

Phosphorus-Containing Epoxy for Flame Retardant.

I. Synthesis, Thermal, and Flame-Retardant Properties

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SYNOPSIS

A new phosphorus-containing oxirane, bis-(3-glycidioxy) phenylphosphine oxide (BGPPPO), was synthesized. Further curing BGPPPO with diamine curing agents, dicyanodiamide (DICY), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenylsulfone (DDS), respectively, resulted in several phosphorylated epoxy resins. Compared with Epon 828, Eponex 1015, and DER 732, BGPPPO showed relatively high reactivity toward diamine agents via DSC studies. Furthermore, the reactivity of the three curing agents toward BGPPPO were found to be in the order of DDM > DICY > DDS. Thermal stability and the weight loss behavior of the cured polymers were studied by TGA. The phosphorylated resins showed lower weight loss temperatures and higher char yields than did the Epon 828-based resins. The high char yields as well as high limited oxygen index (LOI) values of the BGPPPO-based resins confirmed the effectiveness of phosphorus-containing epoxy resins as flame retardants. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins, with the characteristics of toughness, low shrinkage on cure, high adhesion to many substrates, good alkali resistance, and versatility in formulation, are widely used in adhesive, laminating, coating, and casting applications. To meet some application requirements, several approaches have been utilized to enhance the thermal properties of epoxy resins.¹⁻³ Apart from that, the flammability of epoxy resins is a major disadvantage in their application. Flame retardants such as phosphorus-halogen mixtures, ammonium phosphate, and organophosphorous compounds were used to impart flame retardance to epoxy resins.⁴⁻⁷ Among these flame retardants, organophosphorous compounds are the materials of choice. This is because organophosphorous compounds generate little toxic gas and

smoke and exhibit high flame-retardant efficiency while burning. Furthermore, covalently incorporating flame-retardant groups to polymer backbones, i.e., using a reactive flame retardant, has attracted much attention. The permanent attachment of a flame retardant certainly leads to high efficiency in flame retardance.⁸⁻¹³

The introduction of a reactive flame retardant to improve the flame retardance of epoxy resins has been reported in the literature.^{4,7} Several phosphorus-containing curing agents have been synthesized to be utilized as a flame retardant in epoxy resins. When phosphorus was covalently incorporated into the polymer backbones, the polarity of the polymer was improved. Consequently, the solubility in organic solvents, adhesion to metal, and fire resistance of the polymers would be increased. However, these phosphorus-containing curing agents did not have a great effect on the flame retardance of the epoxy resins. In other words, the flame-retardant efficiency was not very high (LOI = 29).⁴ This is mainly due to the low phosphorus contents of the

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Table I Curing Cycles of Epoxy Polymers

Epoxy Resin Compositions	Curing Temperatures (°C)	Curing Time (min)	Postcure Temperatures (°C)	Postcure Time (min)
Epon 828/DDM	115	35	170	30
BGPPO/DDM	95	40	150	30
BGPPO/DDS	145	35	180	25
BGPPO/DICY	135	40	160	25

curing agents and their corresponding cured epoxy resins.

One attempt to raise the phosphorus contents of the epoxy resins is by increasing the phosphorus content of the curing agents. However, the phosphorus content of the epoxy resins can be increased more effectively if the oxiranes are phosphorus-containing instead of the curing agent. This is because one primary amine functional group of the curing agent will react with two oxirane groups of epoxy monomer during curing. In other words, a diamine curing agent would react with two diepoxides stoichiometrically. Therefore, significant improvement of the flame retardance of epoxy resins was achieved through introducing phosphorylated oxirane into the epoxy resins.¹⁴ High phosphorus content was obtained for these epoxy resins. Based on the above, an oxirane compound with phosphorus elements in the backbones was newly synthesized in this study. The synthesized phosphorus-containing oxirane had a high phosphorus content of 11.5% by weight; consequently, a high efficiency on flame retardation of this kind of epoxy resins are expected. Furthermore, the reactivity, curing behavior, thermal properties, degradation behavior, and flame-retardant properties of this phosphorylated oxirane reacted with several commercial curing agents were also studied.

