ELSEVIER

Polymer 42 (2001) 3445–3454

polymer

www.elsevier.nl/locate/polymer

# Flame-retardant epoxy resins from novel phosphorus-containing novolac

Ying Ling Liu*

*Department of Chemical Engineering, Chung Yuan Christian University, Chungli, Taoyuan 32023, Taiwan, ROC*

Received 21 August 2000; accepted 18 September 2000

## Abstract

A novel phosphorus-containing novolac (DOPO-PN) from 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 4-hydroxyl benzoaldehyde was obtained via simple addition reactions. The chemical structure of the obtained DOPO-PN was characterized with FT-IR, $^{1}$H and $^{31}$P NMR and elemental analysis. The DOPO-PN novolac, with multi-phenol groups in the molecular chain, was used as a polyfunctional curing agent for epoxies. The activity and activation energies of the DOPO-PN curing reactions with epoxies were investigated with differential scanning calorimetry (DSC). The thermal properties and thermal degradation behaviors of the DOPO-PN-cured epoxy resins were also studied with DSC and thermogravimetric analysis. High glass transition temperatures (above 160°C) and extremely high thermal stability (above 300°C) were observed for the DOPO-PN/CNE200 (*o*-cresol novolac epoxy)-based resins. High char yields and high limited oxygen index (LOI) values were also found to demonstrate the good flame retardancy of the DOPO-PN-cured epoxy resins. The LOI values of the epoxy resins were proportional to the phosphorus contents of the epoxy resins. A least phosphorus content of 2 wt% is detected for the DOPO-PN-cured epoxy resins to exhibit a LOI value of 26 and to pass the UL 94V-0 test. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Epoxy resin; Phosphorus; Flame retardant

## 1. Introduction

In modern polymer industry, epoxy resins are widely used as advanced composite matrices in the electronic/electrical industrials, owing to their high tensile strength and modulus, low shrinkage in cure, high adhesion property, good chemical and corrosion resistance and excellent dimensional stability [1–2]. Traditionally, brominated compounds and/or antinomy oxide, serving as flame retardants, are imparted into the epoxy resins for compensating the resins' flammability [3–5]. Recently, with the consideration of avoiding the generation of toxic, corrosive and halogenated gases as well as releasing the toxic "environmental hormone" in combustion [6–8], the trend is toward using halogen-free flame retardants. Moreover, organo-phosphorus compounds, generating less toxic gases and smoke, are the materials of choice among the halogen-free flame retardants [9–10]. Additionally, epoxy resins with permanently attached flame-retardant groups exhibit relatively high flame retardancy [11–13]. The above-mentioned permanent attachment coming from covalently incorporating flame-retardant groups onto the epoxy chains could be achieved via using phosphorus-containing oxiranes and/or curing agents. Therefore, investigations on developing flame-retardant epoxy resins from phosphorus-containing epoxides [14–18] and/or curing agents [19–23] have been reported. On the other hand, in recent years, several new processing and packaging techniques for electronics are developed to result in a light, thin, short and small electrical product. These new techniques require advanced materials to ensure the products' quality and high performance. However, some defects in thermal stability, synthesis route, scaling up to mass production and cost were accompanied with the developed materials in the above literature [14–23]. Moreover, the developed surface mounting technology (SMT) and other advanced electronic packaging techniques require materials being able to sustain the solder's and the lead-free solder's temperatures higher than 288°C. Therefore, thermal stability plays an important role for the electronic materials. The present study thus is trying to develop a halogen-free epoxy with high flame retardancy, high thermal stability, simple synthesis route and low cost, to meet the requirements of the current and future electronic applications. In this work, the cyclic phosphorous compound of 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was used to result in a rigid novolac compound via simple addition reactions. The obtained compound with multi-phenol groups was then used as a curing agent for epoxies. The curing reaction, the thermal properties and

---

* Tel.: +886-3-4563171 ext 4130; fax: +886-3-4563171 ext 4199.
*E-mail address:* ylliu@cycu.edu.tw (Y.L. Liu).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00717-5

Table 1
The curing conditions for the epoxy resins

| Epoxy compositions | The initial temperature of the exothermic peak on DSC thermogram (°C) | Curing procedure | |
|---|---|---|---|
| | | 1st cure | 2nd cure |
| BE188/PN | 132.4 | 175°C, 120 min. | 200°C, 180 min. |
| CNE200/PN | 140.3 | 175°C, 120 min. | 200°C, 180 min. |
| BE188/DOPO-PN | 150.6 | 180°C, 120 min. | 200°C, 180 min. |
| CNE200/DOPO-PN | 167.3 | 185°C, 120 min. | 210°C, 180 min. |

the flame-retarding properties of the resulted epoxy resins were studied. The obtained epoxy resins are expected to be qualified for printed circuit boards, encapsulants of electronic devices and other electronic applications.

## 2. Experimental section

### 2.1. Materials

DOPO (**I**) was prepared in our laboratory according to the literature [24]. 4-hydroxybenzaldehyde (4-HBA) and oxalic acid, both from Aldrich Co., were used as received. Tetrahydrofuran (THF) and toluene (from Aldrich Co.) were dried with sodium and distilled out prior to use. Chloroform, from Aldrich Co., was dried with calcium hydride and distilled out prior to use. Diglycidylether bisphenol-A (BE188, epoxy equivalent weight EEW = 188) and *o*-cresol novolac epoxy (CNE200, EEW = 200) were supplied kindly from Chang Chun Plastic Co. (CCP) in Taiwan. Phenolic novolac resin (PN) was also from CCP in Taiwan.

### 2.2. Synthesis of DOPO-HB

DOPO (21.6 g, 0.1 mol), 4-HBA (13.4 g, 0.11 mol) and dried toluene (200 ml) were mixed together and stirred in a 500 ml round-bottom flask. The solution was then heated and refluxed for about 5 h. The reaction solution then became thick due to the precipitation of the formed DOPO-HB. After being cooled to room temperature, the precipitant was filtered and washed with toluene. The obtained solid was then recrystallized from toluene/methanol (2/1 in volume) to give a pure product with a 95% yield. mp: 245–247°C. Elemental analysis: found% (Calc.%): C: 67.01 (67.45), H: 4.32 (4.45), O: 18.85 (18.93), P: 9.23 (9.17).

