The Synthesis and Properties of New Epoxy Resin Containing Phosphorus and Nitrogen Groups for Flame Retardancy

TSUI-SHUANG WANG, JONG-KAE PARNG, MIN-DA SHAU

Department of Applied Chemistry, Chia Nan College of Pharmacy and Science, Tainan, Taiwan, Republic of China

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ABSTRACT: A new type of epoxy resin, which contained phosphorus oxide and nitrogen groups in the main chain, was synthesized. The structure of the new type of epoxy resin was confirmed by infrared (IR) spectroscopy, ¹H nuclear magnetic resonance (¹H-NMR), and ¹³C-NMR spectroscopic techniques. In addition, compositions of the new synthesized epoxy resin (TGDMO) with three curing agents, for example, bis(3-aminophenyl) methylphosphine oxide (BAMP), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenylsulfone (DDS), were used for making a comparison of its curing reactivity, heat, and flame retardancy with that of Epon 828 and DEN 438. The reactivities were measured by differential scanning calorimetry (DSC). Through the evaluation of thermal gravimetric analysis (TGA), those polymers which were obtained through the curing reactions between the new epoxy resin and three curing agents (BAMP, DDM, and DDS) also demonstrated excellent thermal properties as well as a high char yield. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 413–421, 1999

Key words: phosphorus; nitrogen; thermal stability; flame retardancy; char yield

INTRODUCTION

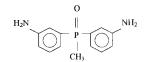
Due to the balance of the properties, the epoxy polymers were used in various industrial fields, such as coating, adhesives, constructions, and insulation materials for electric devices.^{1,2} Recently, chemical synthetic technology and technological applications were significantly developed in the epoxy polymer.^{3–5} However, the common epoxy systems cannot satisfy the demand required by those field applications that require high flame resistance. Considering safety and environment-proofness, epoxy polymers with flame resistance and that are halogen-free have been the focus of attention by researchers in recent

Several techniques have been employed in improving the flame retardancy of epoxy polymers.⁶⁻¹⁰ A feasible approach for improving flame retardation of epoxy polymers involves the application of fire resistant epoxy resins and/or curing agents.⁹⁻¹² The primary objective of this study focuses on improving the flame resistance of epoxy polymers via structure modification. The improvement of flame resistance of epoxy polymers is achieved by introducing the phosphorous and nitrogen groups into the structure of epoxy resin tetraglycidyl–3,3'-diaminodiphenylmethylphosphine oxide (TGDMO). The properties of the

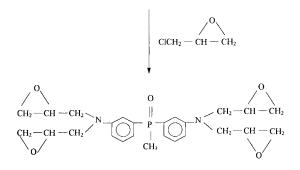
Correspondence to: M.-D. Shau.

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years.^{6–8} According to the previous investigations, it was found that the introduction of phosphorous into the polymer skeleton can improve the fire resistance and decrease contamination on pyrolysis.



Bis (3- aminophenyl)methylphosphine oxide (BAMP)



Tetraglycidyl - 3, 3' - diaminodiphenylmethylphosphine oxide (TGDMO)

Scheme 1 Synthesis of tetraglycidyl-3,3'-diaminodiphenylmethylphosphine oxide (TGDMO).

newly synthesized epoxy resin is compared with commercial epoxy resin, such as Epon 828 and DEN 438. It is found that the newly synthesized epoxy resin demonstrate adequate thermal property as well as high char yields.

EXPERIMENTAL

Reagents

Benzyltrimethylammonium chloride (BTMA), 4,4'-diaminodiphenylmethane (DDM), and 4,4'diaminodiphenylsulfone (DDS) were reagent grade from MERCK, used without further purification. Toluene, acetone, and hexane were distilled at a reduced pressure before the use. BAMP was prepared by a method described previously.⁶ Epon 828 and DEN 438 was purchased from Shell Co. and Dow Chemical Co., respectively.

