging applications.

2. EXPERIMENTAL DETAILS

2.1. Materials

Bisphenol A diglycidyl ether (SE-187) was supplied from our commercial product line from Shin-A T&C Co. Bisphenol Z diglycidyl ether was prepared as below method. The preparation of bisphenol A dibenzolate was based on our previous report. 2-Ethyl-4-methylimidazole was utilized as a catalyst. All the chemicals in this work were used as received from Aldrich Chemical Co. without further purification.

2.2. Measurements

^{1}H spectra were recorded on a Bruker AVANCE 300 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. The epoxy equivalent weights (EEW) were determined by the HBr-acetic acid method.[16] IR measurements were performed on a 6030 Mattson Galaxy Series FT-IR spectrometer; 64-200 scans were signal-averaged at a resolution 2 cm^{-1}. IR Spectroscopic characterization was performed using a pressure cell equipped with quartz and CaF_2 windows. Coefficient of thermal expansion (CTE, based on ASTM E831) and thermogravimetric analysis (TGA) were performed with Mettler Toledo TMA and TGA devices at a heating rate of 10 °C/min, respectively. The D_k and D_f were measured by an RF impedance Material Analyzer (Agilent Co., E4991A, based on JIS-C-6481).

3. RESULTS AND DISCUSSION

Phenolic isocyanate-modified bisphenol-based epoxy resins comprising benzoate group was prepared through 2 step, as shown Scheme 1.

Delivered by Ingenta to: Chinese University of Hong Kong
IP: 37.9.40.66 On: Mon, 24 Oct 2016 16:42:46
Copyright: American Scientific Publishers

Bisphenol Z diglycidyl ether: 4,4′-Cyclohexylidenebisphenol (268.35 g, 1 mol) and epichlorohydrin (740 g, 8 mol) were dissolved in isopropyl alcohol 300 g. NaOH (50% wt. aqueous solution, 192 g) was added dropwise to the reaction vessel, and the reaction allowed to proceed for 4 hr at 50 °C. Removing the residual epichlorohydrin through vacuum, and then NaCl was washed with water ^{1}H NMR ($CDCl_3$, 300 MHz, ppm, TMS): δ 1.43 (6 H of cyclohexane), 2.1 (4 H of cyclohexane), 2.85 (2 H of *oxiran*), 2.92 (2 H of *oxiran*), 3.15 (2 H of *oxiran*), 3.95 (2 H of *methylene*), 4.08 (2 H of *methylene*), 6.9 (4 H of *benzene*), 7.2 (4 H of *benzene*). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm, TMS): δ 158.4, 141.8, 128.4, 114.5, 77.6, 69.0, 50.4, 44.9, 37.6, 23,2.

Poly[(phenyl oxazolidinone bearing bisphenol-based epoxy)-co-formaldehyde] (**P1**, **P2**): Two kinds of bisphenol-isocyanate modified epoxy were prepared. Bisphenol A diglycidyl ether (186 g/eq) and bisphenol Z epoxy (205 g/eq) were respectively allowed to react with poly((phenyl isocyanate)-co-formaldehyde) (Mn∼375). Poly[(phenyl isocyanate)-co-formaldehyde] (100 g) and bisphenol A (or Z) diglycidyl ether (900 g) was loaded into the reaction vessel in the presence of an imidazole catalyst (0.5 g), 2-ethyl-4-methyl-imidazole, and the reaction was allowed to proceed at 150 °C for 2 hr. ^{1}H NMR of **P1** ($CDCl_3$, 300 MHz, ppm, TMS): δ 1.60 ($-CH_3$), 2.78 ($-CH_2$ in oxirane), 2.86 ($-CH_2$ in oxirane), 3.37 (–CH in methine), 3.94 ($-CH_2-O$), 4.19 ($-CH_2-O$) 4.22 (methylene), 6.81 (benzene or phenol), 7.16 (benzene or

