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Synthesis and properties of epoxy resins containing 2-(6-oxid-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)1,4-benzenediol

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2-(6-Oxid-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxa-phosphorin-6-yl)1,4-benzenediol (ODOPB) was prepared by the addition reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and *p*-benzoquinone while DOPO was synthesized through multistep reaction from *o*-phenylphenol and phosphorus trichloride. The compound (ODOPB) was used as a reactive flame-retardant in *o*-cresol formaldehyde novolac epoxy resin (CNE) for electronic application. Owing to the rigid structure of ODOPB and pendant P group, the resultant phosphorus-containing epoxy resin exhibited better flame retardance, higher glass transition temperature and thermal stability than the regular bromine-containing flame-retardant epoxy resin. UL 94-VO rating could be achieved with a phosphorus content of as low as 1.1% (comparable to a bromine content of 6%) in the cured resin and no fume and toxic gas emission were observed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: 2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-benzenediol; flame retardance; epoxy curing)

INTRODUCTION

Epoxy resins have the excellent characteristics of moisture, solvent and chemical resistance, toughness, low shrinkage on cure, superior electrical and mechanical resistance properties, and good adhesion to many substrates. The versatility in formulation also make epoxy resins widely applicable industrially for surface coatings, adhesive, painting materials, pottings, composites, laminates, encapsulants for semiconductors, and insulating materials for electric devices, etc.[1] *o*-Cresol formaldehyde novolac epoxy (CNE) is the resin typically employed in the encapsulation of microelectronic devices[2–6]. Several approaches for modification of epoxy backbone to enhance the thermal properties of epoxy resins have been reported[7–9]. Aromatic bromine compounds in conjunction with antimony oxide are widely used as flame retardants for epoxy resins. Major problems encountered with this system are concerned with the generation of toxic and corrosive fumes during combustion[10,11]. These considerations have led to the search for a new fire retardant. Recently, organophosphorus compounds have demonstrated good ability as flame retardants for epoxy resins and have also been found to generate less toxic gas and smoke than halogen-containing compounds[12–20]. In this study a rigid phosphorus-containing reactive, 2-(6-oxido-6H-dibenzo⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)1,4-benzenediol (ODOPB), was synthesized. The incorporation of this bulky pendant group into epoxy resin is expected to impart the required flame retardance, less fumes and higher thermal stability than the conventional bromine-containing fire retardant systems.

EXPERIMENTAL

Materials

All reagents and solvents were reagent grade or were purified by standard methods before use. *o*-Phenylphenol, phosphorus trichloride, and *p*-benzoquinone (from Aldrich) were used as received. Ethylene glycol monoethyl ether (ethoxyethanol) and methanol (from Acros) were used as solvent and purified before use. The epoxy resins used were *o*-cresol formaldehyde novolac epoxy (CNE, Quatrex 3330, epoxy equivalent weight, EEW 192), and the diglycidyl ether of bisphenol-A (D.E.R.331, EEW 174) (both from Dow Chemicals). A phenol formaldehyde novolac resin was used as curing agent with an average hydroxyl functionality of 6 and a hydroxyl equivalent weight of about 104 (Schenectady Chemical, HRJ-2210). Tetrabromobisphenol-A (TBBA) was purchased from Aldrich. The A-1 catalyst was an ethyl triphenyl phosphonium acetate acetic acid complex, which was used as an advancement catalyst. Triphenyl phosphine (Ph_3P) was used as curing accelerator. Diaminodiphenyl methane (DDM; Aldrich) was used as curing agent for epoxy resins.

Syntheses

Synthesis of 6-chloro-6H-dibenzo⟨c,e⟩⟨1,2⟩oxaphosphinine (CDOP). To a 1 l reaction vessel equipped with a temperature controller, overhead stirrer and a reflux condenser were added 204 g *o*-phenylphenol and 206 g phosphorus trichloride. The mixture was first heated slowly to 30°C to dissolve *o*-phenylphenol and then increased to 50°C. The evolution of HCl gas was detected immediately. The reaction mixture was heated at reflux (145°C) for 2.5 h until HCl evolution has subsided. The mixture was further heated at reflux temperature for another

