

Syntheses, Structure, Reactivity, and Thermal Properties of Epoxy-Imide Resin Cured by Phosphorylated Triamine

TSUI-SHUANG WANG, JIN-FEN YEH, and MIN-DA SHAU*

Department of Applied Chemistry, Chia Nan Junior College of Pharmacy, Tainan, Taiwan, Republic of China

SYNOPSIS

A new phosphorylated epoxy-imide polymer was obtained using diimide-diepoxy (DIDE) cured with tris(3-aminophenyl)phosphine oxide (TAPO). In addition, compositions of the synthesized diimide diepoxy (DIDE), Epon 828, and DEN 438 with common curing agents, e.g., 4,4'-diaminodiphenyl ether (DDE) and 4,4'-diaminodiphenylsulfone (DDS), were compared as to curing reactivity and heat and flame retardation with that of tris(3-aminophenyl)phosphine oxide. The reactivities of those curing agent toward the three kinds of epoxy resins, as measured by differential scanning calorimetry (DSC), were in the order DDE > TAPO > DDS. Through thermal gravimetric analysis (TGA), the thermal and flame resistances of epoxy were confirmed in this study as capable of being significantly improved through introduction of imide and phosphorus groups into the epoxide structure.

© 1996 John Wiley & Sons, Inc.

INTRODUCTION

The special structure and curing method of epoxy resins offer cured materials with the properties of minimum shrinkage, strong resistance to water and chemicals, and good electrical and mechanical properties. The applications of epoxy resin to coatings, adhesives, construction, and insulation of electronic materials are of industrial importance.

Due to the rapid development of electronic materials in aerospace in the past years, it is crucial to improve the heat resistance of epoxy resins and curing materials. Generally, the heat resistance of polymers can be improved through modifying the molecular structure. Epoxy-imide resins have been the focus of attention by researchers in recent years.¹⁻⁸ However, the safety of the materials also needs to be considered. Many techniques have been employed in improving the flame retardation of epoxy resins, such as the addition of fire retardant agents, or the use of fire retardant curing material.^{8,9} According to the previous investigation, it was found that the introduction of phosphorus into the polymer skeleton can improve the fire resistance and adhesion.

In this research, the imide function group was introduced into the structure of the epoxy resin to synthesize epoxy-imide resins with improved heat resistance compared to the conventional epoxy resins. The improvement of flame resistance of the cured epoxy is achieved by introducing the phosphorus group into the structure of a triamine curing agent. The phosphorus-containing triamine curing agent (TAPO) was synthesized. The cured materials from different types of epoxy resins (such as Epon 828, DIDE, and DEN 438) with a variety of hardeners (namely TAPO, DDS, and DDE) were also studied.

EXPERIMENTAL

Reagents

Benzene-1,2,4,5-tetracarboxylic dianhydride was recrystallized from acetic anhydride. 6-Aminohexanoic acid, 4,4'-diaminodiphenylether (DDE), 4,4'-diaminodiphenylsulfone (DDS), and benzyltrimethylammonium chloride were reagent grades as purchased from Merck and used without further purification. *N,N*-Dimethyl formamide was dried over P₂O₅ and then vacuum-distilled. Benzene, toluene, and chloroform were distilled at normal pressure prior to application. Tris(3-aminophenyl)

* To whom correspondence should be addressed.

Table I EA Data of DIDA, DIDE, TNPO, and TAPO

Materials	C (%)		H (%)		N (%)		O (%)	
	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc
DIDA	59.32	59.46	5.41	5.41	6.30	6.31	28.80	28.82
DIDE	60.46	60.43	5.85	5.76	5.02	5.04	28.74	28.78
TNPO	52.27	52.30	2.92	2.91	10.21	10.17	27.15	27.12
TAPO	66.78	66.87	5.62	5.57	12.92	13.06	4.92	4.95

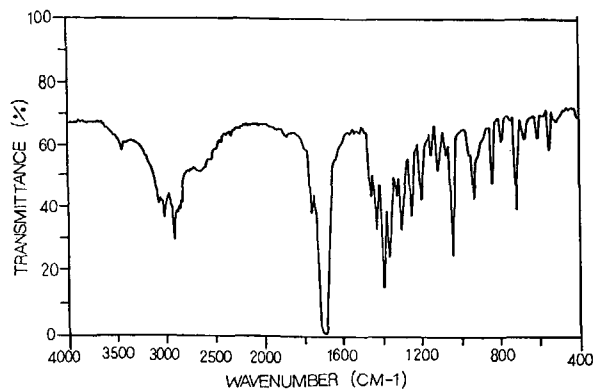
phosphine oxide was prepared by reduction of tris(3-nitrophenyl)phosphine oxide. Epon 828 was purchased from Shell Chemical Co. and novolac epoxy (DEN 438) from Dow Chemical Co.

Synthesis of Diimide-Diacid (DIDA)⁷

A solution of benzene-1,2,4,5-tetracarboxylic dianhydride (21.82 g) in anhydrous *N,N*-dimethyl formamide (80 mL) was gradually added into a stirred solution of 6-aminohexanoic acid (26.26 g) in anhydrous *N,N*-dimethyl formamide (120 mL) under a nitrogen atmosphere. A quantitative amount of anhydrous benzene was added and heated up to 170°C for reaction after being stirred at 80°C for 2 h. Stoichiometric water produced during the course of the reaction was collected by a Dean-Stark trap. The reaction mixture was then cooled to room temperature and DIDA was precipitated in ice water and recrystallized from ethanol. The obtained solid was white and crystalline with the mp near 244°C and the yield 85%.

Synthesis of Diimidediepoxy (DIDE)⁷

A mixture of DIDA (8.88 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.

