European Polymer Journal 36 (2000) 443–452

Synthesis and properties of epoxy resins containing bis(3-hydroxyphenyl) phenyl phosphate

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Received 22 February 1999; accepted 9 March 1999

Abstract

A reactive phosphorus-containing diol compound, bis(3-hydroxyphenyl) phenyl phosphate (BHPP), was synthesized. The compound (BHPP) was used as a reactive flame-retardant for diglycidyl ether of bisphenol-A (DGEBA). Thermal stability and the weight loss behavior of the cured polymers were studied by thermogravimetric analysis. The phosphorous-containing epoxy resin showed lower weight loss temperature and higher char yield than that of DGEBA. The high char yields and limiting oxygen index values as well as excellent UL-94 vertical burn test results of BHPP/DGEBA indicated the flame retardancy of the phosphorous-containing epoxy resins. The resulting phosphorous-containing epoxy resin exhibited better flame retardancy and higher thermal stability than the regular bromine containing flame retardant epoxy resin in encapsulation application. UL 94-VO rating could be achieved with a phosphorus content of as low as 1.5% (comparable to bromine content of 10%) in the cured resin, and no fume and toxic gas emission were observed. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Polymeric materials, which have the potential to simulate the mechanical and chemical behavior of biological tissue better than metals and ceramics, are replacing traditional material. One property of synthetic polymers used in transportation and building, electrical and electronic, and interior furnishing that needs improvement is flame-retardancy. Epoxy resins have the excellent characteristics of moisture, solvent and chemical resistance, low shrinkage on cure, superior electrical and mechanical resistance properties, and good adhesion to many substrate. The versatility in formulation also made epoxy resins widely applied industrially for surface coating, adhesive, painting materials, pottings, composites, laminates, encapsulant for semiconductor, and insulating material for electric devices, etc. [1–3]. However, the common epoxy systems cannot satisfy field applications which require high thermal and flame resistance. Several techniques and approaches for modification of epoxy backbone have been employed in improving the flame retardancy of epoxy polymers [4–7]. A feasible approach for improving flame retardation of epoxy polymers involves the application of fire-retardant epoxy resins and curing agents [8,9]. Aromatic bromine compounds in conjunction with antimony oxide are widely used as flame-retardants for epoxy resin. Major problems encountered with this system concern with the generation of toxic and corrosive fume during combustion [10,11]. Recyclability and environmental concerns about halogenated flame-retardant are driving forces behind the development of cost effective, halogen-free alternatives. These considerations have led to the search of new fire-retardant. In this race, organophosphorus flame-retardants are among the leading contenders. Recently, organophosphorus compounds have

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PII: S0014-3057(99)00091-9

demonstrated good ability as flame-retardant for epoxy resins and also being found to generate less toxic gas and smoke than halogen-containing compounds [12–17]. In this study, a phosphorous-containing reactive bis(3-hydroxyphenyl) phenyl phosphate (BHPP) was incorporated into epoxy resin and is expected to impart the required flame retardancy, less fume and higher thermal stability than the conventional bromine containing fire retardant systems.

2. Experimental

2.1. Materials

All reagents and solvents were reagent grade, or were purified by standard methods before use. Phenyl dichlorophosphate and 1,3-dihydroxybenzene (resorcinol) from Aldrich were used as received. Xylene and methanol from Acros were used as solvent and purified before use. Diglycidyl ether of bisphenol-A (DGEBA, EEW = 189) was obtained from Chang Chun Plastic (Taiwan). A phenol–formaldehyde novolac resin (PN) was used as a curing agent with an average hydroxyl functionality of six and a hydroxyl equivalent weight of about 104 (Schenectady Chemical, HRJ-2210). Tetrabromobisphenol-A (TBBA) was purchased from Aldrich Chemical. The A-1 catalyst was ethyl triphenyl phosphonium acetate acetic acid complex which was used as an advancement catalyst. Ph_3P was triphenyl phosphine that was used as a curing accelerator.

2.2. Synthesis of bis(3-hydroxyphenyl) phenyl phosphate (BHPP)

To a 1 l reaction vessel equipped with a temperature controller, overhead stirrer and a reflux condenser were added 220 g resorcinol and 360 g xylene. The mixture was first heated slowly to 70°C to dissolve resorcinol and then heated to 90°C. To the resultant solution, 195 g of phenyl dichloro phosphate was added continuously at a constant rate over a period of 2 h. The evolution of HCl gas was detected immediately. The reaction mixture was further heated at reflux for 2.5 h until HCl evolution has subsided. The reaction was assumed to be complete when no more HCl evolution was detected at 128°C. After the removal of solvent the resulted residue was recrystallized from tetrahydrofuran to give BHPP (yield 95%), as shown in Scheme 1. The infra-red (IR) spectrum (KBr) exhibited absorption at 1252, 992 cm^{-1} (P–O–P), 1277 cm^{-1} (P=O), 3550–3200 cm^{-1} (HO–P). Anal. Calcd for $C_{18}H_{15}O_6P$: C, 60.34; H, 4.18; O, 26.82; P, 8.66. Found: C, 60.42; H, 4.16; O, 26.62; P, 8.80. FBMS, m/z: 358 (98, M^+).

