Flame Retardancy and Dielectric Properties of Dicyclopentadiene-Based Benzoxazine Cured with a Phosphorus-Containing Phenolic Resin

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ABSTRACT: A dicyclopentadiene-based benzoxazine (DCPDBZ) was prepared and separately copolymerized with melamine–phenol formaldehyde novolac or phosphorus-containing phenolic resin (phosphorus-containing diphenol) at various molar ratios. Their curing behaviors were characterized by differential scanning calorimetry. The electrical properties of the cured resins were studied with a dielectric analyzer. The glass-transition temperatures were measured by dynamic mechanical analysis. The thermal stability and flame retardancy were determined by thermogravimetric analysis and a UL-94 vertical test. These data were compared with those of bisphenol A benzoxazine and 4,4′-biphenol benzoxazine systems. The effects of the diphenol structure and cured composition on the dielectric properties, moisture resistance, glass-transition temperature, thermal stability, and flame retardancy are discussed. The DCPDBZ copolymerized with phosphorus-containing novolac exhibited better dielectric properties, moisture resistance, and flame retardancy than those of the melamine-modified system. The flame retardancy of the cured benzoxazine/phosphorus-containing phenolic resins increased with increasing phosphorus content. The results indicate that the bisphenol A and 4,4′-biphenol systems with a phosphorus content of about 0.6% and the dicyclopentadiene system with a phosphorus content of about 0.8% could achieve a flame-retardancy rating of UL-94 V-0. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2413–2423, 2008

Key words: crosslinking; curing of polymers; dielectric properties; flame retardance; thermosets

INTRODUCTION

Polybenzoxazines can be thermally self-polymerized to produce a crosslinked network through their reactive heterocyclic ring opening at high temperatures in the absence/presence of a catalyst and without the formation of volatile byproducts.[1,2] The network exhibits a high glass-transition temperature (T_g), a high thermal stability, good mechanical properties, excellent electrical properties, and a flame retardancy superior to most epoxy resins. In addition, they provide low water absorption and also excellent dimensional stability because of a near-zero volumetric change upon polymerization. They have become one important class of thermosetting resins in various applications,[3–6] including electronic materials, matrix resins for fiberglass reinforced plastic (FRP), and adhesives.

Dicyclopentadiene (DCPD) is a byproduct of C_5 streams in oil refineries. It is a raw material for low dielectric polymers because of their low polarity, low moisture absorption, and relatively low cost. DCPD-containing thermosetting resins, such as epoxy,[7] dicyanate ester,[8–10] bismaleimide,[11] and bismaleimide–triazine resins,[12] have been developed by our laboratory. The hydrophobic, nonpolar bridging DCPD group contributes to excellent moisture resistance and a dramatic reduction in the dielectric constant without detrimentally affecting the thermal performance. Flame retardancy is now a must for electronic materials for more secure life safety. However, the cycloaliphatic structure of DCPD contains too many hydrogen atoms, which results in a lower flame retardancy. Although many studies have been devoted to benzoxazine (BZ) resins, few have been concerned with flame-retardant BZs containing large cycloaliphatic DCPD moieties.

Traditionally, to enhance flame retardancy, halogen (e.g., bromine, chlorine)-containing compounds or resins are added to electronic materials as a flame retardant. Tetrabromobisphenol A containing advanced epoxy resin shows flame-retardant properties, but halogenated compounds are known to generate toxic, corrosive fumes during combustion and also have the potential to corrode metal components. These drawbacks restrict its usage in electronic

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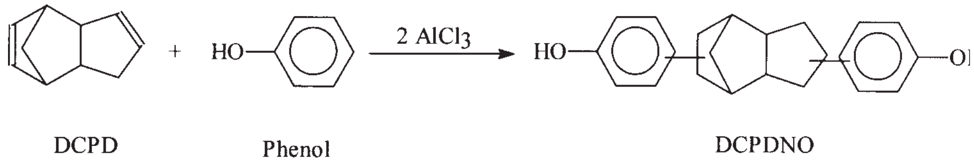


Scheme 1 Reaction of DCPD with phenol to form DCPDNO.

applications.[13–15] Moreover, compounds containing nitrogen (e.g., melamine)[16] and phosphorus have become attractive groups of flame retardants because they are environmentally friendlier than halogen. Their main advantages are a lack of dioxin and halogen acid byproduct formation and a lower evolution of smoke than halogen-containing compounds during combustion; they also exhibit a high flame retardancy.[17,18]

In this study, continuing our research on DCPD, we prepared dicyclopentadiene-based benzoxazine (DCPDBZ) from DCPD phenol adduct. Phosphorus-containing diphenol (DOPO-1X) and melamine–phenol formaldehyde novolac (MPN) containing reactive phenolic OH groups were used as potential flame retardants and were separately copolymerized with BZ at different levels through a ring-opening reaction. The flame retardancy and thermal stability were studied by a UL-94 test and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Bisphenol A benzoxazine (BPABZ) and 4,4′-biphenol benzoxazine (BIPBZ) were prepared as reported by our laboratory.[19] Bisphenol A, 4,4′-biphenol, DCPD, phenol, aniline, paraformaldehyde, and sodium hydroxide were purchased from Acros (Somerville, NJ) and were used as received. 1,4-Dioxane (Tedia Co., Fairfield, OH) was used as received. All other solvents (liquid chromatography (LC) grade) were obtained from various commercial sources and were used without further purification. MPN was received from Gun-Ei Chemical Co. (Takasaki, Japan; nitrogen content = 20%, OH equivalent weight = 148 g/equiv). DOPO-1X with an OH equivalent weight of 228 g/equiv and bearing 9,10-dihydro-9-oxa-10-oxide-10-phosphenanthene-10-yl (DOPO) was obtained from Forte Chemical Co. (Taiwan).

