Phosphorus-Containing Epoxy Resin for an Electronic Application

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ABSTRACT: A phosphorus-containing epoxy resin, 6-H-dibenz[c.e][1.2] oxaphosphorin-6-[2,5-bis(oxiranylmethoxy)phenyl]-6-oxide (DOPO epoxy resin), was synthesized and cured with phenolic novolac (Ph Nov), 4,4'-diaminodiphenylsulfone (DDS), or dicyandiamide (DICY). The reactivity of these three curing agents toward DOPO epoxy resin was found in the order of DICY > DDS > Ph Nov. Thermal stability and the weight loss behavior of the cured polymers were studied by TGA. The phosphorus-containing epoxy resin showed lower weight loss temperature and higher char yield than that of bisphenol-A based epoxy resin. The high char yields and limiting oxygen index (LOI) values as well as excellent UL-94 vertical burn test results of DOPO epoxy resin indicated the flame-retardant effectiveness of phosphorus-containing epoxy resins. The DOPO epoxy resin was investigated as a reactive flame-retardant additive in an electronic encapsulation application. Owing to the rigid structure of DOPO and the pendant P group, the resulting phosphorus-containing encapsulant exhibited better flame retardancy, higher glass transition temperature, and thermal stability than the regular encapsulant containing a brominated epoxy resin. High LOI value and UL-94 V-0 rating could be achieved with a phosphorus content of as low as 1.03% (comparable to bromine content of 7.24%) in the cured epoxy, and no fume and toxic gas emission were observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 353-361, 1999

Key words: phosphorus-containing epoxy resin; 6-H-dibenz[c,e][1,2]oxaphosphorin-6-[2,5-bis(oxiranylmethoxy)phenyl]-6-oxide; phenolic novalac; 4,4'-diaminodiphenylsulfone; dicyandiamide; bisphenol-A; flame retardant; limiting oxygen index; UL-94V test

INTRODUCTION

Epoxy resins have excellent moisture, solvent and chemical resistance, low shrinkage on cure, superior electrical and mechanical properties, and good adhesion to many substrates. The versatility in formulation also makes epoxy resins widely applicable industrially for surface coatings, adhesives, painting materials, pottings, composites, laminates, encapsulants for semiconductors, and insulating materials for electric devices, etc.¹⁻⁴ However, the common epoxy systems cannot satisfy field applications that require high thermal and flame resistance. Considerable environmental attention and health restrictions have been considered in the last three decades in regard to controlling inherent flammability of common organic polymer by incorporation of fire-retardant additives. Several approaches for modification of the epoxy backbone to enhance the thermal properties of epoxy resins have been reported.^{5–8}

Flame retardants such as tetrabromobisphenol A, phosphorus-halogen mixtures, ammonium phosphate, and organophosphorus compounds have been used to impart flame retardancy to epoxy resins.⁹⁻¹² In a fire, halogens (i.e., of bro

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mine and chlorine) produce problems of smoke and possibly enhanced toxicity, and corrosion. Organic phosphates have less tendency to cause these problems. Recently, organophosphorus compounds have demonstrated good ability as flame retardants for epoxy resins, and also have been found to generate less toxic gas and smoke than halogen-containing compounds.^{13–21} Flameretardant epoxy resins can be obtained by chemically bonding flame-retardant groups onto epoxy resins, and the permanent attachment of a flame retardant frequently leads to high efficiency in flame retardancy.^{17–18,22–23}

In this study, a rigid phosphorus-containing reactive 2-(6-oxido-6-H-dibenzo[c,e][1,2] oxaphosphorin-6-yl)-1,4-benzenediol (ODOPB) is converted to a phosphorus-containing epoxy resin, 6-H-dibenz[c,e][1,2] oxaphosphorin-6-[2,5-bis-(oxiranylmethoxy)phenyl]-6-oxide (DOPO epoxy resin), which is expected to exhibit the required flame retardancy, less fumes, and higher thermal stability than the conventional flame-retardant epoxy resin systems containing tetrabromobisphenol A (TBBA).