**Figure 1** IR spectrum of DIDA.

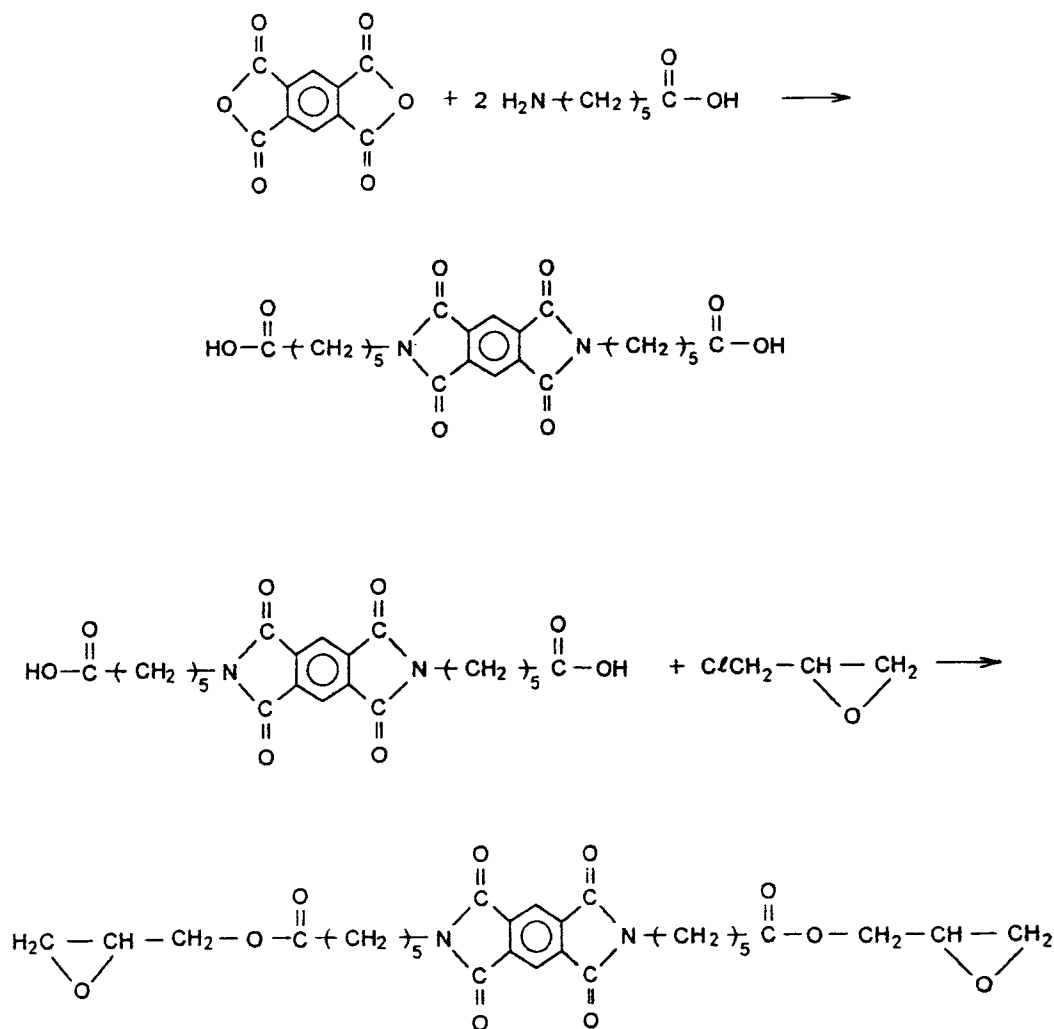
The degree of reaction was controlled by thin-layer chromatography (TLC), using as effluent system chloroform/acetone (8/1). The process was completed in 45 min. The mixture was then cooled to room temperature and washed with water. The unchanged epichlorohydrin was removed from the organic phase by distillation under nitrogen and at reduced pressure. A quantity of toluene was added to the residue and the remaining epichlorohydrin was removed as the toluene azeotrope by distillation. The obtained product after recrystallization from ethanol had mp 121°C, and its epoxy equivalent (E.E.) was 282 g/equiv (calc. 278 g/equiv).¹⁰

Synthesis of Tris(3-nitrophenyl)phosphine Oxide (TNPO)¹¹

A solution of conc. sulfuric acid (20 mL) and concentrated nitric acid (20 mL) was gradually added into a stirred solution of triphenylphosphine oxide (4.25 g) in conc. nitric acid (20 mL) at 10°C for 2 h. The reaction mixture was then cooled to room temperature and TNPO was precipitated in ice water. The obtained solid was a light yellow crystals with melting point 242–244°C, obtained in 82% yield.

Synthesis of Tris(3-aminophenyl)phosphine Oxide (TAPO)

TNPO (4.81 g) reacted with powdered tin(II) chloride dihydrate (28.29 g) in a solution of 45.6 mL ethanol and 31.0 mL fuming hydrochloric acid at room temperature for 2 h. The solution was concentrated until salt come out of solution. The salt was neutralized using 25% NaOH 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 brown crystalline solid with melting point near 260°C; the yield was 55%.



Scheme 1 Synthesis of DIDE.

Characterization and Measurements

The melting point was determined by a Fisher-Johns. Infrared spectra (IR) were examined using a Perkin-Elmer Model 983. Elemental analyses were

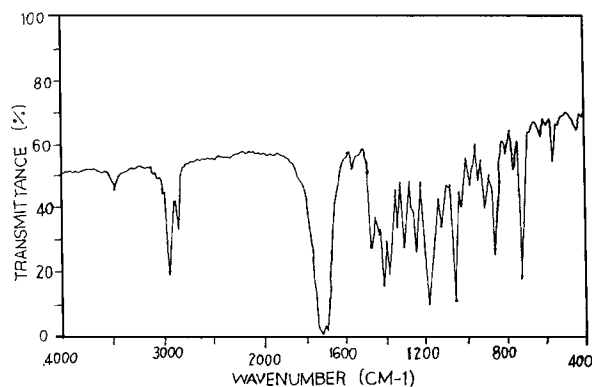


Figure 2 IR spectrum of DIDE.

carried out on a Heraeus CHN-O Rapid Analyzer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained from a Bruker AM-400 where samples were dissolved in $\text{DMSO-}d_6$ with TMS being employed as an internal standard. Thermal resistance was evaluated by thermogravimetric analysis (TGA) on a Du Pont 2100 TGA with a heating rate of $10^\circ\text{C}/\text{min}$. Reactivity was evaluated by differential scanning calorimetry (DSC) on a Du Pont 910 DSC.