EXPERIMENTAL

Reagents

Phenylphosphonic dichloride (PPDC), glycidol, and copper(I) chloride available from the Aldrich Co. were used as received. The curing agents of dicyanodiamide (DICY), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenylsulfone (DDS) were from Aldrich and used as received. Epon 828 was from Shell Chemical Co. Eponex 1015 and DER 732 were from the Dow Chemical Co. Tetrahydrofuran (THF) was dried with sodium and distilled

prior to use. Triethylamine (TEA) was dried with KOH and distilled prior to use.

Synthesis of Bis(3-glycidyloxy)phenylphosphine oxide (BGPPO)

Glycidol (12.5 g, 0.169 mol) was stirred with 60 mL of THF in a 250 mL round-bottom flask. Distilled dry triethylamine (17.1 g, 0.169 mol) was added into the solution and then the solution was cooled to 0°C with ice bathing. After adding Cu₂Cl₂ (0.3 g), a solution of PPDC (15 g, 0.077 mol) in 40 mL THF was added to the reaction solution dropwise over a period of 30 min. The solution then became thick due to the precipitation of the amine hydrochloride. After maintaining it at 0°C for 2 h, the solution was kept at room temperature for another 48 h. The precipitant was filtered and washed with THF. The filtrate was concentrated, washed with an ice aqueous solution of NaOH (2% by weight) and then with distilled water, and finally extracted with ethyl acetate (EA) three times. The extract was dried over MgSO₄ and then concentrated. The obtained product was purified by passing it through column chromatography (using EA/*n*-hexane = 1/1 as the eluent). The final product was obtained with 54% yield and was stored in a refrigerator.

Preparation of Polymers

The epoxy polymers were obtained via thermally curing BGPPO with various curing agents. The reactant compositions were mixed homogeneously with a 1 : 1 molar ratio. The curing cycles were determined by DSC tracing of the respective epoxy/curing agent compositions (Table I).

Instrumental Analysis

Infrared spectra (IR) were obtained using a Perkin-Elmer 842 infrared spectrophotometer. ¹H-NMR and ³¹P-NMR spectra were recorded with a Bruker

MSL-300 (300 MHz) NMR spectrometer using CDCl_3 as a solvent. Elemental analysis was performed by an F002 Heraeus CHN-O Rapid elemental analyzer with acetanilide as a standard. Differential scanning calorimetry (DSC) thermograms were recorded with a Seiko DSC 5200 at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a DuPont 951 thermogravimetric analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen or air atmosphere. Limiting oxygen index (LOI) values were measured on a Stanton Redcroft flame meter by a modified method as reported in the literature.¹⁵ The percentage in the O_2 — N_2 mixture just sufficient to sustain the flame was taken as the LOI.

RESULTS AND DISCUSSION

Synthesis of Phosphorylated Oxiranes and Epoxy Resins

The synthesis of phosphorus-containing oxiranes [bis(3-glycidyloxy) phenylphosphine oxide, BGPPPO] was performed by reacting phenylphosphonic dichloride (PPDC) with glycidol (Fig. 1). The product was purified using column chromatography and was characterized by IR and ^1H - and ^{31}P -NMR. The IR spectrum of BGPPPO is shown in Figure 2. The peak at 1023 cm^{-1} indicates the formation of P—O—CH_2 linkage, i.e., the occurrence of the coupling reaction. Other characteristic absorption peaks of BGPPPO are shown as follows: 914 cm^{-1} (oxirane ring), 1248 cm^{-1} ($—\text{P}=\text{O}$), 1440 cm^{-1} (P—Ph), and 1594 cm^{-1} ($—\text{C}_6\text{H}_5$).¹² The structure of the obtained compound was confirmed via NMR analysis. The chemical shifts of ^1H -NMR analysis are as follows: $\delta = 2.60$ – 3.11 ppm (oxirane ring pro-

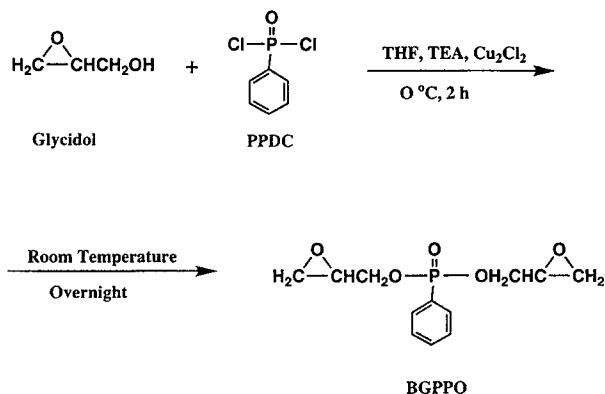


Figure 1 The synthesis scheme of BGPPPO.