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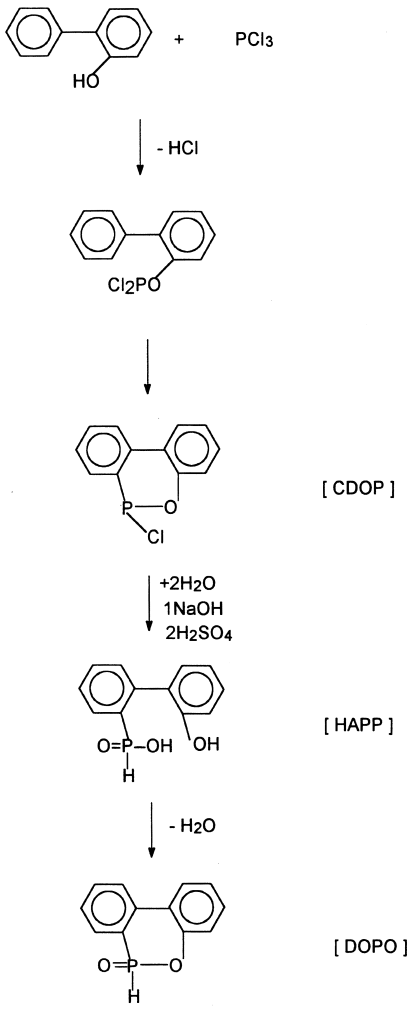
5 h with addition of 1.3 g zinc chloride. The reaction was assumed to be complete when no more HCl evolution was detected at 210°C. Excess phosphorus trichloride was removed under vacuum and the residual solid was recrystallized from tetrahydrofuran to give CDOP. Yield 95%; mp 84–85°C. The i.r. spectrum (KBr) exhibited absorption at 1172, 968 (P–o–Ph), 1583 cm^{-1} (P–Ph). Anal. Calcd. for $C_{12}H_8POCl$: C, 61.54; H, 3.45; O, 6.84; P, 13.24; Cl, 14.94. Found: C, 61.84; H, 3.47; O, 6.62; P, 13.18; Cl, 14.89. EIMS, *m/z*: 234 (86, M^+).

Synthesis of 2-(2-hydroxyphenyl) phenylphosphonic acid (HPPA). CDOP (100 g) was preheated to 100°C and added to a 2 l beaker containing 1 l deionized water with stirring. The mixture was stirred at 100°C for 1 h to precipitate white solids which were filtered. The filtered solids were stirred with 250 ml deionized water and 43 ml 40% aqueous NaOH solution until all solids were dissolved. The solution was heated at 50°C for 1 h, and then 20% aqueous H_2SO_4 was added slowly to neutralize NaOH. The precipitated solid was collected by filtration and thoroughly washed with H_2O and dried. A white crystal of 2-(2-hydroxyphenyl) phenylphosphonic acid (HPPA) was obtained. Yield 96%; mp 105–106°C. I.r. (KBr): 1197 (P=O), 1007 (P–OH), 2384 (P–H), 1587 (P–Ph), 3358, 1362 cm^{-1} (Ph–OH). Anal. Calcd. for $C_{12}H_{11}O_3P$: C, 61.54; H, 4.70; O, 20.51; P, 13.24. Found: C, 61.74; H, 4.71; O, 20.16; P, 13.39. EIMS, *m/z*: 234 (100, M^+).

Synthesis of 9,10-dihydro-oxa-10-phosphaphenanthrene 10-oxide (DOPO). 500 g of HPPA was placed in a 300 ml flask which was connected to a vacuum system. The content was heated to its molten state (106°C) under full vacuum for dehydration. The temperature was slowly increased from 106 to 160°C until the dehydration was complete. White solids of DOPO (yield 93%) with mp 119–120°C after recrystallization from tetrahydrofuran was obtained. I.r.: 1168, 965 (P–Ph), 1196 (P=O), 2384 (P–H), 1587 cm^{-1} (P–Ph). Anal. Calcd. for $C_{12}H_9O_2P$: C, 66.67; H, 4.17; O, 14.81; P, 14.35. Found: C, 66.64; H, 4.31; O, 14.59; P, 14.66. MS, *m/z*: 216 (100, M^+).

The synthetic scheme of above three steps is shown in *Scheme 1.*

Preparation of 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin 6-yl)-1,4-benzenediol (ODOPB). To a 2 l reaction vessel equipped with a temperature controller, overhead stirrer and a reflux condenser were charged 1000 g of ethoxyethanol and 540 g DOPO, then 243 g of powdered *p*-benzoquinone was added incrementally. The temperature of the reaction mixture was raised to 125°C and allowed to react at that temperature for 4 h. After filtration at room temperature, the compound of ODOPB was obtained. The ODOPB was further recrystallized from ethoxyethanol to give mp 255–256°C. Yield 98%. I.r. (KBr): 1168, 925 (P–O–Ph), 1190 (P=O), 1348 (P–OH), 3173 (Ph–OH), 1582 cm^{-1} (P–Ph). The shift and splitting pattern of ^1H n.m.r. spectrum is 6.69 (t, 1H), 6.93 (dd, 1H), 7.16 (dd, 1H), 7.24–7.34 (m, 2H), 7.40–7.51 (m, 2H), 7.66–7.76 (m, 2H), 8.13–8.19 (m, 2H) (*Figure 1A*), ^{31}P n.m.r. (DMSO): a singlet peak at $\delta = 21.5$ ppm (*Figure 1B*). Anal. Calcd. for $C_{18}H_{13}O_4P$: C, 66.67; H, 4.04; O, 19.74; P, 9.52. Found: C, 66.57; H, 4.10; O, 20.04; P, 9.29. MS, *m/z*: 324 (100, M^+).



