

# The Properties of Epoxy–Imide Resin Cured by Phosphorylated Diamines Containing Different Alkyl Groups on Phosphorus

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**ABSTRACT:** Cured networks of epoxy–imide resin cured with four types of phosphorylated diamine curing agents that contained different alkyl groups on phosphorus were studied. The structures of these novel phosphorus-containing curing agents were confirmed by Mass, EA, IR, and  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra characterization. The reactivities were measured by differential scanning calorimetry (DSC). It is found that the reactivities were not affected by the types of alkyl groups in the curing agents. In thermal gravimetric analysis (TGA), those polymers that were ob-

tained through the curing reactions between epoxy–imide resin and four curing agents (BAMP, BAEP, BAPP, and BABP) also demonstrated excellent thermal properties as well as a high char yield. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 141–147, 2002

**Key words:** phosphorylated epoxy–imide polymer; phosphorylated diamine curing agent; thermal properties; 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.<sup>1,2</sup> 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 to enhance flame retardancy.<sup>3–5</sup> It is found that the thermal properties of the epoxy polymers can be improved by introducing heterocyclic rings into the backbone of polymers.<sup>6–9</sup> However, Rao<sup>10</sup> pointed out that the thermal stability was decreased as the flame resistance increased in polymers materials. According to our previous researches, it was found that the introduction of phosphorus and heterocyclic rings into the epoxy polymers can simultaneously improve the thermal and fire resistance stability.

In our previous research,<sup>11</sup> we synthesized a phosphorylated diamine curing agent improving the flame resistance of epoxy polymer via the structure modifi-

cation of the curing agent. In this study, we also synthesized four phosphorylated diamine curing agents containing different alkyl groups on phosphorus and compared their reactivities toward the same epoxy–imide resin. Cured networks of epoxy–imide resin cured with four phosphorylated diamine curing agents were also studied on flame and thermal properties.

## EXPERIMENTAL

### Syntheses of bis(3-aminophenyl)alkylphosphine oxide

#### Synthesis of alkyltriphenyl phosphonium iodide (I)

A mixture of 0.1 mol of triphenyl phosphine and 0.5 mol alkyl iodide in toluene was heated to reflux for 3 h. The white crystal were formed and filtered. The residual solid was washed with toluene several times, and dried in an oven at 100°C for use. Yield was 98%, with an m.p. near 175°C for methyltriphenyl phosphonium iodide.

#### Synthesis of alkyldiphenyl phosphine oxide (II)

A mixture of 0.1 mol of product (I) in 250 mL water and 70 mL 40% potassium hydroxide was heated to reflux. The by-product benzene was removed by distillation. The degree of reaction was controlled by thin-layer chromatography (TLC), using hexane as mobile phase. The product was extracted with chloroform. The chloroform solution was washed with water

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TABLE I  
Curing Cycles of Several Epoxy Systems

Composition	Curing temp. °C	Curing timemin	Postcuring temp. °C	Postcuring time min
DIDE/BAMP	160	45	210	25
DIDE/BAEP	137	45	216	30
DIDE/BAPP	135	45	221	30
DIDE/BABP	137	45	216	30

DIDE: Diimide diepoxide.

BAMP: Bis(3-aminophenyl)methylphosphine oxide.

BAEP: Bis(3-aminophenyl)ethylphosphine oxide.

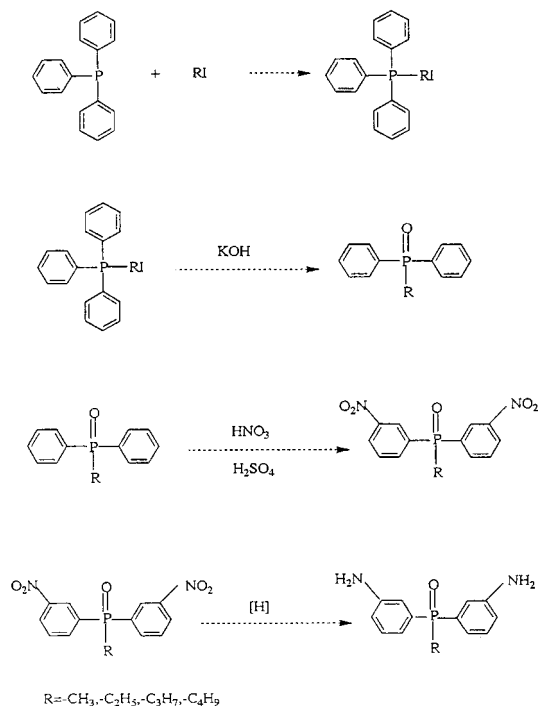
BAPP: Bis(3-aminophenyl)propylphosphine oxide.

