

# Phosphorous-Containing Epoxy Resins from a Novel Synthesis Route

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**ABSTRACT:** The  $\text{—P(O)H}$  in 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was used as an active group to react with the carbonyl group in 4,4'-dihydroxybenzophenone (DHBP) to result a novel phosphorous-containing biphenol compound (DOPO-2OH). Phosphorous-containing epoxy resins were therefore obtained from reacting DOPO-2OH with epichlorohydrin or with diglycidylether bisphenol A. The synthesized compounds were characterized with FTIR,  $^1\text{H}$  and  $^{31}\text{P}$  NMR, elemental analysis, and epoxide equivalent weight titration to demonstrate their chemical structures. Cured epoxy resins were prepared via thermal curing the epoxy resins with various curing agents. Thermal analysis results (differential scanning calorimetry and thermogravimetric analysis) revealed that these cured epoxy resins exhibited high glass transition temperatures and high thermal stability. High char yields at 700°C and high LOI (limited oxygen index) values were also found for the cured epoxy resins to imply that the resins were possessing high flame retardancy. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1697–1701, 2002

**Key words:** resins; thermogravimetric analysis; flame retardance

## INTRODUCTION

Epoxy resins are widely used in the electronic/electrical industrials to serve as advanced composite matrices for manufacturing printed circuit board (PCB), encapsulants for semiconductors, and insulating materials. Among the electronic/electrical applications epoxy resins are required to be within high flame retardancy for securing from fire accidents. Therefore, brominated compounds and antimony oxide were added into the epoxy resins for compensating the resins' flammability.<sup>1,2</sup> However, during recent years, organo-

phosphorous compounds have been considered to replace the traditional brominated flame retardants, with the consideration of avoiding the generation of corrosive and toxic gases as well as releasing the toxic "environmental hormone" under fire.<sup>3–5</sup> Therefore, phosphorous-containing epoxides<sup>6–11</sup> and curing agents<sup>12–16</sup> were synthesized for resulting in halogen-free flame-retardant epoxy resins. Moreover, imparting phosphorous into the epoxy resins via phosphorous epoxide compounds and/or phosphorous curing agents also brought about epoxy resins with permanently attached phosphorous through covalent bonding, to exhibit relatively high flame retardancy.<sup>17</sup>

In this study, phosphorous-containing epoxies were prepared via a novel route with simple synthesis steps and high yields. The phosphorous element was incorporated onto the epoxy compounds by means of a cyclic compound of 9,10-

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dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The rigid DOPO structure enhanced the resulted epoxy resins' thermal stability and showed a high flame retardating effect.<sup>10–12,17</sup> Cured epoxy resins were prepared from curing the synthesized epoxy with various curing agents, and their thermal and flame retardant properties were examined. The obtained epoxy resins are expected to be qualified for printed circuit boards, encapsulants of electronic devices, and other electronic applications.

## EXPERIMENTAL

### Materials

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 4,4'-dihydroxybenzophenone (DHBP) from Aldrich Co. were used as received. Epichlorohydrin (ECH) from Lancaster Synthesis Co. was used as received. Diglycidylether bisphenol A (BE188, epoxy equivalent weight EEW = 188) and phenolic novolac (PN) were supplied from Chang Chun Plastic Co. (CCP) in Taiwan. Dicyandiamide (DICY), 4,4'-diaminodiphenylmethane (DDM), phenol, and triphenylphosphine (TPP) were from the TCI Co. and used as received. Toluene and tetrahydrofuran (THF) from the Fischer Co. were used as received.

### Synthesis of DOPO-2OH

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (21.6 g) (DOPO, 0.10 mol) and 23.5 g of 4,4'-dihydroxybenzophenone (DHBP, 0.11 mol) were put in a 250-mL round-bottom flask. Phenol (150 mL) was added into the flask. The mixture was stirred under refluxing for 5 h. The phenol was distilled out under reduced pressure. Toluene (150 mL) was added into the flask and the precipitant was filtered. The obtained solid was then reprecipitated from THF to give a pure product with a 85% yield. m.p.: 296–298°C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 9.36–9.40 (2H); 7.91–7.93 (2H); 7.61–7.78 (4H); 7.51–7.57 (2H); 7.25–7.30 (2H); 7.02–7.13 (3H); 6.85–6.88 (3H). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, ppm): 31.61. (Elemental analysis found % (Calc. %): C: 69.93 (69.77), H: 4.35 (4.42), P: 7.17 (7.21).

