Phosphorus-Containing Epoxy for Flame Retardant. III: Using Phosphorylated Diamines as Curing Agents

YING-LING LIU,[1] GING-HO HSIUE,[1,2] RONG-HO LEE,[1] YIE-SHUN CHIU[3]

[1]Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

[2]Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan, Republic of China

[3]Chung-San Institute of Science and Technology, Lungtan, Tauyuan, Taiwan, Republic of China

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ABSTRACT: Two phosphorus-containing diamine compounds, bis(4-aminophenoxy)-phenyl phosphine oxide and bis(3-aminophenyl)phenyl phosphine oxide, were synthesized for use as curing agents of epoxy resins. Phosphorylated epoxy resins were obtained by curing Epon 828 and Eponex 1510 with these two diamine agents. For raising the phosphorus contents of the resulting epoxy resins, the phosphorus-containing epoxy, bis(glycidyloxy)phenyl phosphine oxide (BGPPO), was also used. These two diamine agents showed similar reactivity toward epoxies. Their reactivities were higher than DDS and lower than DDM. High char yields in TGA evaluation were found for all the phosphorylated epoxy resins, implying their high flame retardancy. The excellent flame-retardant properties of these phosphorylated epoxy resins were also demonstrated by the high limiting oxygen index (LOI) values of 33 to 51. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 895–901, 1997

Key words: flame retardant; phosphorus-containing epoxy; limiting oxygen index

INTRODUCTION

Epoxy resins are used worldwide on a large scale for adhesive, laminating, coating, and casting applications. The chemistry and technological applications of the epoxy resins are very demanding and there are many new developments each year. For meeting some application requirements, several approaches have been utilized to enhance the thermal properties of epoxy resins.[1–3] Apart from that, a further requirement that has recently gained in importance is the requirement for flame resistance. Therefore, imparting flame retardancy into epoxy resins has received a lot of attention.[4–8] The approaches of flame retardation of epoxy resins can be achieved using additive-type flame retardants and chemically bonding flame retardant groups onto epoxy resins. However, flame retardants of the chemical-bonding type are of interest recently because they exhibit several advantages over those of the additive type.[4–8]

Imparting flame resistance into epoxy resins can be achieved through phosphorus-containing oxiranes.[4,6,8] In our previous study, cured epoxy resins with good flame-retardant properties were also obtained via a newly synthesized phosphorus-containing oxirane of bis(glycidyloxy)phenyl phosphine oxide (BGPPO).[8] On the other hand, flame retardation of epoxy resins can also be achieved by another approach using fire-resistant curing agents.[4,7,9–11] The present study, therefore, focused on the flame retardation of epoxy resins via curing agents. Two phosphorus-containing diamine compounds, bis(4-aminophenoxy)phenyl phosphine oxide and bis(3-aminophenyl)phenyl phosphine oxide, were synthesized for use as cur-

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Correspondence to: G.-H. Hsiue

ing agents. The epoxy compositions of these two phosphorylated diamine compounds curing with commercial epoxy monomers was studied. Moreover, for further raising the flame retardancy of the epoxy resins, the phosphorus-containing oxirane BGPPO was also utilized, curing with these phosphorylated diamine curing agents. The reactivity, curing behavior, thermal properties, degradation behavior, and flame-retardant properties of the above-mentioned phosphorylated epoxy resins were studied.

EXPERIMENTAL

Reagents

Phenyl phosphonic dichloride (PPDC) (Aldrich Company, USA), triphenylphosphine oxide (TCI Company, Japan), *p*-nitrophenol (TCI Company, Japan), copper(I) chloride (Aldrich Company, USA), and tin(II) chloride dihydrated (Aldrich Company, USA) were used as received. The curing agents of dicyanodiamide (DICY), 4,4′-diaminodiphenylmethane (DDM), and 4,4′-diaminodiphenylsulfone (DDS) were available from Aldrich Company and used as received. Epon 828 was from Shell Chemical Co. Eponex 1015 was from Dow Chemical Co. The phosphorus-containing epoxy monomer, bis-(glycidyloxy)phenyl phosphine oxide (BGPPO), was synthesized in our laboratory.[8] 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(4-nitrophenoxy)phenyl Phosphine Oxide (PN-I)

