

# Synthesis and Properties of Novel Phosphorus-Containing Hardener for Epoxy Resins

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**ABSTRACT:** A novel phosphorus-containing curing agent, 2-(6-oxid-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl) phenol formaldehyde novolac [**OD-PN**], was prepared from phenol formaldehyde novolac resin (PN) and a reactive 2-(6-oxid-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)chloride (ODC) while ODC was synthesized through reaction between *o*-phenylphenol and phosphoryl trichloride. The compound (OD-PN) was used as a reactive flame-retardant in *o*-cresol formaldehyde novolac epoxy resin (CNE) for electronic application. Owing to the rigid structure of ODC and pendant P group, the resulted phosphorus containing epoxy resin exhibited better flame retardancy, higher glass transition temperature, and thermal stability than the noncyclic P-containing curing agent or the bromine containing flame-retardant epoxy resin. UL 94-VO rating could be achieved with a phosphorus content of as low as 1.21% (comparable to bromine content of 6%) in the cured resin, and no fumes and toxic gas emission were observed. The relationship between the structure and flammability for both phosphorus containing curing agents OD-PN and TP-PN (triphenyl phosphate-phenol formaldehyde novolac reaction product) are also examined. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1636–1644, 2000

**Key words:** 2-(6-oxido-6H-dibenz(c,e)(1,2) oxaphosphorin-6-yl)chloride; flame retardancy

## INTRODUCTION

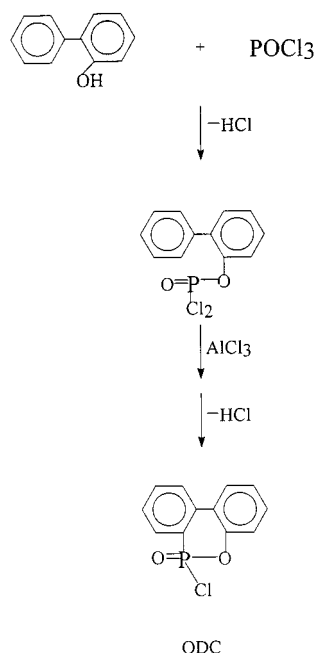
Epoxy resins have the excellent characteristics of moisture, solvent, and chemical resistance, toughness, low shrinkage on cure, superior electrical and mechanical resistance properties, and good adhesion to many substrate. The versatility in formulation also make epoxy resins generally useful industrially for surface coating, adhesive, painting materials, pottings, composites, laminates, encapsulant for semiconductor, insulating

material for electric devices, etc.<sup>1–4</sup> The main drawback of epoxy resins, like many other organic polymers, is their flammability. Traditionally, flame-retardant polymers are obtained 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 the polymer, and this may mean that high loadings 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 groups to polymer, and leads to high ef-

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**Scheme I** Schematic diagram of ODC synthesis.

efficiency in flame retardancy<sup>59</sup> with a consequently much smaller influence upon the physical and mechanical properties of the polymer.

Although bromine compounds in conjunction with antimony oxide are widely used as flame retardants for epoxy resin commercially, many problems with the generation of toxic, corrosive fumes, halogenous gases such as hydrogen bromide during combustion have been reported with this system.<sup>10,11</sup> Consequently, the trend is now towards flame retardants with low or zero halogen content, and increasing use is being made of phosphorus-containing flame retardants. Flame retardation of organic polymers using phosphorus compounds is well established.<sup>12–14</sup> Recently, organophosphorus compounds have demonstrated good ability as a flame retardant for epoxy resins and also to generate less toxic gas and smoke than halogen-containing compounds.<sup>15–23</sup>