Scheme 1

Curing procedure of epoxy resins. Various amounts of ODOPB were added to phenol novolac as a curing agent for cresol formaldehyde novolac epoxy (CNE) resin to determine the flame-retardant effect of phosphorus. The curing agents consisted of ODOPB/PN in various weight ratios (0/100, 25/75, 50/50, 75/25, 100/0) were prepared. Ph_3P was used as a curing accelerator. The CNE resin was mixed with the above curing agents and 0.2% Ph_3P in a mill at 25°C to give thermosettable epoxy resin powders. The resin powders were cured in a mould at 150°C and 50 kg/cm^2 for a period of 1 h and then at 200°C for 2 h and further postcured at 260°C for 4 h to obtain cured specimens.

UL-94V flame retardant test. The UL-94V test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with test specimen bar of 127 mm in length, 12.7 mm in width and up to about 12.7 mm maximum in thickness. The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars suspended vertically over surgical cotton were ignited by a Bunsen burner, two ignitions with 10 s burning time were applied to each sample bar. The samples of cured epoxy resins with various weight ratios of ODOPB/PN and TBBA/PN were subjected to the UL-94V test.

Advancement of epoxy resin with ODOPB. The diglycidyl ether of bisphenol-A (D.E.R.331, Dow) was reacted with ODOPB at 160°C for 90 min in the presence

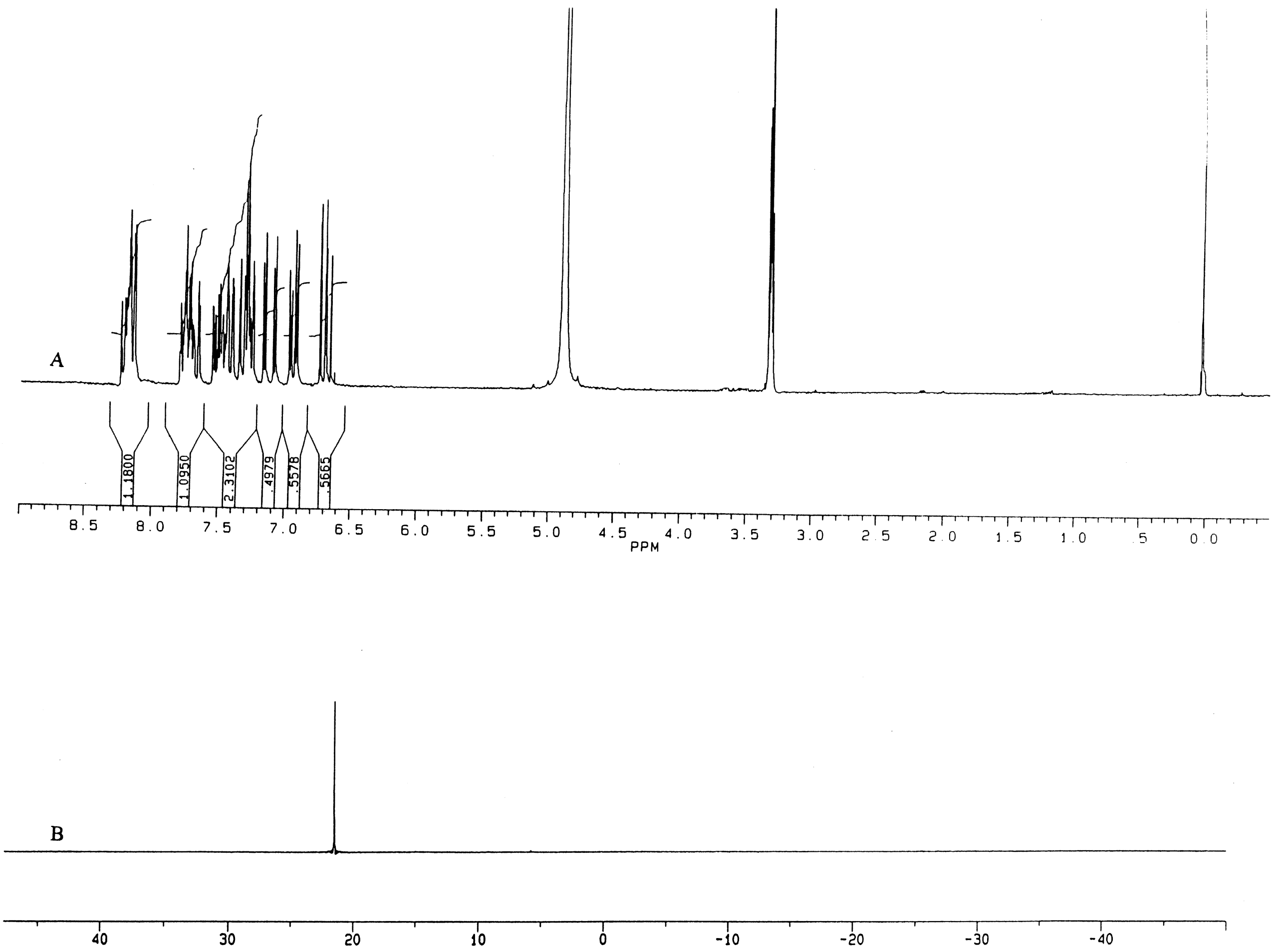
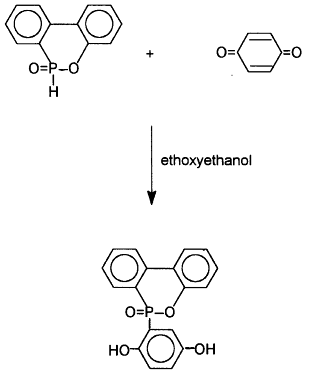