p-Nitrophenol (23.5 g, 0.169 mol) was stirred with 120 mL of THF in a 500 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 in an ice bath. After adding Cu_2Cl_2 (0.3 g), a solution of phenyl phosphonic dichloride (15 g, 0.077 mol) in 60 mL THF was added to the reaction solution dropwise over a period of 30 min. The solution became thick due to the precipitation of the amine hydrochloride. After maintaining 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-cold aqueous solution of NaOH (2% by weight) and with distilled water, and finally extracted with ethyl acetate (EA) three times. The extract was dried over $MgSO_4$ and then concentrated. The product was purified by recrystallization from ethanol. The final product was obtained in an 80% yield. IR (KBr): 854 cm^{-1} ($-C-NO_2$), 1190 cm^{-1} (P—O—Ph), 1233 cm^{-1} ($-P{=}O$), 1344 and 1518 cm^{-1} ($Ph-NO_2$), and 1438 cm^{-1} (P—Ph); ^1H NMR ($CDCl_3$): $\delta = 7.33-7.39$ ppm (aromatic protons near NO_2 groups), $\delta = 7.52-7.98$ ppm ($P-C_6H_5$), and $\delta = 8.00-8.23$ ppm (aromatic protons near O—P=O bonding); ^{31}P NMR ($CDCl_3$): a single peak at $\delta = 13.35$ ppm.

Synthesis of Bis(4-aminophenoxy)phenyl Phosphine Oxide (PA-I)

PN-I (25 g) was placed in a 1000 ml round-bottom flask with 180 g of powder tin(II) chloride dihydrate. A solution of 200 mL fuming hydrochloric acid in 400 mL ethanol was introduced into the flask. The reaction mixture was stirred at room temperature for 5 h. The solution was concentrated and then was neutralized by 25% NaOH aqueous solution. The obtained solution was extracted with chloroform. The organic layer was collected and concentrated under a reduced pressure. The obtained solid was recrystallized from dichloromethane to give a pure product in a 95% yield. IR (KBr): 3499 and 3393 cm^{-1} ($Ph-NH_2$), 1183 cm^{-1} (P—O—Ph), 1240 cm^{-1} (P=O), and 1437 cm^{-1} (P—Ph); ^1H NMR ($CDCl_3$): $\delta = 3.45$ ppm ($-NH_2$), $\delta = 6.52-6.94$ ppm ($C_6H_4-NH_2$), and $\delta = 7.43-7.92$ ppm ($P-C_6H_5$). ^{31}P NMR ($CDCl_3$): single peak at $\delta = 12.97$ ppm.

Synthesis of Bis(3-nitrophenyl)phenyl Phosphine Oxide (PN-II)[12]

Triphenyl phosphine oxide (27.8 g, 0.1 mol) was placed in a 500 mL round-bottom flask equipped with stirrer and nitrogen atmosphere and 200 mL of 96% sulfuric acid was added. The reactant was dissolved and the reaction system was cooled to −5°C with an ice/salt bath. A solution of 14.5 g (0.4 mol) of fuming nitric acid in 100 ml of sulfuric acid was added dropwise over a period of 2 h. The reaction system was kept at room temperature for another 8 h. The reaction solution was hydrolyzed over 2 l of ice. After the ice was melted, the mixture was extracted with chloroform and washed with sodium bicarbonate aqueous solution until neutral pH. The solvent was removed. The solid residue was recrystallized from absolute ethanol. Bis(3-nitrophenyl)phenyl phosphine oxide (PN-

Table I Curing Cycles of Epoxy Resins from Phosphorus-Containing Diamine Curing Agents

Epoxy Resin Compositions	Curing Temperature (°C)	Curing Time (min)	Postcure Temperature (°C)	Postcure Time (min)
Epon 828/PA-I	145	35	170	30
Eponex 1510/PA-I	155	40	175	40
BGPPO/PA-I	125	40	140	35
Epon 828/PA-II	165	50	180	40
Eponex 1510/PA-II	175	45	190	30
BGPPO/PA-II	140	45	170	30

II) was obtained with a 70% yield. IR (KBr): 873 cm^{-1} (—C—NO$_2$), 1193 cm^{-1} (P=O), 1346 and 1528 cm^{-1} (Ph—NO$_2$), and 1434 cm^{-1} (P—Ph); ^{1}H NMR (CDCl$_3$): $\delta = 7.74–8.02$ ppm (P—C$_6$$H_5$), and $\delta = 7.85–8.62$ ppm (P—C$_6$$H_4$—NO$_2$); ^{31}P NMR (CDCl$_3$): a single peak at $\delta = 26.0$ ppm.

