Properties of Cyclic Phosphine Oxide Epoxy Cured by Diacids and Anhydride

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ABSTRACT: New phosphorylated epoxy polymers were obtained with a cyclic phosphine oxide epoxy, 10-phenylphenoxaphosphine-3,8-diglycidylester-10-oxide (EPCAO), cured with three types of curing agents: *N*,*N'*-(4,4'-diphenylsulfone)bis(trimellitimide) (DIDA), 10-phenylphenoxaphosphine-3,8-dicarboxylic acid-10-oxide (PACO), and phthalic anhydride (PA). In addition, compositions of the new EPCAO synthesized with these three curing agents (DIDA, PACO, and PA) were used to make a comparison of EPCAO's curing reactivities and heat and flame retardancy with those of Epon828 and DEN438. The reactivities were measured by differential scanning calorimetry. Through the evaluation of thermogravimetric analysis, those polymers that were obtained through the curing reactions between the cyclic phosphine oxide epoxy resin and the three curing agents mentioned also demonstrated excellent thermal properties and a high char yield. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 950–961, 2002; DOI 10.1002/app.10146

Key words: phosphorylated epoxy; flame retardance; thermal properties; char yield

INTRODUCTION

The special structures and curing methods of epoxy resins produce polymers with useful mechanical properties such as minimum shrinkage after cure and suitable weather, chemical, and thermal resistances. Epoxides can be applied industrially for molding compounds, surface coating and painting materials, matrices of composites, microelectronics-encapsulated materials, and insulating materials for electric devices, adhesives, and so on.[1,2] However, common epoxy systems cannot satisfy the demands of those field applications that require high thermal and flame resistance. Epoxy–imide polymers have received increasing attention during recent years in attempts to enhance their thermal properties.[3–9] The incorporation of halogen and/or phosphorus into the epoxy polymer skeleton can improve its flame properties. Currently, the incorporation of halogen into epoxy polymers is not preferred for environmental reasons. To avoid this problem, epoxy polymers have been modified by the introduction of phosphorus into the molecular structure, which improves its flammability properties.[10,11] According to previous investigations, nonphosphorylated epoxy polymers give about a zero char yield on pyrolysis at higher temperatures in air.[8,12] However, the incorporation of phosphorus into the epoxy polymers can produce adequate char yield on pyrolysis.

The primary objective of this study focused on improving the thermal and flame resistances of an epoxy system via structural modifications of the epoxy and curing agent. Improvement in flammability was achieved by the introduction of a phosphorus group into the structures of the epoxy and curing agent. Thermal properties were improved by the use of imide groups to modify the

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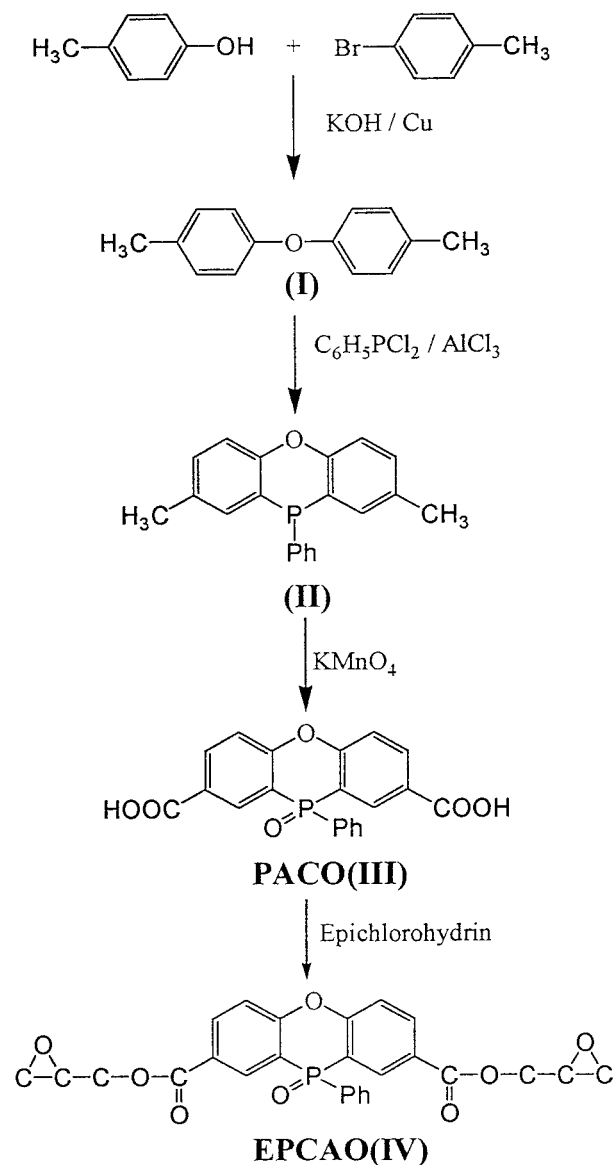
Scheme 1 Synthesis of EPCAO.

backbone structure of the curing agent. The properties of these newly synthesized phosphorylated epoxy or epoxy–imide polymers were compared with commercial products of epoxy resin: Epon828 and DEN438. These newly phosphorylated polymers demonstrated adequate thermal properties and a high char yield up to 700°C in nitrogen and ambient environments.

EXPERIMENTAL

Reagents

Benzyltrimethylammonium chloride (BTMA), 4-methylphenol, and phthalic anhydride (PA)

were reagent grade from Merck and were used without further purification; 4-Bromotoluene and phenylphosphonous dichloride were also reagent grade from Aldrich Co. and were used without further purification. Chloroform, epichlorohydrin (EPC), toluene, and pyridine were distilled at reduced pressure before use. N,N'-(4,4'-diphenylsulfone)bis(trimellitimide) (DIDA) was prepared by a method described previously.[13] Epon828 and DEN438 were purchased from Shell Co. and Dow Chemical Co., respectively.

### Synthesis of 4,4'-Dimethyldiphenyl Ether (I)

A mixture of 24.3 g of 4-methylphenol and 12.5 g of potassium hydroxide was heated to 130°C for 30 min and then cooled to 90°C, at which point 21.4 g of 4-bromotoluene was added in one batch; 0.15 g of copper powder was added, and the mixture was brought to reflux. After 4 h, the reaction mixture was cooled and treated with 20% sodium hydroxide dissolved in 200 mL of water. The chloroform solution was washed with water, and chloroform was removed on a steam bath. The residual solid was purified by column chromatography, with an eluent system of n-hexane. The product was a white crystalline solid with a melting temperature (T_m) of about 43°C.

