

Synthesis and Characterization of Novel Dihydrobenzoxazine Resins

Jeng-Yueh Shieh,¹ Chi-Y. Lin,² Chine-Lin Huang,² Chun-Shan Wang²

¹Department of Industrial Safety and Hygiene, Chun Haw College of Medical Technology, Tainan, Taiwan, Republic of China

²Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, Republic of China

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ABSTRACT: Three dihydrobenzoxazines are synthesized from bisphenol A (BPA), 4,4'-biphenol (BIP), and dicyclopentadiene phenol adduct (DCPD). Polydihydrobenzoxazine containing 4,4'-biphenol (BIPDB) had the most rigid structure of the three and was found to possess the best mechanical and thermal properties. The glass transition temperature of BIPDB was 206°C, and that of BPA-type polydihydrobenzoxazine (BPADB) and dicyclopentadiene type polydihydrobenzoxazine (DCPDDB) were 184 and 183°C, respectively. DCPDDB, with a rigid hydrophobic cy-

cloaliphatic structure, was found to possess excellent properties such as low moisture absorption, low dielectric constant, low polarization. The resulted polymer from DCPDDB had a dielectric constant of 2.94U, which was better than that of polymers derived from BPA (3.31U), BIP (3.45U), and traditional phenolic resin (3.9–4.0U). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 342–347, 2006

Key words: glass transition; thermal properties; dielectric properties

INTRODUCTION

Polybenzoxazines, as a class of thermosetting phenolic resins, offer a number of attractive properties, including high glass transition temperature, high thermal stability, good mechanical properties, and a wide molecular design flexibility.^{1–7} It is well known that benzoxazines possess a number of inherent processing benefits such as low melt viscosity, no release of volatiles during cure, and no need for harsh catalysts to initiate polymerization. In addition, polybenzoxazines possess low water absorption values, good electrical properties, in addition to zero shrinkage or slight expansion upon cure.^{3,8}

Benzoxazines have been used widely in industries, such as in fiber-reinforce laminates, brake shoes for trains, and injection molding.^{9–11} Polymeric materials also play a vital role in electronic packages as a result of their ease of processing, low cost, low dielectric constant, adhesive properties, etc. Moreover, many properties of polymers can be easily improved or altered by preparation of polymer blends or composites.^{12–14}

Electronic applications include printed-wiring circuit boards, thin cards, multichip module laminates

(MCM-L), chip encapsulations, and as a sheet molding compound (SMC).^{15–19} Resin compositions, comprising low melt viscosity polybenzoxazine, have been demonstrated to be useful as die attach adhesives, underfills, and encapsulants, where the characteristics of the resins can be varied in a wide range by copolymerization with functionalized comonomers such as epoxies, phenolics, thermoplastics, and others.^{16,20} The cured resins from benzoxazine compound and epoxy resin or bisoxazine had superior heat resistance, electrical insulation, and water resistance to those of the cured resin from conventional bisphenol A (BPA)-type novolac and epoxy resin or bisoxazoline.^{21–23}

Dicyclopentadiene (DCPD) is a byproduct of C₅ streams in oil refineries, with low cost and high reactivity, and has been incorporated into the polymer backbone.^{24,25} Our previous study²⁵ has demonstrated that this hydrophobic, nonpolar bridging group has contributed to excellent moisture resistance and to a dramatic reduction in the dielectric constant without detrimentally affecting thermal performance, while maintaining epoxy-like processability. Polymers with biphenyl linkages can lead to excellent mechanical properties, low moisture absorption, and thermal expansion.^{26–28}

The objective of this study was to develop a novel DCPD benzoxazine resins with properties such as low dielectric and low dissipation factor for high frequency application, while the polybenzoxazine with rigid biphenyl structure will provide high glass transition temperature and mechanical properties. The

Correspondence to: J.-Y. Shieh (jyshieh@mail.hwai.edu.tw).

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structures of all benzoxazines were characterized by infrared spectroscopy (IR), mass spectroscopy (MS), nuclear magnetic resonance spectroscopy (NMR), and elemental analyses (EA). The resultant benzoxazine resins were cured and their properties were evaluated by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and dielectric analysis (DEA). These test results are compared with those of the BPA-type dihydrobenzoxazine (BPADB).

