

# Synthesis and properties of epoxy resins containing 2-(6-oxid-6*H*-dibenz(c,e)(1,2) oxaphosphorin-6-yl) 1,4-benzenediol (II)

C.-S. Wang<sup>a,\*</sup>, M.-C. Lee<sup>b</sup>

<sup>a</sup>Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan

<sup>b</sup>Department of Electronic Material, Far East College, 49 Chung Hwa Road, Hsin-shin Town, Tainan Prefecture, Taiwan

Received 4 March 1999; received in revised form 2 June 1999; accepted 18 June 1999

## Abstract

Advanced epoxy resins containing naphthalene and flame retardant moiety [tetrabromobisphenol-A (TBBA) or cyclicphosphineoxidediol] in the backbone were synthesized.  $T_g$ s of epoxy resins containing naphthalene structure are higher than that of the diglycidyl ether of bisphenol-A (DGEBA), and a  $T_g$  of 237°C was obtained when the tetrafunctional naphthalene-containing epoxy resin was used. In air, TGA of the phosphorus-containing thermosets displayed 11.5–22.2 wt% char yield at 800°C, while the TBBA-containing network was oxidatively decomposed to nearly zero residue. The efficiency of phosphorus as a flame retardant was found to be much higher than that of bromine. The combination of tetrafunctional naphthalene-containing epoxy resin with cyclic phosphine oxide diol has resulted in high  $T_g$  (239°C) and high limited oxygen index (LOI) 35. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Epoxy; Flame retardancy; Naphthalene

## 1. Introduction

Epoxy resins are widely used in laminating, adhesive, coating and casting applications. However, the thermal and flame resistance of epoxy polymers are inadequate for some applications.

Thermosetting epoxy resins containing bromine atom are particularly useful in circuit boards, electrical laminate, potting, and encapsulation applications in which flame retardant properties are desired [1]. Heat broken bromine atoms proved to serve as free-radical scavengers and convert the radicals of the polymer formed into bromide radicals of lower activity [2]. However, environmental problems encountered with this system are concerned with the generation of toxic and corrosive fumes during combustion [3,4], these drawbacks restrict the range of its applications. Currently, the incorporation of organophosphorus moiety into the epoxy thermosetting structure have been found to generate less toxic gas and smoke than halogen-containing compound [5,6].

During mounting of IC packages on a printed circuit board, both the semiconductor and circuit board have to be exposed to high temperature of 215–260°C during reflow

soldering [7], the introduction of a naphthalene structure into the epoxy skeleton could effectively increase the glass transition temperature and thermal stability [8]. A goal of the present study was to incorporate a phosphorus containing bisphenol into naphthalene epoxy resins to obtain a non-halogen flame retardant epoxy resins with high thermal stability for electronic application. The effect of epoxy functionality upon the flame retardancy and glass transition temperature will be discussed.

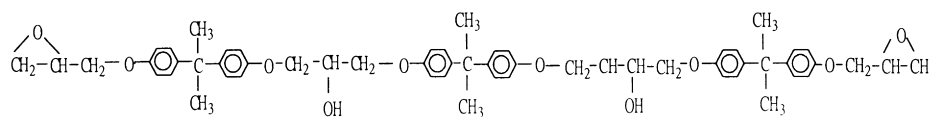
## 2. Experimental

### 2.1. Materials

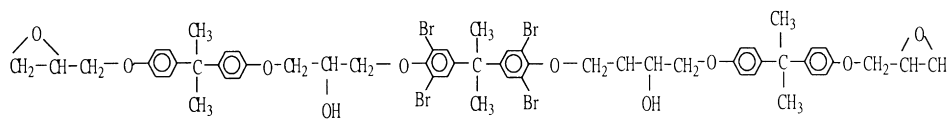
2,7-Dihydroxynaphthalene, bisphenol-A (BPA), and *p*-benzoquinone (BQ) were purchased (from Acros). Epichlorohydrin (from Janssen), 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO, from TCI), tetrabromobisphenol-A (TBBA, from Aldrich) were used as received. Triphenyl phosphine (Ph<sub>3</sub>P) was used as an advancement catalyst. 4,4'-diaminodiphenylsulfone (DDS) was purchased from Jassen and used as a curing agent for epoxy resins. All solvents were obtained from various commercial sources and used without further purification unless otherwise noted. Diglycidyl ether of bisphenol-A

\*Corresponding author. Tel.: +886-6-2757575, ext. 626; fax: +886-6-2344496.