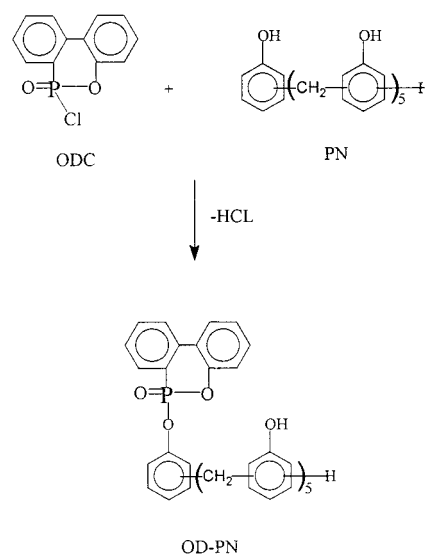
In our previous study,<sup>24</sup> 2-(6-oxid-6H-dibenz(c,e)- $\langle 1,2 \rangle$ oxa-phosphorin-6-yl) 1,4-benzenediol (ODOPB) was synthesized and successfully used to cure the commercial epoxy resins, DGEBA (bisphenol A epoxy) and *o*-cresol formaldehyde novolac epoxy resin (CNE) for laminate and encapsulation applications. The results indicated that the epoxy resins cured with ODOPB demonstrated better flame retardancy, less fumes, and higher thermal stability than the conventional bromine-containing epoxy systems. The present article concerns the synthesis

and characterization of 2-(6-oxid-6H-dibenz(c,e)- $\langle 1,2 \rangle$ oxa-phosphorin-6-yl)chloride (ODC) and its reaction with the phenol formaldehyde novolac resin (PN) to form a polycyclic p-containing curing agent OD-PN (Schemes I and II). The synthesis of ODC is actually a one-step reaction. The intermediate, the dichloride, is not isolated and immediately cyclizes to ODC in very high yield by simply adding a strong Lewis acid catalyst ( $\text{AlCl}_3$ ). Scheme I is much simpler than the previously reported ODOPB synthesis,<sup>24</sup> which involved a tedious four-step reaction and low yield. Therefore, it is advantageous industrially to use OD-PN instead of ODOPB. To compare the p-containing structure on the flame retardancy and the thermal stability of cured epoxy resins, another curing agent TP-PN (Scheme III) was also synthesized and the results discussed.

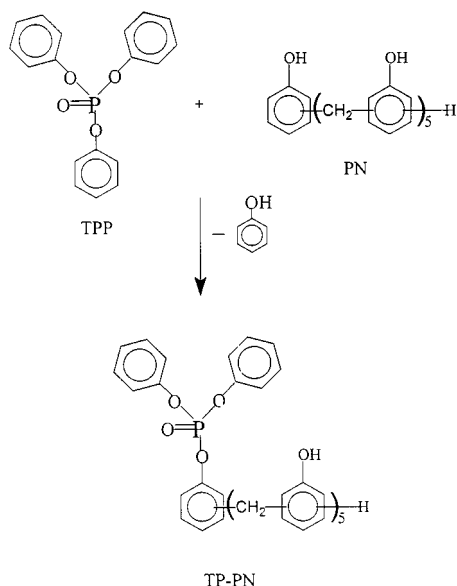
## EXPERIMENTAL

### Reagents

All reagents and solvents were reagent grade, or were purified by standard methods before use. *o*-Phenyl phenol, phosphoryl trichloride, and triphenyl phosphate (TPP) from the Aldrich Co. were used as received. Tetrahydrofuran and methyl isobutyl ketone (MIBK) from the Acros Co. were used as solvents. The epoxy resin used was *o*-cresol-formaldehyde novolac epoxy (CNE, Quatrex 3330, epoxy equivalent weight, EEW



**Scheme II** Schematic diagram for the incorporation of ODC on PN.



**Scheme III** Schematic diagram of TP-PN synthesis.

192). 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). The zinc acetate from the Aldrich Co. was used as a catalyst in TP-PN preparation. Triphenyl phosphine ( $\text{Ph}_3\text{P}$ ) was used as the curing accelerator.

### Syntheses

#### *Preparation of 2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl) chloride (ODC)*

To a 1-L reaction vessel equipped with a temperature controller, overhead stirrer, and a reflux condenser were added 204 g *o*-phenyl phenol and 230 g phosphoryl chloride. The mixture was first heated slowly to 30°C to dissolve *o*-phenyl phenol, and then increased to 50°C. The evolution of HCl gas was detected immediately. The reaction mixture was heated at reflux (145°C) for 5 h until HCl evolution subsided. After the addition of 1.3 g aluminum trichloride, the mixture was further heated at reflux temperature for 8 h. 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 crystallized from tetrahydrofuran to give ODC (yield 93%). The IR spectrum (KBr) exhibited absorption at 1186, 1292  $\text{cm}^{-1}$  (P=O); 1172, 962  $\text{cm}^{-1}$  (P—O—P h); 1462, 1424  $\text{cm}^{-1}$  (P—Ph). Anal. Calcd for  $\text{C}_{12}\text{H}_8\text{PO}_2\text{Cl}$ : C,

