Properties of Epon 828 Resin Cured by Cyclic Phosphine Oxide Tetra Acid

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ABSTRACT: A new phosphorylated epoxy polymer was obtained using Epon 828 resin cured with a phosphorus-containing curing agent, 10-phenylphenoxaphosphine-2,3,7,8-tetracarboxylic acid-10-oxide (PDAC). In addition, compositions of Epon 828 with common curing agents, for example, 4,4′-diaminodiphenylmethane (DDM) and 4,4′-diaminodiphenylsulfone (DDS), were used for making a comparison of its curing reactivity, heat, and flame retardation with that of PDAC. The reactivites of the three curing agents toward Epon 828, as measured by differential scanning calorimetry (DSC), was in the following order: DDM > PDAC > DDS. Through thermal gravimetric analysis evaluation (TGA), the thermal and flame resistance of epoxy polymers were confirmed in this study as capable of being improved through introduction of the cyclic phosphine oxide group into the carboxyl curing agent structure. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1877–1885, 1998

Key words: cyclic phosphine oxide tetra acid; thermal stability; flame retardancy; char yield

INTRODUCTION

The special structures and the variety of curing methods of epoxy resins give satisfactory mechanical properties, such as minimum shrinkage after cure, suitable chemical and weather resistance, and good adhesion. Due to the balance of the properties, the epoxy polymers were used in various industrial fields, such as transportation, insulation materials for electric devices, and construction materials.[1,2] But the thermal and flame resistance of epoxy polymers are inadequate for some applications. It is necessary to introduce new structures into the epoxy polymer skeleton to improve the thermal and flame resistance.

The properties and performances of epoxy polymers are all dependent on the types of epoxy resins and curing agents and the crosslinking density. The incorporation of halogen and/or phosphorus into the epoxy polymer skeleton can improve flame resistance.[3,4] Currently, the incorporation of halogen into epoxy polymers is not preferred for environmental reasons. To prevent this problem, the epoxy polymers were modified by introducing phosphorus into the molecular structure, improving the flame properties.[5,6] According to the previous investigations, it was found that nonphosphorylated curing agents give about a zero char yield on pyrolysis at higher temperature in air.[7,8] On the other hand, the incorporation of phosphorus into the curing agent structure can produce adequate char yield on pyrolysis.[6,9]

In the present work, a phosphorus-containing curing agent, 10-phenylphenoxaphosphine-

3,3' 4,4'-dimethyldiphenyl ether

(I)

2,3,7,8-tetramethyl-10-phenyloxaphosphine

(II)

10-phenylphenoxaphosphine-2,3,7,8-tetracarboxylic-10-oxide

(III)

Scheme 1   Synthesis of PDAC.

2,3,7,8-tetracarboxylic acid-10-oxide (PDAC), was prepared by the reaction of 3,3′,4,4′-tetra-methyldiphenylether with phenylphosphorous dichloride and KMnO$_4$, according to Scheme 1. The curing behaviors and the thermal and flame properties of a new epoxy polymer, Epon 828/PDAC, were studied.

EXPERIMENT

Reagent

3,4-Dimethylphenol (from Jassen Co.), 4-bromo-*o*-xylene (from Aldrich Co., Milwaukee, Wisconsin, U.S.A.), and phenylphosphorous dichloride (from Aldrich Co.) were reagent grade and used without further purification. Chloroform, benzene, methanol, and pyridine were distilled at reduced pressure before use. Epon 828 was purchased from the Shell Chemical Co.

Synthesis of 3,3′,4,4′-Tetramethyldiphenylether (I)

A mixture of 52.5 g 3,4-dimethylphenol and 25.00 g of potassium hydroxide was heated to 150°C for 30 min, then cooled to 90°C, at which point 46.25 g of 4-bromo-*o*-xylene was added in one batch. Copper powder, 0.30 g, was added and the mixture was brought to reflux. After 45 min, the reaction mixture was cooled and treated with 20% 400 mL of sodium hydroxide. The product was extracted with chloroform. The chloroform was removed in the steam bath. The residual solid was purified by column chromatography, using an eluent system of *n*-hexane. The product was a white crystalline solid. Yield was 44%, with an mp about 60°C.

Synthesis of 2,3,7,8-Tetramethyl-10-phenylphenoxaphosphine (II)

A mixture of 25.36 g of 3,3′,4,4′-tetramethyldiphenylether, 54.62 g of phenylphosphorous dichloride, and 18.76 g of aluminum chloride was stirred at 120–130°C for 6 h and then poured into ice water. The precipitate was washed, filtered, and dissolved in benzene (400 mL) in the presence of a 20% NaOH solution. The benzene solution was washed with water and concentrated. The residual was purified by column chromatography, using an eluent system of hexane/acetone (6/4). The product was a colorless crystalline solid. Yield was 55%, with an mp about 245°C.