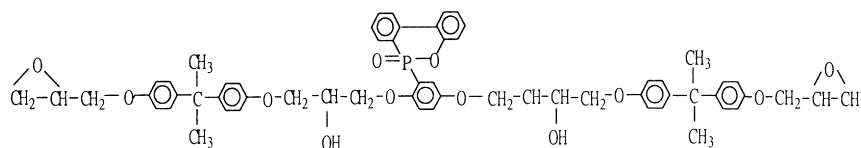
E-mail address: cswang@mail.ncku.edu.tw (C.-S. Wang).



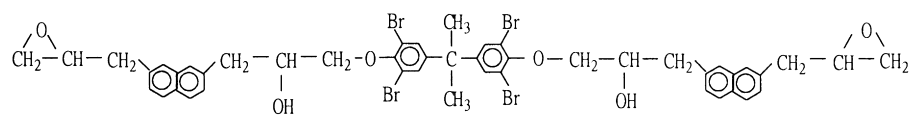
DG-B



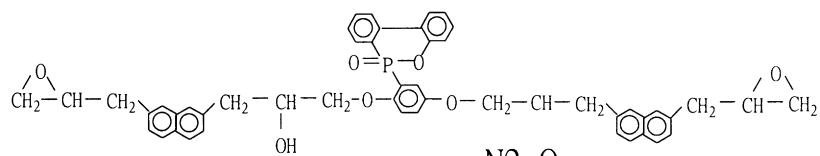
DG-T



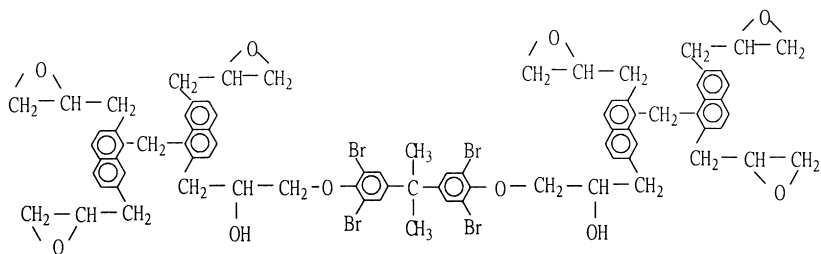
DG-O



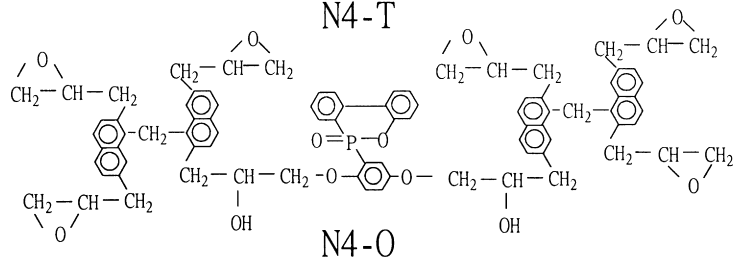
N2-T



N2-O



N4-T



N4-O

Scheme 1.

Table 1  
Advancement composition, reaction condition and EEWs (all compositions are in grams)

	DG-B	DG-T	DG-O	N2-T	N2-O	N4-T	N4-O
<i>Epoxy</i>							
DGEBA	20	20	20				
N2				20	20		
N4						20	20
<i>Diol</i>							
Bisphenol-A	5.520						
TBBA		13.150		16.704		7.358	
ODOPB			7.834		9.951		4.383
<i>Catalyst</i>							
Ph <sub>3</sub> P (500 ppm)	0.128	0.166	0.139	0.184	0.150	0.137	0.122
Reaction (temp., °C)	160	160	160	160	160	140	140
Condition (time, h)	1	1	1	1	1	1	1
EEW	469	591	548	613	508	359	319

(DGEBA, EEW 188) was generously supplied by Nan-Ya Co., Taiwan.

## 2.2. Synthesis

### 2.2.1. Preparation of 2,7-diglycidyloxy-naphthalene (N2)

To a 500 ml four-neck round bottom flask equipped with a stirrer, heating mantle, thermocouple, temperature controller, condenser, nitrogen inlet and addition funnel, were charged 0.1 mol of 2,7-dihydroxynaphthalene, 0.9 mol of epichlorohydrin, 30 g of isopropyl alcohol and 4 ml water. The reaction mixture was heated to 65°C with stirring while 20 wt% aqueous NaOH 40 g (0.2 mol) was added dropwise over a period of 45 min. After the completion of aqueous sodium hydroxide addition, the reaction mixture was maintained at 65°C for an additional 15 min and then the bottom brine layer was removed by siphoning. The organic phase was further reacted with 20 g of 20 wt% aqueous NaOH (0.1 mol) at 65°C for 30 min and then the phases were separated. The organic phase was washed several times with deionized water to remove the residual salt. The organic phase after water washes was placed on a rotary evaporator under a full vacuum at 150°C to remove the excess epichlorohydrin and solvent completely. The epoxy equivalent weight (EEW) of the dark brown colored semi-solid product was 166 (theoretical value 136).