57.48; H, 3.19; O, 12.77; P, 12.38; Cl, 14.17. Found: C, 57.52; H, 3.15; O, 12.65; P, 12.30; Cl, 14.38. EIMS,  $m/z$ : 251 (92,  $\text{M}^+$ ).

#### *Preparation of p-Containing Curing Agent ODC-PN*

To a 2-L reaction vessel equipped with a temperature controller, overhead stirrer, and a reflux condenser were charged 1000 g of MIBK and 624 g phenol formaldehyde novolac resin, then 250 g of ODC was added incrementally. The temperature of the reaction mixture was raised to 120°C, and was allowed to react at that temperature for 4 h. The reaction was assumed to be complete when no more HCl evolution was detected at 120°C. After washing with deionized water at room temperature, MIBK was removed under vacuum to obtain OD-PN. The OD-PN was further recrystallized from MIBK to give a product with a softening point of 125–132°C (yield 98%). GC was used to trace the reaction. Very little reaction takes place between ODC and PN below 90°C, while at 120°C, the reaction completed in 4 h. IR (KBr): 972 (P—O—Ph), 1200, 1280 (P=O), 1424  $\text{cm}^{-1}$  (P—Ph), 3304 (Ph—OH).

#### *Preparation of p-Containing Curing Agent TP-PN*

To a three-necked 500-mL glass vessel equipped with a stirrer and a distillation column, 1 mol (326 g) of triphenyl phosphate (TPP), 1 mol (624 g) of phenol formaldehyde novolac resin and  $6 \times 10^{-3}$  mol of zinc acetate were introduced. The reaction was carried out with stirring under a nitrogen atmosphere at 140°C for 4 h. The reaction mixture was then heated to 190°C and maintained at this temperature, while phenol was continuously removed by distillation under reduced pressure of 180–200 mmHg and then at 200°C and 4–5 mmHg to complete the transesterification. The TP-PN was further recrystallized from MIBK to give product (softening point 46–53°C, yield 98%).

#### *Curing Procedure for Epoxy Resins*

Various amounts of OD-PN and TP-PN were added with phenol novolac (PN) as curing agents for cresol formaldehyde novolac epoxy (CNE) resin to determine the flame-retardant effect of phosphorus and structure. The curing agents consisted of OD-PN/PN and TP-PN/PN in various weight ratios (0/100, 25/75, 50/50, 75/25, 100/0) were prepared.  $\text{Ph}_3\text{P}$  was used as the curing accelerator. The CNE resin was mixed with the

above curing agents and 0.2%  $\text{Ph}_3\text{P}$  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<sup>2</sup> for a period of 1 h, and then at 180°C for 2 h and further postcured at 210°C for 3 h to obtain cured specimens.

### LOI and UL-94V Flame-Retardant Test

The LOI is the minimum fraction of  $\text{O}_2$  in a mixture of  $\text{O}_2$  and  $\text{N}_2$  that will just support flaming combustion. The LOI test was performed according to the testing procedure of ASTM D 2836 Oxygen Index Method with a test specimen bar of 7 to 15 cm in length,  $6.5 \pm 0.5$  mm in width and  $3.0 \pm 0.5$  mm in thickness. Ten sample bars suspended vertically were ignited by a Bunsen burner. The flame was removed and the timer started. The concentration of oxygen must be raised if the specimen is extinguished before burning 3 min or 5 cm: continue to adjust oxygen content until limiting concentration is determined.

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 OD-PN/PN and TP-PN/PN were subjected to the UL-94V test.