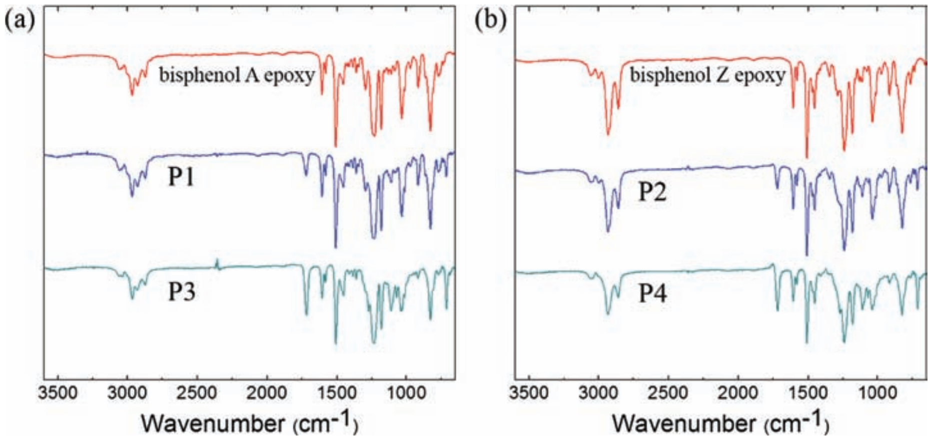


Figure 1. FT-IR spectra of (a) bisphenol A based and (b) bisphenol Z based epoxy resin.

phenol), 7.46 (–CH phenol). ^{1}H NMR of **P2** ($CDCl_3$, 300 MHz, ppm, TMS): δ 1.44 (–CH_2 in cyclohexane), 1.62 (–CH_3), 2.1 (–CH_2 in cyclohexane), 2.78 (–CH_2 in oxirane), 2.86 (–CH_2 in oxirane), 3.37 (–CH in methine), 3.94 (–CH_2–O), 4.19 (–CH_2–O) 4.2 (methylene), 6.81 (benzene or phenol), 7.16 (benzene or phenol), 7.44 (–CH phenol).

Poly[(phenyl oxazolidinone bearing bisphenol-based epoxy)-co-formaldehyde] comprising benzoate group (**P3**, **P4**): **P3** or **P4** was prepared from **P1** or **P2** (100 g) and bisphenol A dibenzolate (20 g) via the transesterification reaction[9] in the presence of an imidazole catalyst (0.02 g), 2-ethyl-4-methyl-imidazole, and the reaction was allowed to proceed at 180 °C for 5 hr. ^{1}H NMR of **P3** ($CDCl_3$, 300 MHz, ppm, TMS): δ 1.60 (–CH_3), 2.78 (–CH_2 in oxirane), 2.86 (–CH_2 in oxirane), 3.37 (–CH in methine), 3.94 (–CH_2–O), 4.17 (–CH_2–O) 4.38 (methylene), 5.62 (methine), 6.81 (benzene or phenol), 7.16 (benzene or phenol), 7.39 (benzoate), 7.46 (–CH in phenol), 7.57 (1H of benzoate), 8.02 (2H of benzoate). ^{1}H NMR of **P4** (CDCl3, 300 MHz, ppm, TMS):): δ 1.44 (–CH_2 in cyclohexane), 1.62 (–CH_3), 2.1 (–CH_2 in cyclohexane), 2.78 (–CH_2 in oxirane), 2.86 (–CH_2 in oxirane), 3.37 (–CH in methine), 3.94 (–CH_2–O), 4.19 (–CH_2–O), 4.3 (methylene), 5.62 (methine), 6.81 (benzene or phenol), 7.16 (benzene or phenol), 7.39 (benzoate), 7.46 (–CH in phenol), 7.57 (1H of benzoate), 8.02 (2H of benzoate). Note that ^{1}H signal of the carbinol methine proton in was appeared at about 5.6 ppm in **P3** or **P4**, which was not observed in **P1** or **P2** state.

Figure 1 shows the FT-IR spectra for epoxy resins prepared as described above. The characteristics absorption bands of the glycidyl group of epoxide were observed at 920 and 835 cm^{-1} in addition to the absorption peaks at 3048 and 1178 cm^{-1}, indicating the presence of an aromatic ring in every epoxy compound. The reaction of cyano and epoxide was confirmed by IR spectrum: $\upsilon_{C=O}$ absorbance at 1720 cm^{-1} i.e., the carbonyl peak of oxazolidone group in **P1** and **2**. After esterification, in particular, the absorption of epoxide peak appeared at around 920 cm^{-1} for **P3** and **P4** decreased when the epoxide was reacted with bisphenol A dibenzolate. Conversely, the absorbance at 1720 cm^{-1} increased due to the carbonyl peak of benzoate group. Thus, these FT-IR spectra could demonstrate the preparation of phenolic-isocyanate-modified bisphenol-based epoxy resins comprising benzoate group.

