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Flame retardant epoxy polymers based on all phosphorus-containing components

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Abstract

A phosphorus-containing epoxy resin, bis(3-*t*-butyl-4-glycidyloxyphenyl-2,4-di-*t*-butylphenyl)resorcinol diphosphate, was synthesized and subsequently cured with non-phosphorus containing amines, and/or novel phosphorus-containing aromatic or polyoxyalkylene amines. Chemical structures of these materials were characterized with FTIR, NMR, elemental analysis, and amine titration. The introduction of soft –P–O– linkage, polyoxyalkyene, or hard aromatic group into the backbones of the synthesized phosphorus-containing amines provides epoxy polymers with high phosphorus contents and tailored flexibility. Thermal analysis of differential scanning calorimeter and thermal gravimetric analysis (TGA) reveals that these resulted epoxy polymers possess moderate T_gs and thermal stability. Furthermore, high char yields in TGA analysis and high limited oxygen index values indicate that these phosphorus-containing epoxy polymers possess excellent flame retardant properties. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phosphorus; Polyetheramine; Epoxy resin; Flame retardant; Limited oxygen index

1. Introduction

Epoxy resins have been extensively investigated because of their superior properties in adhesion, heat resistance, corrosion resistance, and low shrinkage on cure. This leads to wide applications for surface coating, adhesives, laminates, composites, potting, painting materials, encapsulant for semiconductor, and insulating material for electric devices [1–3]. In order to maintain their valid status in the advanced applications, the epoxy materials have to keep up with the requirements for high thermal and flame resistance.

A most feasible approach for improving the flame retardant properties have been developed by incorporating additive- or reactive-type flame retardants into epoxy resins [4–10]. Bromine-containing aromatic compounds in conjunction with antimony oxide and inorganic materials such as metal hydroxides and metal oxide are widely used as additive-type flame retardant for epoxy resins [4]. Major problems encountered with this system concern with the generation of toxic and corrosive fume during combustion [5,6]. To circumvent these problems, non-halogenated flame retardants are materials of choice. Moreover, the reactive type flame retardants are of interest because they are able to sustain the flame retardance for longer time, and reduce the influence on physical, mechanical, and artifactitious properties of polymers [7–10].

Phosphorus-containing compounds for flame retardants are used either by blending with polymers or by reacting onto polymers. It is believed that phosphorus-containing compounds can quench flammable particles like H • or OH • and reduce the energy of the flame in

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the gas phase [11,12]. Moreover, in the solid phase, the phosphorus-containing functional groups are converted by thermal decomposition to phosphoric acid [13]. The polyphosphoric acid esterifies, and dehydrates the polymer, and then forms a protective carbonaceous layer. This protective layer is heat-resistant at higher temperatures, and shields the underlying polymer from attack by oxygen and radiant heat [11–13]. A conventional way to increase the flame resistance of epoxy polymers is to utilize flame-resistant curatives. Several investigations in this regard have been recently reported such as phosphorylated diamines [14,15], hydroxyphenyl phosphate [16], and phosphorus-containing bismaleimide [17]. Furthermore, excellent flame retardancy is also achieved through the introduction of phosphorus-containing functional groups into the backbones of epoxy such as imide-epoxy resin [18], aryl phosphinate epoxyether [19].

Recently, we employed a family of poly(oxyalkylene)diamine derivatives to prepare the curatives for epoxy resins [20–22]. The resulted epoxy polymers were shown to possess well-tuned properties, particularly the flexibility. In this work, a phosphorus-containing epoxy resin, bis(3-*t*-butyl-4-glycidyloxyphenyl-2,4-di-*t*-butyl phenyl)resorcinol diphosphate (GDP), was synthesized and subsequently cured with various non-phosphorus containing amines, and/or novel phosphorus-containing aromatic or polyoxyalkylene amines. The structure–properties relationship was studied. Furthermore, thermal properties, flame retardancy, and degradation behaviors of these resulted phosphorus-containing epoxy polymers were also investigated. As the safety and environmental issues become more significant, the utilization of both phosphorus-containing epoxy resins and curing agents would certainly enhance the flame retardant properties. Furthermore, the flexibility of the epoxy polymers could be tailored through incorporating alkyl or aromatic groups of the aforementioned curing agents.