## RESULTS AND DISCUSSION

### Synthesis of Phosphorus-Containing Compounds

Synthesis of the reactive rigid heterocyclic ring structure containing phosphorus, 2-(6-oxid-6H-dibenz(c,e)(1,2)oxa-phosphorin-6-yl) chloride (ODC), was performed by starting from *o*-phenyl phenol and phosphoryl trichloride in two steps according to Scheme I. The phosphorus-containing curing agent, 2-(6-oxido-6H-dibenz(c,e)(1,2) oxa phosphorin-6-yl) phenol formaldehyde novolac resin (OD-PN), was obtained by the addition of ODC to phenol formaldehyde novolac resin in a quantitative yield (Scheme II). As the reaction proceeded, IR spectrum of the phosphorus-containing curing agent OD-PN exhibited the character-

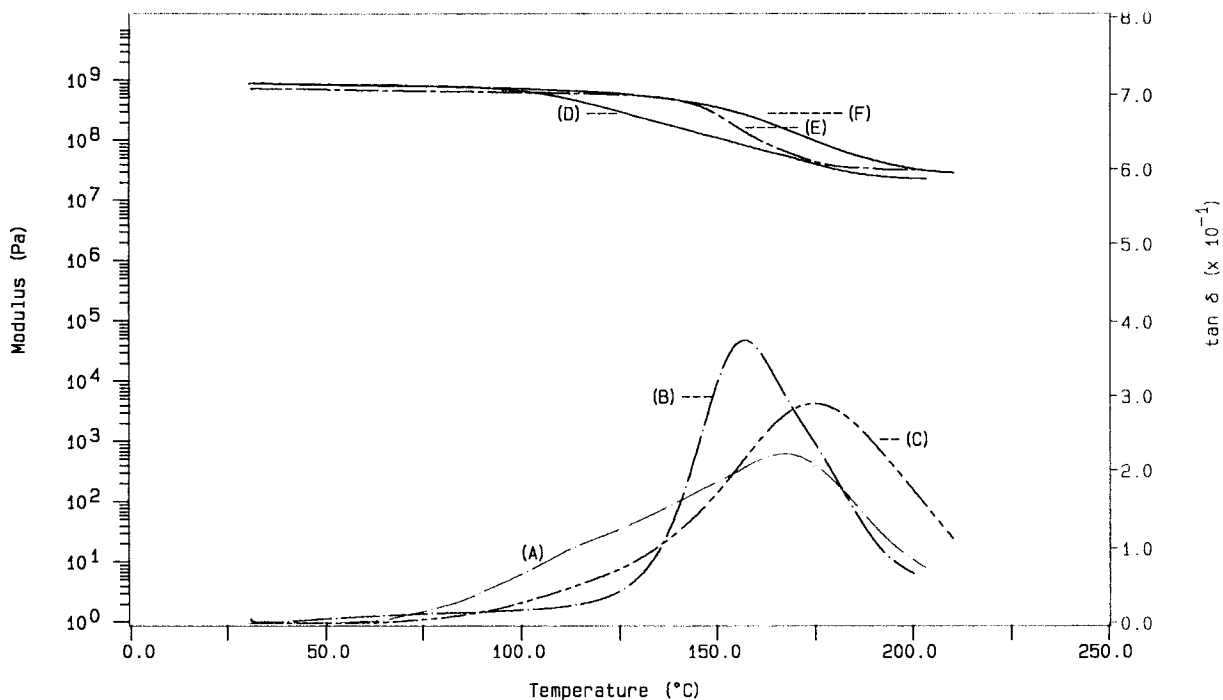
istic phenol-like hydroxyl group absorption at 3304 cm<sup>-1</sup>. The absorption around 1200 and 1280 cm<sup>-1</sup> corresponds to vibration with P=O, which is characteristic of phosphonylated compounds. The OD-PN also showed strong absorption around 972 cm<sup>-1</sup>, corresponding to P—O—C (aromatic) stretching; the P—C (aromatic) stretching absorption around 1424 cm<sup>-1</sup>. A similar IR spectrum for TP-PN was also observed. The noncyclic phosphorus-containing curing agent, TP-PN, was obtained by transesterification between TPP and phenol formaldehyde novolac resin in a quantitative yield (Scheme III). As the reaction proceeded, the IR spectrum of phosphorus-containing curing agent TP-PN exhibited the characteristic phenol-like hydroxyl group absorption at 3372 cm<sup>-1</sup>. The absorption around 1212 and 1284 cm<sup>-1</sup> corresponds to vibration with P=O, which is characteristic of phosphonylated compounds. The TP-PN also showed strong absorption around 972 cm<sup>-1</sup> corresponding to P—O—C (aromatic) stretching, but it was different with OD-PN. The P—C (aromatic) stretching absorption around 1424 cm<sup>-1</sup> was not found in the TP-PN spectrum.