EXPERIMENTAL

Reagents

ODOPB was prepared in our laboratory.²⁶ Epichlorohydrin (EPI) from Janssen Co. and potassium hydroxide from Showa Co. were used as received. All solvents were reagent grade or were purified by standard methods before use. The diglycidyl ether of bisphenol-A [Bis-A epoxy resin, epoxy equivalent weight (EEW) = 189] was obtained from Chang Chun Plastic Co. (Taiwan). 4,4'-Diaminodiphenylsulfone (DDS) and dicyandiamide (DICY) used as curing agents were from Aldrich and used as received. A phenol-formaldehyde novolac resin (Ph Nov) with an average hydroxyl functionality of 6 and a hydroxy equivalent weight of about 104 (Schenectady Chemical, HRJ-2210) was also used as a curing agent. The A-1 catalyst was (ethyl) triphenyl phosphonium acetate acetic complex; Ph3P was triphenylphosphine, which was used as curing accelerator.

Instrumental

Infrared spectra (IR) were obtained using a Nicolet 550 Fourier Transfer Infrared Spectrophotometer. Mass spectra were recorded by a VG 70-250s gas chromatography/mass spectroscopy. Differential scanning calorimetry (DSC) data were obtained in a nitrogen atmosphere at a 20°C min⁻¹ heating rate using a Perkin-Elmer DSC7 differential scanning calorimeter. Thermal gravimetric analysis (TGA) was employed with a Perkin-Elmer TGA7 at a heating rate of 20°C min⁻¹ in nitrogen or air atmosphere. Limiting oxygen index (LOI) values were measured on an ATLAS limiting oxygen index chamber . The percentage of O₂ in the O₂–N₂ mixture just sufficient to sustain the flame was taken as the LOI. EEW of DOPO epoxy resin was determined by the HClO₄/ potentiometric titration method.

Synthesis of DOPO Epoxy Resin

Into a 1-L reaction vessel equipped with temperature and pressure controls and indicators. means for the continuous or intermittent addition of aqueous sodium hydroxide, means for condensing and separating water from a codistillate mixture of water, solvent, and epichlorohydrin, and means for returning the solvent and epichlorohydrin to the reaction vessel was added 64.8 g (1 equivalent) of ODOPB, 185 g (5 equivalents) of epichlorohydrin, and 54 g of the methylether of propylene glycol (1-methoxy-2-hydroxypropane) as a solvent. After stirring at room temperature and atmospheric pressure to thoroughly mix the contents, the temperature was raised to 65°C and the pressure was reduced to 160 mm Hg absolute. To the resultant solution was continuously added 8 g, 2 equivalents of a 50% aqueous sodium hydroxide solution at a constant rate over a period of 1 h. During the addition of the sodium hydroxide, the water was removed by codistilling with epichlorohydrin and solvent. The distillate was condensed, thereby forming two distinct phases, an aqueous phase (top) and an organic epichlorohydrin-solvent phase (bottom). The organic phase was continuously returned to the reactor. After completion of the sodium hydroxide addition, the reaction mixture was maintained at a temperature of 65°C and a pressure of about 160 mm Hg absolute for an additional 30 min. A sample of the reaction mixture was washed to remove salt and subsequently distilled resulting in an epoxidized ODOPB resin (DOPO epoxy resin) having a hydrolyzable chloride content of 0.02% and an epoxide content of $\sim 23.5\%$, which corresponds to an epoxide equivalent weight of about $223 \sim 228$.

Curing Procedure of Epoxy Resins

The thermal and fire retardant properties of the phosphorus- and nonphosphorus-containing epoxy

| Epoxy Resin/ Curing Agent | Precure Temperature (°C) | Precure Time (min) | Curing Temperature (°C) | Curing Time (min) | Postcure Temperature (°C) | Postcure Time (min) |
|------------------------------|--------------------------------|--------------------------|-------------------------------|-------------------------|---------------------------------|---------------------------|
| Bis-A/Ph Nov | 150 | 60 | 175 | 120 | 200 | 180 |
| DOPO/Ph Nov | 150 | 60 | 175 | 120 | 190 | 180 |
| Bis-A/DDS | 150 | 60 | 175 | 120 | 200 | 180 |
| DOPO/DDS | 135 | 60 | 155 | 120 | 175 | 180 |
| Bis-A/DICY | 150 | 60 | 175 | 120 | 200 | 180 |
| DOPO/DICY | 130 | 60 | 145 | 120 | 165 | 180 |

Table I Curing Steps of Epoxy Resins

resin were evaluated by preparing six cured epoxy resins, i.e., DOPO epoxy resin cured with Bis-A/Ph Nov, DOPO/Ph Nov; Bis-A/DDS, DOPO/DDS, Bis-A/DICY, DOPO/DICY. 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. Curing steps were predetermined by DSC thermograms of respective epoxy/ curing agent compositions (Table I).

