

Flame Retardant Epoxy Polymers Using Phosphorus-Containing Polyalkylene Amines as Curing Agents

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ABSTRACT: Two series of novel phosphorus-containing poly(alkylene) amines with or without aromatic groups were synthesized via reacting phosphoryl chloride derivatives with commercially available polyetheramines, ethylenediamine and N-phenyl-1,4-phenylenediamine, respectively. Chemical structures of the amines were characterized with FTIR, NMR, P (phosphorus) content measurement, and amine content titration. These amines were then utilized as curing agents to react with diglycidyl ether of bisphenol A for preparing phosphorus containing epoxy polymers. The introduction of soft —P—O— linkage, polyalkylene, and hard aromatic group into the backbones of the synthesized phosphorus-containing amine (PCA) provides epoxy resins with tunable flexibility. Thermal analysis of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) reveals that these resulted epoxy resins possess moderate T_g 's and thermal stability. Furthermore, high char yields in TGA and high limited oxygen index (LOI) values indicate that these phosphorus-containing epoxy (PCE) resins are capable of exhibiting excellent flame retardant properties. These polymers can be potentially utilized in flame retardant epoxy coatings and other applications. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3526–3538, 2001

Key words: phosphorus; polyalkylene; epoxy resin; flame retardant; limited oxygen index

INTRODUCTION

Epoxy resins, with characteristics of toughness, low shrinkage on cure, excellent attachment to many substrates and good alkali resistance, are widely used in casting, adhesion and lamination.¹ By changing the chemical structure of the curing agents, a wide range of polymer properties of the epoxy resins can be obtained.^{2–4} For example,

using polyalkylene polyamines as curing agents leads to flexible epoxy resins for coating applications.^{5,6} The effect of alkyl and aromatic groups on the above-mentioned curing agents for the flexibility of their corresponding epoxies was also discussed.⁷ The extent of epoxy polymers' flexibility was decided by the balance between hard (aromatic) and soft (alkyl) chemical groups in the same molecule.

One of the main drawbacks of the epoxy resins in many applications is their flammability, because they are organic materials. Therefore, attempts at imparting flame retardancy to epoxy

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resins have been made.^{8–18} Reactive type phosphorous flame retardants for epoxy resins are choice materials for these investigations, as they circumvent the generation of halogenated toxic/corrosive gases under combustion,^{8–10} have high flame retardant efficiency and fewer influences on the resins' properties.^{11–13} Covalent incorporation of phosphorus onto the epoxy resins, via phosphorylating oxiranes and/or curatives, seems to be a reasonable approach to bring about flame retardancy.^{14–18} The epoxy resins reported in the literature exhibit excellent flame retardant capacity, confirming that covalently incorporating phosphorus onto epoxy resins is an efficient way for improving their flame resistance.

Commercially available amines, such as Jeffamines series and their derivatives, used as curing agents for epoxy resins have been previously reported.^{5–7,19,20} However, this kind of phosphorus-containing epoxy (PCE) resins, and their flame retardant properties have not been reported on to date. The purpose of the present article is to develop a series of phosphorus-containing polyalkylene amines with/without aromatic (hard) groups as curatives for epoxy resins. These phosphorus-containing amines (PCA) were obtained from reacting Jeffamines with phosphoryl chlorides. Synthesis, characterization, and curing behavior of the obtained amines are discussed. Thermal properties, flame retardancy, and degradation behavior of the resulted PCE resins were also investigated. As safety and environmental issues become more significant, the utilization of PCE resins in electronic/electrical parts and building/construction products increases rapidly. The developed materials in this study would suit the needs of these applications.

EXPERIMENTAL

Materials

1,3-benzenediphosphoro tetrachloridate $\{\text{Cl}_2\text{P}(\text{O})[\text{OC}_6\text{H}_4\text{OP}(\text{O})\text{Cl}]_n\text{Cl}\}$ (DCP, $n = 1,2$) was synthesized from reacting phosphoryl trichloride (POCl_3 , from Aldrich Co., Milwaukee, WI) with resorcinol (from TCI, Tokyo, Japan) in our laboratory. No chemical shift at 6–7 ppm ($-\text{OH}$) was observed in $^1\text{H-NMR}$. This indicates that the resorcinol groups were completely reacted. Moreover, tris(2-chloroethyl) phosphate (TCEP) was used as an external standard to evaluate the ratio of monomer to dimer for DCP in $^{31}\text{P-NMR}$. The

ratio of monomer ($\delta = 2.5$ ppm; OPOCl_2) to dimer ($\delta = -6.5$ ppm; O_2POCl) according to TCEP ($\delta = -6.5$ ppm; O_3PO) is greater than 19. The monomer ratio is therefore higher than 95%. Phenylphosphonic dichloride (PPDC) was purchased from Aldrich Co. and used as received. Poly(propylene glycol) bis(2-aminopropyl) ether, Jeffamine D230 ($M_w = 230$) and Jeffamine D400 ($M_w = 400$), were from Huntsman Chemical Co., Salt Lake City, UT. Ethylenediamine (EDA, from Fluka Chemical Co., Buchs, Switzerland), *N*-phenyl-1,4-phenylenediamine (PDA, from Forte Chemical Co., Kaoshiung, Taiwan), aluminum oxide (from Lancaster Co., Morecambe, UK), and NaHCO_3 (from Wako Co., Osaka, Japan) were all used as received. Tetrahydrofuran (THF, dried with sodium metal), Toluene (dried with sodium metal), and Chloroform (CHCl_3 , dried with calcium hydride) were made available from Tedia Chemical Co., Fairfield, CT, to be refluxed with the drying agents and distilled out prior to use. Diglycidyl bisphenol-A Epoxy (BE188, EEW = 188) was from Chang Chun Plastic Co., Kaoshiung, Taiwan.