Figure 1 (A) ^{1}H and (B) ^{31}P n.m.r. spectra of ODOPB



Scheme 2

of 500 ppm ethyltriphenyl phosphonium acetate catalyst. The equivalent ratio of epoxy to phenolic hydroxyl of 2.20:1 produced a solid epoxy resin with an EEW of 483.

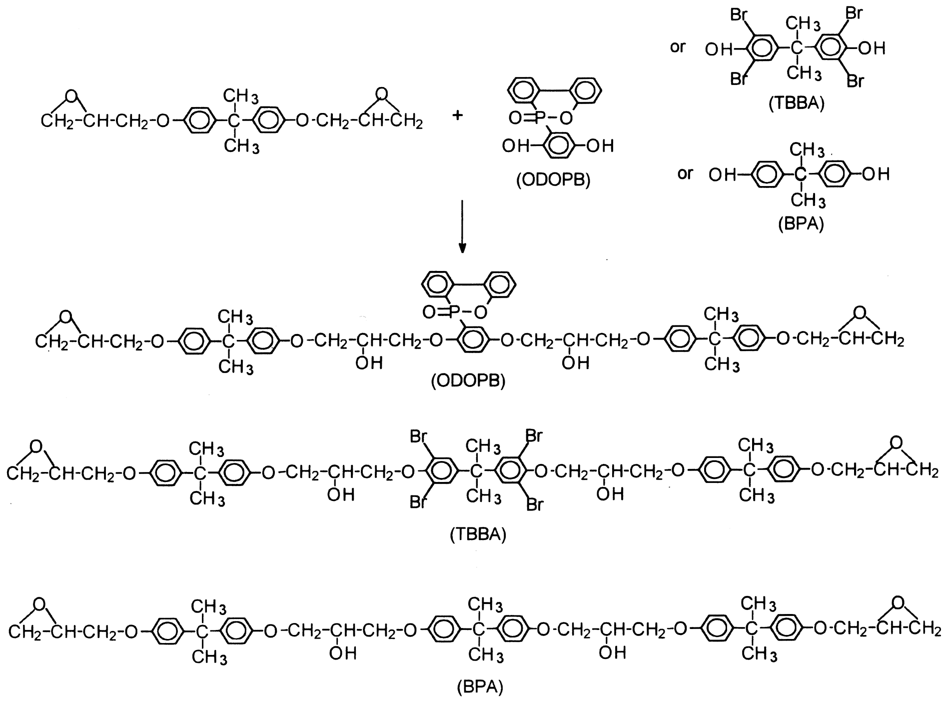
Advancement of epoxy resin with TBBA and BPA. In order to compare the thermal, mechanical and flame-retardant effect of ODOPB *versus* TBBA, the advancements of epoxy resins with TBBA and bisphenol-A (BPA) were also performed. The same advancement procedure as that of ODOPB was applied. The equivalent ratios of epoxy to phenolic hydroxyl of 2.58:1 (for TBBA) and 2.04:1 (for BPA) produced two kinds of solid epoxy resins with the same EEW of 483. The reaction scheme is shown in *Scheme 3*.

Curing procedure for the advanced epoxy resin. Various advanced epoxy resins were mixed with methylene dianiline (MDA) at 150°C poured into a hot aluminum mould, cured in an oven at 175°C for 1 h, and then postcured at 200°C for 2 h. The amounts of the advanced epoxy resins, curing agent, and the glass transition temperatures and thermogravimetric analysis (t.g.a.) data of the cured products are given in *Table 3*.

RESULTS AND DISCUSSION

Synthesis of phosphorus-containing compounds

Synthesis of the reactive rigid heterocyclic ring structure containing phosphorus (9,10-dihydro-9-oxa-10 phospha-phenanthrene 10-oxide, DOPO) was performed by starting with *o*-phenylphenol and phosphorus trichloride in three steps according to *Scheme 1*. The phosphorus-containing diol compound, 2-(6-oxido-6H-dibenzene⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)1,4-benzenediol (ODOPB), was obtained by the addition of DOPO to *p*-benzoquinone in a quantitative yield (*Scheme 2*). As the reaction proceeded, the distinctive absorption at 2384 cm^{-1} for P–H stretching in DOPO disappeared while a broad absorption at around 3173 cm^{-1} for phenolic OH appeared in ODOPB. Consequently, this addition reaction could be monitored by means of these absorptions. The yield in each step was satisfactory and the structures of DOPO, HPPA, CDOP and ODOPB were confirmed by elemental analysis and infrared spectroscopy.