2.3. Curing procedure of epoxy resins

Various amount of BHPP was added to phenol novolac as a curing agent for DGEBA to determine the flame retardant effect of phosphorus. The curing agents consisted of BHPP/PN in various weight ratio (0/100, 25/75, 50/50, 75/25) were prepared. Ph_3P was used as a curing accelerator. The DGEBA 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 mold at 150°C and 50 kg cm^{-2} for a period of 1 h and then at 175°C for 2 h, and further postcured at 200°C for 3 h to obtain cured specimens.

2.4. Limiting oxygen index (LOI) and UL-94V flame retardant test

The LOI is the minimum fraction of O_2 in a mixture of O_2 and N_2 that will just support flaming combustion. The LOI test was performed according to the testing procedure of ASTM D 2836 Oxygen Index Method with test specimen bar of 7–15 cm in length, 6.5 ± 0.5 mm in width and 3.0 ± 0.5 mm in thickness. Ten sample bars suspended vertically were ignited by a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was raised if the specimen was extinguished before burning for 3 min or 5 cm. The oxygen content was adjusted until the limiting concentration was determined.

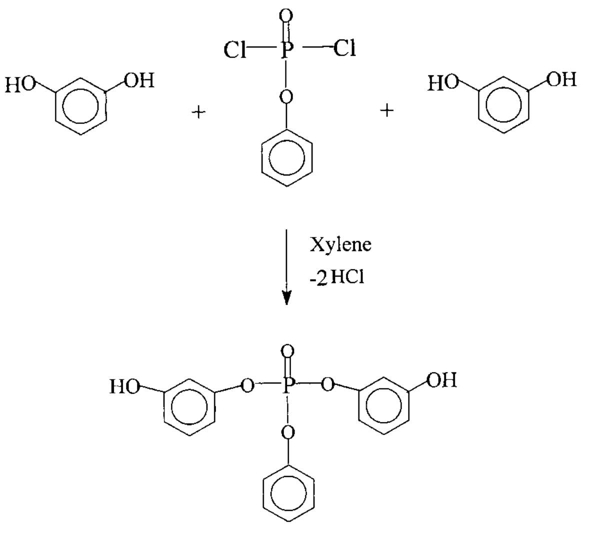
The UL-94V test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with test specimen bars of 127 mm length, 12.7 mm width and about maximum 12.7 mm thickness. The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars suspended vertically over surgical 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 BHPP/PN and TBBA/PN were subjected to the UL-94V test.

2.5. Advancement of epoxy resin with BHPP

DGEBA was reacted with BHPP at 160°C for 90 min in the presence of 500 ppm ethyltriphenyl phosphonium acetate catalyst, as shown in Scheme 2. The equivalent ratio of epoxy to phenolic hydroxyl of 2.20 : 1 produced a solid epoxy resin with an EEW of 483.

2.6. Advancement of epoxy resin with TBBA and BPA

In order to compare the thermal, mechanical and flame-retardant effect of BHPP vs. TBBA, the advancements of epoxy resins with TBBA and bisphenol-A (BPA) were also performed. The same advance-



BHPP

Scheme 1.

ment procedure as that of BHPP was applied. The equivalent ratios of epoxy to phenolic hydroxyl of 2.58 : 1 (for TBBA) and 2.04 : 1 (for BPA) produced two solid epoxy resins with the same EEW of 483, which is shown in Scheme 2.

2.7. Curing procedure for the advanced epoxy resin

Various advanced epoxy resins were mixed with PN at 150°C, poured into a hot aluminum mold, 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, the glass transition temperatures and TGA data of the cured products are given in Table 3.

3. Results and discussion

The synthesis of BHPP is shown in Scheme 1, and its IR spectrum is shown in Fig. 1. The strong absorption around 1277 cm^{-1} corresponds to vibration with P=O, which is a characteristic of phosphate compounds. The BHPP also showed strong absorptions around 1252, 1139 and 992 cm^{-1} corresponding to P–O–C (aromatic) stretching; the HO–P stretching absorptions around 3550–3200 cm^{-1}, which support the BHPP structure. The structure was also confirmed by elemental analysis and FBMASS spectrometry.

