

Structure Characterization, Reactivity, and Thermal Properties of New Cyclic Phosphine Oxide Epoxy Resin Containing Tetra-Oxirane Rings

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Received 3 June 1997; accepted 2 November 1997

ABSTRACT: A new type of epoxy resin, which contained cyclic phosphine oxide and tetra-oxirane rings in the main chain, was synthesized. The structure of the new type of epoxy resin was confirmed by elemental analyses (EA), infrared (IR) spectroscopy, and ^1H nuclear magnetic resonance (NMR) and ^{13}C -NMR spectroscopies. In addition, compositions of the new synthesized cyclic phosphine oxide epoxy resin (TGCAO) with three curing agents, for example, bis(3-aminophenyl)ethylphosphine oxide (BEMP), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenylsulfone (DDS) were used for making a comparison of its curing reactivity, heat, and flame retardancy with those of Epon 828 and DEN438. The reactivities were measured by differential scanning calorimetry. Through the evaluation of thermal gravimetric analysis, those polymers, which were obtained through the curing reactions between the new epoxy resin and three curing agents (BEMP, DDM, and DDS), also demonstrated adequate thermal properties, as well as a high char yield. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1397–1409, 1998

Key words: cyclic phosphine oxide epoxy resin; tetra-oxirane rings; thermal stability; flame retardancy; char yield

INTRODUCTION

Due to the rapid development of electronic materials in aerospace in the past years, it is crucial to improve the flame and thermal resistances of epoxy polymers. There have been many ways for improving flame properties of epoxy polymers, such as the addition of fire retardant agents or the use of fire retardant epoxy resins or curing agents. Modification of the backbone of epoxy resins or curing agents have received increasing attention during recent years in order to enhance

flame retardancy.^{1,2} It is found that the thermal properties of the epoxy polymers can be improved by introducing heterocyclic rings into the backbone of polymers.^{3–6} However, Rao⁷ pointed out that the thermal stability was decreased as the flame resistance increased in polymer materials. According to our previous research,⁸ it was found that the introduction of phosphorus and heterocyclic rings into the epoxy polymers can improve the thermal and fire resistance stability.

The primary objective of this study focuses on improving the thermal and flame resistance of epoxy polymers by structural modification. The thermal resistance of epoxy resin is improved in this study using cyclic phosphine oxide groups to modify the backbone structure of epoxy resin. The improvement of flame resistance of epoxy polymers is achieved by introducing the phosphorus group into the epoxy resin (10-phenylphenoxaphosphine-

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Contract grant sponsor: The National Science Council, Republic of China; contract grant number: NSC 86-2216-E-041-003.

Journal of Applied Polymer Science, Vol. 68, 1397–1409 (1998)
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2,3,7,8-tetraglycidylester-10-oxide, or TGCAO) and the curing agent (bis(3-aminophenyl)ethylphosphine oxide, or BEMP). The properties of the newly synthesized cyclic phosphine oxide epoxy resin are compared with commercial epoxy resins, such as Epon 828 and DEN 438. It is found that the newly synthesized cyclic phosphine oxide epoxy resin demonstrate adequate thermal properties as well as high char yield.

EXPERIMENT

Reagents

Benzyltrimethylammonium chloride (BTMA), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenylsulfone (DDS) were reagent grade from Merck and used without further purification; 4-Bromo-*o*-xylene (from Aldrich Co.), phenylphosphorous dichloride (from Aldrich Co.), and 3,4-dimethylphenol (from Jassen Co.) were also reagent grade and used without further purification. Chloroform, epichlorohydrin, benzene, toluene, and pyridine were distilled at a reduced pressure before the use. BEMP was prepared by a method described previously.⁸ Epon 828 and DEN 438 were purchased from Shell Co. and Dow Chemical Co., respectively.

Synthesis of 3,3',4,4'-tetramethyldiphenylether (I)

A mixture of 52.50 g of 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. 0.30 g of copper powder was added, and the mixture was brought to reflux. After 45 min, the reaction mixture was cooled and treated with 400 mL (20%) of sodium hydroxide. The product was extracted with chloroform. The chloroform solution was washed with water and chloroform was removed on 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 mp at about 60°C.

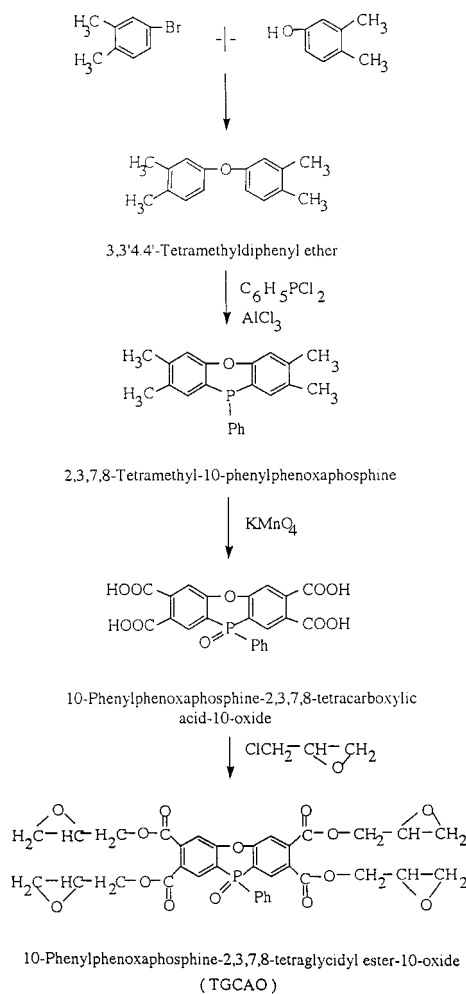
Synthesis of 2,3,7,8-tetramethyl-10-phenylphenoxaphosphine (II)

A mixture of 25.36 g of 3,3',4,4'-tetramethyldiphenylether, 54.62 g of phenylphosphonous 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 off,

and dissolved in benzene (400 mL) in the presence of 20% of aqueous sodium hydroxide. Then the benzene solution was 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. The yield was 55%, with an mp at about 245°C.