### 2.2.2. Preparation of 1,1'-bis(2,7-diglycidyloxy-1-naphthyl) methane (N4)

N4 was synthesized by a procedure analogous to that reported in Ref. [9], the EEW of the dark brown colored solid product was 168 (theoretical value 139).

### 2.2.3. Preparation of 2-(6-oxid-6H-dibenz(c,e) (1,2) oxaphosphorin 6-yl) 1,4-benzenediol (ODOPB)

Into a 500 ml three-neck round bottom flask equipped with a stirrer, heating mantle, thermocouple, temperature controller, nitrogen inlet and reflux assembly, were charged 0.33 mol of DOPO and 300 ml xylene. The temperature of the solution was raised to reflux (ca. 140°C) in order to distill the residual water and returning xylene back to the reaction flask. When the amount of water was completely removed, then 0.3 mol powdered *p*-benzoquinone (BQ) was added incrementally. The reaction mixture was maintained at reflux for an additional 1 h after the completion of BQ addition. The precipitates was filtered and further recrystallized twice from DMAC, and finally dried in a vacuum oven at 190°C to obtain ivory colored ODOPB (60% yield, m.p. 250°C,  $\Delta H_m$  98.10 J/g), MS *m/e* 324 (100, M<sup>+</sup>). IR spectrum 920, 1168 cm<sup>-1</sup> (*p*-*o*-ph), 1190 cm<sup>-1</sup> (*p* = *o*), 1582 cm<sup>-1</sup> (*p*-ph), 3173 cm<sup>-1</sup> (ph-OH).

<sup>1</sup>H NMR (DMSO, d6)  $\delta$ 6.62 (t, 1H),  $\delta$ 6.89 (dd, 1H),  $\delta$ 7.14 – 7.77 (m, 7H),  $\delta$ 8.20 – 8.28 (dd, 2H). <sup>31</sup>P NMR

Table 2  
Experimental curing formulations and physical properties of cured epoxy resins

Advanced epoxies designation	Resin (g/eq)	Curing agent (g/eq)	T <sub>g</sub> <sup>a</sup> (°C)	Density
DG-B/DDS	50/0.107	6.618/0.107	136	1.1673
DG-T/DDS	50/0.085	5.252/0.085	146	1.4501
DG-O/DDS	50/0.091	5.664/0.091	164	1.2586
N2-T/DDS	50/0.082	5.063/0.082	155	1.6042
N2-O/DDS	50/0.098	6.110/0.098	167	1.2892
N4-T/DDS	50/0.139	8.464/0.139	237	1.4501
N4-O/DDS	50/0.157	9.730/0.157	239	1.2628

<sup>a</sup> Peak of tan  $\delta$  curve in dynamic viscoelastic analyses.

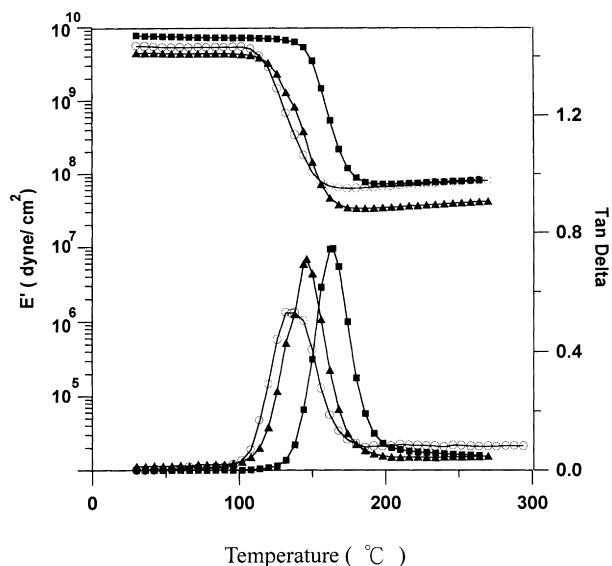


Fig. 1. Dynamic viscoelastic analyses of cured epoxy resins (○) DG-B/DDS (▲) DG-T/DDS (■) DG-O/DDS, curing agent is 4-4'-diaminodiphenyl sulfone (DDS).

(DMSO, d6) a single peak at  $\delta 21.5$ . The reaction was shown previously [11].