Scheme 3

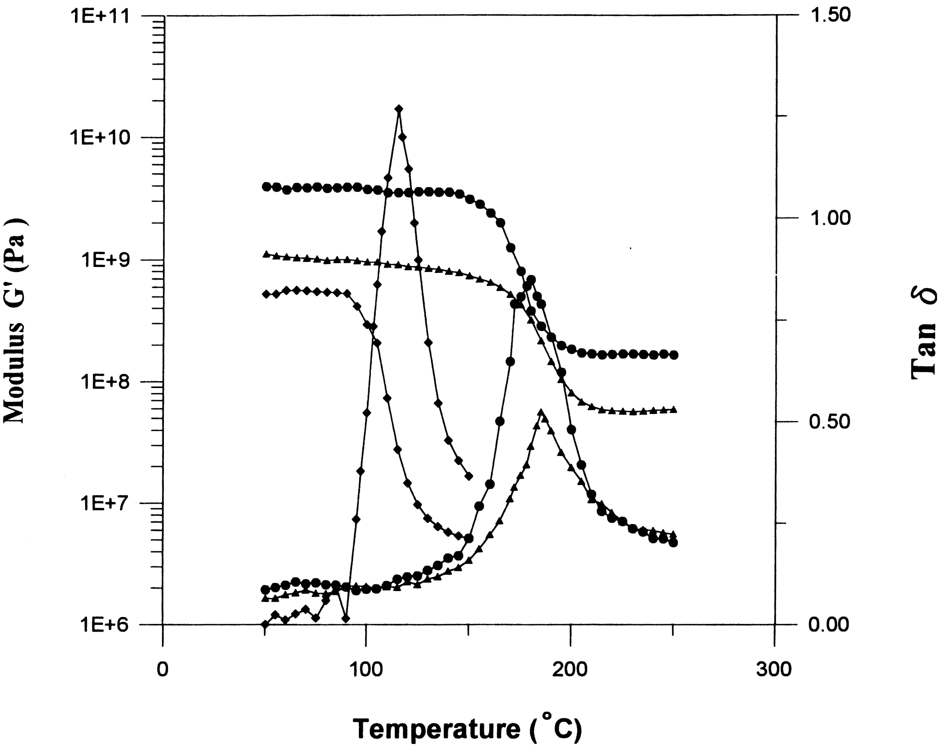


Figure 2 Dynamic viscoelastic analyses of cured CNE resins: (a) ● PN; (b) ▲ ODOPB-D; (c) ◆ TBBA-D

Dynamic viscoelastic analyses of various cured CNE resins

Dynamic viscoelastic analysis can give information on the microstructure of cured epoxy resins. The tan δ curves for the control network exhibit a major relaxation observed in most epoxy polymer[21]. The transition corresponds to the major T_g of the cured epoxy resin, above which significant chain motion takes place. *Figure 2* shows the storage modulus G' and tan δ of cured epoxy resins with PN, ODOPB and TBBA. The results indicate that the epoxy resin cured with ODOPB had a higher T_g than that of the epoxy resin cured with TBBA. This result may be attributed to the incorporation of a bulky rigid group which increased the rotational barrier.

Thermal properties for cured epoxy resins

T.g.a. is the most favoured technique for rapid evaluation in comparing and ranking the thermal stability of various polymers. T.g.a. analyses of the CNE resin cured with PN

Table 1 Thermal properties of cured neat CNE epoxy resin using various ratios of ODOPB/PN and TBBA/PN

Sample design		T_g (°C)	Temperatures of weight loss				Rapid rate T_r (°C)				Char yields at 700°C	
			5%		10%		Step 1		Step 2			
			Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2
	ODOPB/PN											
Control	0/100	182	397	397	419	419	447	450	—	—	26	32
ODOPB-A	25/75	83	401	405	420	421	439	447	598	598	32	40
ODOPB-B	50/50	184	408	415	417	425	431	445	572	585	32	41
ODOPB-C	75/25	185	411	411	425	427	433	445	577	585	34	44
ODOPB-D	100/0	185	411	413	427	431	438	448	587	606	38	49
	TBBA/PN											
TBBA-A	25/75	146	284	403	339	418	348	426	—	—	26	36
TBBA-B	50/50	135	387	396	391	399	393	404	—	—	26	38
TBBA-C	75/25	126	371	390	385	395	389	397	—	—	28	38
TBBA-D	100/0	113	389	409	389	411	395	416	—	—	28	39

