Novel flame retardant epoxy resins

I: Synthesis, characterization, and properties of aryl phosphinate epoxy ether cured with diamine

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Summary

A novel aryl phosphinate epoxy ether, 10-(2',5'-bis(glycidyloxy)phenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DHQEP), was synthesized. The structures of the obtained compounds were confirmed by mass, FTIR, ^{1}H, ^{13}C, ^{31}P-NMR spectroscopies, elemental analysis, and X-ray single crystal analysis. In addition, compositions of DHQEP with common curing agents, e.g., 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenyl sulfone (DDS), and dicyanodiamide (DICY), were studied to compare their thermal and flame resistance with that of commercial epoxy resins. The aryl phosphinate epoxy-resin composites exhibited excellent thermal properties and a quite high limiting oxygen index (LOI) value as well as high char yield. Aryl phosphinate epoxy ether is shown to be an effective flame retardant and thermal stabilizer for epoxy resins.

Introduction

Epoxy resins have many attractive properties as well as good processing characteristics and have been widely used in many applications including both the electronics and aerospace industries. However, the flammability of epoxy resins is a major disadvantage in applications that require high flame resistance. Many techniques have been used to improve the flame retardancy of epoxy resins. Recently, phosphorus-modified epoxy resins have received the most attention in the literature (1,2). This approach involves the synthesis of epoxy resins and/or curing agent from monomers bearing phosphorus groups that were effective as flame-retardant or thermal-stabilizer. Various organic phosphorus groups have been covalently incorporated into the backbone of epoxy resin to enhance their flame retardancy (1-4). However, literature on the synthesis and properties of the epoxy compound containing pendent phosphorus groups is scarce.

Since a cyclic organic phosphorus compound, 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), was developed in the early 1970's (5), a large number of aryl phosphinate derivatives have been synthesized and used as additive flame retardants or incorporated into synthetic resins such as polyesters, by copolymerization to prepared flame-retardant polymers. In our previous article (6), an aryl phosphinate anhydride (DMSA) was synthesized and successfully used to cure commercial epoxy resins, DER331 and DEN438. The resulting aryl phosphinate epoxy-resin composites

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exhibited a quite high LOI value as well as high char yield. In addition, Matsumoto et al. (7) reported a synthesis using aryl phosphinate hydroquinones and that they obtained excellent heat and flame resistance copolyesters by it.

This study deals with the synthesis and characterization of novel epoxy ether which contained a pendent phosphorus group, prepared from an aryl phosphinate hydroquinone. The flame retardancy is expected to be improved through the introduction of phosphorus groups into the structure of epoxy. Furthermore, thermal stability of the epoxy resins can be enhanced by the predominantly aromatic group. The thermal and flame resistance of the newly synthesized epoxy-resin composites are also discussed.

Experiment

Materials
The aryl phosphinate flame retardant agent (DOPO, **1**) was supplied by the Chung-Shan Institute of Science and Technology, Taiwan. 1,4-Benzoquinone, epichlorohydrin, sodium methoxide, dicyanodiamide (DICY), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenyl sulfone (DDS) were reagent grades as purchased from Acros Co. and used without further purification. Bisphenol A epoxy (DER331) and novolac epoxy (DEN438) made by Dow Chemical Co., were chosen as the control epoxy resins.

Monomer synthesis
<u>10-(2',5'-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (**2**)</u>
A solution of 1,4-benzoquinone (27.0 g, 0.25 mol) in anhydrous tetrahydrofuran (100 mL) was added dropwise to a stirred solution of DOPO (60.0 g, 0.28 mol) in anhydrous tetrahydrofuran (100 mL) at 60 °C for 2 h under nitrogen, and the mixture was continuously refluxed at 80 °C for 4 h. The resulting precipitate was filtered and washed several times with tetrahydrofuran, and then dried under vacuum to given 69.7 g of **2** as ivory-white crystalline solid (yield 86 %): mp 248-250 °C MS (70eV): m/z 324 (M$^+$). IR (KBr, cm^{-1}): 3065 (aromatic); 3408 (OH); 1443, 1595 (P-Ar); 1198 (P=O); 925, 750 (P-O-Ar).^{1}H-NMR (DMSO-d_6, ppm): 9.46 (s; 1H), 9.17 (s; 1H); 6.59-8.30 (m, 11H). ^{31}P-NMR (DMSO-d_6, ppm): 22.3.
Anal. Calc. for $C_{18}H_{13}O_4P$: C, 66.67; H, 4.04; P, 9.56. Found: C, 66.60; H, 4.02; P, 9.54.