Synthesis of 3,8-Dimethyl-10-phenylphenoxaphosphine (II)

A mixture of 9.9 g of **I**, 24.82 g of phenylphosphonous dichloride, and 8.52 g of aluminum chloride was stirred at 130°C for 2 h and then poured into ice water. The precipitate was washed, filtered off, and dissolved in chloroform (200 mL) in the presence of 20% NaOH solution. The chloroform solution was washed with water and concentrated. The residue was purified by column chromatography with an eluent system of hexane/acetone (6/4), The product was a colorless crystalline solid ($T_m \sim$ 190°C).

Synthesis of 10-Phenylphenoxaphosphine-3,8-dicarboxylic acid-10-oxide (PACO, III)

A solution of $KmnO_4$ (22.75 g) in water (100 mL) was gradually added to a stirred solution of **II** (3.20 g) in pyridine (150 mL) and H_2O (50 mL) containing NaOH (1.27 g) at 90°C. The mixture was refluxed for 3 h. Manganese dioxide was filtered off, and pyridine was removed by vacuum distillation. $KMnO_4$ (5.25 g) in H_2O (50 mL) was added to the aqueous solution, and the mixture

EPCAO

Epon 828

DEN 438

DIDA

PACO

PA
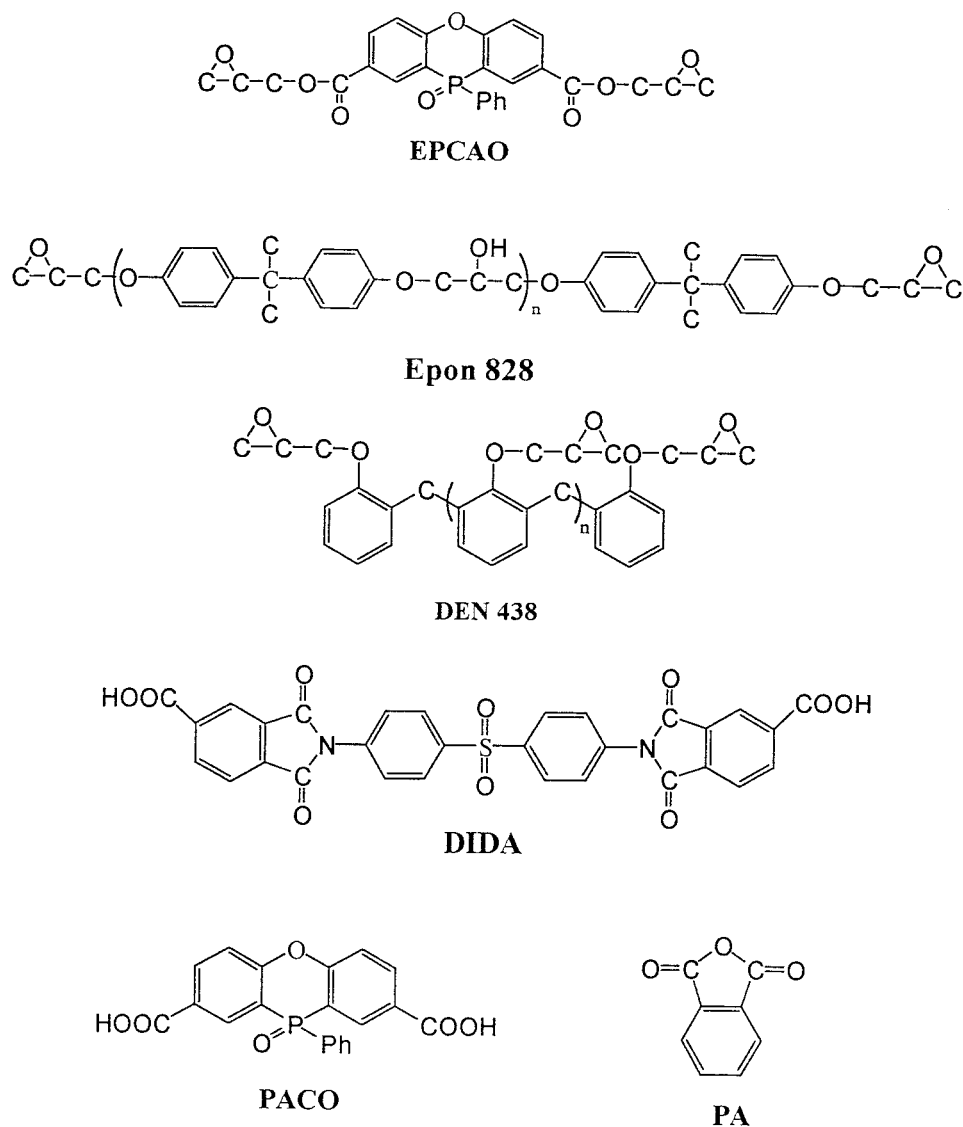
Scheme 2 Structures of various epoxy resins and curing agents.

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

Table I EA Data

Material	C (%)		H (%)	
	Exp	Calculated	Exp.	Calculated
I	84.97	84.73	7.18	7.11
II	78.96	75.09	5.55	5.60
III	63.18	63.18	3.38	3.83
IV	63.45	61.12	4.19	4.10

H_2O and recrystallized from acetic acid. The product was a white crystalline solid ($T_m \sim 350°C$).

Synthesis of 10-Phenylphenoxaphosphine-3,8-diglycidylester-10-oxide (EPCAO, IV)

A mixture of PACO (3.71 g) and EPC (100 mL) was heated to 90°C. Solid BTMA (0.785 g) was added, and the mixture was heated to 120°C. The degree of reaction was measured by thin layer chromatography (TLC) with a mobile phase of hexane/acetone (5/5). The process was completed in 1.5 h.