—, step 2 of rapid rate was not found

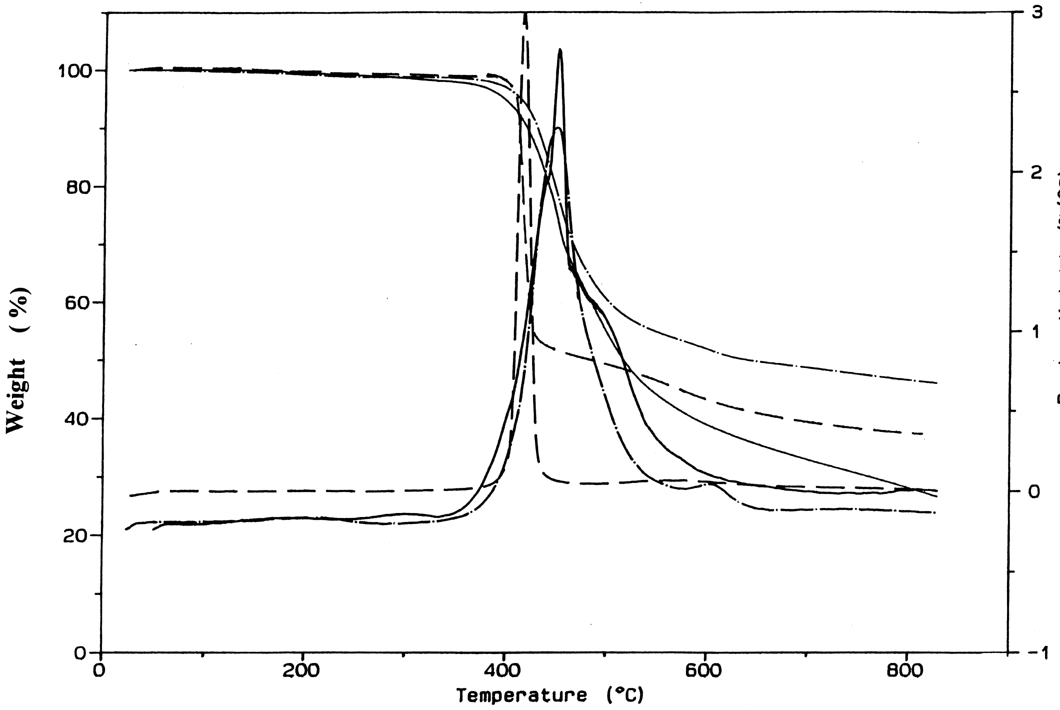


Figure 3 T.g.a. thermograms of cured epoxy resins in N_2: (a) — PN; (b) — · ODOPB-D; (c) – – TBBA-D

(control) and epoxy resins cured with various ratios of ODOPB/PN and TBBA/PN in nitrogen and air are shown in *Table 1*. The results indicated that CNE cured with various weight ratios of ODOPB/PN and TBBA/PN have higher char yield than that of the control CNE resin. It should be noted that the ODOPB-A (1.1% of P-containing) has exhibited higher char yield (40% in N_2 at 700°C) and thermal stability than that of the control CNE resin and all TBBA/PN cured epoxy resins. *Figures 3* and *4* show the t.g.a. traces of the control CNE resin, ODOPB-D and TBBA-D resins in N_2 and air. The control CNE resin exhibited 5% weight loss at 397°C and 10% weight loss at 419°C, and then a rapid weight loss was found at around 450°C in N_2. The cured epoxy resin of TBBA-D exhibited 5% weight loss at 409°C and 10% weight loss at 411°C, and then a rapid weight loss was found at around 416°C. On the other hand the phosphorylated ODOPB/PN resin showed its 5% weight loss at 413°C and 10% weight loss at 431°C. The thermal stability of cured epoxy resin were compared by the temperatures for 5% and 10% weight loss. The following order may be given: ODOPB-D > TBBA-D > Control CNE. Although the rapid weight loss temperature (T_r) of the control CNE resin occurred at 450°C, which is slightly higher than that of ODOPB-D, unlike the one-stage rapid weight loss of the control CNE resin, the ODOPB-D epoxy resin exhibited a second stage of rapid weight loss at 606°C. This phenomenon played an important role in improving the flame retardance of the resins. While burning, the phosphorus-containing groups first decompose at around 440°C, and then form a phosphorus-rich residue, which prevent further decomposition of the epoxy resins, by raising the second decomposition temperature to 606°C and resulting in a high char yield. The char yields at 700°C for the control CNE, TBBA-D and ODOPB-D resins were 32%, 39% and 49%, respectively. The same phenomenon can also be observed in *Figure 3* (in air).