<u>10-(2',5'-bis(glycidyloxy)phenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DHQEP, **3**)</u>
The reaction of **2** (64.8 g, 0.20 mol) and 200 mL (2.56 mol) of epichlorohydrin was carried out using 22.0 g (0.407 mol) of sodium methoxide as catalyst at 65 °C for 18 h. The reaction mixture was diluted with methanol (200 ml), and the produced sodium chloride was filtered off. The filtrate was washed twice with water and dried with anhydrous MgSO$_4$. Excess epichlorohydrin and methanol were evaporated, and then the product thus obtained was purified by silica gel column chromatography using ethyl acetate/n-hexane (4/1) as eluent. The isolated yield of **3** was 47.7 g (53 %). mp 156-157 °C. MS (ESI) m/z 437.1 (MH$^+$) EEW: 225 g/equiv. (calc. 218 g/equiv.). IR (KBr, cm^{-1}): 1490, 1583 (P-Ar); 1278 (C-O); 1219 (P=O); 1039(Ar-O); 916 (epoxy group). ^{1}H-NMR (CDCl$_3$, ppm): 4.40, 4.02, 3.43, 2.99, 2.84 (m, 5H); 3.73, 3.63, 2.43, 2.45, 2.19 (m, 5H); 6.79-8.08 (m; 18H). ^{13}C-NMR (CDCl$_3$, ppm): 70.1, 70.0, 50.5, 49.5, 44.9, 44.7; 114.3-155.1 (aromatic) . ^{31}P-NMR (CDCl$_3$, ppm): 19.1.
Anal. Calc. for $C_{24}H_{21}O_6P$: C, 66.05; H, 4.85; P, 7.10. Found: C, 65.85; H, 4.86; P, 6.87.

Table 1. Curing cycles of several epoxy systems.

Compositions	Curing temperature (℃)	Curing time (min)	Postcure temperature (℃)	Postcure time (min)
DHQEP/DICY	170	120	220	60
DHQEP/DDS	180	120	230	60
DHQEP/DDM	120	120	170	60
DER331/DDS	180	120	230	60
DER331/DDM	120	120	170	60
DEN438/DDS	140	120	230	60
DEN438/DDM	100	120	170	60

Preparation of single crystal of DHQEP
The single crystal used in X-ray analysis was prepared by recrystallization from DHQEP/acetone solution. The very dilute DHQEP/acetone solution in tube was exposed in a closed vessel to a saturated vapor of ethyl ether at room temperature over one day. The size of crystal selected for X-ray analysis was 0.50 X 0.38 X 0.20 mm.

Preparation of polymers
Curing agents such as dicyanodiamide (DICY), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenyl sulfone (DDS) were used. The epoxy polymers were obtained via thermal curing. To obtained a highly crosslinked polymer with good thermal stability, a one epoxy equivalent weight of the epoxy resins was polymerized with 0.25 mol of curing agents. The curing cycles were determined by DSC tracing of the respective epoxy/curing agent compositions (Table 1).