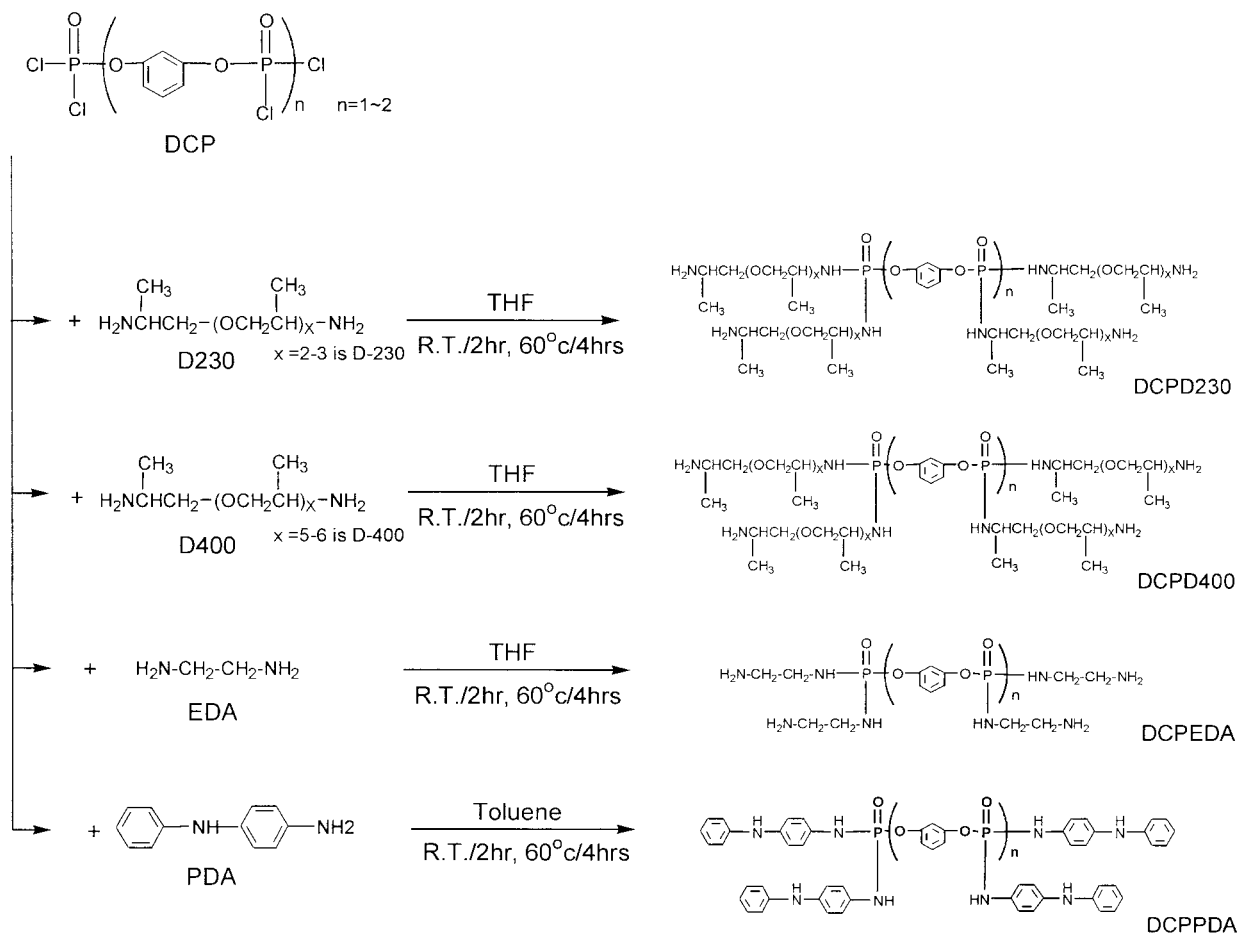
Synthesis of DCP-amines, DCPD230 and DCPD400

A solution of DCP (24 g) in 500 mL of THF was gradually added into a stirred solution of Jeffamine D230 (56 g solute in 50 mL THF) under nitrogen atmosphere. The solution was stirred at room-temperature for 2 h and heated to 60°C for 4 h to complete the reaction. The solvent in the reaction solution was then removed with a rotary evaporator. The product was extracted with CHCl_3 and then washed with $\text{NaHCO}_3(\text{aq})$ three times. The organic layer was collected and concentrated under a reduced pressure. The viscous product DCPD230 was obtained with a yield of 95% (Scheme 1).

DCPD400 was prepared from the above procedure by reacting 32 g DCP with 38 g Jeffamine D400. A viscous liquid with a yield of 95% was obtained (Scheme 1).

Synthesis of DCP-amine, DCPEDA

Ethylenediamine (23 g; EDA) in 500 mL THF with an ice/salt bath was stirred under nitrogen atmosphere. A solution of DCP (38 g) in 500 mL THF was added dropwise to the reaction solution in 1 h. After maintaining at room-temperature for 2 h, the solution was kept at 60°C for another 4 h. The reaction solution was concentrated with a



Scheme 1 Synthesis routes for DCP-amines.

rotary evaporator. The crude product was then dissolved in 300 mL distilled water and mixing with 7.6 g aluminum oxide was utilized to remove Cl^- from the solution. After filtration and concentration, DCPEDA was obtained with a yield of 85% (Scheme 1).

Synthesis of DCP-amine, DCPFDA

N-phenyl-1,4-phenylenediamine (57 g; PDA) in 500 mL toluene was stirred under a nitrogen atmosphere. A solution of DCP (30 g) in 500 mL toluene was added dropwise in 1 h. The reaction mixture was then kept at room temperature and 60°C for 2 and 4 h, respectively. After being concentrated with a rotary evaporator, the reaction mixture was extracted with chloroform and washed with NaHCO_3 aqueous solution three times. The collected organic layer was concentrated. The crude product was then precipitated from the 1:1 mixture of methanol and dichlo-