### Dynamic Viscoelastic Analyses of Various Cured CNE 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 polymers.<sup>25</sup> The transition corresponds to the major  $T_g$  of the cured epoxy resin, above which significant chain motion takes place. Figure 1 shows the storage modulus  $G'$  and  $\tan \delta$  of cured epoxy resins with PN, OD-PN, and TP-PN. The result indicates that the epoxy resin cured with OD-PN has higher  $T_g$  than that of epoxy resin cured with TP-PN. The  $T_g$  of all cured epoxy resins are listed in Table I. It should be noted that  $T_g$  of cured epoxy resins increased with the increase in OD-PN content, while  $T_g$  decreased with the increase in TP-PN content. The increase in  $T_g$  by using OD-PN as a curing agent may be attributed to the incorporation of a bulky rigid group, which increased rotational barrier.

### 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



**Figure 1** Dynamic viscoelastic analyses of cured CNE resins (A) and (D) PN; (B) and (E) ODPN/PN-D; (C) and (F) TPPN/PN-D.

epoxy resins with various curing agents were evaluated by TGA under nitrogen and air.

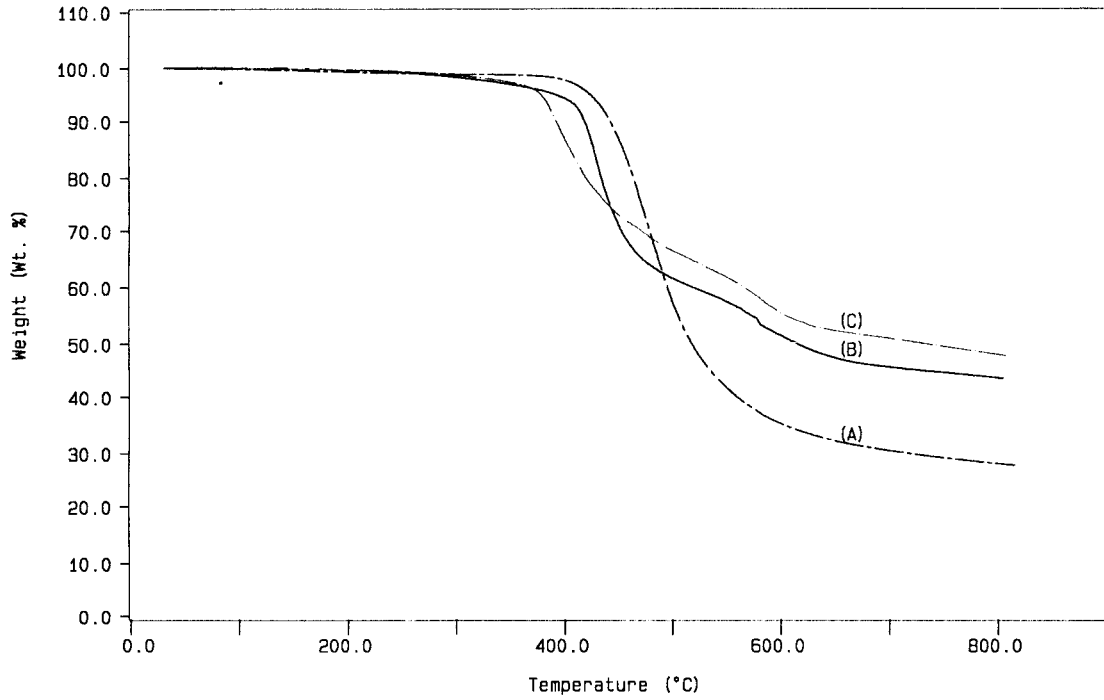
Figures 2 and 3 show the thermogravimetric traces of the control CNE resin, ODPN/PN-D and TPPN/PN-D resins in  $N_2$  and air. The initial de-

composition (5% weight loss), 10% weight loss, the rapid weight loss before 700°C, and the char yield at 700°C in  $N_2$  and air were also summarized in Table I. The results indicate that CNE, cured with various weight ratios of ODPN/PN and