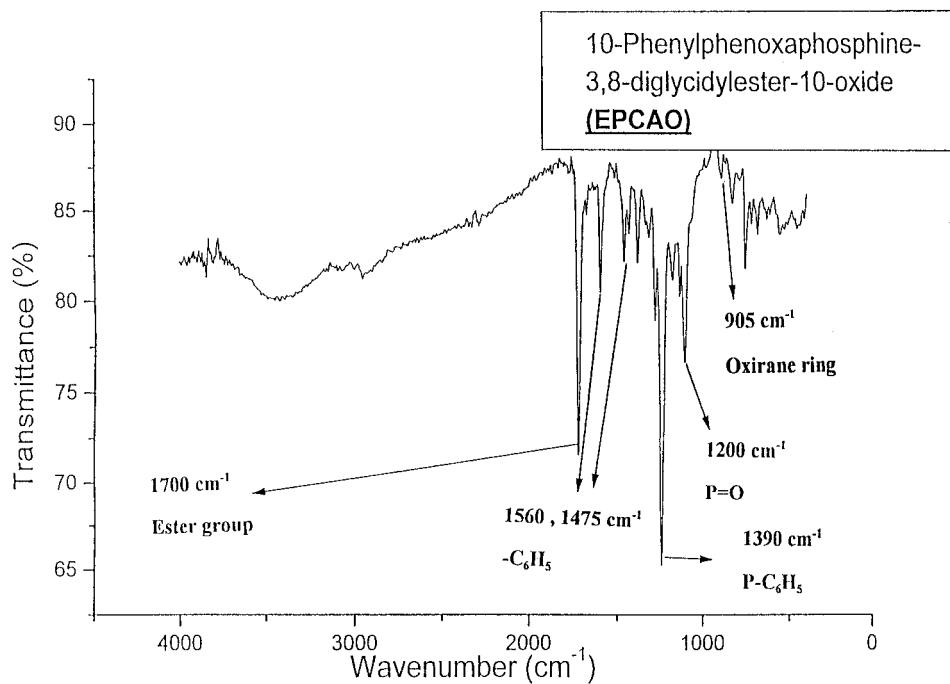The mixture was then cooled to room temperature and washed with water twice. The un-
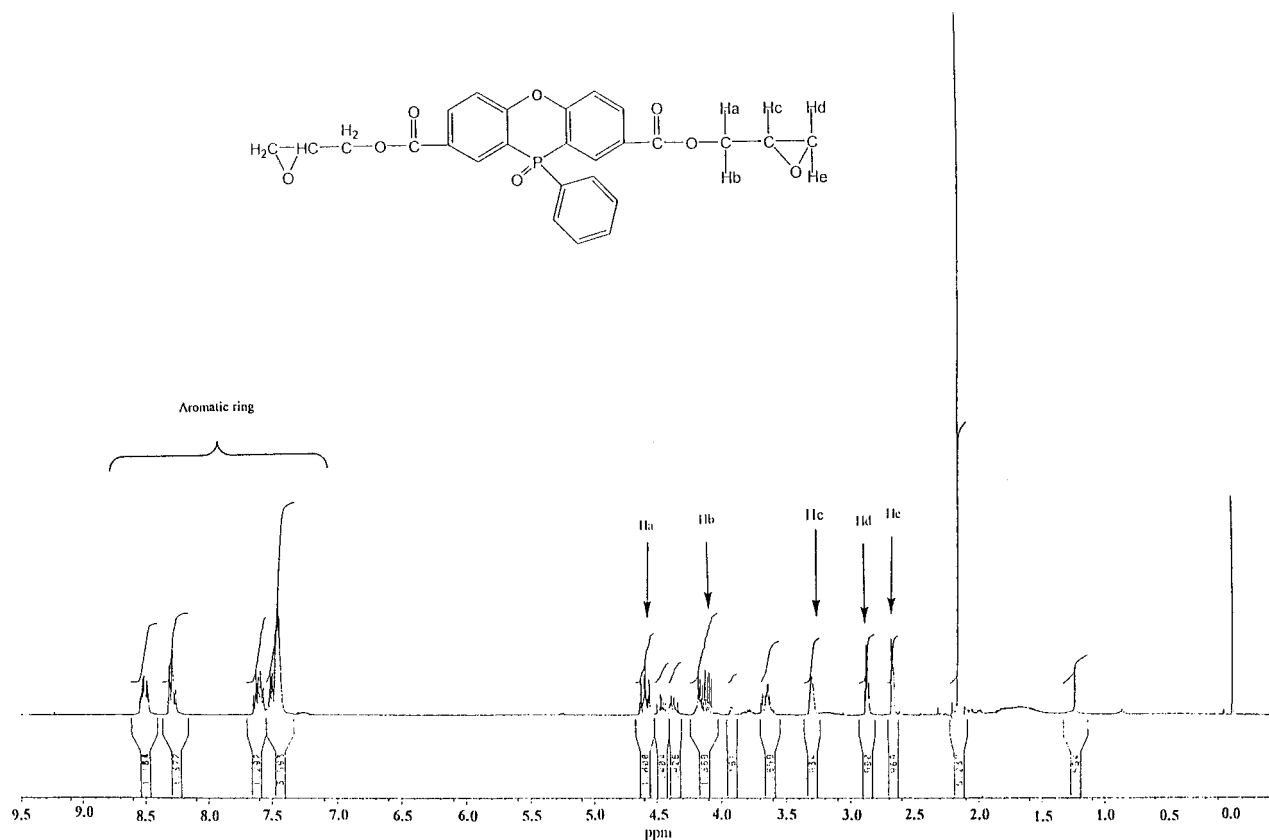
Figure 1 IR spectrum of EPCAO.

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

Table II   ¹H-NMR Data for EPCAO

	Type of Proton					
	Ha	Hb	Hc	Hd	He	Aromatic
Chemical shift (ppm)	4.57 (2H,m)	4.09 (2H,m)	3.28 (2H,m)	2.85 (2H,m)	2.65 (2H,m)	7.24–8.40 (11H,m)

changed EPC was removed from the organic phase by distillation under nitrogen and at reduced pressure. Some toluene was added to the residue, and the remaining EPC was removed as the toluene azeotrope by distillation. The obtained product was purified with column chromatography with the same eluent solvent as TLC, yielding a T_m near 121°C and an epoxy equivalent of 242 g/equiv (calculated 246 g/equiv). The product was a light yellow crystalline solid.