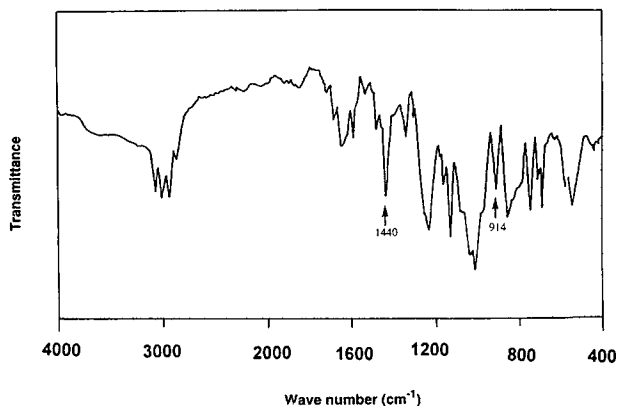


Figure 2 IR spectrum of BGPPPO.

tons), $\delta = 3.90$ – 4.31 ppm (P—O—CH_2 —), and $\delta = 7.35$ – 7.70 ppm (aromatic protons) (Fig. 3). Furthermore, the ^{31}P -NMR spectrum of BGPPPO shows only a peak at around $\delta = 20.6$ ppm (Fig. 4). However, PPDC shows peaks at 36.2 ppm in the ^{31}P -NMR spectrum. The shielding on the phosphorus atom should be caused by the replacement of electron-withdrawing chlorine atoms by $—\text{O—CH}_2—$ groups.¹⁶

The synthesized phosphorus-containing oxirane BGPPPO was then cured by various amine curing agents. The curing conditions were determined via DSC tracing and are collected in Table I. Different curing temperatures imply the variety of reactivity of BGPPPO toward different curing agents.

The curing reaction was observed by an IR spectrophotometer. The IR spectra of BGPPPO/DDS before and after curing are shown in Figure 5. The strong absorption peaks of oxirane ring at 914 cm^{-1} and of primary amine at 3260 and 3512 cm^{-1} almost disappeared after curing. The formation of hydroxyl groups was also found as the broad peak at around 3400 cm^{-1} emerged after curing. This confirmed the occurrence of the reaction between amine and the oxirane ring.

Reactivity of BGPPPO Toward Curing Agents

The curing reactions were studied by DSC. Typical DSC thermograms of BGPPPO and other epoxies with the curing agent DDM are shown in Figure 6. The reactivities of the epoxies were directly read from the starting temperatures of the exothermic peaks.^{4,7} As shown in the DSC thermograms, BGPPPO is more reactive toward amine curing agents than are the other three epoxies. The high reactivity of BGPPPO possibly results from the electronic ef-