#### 2.2.4. Advancement of epoxy resins with various diols

The advancement procedure was as follows: into a 100 ml round bottom flask equipped with a stirrer, heating mantle, thermocouple, temperature controller and vacuum outlet, was initially charged with an epoxy resin (DGEBA, N2 or N4). The epoxy resin was heated under full vacuum at 100°C to drive off the residual water in the epoxy resin for approximately 1 h and then the diol (BPA, TBBA or ODOPB) was added. The reaction mixture was heated to ~140°C to achieve a complete solution, and then 500 ppm  $\text{Ph}_3\text{P}$  was added as a catalyst. The reaction mixture was maintained at ~160°C for 1 h to complete the reaction. The advanced epoxy resins with designated abbreviations are described in Scheme 1, while their compositions, reaction conditions and EEWs of final products are shown in Table 1.

Curing procedure of epoxy resins. Each advanced epoxy resin was mixed well with a stoichiometric amount of curing agent, DDS, at moderate temperature to give a precured epoxy powder, the curing compositions are shown in Table 2. The epoxy powders were poured into aluminum trays and cured in mold under atmospheric pressure at 80°C for 1 h, 180°C for 1 h, and then postcured at 200°C for 2 h to obtain specimen for dynamic viscoelastic analysis and flame retardancy test.

#### 2.3. Measurement and testing

$^1\text{H}$  NMR of the synthesized ODOPB was obtained on a Bruker Analytical WP-100, samples were analyzed in deuterated DMSO using tetramethylsilane (TMS) as an

internal standard. Mass spectrometric analyses were performed on a VG 70-250S GC/MS spectrometer with a solid inlet. Infrared spectra were recorded with a Nicolet 520 FTIR spectrometer operated with a dry air purge. Signal of 32 scans at a resolution of  $4\text{ cm}^{-1}$  were averaged before Fourier transformation. The EEWs of epoxy resins were determined by the  $\text{HClO}_4$ /potentiometric titration method. Differential scanning calorimeter (Perkin-Elmer DSC-7) measurements were made at a scan rate of  $10^\circ\text{C}/\text{min}$  with 4–6 mg samples under nitrogen atmosphere, the melting endotherm can be traced from the change of the specific heat in the heat flow curves, and  $\Delta H_m$  was calculated. Dynamic viscoelastic properties were performed on a Perkin-Elmer 7 Series Thermal Analysis System with DMA mode between 30 and  $280^\circ\text{C}$ , with a heating rate of  $10^\circ\text{C}/\text{min}$  at a frequency of 1 Hz. The temperature/time scan in a three-point bending mode was chosen. The dimension of the specimen was  $20 \times 12.7 \times 1.5\text{ mm}^3$ , the distance of the support span was 10 mm. The mechanical loss factor ( $\tan \delta$ ) was determined. The thermal stability was obtained using a Perkin-Elmer Thermogravimetric analyzer (TGA) with a heating rate  $20^\circ\text{C}/\text{min}$  in nitrogen or air. The density of the cured epoxy resin specimen was determined in a carbon tetrachloride–toluene density gradient column.

Flame retardant properties were measured by either “oxygen index” (ASTM D2863-77) method or by the “UL-94V” (FMVSS 302/ZSO 3975) method. Oxygen index was obtained in the ATLAS instrument, it is defined as the minimum volumetric fraction of oxygen in an  $\text{O}_2\text{-N}_2$  blend required to support the flame under the specific conditions, about 3 min prior to extinguishing. The linear velocity of the gas was fixed at  $4 \pm 1\text{ cm/s}$ , and the samples were 10 cm long, 6 mm wide and 2 mm thick [10]. The UL-94V flame retardancy test was determined according to the reported article [11].

### 3. Results and discussion

#### 3.1. Glass transition temperature ( $T_g$ )

Dynamic storage modulus and damping ( $\tan \delta$ ) for each of the thermoset were measured from the dynamic viscoelastic analyses.  $T_g$  were determined from the peak of the  $\tan \delta$  curves, and the results are shown in Table 2. Effects of diol, epoxy structures and epoxy functionality on  $T_g$  are discussed as follows.

##### 3.1.1. Effect of diol structure

DGEBA was advanced with BPA, TBBA and ODOPB, i.e. the incorporation of diol into the “middle position” of DGEBA backbone.  $T_g$ s of advanced epoxy resins were in the order of  $\text{DG-B/DDS} < \text{DG-T/DDS} < \text{DG-O/DDS}$  (from  $\tan \delta$  of Fig. 1) which is in agreement with the increasing difficulty in chain rotation [12]. The same