### 2.3. Synthesis of DOPO-PN

DOPO-HB (16.9 g, 0.1 mol) was dissolved in 150 ml dried THF in a 250 ml round-bottom flask. About 0.44 g (0.005 mol) of oxalic acid was added into the solution. The reaction mixture was then heated and kept refluxing for 4 h. The reaction solution was concentrated and neutralized by 5 wt% NaOH aqueous solution. The obtained solution was extracted with chloroform. The organic layer was collected and concentrated under a reduced pressure to give a product in a 95% yield. Softening point 135–138°C. Elemental analysis: found% (Calc.%): C: 71.43 (71.25), H: 4.11 (4.06), O: 14.88 (15.00), P: 9.77 (9.69).

### 2.4. Preparation of epoxy resins

The cured epoxy resins were obtained via thermally curing DOPO-PN with epoxies. The phosphorus-free phenolic novolac PN was also used for preparing control samples. 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 novolac curing agents [16]. The curing cycles were determined from differential scanning calorimetry (DSC) tracing of the respective epoxy/curing agent compositions (Table 1).

### 2.5. Instrumental analysis and measurements

Infrared spectra (FT-IR) were obtained from a Perkin–Elemer 2000 FT-IR. $^1$H and $^{31}$P NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer with $CDCl_3$ or DMSO-$d_6$ as a solvent. Elemental analysis was performed with a F002 Heraeaus CHN–O rapid element analyzer employing acetanilides as a standard. The phosphorus contents of the synthesized resins were determined via phosphorus elemental analysis by a micro digestion apparatus with a spectrophotometer. DSC thermograms were recorded with a thermal analysis (TA) DSC-2900 at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a TA TGA-2950 thermogravimetric analyzer at a heating rate of 20°C/min under nitrogen or air atmosphere. Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter by a modified method that has been reported in the literature [25,26]. The percentage in the $O_2$–$N_2$ mixture deemed sufficient to sustain the flame was taken as the LOI. The UL-94V test was performed according to the testing method proposed by Underwriter Laboratory Inc. [27], with test specimen bars of 127 mm length, 12.7 mm width and about 3.2 mm thickness. Five sample bars suspended vertically over surgical cotton were ignited by a Bunsen burner. A flame was applied twice to the lower end of the specimen for 10 s. The class of 94 V-0 is achieved if each after-flame time does not exceed 5 s, and sum of the after-flame time of 10 tests for the five samples does not exceed 50 s. Meanwhile, for UL94 V-0, the surgical cotton below the specimen could not be ignited with the flaming drippings.

### *2.6. Activation energies of curing kinetics from DSC*

#### *2.6.1. Method 1 [28]*

A simple but accurate relationship among activation energy ($E_a$), heating rates ($\varphi$) and temperature of exothermic peak ($T_p$) as

$$E_a = \frac{-R}{1.052}\frac{\Delta \ln \phi}{\Delta(1/T_p)} \qquad (1)$$

is used [20,28–30]. The exothermic peaks at various heating rates of the curing reactions were recorded on a DSC.

#### *2.6.2. Method 2 [20,31]*

From the DSC data, the reaction rate $r$ could be taken as

$$r = dx/dt = \varphi(dx/dT) = A\,e^{(-E_a/RT)}(1-x)^n, \qquad (2)$$

where $\varphi$ = heating rate, $A$ = Arrenihus constant, R = idea gas constant and $T$ = temperature. While at $T = T_p$, it is obtained that $dr/dt = 0$, the above equation could be rearranged into

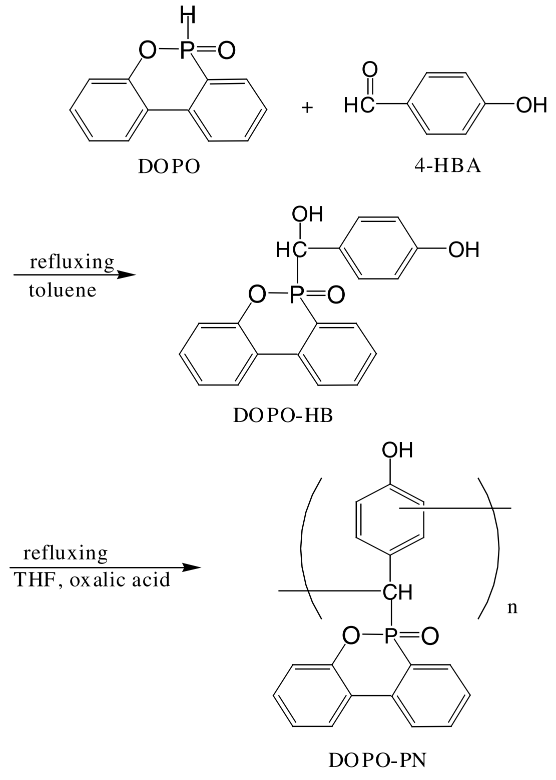
$$-\ln(\varphi/T_p^2) = \ln(E_a/R) - \ln(An) - (n-1)\ln(1-x)P + E/(RT_p). \qquad (3)$$

The activation energy is able to be obtained by a plot of $-\ln(\varphi/T_p^2)$ vs. $(1/T_p)$.