BABP: Bis(3-aminophenyl)butylphosphine oxide.

and concentrated. The residual was purified by column chromatography and dried for use. Yield was 86%, with an m.p. near 115°C for methyl-diphenylphosphine oxide.

#### Synthesis of bis(3-nitrophenyl)alkylphosphine oxide(III)

A solution of 60 mL conc. sulfuric acid and 60 mL conc. nitric acid was gradually added into a stirred solution of 0.1 mol alkyl-diphenylphosphine in 60 mL conc. nitric acid at 10°C for 2 h. The reaction mixture was brought to room temperature and bis(3-nitrophenyl)alkylphosphine oxide was precipitated in iced water. The obtained solid was a light yellow crystals. Yield was 84%, with m.p. near 203°C for bis(3-nitrophenyl)methylphosphine oxide.



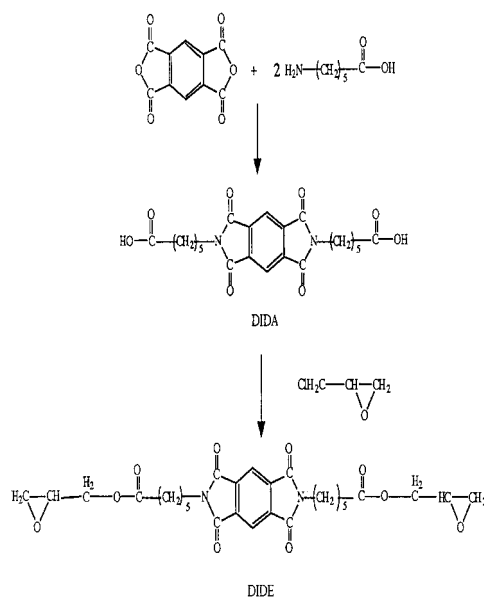
Scheme I Syntheses of bis(3-aminophenyl)alkylphosphine oxide.

#### Synthesis of bis(3-aminophenyl)alkylphosphine oxide(IV)

Bis(3-nitrophenyl)alkylphosphine oxide (0.6 mol) reacted with powder tin(II) chloride dihydrated (110.0 g) in a solution of 120 mL ethanol and 120 mL fuming hydrochloric acid at room temperature for 2 h. The solution was concentrated until salt came out of solution. The salt was neutralized using 25% sodium hydroxide, and the product was extracted with chloroform. Solid residue was obtained when chloroform was removed by distillation at a reduced pressure. The obtained solid was recrystallized from dichloromethane. The product was a light yellow crystalline solid. Yield was 87%, with an m.p. near 146°C for bis(3-aminophenyl)methylphosphine oxide.

#### Preparation of polymers

Polymers studied were prepared as indicated in Table I. To obtain a highly crosslinked polymer with good thermal stability, a 1-epoxy equivalent weight of the



Scheme II Syntheses of diimide-diepoxide.

TABLE II  
The Data of Elemental Analysis

Compounds	Alkyltriphenyl phosphonium iodide				Alkyltriphenyl phosphine oxide				Bis(3-nitrophenyl) alkyl phosphine oxide				Bis(3-aminophenyl) alkyl phosphine oxide								
	C%		H%		C%		H%		C%		H%		N%		C%		H%		N%		
	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	
When alkyl is																					
Methyl	56.46	56.46	4.48	4.49	72.11	72.22	6.10	6.06	50.91	50.99	3.68	3.62	9.15	9.15	63.03	63.41	6.12	6.11	11.32	11.38	
Ethyl	57.41	57.43	4.81	4.81	72.89	73.03	6.63	6.57	52.02	52.50	4.06	4.09	8.69	8.75	63.52	64.60	6.59	6.58	10.52	10.76	
Propyl	58.35	58.24	5.13	5.12	73.82	73.76	7.00	7.01	53.83	53.90	4.52	5.12	8.37	8.38	63.24	65.70	7.01	6.90	9.77	10.20	
<i>n</i> -Butyl	59.20	59.18	5.42	5.42	74.58	74.40	7.56	7.41	55.44	55.18	5.07	4.92	7.90	8.04	65.68	65.65	7.30	7.34	9.53	9.72	

epoxy-imide resin<sup>11</sup> was polymerized with 0.5 mol of curing agent. The epoxy equivalent weight of epoxy-imide resin was 282 g/equiv.