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

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_2O (80 mL) containing sodium hydroxide (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,



Scheme 1

Table I Elemental Analyses Data

Materials ^a	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
Compound III	54.96	56.41	2.44	2.78	34.25	34.16
TGCAO	57.89	58.96	4.25	4.19	32.86	32.37

^a Compound I, 3,3',4,4'-tetramethyldiphenyl ether; compound II, 2,3,7,8-tetramethyl-10-phenylphenoxaphosphine; compound III, 10-phenylphenoxaphosphine-2,3,7,8-tetracarboxylic acid-10-oxide.

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. The yield was 70%. The melting point can not be measured due to the dehydration of compound III.

Synthesis of 10-phenylphenoxaphosphine-2,3,7,8-tetraglycidylester-10-oxide

A mixture of 10-phenylphenoxaphosphine-2,3,7,8-tetracarboxylic-10-oxide (5.21 g) and epichlorohydrin (EPC, 156 mL) was heated to 90°C. The solid benzyltrimethylammonium chloride (BTMA, 0.785 g) was added with the mixture being heated to 120°C. The degree of reaction was controlled by thin layer chromatography (TLC), using a mobile

phase hexane–acetone (4/6). 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 pressure. Some toluene was added to the residue, and the remaining epichlorohydrin was removed as the toluene azeotrope by distillation. The obtained product was purified from column chromatography, with the eluent solvent system as TLC. The product was a light yellow, viscous liquid and epoxy equivalent, 169 g/equiv (calcd 173 g/equiv).

Characterization and Measurements

The melting points were determined by a Yanaco MP-S3. Infrared (IR) spectra were examined us-

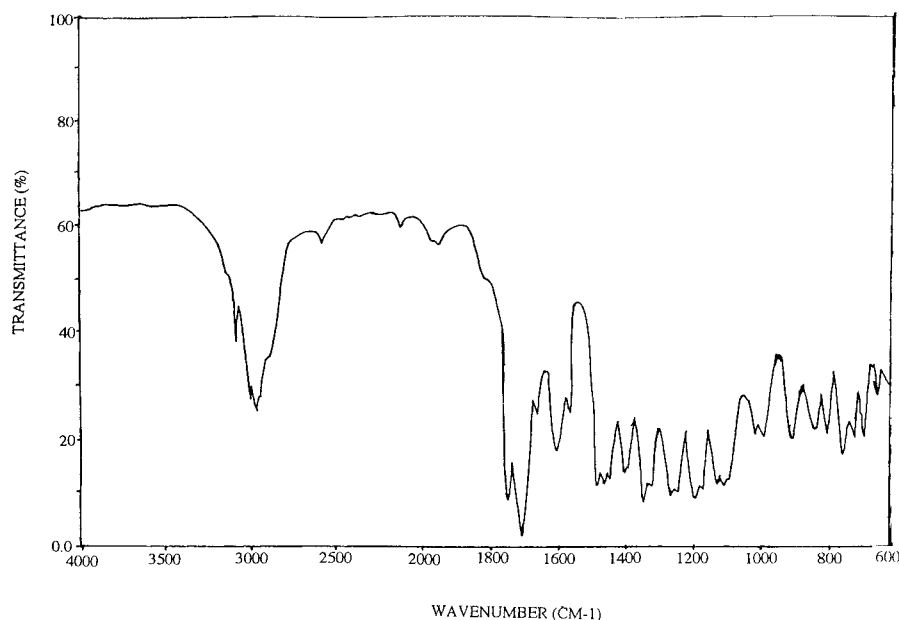


Figure 1 IR spectrum of TGCAO.

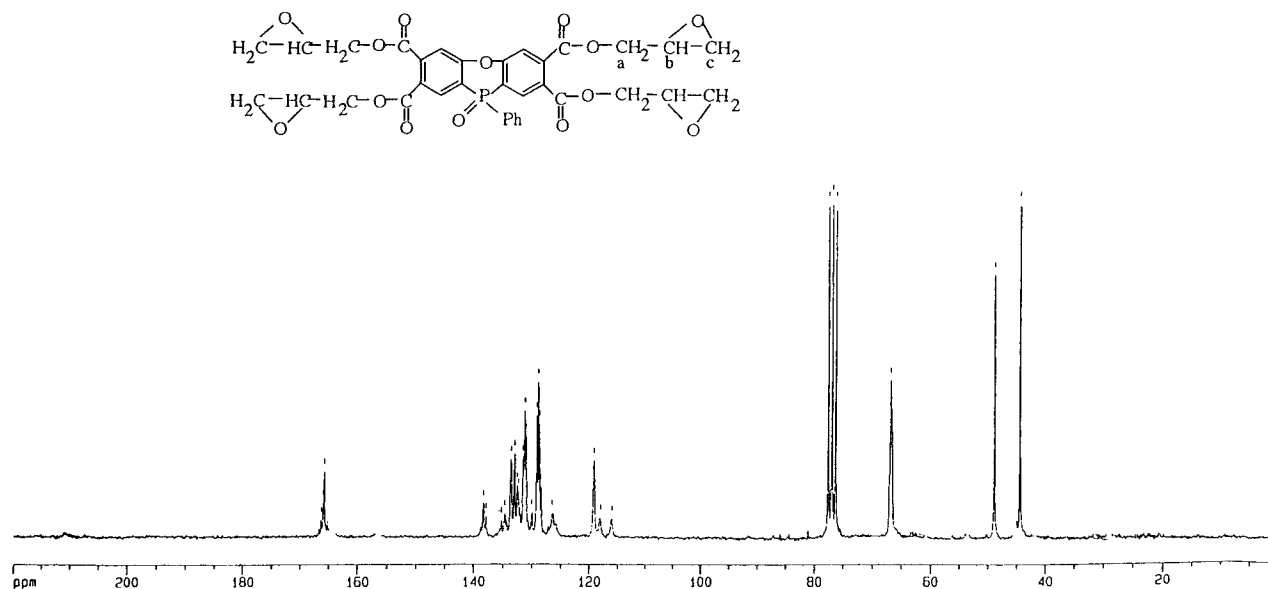


Figure 3 ^{13}C -NMR spectrum of TGCAO.

those compounds were in good agreement with the calculated values. The IR spectrum is shown in Figure 1. The peak at 1725 cm^{-1} represents the absorption of ester group. Absorptions arising because of $\text{P}=\text{O}$ at 1180 cm^{-1} , $\text{Ar}-\text{P}$ at 1375 cm^{-1} , and $-\text{Ar}$ at 1487 and 1564 cm^{-1} were also observed. The characteristic band of the oxirane ring was observed at 910 cm^{-1} .