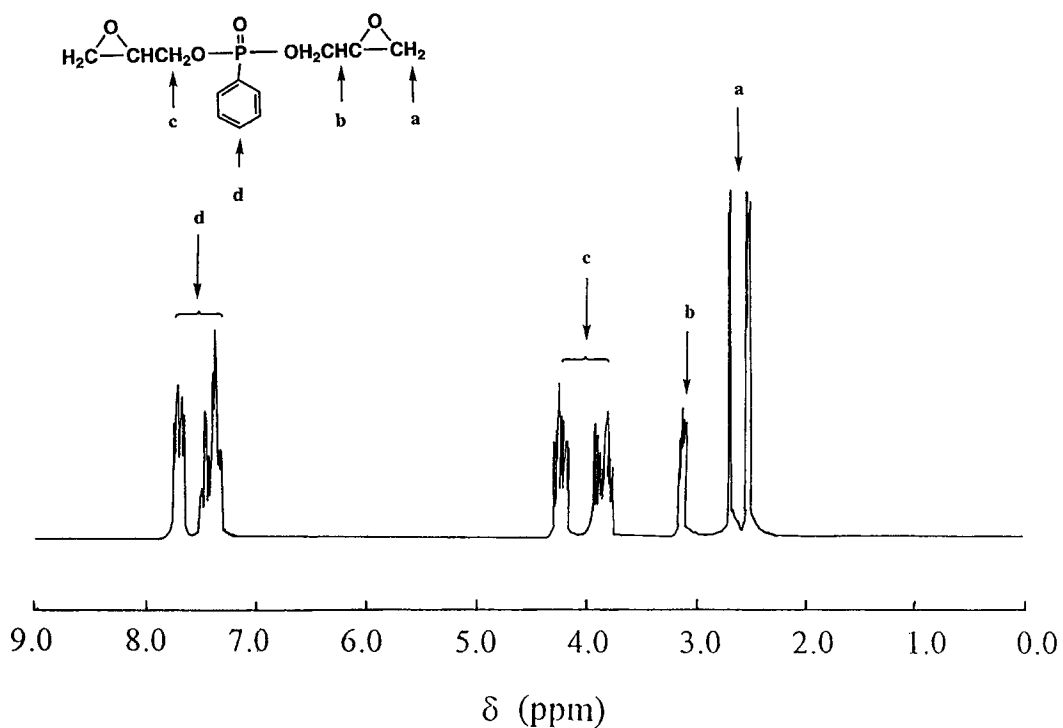


Figure 3 ¹H-NMR spectrum of BGPPPO.

fect.^{4,7} The —P=O serving as an electron-withdrawing group in the epoxy consequently reduced the electron density of the oxirane rings. This effect makes the reaction between the oxirane ring and amine to take place easily. Therefore, the reactivity

of BGPPPO toward amine curing agents is higher than the respective Epon 828, Eponex 1510, and DER 732.

The reactivities of various curing agents toward BGPPPO were also studied via DSC (Fig. 7). DDM

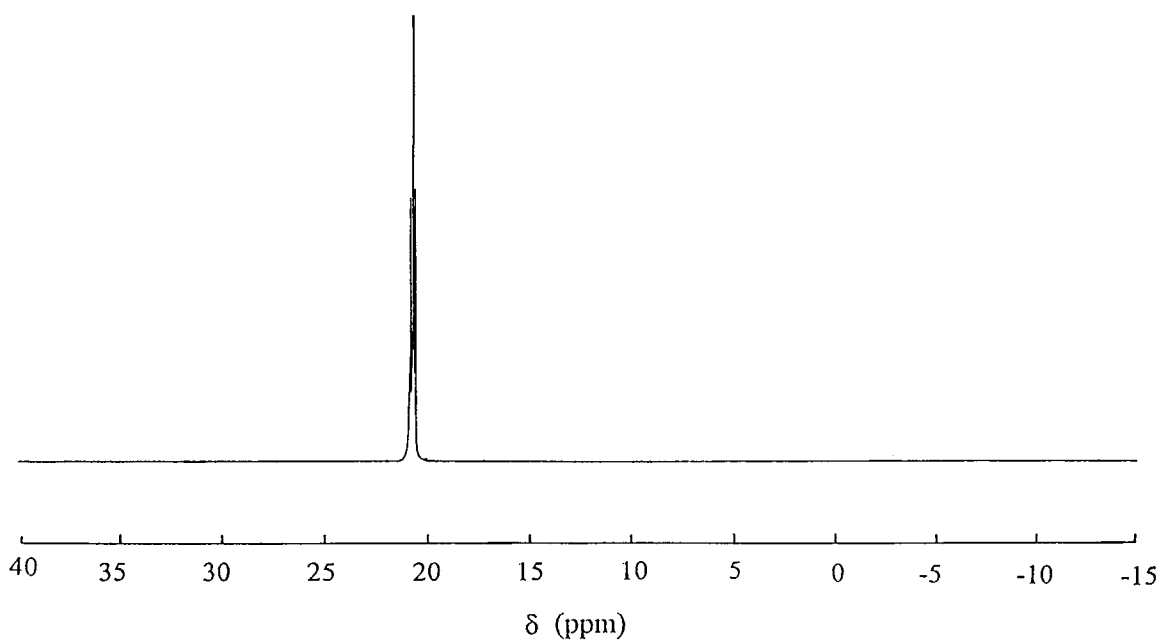


Figure 4 ³¹P-NMR spectrum of BGPPPO.