EXPERIMENTAL

Materials

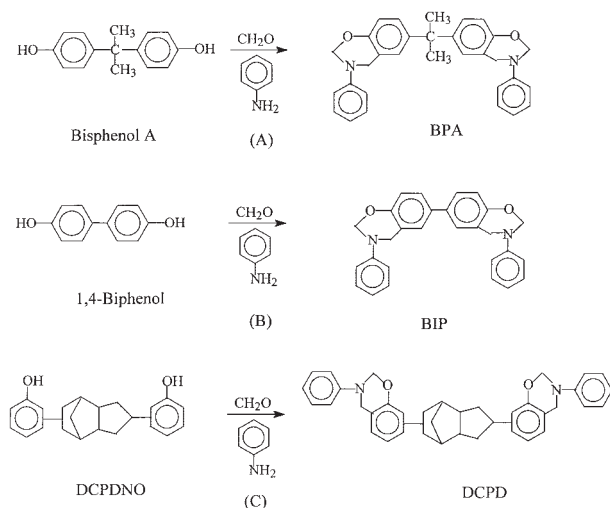
All reagents and solvents were reagent grade or were purified by standard methods before use. 1,4-Dioxane from TEDIA was used as received. Aniline, formaldehyde, bisphenol-A, 4,4'-biphenol (BIP), and sodium chloride from Acros were used as received. Toluene, acetone, and methanol from Acros were used as solvent and purified before use. Aluminum trichloride was used as a catalyst. DCPD phenol novolac (DCP-DNO) was prepared in our laboratory.²⁵

Measurements

¹H NMR spectra were obtained using a Bruker Avance-600 spectrometer, using DMSO-*d*₆ as a solvent. Elemental analyses were carried out with a Heraeus CHN-Rapid elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-550 spectrometer, with KBr pellets or using 10–15 μm film. Spectra in the optical range of 400–4000 cm⁻¹ were obtained by averaging 32 scans at a resolution of 4 cm⁻¹. Differential scanning calorimeter (PerkinElmer DSC-7) measurements were used in this work. Samples of approximately 5–10 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate of 10°C/min in the range of 50–340°C under N₂ atmosphere, and the glass transition temperature (*T*_g) values were obtained as the change of the specific heat in the heat flow curves. Thermogravimetric analyses (TGA) were performed on a PerkinElmer TGA-7 thermal analyzer, using a heating rate of 10°C/min in N₂ at a purge pressure of 25 psi, within the temperature range of 100–800°C. The dielectric constant and dissipation factor were measured with an Agilent 4291B measurement system at 30°C in a nitrogen atmosphere at a flow rate of 500 cm³/min by the two parallel-plate mode at 1 GHz. The applied voltage was 1 V.

Synthesis of BPADB

To a 500 mL reaction vessel equipped with a temperature controller, overhead stirrer, and a reflux condenser were added 34.2 g BPA, 48.6 g formalin, and

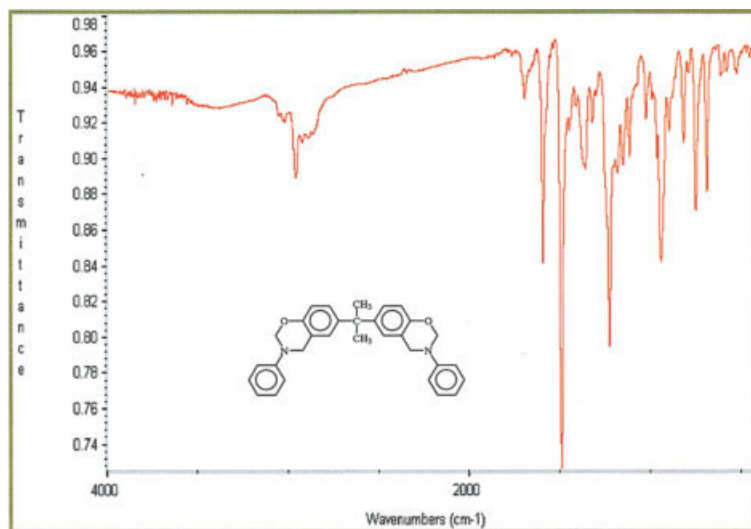


Scheme 1 The synthesis of benzoxazines of (A) BPA, (B) BIP, and (C) DCPD.