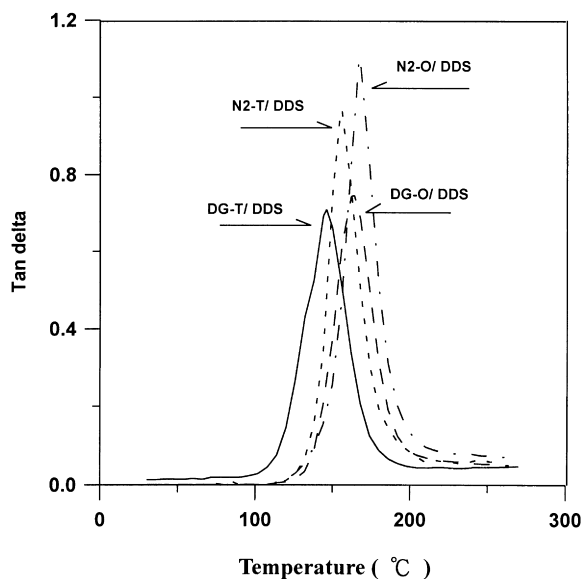


Fig. 2. Tan  $\delta$  curves of difunctional oxirane-terminated thermosets.

tendency was observed for 2-functional (N2) and 4-functional (N4) naphthalene series.

### 3.1.2. Effect of epoxy structure

When difunctional naphthalene-containing epoxy resin (N2) was compared with difunctional DGEBA as a terminal group in advanced epoxy resin, the tan  $\delta$  curves are illustrated in Fig. 2, and the sequences of  $T_g$  N2-T/DDS (155°C) > DG-T/DDS (146°C) and N2-O/DDS (167°C) > DG-O/DDS (164°C). Introduction of rigid naphthalene structure into the epoxy backbone increased the difficulty of chain rotation, hence the  $T_g$  was higher

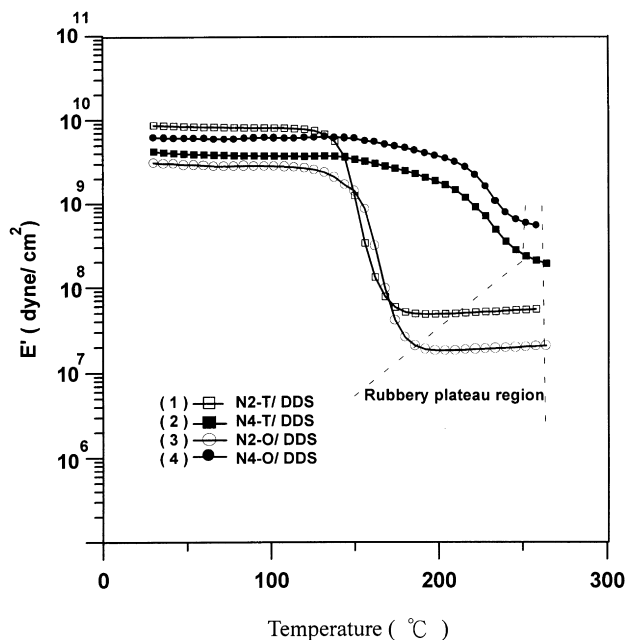


Fig. 3. Rubbery plateau region of crosslinked epoxy networks.

[8]. The  $T_g$  of N2-O/DDS was slightly higher (3°C) than that of DG-O/DDS, indicating that ODOPB played an important role in increasing  $T_g$ .

### 3.1.3. Effect of epoxy functionality

The degree of crosslinking affects the glass transition since the creation of network junctions can alter the chain mobility. In naphthalene-containing epoxy systems, when the same diol was used, the storage modulus ( $E'$ ) beyond the glass transition (i.e. rubbery plateau region) increased with the increase in epoxy functionality [13] (Fig. 3). As indicated in Fig. 3, the storage modulus  $E'$  of N4-T/DDS was greater than that of N2-T/DDS and N4-O/DDS was also greater than that of N2-O/DDS.  $T_g$  increased in the order of N2-T/DDS < N2-O/DDS  $\ll$  N4-T/DDS  $\approx$  N4-O/DDS (Fig. 4). The difference in  $T_g$  for N4-T/DDS and N4-O/DDS is insignificant, indicating crosslinking density played a predominant role in raising  $T_g$  in the multi-functional epoxy resin systems.

## 3.2. Thermal stability

TGA is a convenient technique for rapid evaluation in comparing the thermal stability of various polymers. The thermal and thermo-oxidative stability of cured advanced epoxy resins were evaluated by TGA in nitrogen and air.

### 3.2.1. Effect of diol structure

Fig. 5 showed the TGA thermograms of three different diol containing advanced cured epoxy resins.  $T_{5\%}$  (5% weight loss) of DG-T/DDS was lowest, which began at 374°C and then gave an abrupt drop, maximum decomposition temperature (385°C) was close to  $T_{5\%}$ , it was due to the thermal decomposition character of bromine-containing TBBA. DG-T/DDS had the lowest  $T_{5\%}$  (374°C) indicating the bromine containing structure had exceptionally low thermal stability.