Synthesis of 10-Phenylphenoxaphosphine-2,3,7,8-tetracarboxylic acid-10-oxide (III) (PDAC)

A solution of KMnO$_4$ (80.00 g) in water (100 mL) was gradually added into a stirred solution of 2,3,7,8-tetramethyl-10-phenylphenoxaphosphine (6.70 g) in pyridine (320 mL) and H$_2$O (80

Table I Data of Elemental Analyses

Materials	C (%)		H (%)		O (%)	
	Exp	Calcd	Exp	Calcd	Exp	Calcd
Compound **I**	85.44	84.96	7.72	7.69	6.85	7.08
Compound **II**	76.12	75.86	6.01	6.03	9.03	9.20
PDAC	54.96	56.41	2.44	2.78	34.25	34.16

Compound **I:** 3,3′,4,4′-tetramethyldiphenylether; compound **II:** 2,3,7,8-tetramethyl-10-phenylphenoxaphosphine; PDAC: 10-phenylphenoxaphosphine-2,3,7,8-tetracarboxylic acid-10-oxide.

mL) containing NaOH (2.55 g) at 90°C. The mixture was refluxed for 3 h. Manganese dioxide was filtered off and pyridine was removed by vacuum distillation. In addition, $KMnO_4$ (20.00 g) in H_2O (200 mL) was added to the aqueous solution, and the mixture was stirred under reflux for 5 h. The MnO_2 was filtered off, and the filtrate was acidified with dilute H_2SO_4. The precipitate was washed with H_2O and recrystallized from acetic acid. The product was a white crystalline solid. Yield was 70%. The melting point cannot be measured due to the dehydration of compound **III**.

Characterization and Measurements

Elemental analysis (EA) was carried out on a Heraeus CHN-O Rapid Analyzer. Infrared spectra (IR) and Fourier transform infrared (FTIR) spectra were obtained using a Perkin–Elmer Model 983 and a Bomen DA 3.002 FTS, respectively.^{1}H-NMR and ^{13}C-NMR spectra were obtained from a Bruker AM-400 where the sample was dissolved in DMSO-d_6 with TMS employed as an internal standard. The melting point and curing conditions were determined through dynamic and isothermal thermograms by differ-

Figure 1   IR spectrum of PDAC.

Figure 2 ^{1}H-NMR spectrum of PDAC.

ential scanning calorimetry (DSC) on a DuPont 2000. The thermal resistance was evaluated by thermogravimetric analysis (TGA) on a DuPont 2000 with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Identification of 10-Phenylphenoxaphosphine-2,3,7,8-dicarboxylic acid-10-oxide (PDAC)

The data of the elemental analyses are listed in Table I. The elemental analyses of these compounds were in good agreement with the calculated values. The IR spectrum of PDAC is shown in Figure 1. The peaks at 1720 cm^{-1} represent the stretch absorption of C=O in the acid group. Absorption arising because of the aromatic rings at

1605 and 1560 cm^{-1}, P—Ar at 1375 and 1130 cm^{-1}, Ar—O—Ar at 1200 cm^{-1}, and P=O at 1185 cm^{-1} were also observed. The ^{1}H-NMR spectrum in DMSO-d_6 is shown in Figure 2. Aromatic ring protons are evident at $\delta = 7.48-8.32$ ppm. The ^{13}C-NMR spectrum of PDAC is shown in Figure 3. The chemical shifts of the characterized carbons in PDAC are listed in Table II. This is based on the assigned labels of carbons in Figure 3. Through the structural characterization of EA, IR,^{1}H-NMR, and ^{13}C-NMR, the synthesized compound was confirmed to be 10-phenylphenoxaphosphine-2,3,7,8-tetracarboxylic acid-10-oxide.

Preparation of Tested Samples

To obtain a complete reaction between Epon 828 and the curing agents (PDAC, DDM, DDS) and to avoid formation of residual stress, two parameters that need to be considered in determining the curing period are the curing temperature and time. Determination of the optimum curing temperature and time can be carried out by DSC through isothermal and thermal scanning, respectively. The compositions and curing data of all the tested samples are listed in Table III.

Curing Behaviors of Curing Agents

The polymerization reactions were studied by DSC. Typical DSC thermograms of the three poly-

Figure 3 ^{13}C-NMR spectrum of PDAC.

Table II ^{13}C-NMR Data of PDAC

No. Carbon	C_1	C_2	C_3	C_4	C_5	C_6
Chemical shift (ppm)	167.06	166.42	140.98	120.12	155.54	115.65 116.52

No. carbon	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
Chemical shift (ppm)	132.11	134.88	132.51 130.93	130.90	128.60	128.96

mers, Epon 828/PDAC, Epon 828/DDM, and Epon 828/DDS, as shown in Figure 4, demonstrate the reactivities of the curing agents (PDAC, DDM, and DDS) toward the epoxy resin Epon 828. The influence of the chemical reactivity of the curing agent on the cure behavior indicated in Figure 4 is apparent. For the Epon 828 used, the exothermic starting temperature increases according to the following order: DDM < PDAC < DDS. A

curing agent which exhibits a lower exothermic starting temperature under the same set of curing conditions is more reactive toward the epoxy resins. It is therefore reasonable to propose that the chemical reactivities of these three curing agents toward the epoxy resin are as follows: DDS < PDAC < DDM. From Figure 5, it is found that there is one exothermic peak at 184.7°C and another endothermic peak at 269.5°C in the Epon