The ^1H -NMR spectrum in *d*-chloroform is in Figure 2. The chemical shifts of characterized protons in TGCAO are listed in Table II. This is based on the assigned labels of protons shown in Figure 2. Aromatic ring protons appeared at $\delta = 7.28$ – 8.50 ppm. Ha and Hb of methylene were also observed at 4.58 (4H, m) and 4.09 ppm (4H, m). Hc, Hd, and He of oxirane ring were assigned at 3.27 (4H, m), 2.84 (4H, m), and 2.63 ppm (4H, m) respectively.

The ^{13}C -NMR spectrum of TGCAO is shown in Figure 3. The resonance lines in spectrum fall into the following three main regions: 40 – 70 ppm for the aliphatic carbons, 116 – 140 ppm for the aromatic carbons, and 166 ppm for the carbonyl carbons of the ester group. The chemical shifts of characterized carbons in TGCAO are listed in Table III. 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 cyclic phosphine oxide epoxy, phosphorylated epoxy, and nonphosphorylated epoxy poly-

mers were evaluated here by preparing nine polymers, that is, TGCAO–BEMP, TGCAO–DDM, TGCAO–DDS, Epon 828–BEMP, Epon 828–DDM, Epon 828–DDS, DEN 438–BEMP, DEN 438–DDM, and DEN 438–DDS. To obtain a highly crosslinked polymer with good thermal stability, one epoxy equivalent of the 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 IV.

Reactivities of Epoxy Resins and Curing Agents

The polymerization reactions were studied by DSC. A 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 (Figs. 4–6) demonstrate the reactivities of curing agents (BEMP, DDM, and DDS) toward epoxy resins (TGCAO,

Table III ^{13}C -NMR Data of TGCAO

Aliphatic			Aromatic	Carbonyl
a	b	c		
66.97	48.81	44.43	116.00–138.31	165.95

Table IV Curing Cycles of Several Epoxy Systems

Compositions	Curing Temperature (°C)	Curing Time (min)	Postcure Temperature (°C)	Postcure Time (min)
TGCAO-DDS	125	30	210	20
TGCAO-DDM	85	35	150	25
TGCAO-BEMP	110	35	185	20
Epon 828/DDS	130	30	230	25
Epon 828/DDM	90	35	165	20
Epon 828/BEMP	110	30	185	20
DEN 438/DDS	120	25	225	20
DEN 438/DDM	90	35	165	20
DEN 438/BEMP	110	40	180	20

Epon 828, and DEN 438). The influence of the chemical reactivity of the curing agent on cure behavior is indicated from these figures to be apparent. For all the epoxy resins used, the exothermic starting temperature increases according to the order DDM < BEMP < 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 reactivities of these three curing agents toward epoxy resins increases, as follows: DDS < BEMP < DDM. The lowest reactivity of DDS toward epoxy resins, as compared with that of BEMP and DDM, should be attributed to the electronic effects. The lower reactivity of BEMP toward epoxy

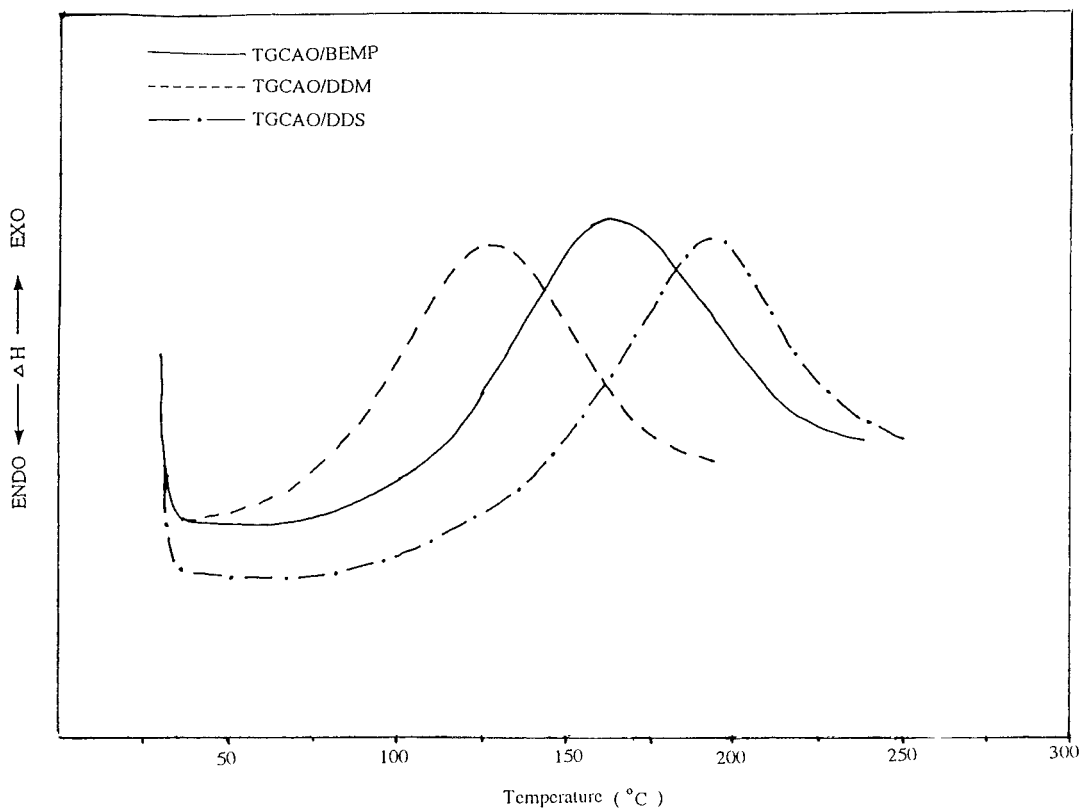


Figure 4 DSC thermograms of three compositions: TGCAO-BEMP, and TGCAO-DDM, TGCAO-DDS. Heating rate: 10°C/min.