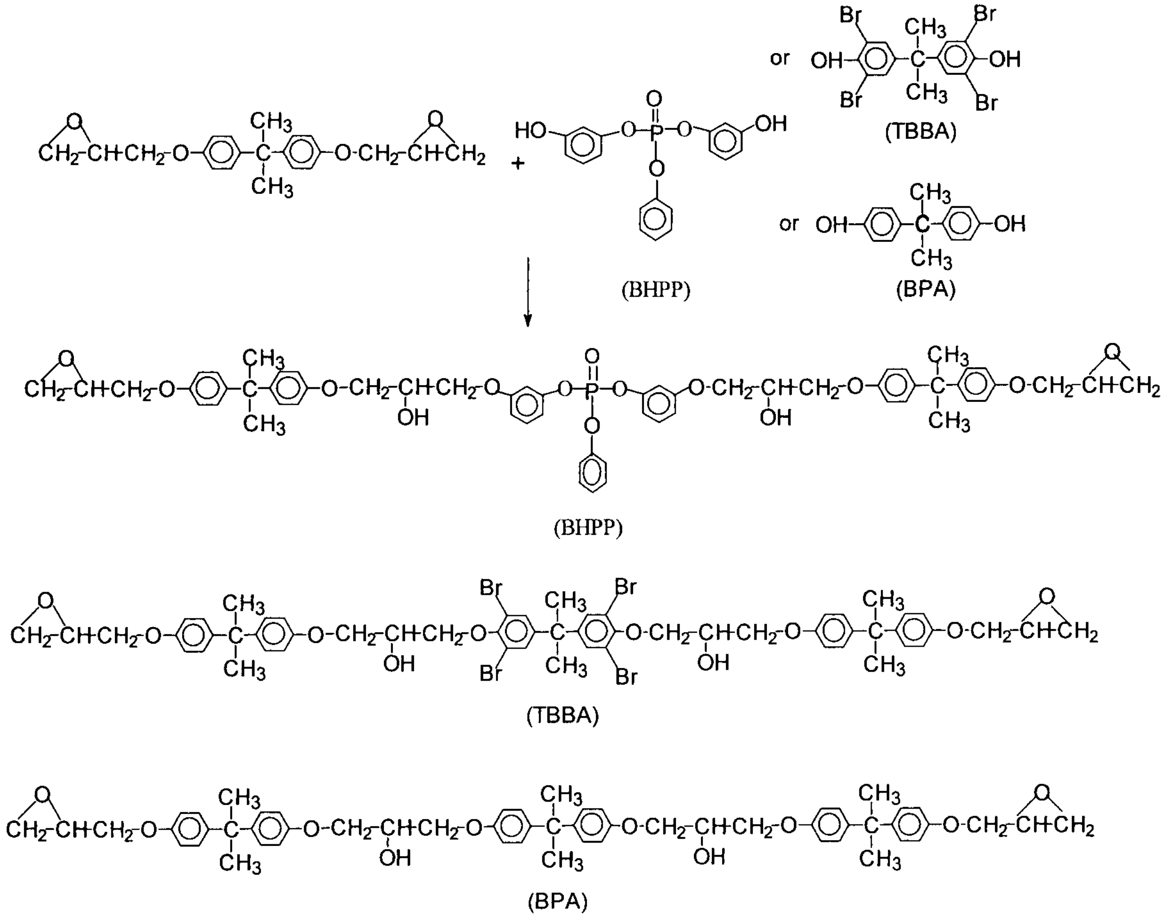
3.1. Thermal properties for cured epoxy resins

Dynamic viscoelastic analysis can give information on the microstructure of cured epoxy resins. The $\tan\delta$ curves for the control network exhibit a major relaxation observed in most epoxy polymer [18]. The transition corresponds to the major T_g of the cured epoxy resin above which significant chain motion takes place. Fig. 2 shows the storage modulus G' and $\tan\delta$ of cured epoxy resins with PN and BHPP. The result indicated that the epoxy resin cured with BHPP had slightly lower T_g than that of DGEBA cured with PN. The result may be attributed to the incorporation of linear phosphorous-containing group which decreased rotational barrier.

The phosphorous-containing cured epoxy resins were investigated by thermogravimetric analysis (TGA). TGA is the most favored technique for rapid evaluation in comparing and ranking the thermal stab-

Table 1
Thermal properties of cured epoxy resin with various phosphorous or bromine contents

			Temperature of weight loss				Rapid weight loss temperature, T_r (°C)				Char yield (%)			
			5%		10%		Step I		Step II		600°C		700°C	
Sample		T_g (°C)	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2
	P%													
Control	0.0	121	421	427	447	441	470	472	–	–	21	24	2	18
BHPP-A	0.75	111	371	371	393	387	414	410	–	607	30	34	23	28
BHPP-B	1.51	102	361	367	377	379	393	386	567	552	32	35	27	32
BHPP-C	2.25	96	345	357	365	367	383	479	565	542	36	38	32	35
	Br%													
TBBA-A	5.10	128	369	383	391	411	423	425	627	–	23	25	0	21
TBBA -B	10.2	121	373	395	387	407	411	412	643	–	25	27	2	24
TBBA-C	15.3	113	353	377	379	387	401	403	657	–	27	30	6	28



Scheme II Schematic of BHPP, TBBA and BPA advanced epoxy resins

Scheme 2.

ility of various polymers. TGAs were performed in N_2 and air using a TGA 7 Perkin–Elmer analyzer, at a heating rate of 20°C/min from 40–800°C. TGAs of DGEBA cured with PN (control) and DGEBA cured with various ratio of BHPP/PN and TBBA/PN in nitrogen and air are shown in Table 1.The results indicated that DGEBA cured with various weight ratio of BHPP/PN and TBBA/PN have higher char yield than that of the control DGEBA/PN system. It should be noted that the BHPP-B (containing 1.51% of phosphorous) has exhibited higher char yield (32% in N_2 at 700°C) and thermal stability than that of the control DGEBA/PN and all TBBA/PN cured systems. Fig. 3 shows TGA traces of the control, BHPP-C and TBBA-C resins in N_2. The control exhibited 5% weight loss at 427°C, 10% weight loss at 441°C and then a rapid weight loss at around 472°C in N_2. The cured epoxy resin of TBBA-C exhibited 5% weight loss at 377°C, 10% weight loss at 387°C and then a rapid weight loss at around 403°C. On the other hand, the BHPP-C/PN system showed 5% weight loss at 357°C and 10% weight loss at 367°C. The thermal stabilities of cured epoxy resins were compared by the temperature of 5 and 10% weight loss, the following order may be given: BHPP-C > TBBA-C > CONTROL. Although the rapid weight loss temperature (T_r) of the control occurred at 472°C which is higher than that of BHPP-C, however, unlike the one stage rapid weight loss of the control, the BHPP-C epoxy resin exhibited a second stage of rapid weight loss at 542°C (Fig. 4). This phenomenon played an important role in improving the flame retardancy of the resins. While on fire, the phosphorous-containing groups first decompose at around 380°C and then form a phosphorus-rich resi-

