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Synthesis of novel flame retardant epoxy hardeners and properties of cured products

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Abstract

Novel flame-retardant curing agents for epoxy resins, [ODOPM–PN] and [ODOPM–MPN], were prepared from phenol formaldehyde novolac (PN), melamine-phenol formaldehyde novolac (MPN) and a reactive 2-(6-oxid-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-methanol (ODOPM) while ODOPM was synthesized through the reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and formaldehyde. The compounds (ODOPM–PN and ODOPM–MPN) were used as flame-retardant hardener for *o*-cresol formaldehyde novolac epoxy (CNE) resin in electronic application. The thermal stability and flame retardancy were determined by thermal gravimetric analysis and UL 94 vertical test. The glass transition temperatures were measured by dynamic mechanical analysis. The phosphorus–nitrogen synergistic effect on flame retardancy combined with the rigid structure of ODOPM have resulted in better flame retardancy, higher glass transition temperature and thermal stability for the phosphorus–nitrogen containing epoxy resin system than the regular phosphorus-containing flame retardant epoxy resin system. UL 94-VO rating could be achieved with a lower phosphorus content of as low as 0.81% with 2.36% nitrogen for the ODOPM–MPN cured epoxy resin system and no fume and toxic gas emission were observed.

Keywords: 2-(6-Oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)methanol; Melamine; Flame retardancy

1. 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 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. [1–4]. The main drawback of epoxy resins which like other organic polymers is their flammability. Traditionally, flame-retardant polymers are achieved by physically blending flame-retardant additive with the polymer. However, a major disadvantage of all flame-retarding additives is that they may be lost in processing and during use of polymer, and this may mean that high loading are initially required. Another way in which to reduce the flammability of polymers is chemically bond the flame retardant to the polymer backbone, i.e. to use a reactive flame retardant. This offers the advantage of permanent attachment of flame-retardant group to polymer and leads to high efficiency in flame retardancy [5–8] with consequently a much smaller influence upon the physical and mechanical properties of the polymer.

Recently, organophosphorus compounds have demonstrated good ability as flame-retardant for epoxy resins and also being found to generate less toxic gas and smoke than halogen-containing compounds [9–17]. According to the previous investigations, it was found that introduction of phosphorus into the polymer skeleton can improve the flame retardancy and decrease contamination on pyrolysis. Generally, the phosphorus moiety decomposes at low temperatures relative to the polymer matrix. However, oxidation of the phosphorus char is observed at temperature above 600°C. Thus, a phosphorus-rich char is formed to reduce the production of combustible gases during fire [18–21].

The main common advantages of nitrogen compounds are their low toxicity, their solid stated and, in case of fire, the absence of dioxin and halogen acid as well as their low evolution of smoke.

Melamine and its salts are widely used as fire retardant additives, particularly of intumescent type [22,23]. It is known that melamine undergoes progressive condensation

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on heating with elimination of ammonia and formation of polymeric products named 'melam', 'melem', and 'melon' which are more thermally stable than melamine itself [24–27]. Therefore, when melamine is incorporated in a polymer, in absence of reactions with the matrix, it should leave the material when thermal degradation occurs, with negligible contribution to charred residue possibly formed.

In this article, the nitrogen–phosphorus synergistic effect on flame retardancy was studied by the incorporation of a rigid cyclophosphoryloxymethyl structure into melamine phenol novolac to form a novel epoxy resin hardener and its effects on flame retardancy and physical properties were investigated.

2. Experimental

2.1. Materials

All reagents and solvents were reagent grade or were purified by standard methods before use. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) which was prepared in our laboratory [28]. Paraformaldehyde and melamine from Aldrich were used as received. Xylene, and methyl isobutyl ketone (MIBK) from Acros were used as solvent. The epoxy resin used was *o*-cresol formaldehyde novolac epoxy (CNE, epoxy equivalent weight, EEW 192) from the Chang Chun Plastic (Taiwan). 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). Ph_3P was triphenyl phosphine that was used as curing accelerator. PTSA was *p*-toluenesulfonic acid that was used as catalyst.

2.2. Syntheses

2.2.1. Preparation of 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphos-phorin-6-yl) methanol (ODOPM)

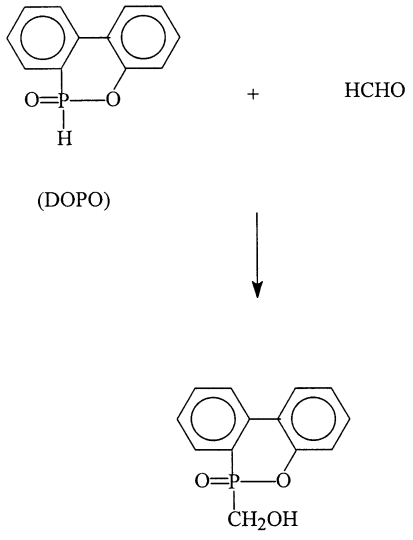
The ODOPM was prepared from paraformaldehyde and DOPO which was prepared by our laboratory [28]. A typical procedure for the preparation of ODOPM is as follows (Scheme 1: schematic diagram of ODOPM synthesis): to a 1 l reaction vessel equipped with a temperature controller, overhead stirrer and a reflux condenser with a Dean-Stark trap were added xylene (400 ml) and DOPO (216 g) and heated to 90°C with stirring under nitrogen atmosphere. To the stirring mixture, paraformaldehyde (30 g) was added incrementally over 2 h. After the completion of paraformaldehyde addition, the reaction mixture was refluxed for another 6 h resulted in precipitation of product. The product was filtered and washed thoroughly with xylene. The yield of ODOPM was 98%; m.p. 155–156°C. The IR spectrum (KBr) exhibited absorption at 1186, 1292 cm^{-1} (P=O); 962 cm^{-1} (P–O–Ph); 1462 cm^{-1} (P–Ph); 1428 cm^{-1} (P–C, aliphatic C); 3308 cm^{-1} (C–OH). EI mass spectrum intensity (%), *m/z*: 246 (92, M^+). The shift and splitting pattern of ^1H NMR spectrum is 4.11–4.38 (m, 2H), 5.59 (t, 1H), 7.25–7.31(m, 2H), 7.45 (t, 1H), 7.61 (t, 1H), 7.76 (t, 1H), 8.02 (t, 1H), 8.15–8.23 (m, 2H), (Fig. 1A), ^{31}P NMR (DMSO): a singlet peak at $\delta = 32.9$ ppm (Fig. 1B). Anal. calcd for $C_{13}H_{11}O_3P$: C, 63.41%; H, 4.47%; O, 19.51%; P, 12.61%. Found: C, 63.32%; H, 4.51%; O, 19.63%; P, 12.54%.