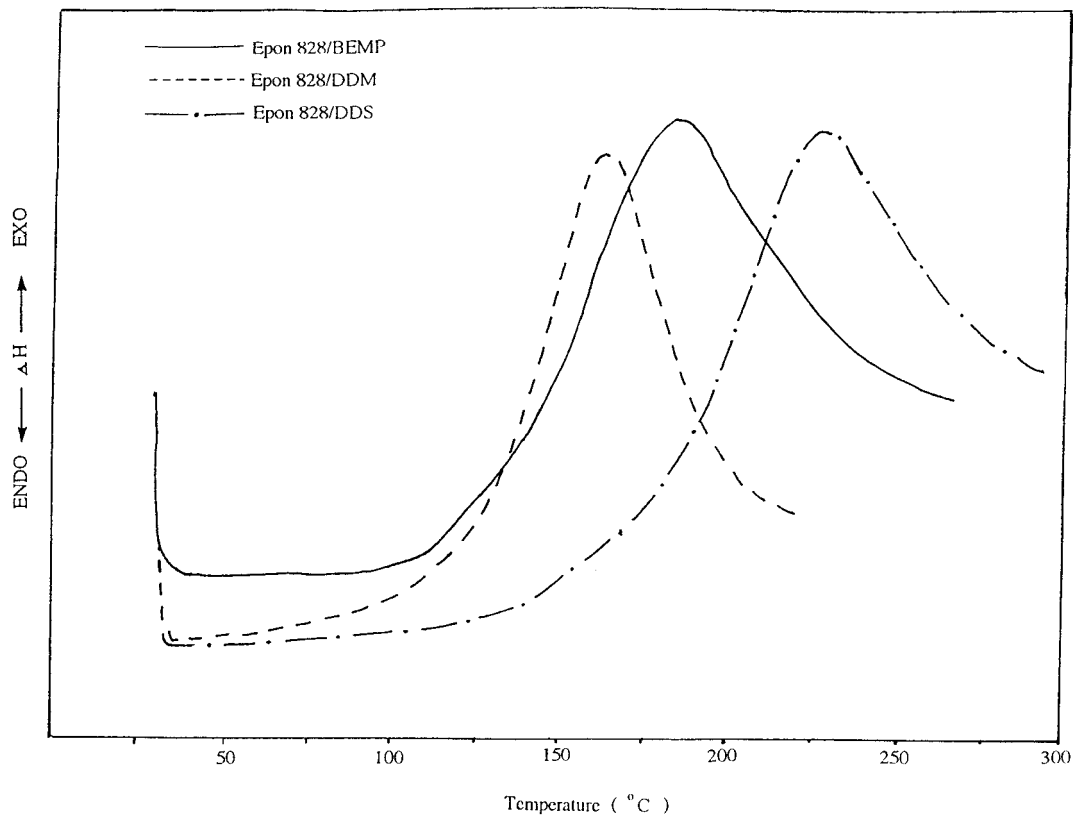


Figure 5 DSC thermograms of three compositions: Epon 828–BEMP, Epon 828–DDM, and Epon 828–DDS. Heating rate: 10 $^{\circ}\text{C}/\text{min}$.

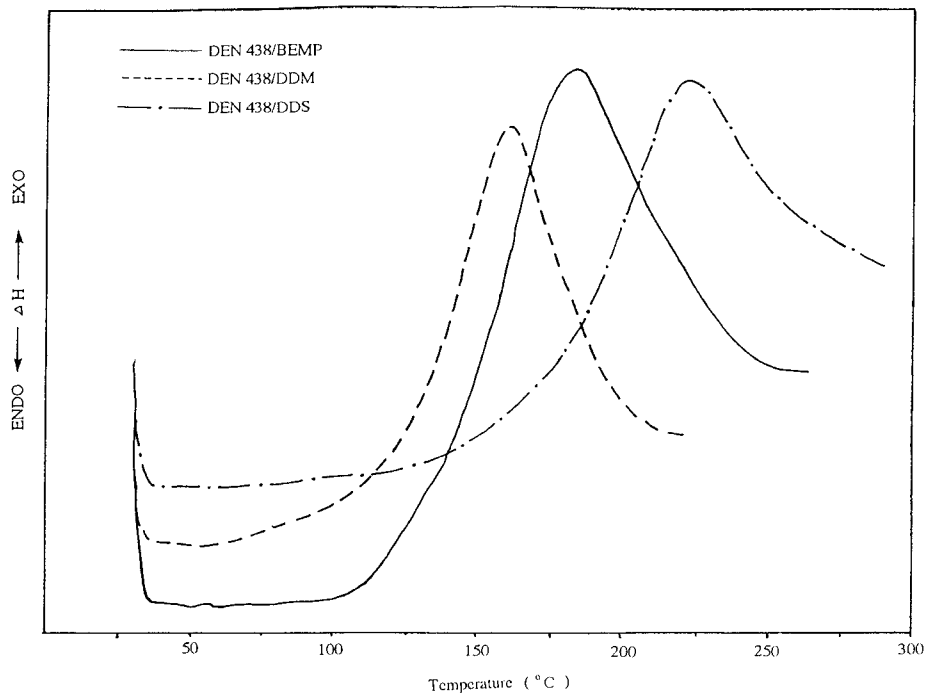


Figure 6 DSC thermograms of three compositions: DEN 438–BEMP, DEN 438–DDM, DEN 438–DDS. Heating rate: 10 $^{\circ}\text{C}/\text{min}$.

