

# The Properties of Epoxy-Imide Resin Cured by Cyclic Phosphine Oxide Diacid

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## SYNOPSIS

A new phosphorylated epoxy-imide polymer synthesized was obtained using diimide-diepoxide (DIDE) resin cured with the new curing agent, 10-phenylphenoxy-phosphine-3,8-dicarboxylic acid-10-oxide (PCAO). In addition, compositions of the synthesized diimide-diepoxide (DIDE), Epon 828, with common curing agents, e.g., 4,4'-diaminodiphenylether (DDE) and 4,4'-diaminodiphenylsulfone (DDS), were used for making a comparison of its curing reactivity and heat, and flame retardation with that of (PCAO). The reactivities of those curing agents toward the two kinds of epoxy resins, as measured by differential scanning calorimetry (DSC), were in the following order: DDE > PCAO > DDS. Through evaluation of thermal gravimetric analysis (TGA), the thermal and flame resistances of epoxy polymers were confirmed in this study as capable of being significantly improved through introduction of imide and cyclic phosphine oxide group into the epoxide and curing agent structures. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxyes have satisfactory mechanical properties, such as minimum shrinkage after cure, suitable weather and chemical resistance, and thermal resistance. Epoxyes are applied industrially for molding compounds, surface coating and painting materials, matrices of composites, microelectronic encapsulated materials, insulated materials for electric devices, adhesives, etc.<sup>1,2</sup> However, the common epoxy systems cannot satisfy field applications that require high thermal and flame resistance.

The properties and performances of cured epoxy polymers are all dependent on the types of epoxy resins used, the types of curing agents used, and on cross-linking density. The types of curing agents used can be amines, anhydrides, salts, or acids. Due to the rapid development of electronic materials in aerospace in past years, it is crucial to improve the heat and flame resistances of epoxy resins and curing agents. Modifications of the backbone of epoxyes

have received increasing attention during recent years in attempts to enhance thermal properties.<sup>3-8</sup>

In this research, the improvement of flame and thermal resistances of the cured epoxy was achieved by introducing the cyclic phosphine oxide group into the structure of a diacid curing agent. The phosphorus-containing diacid curing agent (PCAO) was synthesized. The cured materials from different types of epoxy resins, such as DIDE and Epon 828, with a variety of hardeners, namely PCAO, DDS, and DDE, were also studied.

## EXPERIMENTAL

### Reagents

Benzyltrimethylammonium chloride, 4-methylphenyl, 4,4'-diamino-diphenylether (DDE), 4,4'-diaminodiphenylsulfone (DDS), and 6-aminohexanoic acid were reagent grade from Merck and used without further purification. 4-bromotoluene and phenylphosphonous dichloride were also reagent grade from Aldrich Co. and used without further purification. Benzene-1,2,4,5-tetracarboxylic dianhydride

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was recrystallized from acetic anhydride. *N,N'*-dimethylformamide was dried over  $P_2O_5$  and then vacuum-distilled. Chloroform, epichlorohydrin, benzene, toluene, and pyridine were distilled at reduced pressure before use. Bis(3-aminophenyl) methyl phosphine oxide (BAMP) and diimide-diepoxyde (DIDE) were prepared by a method described previously,<sup>8</sup> Epon 828 was purchased from Shell Chemical Co.

### Synthesis of 4,4'-Dimethyldiphenylether

A mixture of 48.6 g of 4-methylphenol and 25 g of potassium hydroxide was heated to 130°C for 30 min, then cooled to 90°C, at which point 42.8 g of 4-bromotoluene was added in one batch; 0.30 g of copper powder was added, and the mixture was brought to reflux. After 30 min, the reaction mixture was cooled and treated with 12.5 g of sodium hydroxide dissolved in 400 mL of water. The product was extracted with chloroform. The chloroform solution was washed with water, and chloroform was removed in the steam bath. The residual solid was purified by column chromatography using as eluent *n*-hexane. The product was a white crystalline solid. Yield was 85%, with m.p. at about 43°C.