Preparation of DOPO Epoxy Resin Modified Encapsulants

To determine the amount of phosphorus needed to achieve flame retardancy, various amount of DOPO epoxy resin was added to Bis-A epoxy resin and cured with Ph Nov. The mixtures of epoxy resins consisted of Bis-A epoxy/DOPO epoxy (or Bis-A epoxy/ TBBA epoxy) in various weight ratios (87.5/12.5, 77.8/22.2, 71.4/28.6) were prepared. Ph₃P was used as a curing accelerator. Each epoxy mixture was mixed with Ph Nov and 0.2% Ph₃P in a mill at 25°C to give thermosettable epoxy resin powders. The resin powders were cured in a mold at 150°C and 50 kg/cm² for a period of 1 h and then at 185°C for 2 h, and further postcured at 210°C for 3 h to obtain cured specimens.

LOI and UL-94V Flame Retardant Test

The LOI is the minimum fraction of O_2 in a mixture of O_2 and N_2 that will just support flaming combustion. The LOI test was performed according to the testing procedure of ASTM D 2836 Oxygen Index Method with test specimen bar of 7–15 cm in length, 6.5 ± 0.5 mm in width, and 3.0 ± 0.5 mm in thickness. Ten sample bars suspended vertically were ignited by a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was

raised if the specimen extinguished before burning 3 min or 5 cm. The oxygen content was adjusted until the limiting concentration was determined.

The UL-94V test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with test specimen bars of 127 mm length, 12.7 mm width, and about maximum up to 12.7 mm thickness. The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars suspended vertically over surgical cotton were ignited by a Bunsen burner; two ignitions with 10 s burning time were applied to each sample bar. The samples of cured epoxy resins with various curing agents of Ph Nov, DDS, and DICY were subjected to the UL-94V test.

RESULTS AND DISCUSSION

Synthesis of DOPO Epoxy Resin

The synthesis of the phosphorus-containing epoxy resin (DOPO epoxy resin) was performed by reacting ODOPB with EPI (Scheme 1). The product was characterized by IR. The IR spectrum of DOPO epoxy resin is shown in Figure 1. The peak at 917 cm⁻¹ absorption indicates the oxirane ring and the peak at 1180–1120 cm⁻¹ indicates the P—O—Ph linkage. Other absorption peaks of DOPO epoxy resin are 1248 cm⁻¹ (—P—O) and 1400–1500 cm⁻¹ (—P—Ph). The EEW of DOPO epoxy resin was determined by the HClO₄/potentiometric titration method and found to be 229 (theoretical is 218).

Curing Reactivity

The curing behaviors of the mixtures of DOPO epoxy and various curing agents were studied by DSC. The relative reactivities of various curing agents toward DOPO epoxy resin area



Scheme 1 Synthesis of DOPO epoxy resin.

shown in (Fig. 2). For the epoxy resin used, the exothermic starting temperatures increased in the order of DICY < DDS < Ph Nov. A curing agent that exhibits a lower exothermic starting temperature under the same set of curing condition is more reactive toward the epoxy resin. Since the reactivity of the hydroxyl group toward the oxirane ring is lower than that of the amine group, Ph Nov showed lower reactivity than DDS and DICY.

Dynamic Viscoelastic Analyses of DOPO Epoxy Resins with Various Curing Agents

Dynamic viscoelastic analysis can give information on the microstructure of cured epoxy resins. The tan δ curves for the control network exhibit a major relaxation observed in most epoxy polymers.²⁵ The transition corresponds to the major T_g of the cured epoxy resin, above which significant chain motion takes place. Figure 3 showed the storage modulus G' and tan δ of DOPO epoxy and Bis-A epoxy cured with Ph Nov. The results (shown in Table II) indicated that the DOPO epoxy resin cured with Ph Nov, DDS, and DICY had higher T_g (181, 254, and 198°C) than that of Bis-A epoxy resin cured with Ph Nov, DDS, and DICY (123, 212, and 138°C). The result may be attributed to the



Figure 1 IR spectrum of DOPO epoxy.



Figure 2 DSC thermograms of DOPO epoxy resin cured with (A) Ph Nov, (B) DDS, and (C) DICY.

incorporation of a bulky rigid group that increases the rotational barrier.