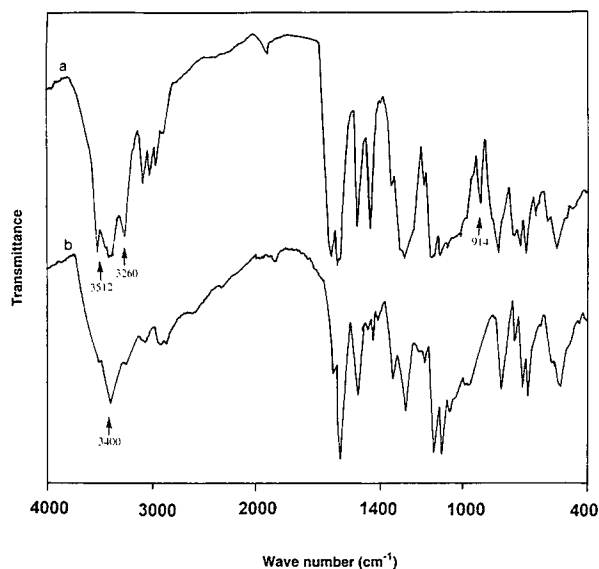


Figure 5 IR spectra of BGPPO/DDS-based resin (a) before and (b) after curing.

showed the highest chemical reactivity toward BGPPO, whereas DDS did otherwise. The variation in reactivity could be due to the aforementioned electron effect. In contrast to the electron-withdrawing effect on the reactivity of oxirane rings, an electron-withdrawing group would decrease the electron density of the amine groups and thus reduce its reactivity. The methylene group of DDM with

the lowest electron-withdrawing effect on the amine groups, therefore, showed the highest reactivity toward BGPPO.

Thermal and Flame-retardant Properties

TGA thermograms of the cured resins BGPPO/DDM and Epon 828/DDM in a nitrogen atmosphere are illustrated in Figure 8. Epon 828/DDM resin exhibited 1% weight loss at 360°C and then a rapid weight loss was found at around 390°C. On the other hand, the phosphorylated BGPPO/DDM resin showed its 1% weight loss at 230°C and a somewhat greater (<10%) weight loss at around 245°C. Unlike the one-stage weight loss behavior of the Epon 828/DDM resin, the BGPPO/DDM resin showed a second stage of weight loss at about 410°C. The first weight loss temperature of 245°C seemed to indicate that the thermal stability of the BGPPO/DDM resins decreased compared with the Epon 828/DDM resin. However, it is noteworthy that the percentage of the weight loss of BGPPO/DDM at 245°C was less than 10%. This low percent weight loss could possibly result from the pyrolysis of the phosphonate groups. Moreover, the rapid weight loss of BGPPO/DDM occurred at 410°C. This temperature is higher than the rapid weight loss temperature (390°C) of Epon 828/DDM. Thus, the thermal stability at high temperatures of the resins was improved as the

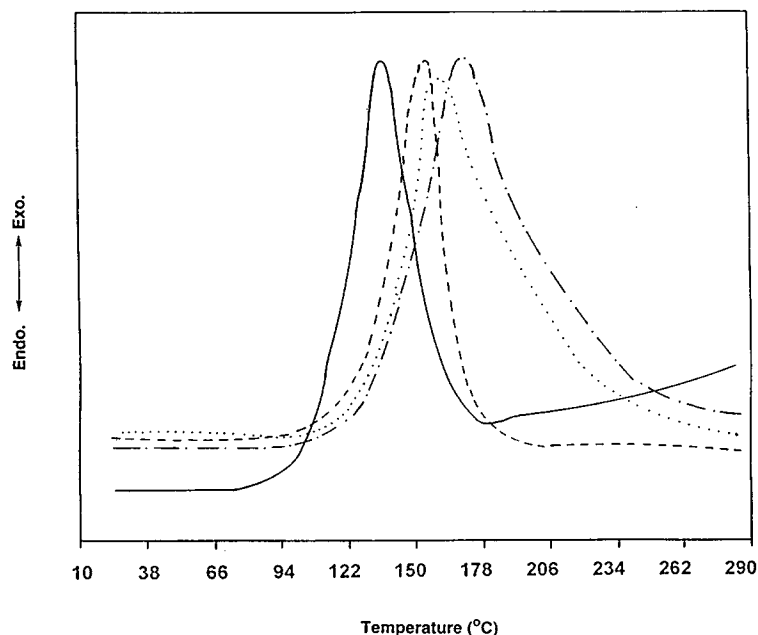


Figure 6 DSC thermograms of (—) BGPPO, (---) Epon 828, (- · -) Eponex 1510, and (· · · ·) DER 732 cured by DDM.