**Characterization and measurements**

Infrared spectra (IR) were examined using a JASCO-200 and Bomen MB-100. Mass spectra were obtained from JEOL SX-102A. Elemental analyses (EA) were carried out on Heraeus CHN-O Rapid Analyser. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained from a Bruker AM-400 where samples dissolved in DMSO-d<sub>6</sub> with TMS being employed as an internal standard. Thermal resistance was evaluated by thermogravimetric analysis (TGA) on a TGA DU PONT 2100 with a heating rate of 10°C/min. The curing cycles and reactivities were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC 7.

**RESULTS AND DISCUSSION**

Bis(3-aminophenyl)alkylphosphine oxide (BAMP, BAEP, BAPP, BABP) were obtained through the following four synthetic steps: synthesis of alkyltriphenyl phosphonium iodide(I), alkyltriphenyl phosphine (II), bis(3-nitrophenyl)alkylphosphine oxide (III), and the hydrogenation of bis(3-nitrophenyl)alkylphosphine oxide using tin (II) chloride dihydrated in acidic condition. The synthetic pathways of bis(3-aminophenyl)alkylphosphine oxide and epoxy-imide resin were shown as in Schemes I and II. The chemical structures of phosphorus-containing curing agents and their precursors are identified.

**Identification of bis(3-nitrophenyl)alkylphosphine oxide (III)**

Elemental analyses data of bis(3-nitrophenyl)alkylphosphine oxides which alkyl is methyl, ethyl, pro-

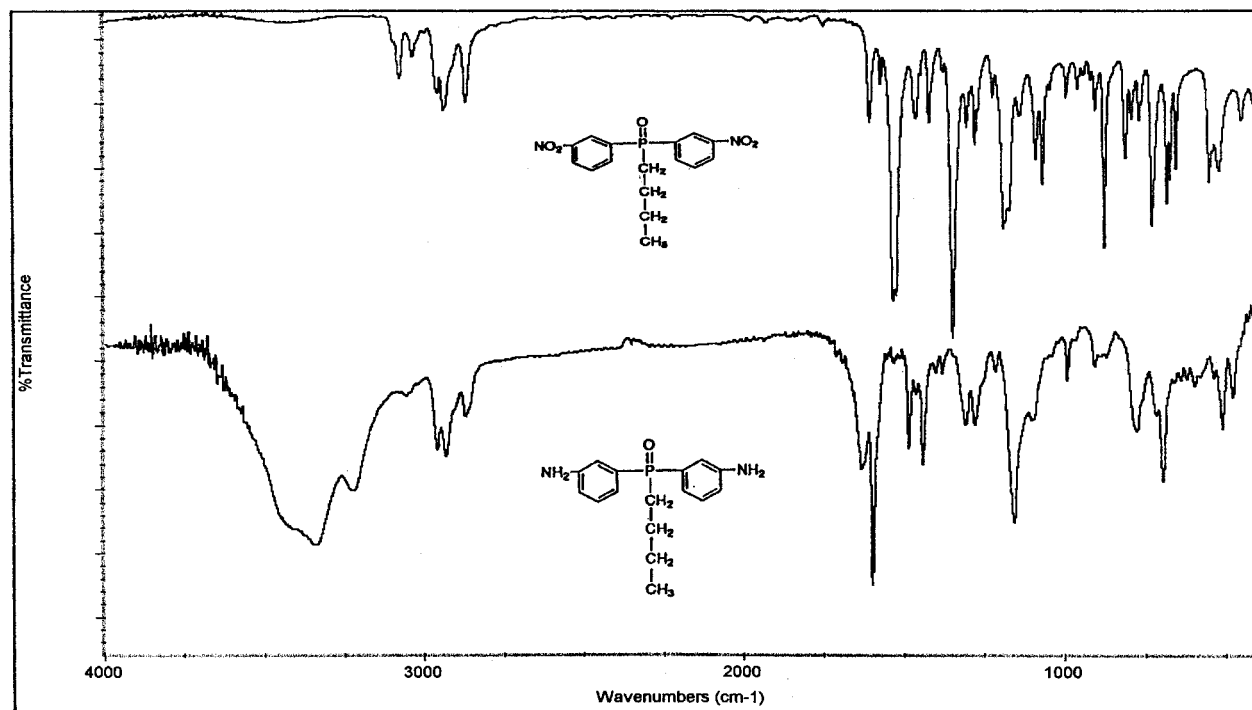


Figure 1 IR spectrum of bis(3-nitrophenyl)butylphosphine oxide and bis(3-aminophenyl)butylphosphine oxide.