### Synthesis of 3,8-Dimethyl-10-Phenylphenoxaphosphine

A mixture of 19.80 g of 4,4'-dimethyldiphenylether, 49.65 g of phenylphosphonous dichloride, and 17.50 g of aluminium chloride was stirred at 120°C for 2 h and then poured into ice water. The precipitate was washed, filtered off, and dissolved in chloroform (400 mL) in the presence of 20% NaOH solution. The chloroform solution was washed with water and concentrated. The residual was purified by column chromatography, using as eluent system of hexane/acetone (6/4). The product was a colorless crystalline solid. Yield was 74%, with m.p. about 190°C (m.p. = 191–192°C).<sup>9</sup>

### Synthesis of 10-Phenylphenoxaphosphine-3,8-Dicarboxylic Acid-10-Oxide

A solution of  $KMnO_4$  (45.50 g) in water (200 mL) was gradually added into a stirred solution of 3,8-dimethyl-10-phenylphenoxaphosphine (6.40 g) in pyridine (300 mL) and  $H_2O$  (100 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,  $KMnO_4$  (10.50 g) in  $H_2O$  (100 mL) was added

to the aqueous solution, and the mixture was stirred under reflux for 2 h.

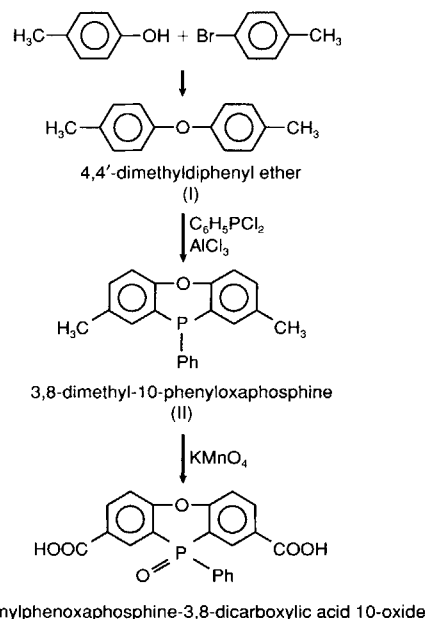
The  $MnO_2$  was filtered off, and the filtrate was acidified with dilute  $H_2SO_4$ . The precipitate was washed with  $H_2O$  and recrystallized from acetic acid. The product was a white crystalline solid. Yield was 81%, with m.p. at about 355°C.

Some characteristic data of IR,  $^1H$ -NMR, and  $^{13}C$ -NMR were shown as follows. IR (KBr) results were  $1732\text{ cm}^{-1}$  ( $\nu_{C=O}$  acid),  $1564\text{ cm}^{-1}$  and  $1487\text{ cm}^{-1}$  ( $\nu_{C_6H_5}$ ),  $1393\text{ cm}^{-1}$  ( $\nu_{P-C_6H_5}$ ), and  $1180\text{ cm}^{-1}$  ( $\nu_{P=O}$ ).  $^1H$ -NMR results were  $\delta = 7.30$ – $8.25$  ppm (aromatic ring protons)  $^{13}C$ -NMR results were  $\delta$ : 119–140 ppm (aromatic carbons) and 171 ppm (carbonyl carbons of the acid group). Scheme I illustrates how PCAO was synthesized.

### Characterization and Measurements

The melting point was determined by a Yanaco MP-S3. Infrared (IR) spectra were examined using a Perkin-Elmer Model 2000. Elemental analyses were carried out on a Heraeus CHN-O Rapid Analyzer.  $^1H$ -NMR and  $^{13}C$ -NMR spectra were obtained from a Bruker AMX-400, in which samples were dissolved in  $DMSO-d_6$ , with TMS used as an internal standard.

The curing cycles and reactivities were measured by DSC on a Perkin Elmer DSC 7. The thermal resistance was evaluated by TGA on a Du Pont 2000 with a heating rate on 10°C/min.



Scheme 1 Synthesis of PCAO.

**Table I Data of Elemental Analyses**

Materials	C%		H%		O%	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Compound I <sup>a</sup>	84.97	84.85	7.18	7.07	8.20	8.08
Compound II	78.96	78.95	5.55	5.59	5.34	5.26
PCAO	63.18	63.16	3.38	3.42	25.28	25.26

<sup>a</sup> Compound I = 4,4'-dimethyldiphenylether; Compound II = 3,8-dimethyl-10-phenylphenoxaphosphine; PCAO = 10-phenylphenoxaphosphine-3,8-dicarboxylic acid-10-oxide.