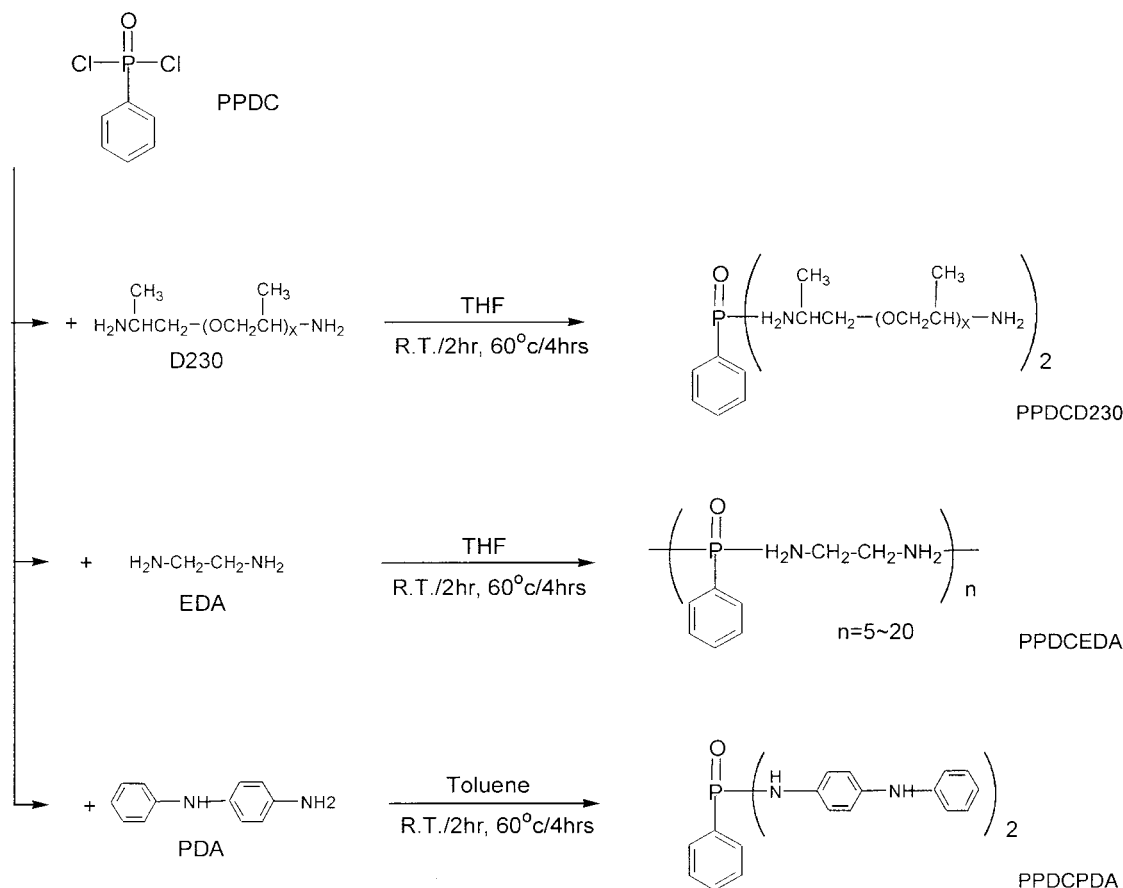
romethane to obtain powder DCPFDA with a yield of 70% (Scheme 1).

Synthesis of PPDC-amines, PPDCD230, PPDCEDA, and PPDCFDA

Synthesis procedures for PPDC-amines are the same as those for DCP-amines except for replacing DCP by PPDC in the operation for the respective products. The yields of the PPDC-amines are also similar to those of their corresponding DCP-amines, respectively (Scheme 2).

Preparation of Epoxy Resins

Epoxy polymers were obtained via thermally curing BE188 with various amine curatives. The reactant compositions were mixed homogeneously with a 1:1 equivalent ratio. The conditions of the curing cycles were determined from DSC tracing of the respective BE188/amine curing agent compositions.



Instrumental Measurements

Amine contents were estimated by using ASTM D2073-92 method.²¹ Infrared spectra were obtained using a PERKIN ELMER PARAGON 500 Fourier Transform Infrared Spectrophotometer (FTIR). ¹H-NMR and ³¹P-NMR spectra were recorded with a Brüker MSL-300 NMR Spectrometer. Differential scanning calorimeter (DSC) thermograms were recorded with a Seiko DSC 5200 at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a Seiko TGA 5200 at a heating rate of 10°C/min under nitrogen or air atmosphere. Elemental Analysis was performed on an F002 Heraeus CHN-O Rapid Elemental Analyzer employing acetanilide as a standard. Phosphorus contents of the chemicals were determined via phosphorus elemental analysis by a Micro Digestion Apparatus with a spectrophotometer. Limited oxygen index (LOI) values were measured on a Stanton Redcraft Flame Meter by a modified method as reported by the literature.^{12,22}

The percentage in the O₂-N₂ mixture that was just sufficient to sustain the flame was taken as the LOI.

Activation Energies of Curing Kinetics from DSC

A simple but accurate relationship among activation energy (E_a), heating rates (ϕ), and temperature of exothermic peak (T_p) as

$$E_a = \frac{-R \Delta \ln \phi}{1.052 \Delta(1/T_p)} \quad (1)$$

is used.²³⁻²⁵ The exothermic peaks at various heating rates of the curing reactions were recorded on a DSC.

Activation Energies of Thermal Degradation from TGA

The integral technique of Ozawa based on the following equation

Table I Structural Characteristics of DCP-Amines

Compounds	Amine Content (meq/g)		Phosphorus Content (wt %)		FTIR Absorption (cm ⁻¹)	¹ H-NMR (ppm)	³¹ P-NMR (ppm)
	Calculated	Measured	Calculated	Measured			
DCPD230	3.44	3.19	5.92	5.60	910 (P—N) 1262 (P=O) 1111 (C—O—C) 3289 (—NH)	δ = 0.6–0.7 (—CH—) δ = 0.9 (—CH ₃) δ = 2.5–2.9 (—NH—, —NH ₂) δ = 3.1–3.4 (—OCH ₂ —) δ = 6.7–7.3 (aromatic protons)	δ = 3.3 (OPO ₂ N) δ = 10.7–11.9 (OPON ₂)
	1.88	1.66	3.72	3.73	910 (P—N) 1261 (P=O) 111 (C—O—C) 3297 (—NH)	δ = 0.6–0.7 (—CH—) δ = 0.9 (—CH ₃) δ = 2.5–2.9 (—NH—, —NH ₂) δ = 3.1–3.4 (—OCH ₂ —) δ = 6.7–7.3 (aromatic protons)	δ = -4.0 (OPO ₂ N) δ = 3.1 (OPON ₂)
	8.12	6.03	14.22	13.98	953 (P—N) 1316 (P=O) 3412 (—NH)	δ = 2.5–2.9 (—CH ₂) δ = 6.7–7.3 (aromatic protons)	δ = -5.9 (OPO ₂ N) δ = 0.7 (OPON ₂)
	5.91	— ^a	7.03	7.21	954 (P—N) 1315 (P=O) 3434 (—NH)	δ = 2.5 (—NH—) δ = 6.7–7.8 (aromatic protons)	δ = 2.9 (OPO ₂ N) δ = 10.7–13.1 (OPON ₂)

^a The value was not obtained because the sample was too dark.

$$\log F(\alpha) = \log(A \times Ea/R) - \log \beta + \log[p \times Ea/RT] \quad (2)$$

is used, where $\log F(\alpha)$ equals $\int d\alpha/(1-\alpha)^n$, Ea equals activation energy, α equals conversion of degradation, β equals heating rate, A equals Arrhenius constant. The Ea can be obtained from a plot of $\log \beta$ against $1/T$ at a constant α .^{26,27} The data of degradation conversion were recorded on a TGA at various heating rates.