2.2.2. Preparation of ODOPM–PN

To a 2 l reaction vessel equipped with a temperature controller, overhead stirrer and a reflux condenser with a Dean-Stark trap were charged 1000 g of xylene, 624 g phenol formaldehyde novolac resin and 1.7 g PTSA, then 246 g of ODOPM was added incrementally. The temperature of the reaction mixture was raised to 130°C and allowed to react at that temperature for 12 h. The reaction was assumed to be complete when no more H_2O evolution was detected at 130°C. The *p*-toluene sulfuric acid was neutralized with NaOH solution and then washed with deionization water at room temperature, xylene was finally removed under vacuum to obtain ODOPM–PN (Scheme 2: schematic diagram of ODOPM–PN synthesis). The ODOPM–PN was further recrystallized from MIBK to give a product with softening point of 64–72°C, yield 98%. HPLC was used to trace the reaction by following the disappearance of ODOPM. Very little reaction took place between ODOPM and PN below 90°C, while at 132°C, the reaction was completed in 12 h. IR (KBr): 972 (P–O–Ph); 1200, 1280 (P=O); 1424 cm^{-1} (P–Ph); 3304 cm^{-1} (Ph–OH); 1432 cm^{-1} (P–C, aliphatic C).

2.2.3. Preparation of melamine-phenol formaldehyde novolac (MPN) resin

Preparation of MPN was performed according to Scheme 3 (synthesis of MPN resin). To a 2 l reaction vessel equipped with a temperature controller, overhead stirrer and a reflux condenser with a Dean-Stark trap were charged 163 g of 37% formaldehyde (2 mol), 126 g (1 mol) of melamine and



Scheme 1.

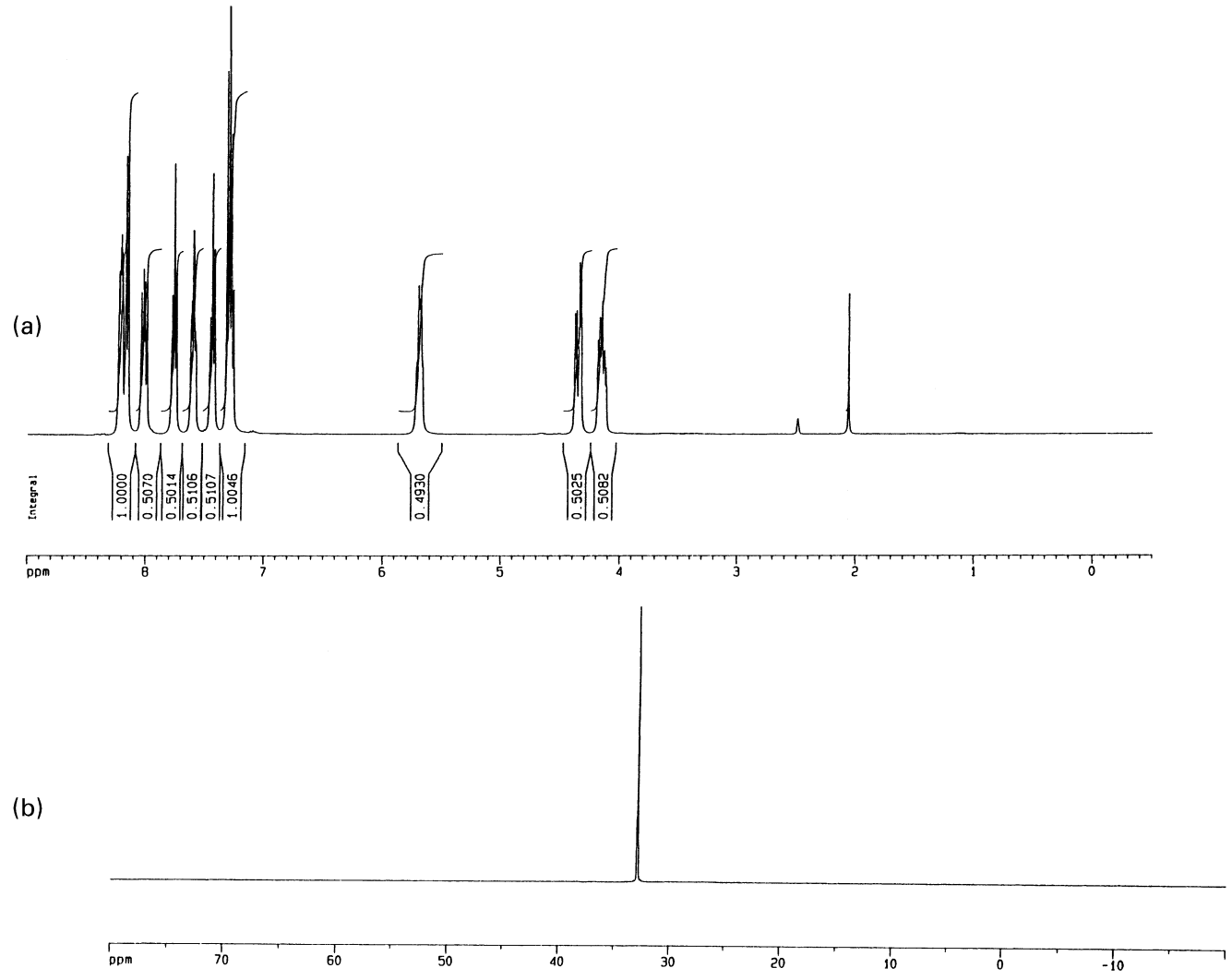
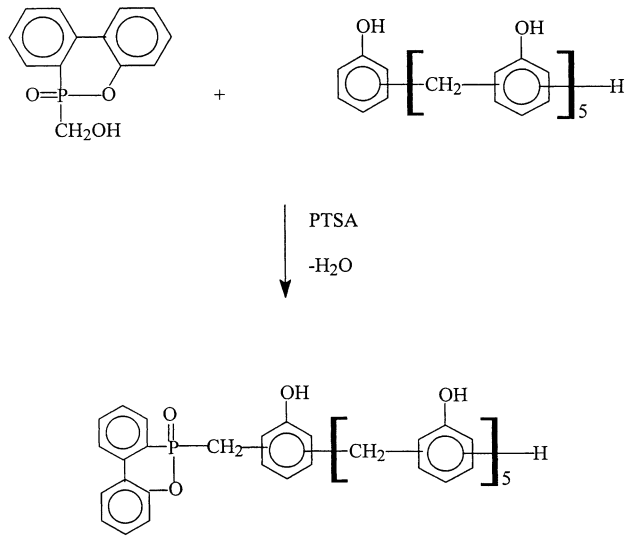