Thermal Properties for Cured Epoxy Resins

TGA is the most favored technique for rapid evaluation in comparing and ranking the ther-

mal stability of various polymers. Themogravimetric analyses of both DOPO and Bis-A epoxy resins cured with various curing agents of Ph Nov, DDS, and DICY in nitrogen and air are shown in Table II. The results indicated that DOPO epoxy resin cured with Ph Nov, DDS,



Figure 3 Dynamic viscoelastic analysis of cured epoxy resins. (A) and (B) Bis-A/Ph Nov; (B) and (D) DOPO/Ph Nov.

| | | | Tem | peratu Lo | re of W | eight | Raj | pid Wei | ight Lo | ss Tem | р (<i>T_r</i> , с | °C) | Ch Yie (% | ar eld 6) |
|--------------|-----|---------------------------|-----|--------------|---------|-------|-----|---------|---------|--------|------------------------------|-------|-----------------|-----------------|
| | | | 1 | % | 1(|)% | Ste | ep I | Ste | p II | Step | o III | 700 |)°C |
| Epoxy Resin/ | | | | | | | | | | | | | | |
| Curing Agent | P% | $T_g \ (^{\rm o}{\rm C})$ | Air | N_2 | Air | N_2 | Air | N_2 | Air | N_2 | Air | N_2 | Air | N_2 |
| Bis-A/Ph Nov | 0.0 | 123 | 267 | 257 | 413 | 367 | 449 | 442 | 621 | | _ | _ | 2 | 19 |
| DOPO/Ph Nov | 4.8 | 181 | 183 | 207 | 373 | 363 | 377 | 376 | 544 | 521 | 745 | | 37 | 48 |
| Bis-A/DDS | 0.0 | 212 | 237 | 277 | 371 | 377 | 424 | 408 | 656 | _ | | | 0 | 11 |
| DOPO/DDS | 4.5 | 254 | 187 | 207 | 347 | 327 | 363 | 363 | 557 | 411 | 753 | | 32 | 40 |
| Bis-A/DICY | 0.0 | 138 | 243 | 243 | 367 | 357 | 398 | 395 | 443 | 429 | 595 | | 0 | 8 |
| DOPO/DICY | 7.2 | 198 | 167 | 159 | 321 | 313 | 212 | 344 | 344 | 491 | 472 | _ | 28 | 32 |

Table II Thermal Properties of Cured Epoxy Resins

and DICY have higher char yield than that of cured Bis-A epoxy resin.

TGA thermograms of cured Bis-A epoxy/Ph Nov and DOPO epoxy/Ph Nov in a nitrogen atmosphere are illustrated in Figure 4. Bis-A /Ph Nov exhibited 1% weight loss at 257°C and then a rapid weight loss at 442°C. On the other hand, DOPO epoxy resin showed its 1% weight loss at 207°C, and a 10% weight loss at around 367°C. DOPO epoxy exhibited a lower first step rapid weight loss temperature (at 376°C) than that of Bis-A epoxy resin (at 442°C). However, unlike the one- stage weight loss behavior of the Bis-A epoxy/Ph Nov system, the DOPO epoxy/Ph Nov showed a second-stage weight loss at around 521°C. This phenomenon indicates an important role in improving the flame retardancy of the resins. While the resin is burning, the phosphorus-containing groups first decompose at around 376°C, and then form a phosphorus-rich residue that prevents further decomposition of the epoxy resin by raising the second decomposition temperature to 521°C and results in a high char yield. The char yields at 700°C for the Bis-A epoxy/Ph Nov system and DOPO epoxy/Ph Nov system were 19 and 48%. TGA thermograms of DOPO and Bis-A epoxy resins cured with various curing agents are shown in Table II.



Figure 4 TGA thermograms of cured epoxy resins in N_2 : (A) Bis-A/Ph Nov, (B) DOPO/Ph Nov and derivative, (C) Bis-A/Ph Nov, and (D) DOPO/Ph Nov.

| Epoxy Resin/ Curing Agent P% | | Average Burning Time (s) | Visible Smoke | Drip | UL 94-V Classification | LOI | |
|---------------------------------|-----|-----------------------------|------------------|--------|---------------------------|-----|--|
| Bis-A/Ph Nov | 0.0 | 78 | Slight | No | V-2 | 26 | |
| DOPO/Ph Nov | 4.8 | 0 | No | No | V-0 | 34 | |
| Bis-A/DDS | 0.0 | 123 | Heavy | Heavy | V-2 | 22 | |
| DOPO/DDS | 4.5 | 0 | No | No | V-0 | 32 | |
| Bis-A/DICY | 0.0 | 158 | Heavy | Slight | V-2 | 21 | |
| DOPO/DICY | 7.2 | 0 | No | No | V-0 | 36 | |