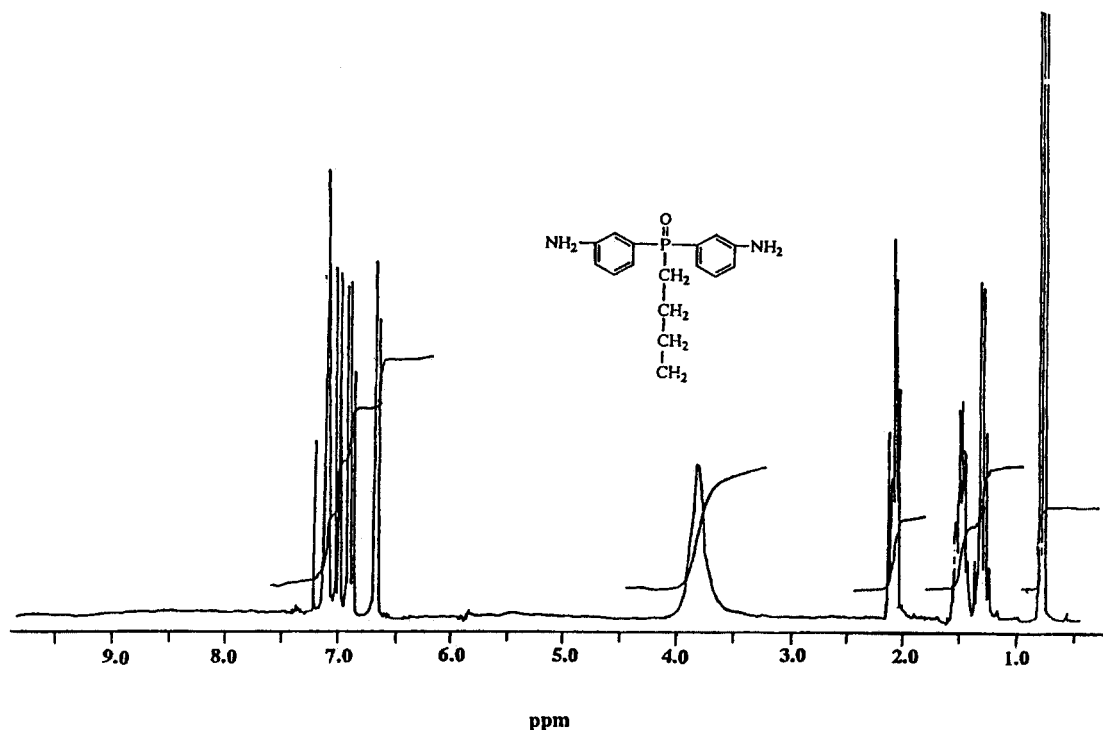


Figure 2  $^1\text{H-NMR}$  spectrum of bis(3-aminophenyl)butylphosphine oxide.

pyl, *n*-butyl are listed in Table II. The IR spectrum of bis(3-nitrophenyl)alkylphosphine oxide is shown in Figure 1. Peaks at  $3000\text{ cm}^{-1}$  and  $3100\text{ cm}^{-1}$  display the absorptions of aromatic C—H. Absorptions arising because of  $-\text{NO}_2$  at  $1530\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$ ,  $-\text{P}=\text{O}$  at  $1170\text{ cm}^{-1}$  were observed.