## RESULTS AND DISCUSSION

### Identification of Diimide-Diepoxide

Diimide diacid was obtained through the reaction of benzene-1,2,4,5-tetracarboxylic dianhydride with 6-aminohexanoic acid. DIDE was obtained through the reaction of the diimide diacid with epichlorohydrin. Products were obtained by distillation and recrystallization. The chemical structure of the diimide diepoxide was characterized by elemental analysis, IR spectroscopy, and <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopies.<sup>8</sup>

### Identification of 10-Phenylphenoxaphosphine-3,8-Dicarboxylic Acid-10-Oxide

The data of elemental analyses are listed in Table I. Elemental analyses of those compounds were in good agreement with the calculated values.

The cyclic phosphine oxide diacid curing agent was confirmed to be 10-phenylphenoxaphosphine-3,8-dicarboxylic acid-10-oxide, as seen from studies of elemental analyses (EA) and IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopies.

### Preparation of Polymers

The thermal and fire retardant properties of the cyclophosphorylated epoxy-imide, non-phosphory-

lated epoxy-imide, cyclophosphorylated epoxy: and nonphosphorylated epoxy polymers were evaluated here by preparing eight polymers, i.e., DIDE/PCAO, DIDE/BAMP, DIDE/DDS, DIDE/DDE, Epon 828/PCAO, Epon 828/BAMP, Epon 828/DDS, and Epon 828/DDE. To obtain a highly cross-linked polymer with good thermal stability, one epoxy equivalent weight of the epoxy resins was polymerized with 0.25M of curing agent. Curing cycles were determined by DSC thermograms. These compositions and curing cycles of polymers are listed in Table II.

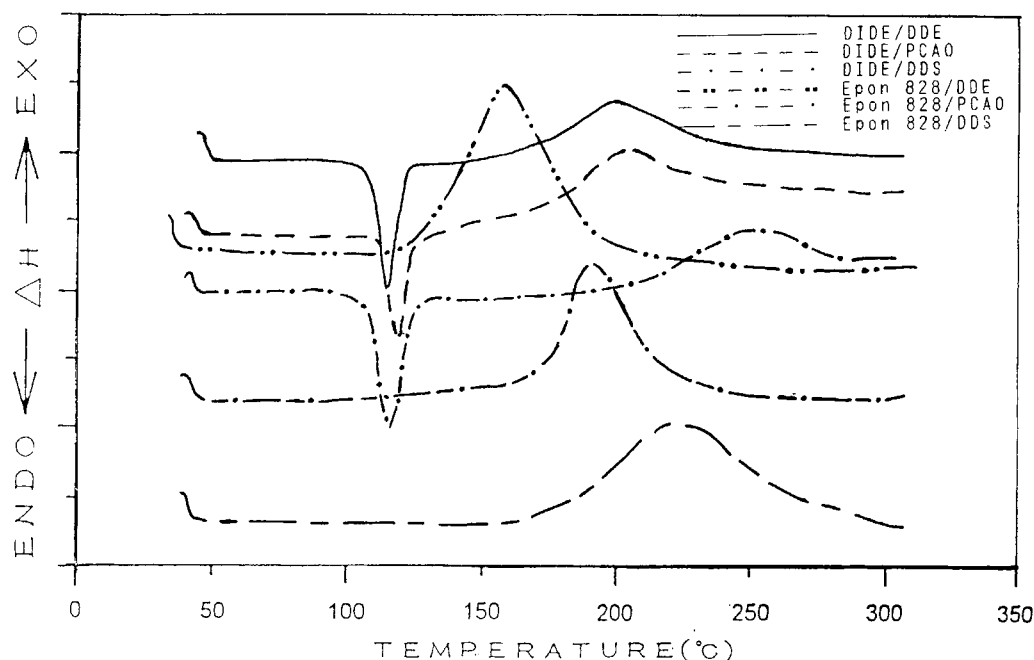
### Reactivities of Curing Agents

The polymerization reactions were studied by DSC. Significant caution was taken during the DSC study of the polymerization reactions to obtain homogeneous mixtures of the epoxy resins and curing agents.