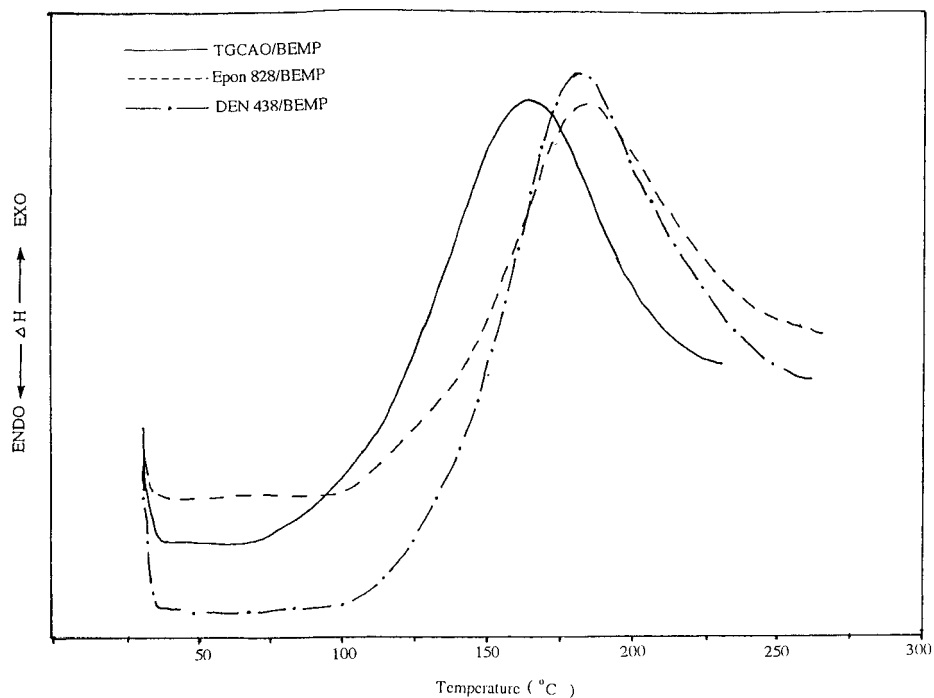


Figure 7 DSC thermograms of three compositions: TGCAO-BEMP, Epon 828-BEMP, DEN 438-BEMP. Heating rate: 10°C/min.

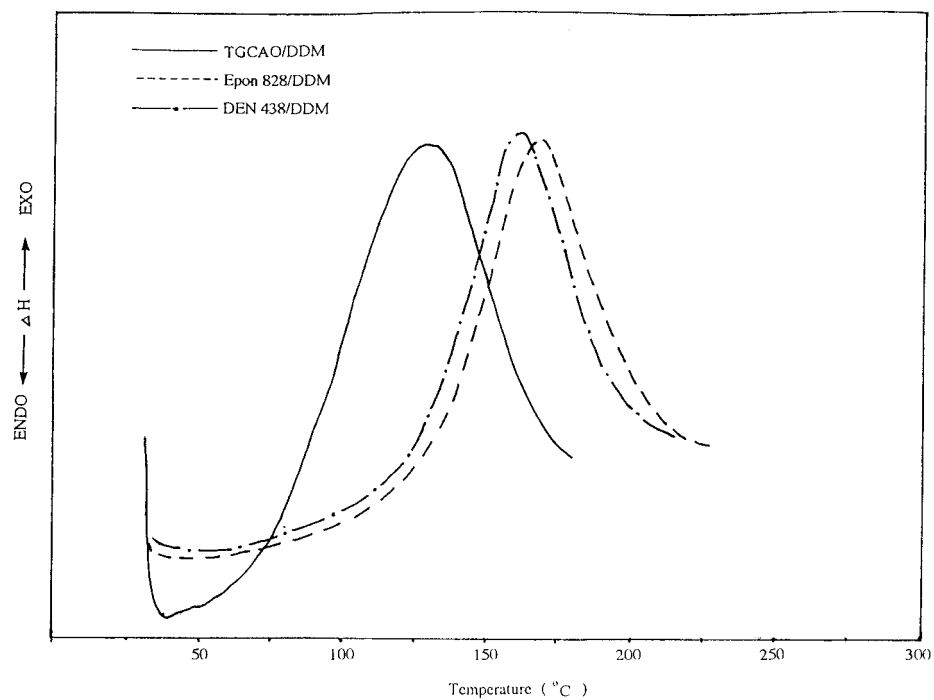


Figure 8 DSC thermograms of three compositions: TGCAO-DDM, Epon 828-DDM, DEN 438-DDM. Heating rate: 10°C/min.

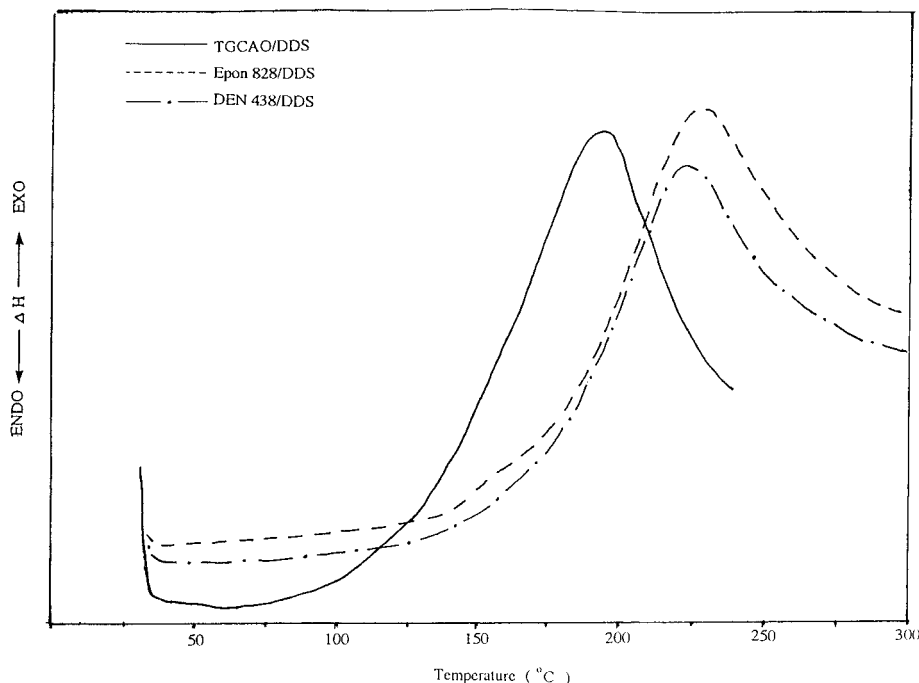


Figure 9 DSC thermograms of three compositions: TGCAO–DDS, Epon 828–DDS, DEN 438–DDS. Heating rate: 10°C/min.

resins, as compared with that of DDM, also should be attributed to electronic effects. In the case of BEMP, the electron-withdrawing group, P=O, reduced the electron density of the amine nitrogen and subsequently reduced their nucleophilic attack on the oxirane ring of the epoxy resins.