Monomer synthesis

Synthesis of dicyclopentadiene phenol novolac (DCPDNO)

The DCPDNO was synthesized by a modified procedure that was reported by our laboratory.[7] Phenol (1 mol, 94 g) and $AlCl_3$ (0.015 mol) were added to a four-necked round-bottom flask equipped with a nitrogen inlet, heating mantle, stirrer, thermocouple, and temperature controller. The reaction mixture was gradually heated to 120°C, and 0.1 mol of DCPD was added gradually over a period of 4 h. After the reaction was completed, 0.06 mol of 5 wt % aqueous NaOH was added, and the mixture was stirred for 1 h. The reaction mixture was filtered, and the filtrate was washed three times with deionized water. Next, the organic phase was separated and distilled in a rotary evaporator to remove excess phenol. The crude products were dissolved in toluene and extracted with warm water several times to remove any remaining trace phenol. The organic phase was finally distilled to remove the solvent, and then, the product was obtained in an almost quantitative yield. The reaction equation is shown in Scheme 1.

ANAL. Calcd for $C_{22}H_{24}O_2$: C, 82.50%; H, 7.50%. Found: C, 82.89%; H, 7.58%. Electron-impact mass spectrometry (*m*/*z*): 320 (60 M^+).

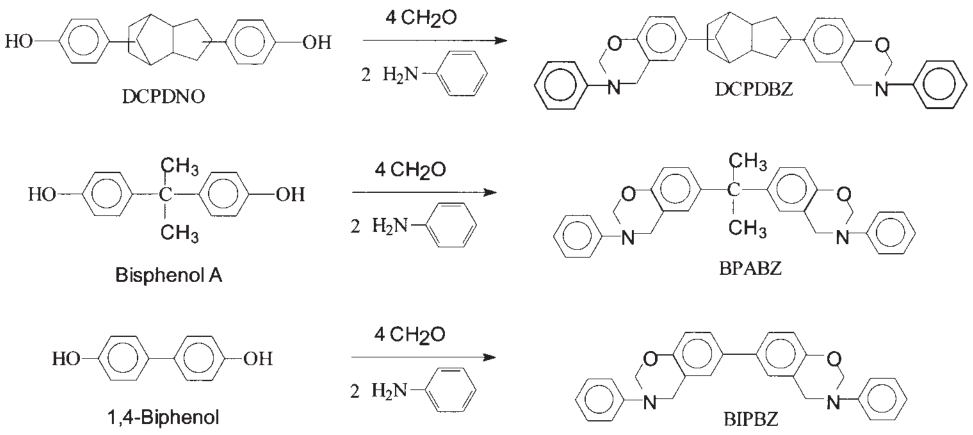
Synthesis of DCPDBZ

Various BZs were synthesized according to previously published procedures from our laboratory,[19] as shown in Scheme 2. DCPDBZ was synthesized as follows: to a 500-mL, round-bottom flask were added 0.1 mol of DCPDNO, 100 mL of 1,4-dioxane, and 32.4 g (0.4 mol) of 37% formalin. A mixed solution of 18.6 g (0.2 mol) of aniline and 30 mL of 1,4-dioxane was added dropwise to the previous mixture. The reaction mixture was heated to reflux for 5 h under a nitrogen atmosphere. After the completion of the reaction, the solvent and monomers were removed *in vacuo,* and the residual yellow solid was collected. The collected solid was dissolved in 300 mL of ethyl ether. It was washed with a 3*N* NaOH aqueous solution and a 1*N* HCl aqueous solution and was finally washed with deionized water several times. The brown product of DCPDBZ was obtained after the solvent was removed *in vacuo.* The yield was 86%.

ANAL. Calcd for $C_{38}H_{38}N_2O_2$: C, 82.31%; H, 6.86%; N, 5.05%. Found: C, 82.50%; H, 6.92%; N, 4.93%.

Measurement

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet (Madison, WI) Magna-520



Scheme 2 Synthesis of BZ monomers.

spectrometer with KBr pellets. Spectra in the optical range 400–4000 cm^{-1} were obtained by the averaging of 16 scans at a resolution of 4 cm^{-1}. ^{1}H-NMR spectra were registered with a Bruker (Rheinstetten, Germany) AC200 spectrometer with dimethyl sulfoxide-d_6 as the solvent. Mass spectrometric analyses were performed on a VG 70–250 gas chromatography/mass spectrometry spectrometer (VG Analytical, Manchester, UK). Differential scanning calorimetry (DSC) scans were obtained from about 5–10 mg samples in a nitrogen atmosphere at a heating rate of 10°C/min with a PerkinElmer (Norwalk, CT) DSC 7. TGA was performed with a PerkinElmer TGA 7 at a heating rate of 20°C/min under nitrogen from 30 to 800°C. The UL-94 vertical test was performed according to the FMVSS 302/ZSO 3975 testing procedure with a test specimen bar 127 mm long, 12.7 mm wide, and about 1.27 mm thick. Dynamic mechanical analysis (DMA) was carried out with a PerkinElmer DMA 7e. The tan δ were determined as the sample was subjected to a temperature scan mode at a programmed heating rate of 10°C/min from ambient to 250°C at a frequency of 1 Hz and an amplitude of 6 μm. A sample 15 mm in length, 10 mm in width, and approximately 1.5 mm in thickness was used. The test method was performed in the three-point bending mode with the tension ratio at 110%. Dielectric measurements were performed with a Agilent (Palo Alto, CA) 4291B measurement system at a temperature of 30°C in the two-parallel-plate mode at 1 GHz. The applied voltage was 1 V. Before testing, the samples (1 × 1 cm^2 and 0.3 cm thick) were dried *in vacuo* at 100°C for 8 h. Moisture absorption was tested as follow: Samples 1 × 1 cm^2 and 0.1 cm thick were dried *in vacuo* at 120°C until the moisture was expelled. After it was cooled to room temperature, the sample was weighed and then placed in 100°C water for 48 h and weighed again. The moisture absorption was calculated as

$$\text{Weight gain } (\%) = (W/W_0 - 1) \times 100\%$$

where W is the weight of the sample after placement in 100°C water for 48 h and W_0 is the weight of sample before placement in water. UL-94 is a testing method for flame retardancy. During the test, the polymer specimen was subjected to two 10-s ignitions. After the first ignition, the flame was removed, and the time for the polymer to self-extinguish for the first ignition (t_1) was recorded. Cotton ignition was noted if polymer dripping occurred during the test. After cooling, a second ignition was performed on the same sample, and the self-extinguishing time for the second ignition (t_2) and dripping characteristics were recorded. If t_1 + t_2 were less than 10 s with no dripping, it would be considered a V-0 material.