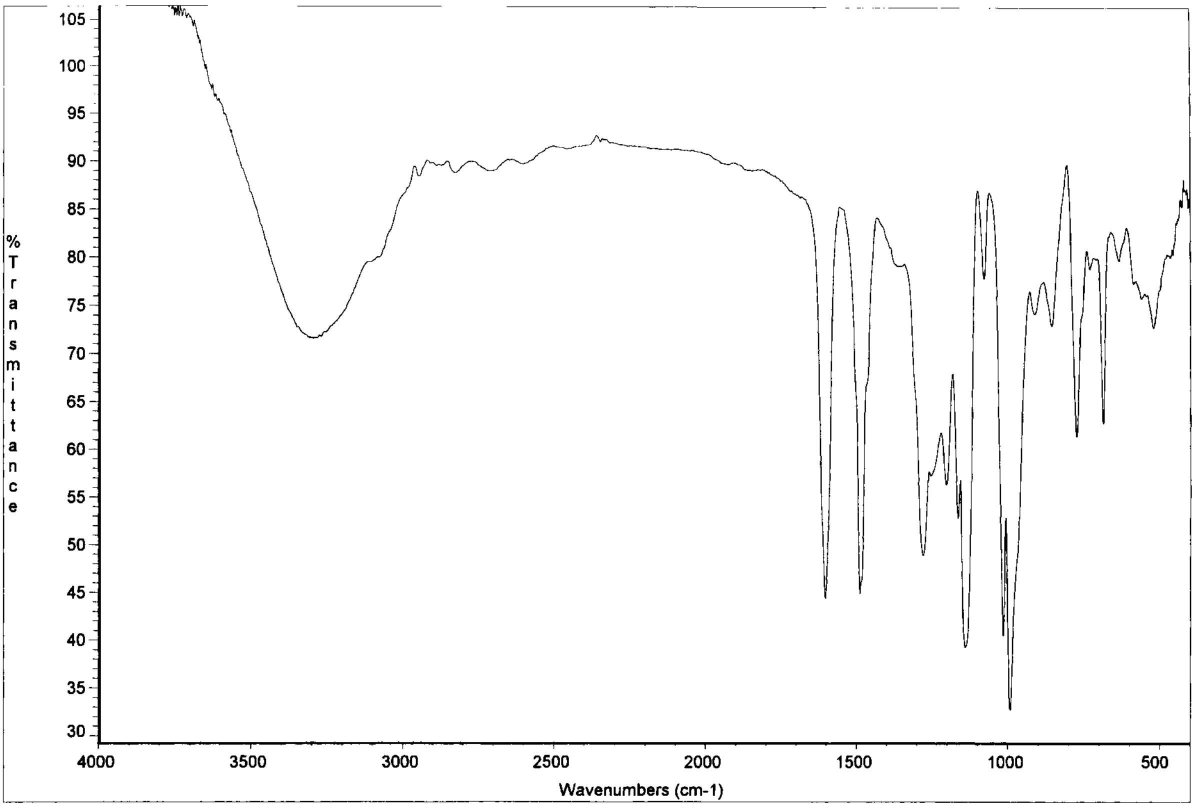


Fig. 1. IR spectrum of BHPP.

due, which prevent further decomposition of the epoxy resins by raising the second decomposition temperature to 542°C and resulted in a high char yield. The char yields at 700°C for the control, TBBA-C resin and BHPP-C resin were 18, 28 and 35%, respectively. The same phenomenon was also observed in Table 1 (in air). Furthermore, raising the phosphorus content of the resin system by using BHPP as the curing agent further raised the char yield from 18 to 35% (phosphorous-content from 0 to 2.36%). These high char yields imply that the flame retardancy of the epoxy resins were elevated via the phosphorous-containing agent [19,20], and the result are shown in Fig. 5.

3.2. LOI and UL-94V test for flame-retardant epoxy resin

Cured epoxy resin with high phosphorus content is expected to have a high char residue on pyrolysis. The

Table 2
UL-94V test rating and LOI value of cured epoxy resins with various phosphorous and bromine content

Sample	Flame-retardant element	Average burning time (s)	Visible smoke	Drip	UL 94V classification	LOI
	P%					
Control	0.0	87	Slight	No	V-2	26
BHPP-A	0.75	42	Slight	No	V-2	28
BHPP-B	1.51	7	No	No	V-0	31
BHPP-C	2.25	0	No	No	V-0	33
	Br%					
TBBA-A	5.12	38	Heavy	No	V-2	28
TBBA-B	10.20	18	Slight	No	V-1	30
TBBA-C	15.30	0	No	No	V-0	35