#### Identification of bis(3-aminophenyl)alkylphosphine oxide (IV)

Elemental analyses data of bis(3-aminophenyl)alkylphosphine oxides which alkyl is methyl, ethyl, propyl, *n*-butyl, respectively, are listed in Table II. The IR spectrum of bis(3-aminophenyl) butylphosphine ox-

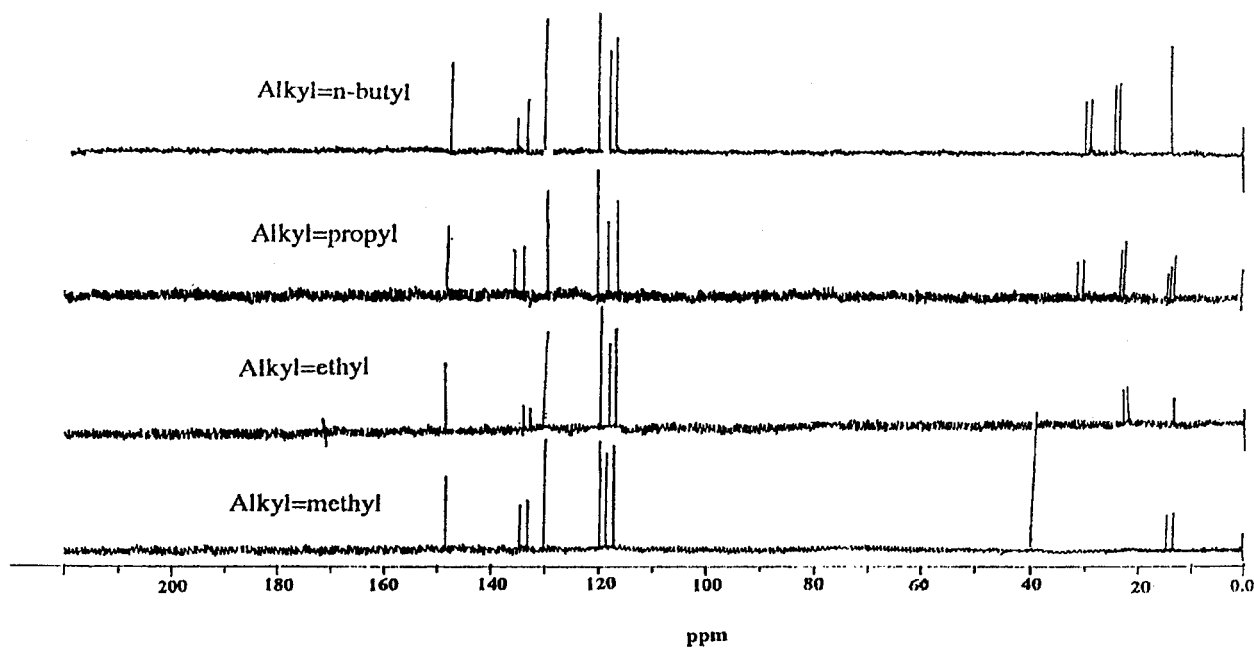
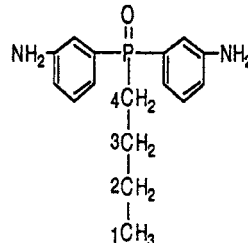
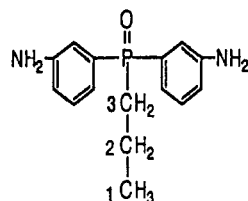
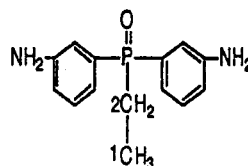
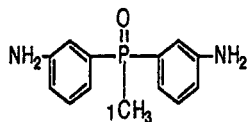


Figure 3  $^{13}\text{C-NMR}$  spectrum of bis(3-aminophenyl)butylphosphine oxide.

**TABLE III**  
**<sup>1</sup>H-NMR Data of Bis(3-aminophenyl)alkyl-phosphine oxide**

Types of proton alkyl	1	2	3	4	NH <sub>2</sub>	Aromatic hydrogens
	Chemical shifts (ppm)					
Methyl	1.82 (3H,m)				4.50–5.36 (4H,s)	6.68–7.16 (8H,br)
Ethyl	1.14 (3H,m)	2.13 (2H,m)			3.12–3.92 (4H,s)	6.69–7.16 (8H,br)
Propyl	1.48 (3H,m)	2.09 (2H,m)	2.62 (2H,m)		3.78–4.63 (4H,s)	6.69–7.16 (8H,br)
<i>n</i> -Butyl	0.83 (3H,m)	1.40 (2H,m)	1.52 (2H,m)	2.11 (2H,m)	3.53–4.05 (4H,s)	6.69–7.16 (8H,br)

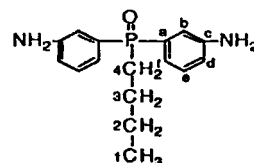
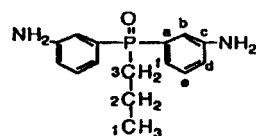
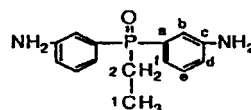
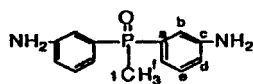