Curing procedure for the BZ/diphenol resins

BPABZ, BIPBZ, and DCPDBZ were separately cured with MPN and DOPO-1X. The reactant composition was mixed in various equivalent molar ratios. The mixture was crushed into a fine powder and then heated on a hot plate with continuous stirring until

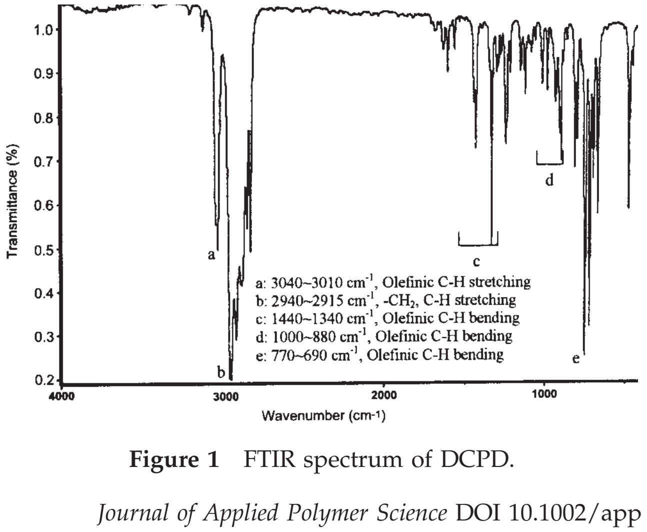


Figure 1 FTIR spectrum of DCPD.

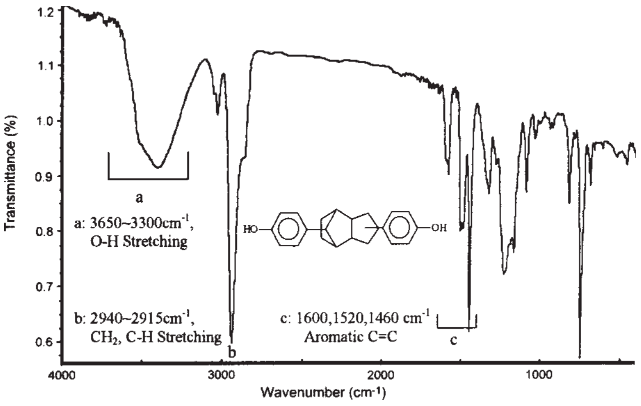


Figure 2 FTIR spectrum of DCPDNO.

a homogeneous solution was obtained. The mixture was cured at 200°C for 2 h, 220°C for 2 h, and 240°C for 1 h for the BPABZ and BIPBZ series. The DCPDBZ series was cured at 220°C for 2 h, 240°C for 2 h, 250°C for 2 h, and 270°C for 1 h. After that, the samples were allowed to cool slowly to room temperature to prevent cracking.

RESULTS AND DISCUSSION

Structure of the DCPDBZ monomer

The mechanism of DCPDNO formation may have been a two-step process. The first step was the reaction of DCPD with $AlCl_3$ to form carbocations with various possible structures, and then, the second step was the further reaction with phenol (Scheme 1). The IR spectra of DCPD and DCPDNO are shown in Figures 1 and 2, respectively. The characteristic absorption peaks of —HC=CH— at 770–690 and 3040–3010 cm^{-1} (from DCPD) disappeared, as shown in Figure 2, which implied that all of the —HC=CH— functional groups reacted with phenol. The characteristic absorption peaks of the aromatic ring at 1600, 1520, and 1460 cm^{-1} and the OH absorption peaks of novolac at 3650–3300 cm^{-1} are shown in Figure 2. The ^1H-NMR spectra of DCPD and DCPDNO are shown in Figures 3 and 4, respectively. The signals of the aliphatic hydrogens in DCPD in the range 1.2–3.2 ppm are shown in Figure 3. The ^1H-NMR signals at 5.4 and 5.9 ppm disappeared because of the olefinic protons of the —HC=CH— functional groups reacting with phenol. The characteristic peaks of the aromatic ring at 6.73–7.17 ppm and the OH absorption peaks at 8.0 ppm are all visible in Figure 4.

The desired BZ monomers were reported by one of the authors in a previous study.[19] The BZ monomer formation is described in Scheme 2. The DCPDBZ compound was synthesized from novolac (DCPDNO), aniline, and formalin. The typical IR spectrum of the DCPDBZ exhibited several distinctive absorptions, as shown in Figure 5. The distinctive absorption at 3650–3300 cm^{-1} for phenolic —OH stretching disappeared, whereas absorptions around 1322 cm^{-1} for the —CH_2 stretching of the BZ ring and 1233 cm^{-1} for C—O—C asymmetric stretching appeared. Additionally, the characteristic absorption assigned to the trisubstituted benzene ring at 950 cm^{-1} was also observed. Consequently this reaction could be monitored by means of these absorptions. Figure 6 shows the typical ^1H-NMR spectra of DCPDBZ. The conversion of DCPDNO to DCPDBZ was confirmed by the disappearance of the phenolic proton (—OH) of DCPDNO at 8.0 ppm in the ^1H-