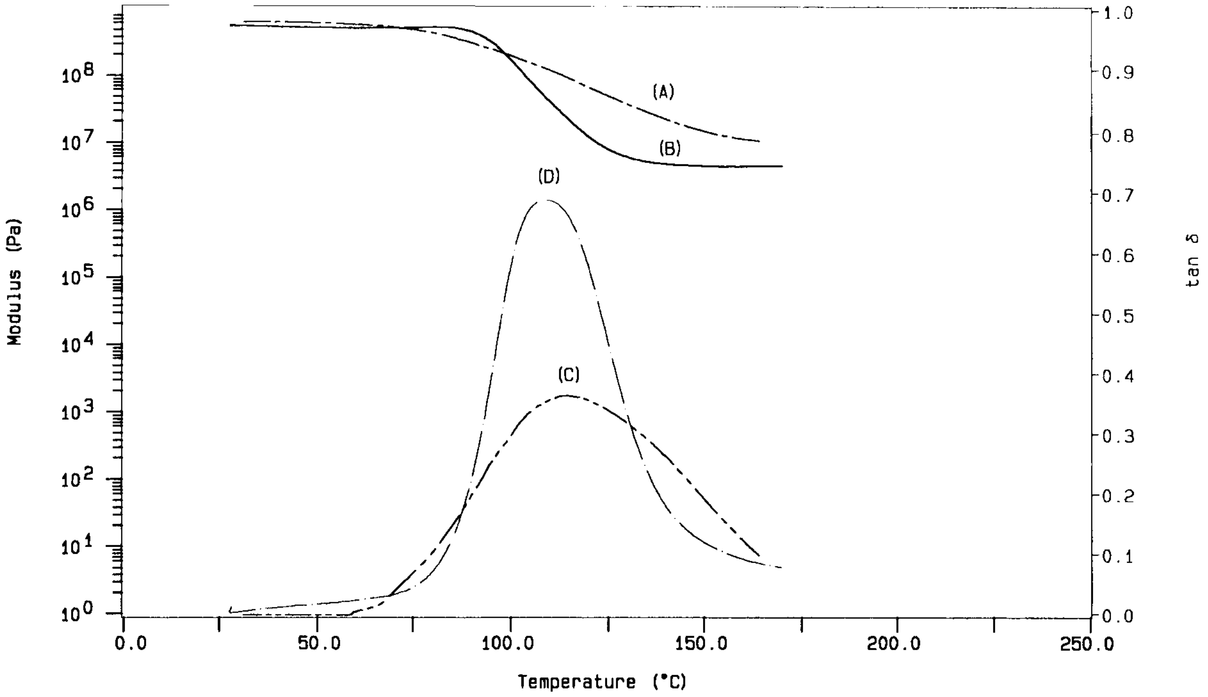


Fig. 2. Dynamic viscoelastic analyses of cured resins: (A) and (C) DGEBA/PN; (B) and (D) DGEBA/BHPP.

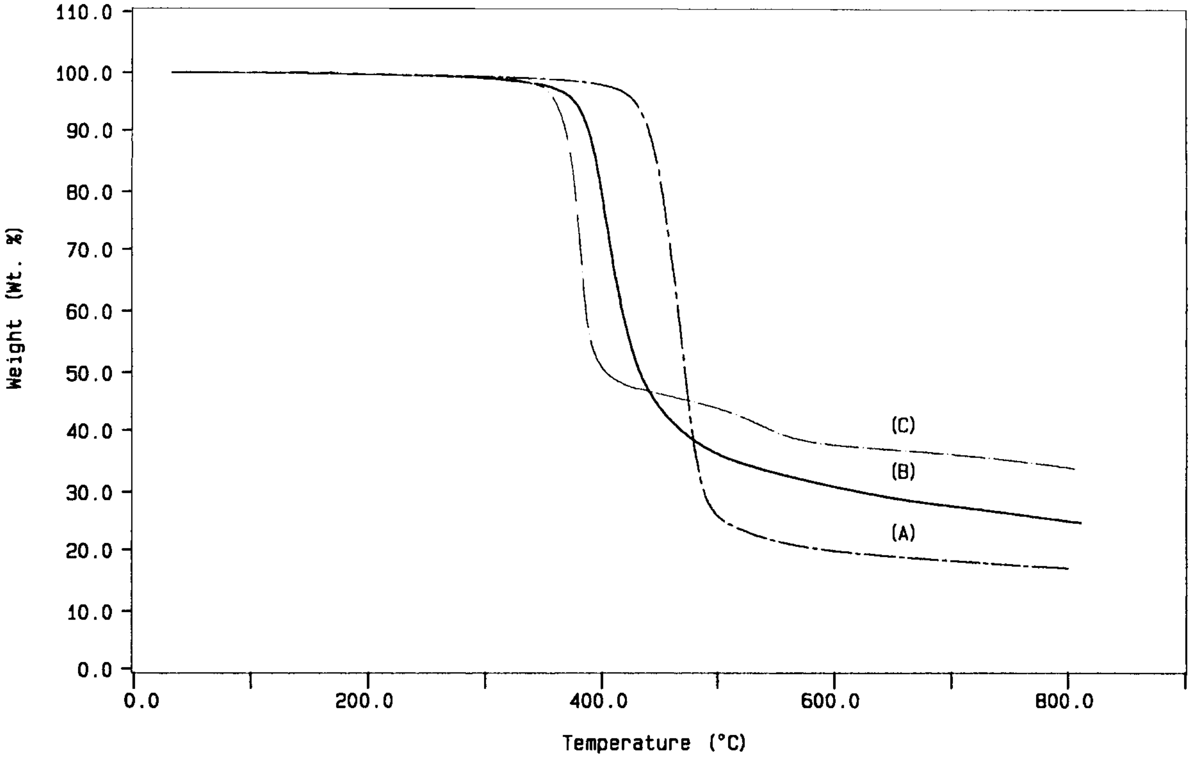


Fig. 3. TG thermograms of cured epoxy resins of N_2: (A) Control, (B) TBBA-C and (C) BHPP-C.