2. Experimental

2.1. Materials

1,3-benzenediphosphoro tetrachloridate $\{Cl_2P(O)$-$[OC_6H_4OP(O)Cl]n Cl\}$ (DCP, $n = 1,2$) was synthesized from reacting phosphoryloxytrichloride ($POCl_3$, from Aldrich Co.) with resorcinol (from TCI, Japan) [23]. Bis(3-*t*-butyl-4-hydroxyphenyl-2,4-di-*t*-butylphenyl)resorcinol diphosphate (HDP, $n = 1,2$) was synthesized by reacting DCP with *t*-butylhydroquinone and 2,4-di-*t*-butylphenol (from TCI Japan) [23]. Phenylphosphonicdichloride (PPDC) and epichlorohydrin were purchased from Aldrich Co. and used as received. Poly(propylene glycol)bis(2-aminopropyl)ether, Jeffamine® D230 (Mw = 230), were from Huntsman Chemical Co. Ethylenediamine (EDA, Fluka Chemical Co.), *N*-phenyl-1,4-phenylenediamine (PDA, Forte Chemical Co., Taiwan), aluminum oxide (Lancaster Co.), 4,4-diaminodiphenylmethane (DDM, JANSSEN CHIMICA Co.), and $NaHCO_3$ (Wako Co.) were all used as received. Tetrahydrofuran (THF), toluene, acetone, methanol, dichloromethane and chloroform etc. were available from Tedia Chemical Co., all reagents and solvents are reagent grade. Diglycidyl ether of bisphenol-A, BE-188 with an epoxide equivalent weight (EEW) of 188 and NPES-901 of 500, were from Chang Chun Plastic Co. and Nan Ya Co., Taiwan, respectively.

2.2. Analytical methods

Amine titration was estimated by using ASTM D2073-92 method for curing process [20–22]. Infrared spectra were recorded by using a Perkin Elmer Paragon 500 FT-IR spectrophotometer. ^1H-NMR and ^{31}P-NMR were obtained with a Brüker MSL-300 NMR spectrometer. Elemental analysis (EA) 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 microdigestion apparatus with a spectrophotometer. Gel permeation chromatography (GPC) analyses were performed in the Waters apparatus (515 HPLC pump, 2410 refractive index detector). Waters Stygel column sets were used with a 1.0 ml/min flow rate of THF, calibrated by polystyrene standards. Differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) were performed on a Seiko SII model SSC/5200. A heating or cooling rate of 10 °C/min under nitrogen atmosphere was used for DSC. TGA was measured by heating the samples at a heating rate of 10 °C/min from 30 to 900 °C in air or nitrogen. Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter by a modified method as reported by literature [24,25]. The percentage in the O_2–N_2 mixture merely sufficient to sustain the flame was taken as the LOI.

2.3. Synthesis

The preparation of the following phosphorus-containing amines was based on the procedures reported previously [26].

2.3.1. Preparation of DCP-amine, DCPD230

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 500 ml THF) under nitrogen atmosphere. The solution was stirred at room temperature for 2 h and heated up to 60 °C for 4 h to complete the reaction. The solvent was then removed with a rotary evaporator. The product was extracted with chloroform and then washed with sodium bicarbonate ($NaHCO_3$) aqueous three times. The organic layer was collected and concentrated under a reduced pressure. The viscous orange product DCPD230 was obtained with a yield of 95%, as shown in Scheme 1. FT-IR exhibited absorption at 1260 cm^{-1} (P=O), 910 cm^{-1} (P–N), 3289 cm^{-1} (vs, –NH), and 1111 cm^{-1} (vs, C–O–C). ^{1}H-NMR($CDCl_3$): $\delta = 0.6$–0.7 ppm (–C*H*–), $\delta = 0.9$ ppm (–C*H*$_3$), $\delta = 2.5$–2.9 ppm (–N*H*– and N*H*$_2$–), $\delta = 3.1$–3.4 ppm (–OC*H*$_2$–), and $\delta = 6.7$–7.3 ppm (aromatic protons). ^{31}P-NMR($CDCl_3$): $\delta = 0.9$ ppm (O*P*O$_2$N), and $\delta = 10.7$ ppm (O*P*ON$_2$). Anal. Calcd. for DCPD230: amine content, 3.44 meq/g; P%, 5.92. Found: amine content, 3.19 meq/g; P%, 5.60.