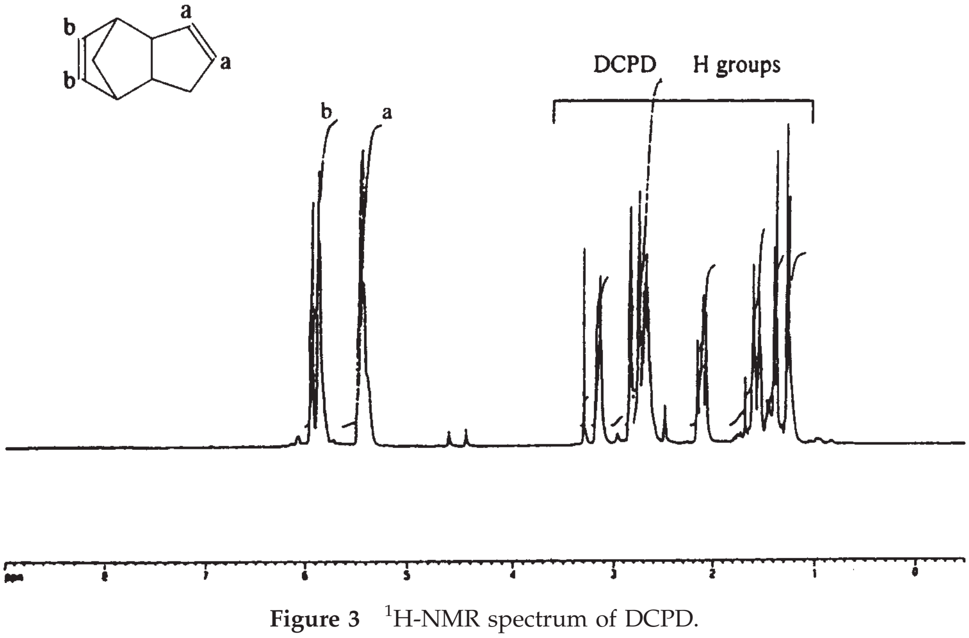


Figure 3 ^1H-NMR spectrum of DCPD.

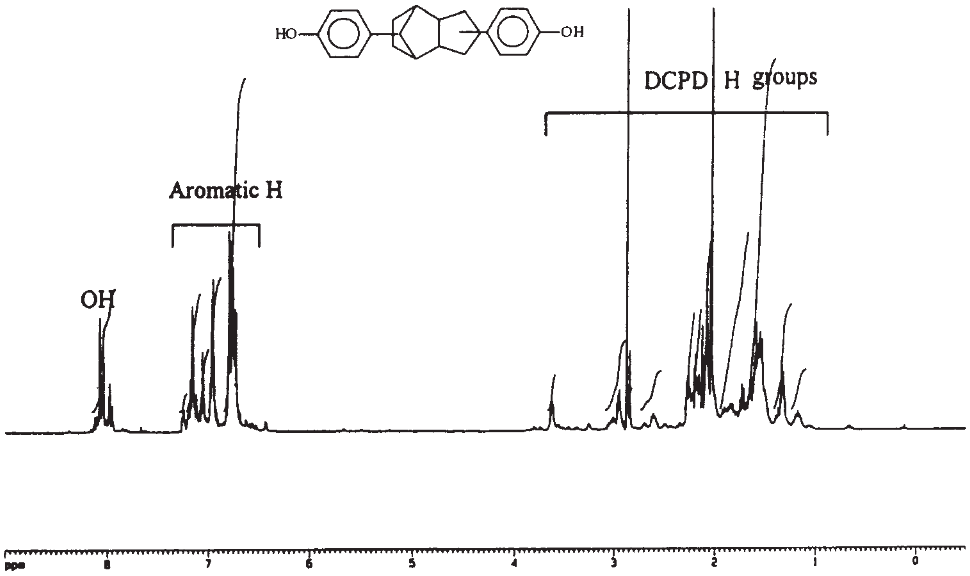


Figure 4 ^{1}H-NMR spectrum of DCPDNO.

NMR spectra. Additionally, the appearance of the characteristic peaks of O—CH$_2$—N at 5.35–5.4 ppm and Ar—CH$_2$—N at 4.58–4.7 ppm was also observed. The structure of DCPDBZ was in good agreement with the proposed structure.

DSC scans of the BZ/diphenol resins and their curing procedure

The curing reaction of the BZ compounds with various molar ratios of curing agents, including MPN and DOPO-1X, were monitored with DSC to evaluate the effect of the structure of the diphenols on the curing behavior of the cured resins. Figures 7 and 8 show the typical DSC scans for the BPABZ/MPN and BPABZ/DOPO-1X resins, respectively, with molar ratios of 100/0, 95/5, 90/10, 85/15, and 80/20. The onset temperature for the curing reaction (T_i) and the exothermic peak temperature (T_{exo}) are reported in Table I. The curing reactivity of the BZ could be judged by its T_i values. The neat BIPBZ had the lowest T_i (186°C), whereas DCPDBZ with the bulky DCPD ring in the backbone required a higher curing temperature (227°C) than BPABZ and BIPBZ.

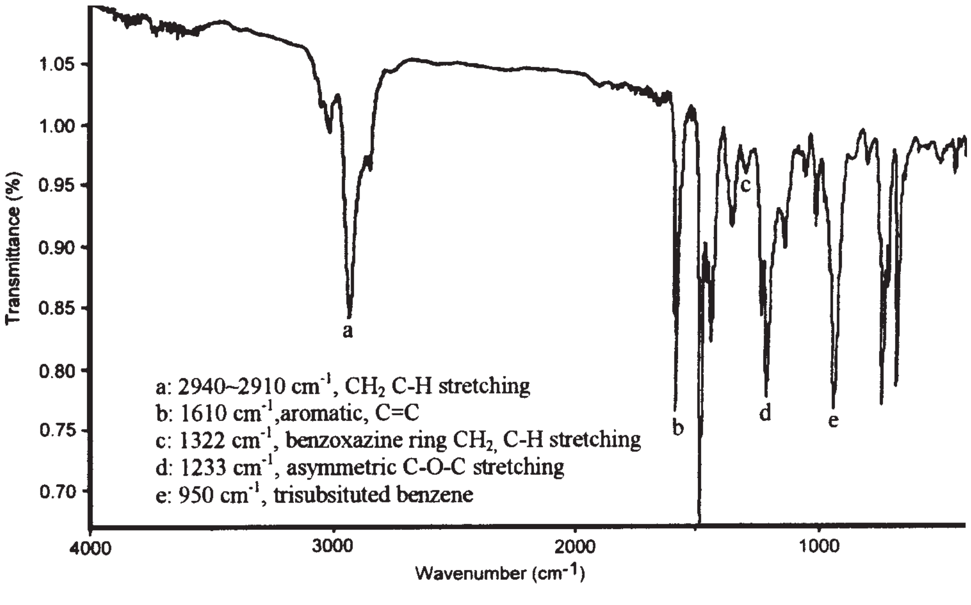


Figure 5 FTIR spectrum of DCPDBZ.