Fig. 1. (a) ^{1}H and (b) ^{31}P NMR spectra of ODOPM.

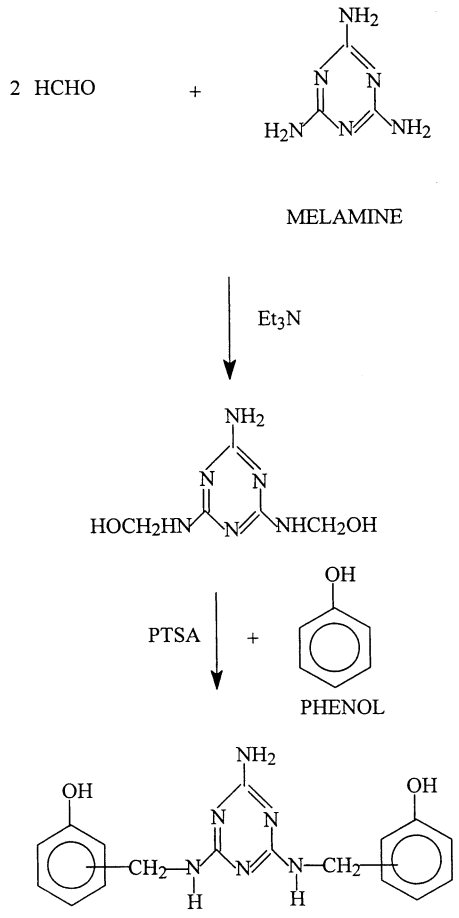
then adjust the PH of reaction mixture to 9.0 using triethylamine. The temperature of the reaction mixture was raised to 75°C and allowed to stir at that temperature for 30 min and then neutralized with dilute H_3PO_4. The temperature of the reaction mixture was raised to 95°C when 846 g of phenol and 0.25 g *p*-toluene sulfuric acid were added, then allowed to react at that temperature for 24 h. The *p*-toluene sulfuric acid was neutralized with NaOH solution. The product was dissolved in MIBK and washed with deionization water at room temperature and finally MIBK was removed under vacuum to obtain MPN. The MPN was further recrystallized from MIBK to give a product with softening point of 101–104°C, yield 96%. The nitrogen content has 24.8% that was determined via elemental analysis. The distribution of the chemical structures of MPN was analyzed by HPLC to be

$$\begin{matrix} & & & & \mathrm{P} & & \\ & & & & | & & \\ \mathrm{M\text{-}P} & : & \mathrm{P\text{-}M\text{-}P} & : & \mathrm{P\text{-}M\text{-}P} & = & 15 : 74 : 11 \end{matrix}$$

where P stands for phenol and M stands for melamine.