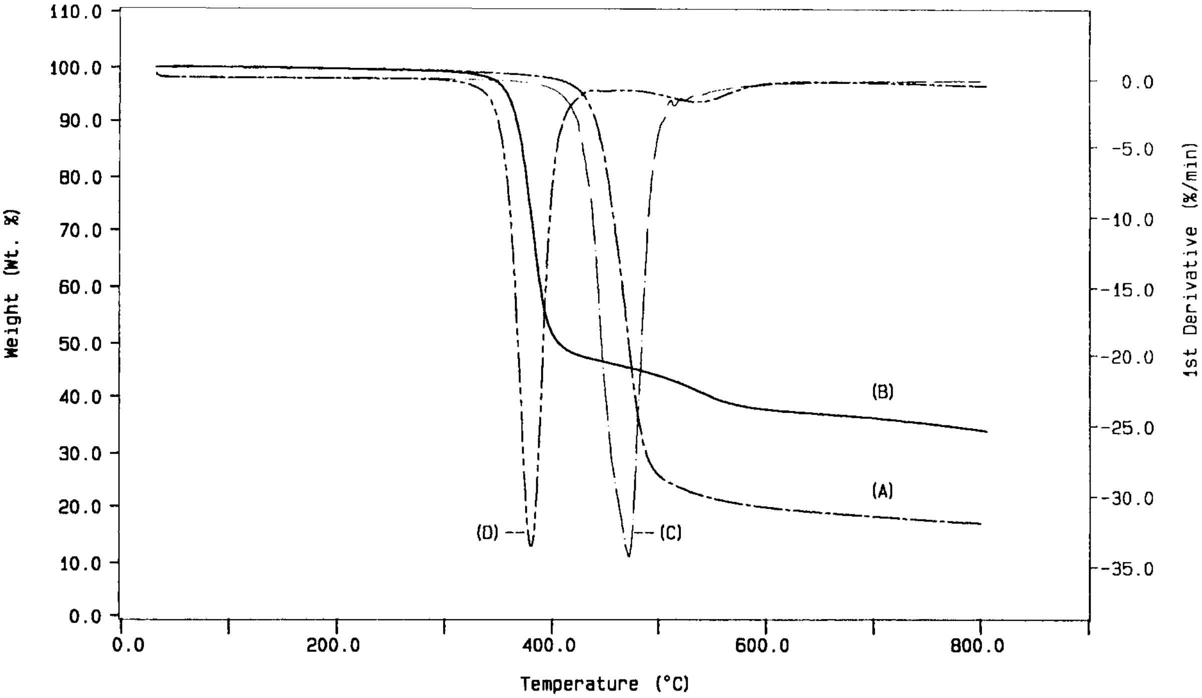


Fig. 4. TGA thermograms of cured epoxy resins: (A) Control, (B) BHPP-C and derivative, (C) Control and (D) BHPP-C.