RESULTS AND DISCUSSION

Synthesis of PCA

Two series of PCA were synthesized according to Schemes 1 and 2. One series, the DCP-amines, contain aromatic groups in their backbones, whereas a pendant phenyl ring is attached directly to P=O group in the backbone of the other series, PPDC-amines. These PCA compounds were obtained by the formation of P—N bond via reacting P—Cl reactive groups of the phosphonic chloride compounds (DCP and PPDC) with the —NH₂ groups of the amines (Jeffamine D-230, Jeffamine D-400, EDA, and PDA). Chemical structures of the obtained products were characterized with IR, ¹H-NMR, ³¹P-NMR, elemental analysis, and amine titration. The analysis data is listed in Table I and Table II. It is noteworthy that the formation of P—N bond was represented by the absorption peaks of the FTIR spectra at about 910 cm⁻¹ for D230 and D400 derivatives, and 950 cm⁻¹ for EDA and PDA derivatives.²⁸ The extent of the above reaction is studied by monitoring emergence of the P—N absorption peaks. Moreover, other specific absorption peaks at 1260 cm⁻¹ (P=O), 1111 cm⁻¹ (C—O—C), and 3289 cm⁻¹ (—NH) in the FTIR spectrum of DCPD230 (Fig. 1) further confirm the correct chemical structure of DCPD230. These absorption peaks were also observed in the FTIR spectra of the other PCA, demonstrating successful synthesis of these compounds. Figure 2 shows the ¹H-NMR spectrum of DCPD230. The chemical shifts at δ equals 0.6–0.7 ppm (—CH—), δ equals 0.9 ppm (—CH₃), δ equals 2.5–2.9 ppm (—NH— and —NH₂), δ equals 3.1–3.4 ppm (—OCH₂—), and δ equals 6.7–7.3 ppm (aromatic protons) also coincide with the chemical structure of DCPD230. However, two major peaks are found in the ³¹P-NMR spectrum of DCPD230. These two different

Table II Structural Characteristics of PPDC-Amines

Compounds	Amine Content (meq/g)		Phosphorus Content (wt %)		FTIR Absorption (cm ⁻¹)	¹ H-NMR (ppm)	³¹ P-NMR (ppm)
	Calculated	Measured	Calculated	Measured			
PPDCD230	6.87	6.18	5.30	5.02	908 (P—N) 1257 (P=O) 1120 (C—O—C) 3360 (—NH) 953 (P—N) 1316 (P=O) 3436 (—NH) 945 (P—N) 1316 (P=O) 3314 (—NH)	δ = 0.9–1.1 (—CH—, —CH ₃) δ = 2.5–2.9 (—NH—, —NH ₂) δ = 3.1–3.6 (—OCH ₂ —) δ = 7.3–7.8 (aromatic protons) δ = 3.0–3.4 (—CH ₂ —) δ = 7.5–7.8 (aromatic protons)	δ = 20.6
PPDCEDA	12.69	10.21	15.74	— ^a			δ = 11.2 δ = 14.6
PPDCPDA	8.16	— ^a	6.30	7.14			δ = 5.8

^a The value was not obtained because the sample was too dark.

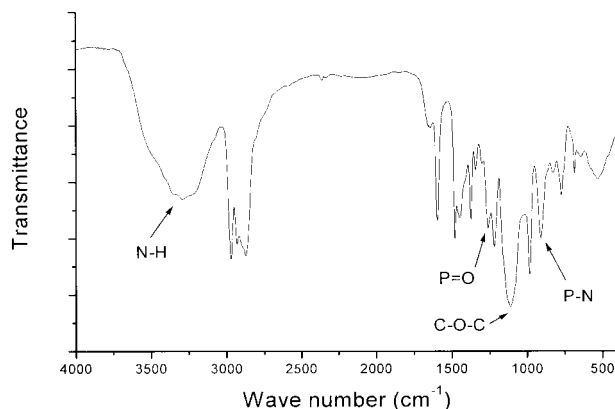


Figure 1 FTIR spectrum of DCPD230.

phosphorus absorption peaks of DCPD230 in ^{31}P -NMR possibly result from the raw material DCP due to the fact that DCP contains a notable amount of dimers ($n = 2$). Therefore, the phosphorus absorption peaks of DCPD230 in ^{31}P -NMR are assigned to be OPO_2N (δ equals 0.9 ppm) and OPON_2 (δ equals 10.7 ppm) (Fig. 3). For PPDCD230 and PPDCPDA, only one peak is found in their ^{31}P -NMR spectrum, revealing that PPDCD230 and PPDCPDA are obtained in pure monomer form. In addition, three peaks are observed in the ^{31}P -NMR spectrum of PPDCEDA, indicating that PPDCEDA is obtained in oligomer form. This coincides with that reported in the literature.²⁹ The data of NMR analysis for the other PCA is listed in Table I and Table II, demonstrating the chemical structures of these compounds.

Phosphorus and amine contents of the synthesized PCA were further determined by EA and amine titration, respectively. The coincidence between the calculated and measured values of the P and amine contents further confirms the chemical structures of the synthesized compounds (Ta-

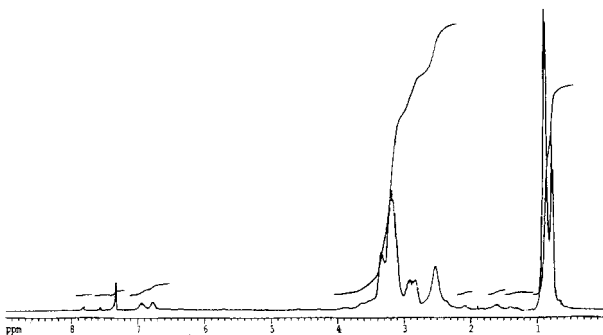


Figure 2 ^1H -NMR spectrum of DCPD230.

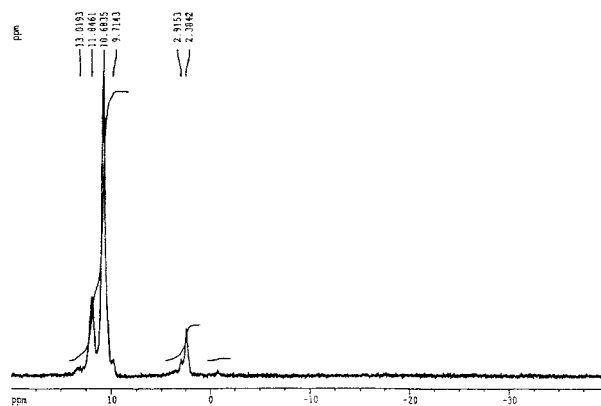


Figure 3 ^{31}P -NMR spectrum of DCPD230.

ble I and Table II). However, some of the phosphorus and amine contents are not measurable due to the dark color of the samples. Nevertheless, the calculated values were used in the following curing reactions and properties estimation given that the aforementioned calculated and measured values are quite close to each other.