Characterization and Measurements

T_m's were determined by a Yanaco Mp-S3. IR spectra were examined with a PerkinElmer model 2000. Elemental analyses were carried out on a Heraeus CHN—O rapid analyzer. ¹H-NMR and ¹³C-NMR spectra were obtained from a Bruker AMX-400, where samples were dissolved in D-chloroform and DMSO-d₆ with TMS 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 thermogravimetric analysis (TGA) on a TA 2050 with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The cyclic phosphine oxide epoxy, EPCAO, was obtained through the following four synthetic
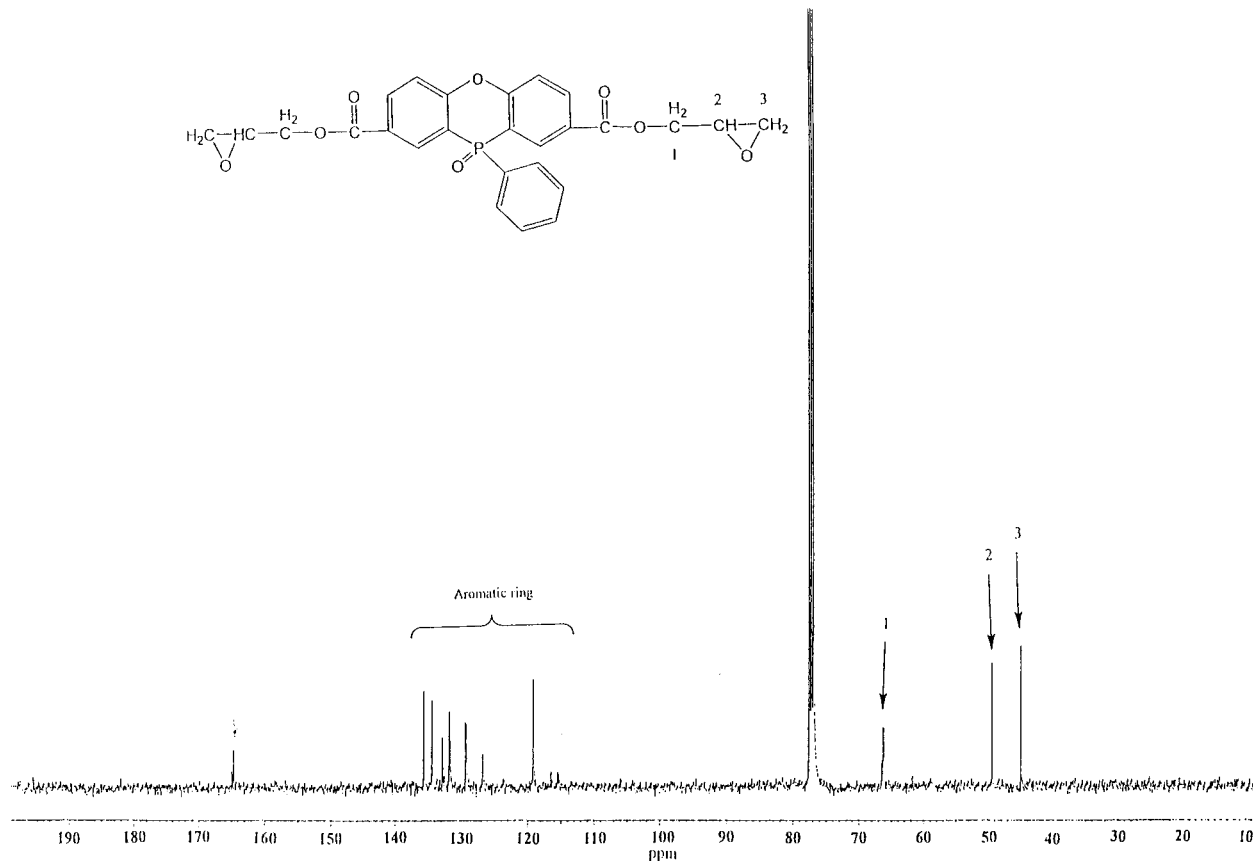
Figure 3   ¹³C-NMR spectrum of EPCAO.

Table III ^{13}C-NMR Data for EPCAO

	Type of Carbon				
	C1	C2	C3	Aromatic	Carbonyl
Chemical shift (ppm)	66.11	49.23	44.77	118.92–135.25	164.43

steps: syntheses of **I**, **II**, and PACO (**III**), and esterification of PACO, according to Scheme 1. The chemical structure of the cyclic phosphine oxide epoxy, EPCAO, was characterized by elemental analysis (EA), IR spectroscopy, and ^{1}H-NMR and ^{13}C-NMR spectroscopies. The structures of Epon828, DEN438, DIDA, and PA are listed in Scheme 2.

Identification of EPCAO

The data of EA are listed in Table I. EAs of these compounds were in good agreement with the calculated values. The IR spectrum is shown in Figure 1. The peak 1730 cm^{-1} represents the absorption of ester group. Absorptions arising because of P=O at 1200 cm^{-1}, P—C$_6$H$_5$ at 1390 cm^{-1}, and —C$_6$H$_5$ at 1560 and 1475 cm^{-1} were also observed. The characteristic band of the oxirane ring was observed at 905 cm^{-1}. The^{1}H-NMR spectrum in D-chloroform is shown in Figure 2. The chemical shifts of characterized protons in EPCAO are listed in Table II; these are based on the assigned labels of protons shown in Figure 2. Aromatic ring protons were found at $\delta = 7.24-8.40$ ppm. Ha and Hb of methylene were also observed at 4.57 and 4.09 ppm (2H,m). Hc, Hd, and He of oxirane ring were assigned at 3.28, 2.85, and 2.65 ppm (2H,m), respectively. The ^{13}C-NMR spectrum of EPCAO is

shown in Figure 3. The resonance lines in the spectrum fell into three main regions: 44.77–66.11 ppm for the aliphatic carbons, 118.92–135.25 ppm for aromatic carbons, and 164.43 ppm for the carbonyl carbons of the ester group. The chemical shifts of characterized carbons in EPCAO are listed in Table III; these are based on the assigned labels of carbons in Figure 3. The synthesized cyclic phosphine oxide epoxy was confirmed to be EPCAO, as shown from EA, IR, ^{1}H-NMR, and ^{13}C-NMR studies.

Preparation of Polymers

The thermal- and fire-retardant properties of the phosphorylated epoxy, phosphorylated epoxy–imide, nonphosphorylated epoxy, and nonphosphorylated epoxy–imide polymers were evaluated by preparing nine polymers (i.e., EPCAO/DIDA, Epon828/DIDA, DEN438/DIDA, EPCAO/PACO, Epon828/PCAO. DEN438 /PACO, EPCAO/PA, Epon828/PA, and DEN438/PA). To obtain a highly crosslinked polymer with good thermal stability, a single equivalent weight of the epoxy was polymerized with 0.25 mol of curing agent. Curing cycles were determined by DSC thermograms. These compositions and the curing cycles of the polymers are listed in Table IV.