DSC thermograms (Figs. 7–9) demonstrate the reactivities of epoxy resins (TGCAO, Epon 828, and DEN 438) toward three curing agents (BEMP, DDM, and DDS). The influence of the chemical reactivity of these epoxy resins on the cure behavior is observed in those figures. For all the curing agents used, the exothermic starting temperature increases according to the order of TGCAO < DEN 438 < Epon 828. From the above data, we confirmed that the new cyclic phosphine oxide epoxy resin, TGCAO, is more reactive than the commercial epoxy resins, Epon 828 and DEN 438. The higher reactivity of TGCAO toward curing agents, as compared with that of Epon 828 and DEN 438, also should be attributed to the electronic effect.

Flame Properties

The oxygen index is commonly used as a measurement of the flame retardancy of material. Van Krevelen⁹ has proposed that the char residue on

pyrolysis is linearly proportional to the oxygen index for the halogen-free polymers. The new synthesized cyclic phosphine oxide epoxy resin, TGCAO, containing 4.48% phosphorus, is expected to have a higher solid char residue on pyrolysis. To demonstrate the properties of the flame retardancy of this new cyclic phosphine oxide epoxy resin, these cured polymers are divided into the following three groups: (1) TGCAO–BEMP, Epon 828–BEMP, and DEN 438–BEMP; (2) TGCAO–DDM, Epon 828–DDM, and DEN 438–DDM; (3) TGCAO–DDS, Epon 828–DDS, and DEN 438–DDS. The char yields of these cured polymers in nitrogen and air are shown in Figures 10–15. For group (1), the cyclophosphorus-containing polymer that has the highest phosphorus content, TGCAO/BEMP, has a higher char yield than the other two polymers, Epon 828–BEMP and DEN 438–BEMP. For group (2), the cyclophosphorus-containing polymer, TGCAO–DDM, has a higher char yield than the other two polymers, Epon 828–DDM and DEN 438–DDM. For group (3), the cyclophosphorus-containing polymer, TGCAO–DDS, has a higher char yield than the other two polymers, Epon 828–DDS and DEN 438–DDS. From the above results, we have found that the new synthesized cyclic phosphine oxide epoxy resin demonstrated adequate flame properties.

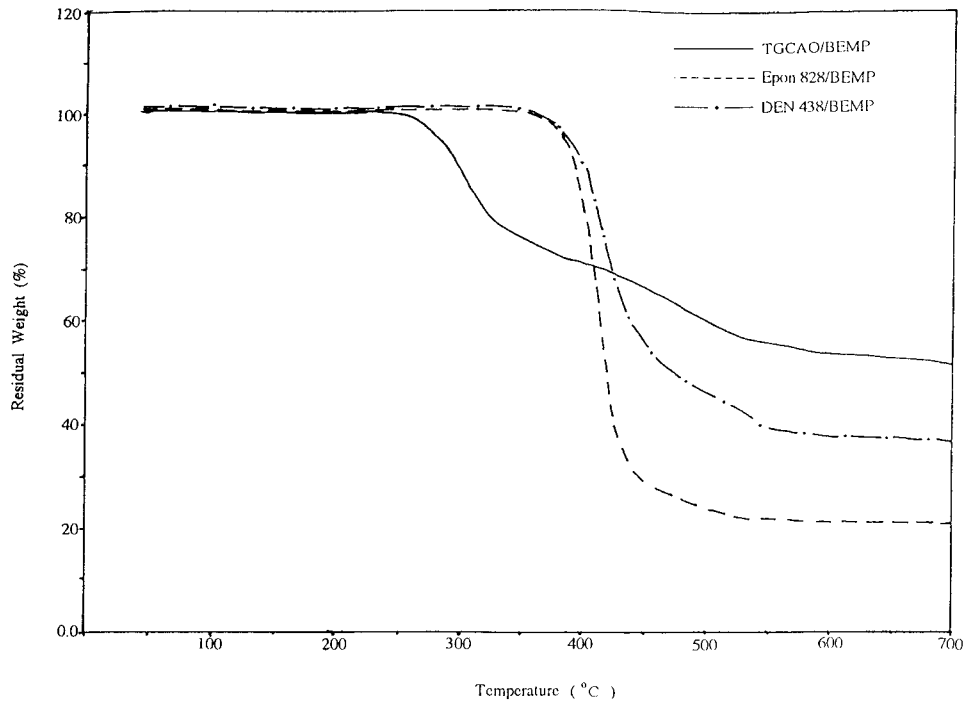


Figure 10 TGA thermograms of TGCAO-BEMP, Epon 828-BEMP, DEN 438-BEMP in a nitrogen environment. Heating rate: 10°C/min.