RESULTS AND DISCUSSION

Identification of DIDE

DIDA was obtained through the reaction of the benzene-1,2,4,5-tetracarboxylic dianhydride with 6-aminohexanoic acid. The chemical structure of the diimide diacid was characterized by elemental analysis (Table I) and infrared spectroscopy (Fig. 1).

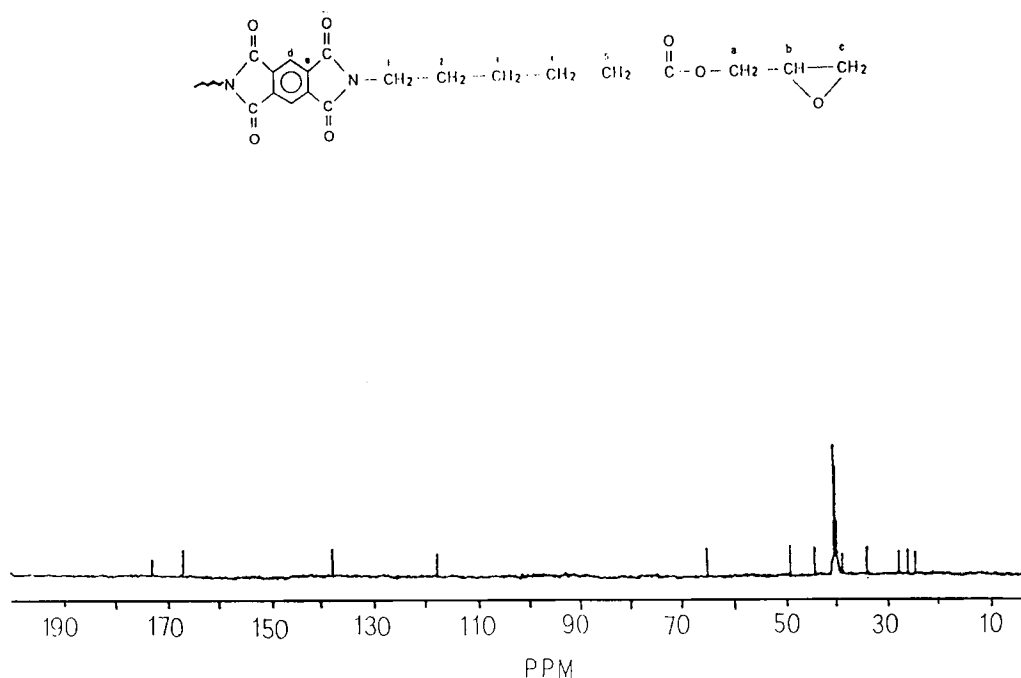


Figure 4 ^{13}C -NMR spectrum of DIDE.

ical structure was characterized by elemental analysis (EA), infrared spectroscopy (IR), ^1H -NMR, and ^{13}C -NMR spectroscopies.

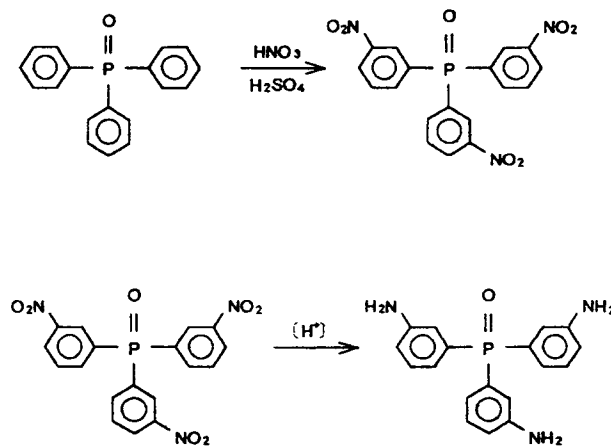
Elemental analysis data are listed in Table I. The IR spectrum is in Figure 5; peaks at 3225 and 3486 cm^{-1} exhibit the absorptions of aromatic primary amine. The ^1H -NMR spectrum is in Figure 6. The chemical shift of characterized protons are listed in Table IV. These shifts are based on the assigned labels of protons in Figure 6. The ^{13}C -NMR spectrum is in Figure 7. The chemical shifts of characterized carbons are listed in Table V. These shifts are based on the assigned label of carbon in Figure 7.

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

Aliphatic Carbons							
1	2	3	4	5	a	b	c
37.81	27.45	25.60	23.94	33.11	64.67	48.99	43.82
Aromatic Carbons				Carbonyl Carbons			
d		e		Imide		Ester	
117.23		137.04		166.41		172.73	

Preparation of Polymers

To obtain a complete reaction between epoxy resins and curing agents and to avoid formation of residual stress, curing temperature and time are two parameters that need to be considered in determining the curing period. Determination of optimum curing temperature and time can be carried out by DSC through isothermal and thermal scanning, respectively. The curing data of all the systems are listed in Table VI.



Scheme 2 Synthesis of TAPO.