Typical DSC thermograms, as seen in Figure 1, demonstrate the reactivities of curing agents (DDE, PCAO, and DDS) toward epoxy resins (DIDE, Epon 828). The influence of the chemical reactivity of the curing agent on cure behavior is indicated in Figure 1 is apparent. For all the epoxy resins used, the exothermic starting temperature increases according to the following order: DDE < PCAO < DDS. A curing agent which exhibits a lower exothermic starting temperature under the same set of curing conditions

**Table II Curing Cycles of Several Epoxy Systems**

Compositions	Curing Temperature (°C)	Curing Time (min)	Postcure Temperature (°C)	Postcure Time (min)
DIDE/PCAO	120	60	194	40
DIDE/BPMP	160	45	210	25
DIDE/DDS	200	30	250	20
DIDE/DDE	160	25	210	20
Epon 828/PCAO	130	50	200	20
Epon 828/BPMP	110	30	185	20
Epon 828/DDS	180	25	230	20
Epon 828/DDE	120	35	170	35



**Figure 1** DSC thermograms of DIDE/PCAO, DIDE/DDS, DIDE/DDE, Epon 828/PCAO, Epon 828/DDS, and Epon 828/DDE. The heating rate is 10°C/min.

is more reactive toward the epoxy resins. It is therefore reasonable to propose that the chemical reactivities of these three curing agents toward epoxy resins increase as follows: DDS < PCAO < DDE. The lowest reactivity of DDS toward epoxy resins, DIDE and Epon 828, as compared with that of PCAO and DDE, should be attributed to electronic effects.

### Thermal Properties

In order to compare the thermal properties of these cured polymers, cured polymers were grouped into

the following four groups: (1) DIDE/PCAO, DIDE/BAMP; (2) DIDE/PCAO, DIDE/DDS, DIDE/DDE; (3) Epon 828/PCAO, Epon 828/BAMP; and (4) Epon 828/PCAO, Epon 828/DDS, Epon 828/DDE. In order to demonstrate the thermal properties of these cured polymers, PDT and temperatures of some characteristic weight losses are listed in Tables III and IV, as well as in Figures 2 to 5. From group (1), it is found that the cyclic phosphine oxide diacid curing agent (PCAO) composition shows better PDT than the other curing agent, BAMP, which also contains a linear phosphorus group. For group (2), the PCAO composition has a slower thermal deg-

**Table III** TGA Data of Curing Epoxy Resins in a Nitrogen Environment

Materials	PDT (°C)	Temperature at Characteristic Weight Loss					Residue (%)	
		10%	20%	30%	40%	50%	600°C	700°C
DIDE/PCAO	390.7	398.1	413.5	423.1	428.9	440.4	31.7%	30.6%
DIDE/BPMP	325.3	378.1	406.3	423.5	442.2	564.2	49.4%	47.9%
DIDE/DDS	383.4	385.9	410.9	425.0	435.9	450.0	31.1%	29.1%
DIDE/DDE	351.0	371.9	396.9	415.0	429.7	453.1	31.9%	30.4%
Epon 828/PCAO	372.3	387.2	412.8	444.7	517.0	—	53.3%	52.0%
Epon 828/BPMP	370.8	390.0	406.0	413.0	417.0	436.1	22.5%	22.0%
Epon 828/DDS	392.5	401.8	408.9	414.3	419.6	426.8	21.8%	19.9%
Epon 828/DDE	255.1	375.2	279.6	386.3	390.8	397.5	19.2%	18.7%

Note: Heating rate = 10°C/min.