Curing Reactions of Epoxy BE188 with The Synthesized Amines

Curing reactions were studied with DSC. Typical DSC thermograms of BE188 cured with amines without/with phosphorus groups are shown in Figures 4–6. The reactivity of the curing agents could be directly read from the starting temperatures of the exothermic peaks.^{14,30} Therefore, the reactivity of the non-phosphorus amines were determined to be in the order of $\text{EDA} > \text{D230} > \text{D400} > \text{PDA}$. This order is coincidental with the electron densities of the $-\text{NH}_2$ groups of these amines, because it is

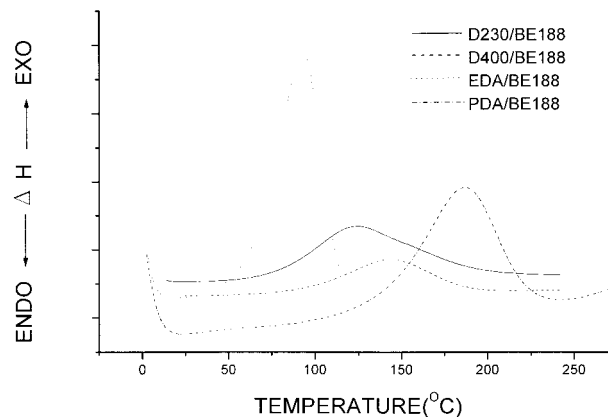


Figure 4 DSC thermograms of BE188 cured with the phosphorus-free amines.

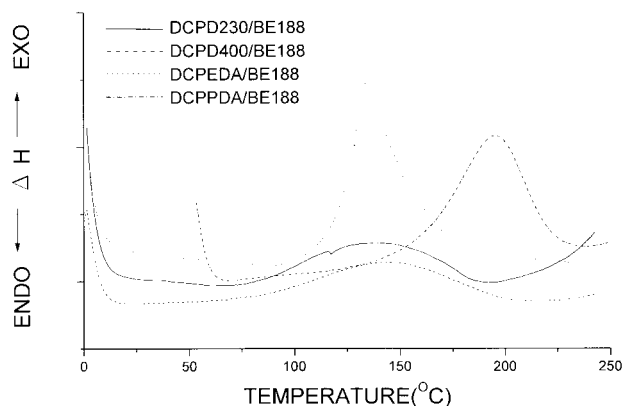


Figure 5 DSC thermograms of BE188 cured with DCP-amines.

reported that the reactivity of an amine toward epoxy is mainly dependent on the electron density of its $-\text{NH}_2$ group.³⁰ The electron-pushing $-\text{CH}_2-$ enriches the electron density of $-\text{NH}_2$ in EDA, and the electron withdrawing benzyl group reduces the electron density of $-\text{NH}-$ in PDA. However, the reactivities of the resulted amines are reduced while the relatively strong electron withdrawing group $-\text{P}=\text{O}$ is introduced into the backbones of these amines. Therefore, taking D230 derivatives as the example, the reactivities of the phosphorus containing amines are determined to be in the order of $\text{D230} > \text{PPDCD230} > \text{DCPD230}$. It is also noteworthy that the reactivities of DCPD230 and PPDCD230 are similar to those of DCPEDA and PPDCEDA, respectively. This could be due to the electron density of $-\text{NH}_2$ in EDA is much more reduced by the electron withdrawing $\text{P}=\text{O}$ group than that in D230, because of the relatively short molecular chain length of EDA.

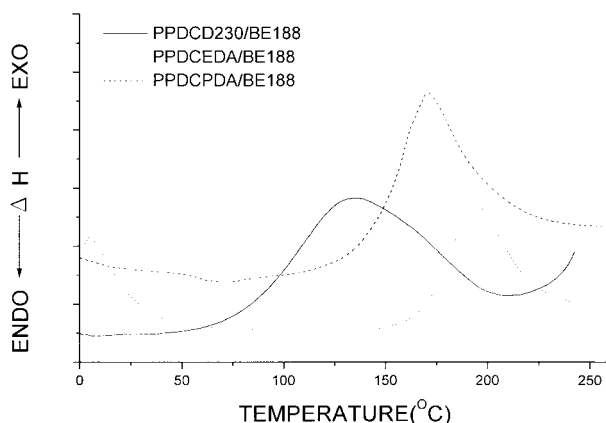


Figure 6 DSC thermograms of BE188 cured with PPDC-amines.

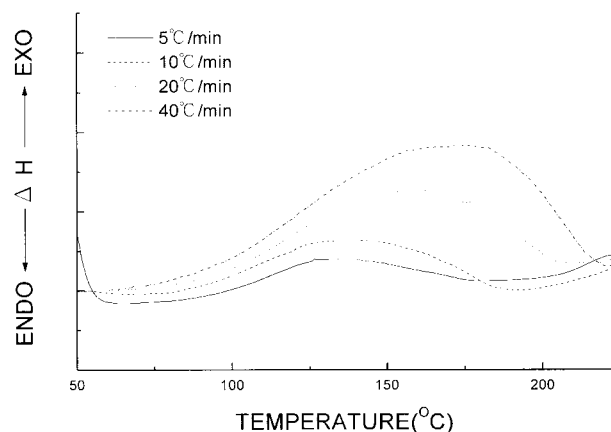


Figure 7 DSC thermograms of BE188 cured with DCPD230 at various heating rates.