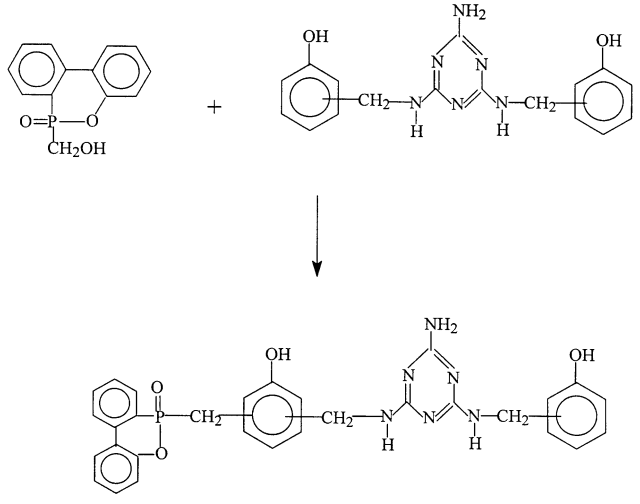
Scheme 2.



Scheme 3.

2.2.4. Preparationof ODOPM–MPN (Scheme 4: synthesis of ODOPM–MPN resin)

To a 2 l reaction vessel equipped with a temperature controller, overhead stirrer and a reflux condenser with a Dean-Stark trap were charged 1000 g of xylene, 311 g MPN resin and 1.7 g PTSA, then 246 g of ODOPM was added incrementally. The temperature of the reaction mixture was raised to 150°C and allowed to react at that temperature for 12 h. The reaction was assumed to be complete when no more H_2O evolution was detected at 150°C. The *p*-toluene sulfuric acid was neutralized with NaOH solution. After washing with deionization water at room temperature, xylene was removed under vacuum to obtain ODOPM–MPN. The ODOPM–MPN was further recrystallized from MIBK to give a product with softening point of 125–127°C, yield 98%. HPLC was used to trace the reaction by following the disappearance of ODOPM. Very little reaction took place between ODOPM and MPN below 90°C, while at 150°C, the reaction was completed in 12 h. IR (KBr): 972 cm^{-1} (P–O–Ph); 1196, 1283 cm^{-1} (P=O); 1424 cm^{-1} (P–Ph); 3298 cm^{-1} (Ph–OH); 1236 cm^{-1}(C–N); 3365 cm^{-1} (N–H).



Scheme 4.

2.2.5. Curing procedure for epoxy resins

Various amounts of ODOPM–PN, MPN and ODPOM–MPN were added with phenol novolac (PN) as curing agents for CNE resin to compare the thermal properties and the flame retardancy of hardeners. The curing agents consisted of ODOPM–PN/PN, MPN/PN and ODPOM–MPN/PN in various weight ratio (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 mold at 150°C and 50 kg cm^{-2} for a period of 1 h and then at 180°C for 2 h and further postcured at 200°C for 3 h to obtain cured specimens.

2.2.6. UL-94V flame retardancy 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 about maximum up to 12.7 mm 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 ODOPM–PN/PN, MPN/PN and ODOPM–MPN/PN were subjected to the UL-94V test

3. Results and discussion

3.1. Synthesis of phosphorus-containing compounds

Synthesis of the reactive rigid heterocyclic ring structure containing phosphorus, ODOPM, was performed by starting with DOPO and paraformaldehyde according to Scheme 1. IR spectrum of phosphorus-containing ODOPM exhibited the characteristic aliphatic hydroxyl group absorption at 3308 cm^{-1}. The absorption around 1186 and 1292 cm^{-1} corresponds to vibration with P=O which is characteristic

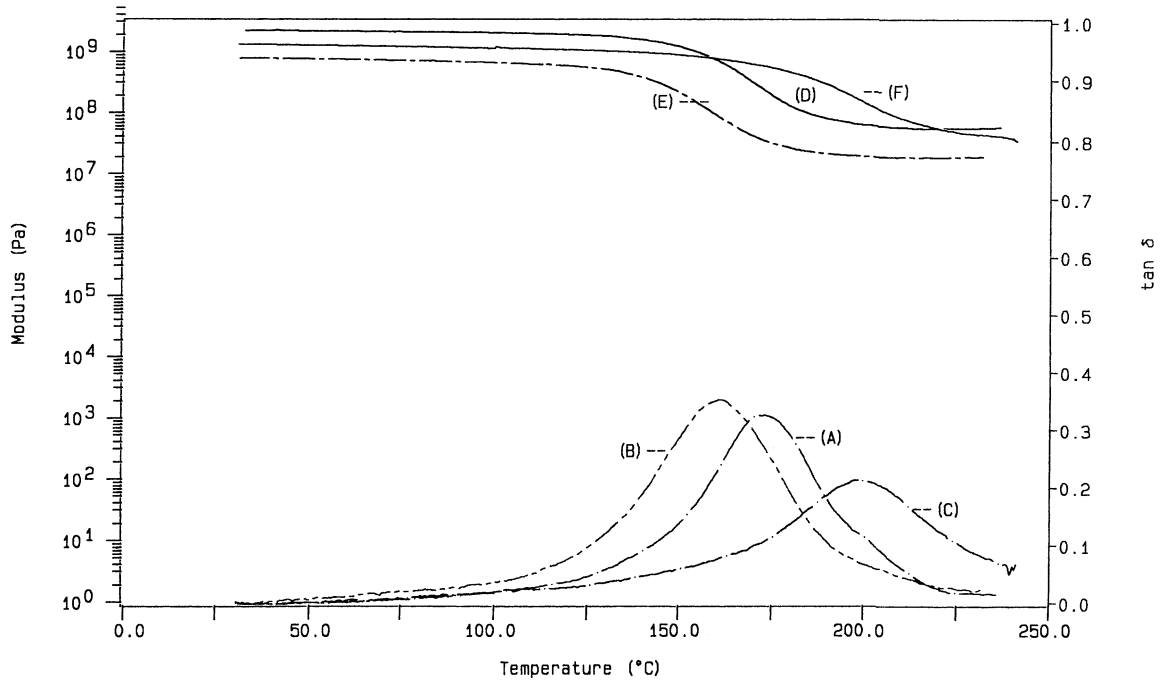


Fig. 2. Dynamic viscoelastic analyses of cured CNE resins (A) and (D) PN; (B) and (E) ODOPM-D; (C) and (F) MPN-D.

of phosphoric compounds. The ODOPM also showed strong absorption around 962 cm^{-1} corresponding to P–O–C (aromatic) stretching; the P–C (aromatic) stretching absorption around 1462 cm^{-1}; and the P–C (aliphatic) stretching absorption around 1428 cm^{-1}.