**Table IV** TGA Data of Curing Epoxy Resins in an Air Environment

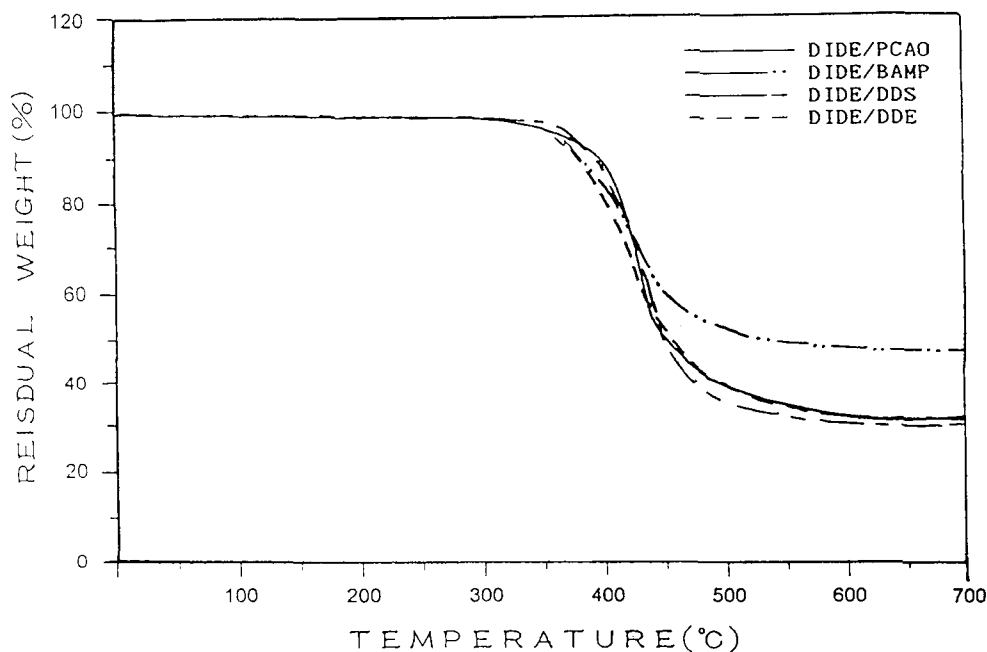
Materials	PDT (°C)	Temperature at Characteristic Weight Loss					Residue (%)	
		10%	20%	30%	40%	50%	600°C	700°C
DIDE/PCAO	387.9	392.3	409.6	423.1	446.2	534.6	35.6%	20.0%
DIDE/BPMP	320.8	375.0	409.4	429.7	471.9	578.2	41.6%	12.8%
DIDE/DDS	382.6	384.4	414.6	431.3	450.0	473.4	20.4%	0%
DIDE/DDE	347.1	362.5	394.6	426.8	458.0	507.1	10.4%	0%
Epon 828/PCAO	375.0	392.4	426.9	476.9	548.1	588.5	48.7%	40.7%
Epon 828/BPMP	372.4	384.0	397.2	407.6	418.9	430.2	26.0%	15.0%
Epon 828/DDS	386.5	392.2	401.8	407.1	414.3	421.4	3.1%	0%
Epon 828/DDE	352.3	368.3	375.0	381.7	397.3	419.6	16.7%	0%

Note: Heating rate = 10°C/min.

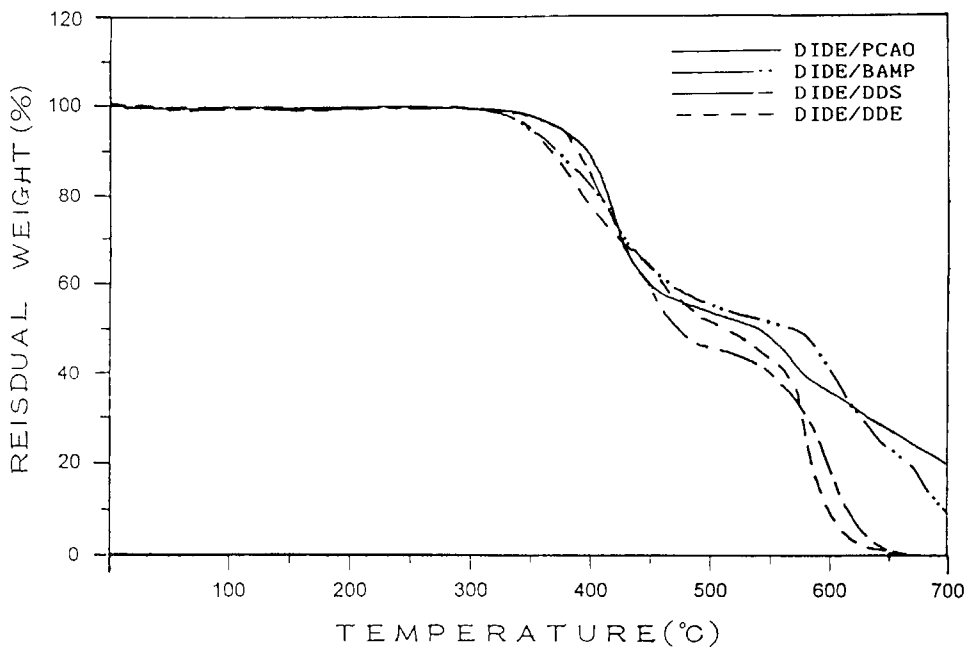
radiation rate than the DDS and DDE compositions. From group (3) and (4), it is found that PCAO compositions show similar PDT to that of BAMP composition; but the PCAO composition has a slower thermal degradation rate than BAMP, DDS, and DDE compositions. In our previous research, we found that the PDT of phosphorylated polymers were lower than those of non-phosphorylated polymers. From the above results, we found that PCAO compositions that contain cyclic phosphine oxide groups demonstrated adequate PDT properties as compared with commercial products of curing agents, DDS and DDE.