Table IV   Curing Cycles of Several Epoxy Systems

| Compositions	Curing Temperature (°C)	Curing Time (min)	Postcure Temperature (°C)	Postcure Time (min)
EPCAO/DIDA	145	50	180	40
EPCAO/PACO	175	70	207	20
EPCAO/PA	125	50	167	20
Epon828/DIDA	140	50	185	30
Epon828/PACO	175	55	227	40
Epon828/PA	130	90	178	30
DEN438/DIDA	138	45	185	25
DEN438/PACO	175	55	230	35
DEN438/PA	106	55	178	25
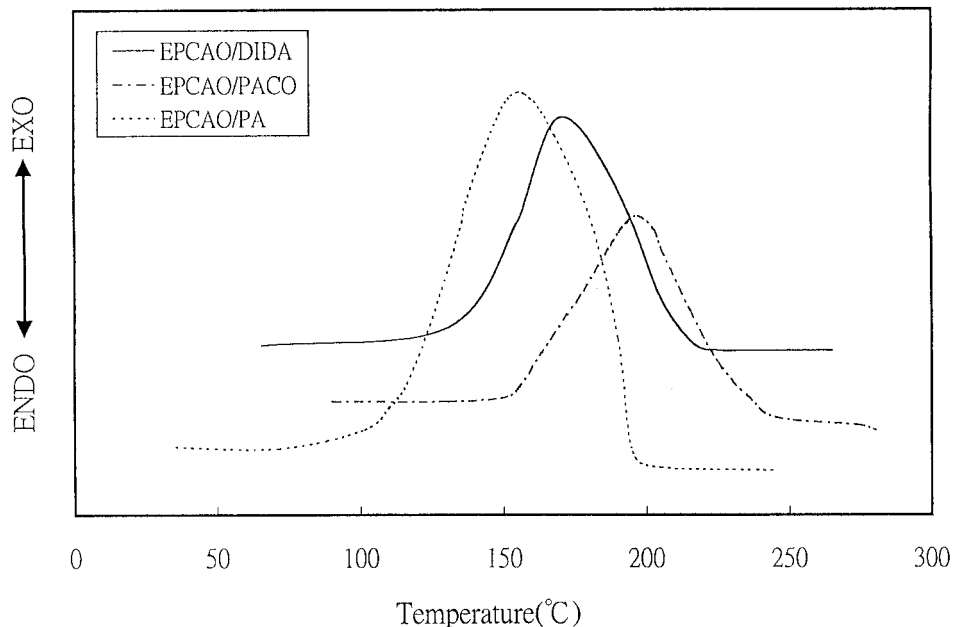
Figure 4 DSC thermograms of three compositions : EPCAO/DIDA, EPCAO/ PACO, and EPCAO/PA (heating rate = 10°C/min).

Reactivities of Epoxy and Curing Agents

The polymerization reactions were studied by DSC. Significant caution was taken during the DSC study of the polymerization reactions to obtain homogenous mixtures of the epoxy and curing agents. Typical DSC thermograms (Figs. 4–6) demonstrated the reactivities of the curing agents (DIDA, PACO, and PA) toward the epoxies (EPCAO, Epon828, and DEN438). The influence of the chemical reactivity of the curing agent on cure
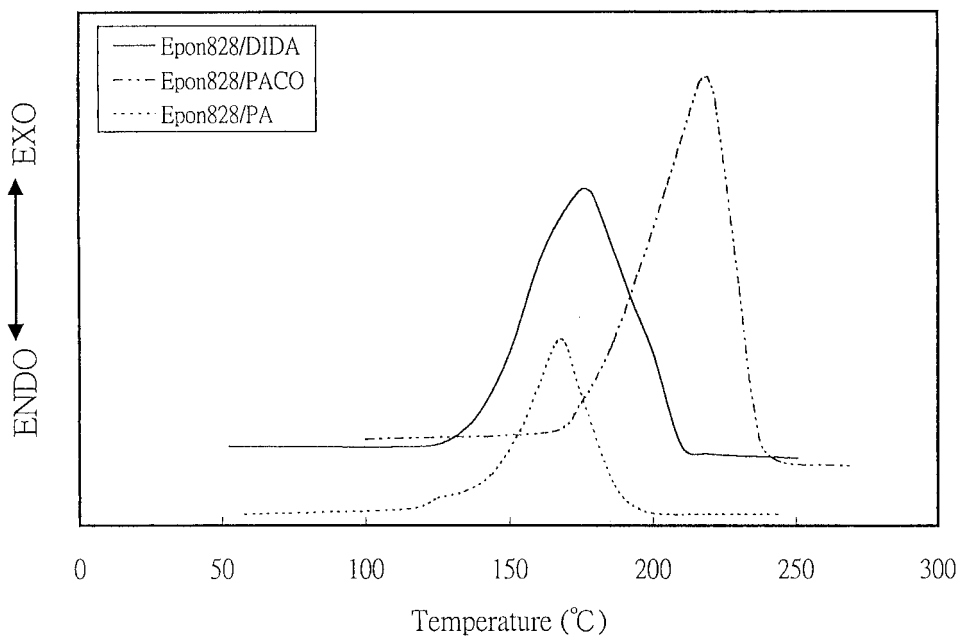
Figure 5 DSC thermograms of three compositions : Epon828/DIDA, Epon828/ PACO, and Epon828/PA (heating rate = 10°C/min).
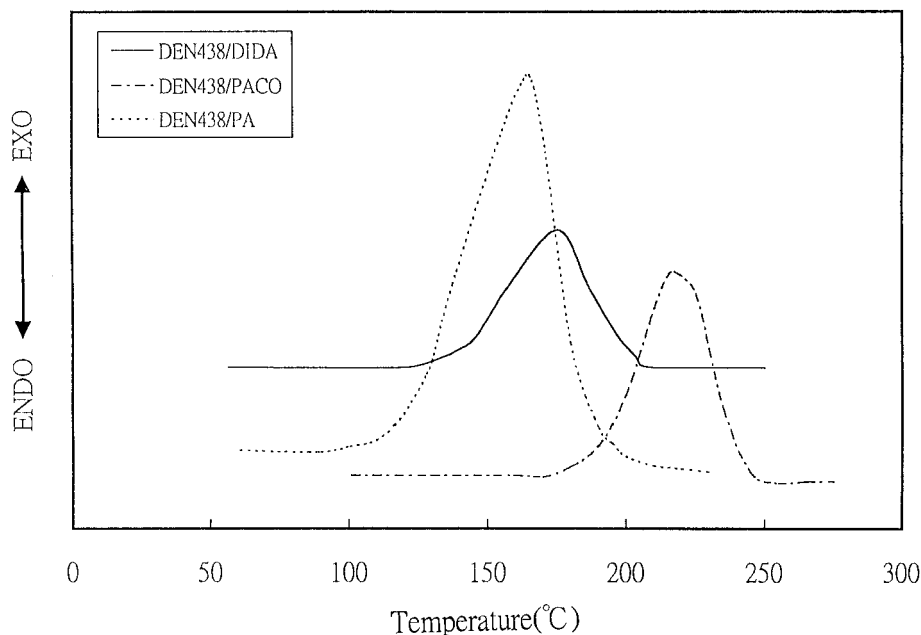
Figure 6   DSC thermograms of three compositions : DEN438/DIDA, DEN438/ PACO, and DEN438/PA (heating rate = 10°C/min).