## 3. Results and discussion

### *3.1. Synthesis of phosphorus-containing compounds*

It is well known that the electrophilic –P(O)–H group could serve as a reactive site to the nucleophilic C=O in aldehydes and ketones via an electrophilic addition reaction [32]. Therefore, the phosphorus-containing compound DOPO-HB was obtained via reacting DOPO with 4-HBA. Furthermore, a self-addition reaction of DOPO-HB between the *ortho*/*para*-reactive sites of phenols and the –C–OH groups in DOPO-HB was performed to result in the phosphorus-containing novolac of DOPO-PN (Scheme 1; the synthesis scheme of phosphorus-containing novolac DOPO-PN). The obtained products were firstly characterized by FT-IR. Fig. 1 shows the FT-IR spectra of DOPO, DOPO-HB and DOPO-PN. As the addition reaction between DOPO and 4-HBA proceeded, the distinctive absorption at 2385 $cm^{-1}$ for P–H stretching in DOPO disappeared while a broad absorption at around 3221 $cm^{-1}$ for phenolic OH appeared in DOPO-HB. The performance of the above reaction was also demonstrated by the appearance of the peak at 3566 $cm^{-1}$ for C–OH in DOPO-HB. The other characteristic absorption peaks at 1186 $cm^{-1}$ (P=O), 1584 $cm^{-1}$ (P–Ph) and 1171 and 931 $cm^{-1}$ (P–O–Ph) [16,24] further confirmed the chemical structure of DOPO-HB (Fig. 1). Moreover, DOPO-PN was obtained via the DOPO-HB self-addition reaction. The proceeding of the dehydration reaction was demonstrated by the disappearance of the peak at 3221 $cm^{-1}$ for C–OH in DOPO-PN. The absorption peak at 3176 $cm^{-1}$ reveals the presence of the Ph–OH groups in DOPO-PN. The absorption peaks at 1213 $cm^{-1}$ (P=O), 1583 $cm^{-1}$ (P–PH) and 1155 and 921 $cm^{-1}$ (P–O–Ph) (Fig. 1) denote that the cyclic DOPO structure in DOPO-PN was still maintained. Furthermore, these two compounds were further characterized with NMR. Fig. 2 depicts the $^1$H NMR spectra of DOPO-HB and DOPO-PN. The absorption of the characteristic proton C–O*H* at $\delta = 6.27$–$6.29$ ppm was found to demonstrate the performance of the addition reaction between DOPO and 4-HBA. With the accomplishment of this reaction, the proton of –C(OH)–*H* in DOPO-HB was also observed by the absorption at $\delta = 5.04$–$5.25$ ppm. The above absorption peaks and the absorption peaks at $\delta = 6.75$–$8.20$ ppm assigned to aromatic protons demonstrate that DOPO-HB with the expected chemical structure was successfully synthesized. The peak integration results were also found to be closely corresponding to the ratios of the above-mentioned protons. This coincidence between the peak



Scheme 1.

integration data and proton ratios provides further evidence on the chemical structure of DOPO-HB. For DOPO-PN, the similar results were found in the $^1$H NMR analysis. The absorption peak of C–O$H$ was not found in the $^1$H NMR spectrum of DOPO-PN (Fig. 2) to denote the performance of the dehydration reaction on DOPO-HB. The chemical structure of DOPO-PN was also confirmed by the other specific absorption peaks at $\delta = 4.48$–$4.53$ ppm (C(OH)–$H$) and $\delta = 6.70$–$8.21$ ppm (aromatic protons) observed in its $^1$H NMR spectrum. Additionally, the peak integration results also coincided with the ratios of the above-mentioned protons in DOPO-PN. Furthermore, DOPO-HB and DOPO-PN exhibit a single peak at $\delta = 31.77$ and 33.50 ppm in their $^{31}$P NMR spectra (Fig. 3), respectively, indicating both the purity and cyclic DOPO structure of the obtained compounds.

### *3.2. Curing reactions of DOPO-PN on epoxies*

The curing reactions of DOPO-PN with epoxies were studied with DSC. Two epoxies based on BE188 and on CNE200 were utilized in the investigation. Fig. 4 shows the typical DSC thermogram of BE188/DOPO-PN-curing reaction. The exothermic peak denotes the proceeding of the curing reaction between BE188 and DOPO-PN. The reactivity of DOPO-PN toward the epoxy could be read from the start point of the exothermic peak [3]. Furthermore, the curing procedures for preparing epoxy resins based on various compositions were also determined from the DSC exothermic peaks, and the results were shown in Table 1. DOPO-PN exhibits a lower reactivity toward epoxies than PN does. The low reactivity of DOPO-PN toward epoxy might be because of the electron effect. The strongly electron-withdrawing group of P=O in the *para*-position of the phenol reduces the electron density of the oxygen atom in phenolic –OH group, and therefore reduces the reactivity of the –OH group toward oxirane rings [3,14]. Moreover, the incorporation of the bulky DOPO group onto the DOPO-PN novolac also reduces DOPO-PN's reactivity owing to the effect of steric hindrance.

Activation energies of the epoxy/DOPO-PN-curing reactions were determined from DSC studies. Two relationships among activation energy ($E_a$), heating rates ($\varphi$) and