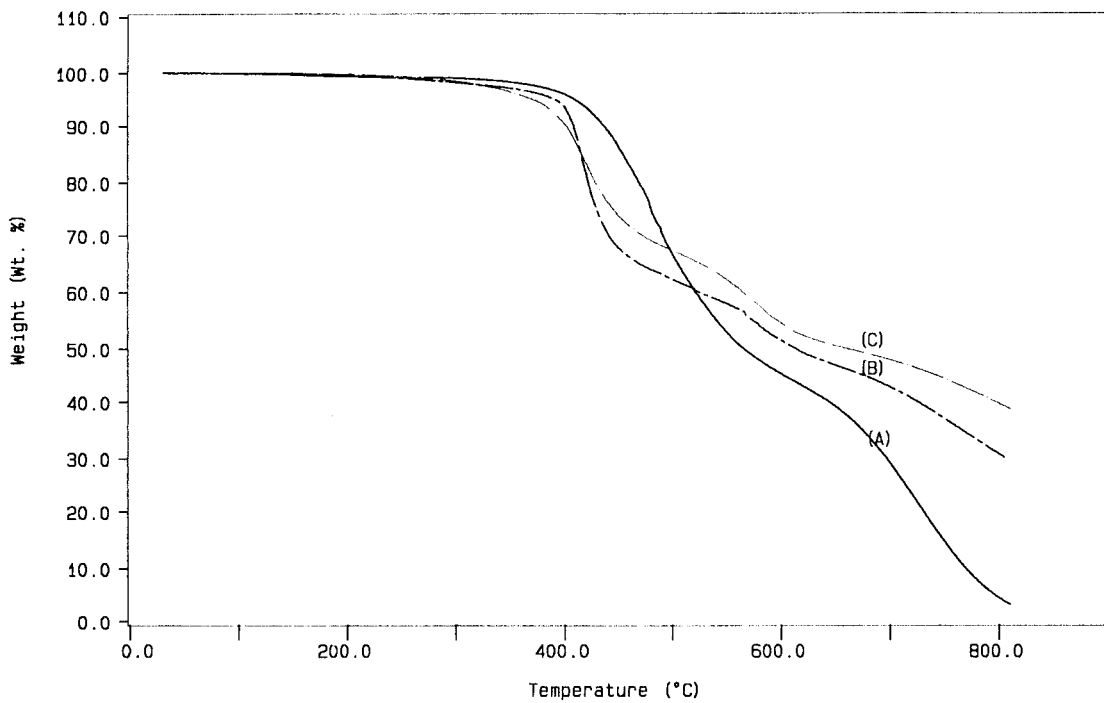
**Table I** Thermal Properties of CNE Epoxy Resin Cured with Various Ratios of OD-PN/PN and TP-PN/PN

Sample Design	OD-PN/PN	$T_g$ (°C)	Temperatures of Weight Loss				Rapid Rate				Char Yields at 700°C	
			5%		10%		$T_r$ (°C)					
			Air	$N_2$	Air	$N_2$	Step 1	Step 2	Air	$N_2$	Air	$N_2$
CONTROL	0/100	167	433	421	453	437	470	473	—	—	27	32
ODPN/PN-A	25/75	169	409	407	435	427	450	455	—	—	41	43
ODPN/PN-B	50/50	171	403	395	427	417	442	437	606	620	43	44
ODPN/PN-C	75/25	175	385	383	419	397	423	409	587	596	44	46
ODPN/PN-D	100/0	178	377	377	401	397	413	401	579	587	46	50
	TP-PN/PN											
TPPN/PN-A	25/75	165	421	412	443	442	461	458	716	631	34	40
TPPN/PN-B	50/50	161	417	406	431	422	441	443	615	597	35	41
TPPN/PN-C	75/25	160	397	395	417	420	424	436	610	590	38	43
TPPN/PN-D	100/0	156	391	389	409	415	419	425	575	584	40	45