### Flame Properties

The oxygen index is commonly used a measurement of the flame retardancy of a material. Van Krevelen<sup>10</sup> has proposed that the char residue on pyrolysis is linearly proportional to the oxygen index for halogen-free polymers. Increased char formation can limit the production of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, and decrease the thermal conductivity of the surface of a burning material.<sup>11</sup> In order to demonstrate the properties of the flame retardancy of this cyclic phosphine oxide diacid curing



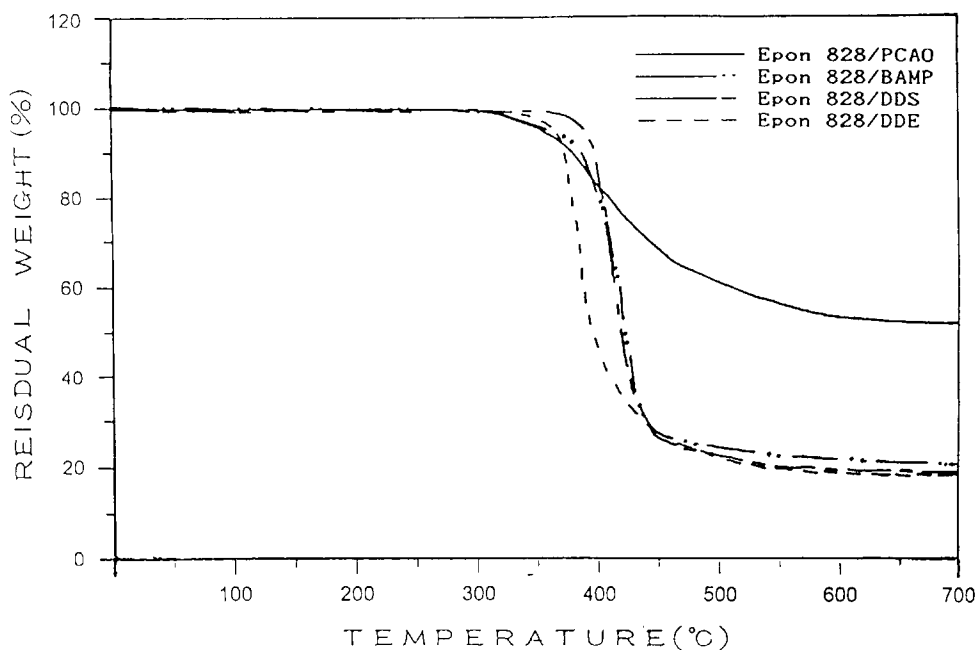
**Figure 2** TGA thermograms of DIDE/PCAO, DIDE/BAMP, DIDE/DDS, and DIDE/DDE in a nitrogen environment. The heating rate is 10°C/min.