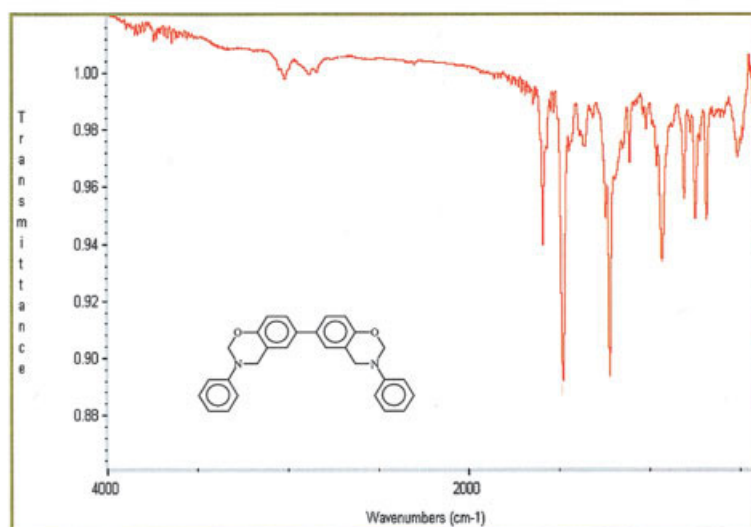
100 mL 1,4-dioxane as solvent. The mixture was first heated and stirred slowly at 30°C to dissolve the reactants. A mixed solution of 27.9 g aniline and 30 mL 1,4-dioxane was added dropwise into the vessel. The reaction mixture was heated to reflux temperature (145°C) and maintained at that temperature for 5 h to complete the reaction. The solvent was removed under vacuum and the residual yellow solid was collected. The solids were dissolved in 300 mL ethyl ether and washed several times with deionized water after a 3N aqueous NaOH and 1N aqueous HCl washes. The yellowish powder of BPA benzoxazine was obtained after the solvent was removed under vacuum (yield 89%; mp 110–112°C). The reaction is shown in Scheme 1(A). The IR spectrum of BPA-type benzoxazine is shown in Figure 1(A). As the reaction proceeded, the distinctive absorption at 3650–3300 cm⁻¹ for phenolic OH stretching disappeared, while an absorption at around 1327 cm⁻¹ for —CH₂— and 1032 cm⁻¹ for —C—O—C— stretching on benzoxazine ring appeared and absorption at around 1500 and 950 cm⁻¹ for trisubstituted benzene as benzoxazine ring appeared. Consequently, this reaction could be monitored by means of these absorptions. The shift and splitting pattern of ¹H NMR spectrum was δ 1.55 (6H, —CH₃), δ 4.58(4H, —N—CH₂—Ph), δ 5.35 (4H, —N—CH₂—O), δ 6.55–7.24 (16H, Ph—H). Anal. Calcd for C₃₁H₃₀N₂O₂: C, 80.50; H, 6.49; N, 6.00. Found: C, 80.00; H, 6.56; N, 6.08. EIMS, *m/z*: 462 (96. M⁺).

Synthesis of biphenyl-type benzoxazine (BIPDB)

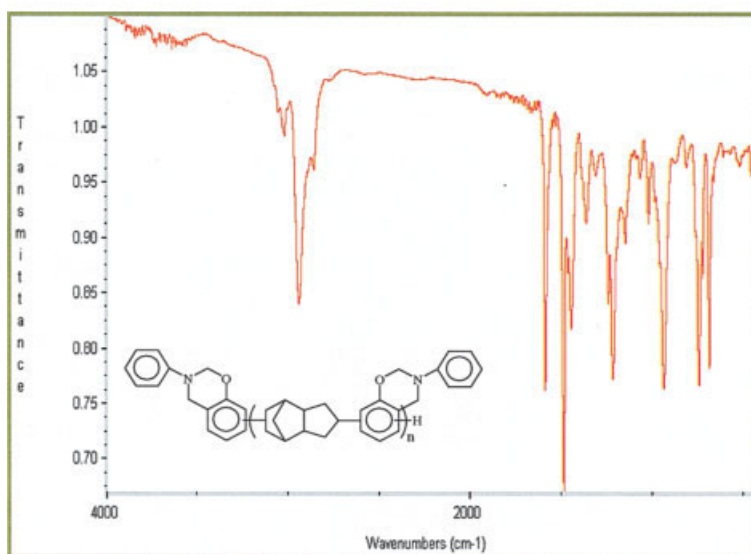
To a 500 mL reaction vessel equipped with a temperature controller, overhead stirrer, and a reflux condenser were added 27.9 g (0.15 mol) BIP, 48.6 g (0.6 mol) formalin, and 100 mL 1,4-dioxane as solvent. The