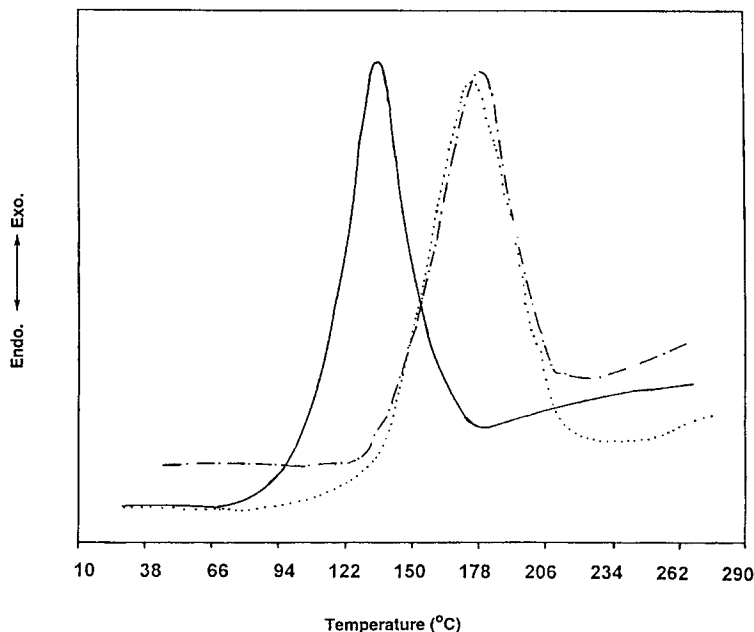


Figure 7 DSC thermograms of BGPPO cured by (—) DDM, (---) DDS, and (····) DICY.

phosphorus was covalently incorporated into the resins. This phenomenon plays an important role in improving the flame retardance of the resins. While in fire, the phosphorus-containing groups first decompose and then form a phosphorus-rich residue. This phosphorus-rich residue would help prevent further decomposition of the polymer, therefore raising the decomposition temperature of the poly-

mer and resulting in a high char yield. This was confirmed by the char yield study. At 700°C, the Epon 828/DDM resin exhibited a char yield of 18%, whereas BGPPO/DDM exhibited 40%.

While in air (Fig. 9), the weight loss behavior showed more stages than that in nitrogen. Another weight loss at higher temperature was observed for Epon 828/DDM and BGPPO/DDM, respectively.

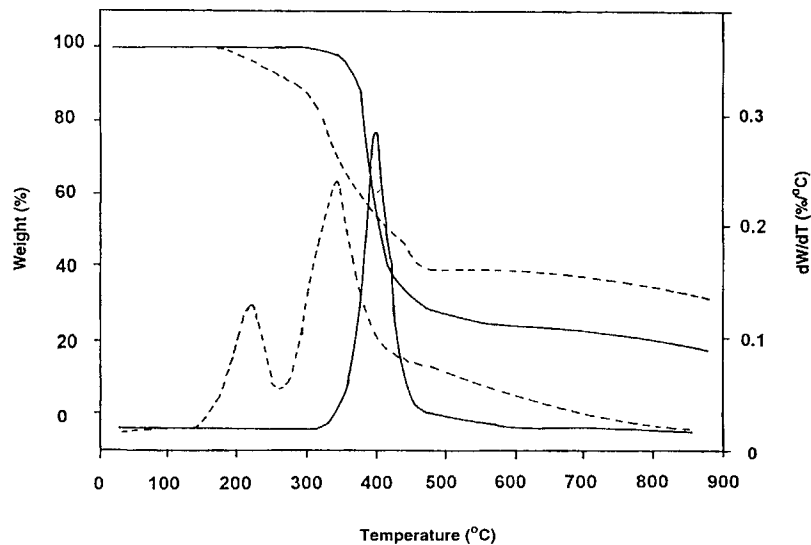


Figure 8 TGA and DTA thermograms of (—) Epon 828/DDM and (---) BGPPO/DDM in nitrogen.