behavior is apparent from these figures. For all the epoxies used, the exothermic starting temperature increased according to the order PA < DIDA < PACO. A curing agent that exhibited a lower exothermic starting temperature under the same set of curing conditions was more reactive toward the epoxy resins. It is, therefore, reasonable to propose that the chemical reactivities of these three curing agents toward epoxy increased as follows : PACO < DIDA < PA. The lowest reactivity of PACO toward epoxy, as compared with that of DIDA and PA, should be attributed to

electronic effects. The lower reactivity of DIDA toward epoxy, as compared with that of PA, also should be attributed to electronic effects. In the case of PACO, the electronic-withdrawing group P=O reduced the electron density of the carbonyl oxygen and, subsequently, reduced the nucleophilic attack on the oxirane ring of the epoxy resins.

Thermal and Flame Properties

To compare the thermal properties of these cured polymers, cured polymers were assigned three

Table V   TGA Data of Cured Epoxy Resins in a Nitrogen Environment

| Material | T_{max} (°C) | Temperature at Characteristic Weight Loss (°C) | | | | | Residue (%) at 700°C |
		10%	20%	30%	40%	50%	
EPCAO/DIDA	425.2	270.1	378.1	417.1	512.5	618.75	47.1
EPCAO/PACO	418.5	376.6	405.5	429.7	442.2	481.2	40.9
EPCAO/PA	380.6	354.7	367.2	381.2	406.2	423.4	32.1
Epon828/DIDA	435.1	375.0	409.6	426.6	470.3	537.5	36.2
Epon828/PACO	414.9	379.7	403.1	415.6	439.1	509.3	39.9
Epon828/PA	399.5	359.4	375.0	384.3	390.6	396.8	0
DEN438/DIDA	468.3	373.4	415.6	473.4	537.4	614.1	46.0
DEN438/PACO	420.6	393.8	418.7	514.1	559.3	700.0	53.8
DEN438/PA	394.5	323.4	368.8	382.8	390.4	396.9	8.8

Heating rate = 10°C/min.

Table VI   TGA Data of Cured Epoxy Resins in an Air Environment

| Material	T_{max} (°C)	Temperature at Characteristic Weight Loss (°C)					Residue (%) at 700°C
		10%	20%	30%	40%	50%	
EPCAO/DIDA	536.0	355.1	389.1	421.9	509.4	570.3	10.4
EPCAO/PACO	415.5	365.6	407.8	426.6	443.8	501.0	33.4
EPCAO/PA	380.2	353.1	365.6	378.1	400.0	418.7	24.2
Epon828/DIDA	526.5	356.2	398.4	425.0	504.7	560.9	1.1
Epon828/PACO	435.2	378.1	403.1	443.8	520.3	543.7	22.64
Epon828/PA	387.5	331.2	367.2	381.3	389.1	396.8	0
DEN438/DIDA	568.5	376.5	440.6	521.8	562.5	579.7	3.8
DEN438/PACO	476.6	396.9	476.6	543.6	560.9	596.8	7.4
DEN438/PA	393.1	357.9	389.1	400.0	412.5	493.8	0

Heating rate = 10°C/min.

groups : (1) EPCAO/DIDA, EPCAO/PACO, and EPCAO/PA; (2) Epon828/DIDA, Epon828/PACO, and Epon828/PA; and (3) DEN438/DIDA, DEN438/PACO, and DEN438/PA. To demonstrate the thermal properties of these cured polymers, the maximum temperature (T_{max}) and temperatures of some characteristic weight losses are listed in Tables V and VI and are also shown in Figures 7–12. The cyclic phosphine oxide epoxy–imide polymer (EPCAO/DIDA) and nonphosphorylated epoxy–imide polymer (Epon828/DIDA, DEN438/DIDA) demonstrated adequate thermal properties that were comparable with other phosphorylated epoxy and nonphosphorylated epoxy polymers. The phosphorus-containing epoxy and epoxy–imide polymers had slower thermal degradation rates than the non-phosphorus-containing epoxy and epoxy–imide polymers. Therefore, the thermal stability and thermal oxidative stability were improved via introduction of cyclophosphorus and imide groups into the structure of the epoxy. The synthesized cyclic phosphine oxide epoxy (EPCAO) and acidic curing agent (PACO) containing 6.3 and 8.5% phosphorus, respectively,
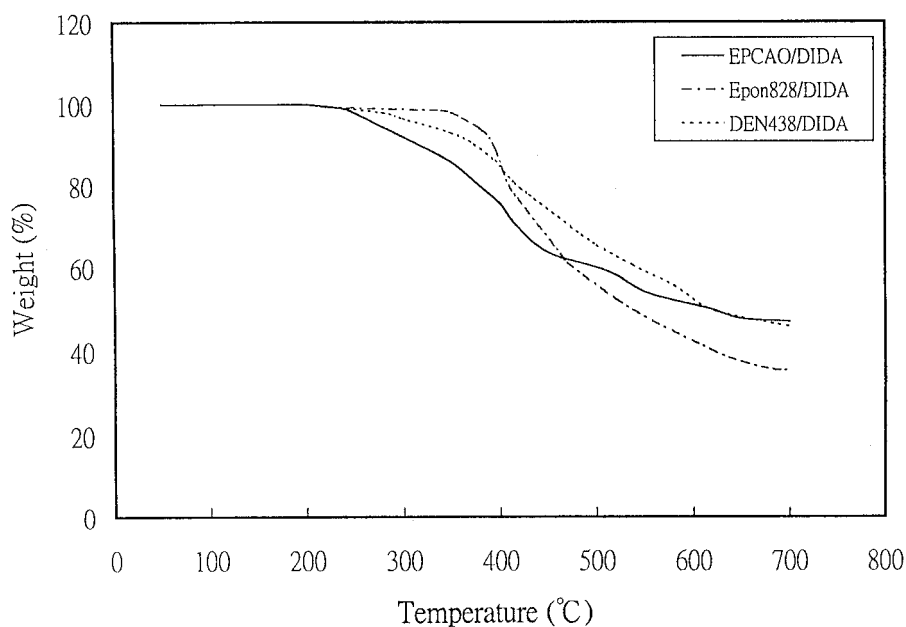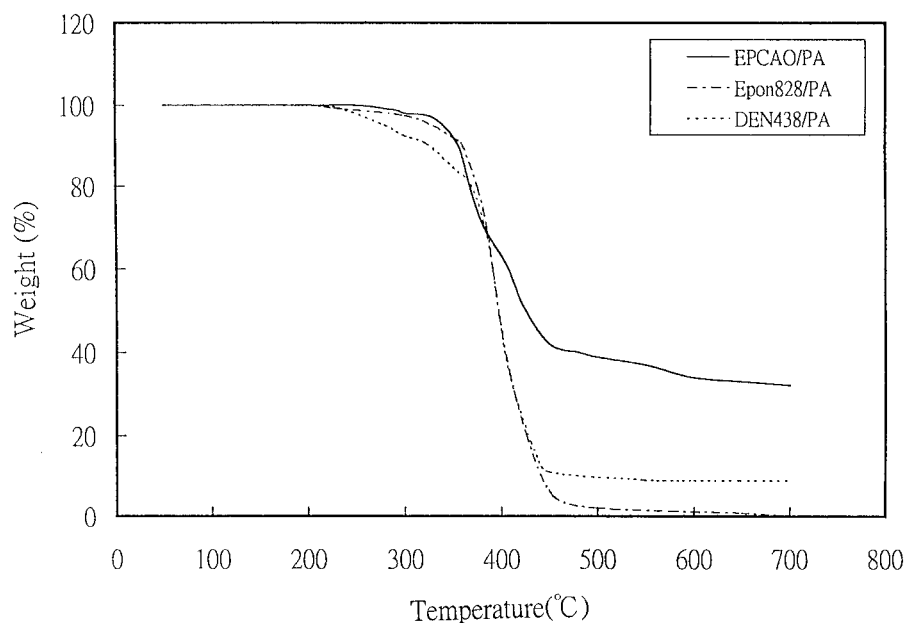