3.2. 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 [29]. 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 δ of cured epoxy resins which were cured with PN, ODOPM-D, and MPN-D. The result indicated that the epoxy resins cured with MPN-D had higher T_g (201°C) than that of epoxy resins cured with ODOPM-D (161°C) and CONTROL (175°C). The T_g of all cured epoxy resins were listed in Table 1. It should be noted that T_g of cured epoxy resins decreased with the increase in ODOPM–PN content while T_g increased with the increase in MPN content. The decrease in T_g by using ODOPM–PN as curing agent may be attributed to the incorporation of bulky rigid group which reduces the crosslink density, while MPN with higher reactive functionality than

Table 1
Thermal properties of cured neat CNE epoxy resin using various ratios of ODOPM/PN and MPN/PN (the curing agent ODOPM–PN is designated as ODOPM. (–) Step 2 of rapid rate was not found)

Sample designation		T_g (°C)	Temperatures of weight loss				Rapid rate, T_r (°C)						Char yields at 700°C	
			5%		10%		Step 1		Step 2		Step 3		Air	N_2
			Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2		
	ODOPM/PN													
CONTROL	0/100	175	393	413	421	437	451	463	671	667	–	–	20	34
ODOPM-A	25/75	173	407	401	420	423	447	441	689	–	–	–	25	37
ODOPM-B	50/50	170	403	383	417	413	439	436	693	615	–	–	27	39
ODOPM-C	75/25	165	383	379	425	411	433	434	599	602	696	–	29	41
ODOPM-D	100/0	161	377	369	407	407	425	430	583	590	709	–	33	43
	MPN/PN													
MPN-A	25/75	185	401	395	429	419	452	455	647	–	–	–	14	34
MPN-B	50/50	190	387	377	417	407	445	447	637	–	–	–	11	33
MPN-C	75/25	194	383	373	413	403	439	445	636	–	–	–	10	31
MPN-D	100/0	201	377	367	397	393	435	441	661	–	–	–	7	29

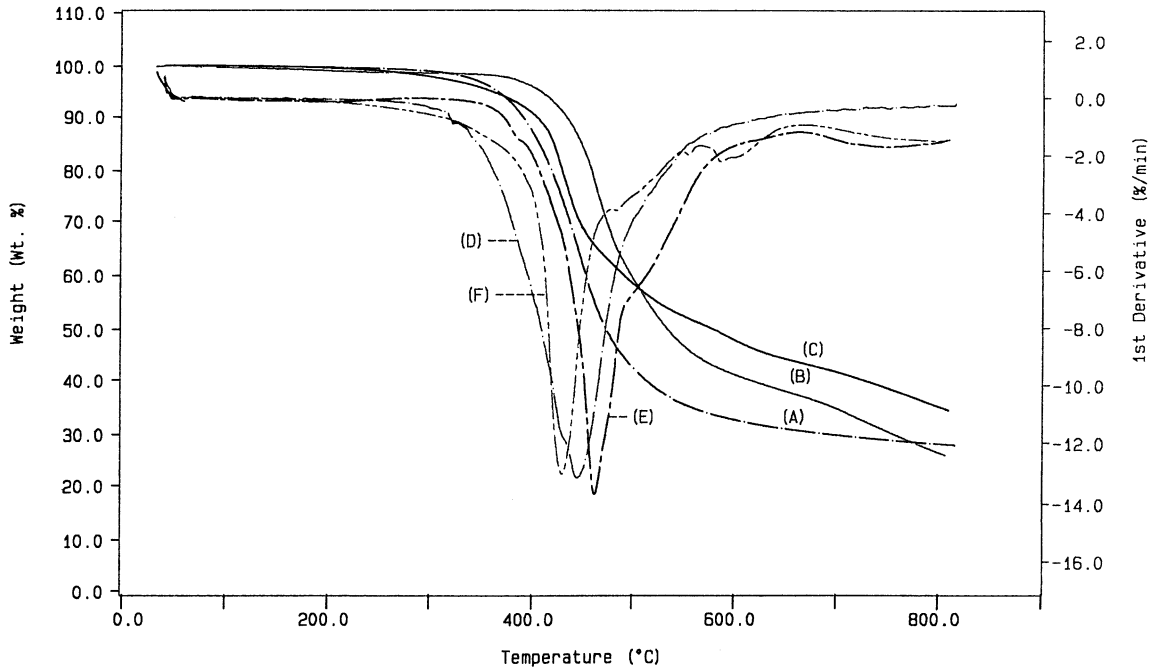


Fig. 3. TGA thermograms of cured epoxy resins in N_2: (A) PN; (B) MPN-D; (C) ODOPM-D and derivative (D) PN; (E) MPN-D; (F) ODOPM-D.