Activation energies of the phosphorus containing amines of DCP series were further determined by a simple but accurate relationship among activation energy (E_a), heating rates (ϕ), and temperature of exothermic peak (T_p) as in Equation 1.

$$E_a = \frac{-R \Delta \ln \phi}{1.052 \Delta(1/T_p)} \quad (1)$$

T_p values at various heating rates for the curing reactions were recorded with DSC measurements (Fig. 7). Therefore, the activation energies of the curing reactions of DCP-amines/BE188 are determined from the slopes of the plots of $\ln(\text{heating rate})$ vs. $1/T_p$ (Fig. 8), and are listed in Table III. The values of the activation energies, 63.4 and

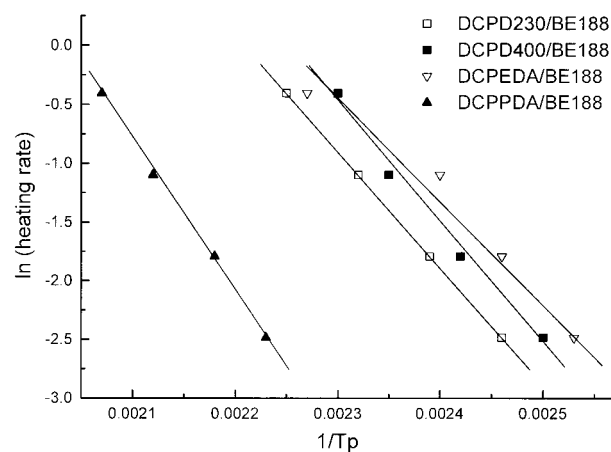


Figure 8 Plots of $\ln(\text{heating rate})$ vs. $1/T$ for BE188/DCPD230 resin under nitrogen atmosphere.

Table III Activation Energies of the Curing Reactions of DCP-Amines with BE188

DCP-amines	Activation Energy (kJ/mol)
DCPD230	76.2
DCPD400	80.8
DCPEDA	63.4
DCPPDA	109.6

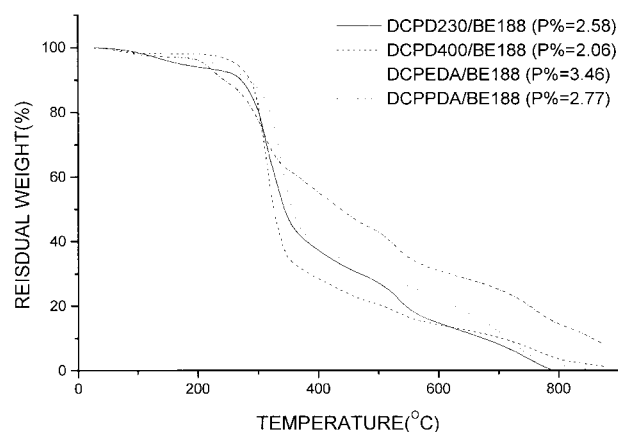
109.6 kJ/mol for the primary and secondary amine reactions toward epoxy, respectively, are similar to those reported in the literature.^{25,31,32}

Thermal and Flame Retardant Properties

PCE polymers were prepared from the synthesized amines and BE188 according to the compositions and curing conditions shown in Table IV. Glass transition temperatures (T_g 's) of the DCP-amines cured epoxy resins are lower than those of their phosphorus free counterparts. The low T_g 's might result from the flexible —P—O— group in the backbones of the cured polymers. Furthermore, introducing the large molecular size of P—O—Ph—O—P into the curing agents also reduces the crosslinking density of the resulted polymers, that is, to reduce their glass transition temperatures. However, the relatively low T_g 's were not observed in the PPDC-amines cured polymers. The polymers from PPDCD230 and PPDCPDPA even exhibited higher T_g 's than the polymers from their counterpart D230 and PDA, respectively. The high T_g 's of the PPDCD230 and PPDCPDPA could possibly result from the rela-

Table IV Epoxy Resins: Curing Conditions and Their Glass Transition Temperatures

Compositions	Curing Cycles			T_g (°C)
	1 h	2 h	2 h	
D230/BE188	50°C	100°C	150°C	69
DCPD230/BE188	50°C	100°C	150°C	45
PPDC230/BE188	50°C	100°C	150°C	72
D400/BE188	50°C	100°C	150°C	41
DCPD400/BE188	50°C	100°C	150°C	7
EDA/BE188	50°C	100°C	150°C	85
DCPEDA/BE188	50°C	100°C	150°C	59
PPDCEDA/BE188	75°C	125°C	175°C	83
PDA/BE188	100°C	150°C	200°C	112
DCPPDA/BE188	100°C	150°C	200°C	91
PPDCPDPA/BE188	100°C	150°C	200°C	120

**Figure 9** TGA thermograms of the BE188/DCP-amine resins under air atmosphere.

tively rigid P—Ph group in the curing agents. However, PPDCEDA cured epoxy polymer does not exhibit high T_g as compared with PPDCD230 and PPDCPDPA cured epoxy polymers. PPDCEDA was obtained in the form of oligomers, which possess a relatively long molecular chain length. This leads to low crosslinking density, i.e., low T_g for the PPDCEDA cured polymers.

TGA thermograms of the DCP-amines cured epoxies under air and N_2 atmosphere are shown in Fig. 9 and Fig. 10, respectively. The weight loss data is listed in Table V and Table VI. Introducing the phosphorus groups into the curing agents would reduce the thermal stability of the resulted epoxy resins. The depressed thermal stability of the PCE polymers could result from the decomposition of the P—O—C bonds.¹⁴ However, the weight loss of the PCE polymers at high temper-

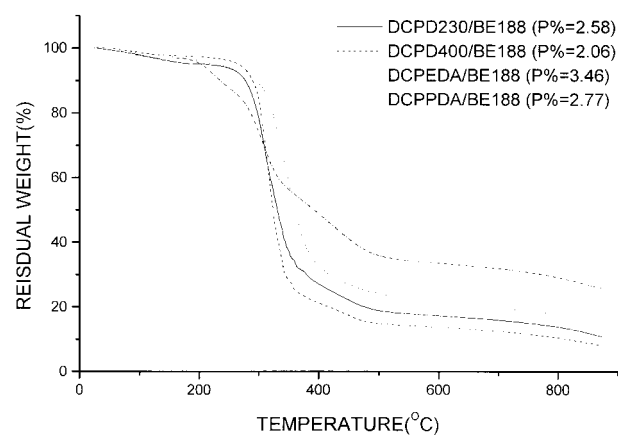
**Figure 10** TGA thermograms of the BE188/DCP-amine resins under nitrogen atmosphere.