Synthesis of Bis(3-aminophenyl)phenyl Phosphine Oxide (PA-II)

The synthesis of bis(3-aminophenyl)phenyl phosphine oxide (PA-II) was performed by the same synthesis procedure as PA-I. The obtained solid was recrystallized from dichloromethane to give a pure product in 90% yield. IR (KBr): 3497 cm^{-1} and 3404 cm^{-1} (—NH$_2$), 1437 cm^{-1} (P—Ph), 1194 cm^{-1} (P=O); ^{1}H NMR (CDCl$_3$): $\delta = 3.60$ ppm (—NH_2), $\delta = 6.78–7.02$ ppm (C$_6$$H_4$—NH$_2$), and $\delta = 7.14–7.66$ ppm (other aromatic protons); ^{31}P NMR (CDCl$_3$): a single peak at $\delta = 30.7$ ppm.

Preparation of Polymers

The epoxy polymers were obtained via thermal curing. 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. ^{1}H NMR and ^{31}P 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°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a DuPont 951 thermogravimetric analyzer at a heating rate of 10°C/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 by the literature. The percentage in the O$_2$–N$_2$ mixture just sufficient to sustain the flame was taken as the LOI.[13]

RESULTS AND DISCUSSION

Synthesis and Characterization of Diamine Compounds

Bis(4-aminophenoxy)phenyl phosphine oxide (PA-I) was synthesized via a two-step route. The synthesis scheme is shown as Figure 1. The dinitro compound, bis(4-nitrophenoxy)phenyl phosphine oxide (PN-I), was first obtained as an intermediate. PN-I was then hydrogenated to result in the diamine compound PA-I. The formation of amine groups was first observed by IR characterization of PA-I. Peaks at 3499 cm^{-1} and 3393 cm^{-1} of the IR spectrum indicate the absorption of aromatic primary amine. The characteristic absorption of nitro groups also emerges. Moreover, other peaks arising from P—O—Ph (1183 cm^{-1}), P=O (1240 cm^{-1}), and P—Ph (1437 cm^{-1}) are observed to confirm that the phosphonate structure is maintained after hydrogenation. Further characterization of ^{1}H and ^{31}P NMR also confirmed the PA-I chemical structure.[15–16]

The other diamine compound, bis(3-aminophenyl)phenyl phosphine oxide (PA-II), was synthesized by means of another two-step route (Figure 2).[12] Nitration and subsequent reduction of triphenylphosphine oxide have been well-estab-

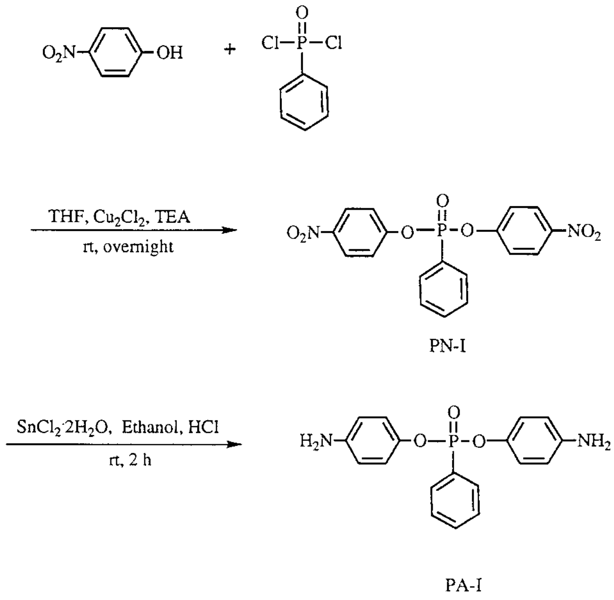

Figure 1 Synthesis scheme of phosphorus-containing diamine PA-I.

lished to obtain meta triamino derivative.[16] On the other hand, the technique of synthesizing dinitro and diamino derivatives is not well-reported. The amount of nitric acid that is required must be carefully controlled in order to obtain a high yield of the diamino compound in the nitration step. The diamino compound bis(3-aminophenyl)-phenyl phosphine oxide (PA-II) was obtained from subsequent hydrogenation. The formation of aromatic primary amine groups is confirmed by IR absorption peaks at 3497 cm^{-1} and 3404 cm^{-1}. The formation of amine was also observed by the ^1H NMR absorption at $\delta = 3.60$ ppm.