PN or ODOPM–PN has provided high T_g products owing to high crosslink density.

3.3. Thermal properties for cured epoxy resins

Thermogravimetric analysis (TGA) is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymers. The thermal properties of the cured epoxy resins with various curing agents were evaluated by TGA under nitrogen and air. The phosphorus-containing (ODOPM–PN) and nitrogen-containing (MPN) cured epoxy resins were investigated by TGA. Fig. 3 shows the thermogravimetric traces of the control CNE resin, ODOPM-D and MPN-D resins in N_2. The initial decomposition (5% weight loss), 10% weight loss, the rapid weight loss before 700°C, and char yield at 700°C in N_2 were summarized in Table 1. The results indicated that CNE cured with various weight ratios of ODOPM–PN/PN have higher char yield than that of the control CNE resin. Moreover, the char yields increased when more phosphorus-containing curing agent ODOPM–PN is introduced in the resin.

The control CNE epoxy resin cured with PN exhibited 5% weight loss at 413°C, 10% weight loss at 437°C and then the first rapid weight loss at 463°C in N_2 (Table 1). This dramatic weight loss was due to the decomposition of the resin matrix and resulted in a constant char yield. However, like most phosphorus-containing compounds [5–7,18], the CNE epoxy resins cured with phosphorus-containing ODOPM–PN showed quite complicated weight loss behavior. The weight loss could be considered as a two-stage process in N_2 environment and a three-stage process in air (Table 1). Although the rapid weight loss temperature (T_r) of the control CNE resin occurred at 463°C in N_2 which is higher than that of ODOPM-D, the phosphorus-containing epoxy resin exhibited a second stage of rapid weight loss at 590°C (ODOPM-D) in N_2. This phenomenon played an important role in improving the flame retardancy of the resins. The decomposition of phosphate group forms a phosphorus-rich residue at the first stage to prevent further decomposition of the resins matrix [5–7,18] and resulted in a high char yield. The char yields at 700°C for the control CNE resin and ODOPM-D resin were 34, 43% in N_2 and 20, 33% in air, respectively. In any case, the epoxy resins cured with ODOPM–PN exhibited higher char yields than the control.

On the other hand, the CNE cured with various weight ratios of MPN/PN had lower char yield than that of the control CNE resin. The char yields at 700°C for the MPM–PN resin were 34–29% in N_2 and 11–5% in air, respectively. It is known that the decomposition of melamine in an open system mostly generates volatiles (e.g. NH_3) above 250°C leaving little residue and resulted in low char yield [24]. MPN-D exhibited 5% weight loss at 367°C and 10% weight loss at 393°C and then a rapid weight loss at around 441°C (in N_2). The behaviors of decomposition similar to the CONTROL epoxy resin only has one stage rapid weight loss.

3.4. UL-94V test of cured epoxy resins

The UL-94Vtest 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

Table 2
UL-94V test of cured CNE with various ODOPM/PN and MPN/PN weight ratios (the curing agent ODOPM–PN is designated as ODOPM. (+ +) Heavy, (+) slightly, (–) scarcely, (—) no)

Sample designation			Average burning time	Fume	Classification
	ODOPM/PN	P (%)			
CONTROL	0/100	0	89	–	V-2
ODOPM-A	25/75	0.51	36	—	V-2
ODOPM-B	50/50	0.97	12	—	V-1
ODOPM-C	75/25	1.45	0	—	V-0
ODOPM-D	100/0	1.81	0	—	V-0
	MPN/PN	N (%)			
MPN-A	25/75	1.80	26	+	V-1
MPN-B	50/50	3.69	5	–	V-0
MPN-C	75/25	5.66	0	–	V-0
MPN-D	100/0	7.50	0	—	V-0

with the increase in phosphorus content of the cured products which is in good agreement with the result from char yield. Although the MPN cured epoxy resins exhibited lower char yield with the increase in nitrogen content, it is found that the epoxy resins cured with MPN had demonstrated less burring time in UL-94V test. The result may be attributed to the dilution of flammable gases by melamine decomposition products.

3.5. Dynamic viscoelastic and thermal properties of ODOPM–MPN epoxy resin

From above results, it can be concluded that the flame retardancy is improved by phosphorus content in char formation, and by nitrogen content from melamine to provide non-combustible gas and high T_g product. ODOPM–MPN which combines both ingredients should provide the cured product with high thermal stability and flame retardancy.

The glass-transition temperatures (T_g) of cured epoxy resins were listed in Table 3. A comparison of storage modulus G' and tan δ curves for the epoxy resins cured with ODOPM–MPN and PN were shown in Fig. 4. T_g increased with ODOPM–MPN content which may attributed to high crosslink density.