Table V Weight Loss Data of the Cured Epoxy Resins Under Nitrogen

Materials	Phosphorus Content (%)	Temperature Recorded at Specific Weight Loss (°C)					Residue (%)
		10%	20%	30%	40%	50%	850°C
DCPD230/BE188	2.58	277	298	309	318	331	11.9
DCPD400/BE188	2.06	290	304	310	317	324	8.9
DCPEDA/BE188	3.46	304	317	329	338	347	16.5
DCPPDA/BE188	2.77	235	286	308	333	392	26.8
PPDCD230/BE188	2.32	293	308	317	329	338	5.9
PPDCEDA/BE188	4.07	307	327	340	354	387	22.9
PPDCPDA/BE188	2.50	304	315	327	347	377	24.2
D230/BE188	0	342	357	365	370	375	1.9
D400/BE188	0	335	353	362	369	374	1.6
EDA/BE188	0	342	352	359	366	372	3.0
PDA/BE188	0	331	347	353	362	373	8.5

ature region are less than those of the phosphorus free ones. This is due to the decomposition of the phosphorus groups at relatively low temperatures forming a phosphorus-rich layer to increase the thermal stability of the residues. This plays an important role for phosphorylated materials in fire resistance via the condensing phase.³³ PPDC-amines cured epoxy polymers exhibit similar behavior on thermal degradation. The 5% weight loss temperatures of these epoxy polymers (ca. 280°) are also lower than those (ca. 320 °) of their phosphorus free counter parts. However, epoxy polymers from PPDC-amines were observed to be more thermally stable than the polymers from DCP-amines since PPDC-amines contain no P—O—C bond. Moreover, the PCE polymers from

glycidyl phosphonate¹⁴ and phosphate¹³ were reported to have degradation temperatures at around 230–250°C. Therefore, the phosphorus-containing curing agents in this study provide a facile way to prepare flame-retardant epoxy polymers with moderate thermal stability and flexibility.

Kinetic study of the thermal degradation behaviors was further investigated by choosing the DCP-amines cured epoxy resins as the sample. The study was performed on TGA with data obtained at different heating rates, and employed the Ozawa analytical method as mentioned in the Experimental section.^{26,27} Activation energy of the resin decomposition at certain decomposition degrees was obtained from the plot of log(heating

Table VI Weight Loss Data of the Cured Epoxy Resins Under Air

Materials	Phosphorus Content (%)	Temperature Recorded at Specific Weight Loss (°C)					Residue (%)
		10%	20%	30%	40%	50%	850°C
DCPD230/BE188	2.58	272	301	314	328	343	0.0
DCPD400/BE188	2.06	286	302	310	317	326	1.8
DCPEDA/BE188	3.46	285	321	333	343	357	0.3
DCPPDA/BE188	2.77	243	293	318	367	438	10.4
PPDCD230/BE188	2.32	290	305	316	328	339	1.9
PPDCEDA/BE188	4.07	294	324	345	380	442	12.2
PPDCPDA/BE188	2.50	303	316	339	375	428	3.4
D230/BE188	0	316	356	363	367	373	0.0
D400/BE188	0	314	356	363	369	373	0.0
EDA/BE188	0	337	349	358	367	383	0.0
PDA/BE188	0	311	342	356	382	410	0.0

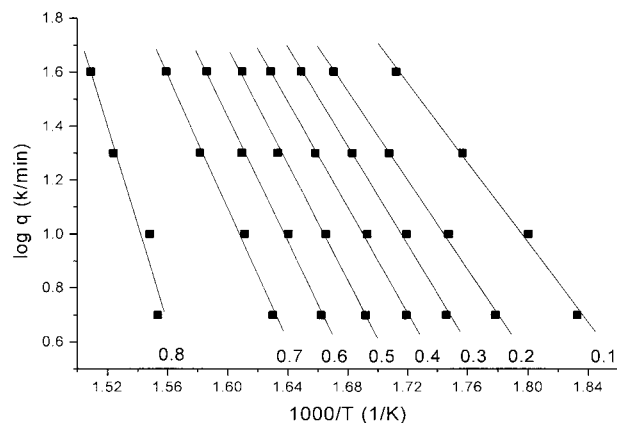


Figure 11 Plots of $\log(\text{heating rate})$ vs. $1/T$ for BE188/DCPD230 resin under nitrogen atmosphere.

rate) vs. $1/T$ (T = temperature) (Fig. 11). The calculated data is listed in Table VII. As shown in the TGA thermograms (Figs. 9 and 10), the degradation of DCP-amines cured resins could be assigned to one-stage and two-stage models for nitrogen and air environment, respectively. The activation energy data also indicates similar degradation behavior as that observed from TGA thermograms. For degradation under nitrogen, the activation energies of the resin decomposition increase with increasing conversion (Fig. 12). It is

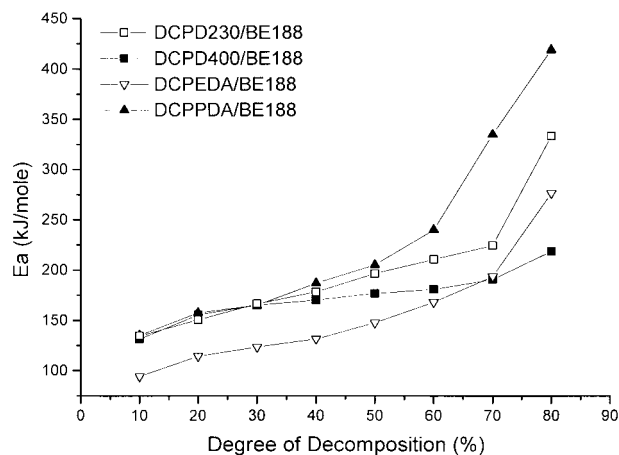


Figure 12 Plots of activation energies of degradation vs. conversions of degradation for BE188/DCP-amine resins under nitrogen atmosphere.

noteworthy that high activation energies were found at degradation conversions higher than 60%. However, a gap is present at about 50% conversion for the activation energies of the resins decomposing under air. At conversions higher than 60%, relatively low values of the activation energies are found (Fig. 13). This implies that the degradation of the resins does not purely result from thermal degradation at the high tempera-

Table VII Activation Energy, EA (KJ/mol) of the Cured DCP-Amines/BE188 for Degradation

Conversion (α)	Activation Energy (kJ/mol)							
	DCPD230/BE188		DCPD400/BE188		DCPEDA/BE188		DCPPDA/BE188	
	In N_2	In Air	In N_2	In Air	In N_2	In Air	In N_2	In Air
0.05	—	95	—	103	—	98	—	94
0.1	135	115	131	132	94	98	135	99
0.15	—	132	—	154	—	99	—	107
0.2	150	146	156	164	114	112	158	130
0.25	—	160	—	169	—	134	—	188
0.3	167	179	165	176	123	180	165	296
0.35	—	209	—	181	—	243	—	— ^a
0.4	178	251	170	196	132	427	187	— ^a
0.45	—	326	—	214	—	— ^a	—	— ^a
0.5	197	507	177	272	148	— ^a	205	— ^a
0.55	—	— ^a	—	381	—	— ^a	—	226
0.6	211	— ^a	181	— ^a	168	274	240	176
0.65	—	— ^a	—	— ^a	—	251	—	146
0.7	225	— ^a	191	— ^a	194	225	335	129
0.75	—	— ^a	—	— ^a	—	226	—	117
0.8	334	— ^a	219	— ^a	276	194	419	113