2.3.2. Preparation of DCP-amine, DCPPDA

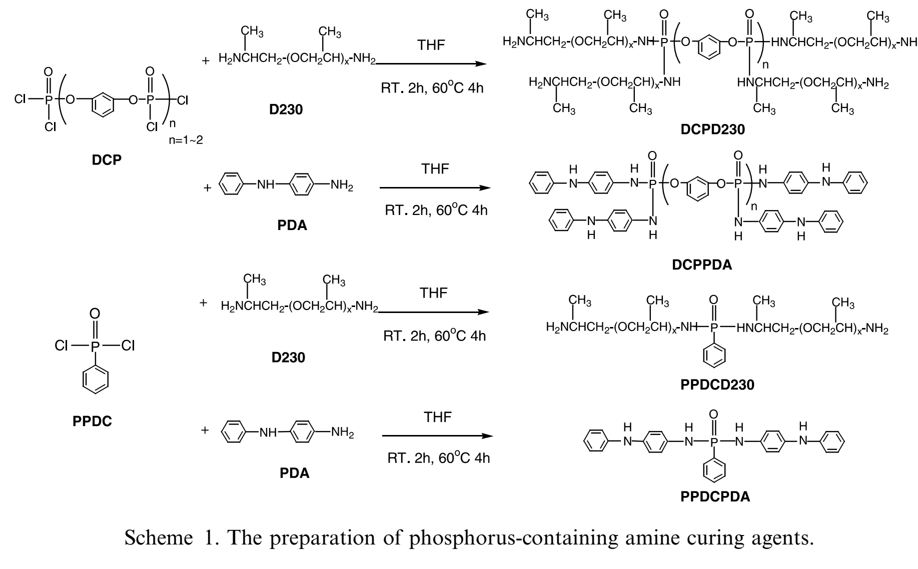
N-phenyl-1,4-phenylenediamine (PDA, 57 g) in 500 ml toluene was stirred under a nitrogen atmosphere. A solution of DCP (30 g) in 500 ml toluene was added dropwise in 1 h. The reactions were then kept at room temperature and 60 °C for 2 and 4 h, respectively. After being concentrated with a rotary evaporator, the reaction mixture was extracted with $CHCl_3$ and washed with $NaHCO_{3(aq)}$ three times. The crude product was collected from organic layer and then precipitated from the 1:1 mixture of methanol and dichloromethane to obtain black powder DCPPDA with a yield of 70%, as shown in Scheme 1. FT-IR exhibited absorption at 1315 cm^{-1} (P=O), 954 cm^{-1} (P–N), and 3434 cm^{-1} (vs, –NH). ^{1}H-NMR($CDCl_3$): $\delta = 2.5$ ppm (–N*H*–) and $\delta = 6.7$–6.8 ppm (aromatic protons). ^{31}P-NMR($CDCl_3$): $\delta = 2.9$ ppm (O*P*O$_2$N), and $\delta = 10.7$–13.1 ppm (O*P*ON$_2$). Anal. Calcd. for DCPD230: P%, 7.03. Found: P%, 7.21.