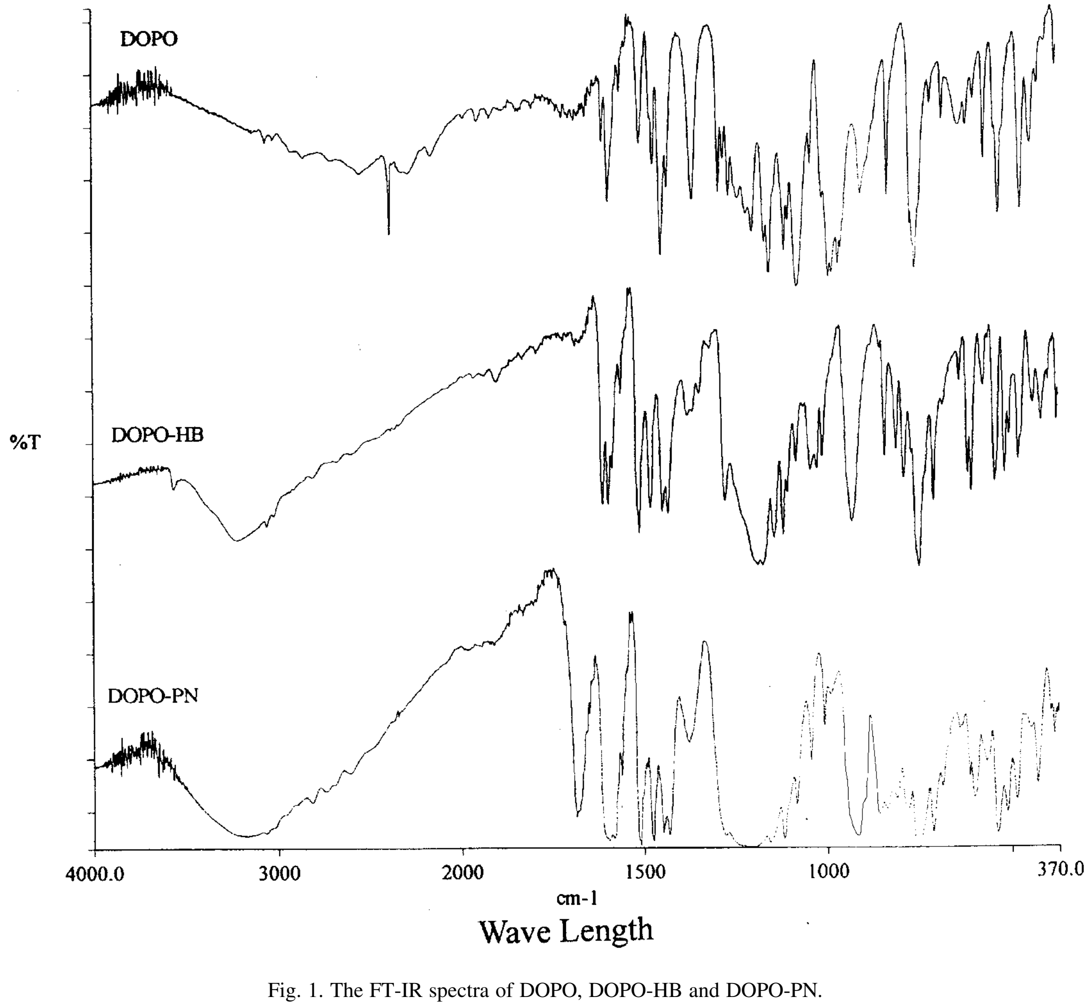


Fig. 1. The FT-IR spectra of DOPO, DOPO-HB and DOPO-PN.

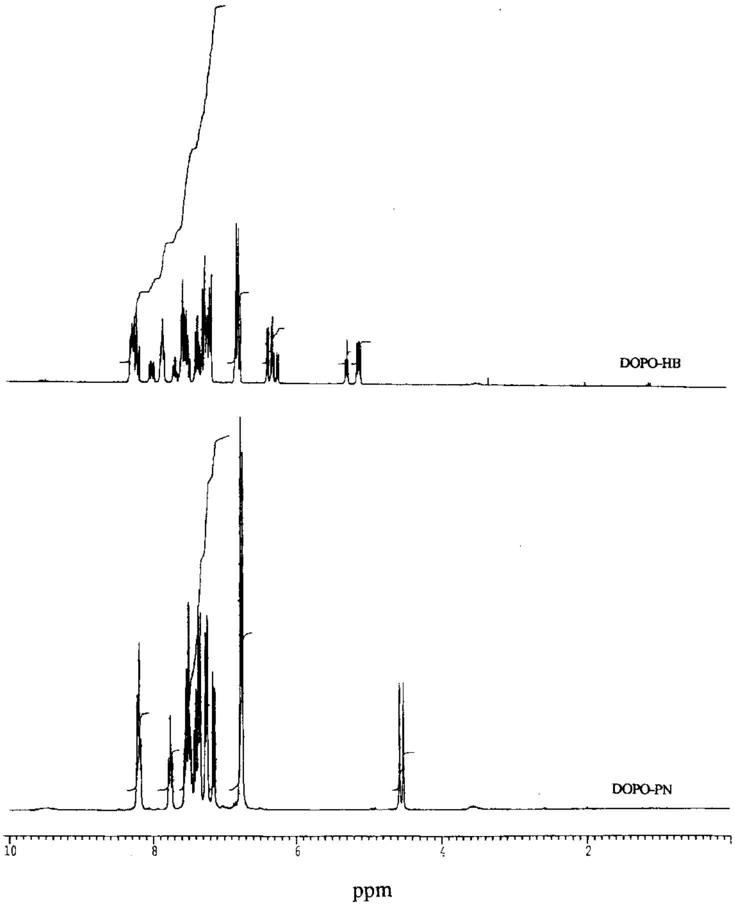


Fig. 2. The $^1$H NMR spectra of DOPO-HB and DOPO-PN.

temperature of exothermic peak ($T_p$) shown as

$$E_a = \frac{-R}{1.052}\frac{\Delta \ln \phi}{\Delta(1/T_p)}$$

and

$$-\ln(\varphi/T_p^2) = \ln(E_a/R) - \ln(An) - (n-1)\ln(1-x)P + E/(RT_p)$$

were utilized. $T_p$s at various heating rates for a curing reaction were recorded with DSC measurements. Therefore, the activation energies of epoxy/DOPO-PN-curing reactions were determined from the slopes of the plots of ln(heating rate) vs. $1/T_p$ (Eq. (1)) and $-\ln(\varphi/T_p^2)$ vs. $(1/T_p)$ (Eq. (3)), respectively. The plots are shown as Fig. 5, and the calculated activation energies of the curing reactions are collected in Table 2. The activation energies of epoxy/DOPO-PN-curing reactions (around 80–85 kJ/mol) are higher than the activation energies of epoxy/amine-curing reactions (around 65 kJ/mol) [20,33], and are comparable to the activation energies of epoxy/PN-curing reactions (about 76–83 kJ/mol). This implies that DOPO-PN exhibits a moderate reaction rate toward epoxies, and involves similar processing conditions for being used in the present PN-cured epoxy systems.