TGA measurements made in air reveal more real information relevant to the behavior of combustion. The presence of oxygen results in a complicated decomposition mechanism of the resins [14]. Comparing  $T_{5\%}$  and char yield of DG-B/DDS with those of DG-O/DDS in different atmosphere (Table 3), the decomposition temperature of DG-B/DDS in air was the same as that of DG-B/DDS in nitrogen while the pyrolysis reaction of DG-O/DDS was activated by the existence of oxygen.

It is noteworthy that the residual weights for all the epoxy resins were almost constant in nitrogen at temperatures up to 800°C, while in air, the residual weights decreased rapidly at temperatures higher than 580°C (Fig. 6) to near zero for BPA and TBBA systems (Figs. 6 and 7), even with naphthalene structure, i.e. N2-T/DDS, N4-T/DDS. One striking difference is that all the ODOPB based epoxy thermosets yielded 11.5–22.2% char even at 800°C in air. It is inferred that the broken bromine atoms were simultaneously blown away by air flow in TGA heating chamber, while the

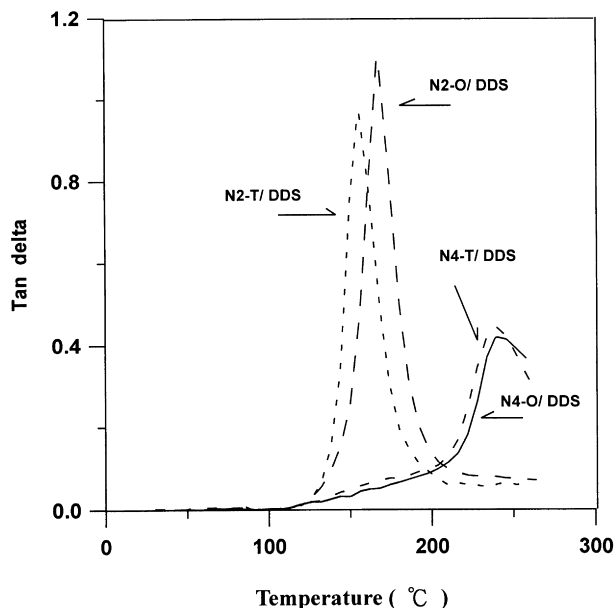


Fig. 4.  $\tan \delta$  curves of multifunctional naphthalene-containing epoxy resins.

phosphorus atoms turned into a char layer covering the surface of the polymer [15]. It is likely that ODOPB, which was incorporated into epoxy resin could be transformed into phosphoric acid or pyrophosphoric acid before the resin was degraded. From the dynamic TGA results, the ODOPB containing epoxy thermosets could be considered to be flame resistant materials.

### 3.2.2. Effect of epoxy structure

Now, the comparative objects were locked on the cured epoxy resins of DGEBA and N2 (both two functional epoxies). The lower  $T_{\max}$  values for N2-T/DDS and N2-O/

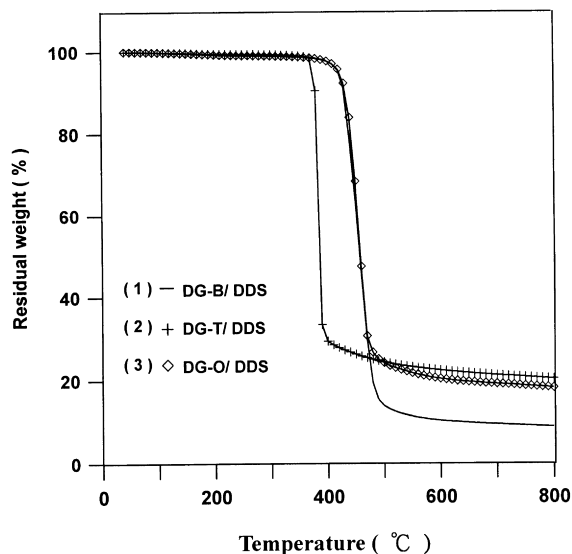


Fig. 5. TGA thermograms of DGEBA-terminated epoxy resins in  $N_2$ .

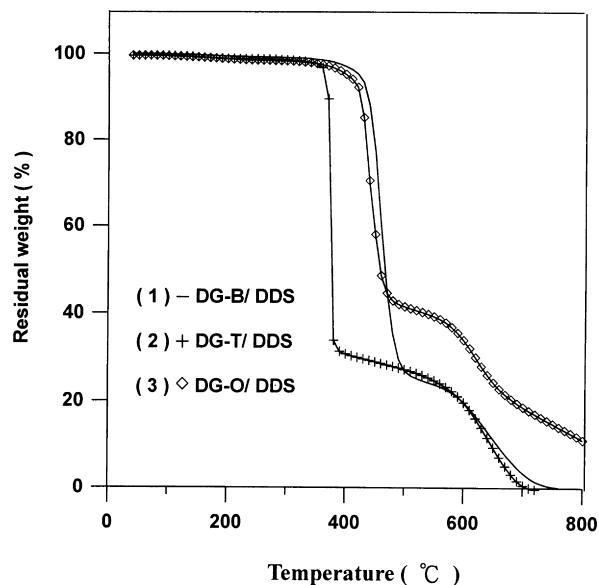


Fig. 6. TGA thermograms of DGEBA-terminated epoxy resins in air.