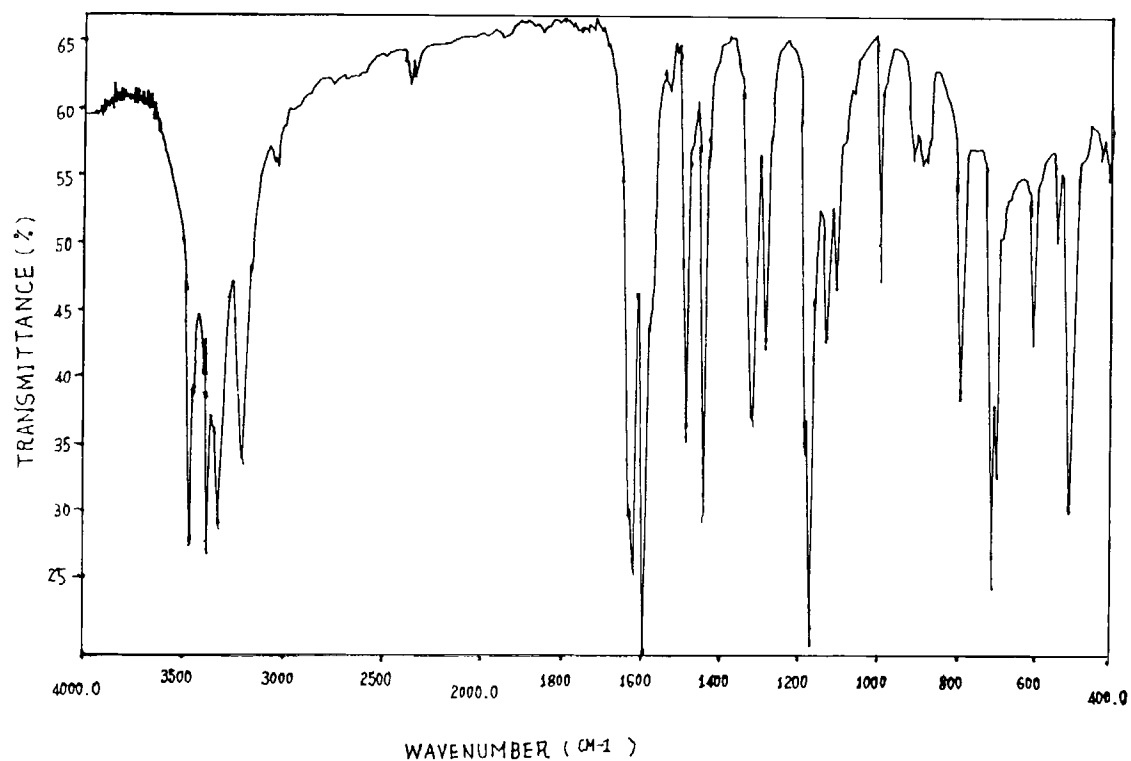


Figure 5 IR spectrum of TAPO.

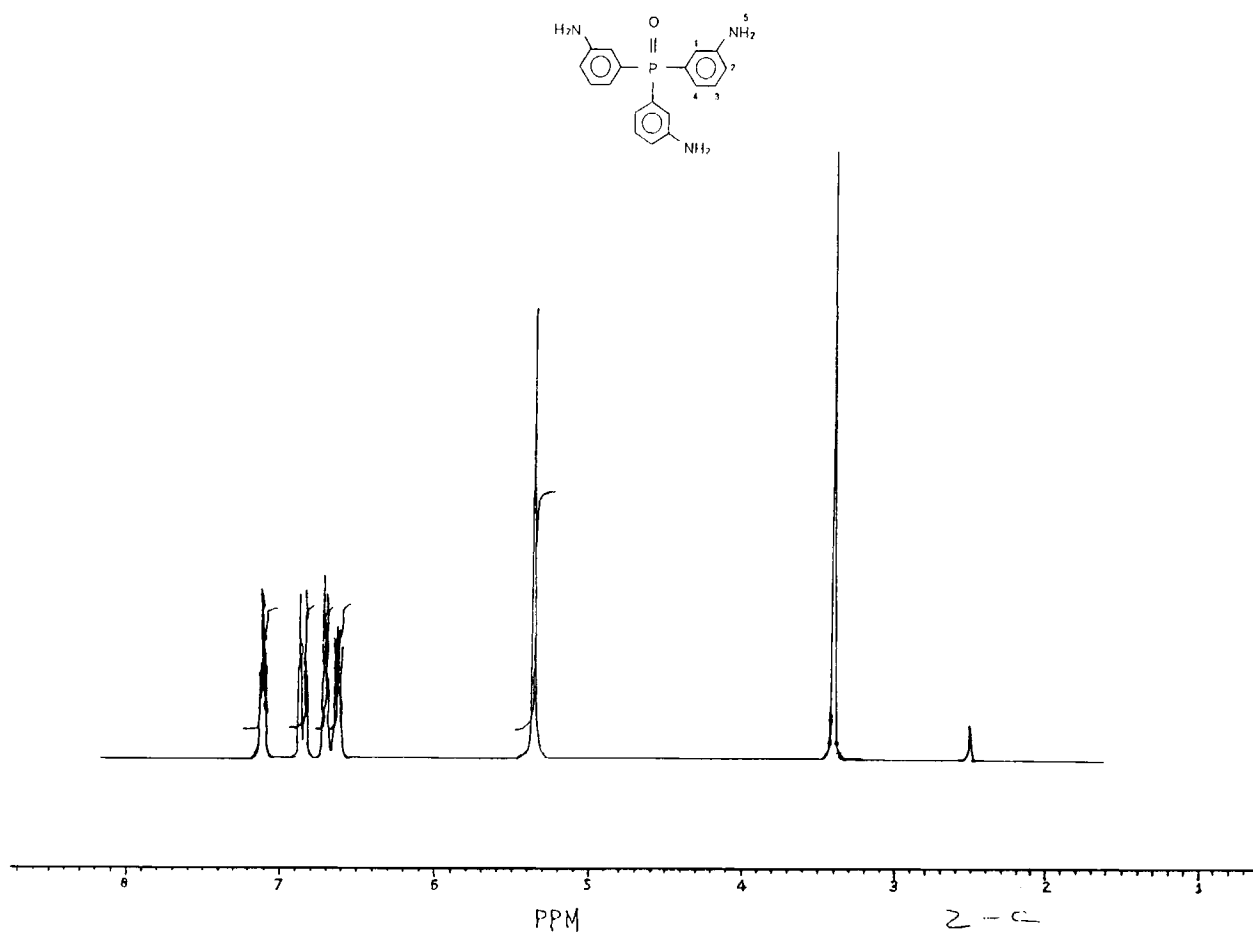


Figure 6 ¹H-NMR spectrum of TAPO.