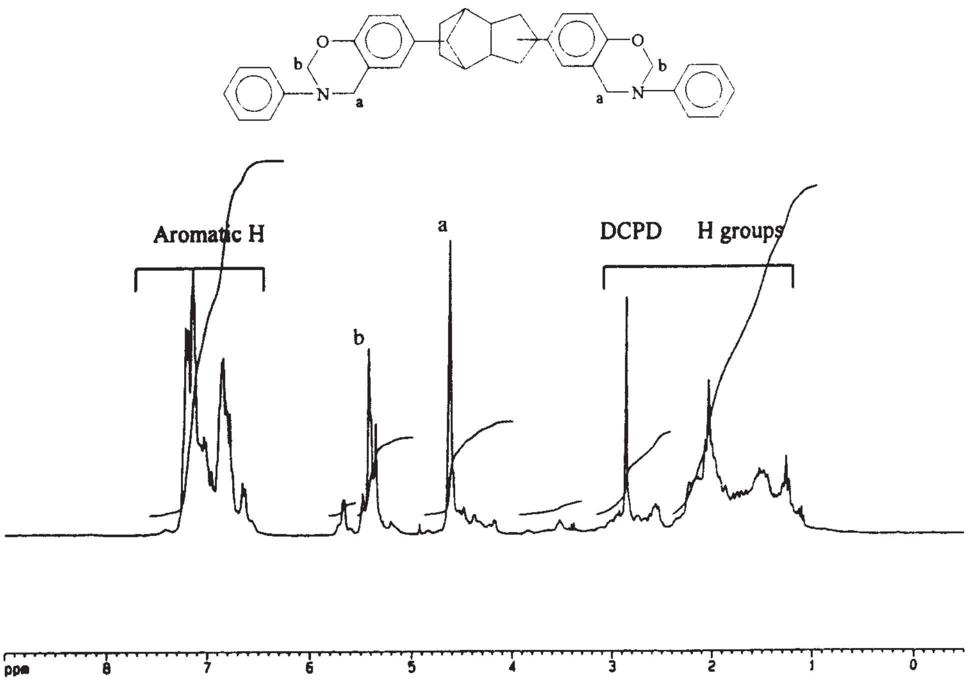


Figure 6 ^{1}H-NMR spectrum of DCPDBZ.

This was attributed to the steric hindrance of the bulky, cycloaliphatic DCPD structure in DCPDBZ, which reduced the reactivity and mobility of the reactive site. The chemical structure of BZ cured with diphenol is shown in Scheme 3.

The curing acceleration was observed from the shift of T_i and T_{exo} to lower temperatures when the amount of phenolic novolac resin (MPN or DOPO-1X) in the mixture increased. The relationship between the exotherm peaks and the amount of phenolic resin in the binary mixture suggested that phenolic hydroxyl groups may have acted as a catalyst with an accelerative effect on the ring-opening curing reaction of the BZ resin. This was in good agreement with past studies reported by Ishida and coworkers.[20–22]

Dielectric properties and water absorption

Table II shows the dielectric constants, dissipation factors, and water absorption values of cured BZ/

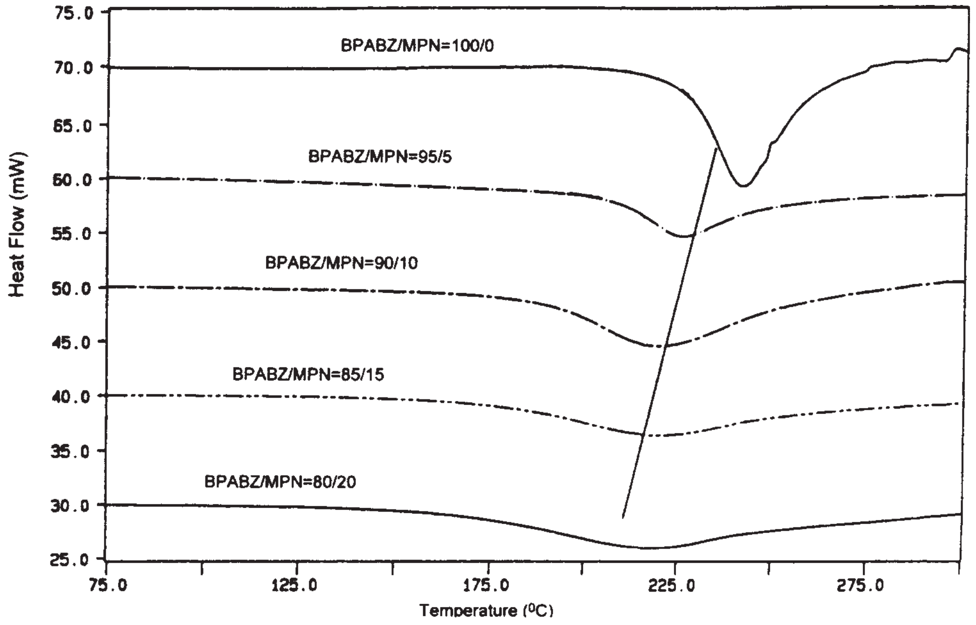


Figure 7 DSC analysis of the BPABZ/MPN resins with various molar ratios.