### Synthesis of DOPO-E-I

DOPO-2OH (17.2 g, 0.04 mol) dissolved in a 20 mL solution of KOH/ethanol (0.5 mol/L) was put

in a 250 mL three-necked flask equipped with a stirrer, condenser, and a nitrogen inlet. The mixture was stirred under nitrogen. After adding 38.4 g ECH the reaction mixture was stirred at room temperature for 48 h. The precipitant was filtered, and the filtrate was washed with a saturated solution of NaHCO<sub>3</sub>(aq) and followed with distilled water for twice. The separated organic layer was dried over MgSO<sub>4</sub> and then concentrated under reduced pressure with a rotary evaporator. A light-yellow solid was obtained with a 90% yield. Softening point: 61–62°C. EEW = 276. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 8.20 (2H); 7.74 (1H); 7.33–7.46 (7H); 7.11 (2H); 6.91–6.93 (4H); 4.33 (2H); 3.82 (2H); 3.33 (2H); 2.88 (2H); 2.73 (2H). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, ppm): 31.56. Elemental analysis found % (Calc. %): C: 67.18 (68.64), H: 4.91 (4.98), P: 5.79 (5.72).

### Synthesis of DOPO-E-II

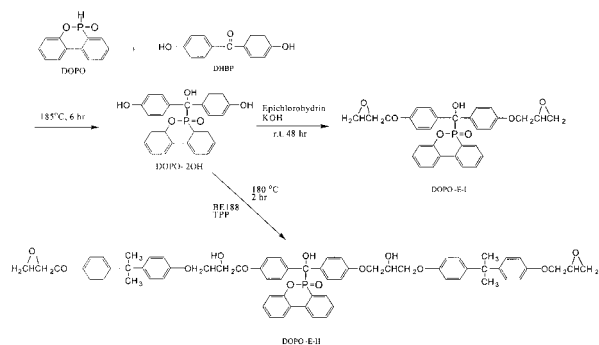
In a 250-mL round-bottom flask, 10.7g DOPO-2OH, 18.8g BE188, and 0.03g TPP were mixed together. The mixture was heated to 180°C and stirred under nitrogen for 2 h. A solid epoxy resin was therefore obtained. Softening point: 125–127°C; EEW = 621. Elemental analysis found % (Calc. %) P: 2.68 (2.62).

### Preparation of Epoxy Resins

The cured epoxy resins were obtained via thermally curing DOPO-epoxy (DOPO-E-I and DOPO-E-II) with various curing agents of DICY, DDM, and PN. To obtain a highly crosslinked polymer with good thermal stability, one epoxy equivalent weight of the epoxy resins was cured with one functional equivalent weight of the curing agents.<sup>13</sup> The curing cycles determined from DSC tracing of the reactions were 155°C for 1 h and 190°C for 1 h.

### Instrumental Analysis and Measurements

Infrared spectra (FTIR) were obtained from a Perkin-Elmer 2000 FTIR. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer with CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as a solvent. Elemental analysis was performed with a Heraeus CHN-O rapid elementary analyzer with benzoic acid as a standard. The phosphorous contents were determined via phosphorous elemental analysis by a Micro Digestion Apparatus with a spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a



**Figure 1** The synthesis route of phosphorous-containing epoxies.

Thermal Analysis (TA) DSC-2900 at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a Thermal Analysis (TA) TGA-2950 Thermogravimetric Analyzer at a heating rate of 10°C/min under nitrogen or air atmosphere. Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter. The percentage in the O<sub>2</sub>-N<sub>2</sub> mixture, deemed sufficient to sustain the flame, was taken as the LOI.

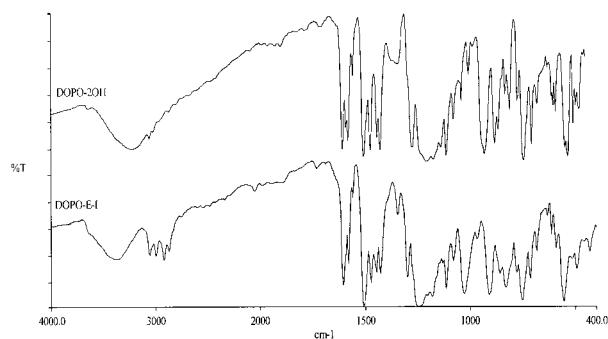
## RESULTS AND DISCUSSION

### Synthesis of Epoxy

The —P(O)-H group could serve as a reactive site to the C=O via a nucleophilic addition reaction.<sup>18</sup> In a previous study<sup>16</sup> DOPO, which contains the —P(O)—H group, was incorporated onto an aldehyde through the above-mentioned reaction to result in a new phosphorous compound with the phenol group. Therefore, through a similar manner a new phosphorous-containing biphenol compound was obtained via reacting DOPO with a benzophenone compound (4,4'-dihydroxybenzophenone, DHBP), as shown in Figure 1. Generally, a ketone is less electrophilic than an aldehyde, to show less reactivity under such nucleophilic addition reactions. However, from DSC tracing of a DOPO/DHBP mixture an exothermic peak starting at 170°C was observed. Therefore, DOPO was expected to be able to react with DHBP at temperatures higher than 170°C. The performance of the above-mentioned reaction was monitored with an FTIR. As the addition reaction proceeded, the —C=O group was attacked with —P(O)—H to form a —P(O)—C—OH group. Therefore, for DOPO-2OH, the distinctive absorp-