^a Not measurable because the regression factor was too small.^{34,35}

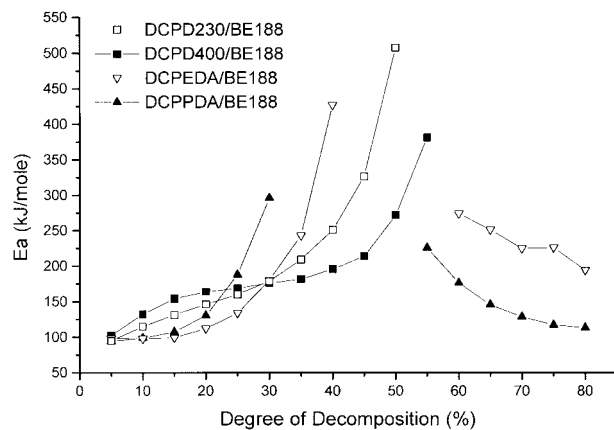


Figure 13 Plots of activation energies of degradation vs. conversions of degradation for BE188/DCP-amine resins under air atmosphere.

ture region under air.^{34,35} Oxidation definitely participates in the degradation at high temperatures. Therefore, increasing the degradation temperature results in lowering the activation energies at the oxidation stage.²⁸

Flame retardant properties of a polymer can be predicted from its char yield at temperatures higher than 700°C.^{8–18} A relationship between char yield ratio (CR) at 850°C under nitrogen, and LOI has been reported.³⁶ Therefore, the char yields at 850°C of the phosphorus-containing polymers are discussed first. As shown in Table V and Table VI, all of the phosphorus-amine cured epoxies resulted in relatively higher char yields than the phosphorus-free ones. As mentioned previously, the high char yields of the PCEs result from the decomposition pattern of the phosphorus-groups, and the subsequent formation of char layer. Therefore, the high char yields imply that introducing phosphorus into the epoxy resins is efficient in improving the epoxies' flame retardancy. The effect of the phosphorus-rich layer on gaining a higher char yield was also observed in the degradation behavior under air. The thermal degradation residues of the phosphorus-free epoxies show a rapid weight loss at 500–600°C under air atmosphere (Fig. 14). However, this rapid weight loss was not observed for their phosphorus-containing counterparts (Fig. 10). Instead, a slow weight loss was found at this temperature range. The formation of the phosphorus-rich layer capable of restraining the char degradation is demonstrated. Moreover, the efficiency of phosphorus groups on improving the flame retardancy of the resins was also illustrated by measuring

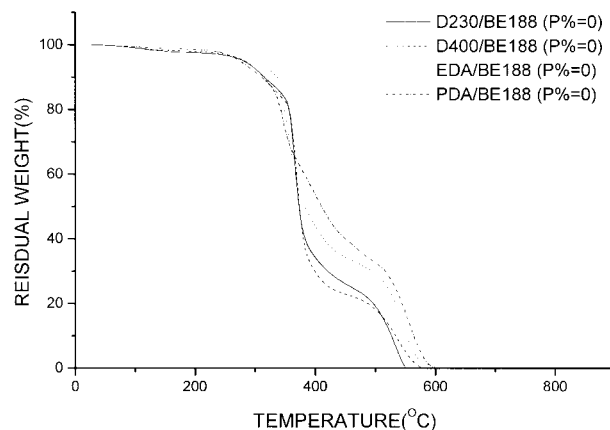


Figure 14 TGA thermograms of BE188/P-free amines under air atmosphere.

LOI values. The phosphorus-free epoxy polymers were found to have LOI values of 18–21, whereas the LOI values of the phosphorus-containing ones were leveled up to 22–31 (Table VIII). A relatively

Table VIII LOI Values^a of the DCP-Amines and PPDC-Amines Cured Epoxy Resins with Various Phosphorus Contents

Resin Composition	Phosphorus Contents (%)	LOI ^a
DCPD230/BE188	2.58	23
DCPD230/D230/BE188	1.94	23
DCPD230/D230/BE188	1.29	22
DCPD230/D230/BE188	0.65	21
D230/BE188	0	18
DCPD400/BE188	2.06	22
DCPD400/D400/BE188	1.55	22
DCPD400/D400/BE188	1.03	21
DCPD400/D400/BE188	0.52	21
D400/BE188	0	18
DCPEDA/BE188	3.46	27
DCPEDA/EDA/BE188	2.60	25
DCPEDA/EDA/BE188	1.73	24
DCPEDA/EDA/BE188	0.87	21
EDA/BE188	0	19
DCPPDA/BE188	2.77	28
DCPPDA/PDA/BE188	2.08	26
DCPPDA/PDA/BE188	1.39	25
DCPPDA/PDA/BE188	0.69	24
PDA/BE188	0	21
PPDCD230/BE188	2.32	23
PPDCEDA/BE188	4.07	31
PPDCPDA/BE188	2.50	28

^a LOI, limited oxygen index.

high LOI value was obtained for the DCPEDA cured epoxy polymer. Moreover, high phosphorus contents resulting in high LOI values was also observed (Table VIII). For example, the DCPEDA (P content = 3.46%) and PPDCEDA (P content = 4.07%) cured resins containing higher phosphorus contents show relatively high LOI values of 27 and 31, respectively.

CONCLUSIONS

Two series of phosphorus-containing poly(alkylene) amines were successfully synthesized and used as epoxy curing agents. Characterization using FTIR, NMR, and elemental analysis along with amine titration confirm the chemical structures of the obtained amines. The kinetic study of curing reaction of the amines with BE188 reveals the optimized process for preparing the corresponding epoxy resins. Thermal analysis and LOI measurements show that the resulted epoxy resins contained efficient improvement in flame-retardant properties. The introduction of soft —P—O— linkage, polyalkylene, and a hard aromatic group into the backbones of the synthesized phosphorus-containing amine provides epoxy resins with tunable flexibility. Furthermore, the moderate reactivities (curing reaction rate) of the synthesized amines, along with their versatility in structure variations, can be very useful in certain industrial applications, such as epoxy and polyurea.^{37,38} More specifically, the use of these amines in epoxy curing exhibits great potential in coating, adhesive, composite fabrication, and further applications.

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