Synthesis of Tetraglycidyl-3,3'-Diaminodiphenylmethylphosphine Oxide

A mixture of bis(3-aminophenyl) methylphosphine oxide (2.321 g) and epichlorohydrin (EPC, 121.11 g) was heated to 90°C. The solid benzyltrimethylammonium chloride (BTMA, 0.696 g) was added with the mixture being heated to 120°C. The process was completed in 1.5 h. The mixture was then cooled to room temperature and washed with water twice. The unreacted epichlorohydrin was removed from the organic phase by distillation under nitrogen and at a reduced pres-

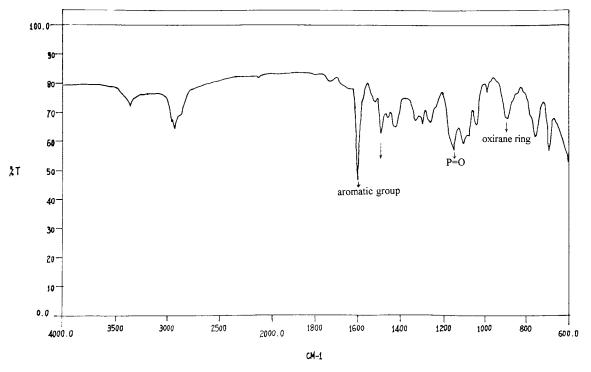
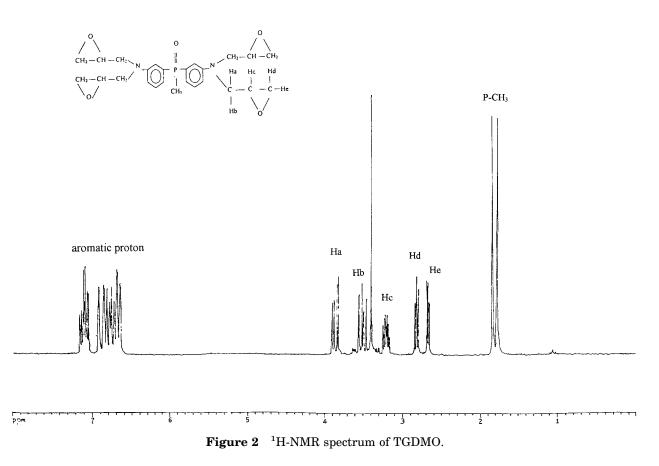


Figure 1 IR spectrum of TGDMO.



sure. The obtained product was purified from column chromatography, using an eluent solvent system of hexane-acetone (2/3). The product was a light brown, viscous liquid and epoxy equivalent to 120 g/equiv (calc 118 g/equiv).

Characterization and Measurements

The melting points were determined by a Yanaco MP-S3. Infrared (IR) spectra were examined using a Perkin–Elmer Model 2000. ¹H nuclear magnetic resonance (¹H-NMR) and ¹³C-NMR spectra were obtained from a Bruker AMX-400, where samples were dissolved in d_6 –DMSO with TMS employed as an internal standard. The curing

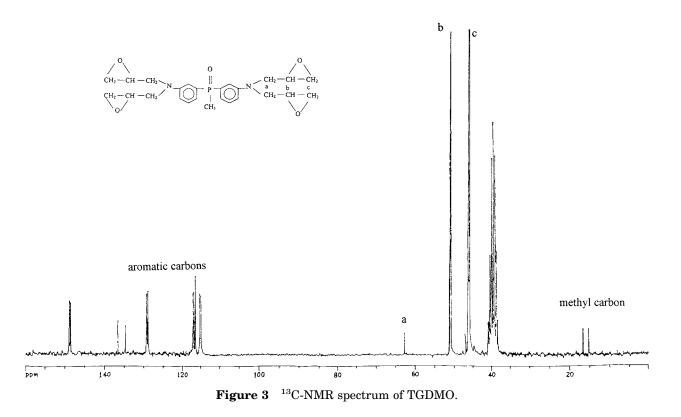
cycles and reactivities were measured by differential scanning calorimetry (DSC) on a TA 2010. Thermal resistance was evaluated by thermal gravimetric analysis (TGA) on a TA 2050 with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The new synthesized epoxy resin, which contained phosphorous and nitrogen groups, TG-DMO, was obtained through the following five synthetic steps: synthesis of methyltriphenyl phosphonium iodide, methyltriphenyl phosphine

Type of Proton	P — CH_3	а	b	с	d	е	Aromatic
Chemical shifts	1.81	3.90	3.55	3.24	2.85	2.67	$6.66 \sim 7.11$ 8H, m
(ppm)	3H, d	4H, m					

Table I ¹H-NMR Data of TGDMO



oxide, bis(3-nitrophenyl) methylphosphine oxide, bis(3-aminophenyl) methylphosphine oxide (BAMP), and tetraglycidyl-3,3'-diaminodiphenylmethylphosphine oxide (TGDMO), according to Scheme 1. The chemical structure of the new epoxy resin, TGDMO, was characterized by infrared (IR) spectroscopy, ¹H-NMR, and ¹³C-NMR spectroscopies.