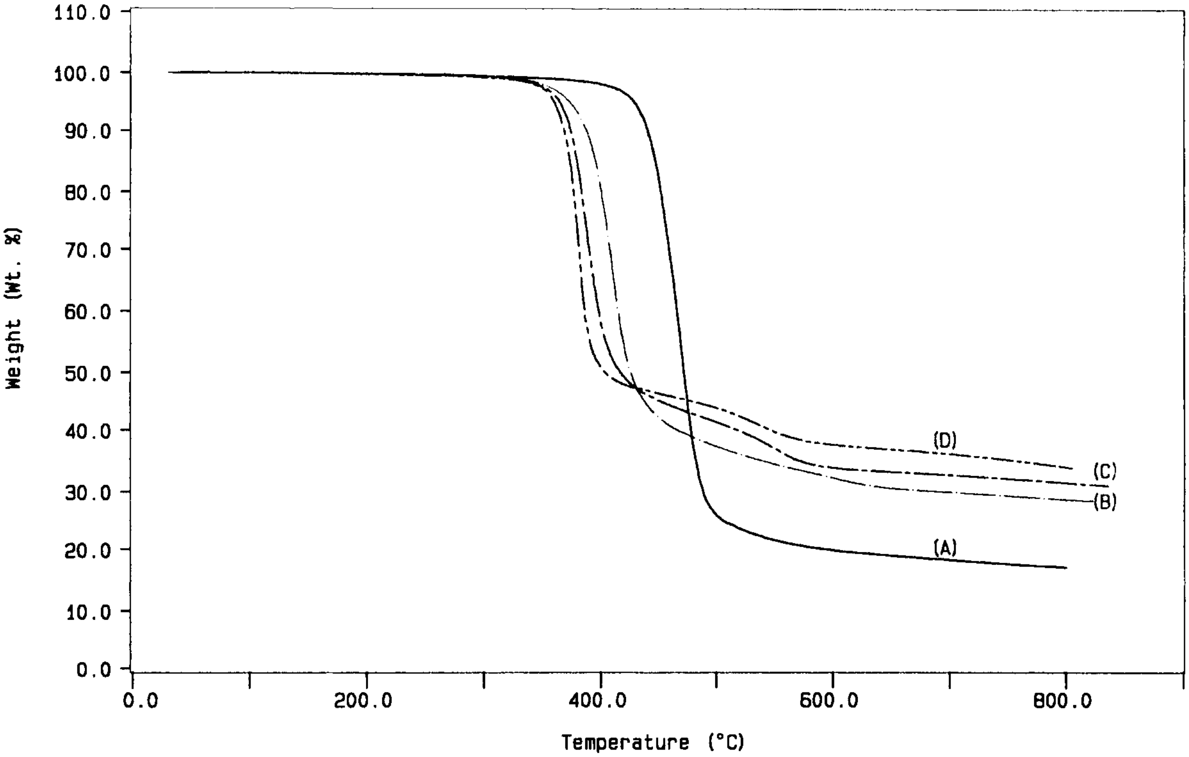


Fig. 5. TGA thermograms of cured epoxy resins: (A) Control, (B) BHPP-A, (C) BHPP-B and (D) BHPP-C.

Table 3
Thermal properties of cured advancement resins

Sample design				Temperature of weight loss				Rapid rate *Tr* (°C)				Char yield at 700°C	
				5%		10%		Step 1		Step 2			
Advancem Resin	Ent (g/eq)	PN curing agent (g/eq)	T_g (°C)	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2
BPA	50/0.105	10.5/0.106	112	377	421	413	437	449	466	–[a]	–[a]	5	14
TBBA	50/0.106	10.4/0.105	124	361	363	365	367	386	380	–[a]	–[a]	10	23
BHPP	50/0.105	10.4/0.105	105	345	347	361	361	380	376	532	530	35	37

[a] Step 2 of rapid rate was not found.

char residue on pyrolysis is reported to be linearly proportional to the oxygen index for halogen-free polymers [21]. The flame-retardant properties of cured epoxy resins with various phosphorus or bromine contents were examined by measuring their oxygen indexes (LOI). It is clear from the result of Table 2 that higher the phosphorus content, higher is the LOI value which agrees well with previous reports [22,23].

The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars of each cured epoxy resins 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 retardancy 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% phosphorous is better than 6% bromine by comparing BHPP-C with TBBA-C), it also generates much less fume than bromine.

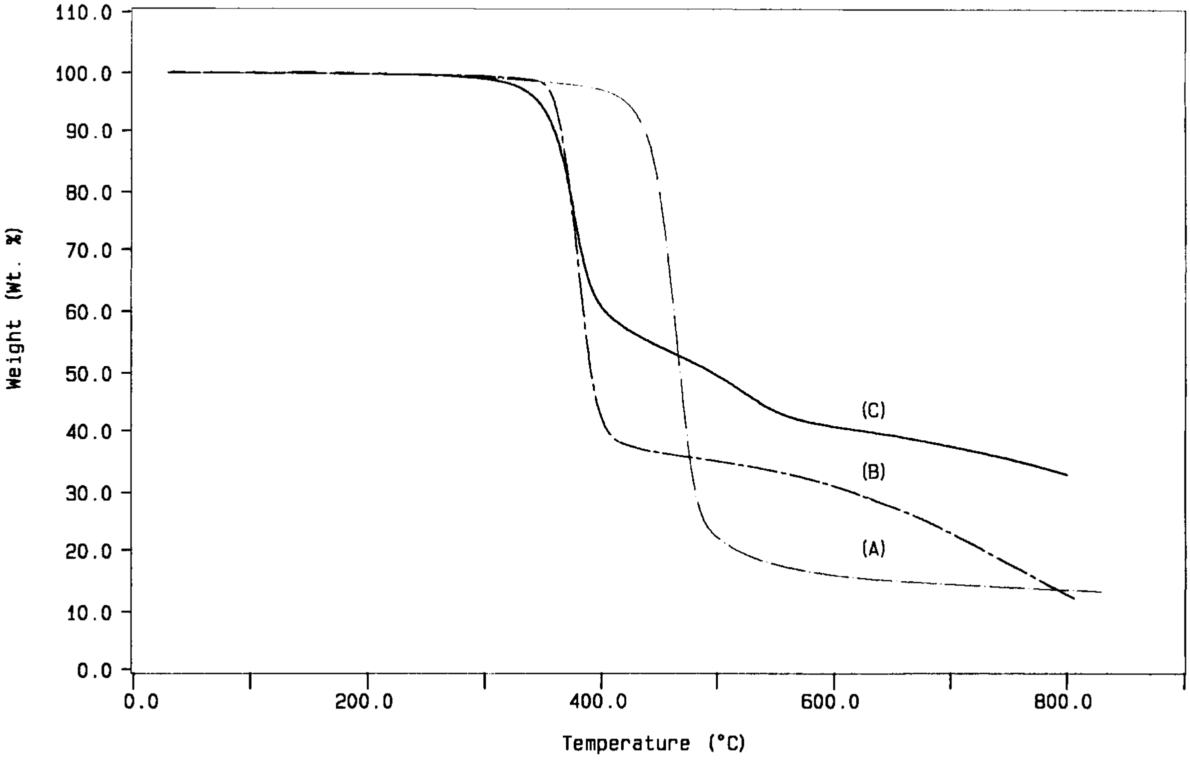


Fig. 6. TGA thermograms of the advanced epoxy resins: (A) ADBPA, (B) ADTBBA and (C) ADBHPP.