Table IV $^1\text{H-NMR}$ Data of TAPO

Type of Proton	1	2	3	4	5
Chemical shifts (ppm)	6.85	6.71	6.62	7.10	5.34
	3H,d	3H,m	3H,m	3H,m	6H,s

Reactivity of Epoxy Resins and Curing Agents

Typical DSC thermograms of the epoxy-imide (DIDE) resin and curing agent compositions are shown in Figure 8. The influence of the chemical reactivity of the curing agent on cure behavior is apparent from this figure. For the epoxy-imide resin (DIDE) used, the exothermic starting temperature increases according to the order $\text{DDE} < \text{TAPO} < \text{DDS}$. A curing agent that exhibits a lower exothermal starting temperature under the same set of curing condition is more reactive toward the epoxy-imide resin. It is therefore reasonable to propose that the chemical reactivity of these three different curing agents toward the epoxy-imide resin increases as follow: $\text{DDS} < \text{TAPO} < \text{DDE}$. The typical

DSC thermograms of Epon 828 with three curing agents are shown in Figure 9. The exothermic starting temperature is in the order $\text{DDS} > \text{TAPO} > \text{DDE}$, so the order of reactivity is $\text{DDE} > \text{TAPO} > \text{DDS}$. DSC thermograms of DEN 438 with three curing agents are shown in Figure 10. The exothermic starting temperatures are in the order $\text{DDS} > \text{TAPO} > \text{DDE}$, so the order of reactivity is $\text{DDE} > \text{TAPO} > \text{DDS}$. From the above data, the lower reactivity of TAPO toward epoxy resin, as compared with DDE, should be attributed to electronic effects. In the case of TAPO, the electron withdrawing group, $\text{P} = \text{O}$, reduced the electron density of the amine nitrogen and subsequently reduced their nucleophilic attack on the oxirane ring of the epoxy resins. From Figures 8 to 10, we also found that the order of reactivity of three different resins (DEN 438, Epon 828, and DIDE) toward three kinds curing agents is $\text{DEN 438} > \text{Epon 828} > \text{DIDE}$.

Thermal Properties

To compare the thermal properties of these cured polymers, cured polymers were divided into six

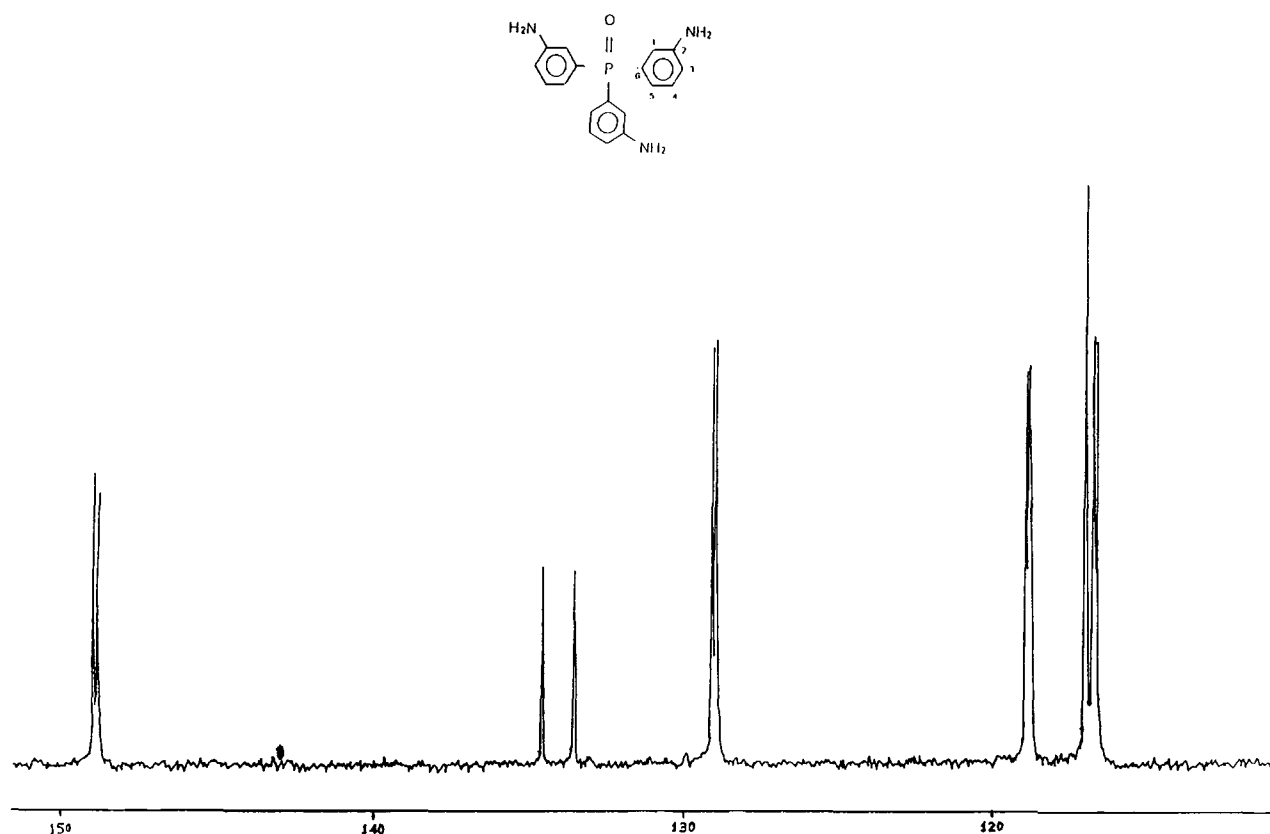
**Figure 7** $^{13}\text{C-NMR}$ spectrum of TAPO.