(A)



(B)



(C)

Figure 1 IR spectra of (A) BPA, (B) BIP, and (C) DCPD benzoxazines. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

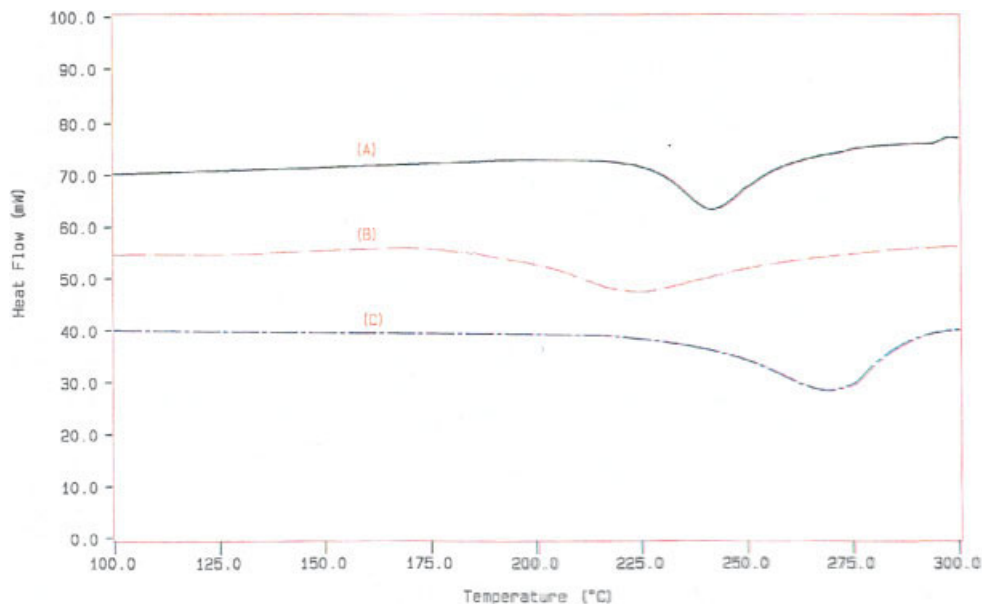


Figure 2 DSC thermograph of (A) BPA, (B) BIP, and (C) DCPD benzoxazines. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mixture was first heated and stirred slowly at 30°C to dissolve the reactants. A mixed solution of 27.9 g (0.3 mol) aniline and 30 mL 1,4-dioxane was added dropwise into the vessel. The reaction mixture was heated to reflux temperature (145°C) and maintained at that temperature for 10 h to complete the reaction. The solvent was removed under vacuum and the residual yellow solid was collected. The collected solids were dissolved in 300 mL ethyl ether and washed several times with deionized water after a 3N aqueous NaOH and 1N aqueous HCl washes. The yellow powder of BIPDB was obtained after the solvent was removed under vacuum (yield 89%; mp 170°C). The reaction is shown in Scheme 1(B). The conversion of the biphenol to the BIP benzoxazine was confirmed by the disappearance of the —OH proton in ^1H NMR and IR spectra. The shift and splitting pattern of ^1H NMR spectrum was δ 4.71 (4H, —N—CH₂—Ph), δ 5.40 (4H, —N—CH₂—O), δ 6.55–7.24 (16H, Ph—H). Anal. Calcd for C₂₈H₂₄N₂O₂: C, 80.00; H, 5.71; N, 6.66. Found: C, 80.30; H, 5.73; N, 6.56. EIMS, m/z : 420 (38. M⁺). The IR spectrum of BIP benzoxazine is shown in Figure 1(B).