TGAs shown in Table 3 indicated similar results as previous ODOPM–PN system that the ODOPM–MPN/PN cured products had a lower decomposition temperature for 5% weight loss and 10% weight loss in N_2 and air than that of CONTROL. However, they also exhibited a higher second step rapid weight loss temperature at 564°C in N_2 and the char yields were higher than CONTROL in N_2. Furthermore, the char yields at 700°C for various

Table 3
Thermal properties of cured neat CNE epoxy resin using various ratios of ODOPM–MPN/PN (the curing agent ODOPM–MPN is designated as DOMPN. (–) Step 2 of rapid rate was not found)

Sample designation	DOMPN/PN	T_g (°C)	Temperatures of weight loss				Rapid rate, T_r (°C)						Char yields at 700°C	
			5%		10%		Step 1		Step 2		Step 3		Air	N_2
			Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2		
CONTROL	0/100	175	393	413	421	437	451	463	667	–	–	–	18	34
DOMPN-A	25/75	178	397	403	423	427	440	440	652	–	–	–	12	39
DOMPN-B	50/50	184	387	383	413	403	455	441	587	609	674	–	21	41
DOMPN-C	75/25	189	377	361	407	393	429	432	575	587	669	–	24	36
DOMPN-D	100/0	195	367	357	393	387	420	421	556	564	696	–	32	37

Table 4
UL-94V test of cured CNE with various ODOPM–PN/PN weight ratios ODOPM–MPN/PN (the curing agent ODOPM–MPN is designated as DOMPN. (+ +) Heavy, (+) slightly, (–) scarcely, (—) no)

Sample designation	DOMPN/PN	P/N (%)	Average burning time	Fume	Classification
CONTROL	0/100	0/0	89	–	V-2
DOMPN-A	25/75	0.81/2.36	8	—	V-0
DOMPN-B	50/50	1.32/3.53	0	—	V-0
DOMPN-C	75/25	1.91/5.12	0	—	V-0
DOMPN-D	100/0	2.47/6.70	0	—	V-0

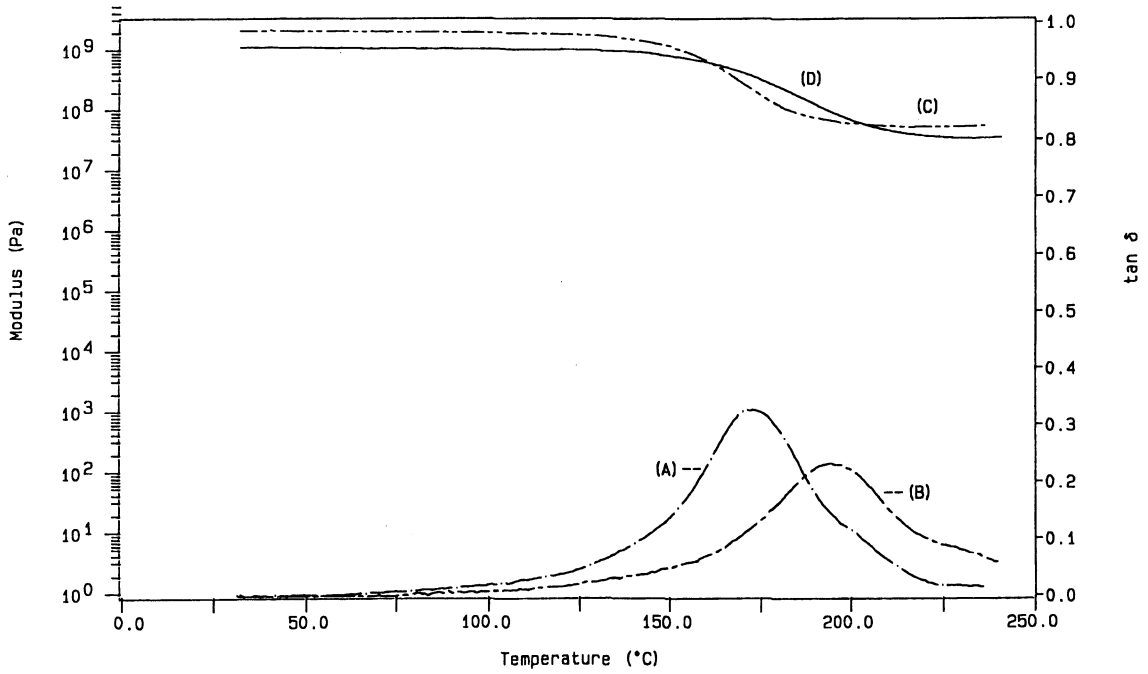


Fig. 4. Dynamic viscoelastic analyses of cured CNE resins (A) and (C) PN; (B) and (D) DOMPN-D.

ODOPM–MPN cured epoxy resins increased with increasing phosphorus–nitrogen content in air environment (from 12 to 32) as shown in Fig. 5 and Table 3. Moreover, in air, one additional rapid weight loss was found at temperatures higher than 669°C. This weight loss at high temperatures is due to the oxidation of char. This phenomenon also played an important role in improving the flame retardancy of the ODOPM–MPN cured system.

3.6. UL-94V test for epoxy resin cured with ODOPM–MPN

For UL-94V test, five specimens of each cured epoxy resins containing ODOPM–MPN were prepared and the test results were shown in Table 4. The CONTROL epoxy resin without phosphorus or nitrogen had a 89 s burning time after the Bunsen burner was removed while epoxy resins cured with ODOPM–MPN all passed UL-94 V0 flame retardancy test. It