Table V ^{13}C -NMR Data of TAPO

Type of Carbon	C-1	C-3	C-4	C-5	Aromatic Carbon (C-2, C-6)
Chemical shifts (ppm)	133.56, 134.56	148.75, 148.89	116.91	128.93, 129.07	116.57, 116.67; 118.78, 118.88

Table VI Curing Cycle of Epoxy Systems

Compositions	Curing Temperature (°C)	Curing Time (min)	Postcure Temperature (°C)	Postcure Time (min)
DIDE/TAPO	140	80	230	30
DIDE/DDE	160	25	210	20
DIDE/DDS	200	30	250	20
DEN 438/TAPO	130	90	200	20
DEN 438/DDE	100	90	170	30
DEN 438/DDS	140	100	230	30
Epon 828/TAPO	140	80	210	30
Epon 828/DDE	120	35	170	35
Epon 828/DDS	180	25	230	20

groups: (1) DIDE/TAPO, Epon 828/TAPO, DEN 438/TAPO; (2) DIDE/DDS, Epon 828/DDS, DEN 438/DDS; (3) DIDE/DDE, Epon 828/DDE, DEN 438/DDE; (4) DIDE/TAPO, DIDE/DDS, DIDE/DDE; (5) Epon 828/TAPO, Epon 828/DDS, Epon 828/DDE; (6) DEN 438/TAPO, DEN 438/DDS, DEN 438/DDE (Figs. 11–16). To demonstrate the thermal properties of these cured polymers, T_{max} and temperatures of some characteristic weight losses are listed in Tables VII and VIII. From groups (1), (2), and (3), it is found that the epoxy-imide resin (DIDE) compositions show better thermal properties than the other epoxy resins. The heat resistance

and thermal oxidative stability could be improved via an introduction of an imide group into the structure of epoxy. From group (6), it is found that the TAPO curing agent composition shows better thermal properties for the DEN 438 resin.

Flame Properties

Flame resistance can be evaluated from the char residue on pyrolysis. A linear relationship between oxygen index (OI) and char residue for halogen-free polymers has been established by Van Krevelen.¹²

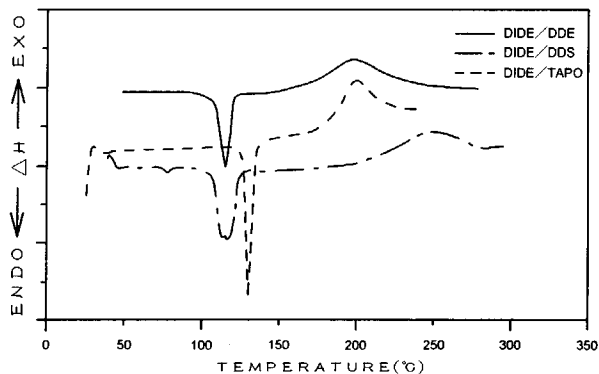


Figure 8 DSC thermograms of three polymers (DIDE/DDE, DIDE/DDS, DIDE/TAPO). The heating rate is 10°C/min.

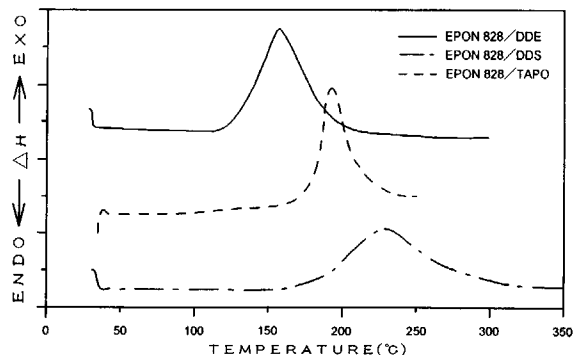


Figure 9 DSC thermograms of three polymers (Epon 828/DDE, Epon 828/DDS, Epon 828/TAPO). The heating rate is 10°C/min.

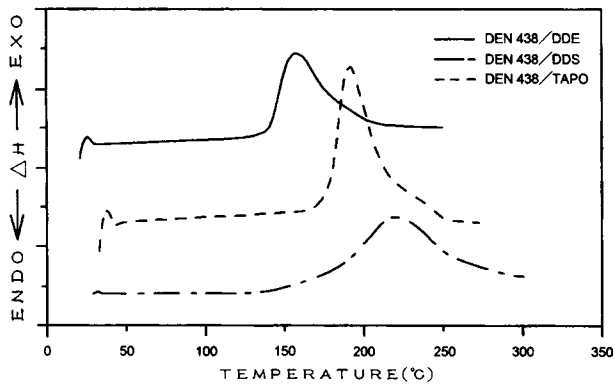


Figure 10 DSC thermograms of three polymers (DEN 438/DDE, DEN 438/DDS, DEN 438/TAPO). The heating rate is 10°C/min.