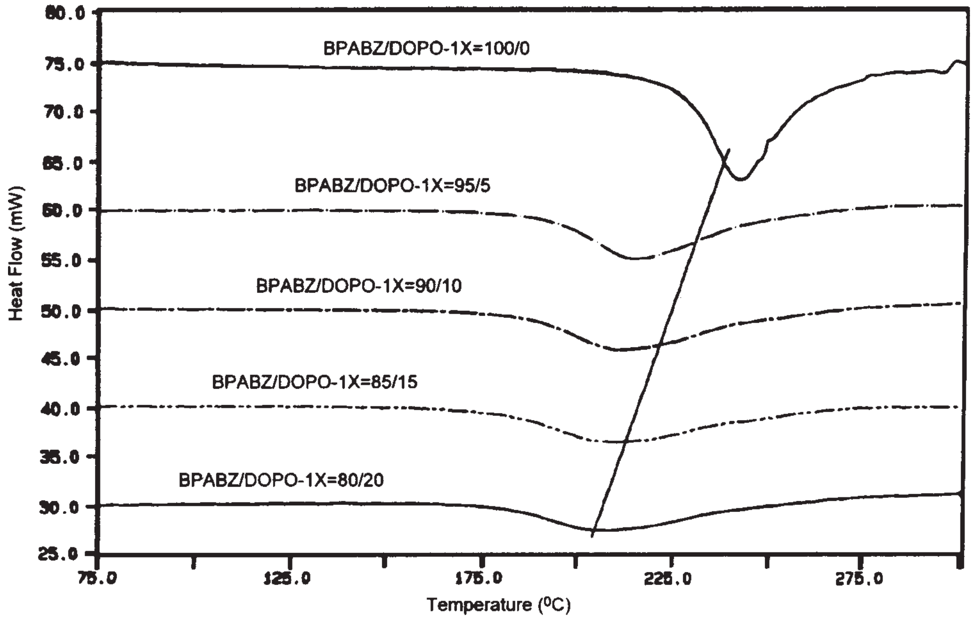


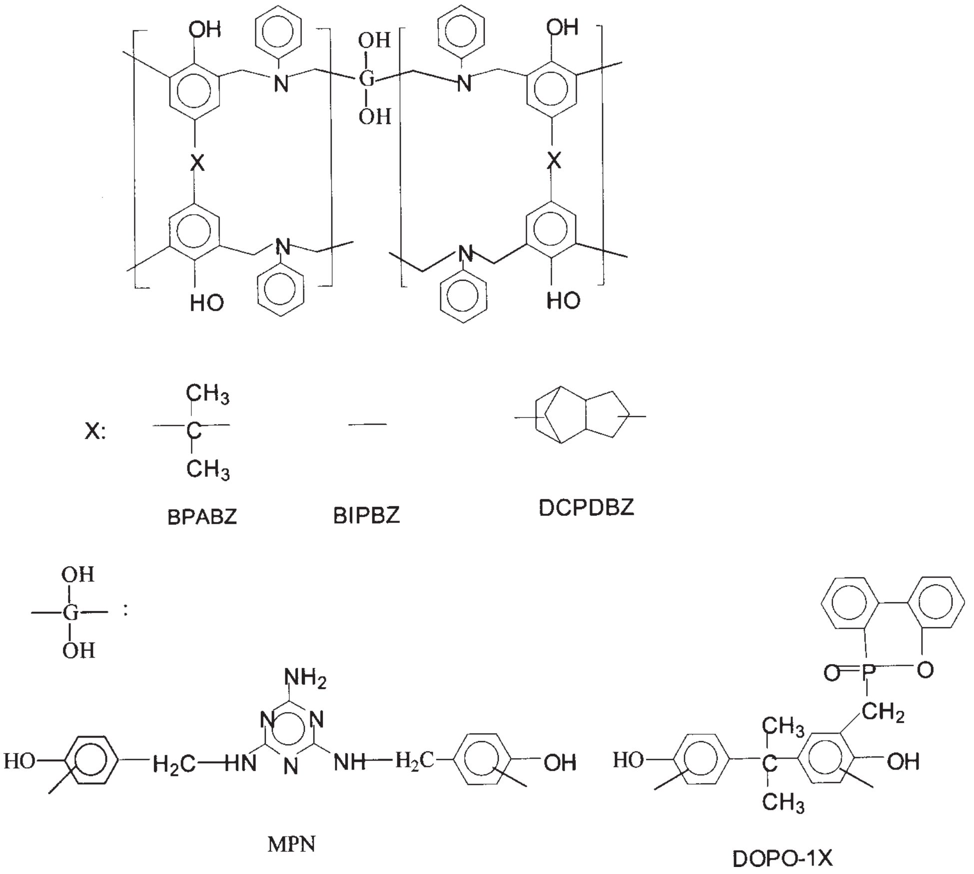
Figure 8 DSC analysis of the BPABZ/DOPO-1X resins with various molar ratios.

diphenol resins. No matter which molar ratio of BZ/diphenol was used, the dielectric constant, dissipation factor, and water absorption of the DCPDBZ systems were lower than those of the BPABZ and BIPBZ systems. The DCPD system, with low polar cycloaliphatic DCPD linkages, had reduced interchain electronic interaction and increased hydrophobicity, which thus decreased the dielectric constant, dissipation factor, and water absorption.