2.3.3. Preparation of DCP-amines, PPDCD230 and PPDCPPDA

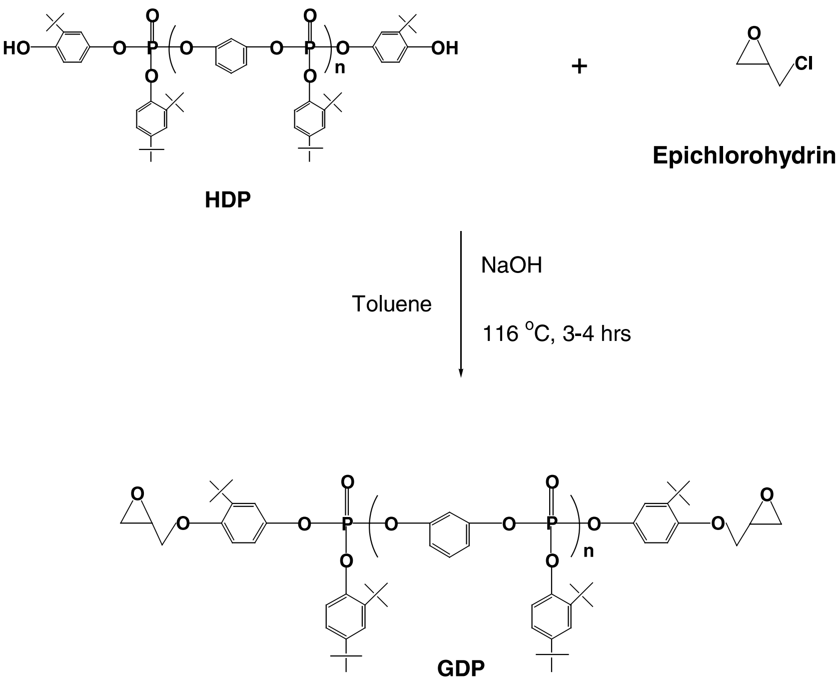
Synthesis procedures for PPDC-amines are the same as those for DCP-amines expect replacing DCP by PPDC in the syntheses for respective products, as shown in Scheme 1. The structures were also confirmed by that analysis above. It was found that the PPDCD230 exhibited IR absorption at 1257 cm^{-1} (P=O), 908 cm^{-1} (P–N), 3360 cm^{-1} (vs, –N*H*), and 1120 cm^{-1} (vs, C–O–C). ^{1}H-NMR: $\delta = 0.6$–1.1 ppm (–C*H*–, –C*H*$_3$), $\delta = 2.5$–2.9 ppm (–N*H*– and N*H*$_2$–), $\delta = 3.1$–3.6 ppm (–OC*H*$_2$–), and $\delta = 7.3$–7.8 ppm (aromatic protons). ^{31}P-NMR: $\delta = 20.6$ ppm. Anal. Calcd. for PPDCD230: P%, 5.30; amine content, 6.87 meq/g. Found: P%, 5.02; amine content, 6.18 meq/g. On the other hand, PPDCPDA exhibits IR absorption at 1316 cm^{-1} (P=O), 945 cm^{-1} (P–N), and 3314 cm^{-1} (–N*H*). ^{1}H-NMR: $\delta = 6.5$–8.6 ppm (aromatic protons). ^{31}P-NMR: $\delta = 5.8$ ppm. Anal. Calcd. for PPDCPDA: P%, 6.30. Found: P%, 7.14.

2.3.4. Preparation of bis(3-t-butyl-4-glycidyloxyphenyl-2,4-di-t-butylphenyl)resorcinol diphosphate

HDP, 80 g was stirred with 320 ml of epichlorohydrin in a 500 ml round-bottom flask at 90 °C. A 40 wt.% sodium hydroxide (NaOH, 5.21 g) aqueous was added to the reaction solution dropwise over 20 min and then refluxed for 3–4 h at 116 °C. The reaction mixture was diluted with toluene, and the resulted sodium chloride was filtered off three times. The remainder of epichlorohydrin, and toluene were evaporated, and the deep red thick liquid phosphorus-containing epoxy thus obtained (Scheme 2). The final product was obtained with 93% yield. The FT-IR exhibited absorption at 1270 cm^{-1} (s, P=O), 872 cm^{-1} (w, oxirane ring), 1179 and 982 cm^{-1} (s, O=P-aromatic), and 3328 cm^{-1} (w, OH of



Scheme 1. The preparation of phosphorus-containing amine curing agents.



Scheme 2. The preparation of phosphorus-containing epoxy GDP.

HDP). ^{1}H-NMR(CDCl$_3$): $\delta = 2.38$–4.02 ppm (oxirane ring protons), $\delta = 1.29$–1.43 ppm (*tetra*-butyl groups), and $\delta = 6.25$–7.54 ppm (aromatic protons). Anal. Calcd. for GDP: P%: 5.1, EEW: 513. Found: P%, 4.5, EEW: 520–550. GPC: $M_n = 978$, PD = 1.08, 96.52% (HDP). $M_n = 1128$, (PD = 1.19, 92.27% (GDP).