Table III UL-94v Test Rating and LOI Values for Cured Epoxy Resins

LOI and UL-94V Test for Cured Epoxy Resins

The flame-retardant properties of cured epoxy resins were examined by measuring the LOI. To demonstrate the flame-retardant properties of DOPO epoxy resin, DOPO epoxy, and Bis-A epoxy were cured with (1) Ph Nov, (2) DDS, and (3) DICY for comparison. The LOI values are shown in Table III. Increased char formation can limit the production of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, as well as decrease the thermal conductivity of the surface of a burning material.²⁴ DOPO epoxy cured with Ph Nov, DDS, and DICY had LOI values of 34, 32, and 36 that were higher than those of Bis-A epoxy cured with Ph Nov, DDS, and DICY (LOI = 26, 22, 21). The UL-94Vtest determines the upward-burning characteristics of a solid. Five sample bars of each cured epoxy resins suspended vertically over surgical cotton were ignited by a Bunsen burner; two ignitions of 10 s each were applied to the sample. The results of UL-94V and LOI test are listed in Table III. DOPO epoxy resin, besides being superior to phosphorus-free epoxy resin in flame retardancy, also generated much less visible smoke than phosphorus-free epoxy resin.

Dynamic Viscoelastic and Thermal Properties of Flame-Retardant Epoxy Encapsulants

Owing to excellent heat, solvent and chemicalresistance, good adhesion and inexpensiveness, epoxy resin has been widely employed in the encapsulation of microelectronic devices. In this study, DOPO epoxy and TBBA epoxy (tetrabromobisphenol A epoxy resin) were compared for their flame retardancy in the encapsulation formulation. Bis-A epoxy was blended with various amount of DOPO epoxy and then cured with Ph Nov to give the cured products with phosphorus content of 0, 0.58, 1.03, and 1.45% (Bis-A/Ph Nov, DOPO-A, DOPO-B, DOPO-C). In the same manner, Bis-A epoxy was blended with TBBA epoxy and then cured with Ph Nov to give the cured products with bromine content of 4.01, 7.24, and 9.91% (TBBA-A, TBBA-B, TBBA-C). Thermal properties of cured epoxy resins are shown in Table IV. It should be noted that T_{g} of cured epoxy resins increased with the increase in phosphorus

Table IV Thermal Properties of Cured Epoxy Resin with Various P or Br Contents

| | | | Temperature of Weight Loss | | | $\begin{array}{c} \text{Rapid Weight Loss Temp} \\ (T_r, \ ^{\circ}\text{C}) \end{array}$ | | | Char Yield (%) | | | | | |
|--------------|-------------|-------------------------|-------------------------------|----------------|-----|---|-----|----------------|-------------------|----------------|-----|-------|-----|----------------|
| | | | 1 | % | 10 |)% | Ste | ep I | Ste | p II | 600 |)°C | 700 | 0°C |
| Sample | P% | $T_g~(^{\rm o}{\rm C})$ | Air | N_2 | Air | ${ m N}_2$ | Air | N_2 | Air | N_2 | Air | N_2 | Air | N_2 |
| Bis-A/Ph Nov | 0.0 | 122 | 267 | 257 | 413 | 367 | 449 | 442 | | | 21 | 25 | 0 | 19 |
| DOPO-A | 0.58 | 133 | 267 | 277 | 403 | 403 | 424 | 428 | | 603 | 31 | 36 | 7 | 31 |
| DOPO-B | 1.03 | 135 | 253 | 273 | 393 | 397 | 409 | 419 | _ | 599 | 33 | 38 | 11 | 34 |
| DOPO-C | 1.45 Br% | 138 | 247 | 269 | 383 | 387 | 399 | 414 | 548 | 587 | 39 | 43 | 21 | 36 |
| TBBA-A | 4.01 | 130 | 273 | 247 | 387 | 377 | 403 | 411 | 625 | _ | 27 | 27 | 0 | 23 |
| TBBA-B | 7.24 | 127 | 277 | 261 | 387 | 357 | 406 | 393 | 641 | _ | 29 | 30 | 2 | 26 |
| TBBA-C | 9.91 | 124 | 297 | 267 | 367 | 383 | 400 | 388 | 647 | — | 31 | 34 | 4 | 29 |



Figure 5 TGA thermograms of cured epoxy resins in N_2 : (A) Bis-A/Ph Nov, (B) TBBA-C, and (C) DOPO-C.

content while T_g decreased with the increase in bromine content. The result may be attributed to the bulky rigid phosphorus-containing group.