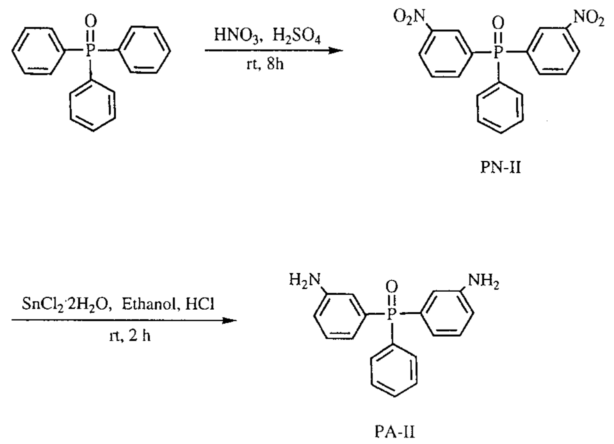

Figure 2 Synthesis scheme of phosphorus-containing diamine PA-II.

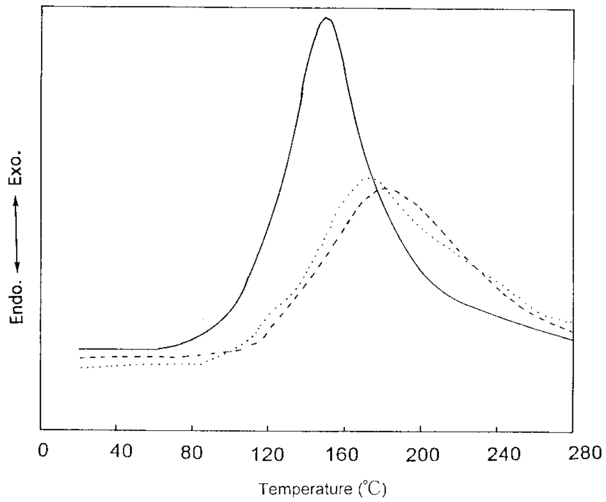

Figure 3 DSC thermograms of BGPPO (——), Epon 828 (---) and Eponex 1510 (····) cured by PA-I.

The phosphorus-containing diamine compounds were obtained and characterized. The curing reaction of these diamines with epoxides and the characterization of their resulting epoxy resins were discussed as follows.

Curing Reactions of Diamines

The curing reactions of the diamine compounds toward oxirane-containing monomers were studied by DSC. Typical DSC thermograms of various epoxies with PA-I are shown in Figure 3. These thermograms, as well as isothermal DSC curing studies, provide information for determining the conditions of curing reactions. The results are collected in Table I and are used as curing cycles for preparing cured epoxy resins. Furthermore, the reactivity of the diamine curing agents could be directly read from the starting temperatures of the exothermic peaks in DSC thermograms. As shown in Figure 4, both of the synthesized phosphorus-containing diamine curing agents exhibit similar reactivity toward Epon 828. Compared with other curing agents, PA-I and PA-II show lower reactivity than DDM and higher reactivity than DDS and DICY. The variation in reactivity could be due to the electronic effect.[7–8] An electron-donating group in the amine compound, for example, the methylene group in DDM, would enrich the electron density of the amine group and therefore increase the reactivity of amine toward oxirane rings. However, for PA-I and PA-II, the —P=O group serves as an electron-withdrawing group, consequently reducing their activity in cur-

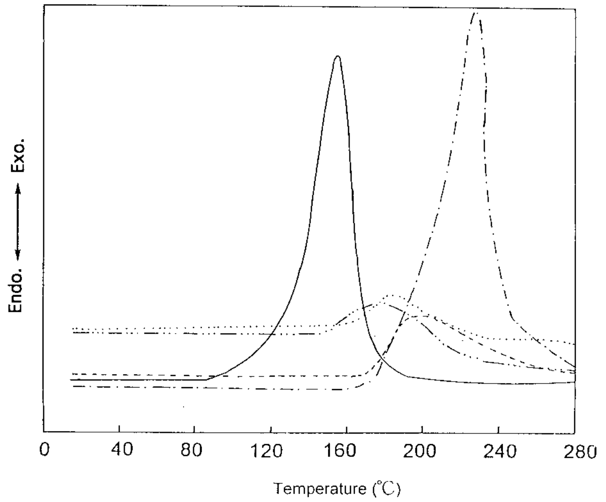

Figure 4 DSC thermograms of Epon 828 cured with DDM (——), PA-I (····), PA-II (–····–), DDS (– – –) and DICY (– · –).

ing with epoxies. On the other hand, DDS, which contains a strong electron-withdrawing group —SO_2—, shows lower reactivity than PA-I and PA-II. Moreover, the phosphonate group decreases the electron-withdrawing effect of P=O bonding. This leads to the result that PA-I is a little more reactive than PA-II.