### 3.3. Thermal properties of the cured epoxy

The cured polymers were prepared according to the curing procedures determined from DSC (Table 1). Moreover, epoxy resins with various phosphorus contents (cured from DOPO-PN/PN blending curing agents) were also prepared for evaluating their application potential in the encapsulation of microelectronic devices. The compositions and thermal properties of the cured epoxy resins are shown in Table 3. The glass transition temperatures ($T_g$s) of these cured epoxy resins are noteworthy. It has been reported that incorporating the bulky rigid DOPO group into the epoxy chain would increase the rotational barrier of the epoxy, therefore, increasing the $T_g$s of the polymers [16]. However, an opposite tendency in $T_g$s of the DOPO-PN-cured epoxy resins was observed in the present study. The $T_g$s of the DOPO-PN-cured epoxy resins were found to be lower than that of the PN-cured epoxy resins. The opposite result of the DOPO's effect on epoxy resins' $T_g$s might be understood by the steric hindrance of the bulky DOPO group in DOPO-PN. In Wang's work [16], a DOPO group-containing bis-oxirane compound (DOPO-epoxy) was used for

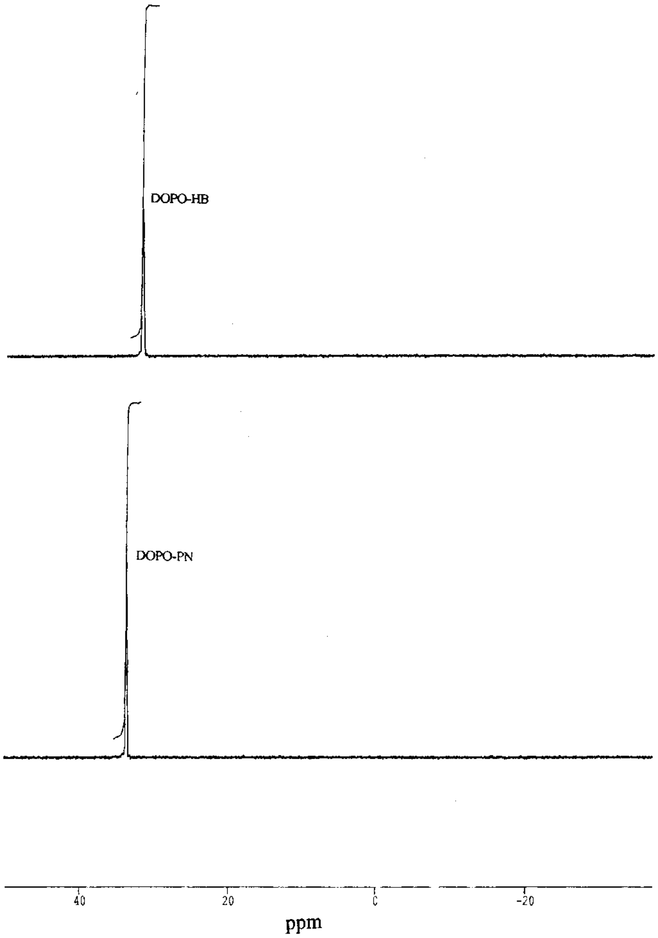


Fig. 3. The $^{31}P$ NMR spectra of DOPO-HB and DOPO-PN.

preparing the epoxy resins. For the small molecule of DOPO-epoxy, the DOPO group provides less hindrance effect in curing reaction, and attributes significantly rational barrier to the cured polymers. However, DOPO-PN contains multi-DOPO groups with closely neighboring distance in one molecular chain, consequently bringing a much apparent steric hindrance in the curing reactions. Therefore, owing to the steric hindrance effect, the crosslinking density of the DOPO-PN-cured epoxy is decreased, consequently lowering the $T_g$ of the polymer. In other aspects, though the DOPO-PN-cured epoxy resins exhibit lower $T_g$s than the PN-cured resins, the $T_g$s of the epoxy resins based on BE188/DOPO-PN (115.5–134.5°C) and CNE200/DOPO-PN (133.9–172.8°C) are still as high to reach the requirements for electronic applications. Additionally, the $T_g$s of the DOPO-PN-cured epoxy resins were found to be proportional to the contents of DOPO-PN, i.e. the phosphorus contents, of the resulted polymers (Fig. 6). It is revealed that the properties of the DOPO-PN-cured epoxy resins could be conveniently tailored by the curing compositions.

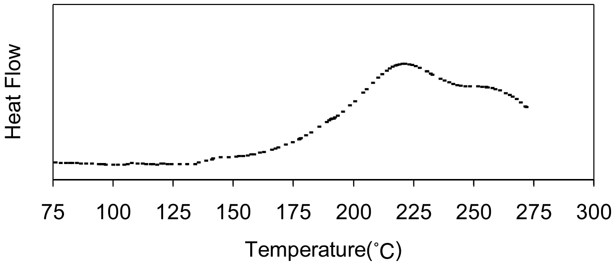


Fig. 4. The DSC thermograms of the BE188/DOPO-PN reactions at a heating rate of 20°C/min.

The cured phosphorus-containing epoxy resins were further investigated by TGA. Figs. 7 and 8 show the TGA thermograms of the DOPO-PN-cured epoxy resins under nitrogen and air atmosphere, respectively. The DOPO-PN-cured epoxy resins are not as thermally stable as the phosphorus-free PN-cured resins. The relatively poor thermal stability of the DOPO-PN-cured epoxy resins comes from

Table 2
The activation energies of the epoxy curing reactions

| Epoxy composition | Method 1 (kJ/mol) | Method 2 (kJ/mol) |
|---|---|---|
| BE188/PN | 76.2 | 72.5 |
| CNE200/PN | 83.2 | 74.3 |
| BE188/DOPO-PN | 80.3 | 76.4 |
| CNE200/DOPO-PN | 85.1 | 81.1 |