Table III Curing Cycles of Several Epoxy Systems

Compositions	Curing Temperature (°C)	Curing Time (min)	Postcure Temperature (°C)	Postcure Time (min)
Epon 828/PDAC (1 : 0.6)	115	30	188	20
Epon 828/PDAC (1 : 0.8)	115	30	188	20
Epon 828/PDAC (1 : 1)	115	30	188	20
Epon 828/DDM	90	35	165	20
Epon 828/DDS	130	30	230	25

Figure 4 DSC thermograms of Epon 828/PDAC (1/0.8), Epon 828/DDM, Epon 828/DDS, The heating rate is 10°C/min.

Figure 5 DSC thermograms of Epon 828/PDAC (1/0.8). The heating rate is 10°C/min.

828/PDAC DSC cure. The exothermic peak at 184.7°C was due to the reaction between Epon 828 and PDAC and the endothermic peak at 269.5°C was due to the dehydration of the unreacted PDAC.

Thermal and Flame Properties of Epon 828/PDAC System

Three ratios of epoxide to acid were studied in the condition as shown in Table III. From Figures 6 and 7, it is evident that the Epon 828/PDAC = 1/0.8 system has the best thermal properties. To compare the thermal properties between Epon 828/PDAC (1/0.8) and the other epoxy polymers (Epon 828/DDM, Epon 828/DDS), the PDT, T_{max}, and temperatures of some characteristic weight losses are listed in Tables IV and V as well as shown in Figures 8 and 9. From the above data, we found that the PDT of the phosphorylated polymer (Epon 828/PDAC) was lower than that of the nonphosphorylated polymers (Epon 828/DDM and Epon 828/DD) and the PDAC composition has a

Figure 6 TGA thermograms of Epon 828/PDAC (1/0.6, 1/0.8, 1/1) in nitrogen environment. The heating rate is 10°C/min.

Figure 7   TGA thermograms of Epon 828/PDAC (1/0.6, 1/0.8, 1/1) in air environment. The heating rate is 10°C/min.

slower thermal degradation rate than that of DDM and DDS.

Van Krevelen[10] proposed that the char residue on pyrolysis is linearly proportional to the oxygen index for halogen-free polymers. The char yield of these cured polymers in nitrogen and air environments are shown in Figures 8 and 9. The char yields at the characteristic temperature of 650°C are listed in Tables IV and V. It was found that the phosphorus-containing polymer, Epon 828/PDAC, has a higher char yield than that of the two nonphosphorylated polymers, Epon 828/DDM and Epon 828/DDS.

Table IV   TGA Data of Cured Epoxy Resins in Nitrogen Environment with Heating Rate of 10°C/min

| Materials | T_{max} (°C) | PDT (°C) | Temperature at Characteristic Weight Loss (°C) | | | | | Residue (%) |
			10%	20%	30%	40%	50%	650°C
Epon 828/PDAC (1 : 0.8)	370	336.7	349	368.1	415	449.4	546	34.8
Epon 828/DDM	391.7	366.7	378.1	387.5	392.2	396.9	403.1	20.6
Epon 828/DDS	420	392.7	396.9	407.8	412.5	417.2	423.4	16

PDT: initial decomposition temperature of the polymer; T_{max}: maximum decomposition rate temperature.

Table V   TGA Data of Cured Epoxy Resins in Air Environment with Heating Rate of 10°C/min

| Materials | T_{max} (°C) | PDT (°C) | Temperature at Characteristic Weight Loss (°C) | | | | | Residue (%) |
			10%	20%	30%	40%	50%	650°C
Epon 828/PDAC (1 : 0.8)	360	316.7	331.6	361.3	395.6	456.6	550.3	17.2
Epon 828/DDM	384	375	382.3	389.0	394.8	412.0	441.6	5.1
Epon 828/DDS	408.3	390	396.9	403.1	407.8	415.6	426.6	3.4

Figure 8   TGA thermograms of Epon 828/PDAC (1/0.8), Epon 828/DD, and Epon 828/DDS in nitrogen environment. The heating rate is 10°C/min.

CONCLUSIONS

The structure of the synthesized cyclic phosphine oxide tetra acid curing agent (PDAC) was confirmed through EA, IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy characterizations. The PDAC compositions demonstrated an adequate thermal degradation rate when compared with the DDM and DDS compositions. The flame retardancy of the epoxy polymer could be significantly improved through the introduction of a cyclic phosphine oxide group into the structure of the curing agent. The cyclophosphorous-containing epoxy polymers were observed to have a higher char yield on pyrolysis than that of the nonphosphorylated epoxy polymers.

Figure 9   TGA thermograms of Epon 828/PDAC (1/0.8), Epon 828/DDM, Epon828/DDS in air environment. The heating rate is 10°C/min.

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