Delivered by Ingenta to: Chinese University of Hong Kong
IP: 37.9.40.66 On: Mon, 24 Oct 2016 16:42:46
Copyright: American Scientific Publishers

The resin properties such as epoxy equivalent weight (E.E.W), water absorption values and thermal property were summarized in Table I (5 times test and their average value). After introduction of polymeric isocyanate, the formation of oxazolidone led to the increased glass-transition temperature in **P1** and **P2**. Also, due to the hydrophilic

Table I. Characterization of epoxy resins.

Epoxy resin	E.E.W.^{a}/g equiv^{-1}	T_g^b/°C	CTE (°)^C ppm	Water uptake	Td_5^d/°C	D_k	D_f
						at 1 GHz	
bisphenol A	187	145.5	66.2	0.47	397.6	3.22	0.023
P1	224.6	153.3	57.9	0.54	393.1	3.21	0.022
P3	377.55	119.6	59.2	0.35	384.1	3.09	0.016
bisphenol Z	205	146.8	69.1	0.53	398.2	3.17	0.025
P2	272.8	174.7	57.4	0.61	396.7	3.16	0.020
P4	495.2	130.0	68.9	0.41	387.2	3.00	0.014

Notes: ^{a}Determined by the HBr acetic acid method; ^{b}Determined by differential scanning calorimetry; ^{c}Calculated by thermomechanical analysis; ^{d}Determined by thermogravimetric analysis.

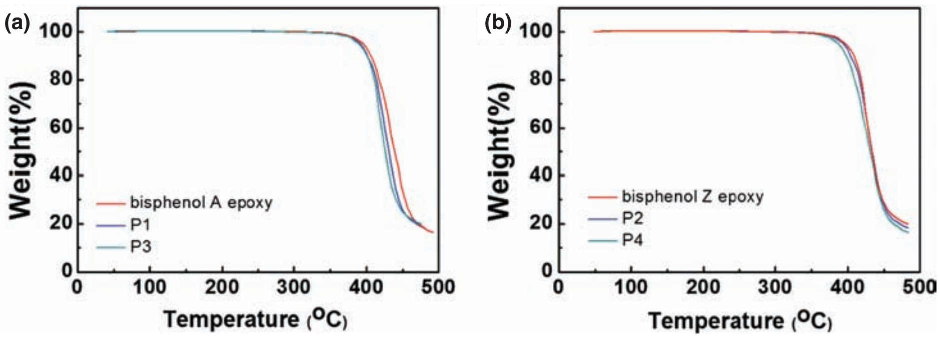


Figure 2. TGA of (a) bisphenol A based and (b) bisphenol Z based epoxy resin.

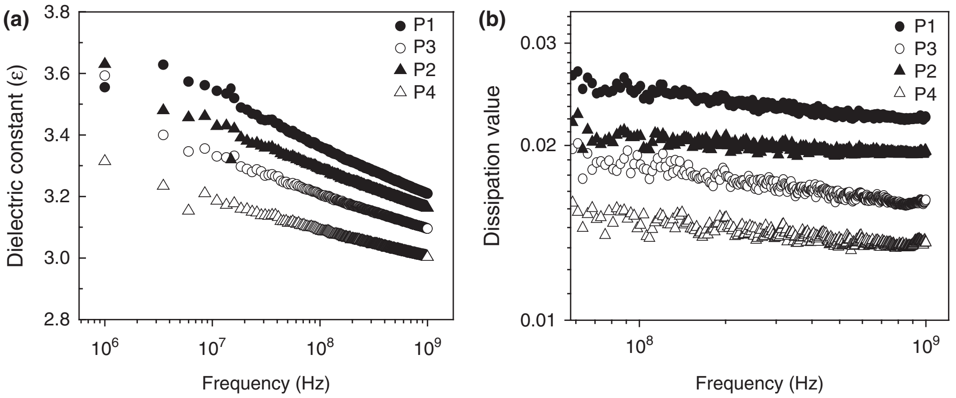


Figure 3. (a) Frequency-dependent dielectric constant, and (b) dissipation value of epoxy resins.

Delivered by Ingenta to: Chinese University of Hong Kong
IP: 37.9.40.66 On: Mon, 24 Oct 2016 16:42:46
Copyright: American Scientific Publishers

property of oxazolidone, the water absorption values of **P1** and **P2** slightly increased, which were not desirable. However, after esterification, the water absorption values of **P3** and **P4** were improved by increasing the portion of hydrophobic moiety, i.e., benzoate, in molecular structure.