Thermal and Flame Retardant Properties

The thermal properties of the cured epoxy resins were evaluated by thermogravimetric analyses (TGA) under nitrogen and air. Figure 5 shows the TGA thermograms of Epon 828/PA-I and Epon 828/PA-II. While being heated under nitrogen, the epoxies from both curing agents showed a one-stage weight loss behavior. In our previous study,[8] the phosphonate-based epoxy resins from phosphorus-containing oxirane showed a two-stage weight loss in heating under nitrogen. The first-stage weight loss was caused from the pyrolysis of the phosphonate groups. However, for PA-I cured epoxy resins, where the phosphonate groups in the epoxy resins were from the curing agent, the decomposition of the phosphonate groups was not so clearly distinguishable from the decomposition of the polymer backbones. As observed for Epon 828/PA-I, weight loss begins at around 285°C and then gives a rapid weight loss at about 325°C, to result in an one-stage weight loss. The one-stage weight loss behavior was also found in other phosphorus-containing diamine cured epoxy resins.[7] Furthermore, the 1% weight loss temperatures of PA-I and PA-II cured resins were found at about 280°C and 321°C, respectively. This implies that the resin from the phosphine curing agent (PA-II) was more thermally stable than that from the phosphonate curing agent (PA-I). Since the weight loss of Epon 828/DDM and Epon 828/DDS resins show their weight loss at 390°C[8] and 401°C,[7] respectively, the weight loss temperatures of the phosphorus-containing diamine cured epoxies were lower than those phosphorus-free epoxy resins. This low weight loss temperature could be due to the decomposition of phosphorus-containing groups. Consequently, phosphorus-rich residues were formed in this stage of decomposition to prevent further decomposition of the resins. This phenomenon plays an important role in improving the flame-retardant properties of the resins and will be discussed later.

The TGA thermograms of the phosphorus-containing diamine cured epoxy in air are shown in Figure 5. The temperatures of 1% weight losses in air are very near to those in nitrogen. This demonstrates that the thermal stability of phosphorus-containing epoxy resins does not decrease while they are being heated together with oxygen. Furthermore, the following step of weight loss in air is not as rapid as that in nitrogen. A two- or three-stage weight loss was found for the epoxy resins heated in air. The presence of oxygen results in a complicated decomposition mechanism of the resins. Moreover, in air, one additional weight loss was found at temperatures higher than 650°C. This weight loss at high temperatures is due to the oxidation of char. As shown in Figure 6, this oxidation reduces the char yields at high temperatures.

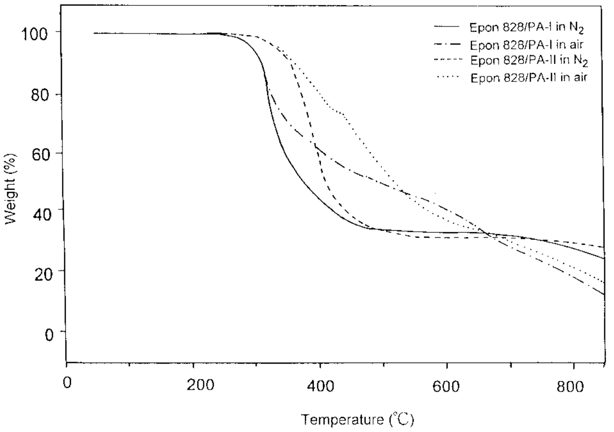

Figure 5 TGA thermograms of epoxy resins of Epon 828 cured with phosphorus-containing diamines.

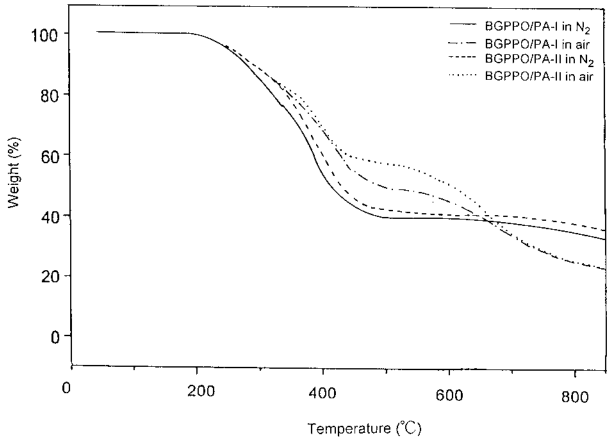

Figure 6 TGA thermograms of epoxy resins of BGPPO cured with phosphorus-containing diamines.