tion at 2385 cm<sup>-1</sup> for P—H stretching in DOPO and absorption at 1627 cm<sup>-1</sup> for the C=O group disappeared, while an absorption at 3560 cm<sup>-1</sup> for C—OH appeared (Fig. 2). Moreover, for the resulting product, the other characteristic absorptions at 3226 cm<sup>-1</sup> (Ph—OH), 1584 cm<sup>-1</sup> (P—Ph), 1210 cm<sup>-1</sup> (P=O), 1182 and 935 cm<sup>-1</sup> (P—O—Ph) were also observed to confirm the chemical structure of DOPO-2OH. From this synthesis route, a phosphorous diol with Ph—C—OH reactive group was obtained. The two phenol groups were utilized for preparing epoxy resins in the following experiments of this work. Moreover, the Ph—C—OH group of DOPO-2OH could be further modified to result in various functional compounds.

The phosphorous-containing diol compound DOPO-2OH was reacted with epichlorohydrin and diglycidylether bisphenol A (DGEBA, a commercial product of BE188 from the CCP Co. was used), respectively, to result in phosphorous-containing epoxies. The performance of the glycidyletherification reaction between DOPO-2OH and epichlorohydrin was confirmed by FTIR, characterization with the observation of the absorption peak of oxirane ring at 913 cm<sup>-1</sup>. Other peaks at 1581 cm<sup>-1</sup> (P—Ph), 1211 cm<sup>-1</sup> (P=O), 1182 and 937 cm<sup>-1</sup> (P—O—Ph) were also observed to confirm that DOPO-E-I maintains the cyclic DOPO structure. The incorporation of epoxide group onto DOPO-2OH was also demonstrated by <sup>1</sup>H-NMR analysis, where showing five specific absorption peaks at  $\delta$  = 4.33, 3.82, 3.33, 2.88, and 2.73 ppm were denoted to the protons of the oxirane ring. Moreover, DOPO-E-I exhibits a single peak at  $\delta$  = 31.56 ppm in its <sup>31</sup>P NMR spectrum, further indicating that the cyclic DOPO structure was still maintained after the glycidyletherification reaction. Moreover, phos-



**Figure 2** The FTIR spectra of DOPO-2OH and DOPO-E-I.

**Table I Thermal Analysis Data of Cured Epoxy Resins**

Epoxy Resins	P Content (wt %)	$T_g$ (°C)	Temp. of 5% Weight Loss (°C)		Char Yield at 800°C (wt %)		LOI
			N <sub>2</sub>	Air	N <sub>2</sub>	Air	
E-I/DDM	4.60	152	341	334	41.4	30.4	36
E-I/DICY	5.00	165	340	327	43.9	32.1	45
E-I/PN	3.64	152	371	353	36.1	23.6	31
E-II/DDM	2.00	140	375	368	29.4	16.1	29
E-II/DICY	2.18	155	375	361	34.7	20.2	30
E-II/PN	1.59	142	385	375	23.6	14.1	26
BE188/DDM	0.00	132	405	382	15.1	0.0	22

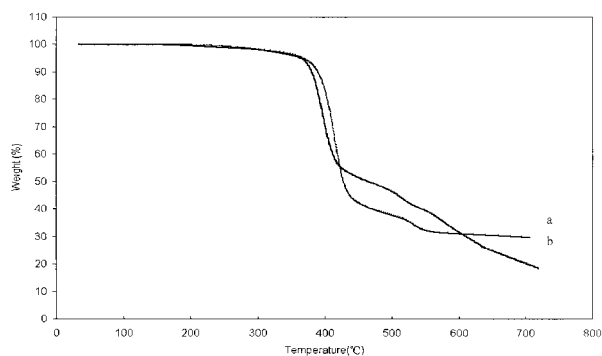
phorous-containing epoxy resin was also obtained via advancement of DOPO-2OH and BE188 with triphenylphosphine as a catalyst.<sup>9</sup> The equivalent ratio of epoxy to phenolic hydroxyl of 1.0 : 1.0 was utilized to result in an epoxy (DOPO-E-II) with an EEW of 621.