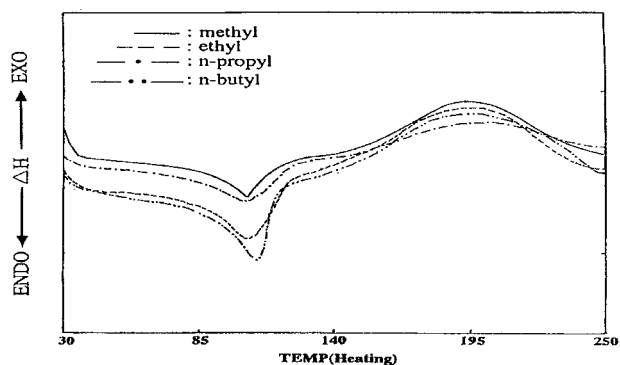
ide is shown in Figure 1. Peaks at  $3400\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$  display the absorptions of aromatic primary amine. Absorptions arising because of  $\text{P}-\text{C}_6\text{H}_4$  at  $1440\text{ cm}^{-1}$ ,  $-\text{C}-\text{N}$  at  $1300\text{ cm}^{-1}$ ,  $-\text{P}=\text{O}$  at  $1160\text{ cm}^{-1}$  were observed. The mass data of bis(3-aminophenyl)alkylphosphine oxide were in good agreement

with the calculated values. The <sup>1</sup>H-NMR spectrum of bis(3-aminophenyl) butylphosphine oxide is shown in Figure 3. The chemical shifts of characterized protons in bis(3-aminophenyl)alkylphosphine oxides are listed in Table III. These resonance lines arising because of aliphatic hydrogens at 1.0–1.2 ppm, amino group hy-

**TABLE IV**  
**<sup>13</sup>C-NMR Data of Bis(3-aminophenyl)alkylphosphine oxide**

Type of proton When alkyl is	1	2	3	4	a	b	c	d	e	f
	Chemical shifts (ppm)									
Methyl	16.00				135.71	116.65	148.85	115.26	129.15	117.12
Ethyl	15.54	23.70			132.52	117.07	146.76	117.96	129.47	120.21
Propyl	15.21	25.44	32.34		134.99	117.16	146.69	117.88	129.47	120.24
<i>n</i> -Butyl	13.50	23.43	24.16	28.50	134.98	116.94	146.79	117.8	129.18	119.93



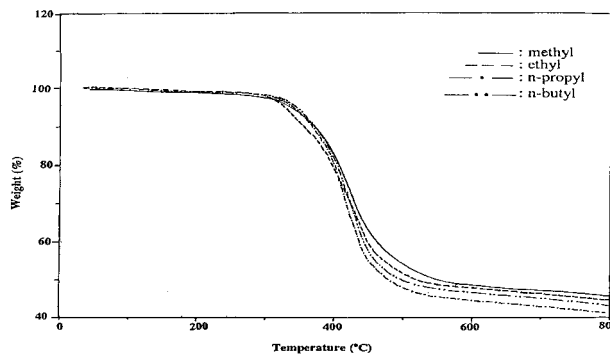


**Figure 4** DSC thermograms of bis(3-aminophenyl)butylphosphine oxide/diimide-diepoxy, the heating rate is 10°C/min.

drogens at 3.5–5.5 ppm, and aromatic hydrogen at 6.6–7.3 ppm were observed. The  $^{13}\text{C}$ -NMR spectra are shown in Figure 3. These resonance lines in spectra fall into two regions, i.e., 10–20 ppm for the aliphatic carbon, 110–150 ppm for the aromatic carbon. These chemical shifts of characterized carbon in bis(3-aminophenyl)alkylphosphine oxides are listed in Table IV.

#### Reactivity of diimide-diepoxy and bis(3-aminophenyl)alkyl-phosphine oxides

The polymerization reaction were studied by DSC. Significant caution was taken during the DSC study of polymerization reaction to obtain homogenous mixtures of the epoxy resin and those curing agents. Typical DSC thermograms of the epoxy-imide resin and curing agents compositions are shown in Figure 4. The influence of the chemical reactivity of the curing agents on cure behavior is indicated from this figure to be apparent. For the epoxy-imide resin used, the exotherm starting temperatures were similar. A curing agent that exhibits a lower exothermic starting temperature under the same set of curing condition is



**Figure 5** TGA thermograms of bis(3-aminophenyl)butylphosphine oxide/diimide-diepoxy in a nitrogen environment; the heating rate is 10°C/min.

more reactive toward the epoxy-imide resin. It is, therefore, reasonable to propose that the chemical reactivity of these four different curing agents toward epoxy-imide resin were not affected by the bulk of alkyl group in the phosphorus group.