These two phosphorus-containing curing agents were further utilized to cure the phosphorus-containing oxirane compound bis-(glycidyloxy)phenyl phosphine oxide (BGPPO). Figure 6 shows the TGA thermograms of epoxy resins basing on BGPPO/PA-I and BGPPO/PA-II. The weight loss was found to begin at around 225°C. This weight loss temperature is lower than that of the above-discussed Epon 828 based resins. This weight loss at such a low temperature should come from the decomposition of the phosphonate groups in BGPPO, since DDM and DDS cured BGPPO resins showed similar weight loss temperatures at about 230°C.[8] After the weight loss at 225°C, the following weight loss behavior of BGPPO-based epoxy resins was similar to that of the Epon 828-based epoxy resins. The specific weight loss temperatures of BGPPO-based resins were a little lower than those of Epon 828-based resins. The decrease in thermal stability of BGPPO-based resins was due to the less thermally stable group of alkyl-phosphonate structures in BGPPO. This effect of decreasing in thermal stability was also observed for DDM cured BGPPO resin.[8] Furthermore, while being examined in air, weight loss was also found at temperatures higher than 650°C for BGPPO-based resins to reduce the char yields.

The relationship between char yields and flame retardancy has been discussed.[17] Increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and decrease the thermal conductivity of the burning materials[18] and consequently limit the flammability of the materials. Therefore, the flame-retardant properties of the phosphorus-containing epoxy resins were first examined by the char yields of the resins at 700°C (Table II). All of the phosphorus-containing diamine cured epoxies showed char yields higher than 35% in nitrogen. As the phosphorus-free Epon 828/DDM resin gives a char yield of 18%, the char-yield enriching effect of phosphorus is demonstrated. While in air, the char yields of phosphorus-free epoxy resins at 700°C are less than 10%. Therefore, the high char yields (higher than 26%) of these PA-I and PA-II cured epoxy resins in air are especially noteworthy. Moreover, the char yields are further raised when the phosphorus-containing oxirane BGPPO is introduced in the resin. Char yields of BGPPO/PA-I resin in nitrogen and in air are found to be 43% and 37%, respectively. These high char yields imply the flame retardancy of the epoxy resins was elevated via the phosphorus-containing diamine curing agents.

The flame-retardant properties of these epoxy resins were further examined by measuring the limiting oxygen index (LOI). When Epon 828 was cured with PA-I and PA-II, the resulting epoxy

Table II Thermogravimetric Data and LOI Values of the Phosphorylated Epoxy Resins

Epoxy Resin Compositions	Temperature of 1% Weight Loss (°C)		Char Yields at 700°C (%)		Phosphorus Contents (%)	LOI Values
	N_2	Air	N_2	Air		
Epon 828/DDM	360	280	18	7	0	24
Epon 828/PA-I	285	280	37	32	4.16	34
Epon 828/PA-II	321	321	37	29	5.10	35
Eponex 1510/PA-I	235	235	35	26	4.03	33
Eponex 1510/PA-II	294	290	35	28	4.25	33
BGPPO/PA-I	225	225	43	37	10.23	49
BGPPO/PA-II	225	225	45	37	10.80	51

resins had LOI values of about 35. The LOI values are higher than that of Epon 828/DDM resin (LOI = 24). The flame-retarding effect of the phosphorus-containing curing agents is demonstrated. Furthermore, the LOI values were raised to 51 for BGPPO/PA-II resin. This high LOI value mainly comes from the high phosphorus content of BGPPO/PA-II resin, since both the epoxy and curing agent contain phosphorus. The increase in LOI values with the increase of phosphorus contents was previously observed.[19–20] Therefore, the high LOI values imply these phosphorus-containing diamine curing agents are applicable in flame retarding epoxy resins.

CONCLUSIONS

New phosphorus-containing diamine compounds were synthesized. These diamine compounds were utilized as curing agents for epoxy resins. While curing with Epon 828 and Eponex 1510, the resulting epoxy resins showed high char yields and LOI values, implying their good flame-retardant properties. The flame-retardant efficiency was further raised using the phosphorus-containing oxirane compound BGPPO as a monomer. Phosphorus-containing epoxy and diamine curing agents yielded epoxy resins with a phosphorus content higher than 10%. This high phosphorus content thus leads to excellent flame retardant properties, demonstrated by the high char yield of 45% and high LOI value of 51. These phosphorus-containing diamine curing agents were determined to be effective in flame retarding epoxy resins.

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