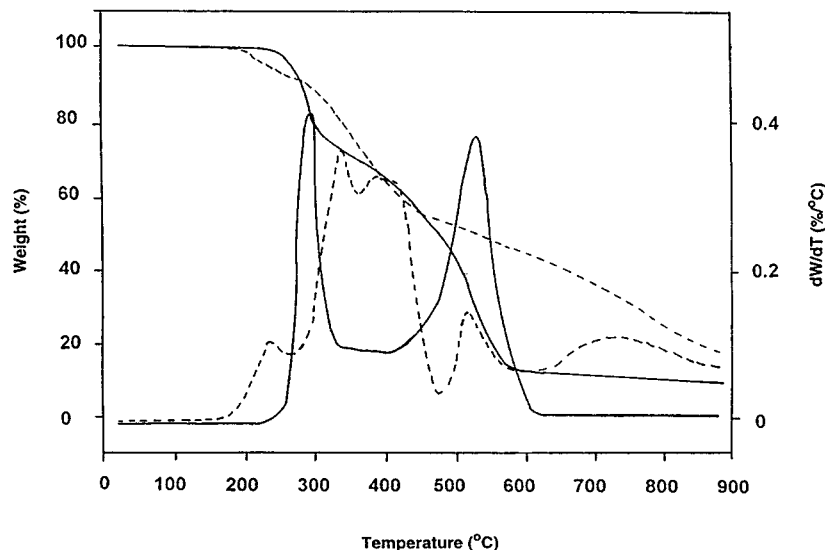


Figure 9 TGA and DTA thermograms of (—) Epon 828/DDM and (---) BGPPO/DDM in air.

This weight loss was brought about by the oxidation of the polymers at high temperatures. As a result of this oxidation process, the char yields were decreased. Char yields of Epon 828/DDM and BGPPO/DDM in air were found to be 7 and 33%, respectively. Furthermore, the phosphorus-free resin, Epon 828/DDM, was less thermally stable in air than in nitrogen. The temperature of the first rapid weight loss dropped from 390 to 296°C while in air instead of being in nitrogen. On the other hand, the decreased thermal stability was not observed for

the phosphorus-containing epoxy resin BGPPO/DDM in air, as shown in Figure 9.

More TGA thermograms of BGPPO-based resins cured by various curing agents are shown in Figures 10 and 11. Polymers of BGPPO reacted with various curing agents showed a similar weight loss behavior (Table II). The pyrolysis temperatures of the resins were increased when the phosphorus-containing BGPPO epoxy was incorporated. The rapid weight loss temperatures of BGPPO-based resins, as aforementioned, were about 130°C higher than that of

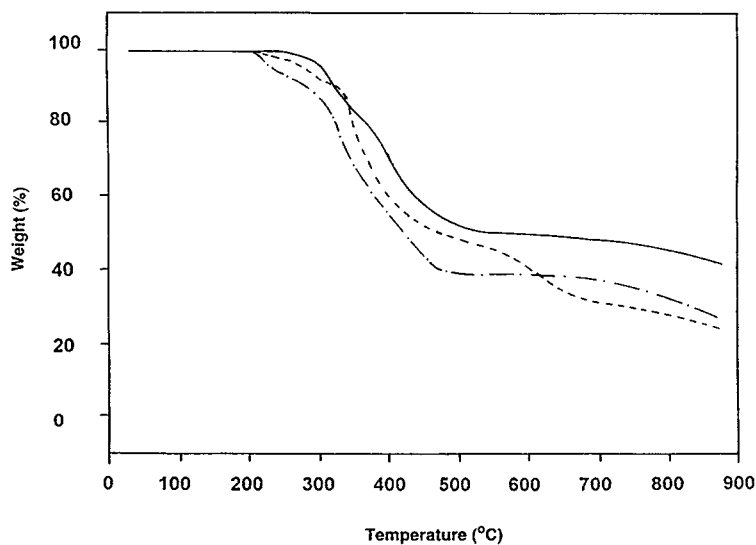


Figure 10 TGA thermograms of BGPPO-based resins cured by (—) DICY, (- - -) DDM, and (- · -) DDS in nitrogen.