Identification of Tetraglycidyl-3,3'-Diaminediphenylmethyl Phosphine Oxide

The epoxy equivalent weight of TGDMO was found to be 120 (calcd 118). The IR spectrum is shown in Figure 1. The peaks at 1596 and 1488 cm⁻¹ represent the absorption of aromatic group. Absorptions arising because of P=O at 1154 cm⁻¹, P-C₆H₄ at 1323 cm⁻¹ were also observed. The characteristic band of the oxirane ring was observed at 890 cm⁻¹.

The ¹H-NMR spectrum in d₆–DMSO is shown in Figure 2. The chemical shifts of characteristic protons in TGDMO are listed in Table I. This is based on the assigned label of protons shown in Figure 2. Aromatic ring protons appeared at δ = 6.66–7.11 ppm. The Ha and Hb of methylene were also observed at 3.90 (4H, m) and 3.55 (4H, m), respectively. The Hc, Hd, and He of the oxirane ring were assigned at 3.24 (4H, m), 2.85 (4H, m), and 2.67 (4H, m), respectively. Protons of P—CH₃ also appeared at 1.81 (3H, d).

The ¹³C-NMR spectrum of TGDMO is shown in Figure 3. The resonance lines in spectrum fall into the following three main regions: 15.98 ppm for the aliphatic carbon near phosphine oxide group, 45.93–62.73 ppm for the aliphatic carbons, and 115.01–148.79 ppm for the aromatic carbons. The chemical shifts of characterized carbons in TGDMO are listed in Table II. This is based on the assigned labels of carbons in Figure 3.

Preparation of Tested Samples

The thermal and flame-retardant properties of the new epoxy phosphorylated epoxy and non-

Table II	¹³ C-NMR	Data o	f TGDMO
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Aliphatic Carbons						
a	a b c		Aromatic Carbons	Methyl Carbon		
62.73	50.09	45.93	115.01-148.79	15.98		

DSC study of the polymerization reactions to ob-

tain homogeneous mixtures of the epoxy resins

strate the reactivities of epoxy resin (TGDMO)

toward three curing agents (BAMP, DDM, and

DDS). The influence of the chemical reactivity of

the curing agent on cure behavior is indicated

from this figure to be apparent. For the new epoxy

resin (TGDMO) used, the exothermic starting

temperature increase according to the order of

DDM < BAMP < DDS. A curing agent that exhibits a lower exothermic starting temperature under the same set of curing conditions is more

reactive toward the epoxy resin. It is therefore

reasonable to propose that the chemical reactivi-

ties of these three curing agents toward epoxy

Typical DSC thermograms (Fig. 4) demon-

and curing agents.

Compositions	Curing Temperature (°C)	Curing Time (min)	Postcure Temperature (°C)	Postcure Time (min)
TGDMO-BAMP	145	35	205	40
TGDMO–DDM	93	35	174	30
TGDMO–DDS	170	30	236	30
Epon 828–BAMP	130	30	194	30
Epon 828–DDM	102	35	174	30
Epon 828–DDS	174	35	242	30
DEN 438–BAMP	110	30	190	30
DEN 438–DDM	102	35	174	30
DEN 438–DDS	120	25	190	30

Table IIICuring Cycles of Several Epoxy Systems

phosphorylated epoxy polymers were evaluated here by preparing nine polymers; that is, TGD-MO-BAMP, TGDMO-DDM, TGDMO-DDS, Epon 828-BAMP, Epon 828-DDM, Epon 828-DDS, DEN 438-BAMP, DEN 438-DDM, and DEN 438-DDS. To obtain a highly crosslinked polymer with good thermal stability, one epoxy equivalent of epoxy resins was polymerized with 0.25 mol of curing agents. Curing cycles were determined by DSC thermograms. These compositions and curing cycles of polymers are listed in Table III.