Characterization and measurements
The elemental analyses were determined by the digestion treat and colorimetry and run in a Carlo-Erba EA-1106 analyzer. IR spectra were generated on a Bio-Rad FTS-40 Fourier transfer infrared spectrometer (KBr pellets). Mass spectra were performed by EI (electron ionization) or ESI (electrospray ionization) technique using a Finnigan MAT-95S and a VG Platform mass spectrometer, respectively. X-ray single crystal analysis was done using a Nonius CAD-4 diffractometer. ^{1}H, ^{13}C and ^{31}P-NMR spectra were obtained using a Bruker Avance-300 spectrometer with DMSO-d_6 or CDCl$_3$ as solvent, working at 300, 75 and 121 MHz, respectively. The epoxy equivalent weight (EEW) was expressed in g/equiv. and determined by the pyridinium chloride method (8). The melting points were measured by a Perkin-Elmer DSC-7 at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) thermograms were recorded with a Perkin-Elmer DSC-7 at a heating rate of 10 °C /min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a Perkin-Elmer TGA-7 with a heating rate of 10 °C /min under nitrogen or air atmosphere. Limiting oxygen index (LOI) values were measured on a Custom Scientific flame meter by a modified method as reported in the literature (9).

Results and discussion

Monomer synthesis and characterization
The synthesis of the aryl phosphinate hydroquinone **2** was carried out by the reaction of **1** with 1,4-benzoquinone through a modified literature method (10), and the structure was confirmed by mass, FTIR, ^{1}H, ^{31}P-NMR spectroscopies, and elemental analyses.
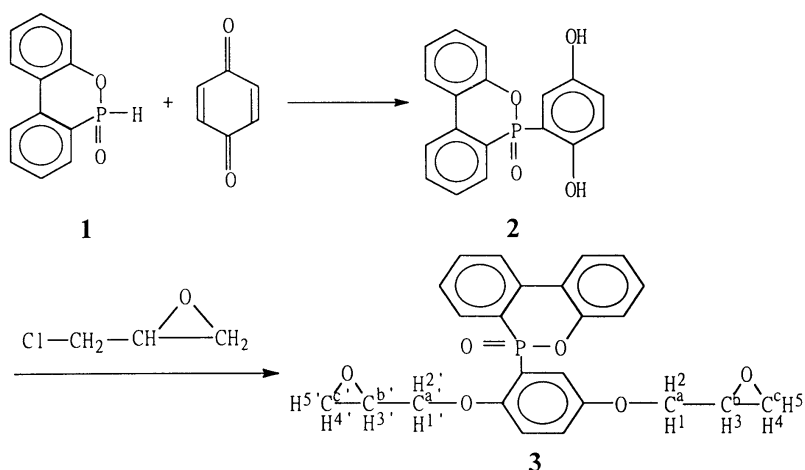
Fig.1. Synthetic scheme of DHQEP

The epoxy ether **3** was synthesized by glycidyletherification of **2** with epichlorohydrin in excess and using sodium methoxide as catalyst (Figure 1). The structure of the epoxy ether was confirmed by mass, FTIR, ^{1}H, ^{13}C, ^{31}P-NMR spectroscopies, elemental analyses, and X-ray single crystal analysis.

The ^{31}P-NMR spectrum of 3 shows a single peak. The assignment of the ^{13}C-NMR signals of **3** was confirmed by C-H correlation (Figure 2). The assignment of the ^{1}H-NMR signals of **3** was confirmed by the COSY experiment (Figure 3). The chemical shifts of protons of the glycidyl ether group of diglycidyl ether of bisphenol A (DGEBA, Figure 4) have been assigned at 4.16, 4.02, 3.31, 2.87, 2.73 (CDCl3, ppm) (11). It is found that the
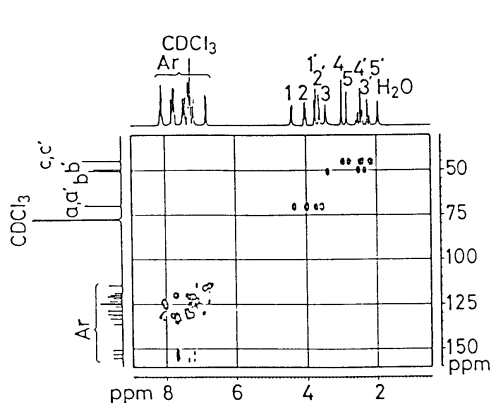
Fig.2. 2D-NMR spectrum of DHQEP (C-H)
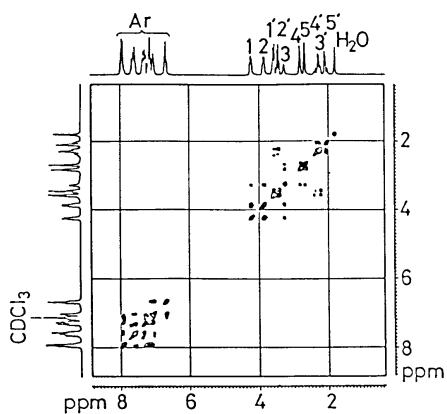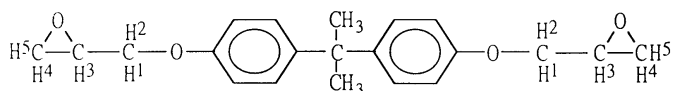