2.4. Preparation of epoxy resins

Epoxy polymers were obtained by homogeneously thermally curing respective BE-188, NPES-901, and GDP with amine curatives. The curing cycles were determined from DSC reaction scans of the respective epoxy/curing agent compositions. Taking D230/BE-188 as the example, general curing cycles are determined based on Fig. 1: mixed at room temperature, heated at 50 °C for 1 h, 120 °C for 2 h, and post-cured at 150 °C for one additional hour. The post-curing temperature of each phosphorus-containing composition is intentionally set at temperatures lower than 200 °C to avoid decomposition of phosphorus functional groups.

3. Results and discussion

3.1. Synthesis and characterization of the phosphorus-containing amines and epoxy

Two series of phosphorus-containing amine curing agents were prepared according to Scheme 1 [26]. These compounds were obtained by the P–N bond formation through reacting P–Cl in the phosphonic chloride (DCP and PPDC) with the –NH$_2$ groups of the amine compounds. Chemical structures of these products were characterized with FT-IR, ^{1}H-NMR, ^{31}P-NMR, EA, and amine titration. The IR absorption peaks of P–N bond appeared at 910 cm^{-1} for D230, and 950 cm^{-1} for PDA derivatives. Other specific absorption peaks at 1260 cm^{-1} (P=O), 1100 cm^{-1} (C–O–C), and 3300 cm^{-1} (–NH) were also present. Two major peaks were found in ^{31}P-NMR spectrum for DCP ($\delta = -6$ and 3.3 ppm), whereas single peak was found for PPDC ($\delta = 34$ ppm).

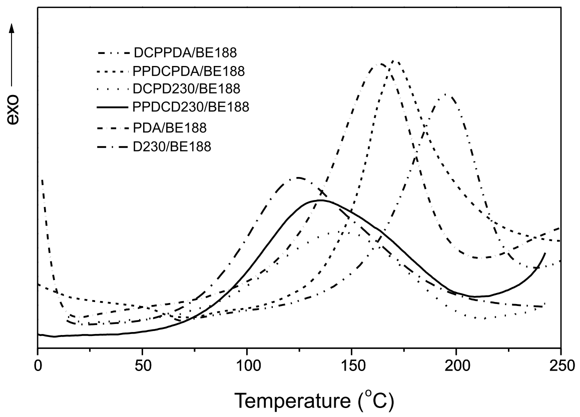


Fig. 1. DSC thermograms of BE188 cured by phosphorus-free and phosphorus-containing curing agents.

Their corresponding amine derivatives showed similar results in NMR spectra. The amine contents are not measurable for PDA-containing curing agents due to the dark color of the samples. The phosphorus contents were measured by EA.

The synthesis of phosphorus-containing oxiranes (GDP) was performed by reacting HDP with epichlorohydrin as shown in Scheme 2. IR spectra of HDP and GDP showed the same characteristic absorptions at 1270 cm^{-1} (P=O), 1607 (benzene ring), 2841–2993 (*tetra*-butyl groups), 1179 and 982 cm^{-1} (O=P-aromatic) due to the presence of aromatic phosphate linkages. The strong and narrow absorption peak of –OH at 3328 cm^{-1} for HDP became weak and broad after reacting with epichlorohydrin.The absorption peak of oxirane ring at 872 cm^{-1} was also found. Moreover, the chemical shifts of oxirane ring in ^{1}H-NMR for GDP were found at 2.38–4.02 ppm. Furthermore, the GPC analyses revealed the similar molecular weight distributions for HDP and GDP.