DDS than those of DG-T/DDS and DG-O/DDS were due to higher bromine or phosphorus content of the formers (Tables 3 and 4). The higher char yields for N2 systems than those for DGEBA systems with the same diol moiety were the contribution of naphthalene structure. However, in air, phosphate played an important role upon raising the amount of char yield.

### 3.2.3. Effect of epoxy functionality

It has been reported that the thermal decomposition temperatures of epoxy resins were affected by the degree of crosslinking in the same cured system [16]. As shown in Fig. 8, the  $T_{5\%}$  of N4-T/DDS exceeded that of N2-T/DDS, but N4-O/DDS fell behind N2-O/DDS, this may be attributed to the incomplete cure of N4-O/DDS at the same post-cured temperature. The higher char yield for N4 system was the combined contribution of crosslinking effect and naphthalene structure (refer to the composition of Table 1).

### 3.3. Flame retardancy

The flame-retardant properties of these epoxy resins were further examined by measuring the limiting oxygen index (LOI) and UL-94V classification test. The LOI represents a universal criterion, which is found to be reliable and reproducible for most materials, including foams and coatings [10]. A material is considered "flammable" when the oxygen index value is less than 26 [17], while it is considered "self-extinguishing" when it is above 26 [18]. Some smokes were observed for TBBA containing cured epoxy resins in the combustion chamber of LOI tester. This thick and heavy bromine-containing smoke can effectively interfere with the diffusion of oxygen into the combustible materials. As shown in Table 4, the LOI values increased with the increase in bromine content (from 32 to 39 when

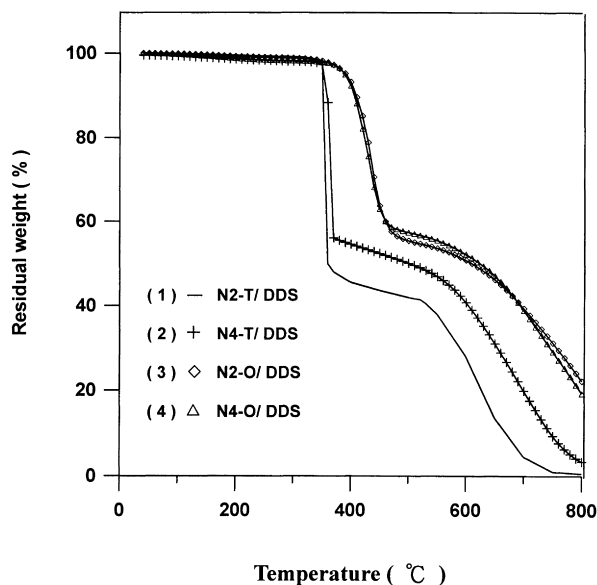


Fig. 7. TGA thermograms of multifunctional naphthalene-containing epoxy resins in air.

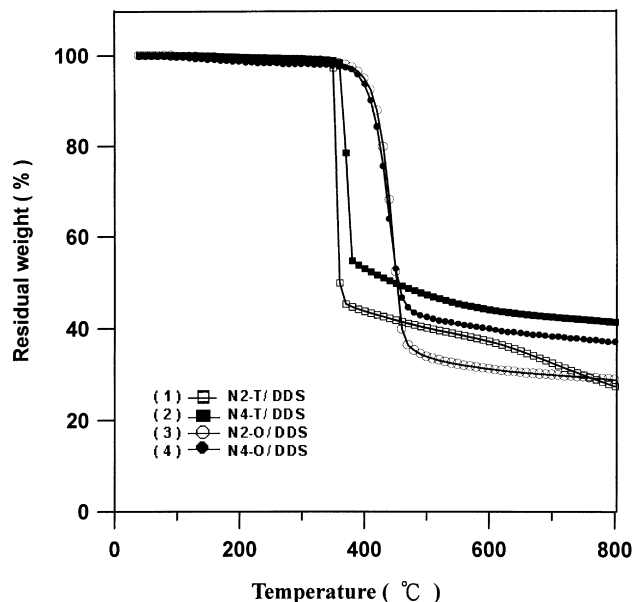


Fig. 8. TGA thermograms of multifunctional naphthalene-containing epoxy resins in  $N_2$ .

bromine content was increased from 13.4 to 22.7). Phosphorus was found to be much more effective than bromine in attaining flame retardant property (2% phosphorus seemed to be as effective as 20% bromine in Table 4). Besides the effect of flame-retarding elements, the oxygen index (OI) of a polymer material may be affected by the

degree of crosslinking in its polymer matrix [16]. A flame resistant grade can be achieved with as low as 1.4 wt% in phosphorus and 13.4 wt% in bromine for highly crosslinked N4 series.