Synthesis of DCPD-type dihydrobenzoxazine (DCPDDB)

To a 500 mL reaction vessel equipped with a temperature controller, overhead stirrer, and a reflux condenser were added 33 g (0.2 mol) DCPDNO, which was prepared in our laboratory,²⁵ 32.4 g (0.4 mol) formalin, and 100 mL 1,4-dioxane as solvent. The mixture was first heated and stirred slowly at 30°C to dissolve the reactants. A mixed solution of 18.6 g (0.2 mol) aniline and 30 mL 1,4-dioxane was added drop-

wise into the vessel. The reaction mixture was heated to reflux temperature (145°C) and maintained at that temperature for 5 h to complete the reaction. The solvent was removed under vacuum and the residual yellow solid was collected. The collected solids were dissolved in 300 mL ethyl ether and washed several times with deionized water after a 3N aqueous NaOH and 1N aqueous HCl washes. The brown solid of DCPD benzoxazine was obtained after the solvent was removed under vacuum (yield 86%). The reaction is shown in Scheme 1(C). The conversion of the DCPDNO to the DCPD benzoxazine was confirmed by the disappearance of the —OH proton in ^1H NMR and IR spectra. The shift and splitting pattern of ^1H NMR spectrum was δ 1.36 (7H, aliphatic DCPD), δ 4.63 (4H, —N—CH₂—Ph), δ 5.42 (4H, —N—CH₂—O), δ 6.55–7.24 (16H, Ph—H). EIMS, m/z : 554 (40. M⁺). The IR spectrum of DCPD-type dihydrobenzoxazine (DCPDDB) was shown in Figure 1(C).

Curing procedure

The curing behaviors of various benzoxazines were examined by DSC. Representative thermograms of three monomers are shown in Figure 2. The benzoxazines were heated at 150°C, poured into a hot aluminum mold, and cured, according to the procedures shown in Table I.

RESULTS AND DISCUSSION

Dynamic viscoelastic analyses of cured benzoxazine resins

Dynamic viscoelastic analysis can give information on the microstructure of cured polymer. The $\tan \delta$ curve

TABLE I
The Curing Procedures for Benzoxazine Resins

	Precure step		Curing step		Postcure step	
	Temp (°C)	Time (h)	Temp (°C)	Time (h)	Temp (°C)	Time (h)
BPA	200	2	220	2	240	1
BIP	200	2	220	2	230	1
DCPD	230	2	250	2	270	2

for the control network exhibits a major relaxation observed in most thermoset polymers.²⁹ The transition corresponds to the major T_g of the cured benzoxazines above which significant chain motion takes place. Figure 3 shows the $\tan \delta$ of cured BPADB, BIPDB, and DCPDDB resins. The T_g 's of all cured benzoxazines were listed in Table II. The results indicate that the cured BIPDB had higher T_g (206°C) than that of cured BAPDB (184°C) and DCPDDB (183°C). The results may be attributed to the more densely packed structure and less free volume, which results in less intermolecular motion, of cured BIPDB than other benzoxazines. The balance of intramolecular and intermolecular motions determines the thermal properties of polymer.³⁰ However, T_g 's of three cured benzoxazines were above 180°C, much higher than traditional epoxy resin (~150°C) and epoxy-cyanate ester resin (~180°C).³¹

Thermal properties for cured benzoxazine resins

Thermogravimetric analysis (TGA) is the most favored technique for rapid evaluation in tracking and ranking the thermal stability and thermal degradation

behavior of various polymers. TGA results for various cured benzoxazine resins containing BPA, BIP, and DCPD structure are shown in Table II. The results indicate that BIPDB has better thermal stability than the others, because BIPDB has higher $T_{d5\%}$ degradation temperature (396°C) and higher char yield (58.7%) at 800°C. The results may also be attributed to its rigid structure.

Moisture absorption

Absorbed moisture acts as a plasticizer, which reduces the mechanical and thermal properties of cured resins. Moisture absorption will reduce T_g of a laminate material and may cause a popcorn effect when in contact with solder at a high temperature. Moisture absorption will also ionize ionic impurities (e.g., Cl^-) and, therefore, corrode an integrated circuit. Furthermore, moisture absorption will increase the dielectric constant of laminate board material. Therefore, lower moisture absorption is necessary for laminate materials.²⁵ Before the moisture absorption was tested, the sample was prepared as follows. The sample (1 cm × 1 cm × 0.1 cm) was dried in vacuo at 120°C until moisture had been expelled. After cooling to room temperature, the sample was weighed, placed in 100°C water for 24 h, and weighed again. The moisture absorption was calculated as the percentage weight gain, $(W/W_0 - 1) \times 100$, where W_0 is the weight of the sample before placed in water and W is the weight of the sample after it is immersed in 100°C water for 24 h.