Fig.3. 2D-NMR spectrum of DHQEP (H-H)

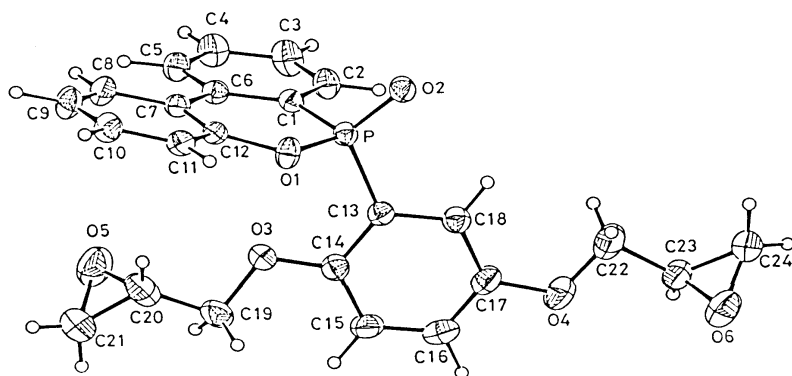**Fig.4.** The schematic structure of DGEBA

Fig.5. The ORTEP drawing of the structure of DHQEP

chemical shifts of protons of the glycidyl ether group on the one end of **3** were similar to those observed in glycidyl ether group of DGEBA. However, the chemical shifts of protons of the glycidyl ether group on the other end of **3** are quite different from those observed in DGEBA. One possible reason for the unusual chemical shifts is due to cyclic organic phosphorus group grafted on the main chain. The chemical shifts of ,$H^{1'}$, $H^{2'}$, $H^{3'}$, $H^{4'}$, and $H^{5'}$ (the label of prontons are show in Figure 1) of **3** are significantly reduced due to the "ring current effect (12)" that arises when these atoms are positioned below the pendent aryl phosphinate group (see Figure 5).

Single-crystal X-ray diffraction shows a disorder at the epoxide ring far away from the pendent aryl phosphinate group (see Figure 6a and 6b). A similar disorder at one epoxide ring of DGEBA crystal has been reported (13). The disorder consists of two alternative orientations for the epoxide ring connected C(22). Both alternatives have one atomic position in common and it is occupied by oxygen atom. Occupancies for the C(23) and C(24) are 0.6 (14).
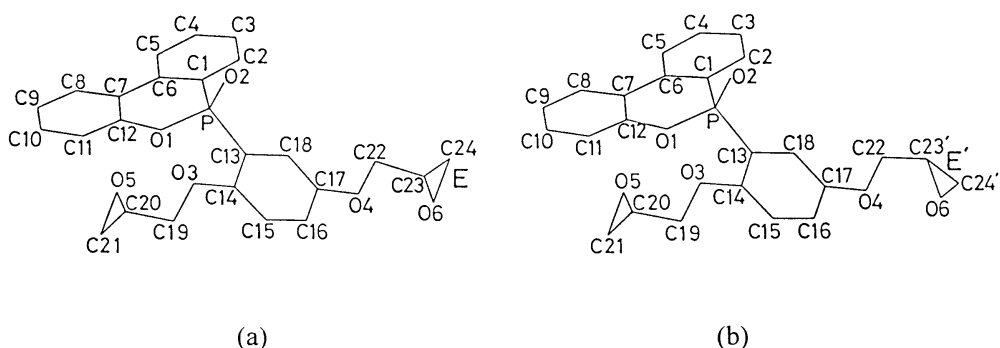

(a)

(b)

Fig.6. Two alternative structure of DHQEP bonds to the alternative position of epoxide ring were blackened. (a) E (b) E'.