Reactivities of Epoxy Resins and Curing Agents

The polymerization reactions were studied by DSC. Significant caution was taken during the

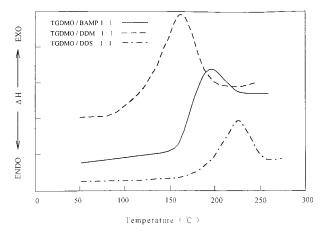


Figure 4 DSC thermograms of TGDMO–BAMP, TGDMO–DDM, and TGDMO–DDS; the heating rate is 10°C/min.

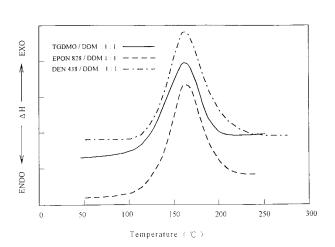


Figure 5 DSC thermograms of TGDMO–DDM, Epon 828–DDM, and DEN 438–DDM; the heating rate is 10°C/min.

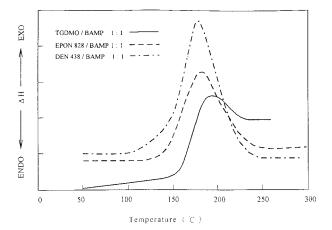


Figure 6 DSC thermograms of TGDMO–BAMP, Epon 828–BAMP, and DEN 438–BAMP; the heating rate is 10°C/min.

resin increases as follows: DDS < BAMP < DDM. The lowest reactivity of DDS toward epoxy resin, as compared with that of BAMP and DDM, should be attributed to the electronic effects. The lower reactivity of BAMP toward epoxy resin, as compared with that of DDM, also should be attributed to electronic effects. In the case of BAMP, the electron-withdrawing group, P=O, reduced the electron density of the amine nitrogen and subse-

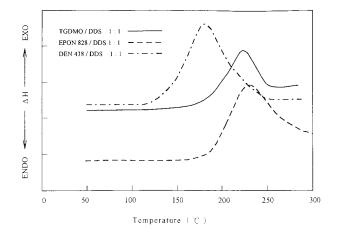


Figure 7 DSC thermograms of TGDMO–DDS, Epon 828–DDS, and DEN 438–DDS; the heating rate is 10°C/min.

quently reduced their nucleophilic attack on the oxirane ring of the epoxy resin.

DSC thermograms (Figs. 5–7) demonstrate the reactivities of three curing agents (DDM, BAMP, and DDS) toward epoxy resins (TGDMO, Epon 828, and DEN 438). The influence of the chemical reactivity of these epoxy resins on the cure behavior is observed in those figures. For the DDM used, the exothermic starting temperatures of

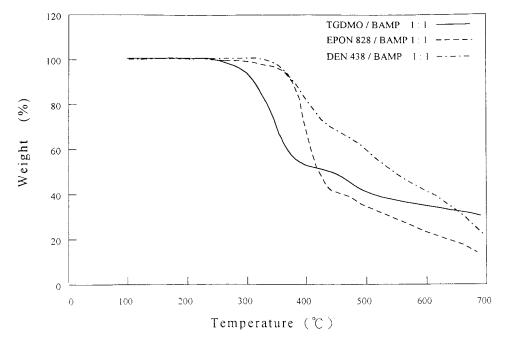


Figure 8 TGA thermograms of TGDMO–DDS, Epon 828–DDS, and DEN 438–DDS in air atmosphere; the heating rate is 10°C/min.

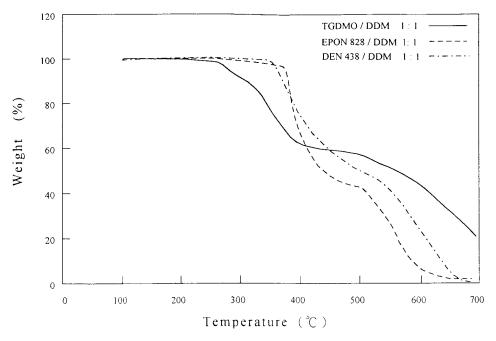


Figure 9 TGA thermograms of TGDMO–BAMP, Epon 828–BAMP, and DEN 438–BAMP, in air atmosphere; the heating rate is 10°C/min.