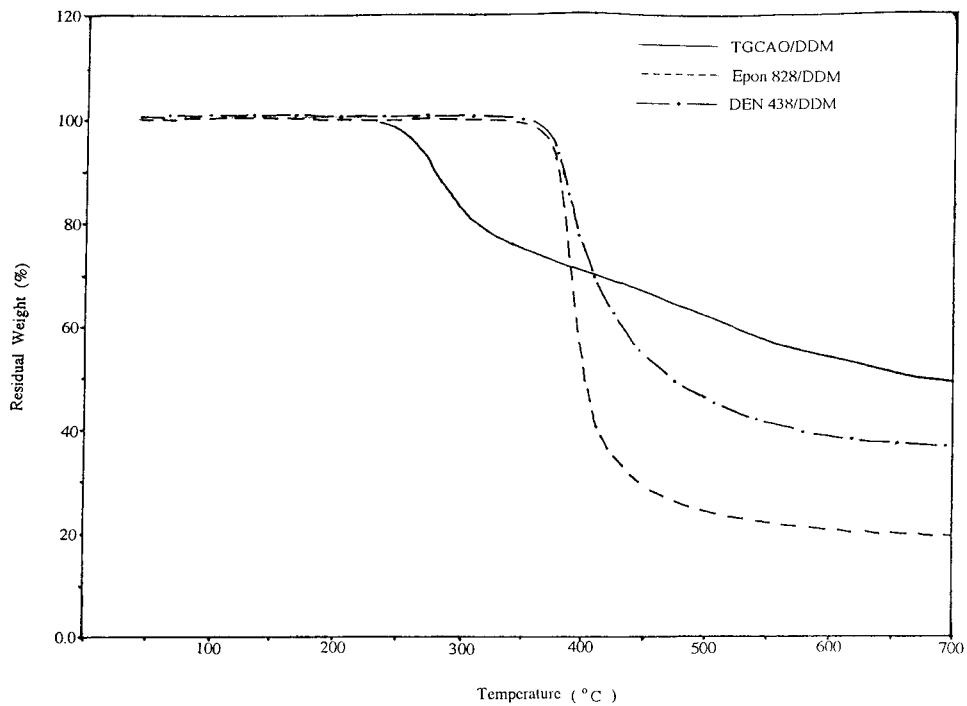


Figure 11 TGA thermograms of TGCAO-DDM, Epon 828-DDM, DEN 438-DDM in a nitrogen environment. Heating rate: 10°C/min.

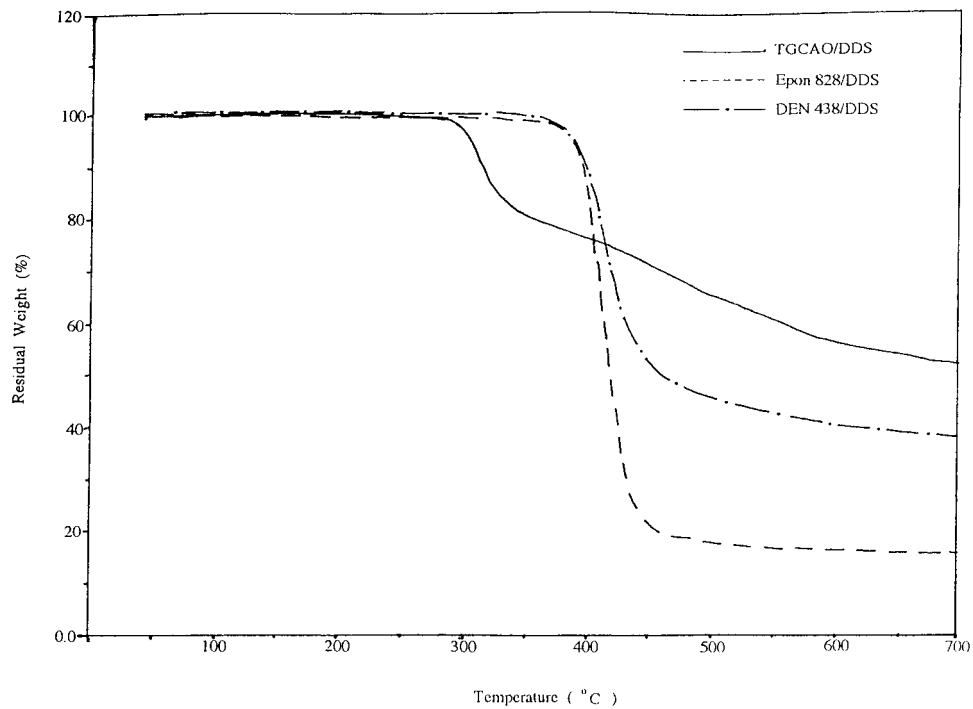


Figure 12 TGA thermograms of TGCAO-DDS, Epon 828-DDS, DEN 438-DDS in a nitrogen environment. Heating rate: 10°C/min.

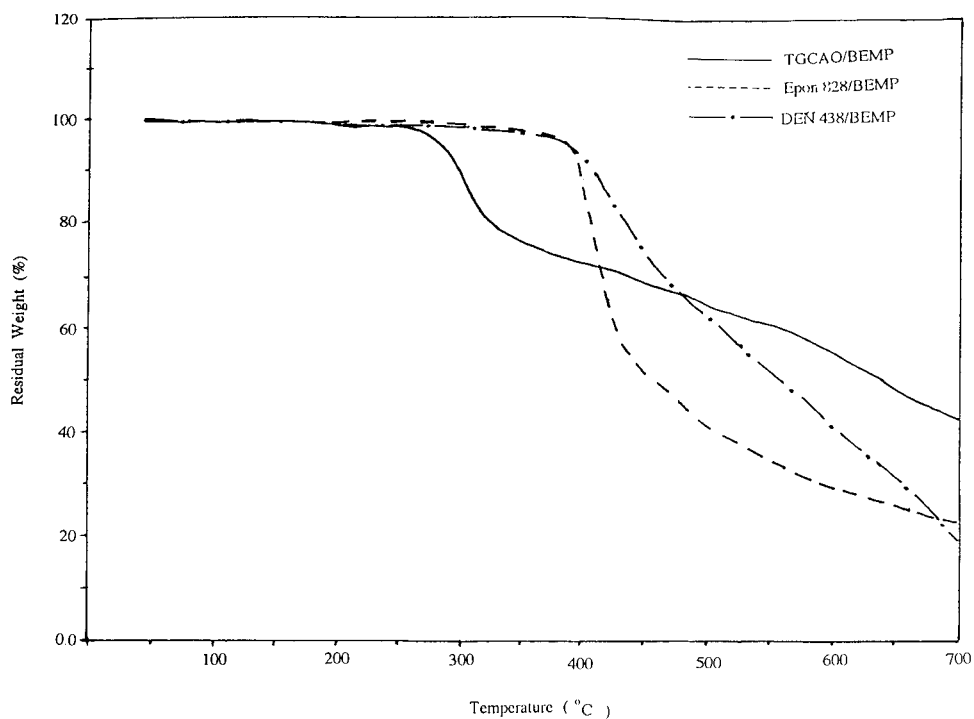


Figure 13 TGA thermograms of TGCAO-BEMP, Epon 828-BEMP, DEN 438-BEMP in an air environment. Heating rate: 10°C/min.