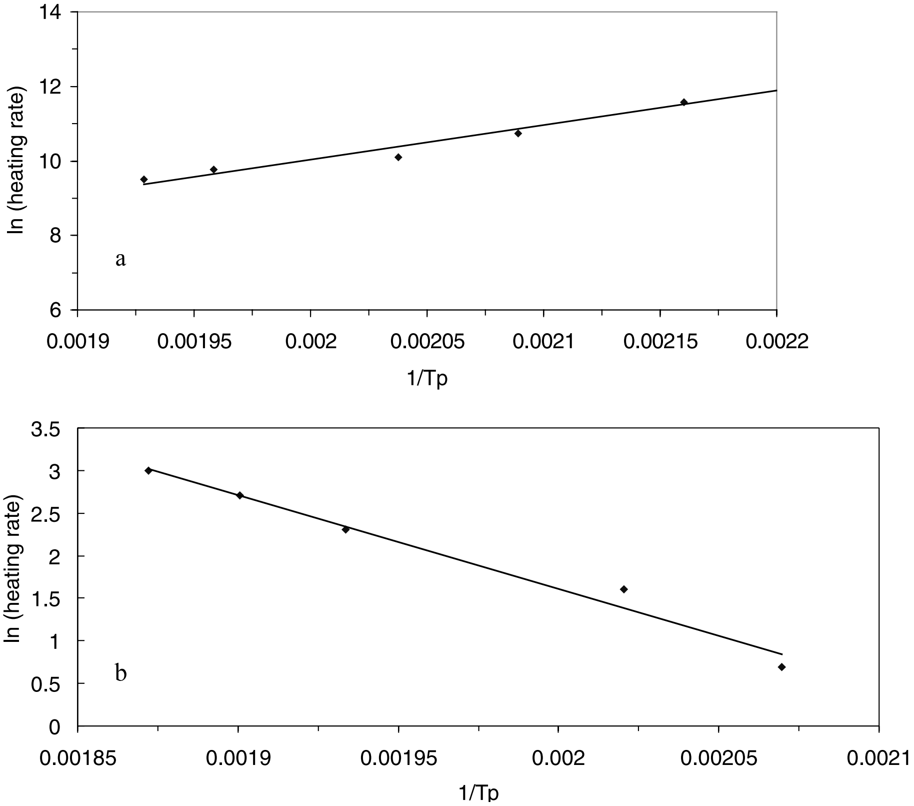


Fig. 5. The plots of ln(heating rate) vs. $1/T_p$ for: CNE200/DOPO-PN curing reactions at various heating rates: (a) method 1; and (b) method 2.

the phosphorous DOPO group degrading at relatively low temperatures. The same phenomenon was also observed for other phosphorylated epoxy resins [14–17] and other polymers [34–36]. However, the thermal stability of the DOPO-PN-cured resins is found to be much higher than that of other phosphorylated epoxy resins. For example, the temperature of 1% weight loss of BE188/DOPO-PN resin is measured to be about 305°C, which is higher than those of DOPO-epoxy/PN resin (207°C) [16], bis-glycidyl phosphonate/diaminodiphenylmethane (DDM) (225°C) [14] and cyclotriphosphazene epoxy/DDM (281°C for 5% weight loss) [18]. High thermal stability is especially important for the halogen-free epoxy resins while being utilized in the advanced electronic application. The developed SMT and other advanced electronic packaging techniques require materials to be able to sustain the solder's and the lead-free solder's temperatures higher than 288°C. The developed DOPO-PN-cured epoxy resins reach the above-mentioned requirements and therefore are qualified for applying in advanced electronics.

Table 3
Thermal properties of cured epoxy resins with various phosphorus contents

| Epoxy resins | P content (wt%) | Tg (°C) | Temp. of 1% weight loss (°C) | | Char yield at 800°C (wt%) | |
|---|---|---|---|---|---|---|
| | | | $N_2$ | Air | $N_2$ | Air |
| *BE188/DOPO-PN* | | | | | | |
| DN188-0 | 0 | 142.3 | 385 | 387 | 19.5 | 2.5 |
| DN188-15 | 1.50 | 134.5 | 311 | 310 | 31.4 | 7.5 |
| DN188-32 | 3.22 | 127.1 | 307 | 305 | 33.7 | 12.2 |
| DN188-41 | 4.11 | 121.5 | 307 | 305 | 37.9 | 16.2 |
| DN188-52 | 5.20 | 115.5 | 304 | 305 | 40.2 | 14.9 |
| *CNE200/DOPO-PN* | | | | | | |
| DN200-0 | 0 | 181.6 | 343 | 350 | 34.4 | 7.0 |
| DN200-15 | 1.45 | 172.8 | 337 | 340 | 36.7 | 16.7 |
| DN200-32 | 3.11 | 157.8 | 331 | 333 | 37.8 | 19.9 |
| DN200-41 | 3.99 | 146.5 | 330 | 327 | 41.1 | 23.1 |
| DN200-52 | 5.05 | 133.9 | 324 | 324 | 45.3 | 28.5 |

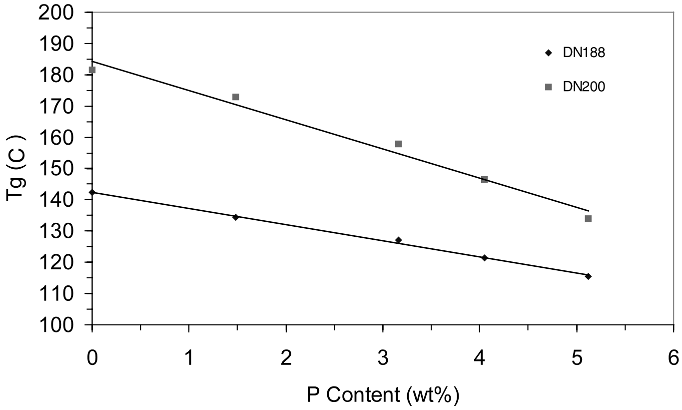


Fig. 6. The plots of $T_g$s of DOPO-PN-cured epoxy resins vs. the resins' phosphorus contents.