Figure 7   TGA thermograms of EPCAO/DIDA, Epon828/DIDA, and DEN438/DIDA in a nitrogen environment (heating rate = 10°C/min).
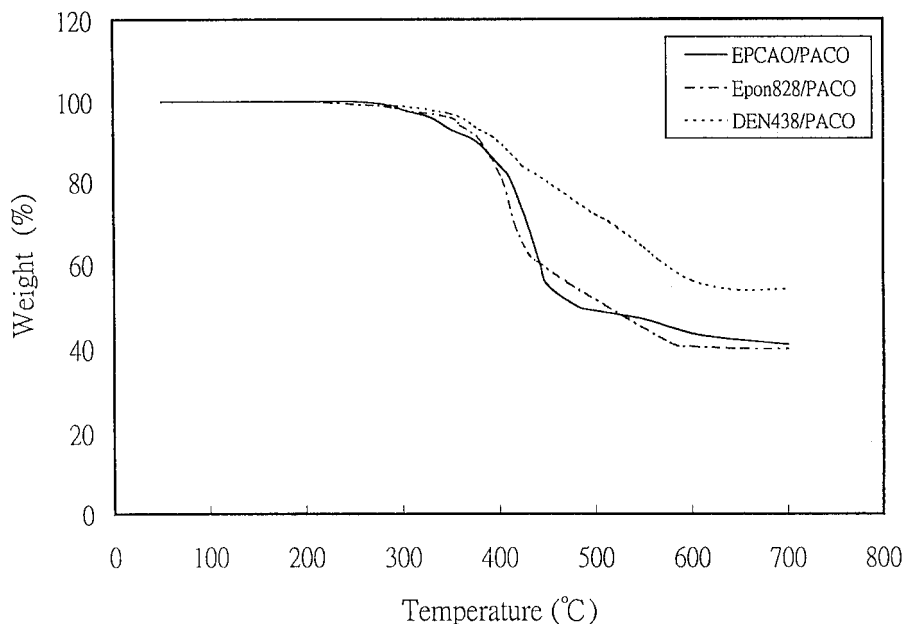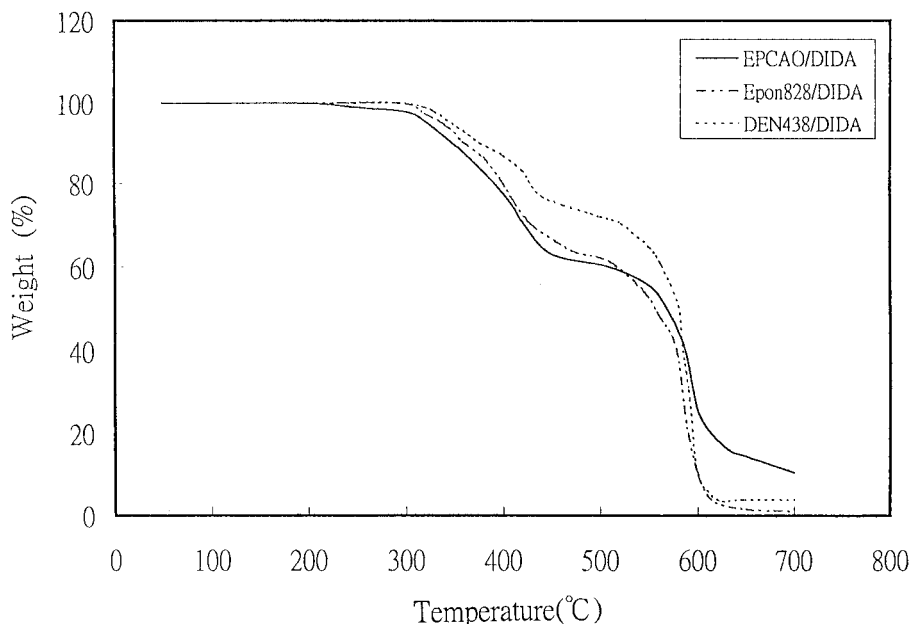
Figure 8   TGA thermograms of EPCAO/PACO, Epon828/PACO, and DEN438/PACO in a nitrogen environment (heating rate = 10°C/min).