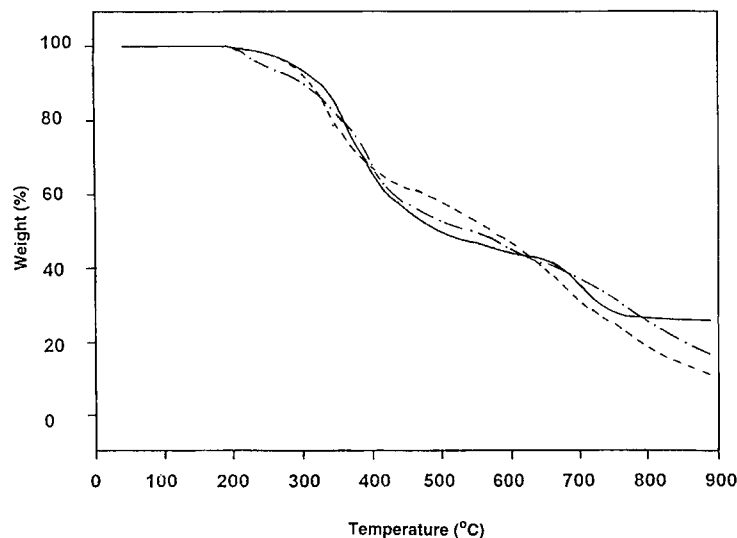


Figure 11 TGA thermograms of BGPPO-based resins cured by (—) DICY, (---) DDM, and (- · -) DDS in air.

the Epon 828-based resin. The temperatures of the oxidation pyrolysis of BGPPO-based resins in air were as high as about 700°C. On the other hand, the phosphorus-free Epon 828-based resins showed an oxidation pyrolysis temperature of 550°C. Moreover, the BGPPO based resins did not show a notable reduction in thermal stability while in air instead of being in nitrogen. Furthermore, it was found that the resin cured with DICY showed a relatively higher char yield and thermal stability than did the resins cured by, respectively, DDM and DDS. This could be due to the high phosphorus content of DICY cured resin. It is important to note that the DICY-cured resin showed an LOI value larger than 43, while the other resins cured by DDM and DDS exhibited LOI values of about 33. The high LOI value of the DICY-based resin certainly resulted from the high phosphorus content. Moreover, the synergism of phosphorus–nitrogen in flame retardance should

also be taken into consideration.¹⁷ DICY contains a high nitrogen weight percent (42%) in the molecule. This high nitrogen content along with high phosphorus content help enhance the char yield and the LOI value as well as the flame retardance of the resin.

CONCLUSION

A new phosphorus-containing epoxy monomer BGPPO was synthesized. The flame-retardant epoxy resins could be prepared via BGPPO cured by several curing agents. Compared with Epon 828, Eponex 1015, and DER 732, the higher reactivity of BGPPO toward diamine curing agents is attributed to the presence of the electron-withdrawing phosphinyl group in the BGPPO molecule. Furthermore, the curing agents exhibiting different reactivity to-

Table II Thermogravimetric and LOI Data of the Phosphorylated Epoxy Resins

Epoxy Resin Compositions	Specific Temperatures of Weight Loss from TGA (°C)								Char % at 700°C		Phosphorus Content %	LOI
	1% Loss		Step 1		Step 2		Step 3		Air	N ₂		
	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂				
Epon 828/DDM	280	360	296	390	535	—	—	—	7	18	0.0	27
BGPPO/DDM	220	230	242	245	420	410	732	—	33	40	6.8	34
BGPPO/DDS	225	235	247	248	355	350	683	607	20	28	5.8	33
BGPPO/DICY	280	285	313	315	407	418	715	—	33	50	8.4	> 43

ward BGPPO is shown in the order of DDM > DICY > DDS. For all phosphorylated epoxy resins, high char yields were found by thermogravimetric analysis. The high char yields as well as high LOI values indicates that the excellent flame-retardant properties of the epoxy resins were obtained.

Financial support of this work by the National Science Council and the Ministry of Economic Affairs, Republic of China, is gratefully acknowledged.

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Received August 28, 1995

Accepted December 18, 1995