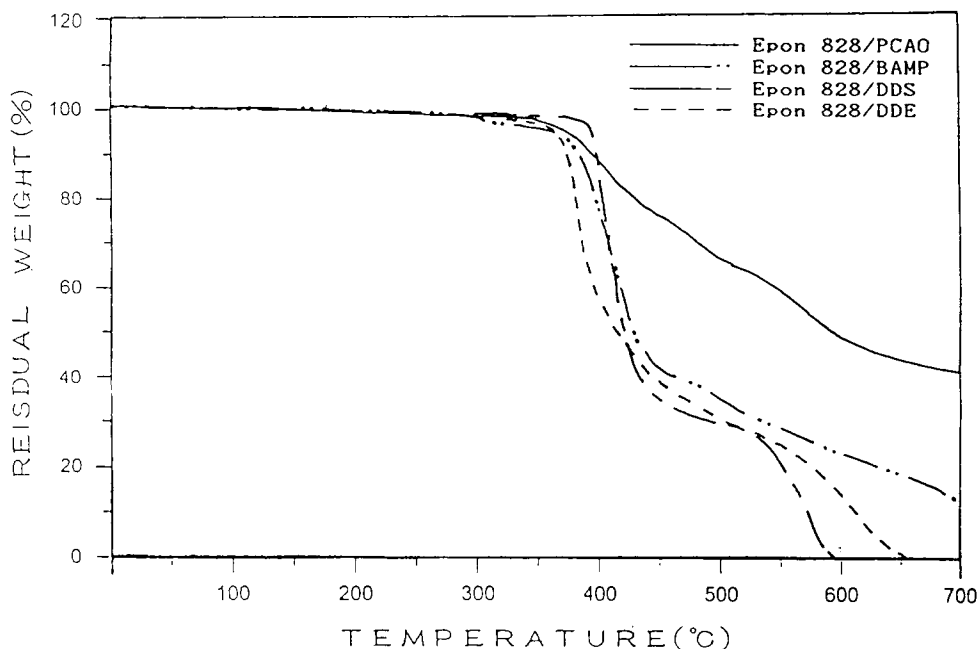
**Figure 3** TGA thermograms of DIDE/PCAO, DIDE/BAMP, DIDE/DDS, and DIDE/DDE in an air environment. The heating rate is 10°C/min.

agent, these cured polymers are divided into four groups: (1) DIDE/PCAO, DIDE/BAMP; (2) DIDE/PCAO, DIDE/DDS, DIDE/DDE; (3) Epon 828/PCAO, Epon 828/BAMP; and (4) Epon 828/PCAO, Epon 828/DDS, Epon 828/DDE. Char yields of these cured polymers in air are shown in Figures 3

and 5. The char yields at characteristic temperatures of 600 and 700°C are listed in Table IV. For group (1), the cyclophosphorus-containing polymer, DIDE/PCAO, has a higher char yield than the other polymer, DIDE/BAMP, which contains linear phosphorus groups. For group (2), the cyclophos-



**Figure 4** TGA thermograms of Epon 828/PCAO, Epon 828/BAMP, Epon 828/DDE, and Epon 828/DDS in a nitrogen environment. The heating rate is 10°C/min.



**Figure 5** TGA thermograms of Epon 828/PCAO, Epon 828/BAMP, Epon 828/DDE, and Epon 828/DDS in an air environment. The heating rate is 10°C/min.

phorus-containing polymer DIDE/PCAO, has a higher char yield than the other two non-phosphorylated polymers, DIDE/DDS and DIDE/DDE. For group (3), the cyclophosphorus-containing polymer, Epon 828/PCAO, has a higher char yield than the other polymer, Epon 828/BAMP, which contains linear phosphorus groups. For group (4), the cyclophosphorus-containing polymer has a higher char yield than the other two non-phosphorylated polymers, Epon 828/DDS and Epon 828/DDE. From the above results, we have found that the newly synthesized cyclic phosphine oxide epoxy polymers, DIDE/PCAO and Epon 828/PCAO, demonstrated a higher char yield.

## CONCLUSION

The structure of the synthesized cyclic phosphine oxide diacid curing agent (PCAO) was confirmed through EA and IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopy characterizations. The PCAO compositions demonstrated adequate thermal properties when compared with the BAMP, DDS, and DDE composition. The flame retardancy of the epoxy resins was confirmed in this study as capable of being significantly improved through introduction of a cyclophosphorus group into the structure of the curing agent. The cyclophosphorus-containing epoxy polymers were observed to have a higher char yield on

pholysis than non-cyclic phosphine oxide and non-phosphorylated epoxy polymers.

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