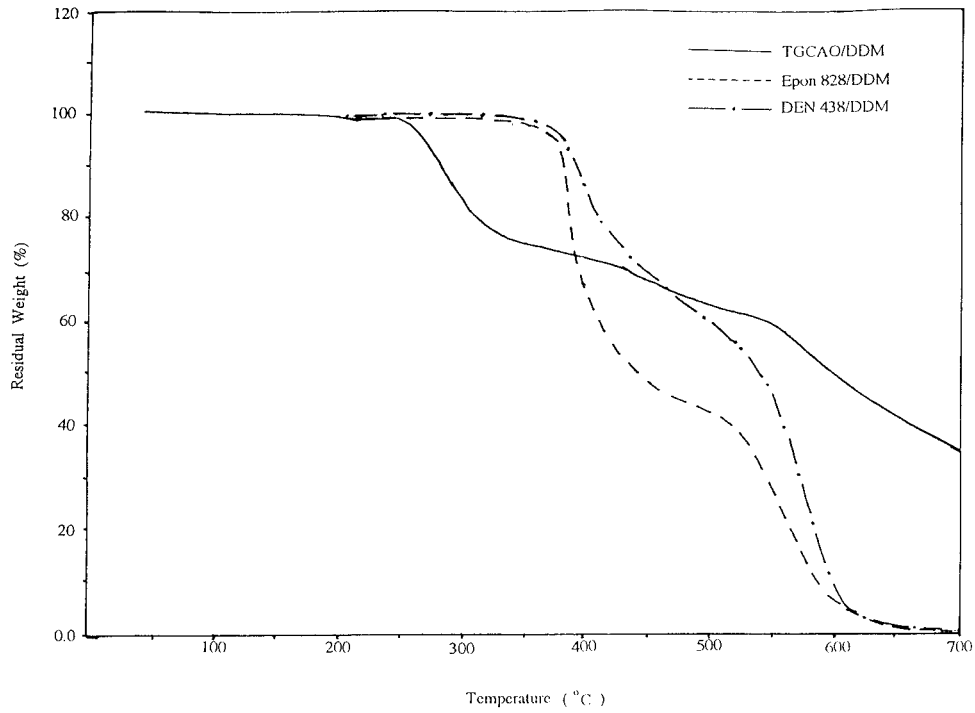


Figure 14 TGA thermograms of TGCAO–DDM, Epon 828–DDM, DEN 438–DDM in an air environment. Heating rate: 10°C/min.

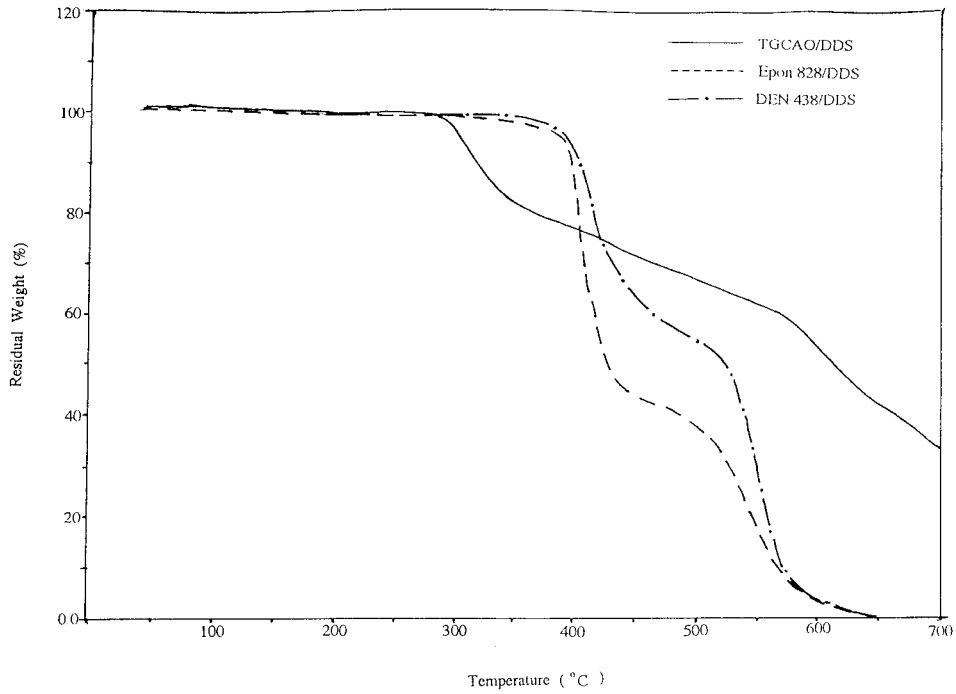


Figure 15 TGA thermograms of TGCAO–DDS, Epon 828–DDS, DEN 438–DDS in an air environment. Heating rate: 10°C/min.

Thermal Properties

To compare the thermal properties of these cured polymers, they were divided into the following three groups: (1) TGCAO–BEMP, Epon 828–BEMP, and DEN 438–BEMP; (2) TGCAO–DDM, Epon 828–DDM, and DEN 438–DDM; (3) TGCAO–DDS, Epon 828–DDS, and DEN 438–DDS. From PDTs and temperatures of some characteristic weight losses, which are shown in Figures 10–15, we can compare the thermal properties of these cured polymers. It is found that polymers containing the cyclic phosphine oxide epoxy resin demonstrated adequate thermal properties, which are compared with the commercial products of epoxy resins, Epon 828 and DEN 438. The cyclic phosphine oxide epoxy resin compositions have a slower thermal degradation rate than Epon 828 and DEN 438 compositions. From TGA cures, we found that PDTs of phosphorylated polymers, TGCAO–BEMP, TGCAO–DDM, and TGCAO–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.

CONCLUSIONS

The structure of the new synthesized cyclic phosphine oxide epoxy resin, TGCAO, was confirmed through epoxy equivalent weight, EA, IR, and ^1H -

and ^{13}C -NMR characterizations. The synthesized TGCAO cured with BEMP, 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 a cyclophosphorus group into the epoxy structure. The cyclophosphorus-containing epoxy polymers were observed to have a higher char yield on pyrolysis than noncyclic phosphine oxide and nonphosphorylated epoxy polymers.

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