these epoxy resins are slightly different. It is reasonable to propose that the chemical reactivities of these three epoxy resins are similar for the curing agent. But for the BAMP and DDS used, we found that the exothermic starting temperature of DEN 438 are slightly lower than TGDMO and Epon 828. From the above data, we confirmed that DEN 438 epoxy resin are more reactive than

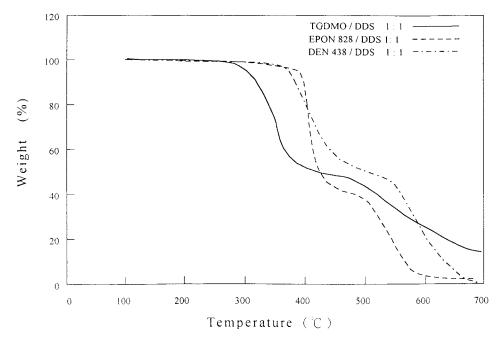


Figure 10 TGA thermograms of TGDMO–DDM, Epon 828–DDM, and DEN 438–DDM, in air atmosphere; the heating rate is 10°C/min.

Materials		Tem	mperature at Characteristic Weight Loss (°C)				Residue
	PDT (°C)	10%	20%	30%	40%	50%	(%) 650°C
TGDMO-BAMP	284	312	336	352	372	448	33.2
TGDMO–DDM	256	310	346	372	436	568	32.6
TGDMO–DDS	304	316	340	354	370	428	7.9

 Table IV
 TGA Data of Cured Epoxy Resins in Air Atmosphere

Heating rate is equal to 10°C/min. PDT is the initial decomposition temperature of polymer.

TGDMO and Epon 828 for lower reactive curing agent, namely, BAMP and DDS.

Thermal and Flame Properties

To compare the thermal properties of these cured polymers, they were divided into the following three groups: (1)TGDMO-BAMP, Epon 828-BAMP, and DEN 438-BAMP; (2) TGDMO-DDM, Epon 828–DDM, and DEN 438–DDM; (3) TGDMO-DDS, Epon 828-DDS, and DEN 438-DDS. From PDTs and temperatures of some characteristic weight losses, which are shown in Figures 8–10. We can compare the thermal properties of these cured polymers. The new epoxy resin (TGDMO) compositions have a lower thermal degradation rate than Epon 828 and DEN 438 compositions. From TGA curves, we found that PDTs of phosphorylated polymer, TGDMO-BAMP, TGDMO-DDM, and TGDMO-DDS, were lower than the other polymers. It is possible that phosphorus in these phosphorylated polymers became phosphoric acid that catalyzed the dehydration of these polymers at lower temperature.

The new synthesized epoxy resin TGDMO is expected to have a higher solid char residue on pyrolysis. To demonstrate the properties of the flame retardancy of this new epoxy resin, these cured polymers are divided into the following three groups: (1) TGDMO-BAMP, Epon 828-BAMP, and DEN 438-BAMP; (2) TGDMO-DDM, Epon 828–DDM, and DEN 438–DDM; (3) TGDMO-DDS, Epon 828-DDS, and DEN 438-DDS. The char yield of these cured polymers in air are shown in Figures 8-10. For group (1), the TGDMO-containing polymer that has the highest phosphorous content, TGDMO-BAMP, has a higher char yield than the other two polymers, Epon 828-BAMP, and DEN 438-BAMP. For group (2), the TGDMO-containing polymer,

TGDMO–DDM, has a higher char yield than the other two polymers, Epon 828–DDM and DEN 438–DDM. For group (3), the TGDMO-containing polymer, TGDMO–DDS, has a higher char yield than the other two polymers, Epon 828–DDS and DEN 438–DDS. Temperatures of some characteristic weight losses and PDTs in air are listed in Table IV. From the above results, we have found that the new epoxy resin demonstrated adequate flame properties.

CONCLUSIONS

The structure of the new epoxy resin, TGDMO, was confirmed through epoxy equivalent weight, IR, ¹H-NMR, and ¹³C-NMR characterization. The synthesized TGDMO cured with BAMP, DDM, or DDS diamines showed a slower thermal degradation rate than Epon 828 and DEN 438 resins cured with the same curing agents. The flame retardancy of the epoxy resin was confirmed in this study as capable of being significantly improved through introduction of phosphorus and nitrogen groups into the epoxy structure. The TGDMO-containing epoxy polymers were observed to have a higher char yield on pyrolysis.

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