TGA were also performed to compare the thermal stabilities of the cured epoxy resins; the results are also shown in Table IV. DOPO-A (0.58% P) exhibited higher char yield (31% in N₂ at 700°C) and higher thermal stability than any TBBA containing resins studied. The result indicates that 0.58% P provided a char yield equivalent to that of 9.91% Br. Figure 5 shows the thermogravimetric traces of cured resins of Bis-A , DOPO-C, and TBBA-C in N₂. The Bis-A resin exhibited 1% weight loss at 257°C and 10% weight loss at 367°C, and then a rapid weight loss at around 442°C in N₂. TBBA-C exhibited 1% weight loss at 247°C and 10%

weight loss at 267°C, and then a rapid weight loss at around 388°C. On the other hand, the phosphorus-containing DOPO-C showed 1% weight loss at 269°C and 10% weight loss at 387°C. If the thermal stability of cured epoxy resins were compared by 1% and 10% weight loss, the following order may be given: DOPO-C > TBBA-C > Bis-A. The rapid weight loss temperature (T_r) of Bis-A epoxy resin occurred at 442°C, slightly higher than that of DOPO-C; however, it is unlike the one-stage rapid weight loss of the Bis-A epoxy resin. DOPO-C exhibited a higher second-stage rapid weight loss at 587°C. This phenomenon played an important role in providing the flame retardancy to the cured epoxy resin, and was confirmed by the higher char yields at 600°C (DOPO-C 43%; TBBA-C 34%;

| Sample | Flame-Retardant Element | Average Burning Time (s) | Visible Smoke | Drip | UL 94-V Classification | LOI | |
|--------------|----------------------------|-----------------------------|------------------|------|---------------------------|-----|--|
| | P% | | | | | | |
| Bis-A/Ph Nov | 0.0 | 78 | Slight | No | V-2 | 26 | |
| DOPO-A | 0.58 | 32 | Very slight | No | V-2 | 28 | |
| DOPO-B | 1.03 | 6 | No | No | V-0 | 30 | |
| DOPO-C | 1.45 | 0 | No | No | V-0 | 34 | |
| | $\mathrm{Br}\%$ | | | | | | |
| TBBA-A | 4.01 | 38 | Heavy | No | V-2 | 27 | |
| TBBA-B | 7.24 | 4 | Slight | No | V-0 | 30 | |
| TBBA-C | 9.91 | 0 | No | No | V-0 | 35 | |

Table V UL-94v Test Rating and LOI Value of Cured Epoxy Resins with Various P and Br Content

LOI and UL-94V Test for Flame-Retardant Epoxy Resin

Cured epoxy resin with high phosphorus content is expected to have a high char residue on pyrolysis. The char residue on pyrolysis is reported to be linearly proportional to the oxygen index for halogen-free polymers.²⁷ The flame-retardant properties of cured epoxy resins with various phosphorus or bromine contents were examined by measuring their oxygen index (LOI). It is clear from the results of Table V that the higher the phosphorus content the higher the LOI value, which agrees well with previous reports.^{28,29}

For the UL-94 test, five specimens of each cured epoxy resin were prepared and the test results are also shown in Table V. The flame retardancy of cured epoxy resins increases with phosphorus or bromine content in the cured products. Besides phosphorus being much more effective than bromine as a flame retardant (1.03% P is almost equivalent to 7.24% bromine by comparing DOPO-B with TBBA-B), it also generates much less visible smoke than the bromine-containing resin.

CONCLUSION

The phosphorus-containing DOPO epoxy resin was successfully synthesized. DOPO epoxy resin cured with Ph Nov, DDS, or DICY yields products with higher T_g , thermal stability, and better flame retardancy than those of Bis-A epoxy resin. DOPO epoxy resin may be suitable as a reactive flame retardant by mixing with Bis-A epoxy resin for encapsulation applications. DOPO epoxy resin exhibits better flame retardancy and thermal stability than that of TBBA, but also generated much less visible smoke during combustion.

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