### Thermal Analysis of Cured Epoxy Resins

The cured polymers were prepared from the phosphorous-containing epoxies with various curing agents. The glass transition temperatures of the epoxy resins determined from DSC analysis were noteworthy (Table I). The  $T_g$ s of the cured epoxy resins was leveled from 132 up to 152°C, while the phosphorous-containing epoxy DOPO-E-I was used in the curing system to be instead of the ordinary bisphenol A-type epoxy BE188. The relatively high  $T_g$ s of the DOPO-E-I-based epoxy resins should come from the high rigidity of the DOPO group. Owing to reducing crosslinking density, it was observed that introducing DOPO group into the epoxy resin systems resulted in polymers with low  $T_g$ s in other works.<sup>16,19</sup> However, this flaw did not appear in the present study. Moreover, the resins based on DOPO-E-I exhibited higher  $T_g$ s than the DOPO-E-II-based polymer did, because DOPO-E-II-based polymers have relatively low crosslinking density as a consequent result from the high EEW value of DOPO-E-II. On the other hand, the PN cured epoxy resins often show relatively high glass transition temperatures, because PN was known as a multifunctional curing agent. However, an opposite result against the above inference was observed in the present work. This uncommon result could be understood by the hindrance effect of the bulky DOPO group. A similar result was

also seen in the reported result, in which a DOPO-containing epoxy cured with PN showing relatively low  $T_g$ .<sup>16,19</sup>

The thermal stability and thermal degradation behavior of the cured phosphorous-containing epoxy resins were investigated with TGA. Typical TGA thermograms of DOPO-E-II/DICY epoxy resin were shown in Figure 3, and the analysis data was collected in Table I. As shown in Figure 3, the weight loss of the resin began at about 368°C, and then a dramatic weight loss followed. In contrast to other phosphorous-containing polymers based on phosphate and phosphine structures,<sup>6,7</sup> the DOPO containing epoxy resins showed relatively high thermal stability. The degradation temperatures of the DOPO group and the polymer matrix were near to each other, and therefore not to show a clear two-stage weight loss behavior, which was observed for other phosphorous-containing polymers. Furthermore, the phosphorous-containing group degraded at low



**Figure 3** Typical TGA thermograms of phosphorous-containing epoxy resins. (a) DOPO-E-II/DICY under nitrogen; and (b) DOPO-E-II/DICY under air.

temperature region and formed a phosphorous-rich char to lead to flame retardant effect on the polymers.<sup>6,7</sup> The cyclic structure and phenyl groups of DOPO group both enhance this char formation. Moreover, the weight loss rates of the phosphorous-containing epoxy resins under air were retarded at temperatures higher than 500°C. The phosphorous-rich char serves as a heat barrier, and protects the resins from further degradation at the high temperature region. In contrast to the phosphorous-free resins, this retardation in degradation was also from the formed phosphorous char that exhibits efficient capability of antioxidation.

From Table I it can be seen that the char yields of the epoxy resins were effectively leveled up while the phosphorous DOPO group was introduced into the resins. The char yields were also found to increase when the phosphorous contents increased to further demonstrate that phosphorous play an important role in the char formation. Because char yield has been correlated to be a representation of polymer's flame retardancy,<sup>20</sup> the prepared epoxy resins in the study were expected to possess good flame-retardant properties. Based on the above, LOI value, which can be taken as an indicator for evaluating polymers' flame retardancy, of the prepared epoxy resins were also measured and shown in Table I. All of the phosphorous-containing epoxy resins exhibited higher LOI values than the phosphorous-free BE188/DDM resin, as increasing the phosphorous contents of the resins also results in increasing the polymers' LOI values. This is coincident with the above-mentioned relationship between phosphorous contents and char yields. Furthermore, the DICY-cured epoxy resins showed high LOI values owing to the contribution of phosphorous-nitrogen synergistic effect.<sup>6,19</sup>

## CONCLUSIONS

Novel epoxy resins containing a cyclic phosphorous group were obtained via a simple synthetic route. The prepared epoxy was cured with various curing agents to result in epoxy resins exhibiting high glass transition temperatures, high thermal stability, and excellent flame retardant properties. Because new packaging techniques, encapsulating methods, and halogen-free products are developing for the demands of the modern electronics, these properties were especially impor-

tant for epoxy resins using in the electrical/electronic application. Therefore, the developed epoxy resins in this study, within a simple synthetic route and outstanding properties, were expected to be potential in industrial application.

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