The moisture absorptions of various cured benzoxazines are shown in Table II. The moisture absorption of cured DCPDDB is 0.21%, which is much lower than

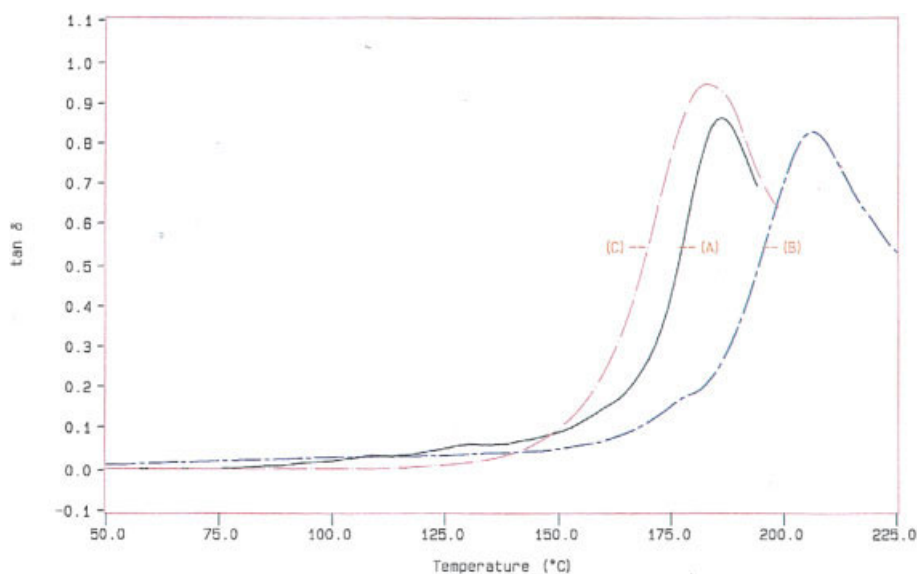


Figure 3 DMA analysis of benzoxazines of (A) BPADB, (B) BIPDB, and (C) DCPDDB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Thermal Moisture Absorption and Dielectric Properties of Cured Bezoxazine Resin

	T_g (°C)	$T_{d5\%}$ (°C)	Char yield at 800°C (%)	Moisture absorption	Dielectric constant at 1 MHz	Tan δ
BPADB	184	364	35.2	0.33	3.31	0.0145
BIPDB	206	396	58.7	0.51	3.45	0.0181
DCPDDB	183	391	30.5	0.21	2.95	0.0095

that of cured BPADB (0.33%) and BIPDB (0.51%). The low moisture absorption may be attributed to the hydrophobic nature of the cycloaliphatic DCPD structure.^{32,33}

Dielectric constant and dissipation factor

Agilent 4291B determines the dielectric constant and dissipation factor of a solid. Before testing, the cured 1 cm × 1 cm × 0.3 cm samples were dried in vacuo at 100°C for 8 h. It is clear from the results of Table II that the dielectric constant ($U_k = 2.95$) and dissipation factor ($\tan \delta = 0.0095$) of cured DCPDDB are much lower than those of cured BPADB and BIPDB.

The dielectric constant could be reduced by increasing the free volume of molecule or by decreasing the polarization.^{34–36} Hougham et al.³⁴ reported that the dielectric constant could be reduced by increasing the hydrophobicity and free volume and also by decreasing polarization of the molecule. The nonplanar structure of DCPD led to more spacing between polymer molecules, resulting in less efficient chain packing and an increase in the free volume of the polymer. Furthermore, the presence of low polar aliphatic DCPD linkages may reduce intermolecular electronic interaction and increase the hydrophobicity, thus decreasing the dielectric constant and dissipation factor.

CONCLUSIONS

Three dihydrobenzoxazines were synthesized, which contained the main structure of BPA, BIP, and DCPD. BIP had the most rigid structure of the three and hence possessed the best mechanical and thermal properties. The glass transition temperature of BIPDB was 206°C, and that of BPADB, and DCPDDB were 184 and 183°C, respectively. DCPD with a rigid cycloaliphatic structure possessed excellent properties such as low moisture absorption, low dielectric constant, and low polarization. The polymer from DCPD benzoxazine had a dielectric constant of 2.94U, which was better than that of polymers derived from BPA benzoxazine (3.31U), BIP (3.45U), and traditional phenolic resin (3.9–4.0U).

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