were expected to have a higher solid char residue on pyrolysis. The oxygen index is commonly used as a measurement of the flame retardancy of material. Van Krevelen[14] proposed that the char residue on pyrolysis is linearly proportional to the oxygen index for halogen-free polymers. In-

creased 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.[15] To demonstrate the properties of flame retardancy, these cured polymers
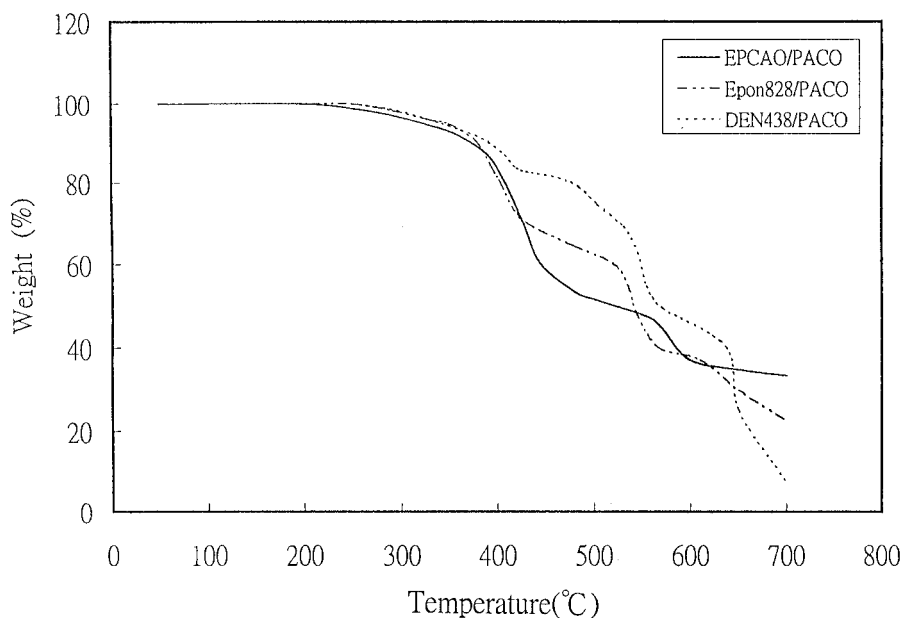

Figure 9   TGA thermograms of EPCAO/PA, Epon828/PA, and DEN438/PA in a nitrogen environment (heating rate = 10°C/min).
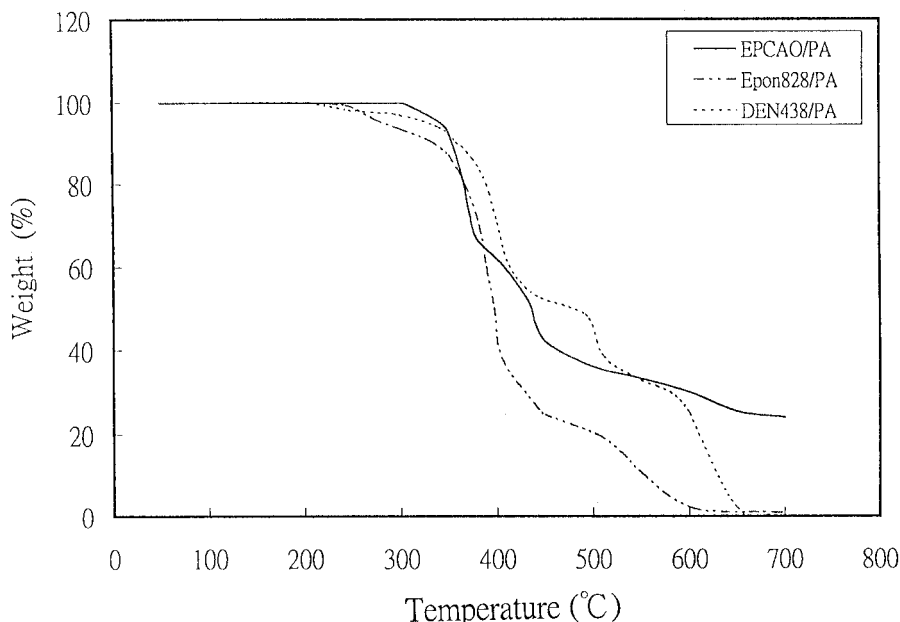
Figure 10   TGA thermograms of EPCAO/DIDA, Epon828/DIDA, and DEN438/DIDA in an air environment (heating rate = 10°C/min).

were divided into three groups : (1) EPCAO/DIDA, Epon828/DIDA, and DEN438/DIDA; (2) EPCAO/PACO, Epon828/PACO, and DEN438/PACO; and (3) EPCAO/PA, Epon828/PA, and DEN438/PA. The char yields of these cured polymers in nitrogen and air are shown in Figures

7–12. The char yields at characteristic temperatures of 600 and 700°C are listed in Tables V and VI. For Group 1, the cyclophosphorus-containing polymer that had the highest phosphorus content, EPCAO/DIDA, had a higher char yield than the other two polymers, Epon828/DIDA and DEN438/

Figure 11   TGA thermograms of EPCAO/PACO, Epon828/PACO, and DEN438/PACO in an air environment (heating rate = 10°C/min).

Figure 12 TGA thermograms of EPCAO/PA, Epon828/PA, and DEN438/PA in an air environment (heating rate = 10°C/min).

DIDA. For Group 2, the cyclophosphorus-containing polymer that had the highest phosphorus content (EPCAO/PACO) had a higher char yield than the other two polymers, Epon828/ PACO and DEN438/PACO. For Group 3, the cyclophosphorus-containing polymer, EPCAO/PA, had a higher char yield than the other two polymers, Epon828/PA and DEN438/PA. From these results, we found that the phosphorus-containing polymers produced a higher char yield.

CONCLUSIONS

The structure of the synthesized cyclic phosphine oxide epoxy (EPCAO) was confirmed by EA, IR, ^{1}H-NMR, and ^{13}C-NMR characterizations. The synthesized EPCAO cured with DIDA, PACO, or PA curing agents showed slower thermal degradation rates than Epon828 and DEN438 resins cured with the same curing agents. The flame retardancy of the epoxy resins was confirmed in this study as capable of being significantly improved through the introduction of a cyclophosphorus group into the epoxy structure. The cyclophosphorus-containing epoxy polymers were observed to have a higher char yield on pyrolysis than nonphosphorylated epoxy polymers.

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