UL-94V test for cured epoxy resins

The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars of each cured epoxy

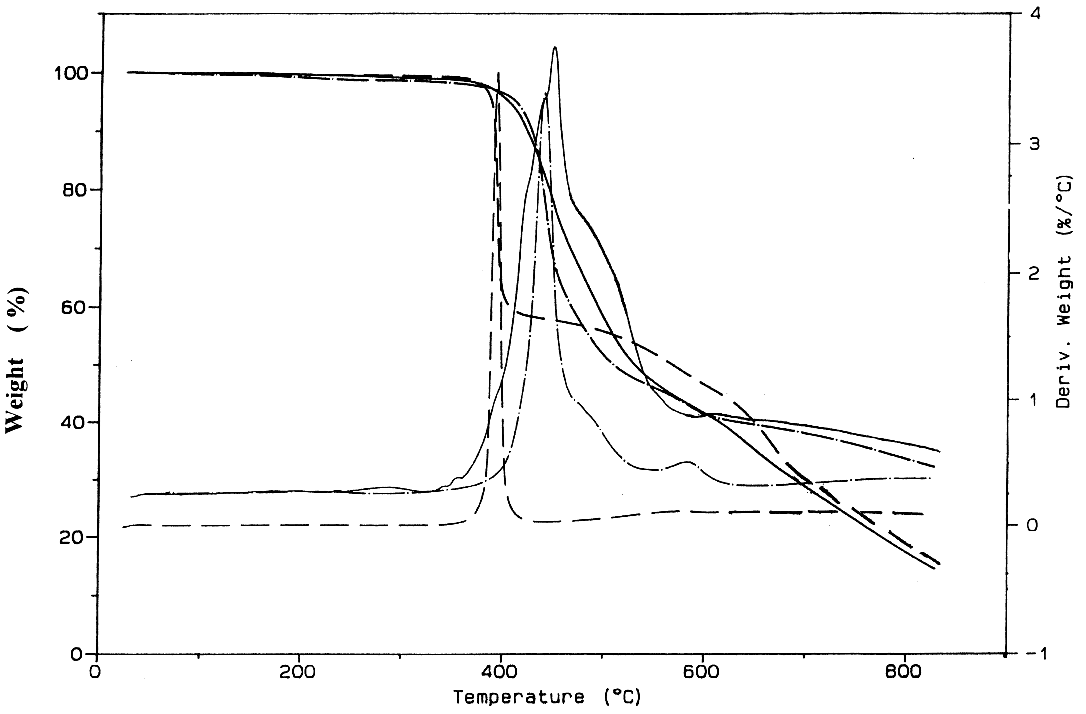


Figure 4 T.g.a. thermograms of the cured epoxy resins in air: (a) — PN; (b) — · ODOPB-D; (c) – – TBBA-D

Table 2 UL-94V test of cured CNE with various ODOPB/PN and TBBA/PN weight ratios

Sample designation			Average burning time	Fume	Classification
	ODOPB/PN	P (%)			
Control	0/100	0	85.6	–	V-2
ODOPB-A	25/75	1.1	8.3	– –	V-0
ODOPB-B	50/50	2.0	< 1	– –	V-0
ODOPB-C	75/25	3.1	0	– –	V-0
ODOPB-C	100/0	4.4	0	– –	V-0
	TBBA/PN	Br (%)			
TBBA-A	25/75	5.8	16	+ +	V-1
TBBA-B	50/50	12.9	< 1	+ +	V-0
TBBA-C	75/25	22.1	0	+	V-0
TBBA-D	100/0	34.4	0	–	V-0

+ + , heavy; + , slightly; –, scarcely; – –, no

Table 3 Thermal properties of cured advancement resins

Sample design		MDA curing agent (g/eq)	T_g (°C)	Temperature of weight loss				Rapid rate T_r (°C)				Char yield at 700°C	
Advancement resin	(g/eq)			5%		10%		Step 1		Step 2			
				Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2
BPA	50/0.105	10.5/0.106	134	369	389	401	406	463	467	—	—	6	12
TBBA	50/0.106	10.4/0.105	155	311	370	335	373	339	376	—	—	14	21
ODOPB	50/0.105	10.4/0.105	161	394	397	407	407	450	451	496	499	22	26

—, step 2 of rapid rate was not found

resin, suspended vertically over surgical cotton, were ignited by a Bunsen burner, two ignitions of 10 s each were applied to the sample. It is clear from the result of *Table 2* that the flame retardance of cured epoxy resins increased with phosphorus or bromine content in the cured products. Besides phosphorus being much more effective than bromine as a flame retardant (1% P is better than 6% bromine by comparing ODPOB-A with TBBA-A), it also generated much less fumes than bromine.