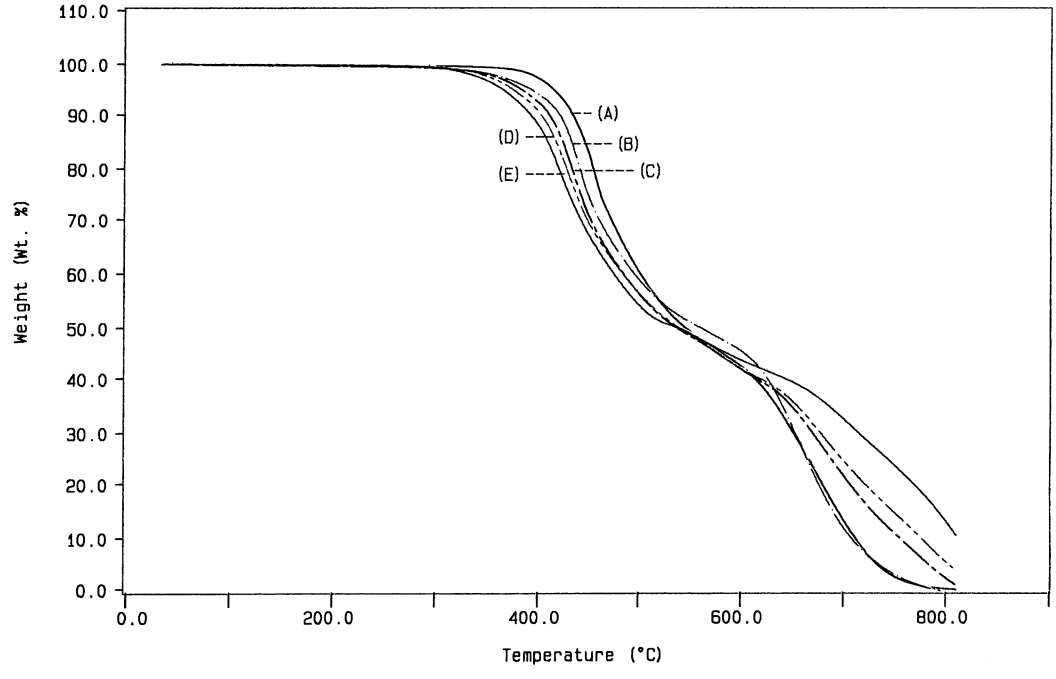


Fig. 5. TGA thermograms of cured epoxy resins in air (A) PN; (B) DOMPN-A; (C) DOMPN-B; (D) DOMPN-C; (E) DOMPN-D.

should be noted that the V-0 rating can be achieved with 0.81% P and 2.36% N. The most important feature of P–N flame retardant is that no fume was generated.

4. Conclusions

Novel flame-retardant curing agents [ODOPM–PN] and [ODOPM–MPN] were successfully synthesized from PN, MPN and ODOPM. The compounds were used as curing agent for CNE resins in semiconductor encapsulation and in electrical laminate applications. The ODOPM–PN and ODOPM–MPN cured system provided not only better mechanical property, flame retardancy and thermal stability but also much less fume in combustion test than the PN cured system. Furthermore, the N–P synergistic effect on flame retardancy and high glass-transition temperature (T_g) resulted from melamine were observed.

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References

[1] Kinjo N, Ogata M, Nishi K, Kaneda A. Adv Polym Sci 1989;88:1.
[2] Wang CS, Liao JK. Polym Bull 1991;25:559.
[3] Nakamura Y, Yamaguchi M, Okubo M, Matsumoto T. J Appl Polym Sci 1992;45:1281.
[4] Shieh JY, Ho TH, Wang CS. Angew Makromol Chem 1995;224:51.
[5] Annakurtty KS, Kishore K. Polymer 1988;29: 756.
[6] Kannan P, Kishore K. Polymer 1992;33:419.
[7] Banks M, Ebdon JR, Johnson M. Polymer 1993;34:4547.
[8] Liu YL, Hsiu GH, Chiu YS, Jeng RJ. J Appl Polym Sci 1996;61:1789.
[9] Maiti S, Banerjee S, Palit SK. Prog Polym Sci 1993;18:227.
[10] Sirrier H, Gorgier S, Borissov G. Eur Polym J 1990;26:73.
[11] Shau MD, Wang TS. J Polym Sci: Polym Chem 1996;34:387.
[12] Liu YL, Hsiu GH, Chiu YS. J Polym Sci: Polym Chem 1997;35:565.
[13] Banerjee S, Palit SK, Maiti S. J Polym Sci: Polym Chem 1984;22:1259.
[14] Mikroyannidis JA, Kourtides DA. J Appl Polym Sci 1984;29:941.
[15] Wang CS, Lin CH. J Polym Sci: Polym Chem 1999;37:3906.
[16] Wang CS, Lin CH. J Appl Polym Sci 2000;75:429.
[17] Cho CS, Fu SC, Chen LW, Wu TR. Polym Int 1998;47:203.
[18] Liu YL, Hsiue GH, Chiu YS, Jeng RJ, Ma C. J Appl Polym Sci 1996;59:1619.
[19] Liu YL, Hsiue GH, Lan CW, Chiu YS. J Polym Sci: Polym Chem 1997;35:1796.
[20] Banerjee S, Palit SK, Maiti S. J Polym Sci: Polym Chem 1994;32:219.
[21] Banks M, Ebdon JR, Johnson M. Polymer 1994;35:3470.
[22] Camino G, Costa L. Polym Degrad Stab 1989;23:359.
[23] Kay M, Price AF, Lavery I. J Fire Retardant Chem 1979;6:69.
[24] Nelson GL, editor. Fire and polymer. ACS symposium series 425. Dallas, TX: ACS, 1989.
[25] Horacek H, Grabner R. Polym Degrad Stab 1996;54:205 (twice).
[26] Bann B, Miller SA. Chem Rev 1958;58:131.
[27] Costa L, Camino G. J Therm Anal 1983;43:423.
[28] Wang CS, Shieh JY. Polymer 1998;39:5819.
[29] Yorkgitis EM, Eiss Jr. NS, Tran C, Willkes GL, McGrath JE. Advances in polymer science, vol. 72. New York: Springer, 1985. p. 79.