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

Sample design	Element for flame-retardant	Average burning time (s)	Fume	Drip	UL-94 classification	LOI
BPA	NO	87	– –[a]	Yes	V-2	24
TBBA	Br (17.27 %)	< 1	+ +[b]	Yes	V-0	33
BHPP	P (4.27%)	0	– –[a]	No	V-0	34

[a] – – : no.
[b] + + : heavy.

3.3. Thermal properties of advanced epoxy resin

Advanced epoxy resins are particularly useful in the printed circuit boards and other electrical laminate application [24]. These types of resins are prepared by reacting an epoxy resin (DGEBA) with bisphenol-A (BPA), TBBA or BHPP. The advanced epoxy resins are shown in Scheme 2. The amount of advanced epoxy resins, curing agent and the glass-transition temperature (T_g) of cured products were listed in Table 3. The advanced epoxy resin made from BHPP had a slightly lower T_g (105°C) than that of the other two advanced epoxy resins, which may attributed to the phosphorous-containing linear structure.

TGAs were also performed to compare the thermal stability of the advanced epoxy resins made from three diols (BPA, TBBA, BHPP), and the results are shown in Fig. 6 and Table 3. The results indicated that the advanced epoxy resin made from BHPP although had a lower decomposition temperature at 5% weight loss (347°C in N_2) and 10% weight loss (361°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 BHPP exhibited a higher second step rapid weight loss temperature at 530°C. This phenomenon played an important role in improving the flame retardancy of the advanced epoxy resin, and was confirmed by the higher char yield at 700°C than that of the other two advanced epoxy resin made from BPA and TBBA.

3.4. UL-94V test for advanced epoxy resin

For UL-94V test, five specimens of each advanced epoxy resins were prepared and the test results were shown in Table 4. The advancement resin made from BPA had a 87 s burning-time after the Bensen burner was removed, while advancement resins made from TBBA and BHPP both passed UL-94 V0 flame retardancy test. It should be noted that the advancement resin containing 4.27% P has exhibited better flame retardancy than the advancement resin containing 17.27% Br. The most important feature of phosphorous flame retardant is that no fume was generated.

4. Conclusions

A reactive phosphorous-containing flame-retardant compound BHPP was successfully synthesized. The compound was used as a curing agent for DGEBA resins for semiconductor encapsulation application, and also used to prepare advanced epoxy resin for electrical laminate application. The BHPP compound provided not only the better flame-retardant effect than that of TBBA but also generated much less fume in combustion test.

Acknowledgements

Financial support of this work by the National Science Council of the Republic of China is gratefully appreciate (NSC 88-2214-E006-002).

References

[1] Kinjo N, Ogata M, Nishi K, Kaneda A. Adv Polym Sci 1989;88:1.
[2] Lubin G, editor. Handbook of composite. New York: Van Nostrand Reinhold, 1982.
[3] Wang CS, Liao JK. Polym Bull 1991;25:559.
[4] Shau MD, Wang TS. J Appl Polym Sci Part A: Polym Chem 1996;34:387.
[5] Ichino T, Hasuda Y. J Appl Polym Sci 1987;34:1667.
[6] Mantecon A, Cadiz V, Serra A, Martinez PA. Eur Polym J 1987;23:481.
[7] Martinez PA, Cadiz V, Mantecon A, Serra A. Angew Makromol Chem 1985;133:97.
[8] Mikroyannidis JA, Kourtides DA. J Appl Polym Sci 1987;29:197.
[9] Chin WK, Shau MD, Tsai WC. J Polym Sci Part A: Polym Chem 1995;33:373.
[10] Derouet D, Morvan F, Bross JC. J Appl Polym Sci 1996;62:1885.

[11] Camino G, Costa L, Martinasso G. Polym Deg Stab 1989;23:359.

[12] Maiti S, Banerjee S, Palit SK. Prog Polym Sci 1993;18:227.

[13] Sirrier H, Gorgier S, Borissov G. Eur Polym J 1990;26:73.

[14] Wang CS, Shieh JY. Polymer 1998;39:5819.

[15] Banks M, Ebdon JR, Johnson M. Polymer 1994;35:3470.

[16] Annakurtty KS, Kishore K. Polymer 1988;29:756.

[17] Mikroyannidis JA, Kourtides DA. J Appl Polym Sci 1984;29:941.

[18] Yorkgitis EM, Eiss Jr. NS, Tran C, Willkes GL, McGrath JE. In: Advances in polymer science, vol. 72. New York: Springer–Verlag, 1985.

[19] van Krevelen DW. Polymer 1975;16:615.

[20] Liu YL, Hsiue GH, Chiu YS. J Polym Sci A: Polym Chem 1997;35:565.

[21] Pearce EM, Liepins R. Environ Health Perspectives 1975;11:69.

[22] Sato M, Yokoyama M. Eur Polym J 1975;15:75.

[23] Liu YL, Hsiue GH, Chiu YS, Jeng RJ, Ma C. J Appl Polym Sci 1996;59:1619.

[24] Wang CS, Berman JR, Walker LL, Mendoza A. J Appl Polym Sci 1991;43:1315.