UL-94V test determines the upward-burning characteristics of a solid and the results of UL-94V classification

Table 3  
Thermal stability of cured epoxy resins by thermogravimetric analyses

Advanced epoxies designation	Nitrogen			Air		
	$T_{5\%}$	$T_{max}$	Char yield (800°C)	$T_{5\%}$	$T_{max}$	Char yield (800°C)
DG-B/DDS	421	457	8.7	421	457	0
DG-T/DDS	374	385	20.2	363	376	0.3
DG-O/DDS	422	460	18.2	406	437	11.5
N2-T/DDS	351	354	27.5	348	358	1.0
N2-O/DDS	399	449	28.9	391	437	22.2
N4-T/DDS	362	370	41.4	353	362	3.7
N4-O/DDS	395	445	37.0	391	437	19.3

Table 4  
Flame retardancy of the advanced epoxy resins

Advanced epoxies designation	Bromine or phosphorus (wt%)	Oxygen index (OI)	Fume	UL-94V Classification
DG-B/DDS	0.0	21	— <sup>a</sup>	v-2
DG-T/DDS	20.0	35	— <sup>a</sup>	v-0
DG-O/DDS	2.4	32	— <sup>b</sup>	v-0
N2-T/DDS	22.7	39	— <sup>a</sup>	v-0
N2-O/DDS	2.6	33	— <sup>b</sup>	v-0
N4-T/DDS	13.4	32	— <sup>b</sup>	v-0
N4-O/DDS	1.4	35	— <sup>b</sup>	v-0

<sup>a</sup> —, Scarcely.

<sup>b</sup> —, No.

are also shown in Table 4. Phosphorus-containing epoxy resins generated less smoke than bromine-containing thermosets as expected.

#### 4. Conclusions

A series of advanced epoxy resins were synthesized by using various diols and epoxy resins. Thermogravimetric analyses revealed that, either in nitrogen or air atmosphere, the advanced resins made from phosphorylated diol were thermally more stable than the advanced resins made from TBBA diol owing to the rigid structure of ODOPB and pendant P group. The resultant phosphorus containing epoxy resin exhibited better flame retardance than the regular bromine containing flame retardant epoxy resin. UL 94-VO (non-combustible) rating could be achieved with a phosphorus content as low as 1.4% (comparable to a bromine content of 13.4%) in the cured N4 resin.

#### References

- [1] Wang CS, Berman JR, Walker LL, Mendoza A. *J Appl Polym Sci* 1991;43:1315.
- [2] Kuryla WC, Papa A. *Flame retardance of materials, 1*. New York: Marcel Dekker, 1973.
- [3] Derouet D, Morvan F, Bross JC. *J Appl Polym Sci* 1996;62:1885.
- [4] Camino G, Costa L, Martinasso G. *Polym Deg Stab* 1989;23:359.
- [5] Annakurthy KS, Kishore K. *Polymer* 1988;29:752.
- [6] Bank M, Ebdon JR, Johnson M. *Polymer* 1994;35:3470.
- [7] Asai S, Saruta U, Tobita M. *J Appl Polym Sci* 1994;51:1945.
- [8] Wang CS, Lee MC. *J Appl Polym Sci* 1998;70:1907.
- [9] Wang CS, Lee MC. *Polym Bull* 1998;40:623.
- [10] Arie R, Arie C. *J Appl Polym Sci* 1979;23:797.
- [11] Wang CS, Shieh JY. *Polymer* 1998;39:5819.
- [12] Boyer RF. *Rubber Chem Technol* 1963;36:1303.
- [13] Sperling LH. *Introduction to physical polymer science*, New York: Wiley, 1993.
- [14] Liu YL, Hsiue GH, Lee RH, Chiu YS. *J Appl Polym Sci* 1997;63:895.
- [15] Li J, Chen S. *J Appl Polym Sci* 1990;40:417.
- [16] Yang CP, Lee TM. *J Polym Sci, Part A: Polym Chem* 1990;28:887.
- [17] Van Krevelen DW. *Polym J* 1975;16:615.
- [18] Gungor G, Sukro O. *Polym-Plast Technol Engng* 1994;33(3):245.