The thermal degradation behavior of the prepared epoxy resins was also observed from TGA thermograms. As mentioned earlier, the phosphorus-containing epoxy resins thermally decompose in the relatively low temperature region. However, at the region of temperatures higher than 450°C, the degradation rates of the phosphorus-containing resins were observed as being slower than the degradation rates of the phosphorus-free resins. A retarded-degradation phenomenon has been observed in other phosporylated polymer systems, and is classified to play an important role in improving the flame retardancy of the phosphorylated polymers [13–17,37]. On heating the phosphorous groups of the resins first decompose to form a phosphorus-rich residue [18,38], which prevents further decomposition of the epoxy resin by raising the decomposition temperatures and consequently results in a high char yield. The char yield has been correlated to denote the flame retardancy [39] and has been widely referenced in the studies of the polymers' flame property [11–21,33–37]. Increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction and inhibit the thermal conductivity of the burning materials [40]. Therefore, through the condensed-phase mechanism the flame retardancy of the phosphorus-containing epoxy resins is leveled up [37]. The char yields of the prepared epoxy resins at 800°C in the present work are shown in Table 3. All the phosphorylated (DOPO-PN cured) epoxy resins show high char yields than the phosphorus-free (PN cured) epoxy resins do, implying that the phosphorus-containing epoxy resins would exhibit relatively high flame retardancy. Moreover, the char yields increase with increasing phosphorus contents of the polymers. And, the epoxy resins based on CNE200 also show higher char yields than the epoxy resins based on BE188. These two results imply that an epoxy resin with a high phosphorus content and a high phenyl group content is highly flame retardant. This inference would be discussed in the following LOI and UL 94-V test section.

### 3.4. LOI and UL 94-V test

The flame-retardant properties of the obtained epoxy resins were examined by measuring the LOI of the resins. A significant increase in LOI (from 21 to 35.5) was observed when DOPO-PN was utilized in the epoxy curing compositions (Table 4). This indicates that incorporating phosphorus has an efficient effect on leveling up the flame retardancy of the epoxy resins. It is also noteworthy that the LOI values

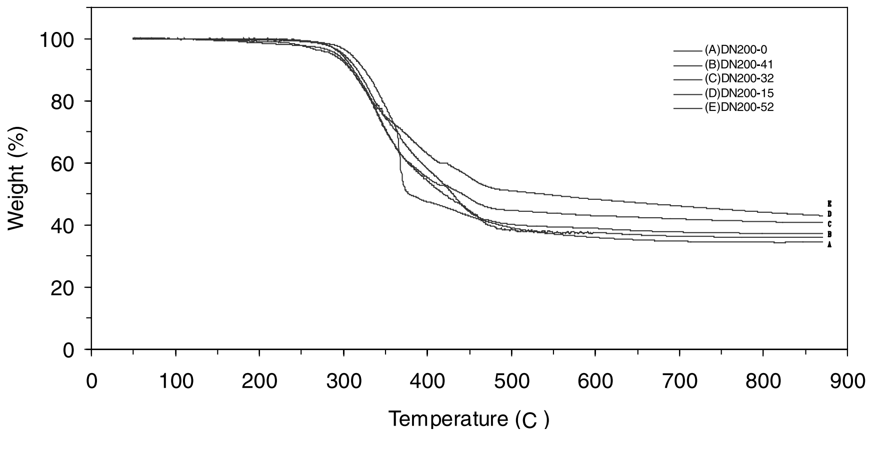


Fig. 7. The TGA thermograms of CNE200/DOPO-PN-based epoxy resins under nitrogen atmosphere.

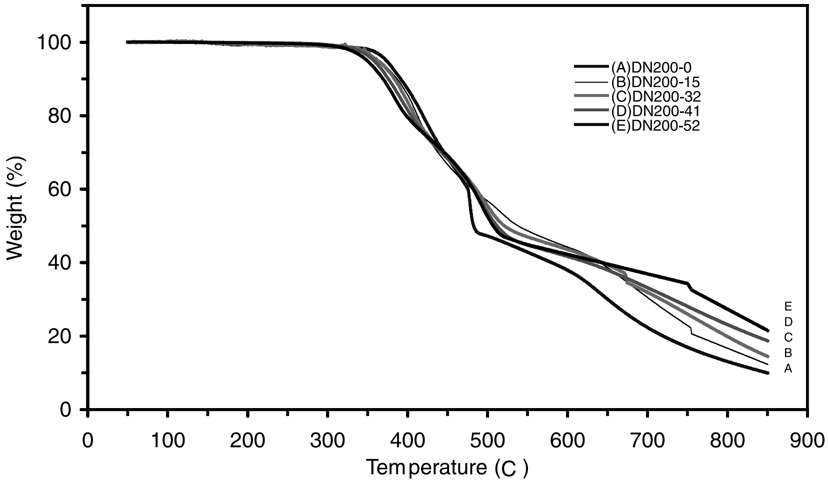


Fig. 8. The TGA thermograms of CNE200/DOPO-PN-based epoxy resins under air atmosphere.

increase with an increase in the phosphorus contents of the resins (Fig. 9). The LOI values of the CNE200-based resins are also found to be higher than that of the BE188-based resins. This result is coincident with the above inference from the char yield data, demonstrating that increasing the contents of phosphorus and phenyl groups in the epoxy resins would improve the flame-retardant property of the polymers. Moreover, the UL 94-V test was also applied to probe the flame retardancy of the phosphorus-containing epoxy resins and to rank it into an industrial expression. The results of UL 94-V test on the epoxy resins are also shown in Table 4. The epoxy resins with phosphorus contents higher than 3 wt% passed the UL 94V-0 test in this table. However, a detailed experiment was performed for evaluating the critical P-content in DOPO-PN-cured epoxy resins for passing the UL 94V-0 test. The critical value was found to be about 2.0 wt% phosphorus content. Basing on the above, the BE188/DOPO-PN/PN and CNE200/DOPO-PN/PN-cured epoxy resins containing a phosphorus content of 2.0 wt% were prepared. These epoxy resins with high $T_g$s (132.3°C for BE188-based resin and 169.2°C for CNE200-based resin), good flame retardancy (LOI = 26, UL 94V-0 grade) and excellent thermal stability (higher than 300°C) are considered to be sufficient for applications in green electrical/electronic materials.