Thermal and flame properties

The thermal properties of the epoxy-resin composites were evaluated by thermogravimertric analyses (TGA) under nitrogen and air. The TGA thermograms of the epoxy-resin composites are show in Figures 7 and 8. The initial decomposition of polymer (PDT), the temperature of maximum decomposition rate (T_{max}), and the char yield in percent at 800 °C are shown in Table 2. It is found that the aryl phosphinate epoxy-resin composites demonstrated adequated thermal properties which was compared with commercial products of epoxy resins. The aryl phosphinate epoxy-resin composites
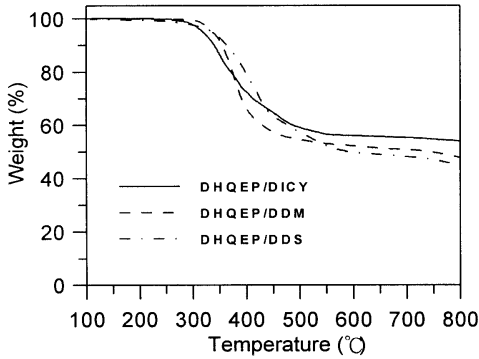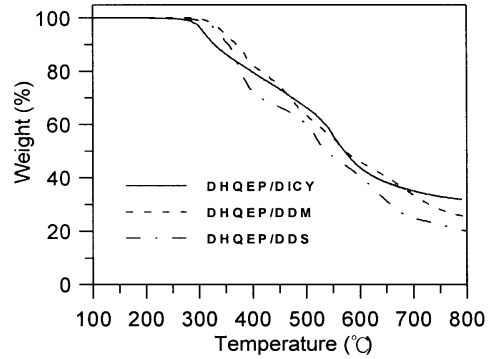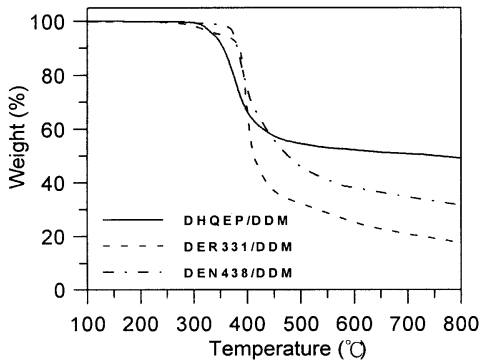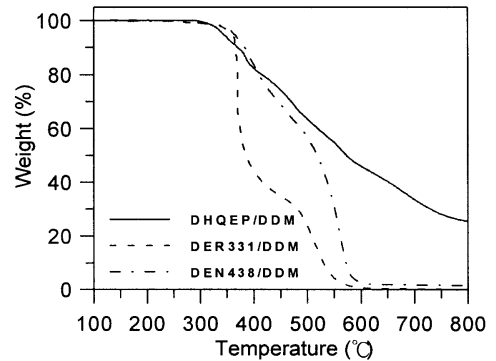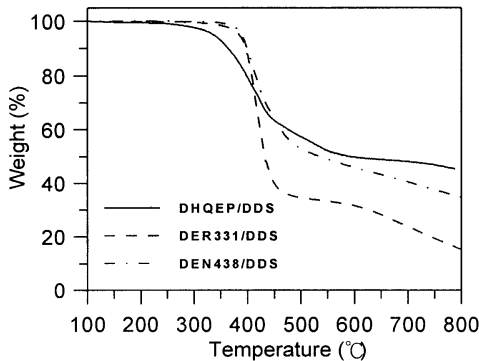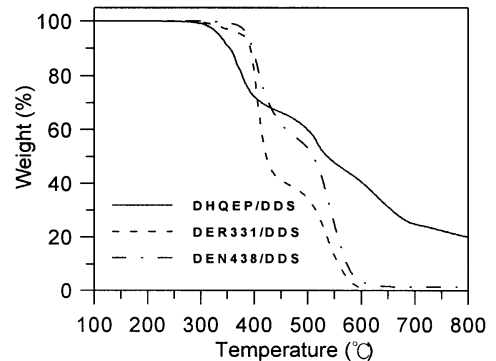

Fig.7. The TGA thermograms of the epoxy-resin composites under nitrogen.