MPN with several amine groups (two NH groups and one NH_2 group) had a relatively large dipole moment, and its location on the backbone permitted considerable rotational freedom; this significantly affected the dielectric constant, dissipation factor, and water absorption. On the contrary, DOPO-1X possessed relatively low polarization and low hydrophilic characteristics. In addition, the bulky and rigid DOPO structure had a low rotational freedom because of a high degree of steric hindrance, which resulted in less efficient chain packing and an increase in the free volume of the polymers. Thus, BZ copolymerized with DOPO-1X had better dielectric properties than those copolymerized with the MPN systems. In addition, the higher the diphenol content in the formulation was, the higher the dielectric constant, dissipation factor, and water

TABLE I
Results of the Thermal Analysis of the Neat BZs and BZ/Diphenol Mixtures

		MPN		DOPO-1X	
	BZ/diphenol molar ratio	T_i (°C)	T_{exo} (°C)	T_i (°C)	T_{exo} (°C)
BPABZ	100/0	220	243	220	243
	95/5	204	226	188	213
	90/10	185	218	181	209
	85/15	179	215	177	206
	80/20	171	214	175	204
BIPBZ	100/0	186	227	186	227
	95/5	184	226	179	226
	90/10	182	225	175	224
	85/15	179	223	173	223
	80/20	175	222	170	220
DCPDBZ	100/0	227	268	227	268
	95/5	217	260	200	240
	90/10	206	257	193	236
	85/15	190	252	188	232
	80/20	183	245	181	228



Scheme 3 Structure of BZ cured with a diphenolic resin.

absorption of the cured resins were; this was attributed to an increase in the high polar sites of the diphenols, either from NH and NH_2 sites of melamine (MPN systems) or O=P—O groups of the cured resins (DOPO systems).

T_g values of the polymers

The T_g values of all of the cured resins with various molar ratios of BZ to diphenol were examined and are listed in Table III. The typical dynamic mechanical properties of the cured BZ/diphenol are shown

TABLE II
Dielectric Constant, Dissipation Factor at Room Temperature, and Moisture Absorption Values for the BZ/Diphenol Resins with Various Molar Ratios

		MPN			DOPO-1X		
	BZ/diphenol molar ratio	Dieletric constant (U, 1G)	Dissipation factor (U, 1G)	Moisture absorption (%)	Dieletric constant (U, 1G)	Dissipation factor (U, 1G)	Moisture absorption (%)
BPABZ	100/0	3.31	0.0145	0.33	3.31	0.0145	0.33
	95/5	3.35	0.0175	0.38	3.33	0.0161	0.37
	90/10	3.39	0.0201	0.46	3.38	0.0186	0.44
	85/15	3.43	0.0204	0.53	3.41	0.0199	0.50
	80/20	3.49	0.0224	0.65	3.48	0.0219	0.58
BIPBZ	100/0	3.45	0.0181	0.51	3.45	0.0181	0.51
	95/5	3.46	0.0197	0.57	3.44	0.0195	0.52
	90/10	3.54	0.0228	0.62	3.52	0.0221	0.58
	85/15	3.58	0.0249	0.68	3.56	0.0243	0.65
	80/20	3.65	0.0280	0.74	3.60	0.0272	0.70
DCPDBZ	100/0	2.95	0.0095	0.21	2.95	0.0095	0.21
	95/5	3.05	0.0119	0.28	2.98	0.0114	0.26
	90/10	3.15	0.0143	0.33	3.04	0.0121	0.31
	85/15	3.23	0.0152	0.39	3.11	0.0139	0.34
	80/20	3.37	0.0153	0.48	3.25	0.0144	0.41

TABLE III
T_g and TGA Results for the BZ/Diphenol Resins with Various Molar Ratios

		MPN			DOPO-1X		
	BZ/diphenol molar ratio	T_g (°C)	$T_{5\%}$ (°C)	Y_c (%)	T_g (°C)	$T_{5\%}$ (°C)	Y_c (%)
BPABZ	100/0	184	364	35.2	184	364	35.2
	95/5	189	379	36.5	187	378	42.2
	90/10	190	393	38.2	184	384	41.9
	85/15	188	403	38.1	182	386	42.6
	80/20	186	402	39.6	179	373	42.0
BIPBZ	100/0	206	396	58.7	206	396	58.7
	95/5	207	397	56.2	199	395	58.7
	90/10	207	399	56.6	198	391	58.4
	85/15	202	401	58.0	189	382	59.5
	80/20	196	393	57.2	185	379	60.1
DCPDBZ	100/0	183	391	30.5	183	391	30.5
	95/5	184	393	29.6	182	396	32.6
	90/10	185	400	30.6	184	396	34.2
	85/15	183	395	31.5	181	405	35.1
	80/20	181	393	34.5	179	397	36.0

in Figure 9. The T_g of the cured neat BPABZ, BIPBZ, and DCPDBZ were 184, 206, and 183°C, respectively. In the MPN-containing systems, as expected, the BIPBZ resin systems (196–207°C) showed higher T_g values than those of the corresponding BPABZ and DCPDBZ systems. These results were attributed to the fact that the cured BIPBZ systems had a more rigid biphenyl structure than those of the other cured resins. The T_g of the cured DCPDBZ systems (181–185°C) was slightly lower than those of the BPABZ systems (184–190°C). This result was attributed to the bulky cylcoaliphatic DCPD structure. Similar tendencies were observed in the other DOPO-1X-containing systems.

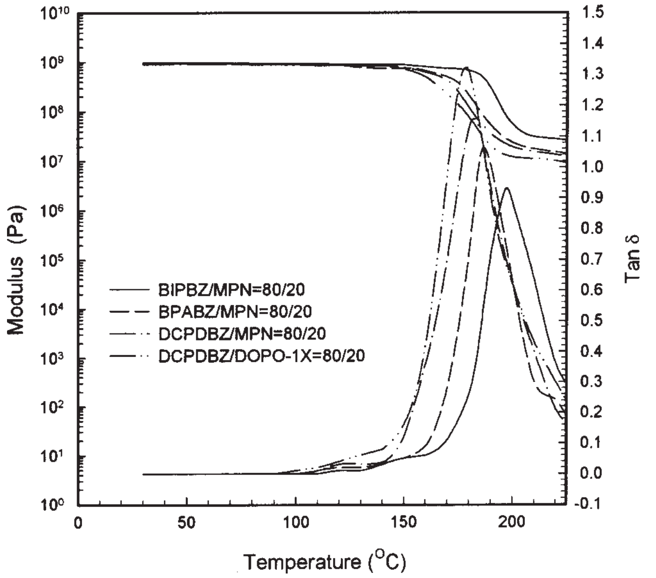


Figure 9 Typical DMA results for BZ cured with diphenol.