Table 4
LOI Values and UL 94-V test results of cured epoxy resins with various phosphorus contents

| Epoxy resins | P content (wt%) | LOI | UL 94 V Test |
|---|---|---|---|
| *BE188/DOPO-PN* | | | |
| DN188-0 | 0 | 21.0 | V-2 |
| DN188-15 | 1.50 | 24.5 | V-1 |
| DN188-32 | 3.22 | 29.0 | V-0 |
| DN188-41 | 4.11 | 32.0 | V-0 |
| DN188-52 | 5.20 | 34.0 | V-0 |
| *CNE200/DOPO-PN* | | | |
| DN200-0 | 0 | 21.0 | V-2 |
| DN200-15 | 1.45 | 25.0 | V-1 |
| DN200-32 | 3.11 | 29.5 | V-0 |
| DN200-41 | 3.99 | 32.5 | V-0 |
| DN200-52 | 5.05 | 35.5 | V-0 |

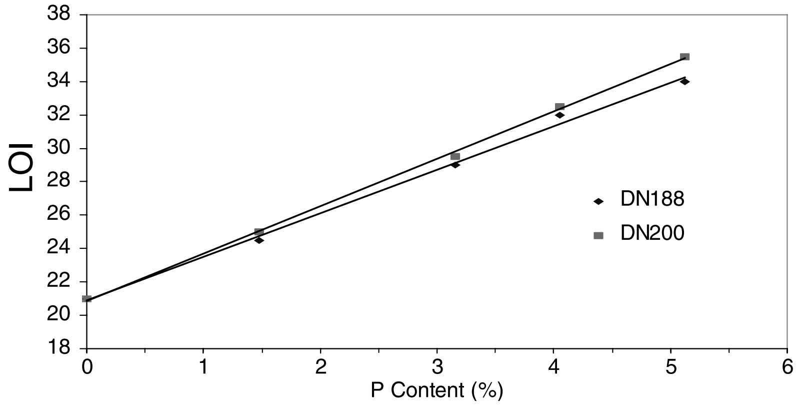


Fig. 9. The plots of LOI values vs. the phosphorus contents of the prepared epoxy resins.

## 4. Conclusions

The phosphorus-containing novolac DOPO-PN was successfully synthesized and used as a curing agent with bisphenol-A-type and *o*-cresol novolac-type epoxies. The cured epoxy resins were found to have high glass transition temperatures, excellent thermal stability and good flame-retardant properties. The synthesized DOPO-PN is therefore suitable to be used as a reactive flame retardant in the epoxy systems for application in green electrical/electronic materials.

## References

[1] Potter WG. Epoxy resins. New York: Springer, 1970.
[2] Kinjo N, Ogata K, Keneda A. Adv Polym Sci 1989;88:1.
[3] Mikroyannidis JA, Kourtides DA. J Appl Polym Sci 1984;29:197.
[4] Yang CP, Hsiao SH. J Appl Polym Sci 1988;36:1221.
[5] Camino G, Costa L. Polym Degrad Stab 1988;20:271.
[6] Luijk P, Govers HAJ, Eijkel GB, Boon JJ. J Appl Pyro 1991;20:303.
[7] Dumler R, Thoma H. Chemosphere 1989;19:305.
[8] Bergman A. Proceedings of International Conference on Halogen-Free materials for Electronic and Electrical Products, Gotherburg, Sweden, November, 1999 (chap. 8).
[9] Green J. J Fire Sci 1992;10:470.
[10] Schut JH. Plas World 1995:31.
[11] Annakurtty KS, Kishore K. Polymer 1988;29:756.
[12] Kishore K, Annakurtty KS. Polymer 1988;29:762.
[13] Banks M, Ebdon JR, Johnson M. Polymer 1993;34:4547.
[14] Liu YL, Hsiue GH, Chiu YS, Jeng RJ, Perng LH. J Appl Polym Sci 1996;61:613.
[15] Liu YL, Hsiue GH, Chiu YS. J Polym Sci Polym Chem Ed 1997;35:565.
[16] Wang CS, Shieh JY. J Appl Polym Sci 1999;73:353.
[17] Wang TS, Parng JK, Shau MD. J Appl Polym Sci 1999;74:413.
[18] Chen-Yang YW, Lee HF, Yuan CY. J Polym Sci Polym Chem Ed 2000;38:972.
[19] Liu YL, Hsiue GH, Lee RH, Chiu YS. J Appl Polym Sci 1997;63:895.
[20] Wang CS, Lin CH. J Appl Polym Sci 1999;74:1635.
[21] Wang TS, Shau MD. J Appl Polym Sci 1998;70:1877.
[22] Buckingham MR, Lindsay AJ, Stevenson DE, Muller G, Morel E, Costes B, Henry Y. Polym Degrad Stab 1996;54:311.
[23] Derouet D, Morvan F, Brosse C. J Appl Polym Sci 1996;62:1855.
[24] Wang CS, Shieh JY. Polymer 1998;39:5819.
[25] Skorna G, Ugi I. Angew Chem Int Ed 1977;16:259.
[26] Nair CPR, Glouet G, Guilbert Y. Polym Degrad Stab 1989;26:305.
[27] Underwriter Laboratory, Materials issued for UL standard for safety, June, 2000.
[28] Ozawa T. J Therm Anal 1970;2:301.
[29] Camba JG, Abajo J, Mantecon A, Cadiz V. Eur Polym J 1987;23:961.
[30] Liu YL, Hsiue GH, Chiu YS, Jeng RJ. J Appl Polym Sci 1996;61:1789.
[31] Kissinger HE. Anal Chem 1957;29:1072.
[32] Wade LG. Organic chemistry. Int. ed. Englewood Cliffs, NJ: Prentice-Hall, 1984 (chap. 18).
[33] Foun CC, Moroni A, Pearce EM, Mijovic J. Polym Mater Sci Engng 1984;51:411.
[34] Liu YL, Hsiue GH, Chiu YS, Jeng RJ, Ma C. J Appl Polym Sci 1996;59:1619.
[35] Liu YL, Hsiue GH, Lan CW, Chiu YS. J Polym Sci Polym Chem Ed 1997;35:1769.
[36] Banerjee S, Palit SK, Maiti S. J Polym Sci Polym Chem Ed 1994;32:219.
[37] Banks M, Ebdon JR, Johnson M. Polymer 1994;35:3470.
[38] Liu YL, Hsiue GH, Lan CW, Chiu YS. Polym Degrad Stab 1997;56:291.
[39] Krevelen DW. Polymer 1975;16:615.
[40] Pearce EM, Liepins R. Environ Health Perspect 1975;11:69.