Fig.8. The TGA thermograms of the epoxy-resin composites under air.

Table 2. Thermogravimetric data and LOI values of the epoxy-resin compositions.

compositions	In nitrogen			In air			Nitrogen contents (%)	Phosphorus contents (%)	LOI values (%)
	PDT[a] (℃)	T$_{max}$[b] (℃)	Char yield (%, 800 ℃)	PDT[a] (℃)	T$_{max}$[b] (℃)	Char yield (%, 800 ℃)			
DHQEP/DICY	319.0	355.1	54.0	296.4	303.0	31.8	5.7	6.4	54.3
DHQEP/DDM	336.9	401.4	49.1	334.7	384.7	25.6	2.5	5.8	46.5
DHQEP/DDS	336.4	397.2	44.8	337.9	376.6	20.1	2.4	5.6	45.0
DER331/DDM	350.8	396.4	17.5	353.5	368.4	0.0	3.0	0	22.6
DER331/DDS	384.5	417.4	12.3	377.2	405.3	0.0	2.8	0	21.9
DEN438/DDM	375.0	386.7	31.6	360.3	560.4	1.5	3.1	0	29.1
DEN438/DDS	388.7	413.5	34.8	384.8	413.5	1.4	2.9	0	28.7

have slower thermal degradation rate than the DER331 and DEN438 composites. Moreover, the initial decomposition of the aryl phosphinate epoxy-resin composites is earlier and the char yield is higher. This behavior is probably due to the products of acidic decomposition from phosphorus group that act as dehydrating agents in the earlier stages and thus promote char formation (15,16). Increasing char formation can limit the production of flammable volatile gases and decrease the exothermicity of the pyrolysis reaction (17). Consequently, the flame retardancy of the composites is improved.

A material must be considered flammable as long as the LOI value $\leq$ 26 (18). This LOI is defined as the minimum fraction of oxygen in an oxygen-nitrogen mixture that is just sufficient to sustain combustion (after ignition) of the specimen. The flame retardancy of epoxy-resin composites was determined by the LOI values of the specimen, are also listed in Table 2. It is found that the composites of the epoxy ether **3** exhibited a significantly higher LOI value than DER331 and DEN438 composites. Furthermore, the synergism between phosphorus and nitrogen in flame retardancy should also be taken into consideration (18). Therefore, it can be seen that the epoxy ether **3** cured with DICY gave the highest LOI value. The high phosphorus content along with high nitrogen content helps enhance the LOI value and char yield as well as the flame retardancy of epoxy-resin composites. From the above results, the aryl phosphinate epoxy ether **3** has a high effectiveness in improving thermal stability and thermal oxidative stability as well as flame retardancy of epoxy-resin composites.

Conclusions

DHQEP was synthesized through the reaction of a cyclic organic phosphorus compound with 1,4-benzoquinone, followed by glycidyletherification with epichlorohydrin in excess and using sodium methoxide as a catalyst. The chemical structures of the aryl phosphinate hydroquinone **2** and DHQEP were confirmed by elemental analysis, FTIR, mass, X-ray single crystal analysis, ^{1}H, ^{13}C and ^{31}P-NMR spectroscopies. The unusual chemical shifts of prontons of the glycidyl ether group positioned under the pendent aryl phosphinate group are due to the "ring current effect". The epoxide ring of the other glycidy ether group far away from the pendent aryl phosphinate group is disordered. The resulting aryl phosphinate epoxy-resin composites demonstrated excellent heat resistance and flame retardancy, confirming the effectiveness of aryl phosphinate epoxide as flame retardant and thermal stabilizer.

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