Dynamic viscoelastic and thermal properties of advanced epoxy resin

Advanced epoxy resins are particularly useful in printed circuit boards and other electrical laminate applications[22]. These types of resins are prepared by reacting an epoxy resin (diglycidyl ether of bisphenol-A) with bisphenol-A (BPA), tetrabromobisphenol-A (TBBA) or ODOPB. The advanced epoxy resins are shown in *Scheme 3*. The amount of advanced epoxy resins, curing agent and the

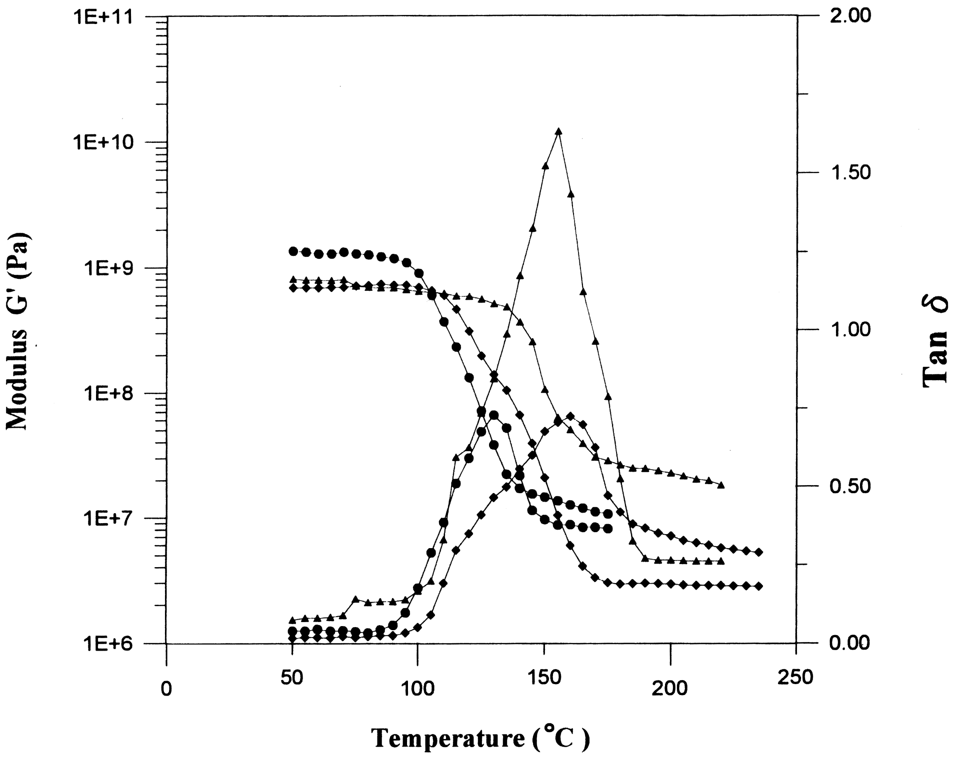


Figure 5 Dynamic viscoelastic analyses of various advancement resins made from: (a) ● BPA; (b) ▲ TBBA; (c) ◆ ODOPB

Table 4 UL-94V test and rating for various advanced epoxy resins

Sample design	Element for flame retardant	Average burning time (s)	Fume	Drip	Classification
BPA	NO	93	– –	Yes	V-2
TBBA	Br (17.26%)	< 1	+ +	Yes	V-0
ODOPB	P (2.12%)	0	– –	No	V-0

– –, no; + +, heavy

glass-transition temperature (T_g) of cured products are listed in *Table 3*. A comparison of storage modulus G' and tan δ curves for the advanced epoxy resins made from three diols are shown in *Figure 5*. The advanced epoxy resin made from ODOPB had a higher T_g (161°C) than the other two advanced epoxy resins, which may also be attributed to the rigid, bulky P-containing cyclic structure.

T.g.a. were also performed to compare the thermal stability of the advanced epoxy resins made from three diols (BPA, TBBA, ODOPB) and the results are shown in *Table 3*. The results indicated that the advanced epoxy resin made from ODOPB had a higher decomposition temperature at 5% weight loss (397°C in N_2) and 10% weight loss (407°C in N_2) than the other two advanced epoxy resins made from BPA and TBBA. Unlike the one-step rapid weight loss of advanced epoxy resins made from BPA and TBBA, the resins made from ODOPB exhibited a higher second step rapid weight loss temperature at 499°C. This phenomenon played an important role in improving the flame retardance of the advanced epoxy resin, which was confirmed by the higher char yield at 700°C than that of the other two advanced epoxy resin made from BPA and TBBA.

UL-94V test for advanced epoxy resin

For the UL-94V test, five specimens of each advanced epoxy resin were prepared and the test results are shown in *Table 4*. The advancement resin made from BPA had a 93 s burning time after the Bunsen burner was removed while advancement resins made from TBBA and ODOPB both passed the UL-94VO flame retardance test. It should be noted that the advancement resin containing 2.1% P has exhibited better flame retardance than the advancement resin containing 17.26% bromine. The most important feature of the P flame retardant is that no fumes were generated.

CONCLUSIONS

A reactive phosphorus-containing flame-retardant compound, 2-(6-oxido-6H-dibenz⟨*c*,*e*⟩⟨1,2⟩oxaphosphorin-6-yl)1,4-benzenediol (ODOPB) was successfully synthesized. The compound was used as curing agent for CNE resins to be used for semiconductor encapsulation applications and also to prepare advanced epoxy resin for electrical laminate applications. The ODOPB compound provided not only the better flame-retardant effect and thermal stability than that of TBBA, but also generated much less fumes in the combustion test.

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