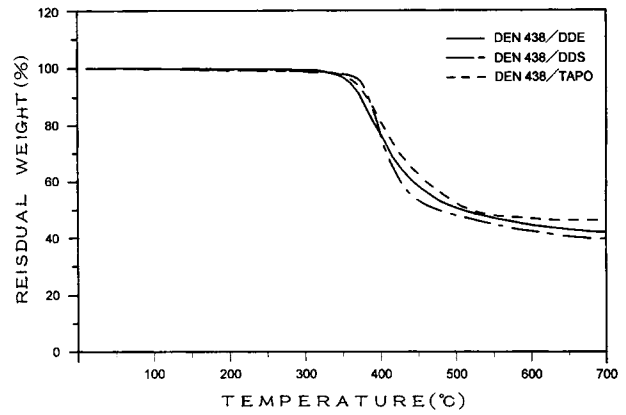


Figure 13 TGA thermograms of DEN 438/DDE, DEN 438/DDS, and DEN 438/TAPO in nitrogen environment. The heating rate is 10°C/min.

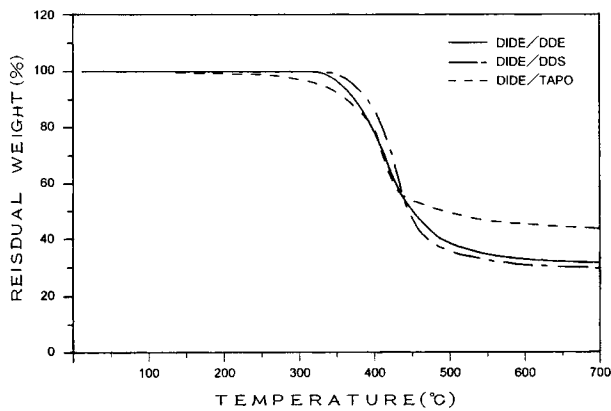


Figure 11 TGA thermograms of DIDE/DDE, DIDE/DDS, and DIDE/TAPO in nitrogen environment. The heating rate is 10°C/min.

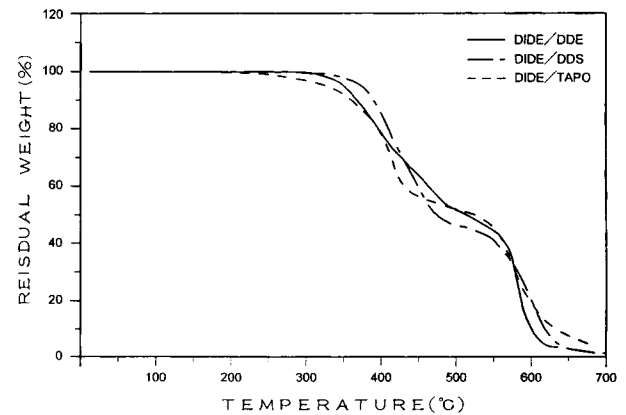


Figure 14 TGA thermograms of DIDE/DDE, DIDE/DDS, and DIDE/TAPO in air. The heating rate is 10°C/min.

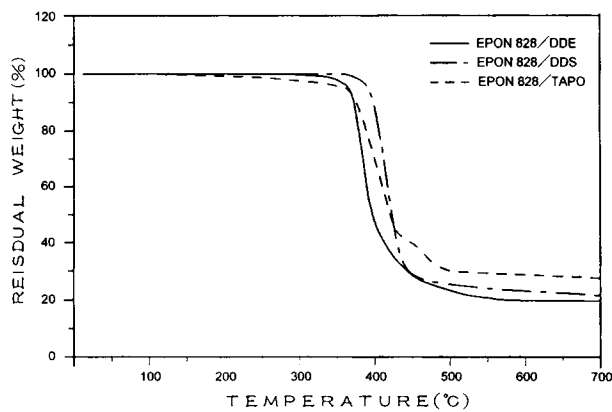


Figure 12 TGA thermograms of Epon 828/DDE, Epon 828/DDS, and Epon/TAPO in nitrogen environment. The heating rate is 10°C/min.

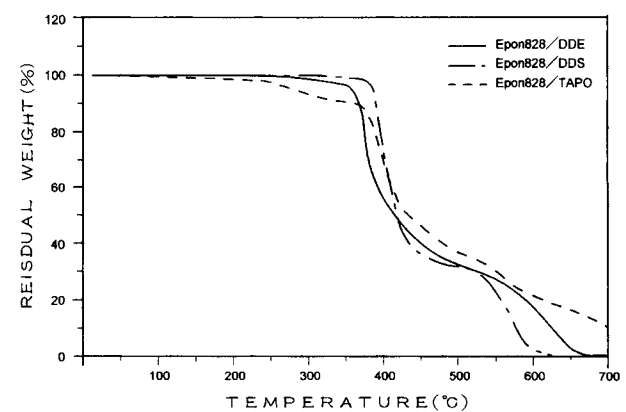


Figure 15 TGA thermograms of Epon 828/DDE, Epon 828/DDS, and Epon/TAPO in air. The heating rate is 10°C/min.

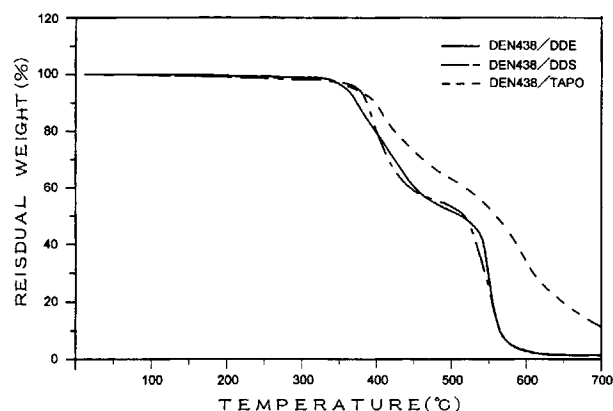


Figure 16 TGA thermograms of DEN 438/DDE, DEN 438/DDS, and DEN 438/TAPO in air. The heating rate is 10°C/min.