In the melamine-containing systems, the incorporation of the high polar melamine structure, which increased molecular interaction and hydrogen bonding, led to a higher T_g than that of the corresponding DOPO-1X-containing system.

Thermal stability of the polymers

The relative thermal stabilities of the cured resins were compared by the temperature at 5% weight loss ($T_{5\%}$) and the percentage char yield at 800°C (Y_c). The TGA data for the cured resins of BZ/diphenol at various molar ratios under a nitrogen atmosphere are listed in Table III, and typical thermogravimetric traces are given in Figure 10. The Y_c values of the BIPBZ systems were higher than those of the corresponding BPABZ and DCPDBZ systems. This was attributed to the high aromatic content and biphenyl structure of the cured BIPBZ systems. The char yield of the DCPD systems was lower than that

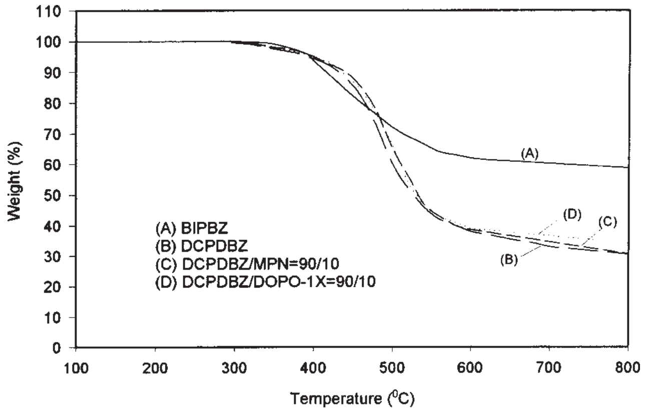


Figure 10 Typical TGA thermograms of BZ cured with diphenol in nitrogen.

TABLE IV
UL-94 Test Results for the BZ/Diphenol Resins with Various Molar Ratios

	BZ/diphenol molar ratio	MPN		DOPO-1X	
		P/N (wt %)[a]	UL-94	P/N (wt %)	UL-94
BPABZ	100/0	0/6.06	V-2	0/6.06	V-2
	95/5	0/6.51	V-2	0.34/5.76	V-1
	90/10	0/6.98	V-2	0.67/5.46	V-0
	85/15	0/7.47	V-2	1.00/5.16	V-0
	80/20	0/7.98	V-2	1.36/4.86	V-0
BIPBZ	100/0	0/6.66	V-2	0/6.66	V-2
	95/5	0/7.13	V-2	0.36/6.30	V-1
	90/10	0/7.62	V-2	0.73/5.94	V-0
	85/15	0/8.14	V-2	1.10/5.59	V-0
	80/20	0/8.66	V-2	1.45/5.23	V-0
DCPDBZ	100/0	0/4.94	V-2	0/4.94	V-2
	95/5	0/5.34	V-2	0.28/4.73	V-1
	90/10	0/5.77	V-2	0.56/4.53	V-1
	85/15	0/6.21	V-2	0.84/4.32	V-0
	80/20	0/6.68	V-2	1.12/4.10	V-0

[a] Calculated value.

of other systems because of the cycloaliphatic structure of DCPD, which increased the flammability.

In those DOPO-1X-containing systems, the results from Table III indicate that the enhancement of char formation in BZ/DOPO-1X could be explained by the incorporation of a phosphorus group into the curing compositions and by the rigid biphenyl structure existing in DOPO-1X.

UL-94 measurements

As shown in Table IV, the UL-94 rating improved from V-2 grade for the BZ/MPN series to V-0 grade for the BZ/DOPO-1X series. In the DCPDBZ/MPN series, the increase in nitrogen content (from 4.94 to 6.68%) with increasing molar ratio of the MPN (MPN contained a nitrogen atom) to DCPDBZ did not show a significant effect in increasing the flame retardancy by the UL-94 test. A similar tendency was observed in the BPABZ/MPN and BIPBZ/MPN systems. The UL-94 V-2 properties of DCPDBZ/MPN may have originated from the presence of the nitrogen atom in BZ; however, the slight increase in nitrogen content with MPN as a curing agent did not dramatically enhance the flame retardancy.

As expected, the addition of DOPO-1X to the BZs effectively enhanced the flame retardancy of the BZ/diphenol systems. The flame retardancy of the cured BZ resins increased with increasing phosphorus content of the cured products. This phenomenon was in good agreement with the results from char yield. A UL-94 V-0 grade was achieved with a phosphorus content of 0.67 wt % for the BPABZ system, 0.73 wt % for the BIPBZ system, and 0.84 wt % for the DCPDBZ system as compared to a 1.5 wt % phosphorus content for our earlier study on flame-retardant epoxy systems.[23] However, it is especially noteworthy that the cured BZ/DOPO-1X resins exhibited a high char yield and better flame retardancy, which were attributed to the phosphorus–nitrogen synergistic effect.

CONCLUSIONS

A series of DCPD-containing BZ/diphenol novolac resins were prepared from various molar ratios of MPN or DOPO-1X to DCPDBZ. Because of the low polarity and hydrophobic nature of the cycloaliphatic DCPD structure, the cured DCPDBZ/diphenolic resins exhibited lower dielectric constant, dissipation factor, and moisture absorption values than those of the bisphenol A and 4,4′-biphenol based systems. All DCPD-based resins still retained good thermal properties. Furthermore, the DCPDBZ/DOPO-1X series offered better dielectric properties and moisture resistance and higher flame retardancy than the melamine-containing (MPN) diphenol series. A UL-94 V-0 rating was achieved with a phosphorus content of less than 1% for DCPDBZ/DOPO-1X. The combination of low dielectric constant, low dissipation factor, outstanding resistance to moisture absorption, and V-0 rating flame retardancy with good thermal properties should make DCPDBZ/DOPO-1X resins attractive for practical applications such as flame-retardant laminates.

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