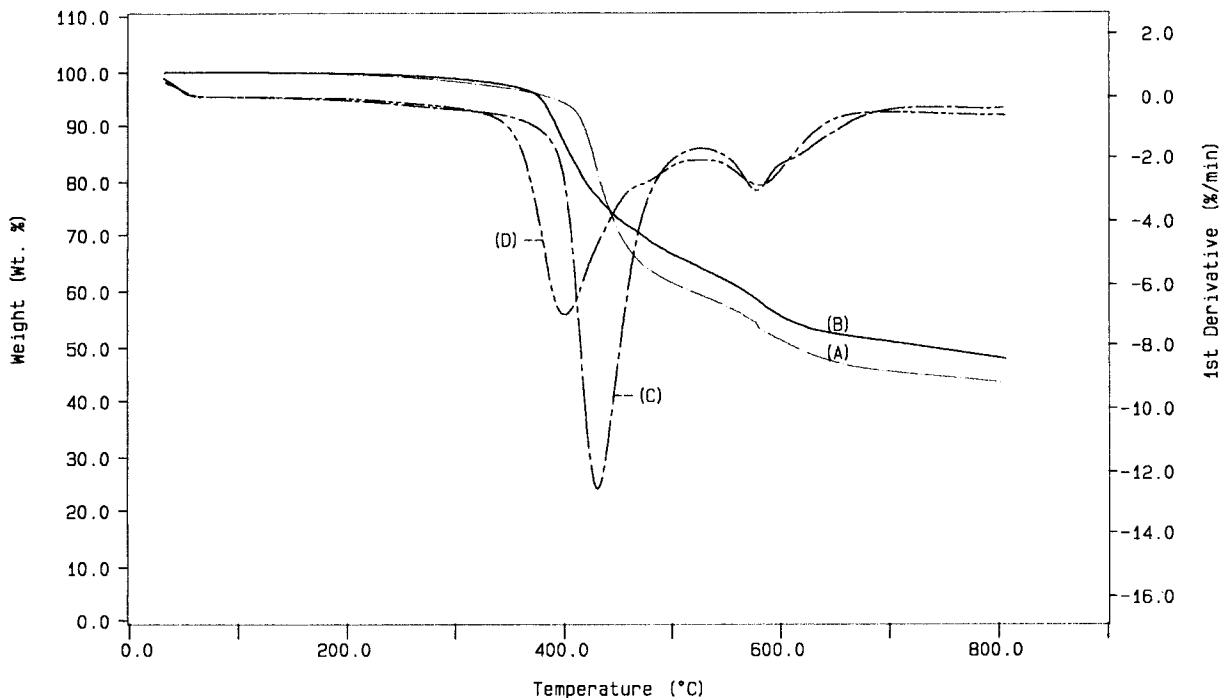
—: Step 2 of rapid rate was not found.



**Figure 2** TGA thermograms of cured epoxy resins in  $N_2$ : (A) PN; (B) TPPN/PN-D; (C) ODPH/PN-D.



**Figure 3** TGA thermograms of cured epoxy resins in air: (A) PN; (B) TPPN/PN-D; (C) ODPH/PN-D.



**Figure 4** TGA thermograms of cured epoxy resins in  $N_2$ ; (A) TPPN/PN-D; (B) ODPH/PN-D and derivatives; (C) TPPN/PN-D; (D) ODPN/PN-D.

TPPN/PN, has a higher char yield than that of the control CNE resin. This may be attributed to both phosphorus-containing curing agents in the cured CNE backbone.

The control CNE epoxy resin cured with PN exhibited 5% weight loss at 421°C, 10% weight loss at 437°C, and then a one-stage rapid weight loss was found at 473°C in  $N_2$  (Table I). 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,<sup>5-7, 18</sup> the CNE epoxy resins cured with either curing agent ODPN or TPPN showed complicated weight loss behavior. The weight loss could be considered as a three-stage process (Table I and Fig. 4). The cured epoxy resin of TPPN/PN-D exhibited 5% weight loss at 389°C and 10% weight loss at 415°C, and then a rapid weight loss was found at around 425°C (in  $N_2$ ). On the other hand, the ODPN/PN-D resin showed its 5% weight loss at 377°C and 10% weight loss at 397°C, and then a rapid weight loss was found at around 401°C. Although the rapid weight loss temperature ( $T_r$ ) of the control CNE resin occurred at 473°C, which is higher than that of ODPN/PN-D and TPPN/PN-D, both phosphorus-containing epoxy resins exhibited a second stage of rapid weight loss at 587°C (ODPN/PN-D)