Increased char formation can limit production of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, as well as

decrease the thermal conductivity of the surface of burning materials.¹³

Those phosphorus-containing polymers are expected to have a higher char yield on pyrolysis. To demonstrate the flame retardation of those phosphorus-containing polymers, those cured polymers are divided into three groups: (1) DIDE/TAPO, DIDE/DDS, DIDE/DDE; (2) Epon 828/TAPO, Epon 828/DDS, Epon 828/DDE; (3) DEN 438/TAPO, DEN 438/DDS, DEN 438/DDE. Char yields of those cured polymer in nitrogen and air at 600 and 700°C are listed in Tables VII and VIII. For group (1) the phosphorus-containing polymer, DIDE/TAPO, has a higher char yield than the other two polymers, DIDE/DDS and DIDE/DDE. For group (2), the phosphorus-containing polymer, Epon 828/TAPO, has a higher char yield than the other two polymers, Epon 828/DDS and Epon 828/DDE. For group (3), the phosphorus-containing polymer, DEN 438/TAPO, has a higher char yield

Table VII TGA Data of Cured Epoxy Resins in Nitrogen Environment^a

Materials	T_{\max} (°C)	Temperature at Characteristic Weight Loss (%)					Residue (%)	
		10%	20%	30%	40%	50%	600°C	700°C
DIDE/TAPO	414.3	368.0	400.0	414.0	428.0	488.0	45.0	43.3
DIDE/DDS	428.2	385.9	410.9	425.0	435.9	450.0	31.1	29.1
DIDE/DDE	418.2	371.9	396.9	415.0	429.7	453.1	31.9	30.4
Epon 828/TAPO	407.1	380.0	396.0	406.0	413.0	423.0	27.8	26.4
Epon 828/DDS	420.1	401.8	408.9	414.3	419.6	426.8	21.8	19.9
Epon 828/DDE	382.2	375.2	379.6	386.3	390.8	397.5	19.2	18.7
DEN 438/TAPO	407.1	391.0	410.0	434.0	470.0	525.0	47.0	45.9
DEN 438/DDS	400.0	387.0	401.0	413.0	432.0	470.0	41.9	39.2
DEN 438/DDE	388.1	372.0	394.0	420.0	449.0	504.0	43.7	40.5

^a Heating rate: 10°C/min.

Table VIII TGA Data of Cured Epoxy Resins in Air^a

Materials	T_{\max} (°C)	Temperature at Characteristic Weight Loss (%)					Residue (%)	
		10%	20%	30%	40%	50%	600°C	700°C
DIDE/TAPO	414.3	367.0	401.0	418.0	438.0	525.0	21.0	4.1
DIDE/DDS	422.4	384.4	414.6	431.3	450.0	473.4	20.4	0
DIDE/DDE	385.5	362.5	394.6	426.8	458.0	507.1	10.4	0
Epon 828/TAPO	407.7	365.0	394.0	402.0	412.0	427.0	20.9	9.8
Epon 828/DDS	395.8	392.2	401.8	407.1	414.3	421.4	3.1	0
Epon 828/DDE	374.4	368.3	375.0	381.7	397.3	419.6	16.7	0
DEN 438/TAPO	446.2	402.0	431.0	468.0	522.0	564.0	35.2	11.7
DEN 438/DDS	405.8	387.0	402.0	419.0	448.0	517.0	2.6	1.4
DEN 438/DDE	417.3	373.0	404.0	429.0	460.0	514.0	2.6	1.3

^a Heating rate: 10°C/min.

than the other two polymers, DEN 438/DDS and DEN 438/DDE.

From above results, we have found that the phosphorylated epoxy polymers demonstrated a higher char yield than nonphosphorylated polymers.

CONCLUSIONS

The structures of synthesized DIDE and phosphorus-containing triamine curing agent (TAPO) were confirmed through EA, IR, ¹H-NMR, and ¹³C-NMR characterization. The thermal and flame resistances of epoxy were confirmed in this study as capable of being significantly improved through introduction of imide and phosphorus groups into the epoxic structure. The phosphorus-containing epoxy polymers were observed to have a high char yield on pyrolysis than nonphosphorylated epoxy polymers.

This work was supported by the National Science Council, Republic of China, under Grant NSC 83-0117-C041-002E.

REFERENCES

1. P. A. Martínez, V. Cádiz, A. Mantecón, and A. Serra, *Angew. Makromol. Chem.*, **133**, 97 (1985).
2. P. A. Martínez, V. Cádiz, A. Mantecón, and A. Serra, *Angew. Makromol. Chem.*, **140**, 133 (1986).
3. P. A. Martínez, V. Cádiz, A. Mantecón, and A. Serra, *Eur. Polym. J.*, **23**, 481 (1987).
4. V. Cádiz, A. Mantecón, and A. Serra, *Angew. Makromol. Chem.*, **152**, 55 (1987).
5. P. A. Martínez, V. Cádiz, A. Mantecón, and A. Serra, *Angew. Makromol. Chem.*, **156**, 37 (1988).
6. B. S. Rao, *J. Polym. Sci., Polym. Lett.*, **26**, 3 (1988).
7. M. D. Shau and W.-K. Chin, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 1653 (1993).
8. M.-D. Shau, W.-C. Tsai, and W.-K. Chin, *J. Polym. Sci., Part A: Polym. Chem.* (to appear).
9. J. A. Mikroyannidis and P. A. Kourtidis, *J. Appl. Polym. Sci.*, **29**, 197 (1984).
10. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, pp. 4-18.
11. F. Challenger, J. F. Wilkinson, et al., *J. Chem. Soc.*, **125**, 2675 (1924).
12. D. W. Van Krevelen, *Polymer*, **16**, 615 (1975).
13. E. M. Pearce and R. Liepins, *Environ. Health Perspect.*, **11**, 69 (1975).

Received January 19, 1995

Accepted April 27, 1995