#### Thermal and flame properties

Glass transition temperature ( $T_g$ ) of these cured phosphorus-containing epoxy-imide polymers (DIDE/BAMP, DIDE/BAEP, DIDE/BAPP, DIDE/BABP) are listed in Table V.

The thermal stability of synthesized phosphorylated epoxy-imide polymers through the reaction between epoxy-imide resin and various phosphorylated curing agents (BAMP, BAEP, BAPP, BABP) were evaluated by thermal gravimetric analysis (TGA). The TGA thermograms of polymers in nitrogen and air environments are shown in Figures 5 and 6, respectively. The polymers began to decompose in a nitrogen environment at a temperature higher than ca. 330°C. The residual weight contents in a nitrogen environment were ca. 45% at 800°C. The decomposition in an air environment, how-

**TABLE V**  
Decomposition Temperatures, Weight Residues, and  $T_g$  of Cured Epoxy Resins, the Heating Rate is 10°C/min

Environment	Resin	Curing agent	Weight loss at temp (°C)					Weight residue (%)		$T_g$
			10%	20%	30%	40%	50%	600°C	700°C	
N <sub>2</sub>	DIDE	BAMP	378.1	406.3	423.5	442.2	564.2	49.4	47.9	121
		BAEP	354.4	395.5	424.1	447.3	518.7	49.9	48.0	123
		BAPP	366.1	400.0	417.9	435.7	480.4	46.9	45.1	124
		BABP	366.1	403.6	425.0	443.9	498.2	48.5	46.1	122
Air	DIDE	BAMP	375.0	409.4	429.7	471.9	578.2	41.6	25.8	127
		BAEP	358.9	396.4	426.7	496.4	589.2	48.0	34.1	126
		BAPP	362.5	403.6	432.1	503.6	617.8	52.0	41.9	123
		BABP	365.2	402.7	431.3	472.3	599.1	49.9	41.0	119

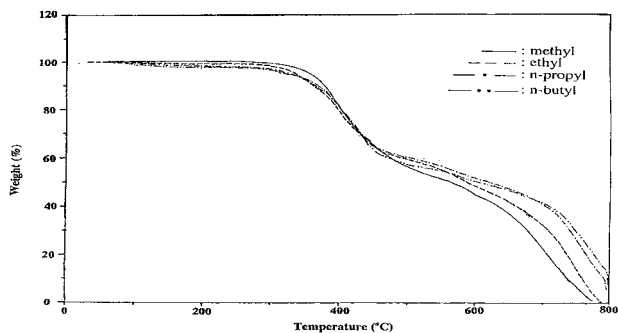
DIDE: Diimide diepoxy.

BAMP: Bis(3-aminophenyl)methylphosphine oxide.

BAEP: Bis(3-aminophenyl)ethylphosphine oxide.

BAPP: Bis(3-aminophenyl)propylphosphine oxide.

BABP: Bis(3-aminophenyl)butylphosphine oxide.



**Figure 6** TGA thermograms of bis(3-aminophenyl)butylphosphine oxide/diimide-diepoxy in an atmosphere environment, the heating rate is 10°C/min.

ever, falls into two steps. The first region of decomposition was ca. 330–430°C with the residual weight contents being ca. 60%. The second step of decomposition started at 705°C. The synthesized phosphorylated epoxy-imide polymers showing good thermal stability and flame resistance (higher char residual on pyrolysis) were found in the TGA study.

### CONCLUSIONS

The structures of these novel curing agents of epoxy resins were confirmed through Mass, EA, IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR characterizations. Using imide

and phosphorus groups to modify the epoxy, the thermal and flame resistance of epoxy can be improved. Some novel phosphorylated epoxy-imide polymers have been synthesized here, where the imide and phosphorus were incorporated into the main chain of epoxy polymers. These polymers showed good thermal and flame resistance. In this study, we found that the synthesized curing agents have excellent flameless properties for epoxy polymers.

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