and 584°C (TPPN/PN-D). This phenomenon played an important role in improving the flame retardancy of the resins. While on fire, the first-stage weight loss at lower temperature could be considered to result from the decomposition of the phosphorus-containing group in both phosphorus-containing epoxy resins to form a phosphate group. The following two stages of weight loss resulted from the complicated decomposition of phosphate groups in both phosphorus-containing epoxy resins and the resin matrix. The decomposition of phosphate groups forms a phosphorus-rich residue at the initial stage to prevent further decomposition of the resins matrix,<sup>5-7,18</sup> and resulted in a high char yield. The char yields at 700°C for the control CNE resin, TPPN/PN-D resin, and ODPN/PN-D resin were 32, 45, and 50%, respectively. In any case, the epoxy resins cured with OD-PN exhibited higher char yields than the TP-PN system.

#### LOI and UL-94V Test for Flame-Retardant Epoxy Resins

Phosphorus compound appears to exert a flame-retarding effect through mainly a condensed-phase mechanism in which dehydration of polymer is catalyzed, leading ultimately to production

**Table II UL-94V Test and LOI Value for Cured CNE with Various OD-PN/PN and TP-PN/PN Weight Ratios**

Sample Designation	OD-PN/PN	P %	Average Burning Time	Fumes	Classification	LOI
CONTROL	0/100	0	86	-	V-2	26
ODPN/PN-A	25/75	0.50	42	--	V-2	28
ODPN/PN-B	50/50	0.95	16	--	V-1	31
ODPN/PN-C	75/25	1.35	0	--	V-0	33
ODPN/PN-D	100/0	1.72	0	--	V-0	35
	TP-PN/PN	P %				
TPPN/PN-A	25/75	0.49	56	-	V-2	27
TPPN/PN-B	50/50	0.94	30	-	V-1	29
TPPN/PN-C	75/25	1.34	12	--	V-1~V-0	31
TPPN/PN-D	100/0	1.71	2	--	V-0	33

-. slightly; --: scarcely; ---: no.

of a relatively incombustible, carbonaceous char. The char insulates the underlying polymer from heat and oxygen, and vapor from the dehydration reaction dilutes flammable gases and quenches the flame.<sup>7</sup> The flame-retardant properties of these cured epoxy resins were compared from their LOI and UL-94V test results (Table II). The char residue on pyrolysis is reported to be linearly proportional to the oxygen index for halogen-free polymers.<sup>26</sup> The flame-retardant properties of cured epoxy resins with various phosphorus or bromine contents were examined by measuring their oxygen index (LOI). It is clear from the results of Table II that the higher the phosphorus content, the higher the LOI value, which agrees well with previous reports.<sup>27,28</sup>

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 results of Table II that the flame retardancy of cured epoxy resins increased with the increase in phosphorus-containing curing agent in the cured products.

Furthermore, by comparing the efficiency in flame-retarding property of OD-PN with TP-PN (Table II), it was found that the epoxy resins cured with OD-PN demonstrated higher LOI value and less burning time in UL-94V test than TP-PN (1.35% P in ODPN/PN-C is better than 1.71% P in TPPN/PN-D). The result is in good agreement with the result from char yield. The rigid polycyclic structure of ODC has demonstrated better flame retardancy than TP.

## CONCLUSION

A novel phosphorus-containing curing agent [OD-PN] was successfully synthesized from phenol formaldehyde novolac resin (PN) and 2-(6-oxid-6H-dibenz(c,e)(1,2)oxa-phosphorin-6-yl) chloride (ODC). The compound was used as a curing agent for CNE resins in semiconductor encapsulation and in electrical laminate applications. The OD-PN provided better flame retardancy and thermal stability than that of TP-PN. Although the flame-retardant effect of OD-PN is generally equivalent to previously reported ODOPB,<sup>24</sup> it is much more advantageous to produce OD-PN than ODOPB industrially because of its simpler process and high yield.

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