To investigate the thermal stability for developed epoxy resins, TGA was performed at a heating rate of 10 °C/min, as shown in Figure 2. 5% weight loss temperature (Td_5) relatively decreased to 384 °C and 387 °C for **P3** and **P4**, respectively. However, these values could be still regarded as stable. Therefore, it could be concluded that the effect of the introduction of polymeric isocyanate or benzoate group on the thermal stability is not critical or negligible.

Figure 3 shows the dielectric properties of the developed epoxy resins. For the applications of high-frequency appliances, the D_k and D_f values are very important factors. In the case of the cured sample of **P3**, its D_k and D_f values were 3.09 and 0.016 at 1 GHz, respectively.

On the other hand, in the case of the cured sample of **P4**, its D_k and Df values were 3.00 and 0.013 at 1 GHz, respectively. Compared with **P1** or **P2**, the decreased dielectric constant and dissipation value of both **P3** and **P4** were attributed to its increased hydrophobic character caused by substitution of the benzoate group. From these results, **P3** and **P4** would be expected to be applicable to various applications employing electrical devices.

4. CONCLUSIONS

In summary, the phenolic isocyanate-modified bisphenol-based epoxy resins comprising benzoate group were synthesized from the commercial product line, and thermal and dielectrical properties (D_k and D_f) were investigated. The polymeric isocyanate modified epoxy resins, **P1** and **P2**, showed lower coefficient of thermal expansion (CTE) than the corresponding bisphenol A and Z epoxy. More curiously, phenolic isocyanate-modified bisphenol-based epoxy resins comprising benzoate group, **P3** and **P4**, exhibited low water absorption values and intriguing dielectrical behavior, which were ascribed to the hydrophobic character of benzoate group.

References and Notes

1. X. Huang, C. Zhi, P. Jiang, D. Golberg, Y. Bando, and T. Tanaka, *Adv. Funct. Mater.* 23, 1824 **(2013)**.
2. J. Alam, S. H. Ryu, and A. M. Shanmughara, *Sci. Adv. Mater.* 7, 993 **(2015)**.
3. X. Y. Huang, T. Iizuka, P. K. Jiang, Y. Ohki, and T. Tanaka, *J. Phys. Chem. C* 116, 13629 **(2012)**.
4. K. C. Yung, B. L. Zhu, T. M. Yue, and C. S. Xie, *Appl. Polym. Sci.* 116, 518 **(2010)**.
5. S. Shin, D. G. Lim, T. Kang, H. Chun, and J. K. Cho, *Polym. Int.* 61, 1411 **(2012)**.
6. J. D. Boysere and A. Beard, *Circuit World* 32, 8 **(2006)**.
7. N. Patton, *Circuit World* 33, 28 **(2007)**.
8. B. Hoevel, L. Valette, and J. Gan, *Circuit World* 33, 17 **(2007)**.

9. S. Lu and I. Hamerton, *Prog. Polym. Sci.* 27, 1661 (**2002**).

10. M. Flores, X. Fernández-Francos, J. M. Morancho, À. Serra, and X. Ramis, *J. Appl. Polym. Sci.* 125, 2779 (**2012**).

11. K. S. Chian and S. Yi, *J. Appl. Polym. Sci.* 82, 879 (**2001**).

12. V. Sendijarevic, A. Sendijarevic, K. C. Frisch, and P. Reulen, *Polym. Composite* 17, 180 (**1996**).

13. X. Su and X. Jing, *J. Appl. Poly. Sci.* 106, 737 (**2007**).

14. E. Y. Lee, I. S. Chae, J. Hong, and S. W. Kang, *Ind. Eng. Chem. Res.* 52, 15713 (**2013**).

15. D. Pan, L. Spanu, B. Harrison, D. A. Sverjensky, and G. Galli, *Proc. Natl. Acad. Sci. USA* 110, 6646 (**2013**).

16. T. Nishikubo and A. Kameyama, *Prog. Polym. Sci.* 18, 963 (**1993**).

Received: 21 February 2015. Accepted: 21 March 2015.

Delivered by Ingenta to: Chinese University of Hong Kong
IP: 37.9.40.66 On: Mon, 24 Oct 2016 16:42:46
Copyright: American Scientific Publishers