3.2. Reactivity of GDP toward curing agents, and properties of cured epoxy polymers

DSC thermograms of BE-188 cured with phosphorus-free and phosphorus-containing amine curing agents, and GDP or NPES-901 cured with commercial amines are shown in Figs. 1 and 2, respectively. The reactivities of the epoxies were directly read from the starting temperatures of the exothermic peaks [9,10]. As shown in DSC thermograms, the reactivity of the phosphorus-free amines were determined to be the order of EDA > D230 > PDA. It is coincidental with the electron densities of those amines [9]. An electron-donating group in the amine compound, for example, the methylene group in EDA, would enrich the electron density of the amine group and therefore, increases the reactivity of amine group toward oxirane rings. However, the electron-withdrawing group, –P=O, reduced the electron density of the amine group and subsequently reduced their nucleophilic attack on the oxirane ring of the epoxy resins [15]. Taking D230 derivatives as the example, the reactivities of these amines are determined to follow the order of D230 > PPDCD230 > DCPD230, as shown in Fig. 1. Likewise, PDA derivatives exhibited similar order of reactivity at higher temperatures. Moreover, as shown in Fig. 2, GDP is more reactive toward amine curing agents than NPES-901. The high reactivity of GDP possibly results from the electronic effect. The –P=O serving as an electron-withdrawing group in the epoxy reduced the electron density of the oxirane rings, and consequently made the oxirane rings more reactive toward amines [18,27].

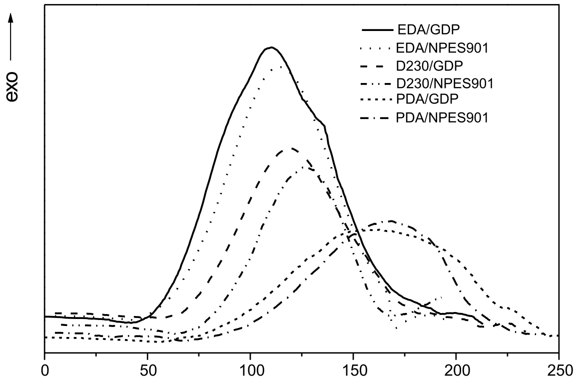


Fig. 2. DSC thermograms of GDP and NPES-901 cured by phosphorus-free curing agents.

3.3. Thermal and flame retardant properties

3.3.1. Glass transition temperatures (T_gs) of the epoxy polymers

To compare the thermal properties, the cured epoxy polymers were divided into four groups: (1) commercially phosphorus-free curing agent/phosphorus-free epoxy; (2) phosphorus-free curing agent/phosphorus-containing epoxy; (3) phosphorus- containing curing agent/phosphorus-free epoxy; (4) phosphorus-containing curing agent/phosphorus-containing epoxy. T_gs of the epoxy polymers were determined by DSC. The compositions, phosphorus, nitrogen and aromatic group contents, and T_gs for the cured epoxy polymers are listed in Table 1. Relatively higher T_gs were found for the compositions with high aromatic contents such as compositions containing PDA or DDM. However, the compositions with high phosphorus contents (5.31–6.19), especially for all phosphorus-containing compositions, exhibited relatively lower T_gs (55–65 °C) despite high aromatic contents for DCPPDA/GDP or PPDCPDA/GDP. This was further corroborated by the relatively higher T_gs (68–95 °C) for compositions with NPES-901 in comparison with the compositions with GDP. It is important to note that NPES-901 possessed similar crosslinking density and lower aromatic contents as compared to the cured GDP compositions (Table 1). Moreover, similar results were also observed for GDP and NPES-901 cured with phosphorus-free amines (T_gs of 60–82 °C for the cured GDP and T_gs of 85–114 °C for the cured NPES-901). Fig. 3 shows T_gs of the aromatic PDA derivatives cured GDP and NPES-901 epoxy resins as a function of phosphorus and aromatic contents. It is important to note that GDP and NPES-901 possessed similar epoxide equivalent weight. The T_g was decreased with increasing phosphorus content. Moreover, the epoxy polymers with high phosphorus contents also possessed high aromatic contents because of high aromatic contents of phosphorus compounds. This indicates that incorporation of linear phosphate groups

Table 1
Compositions and T_gs of the cured epoxy polymers

Compositions	Phosphorus content (%)	Nitrogen content (%)	Aromatic content (%)	T_g (°C)
D230/BE188	0	2.85	30.9	69
EDA/BE188	0	3.45	37.4	85
PDA/BE188	0	3.74	50.8	112
DDM/BE188	0	2.95	47.9	133
D230/NPES-901	0	1.34	24.6	85
EDA/NPES-901	0	1.37	26.7	89
PDA/NPES-901	0	1.67	24.6	100
DDM/NPES-901	0	1.27	25.1	114
DCPD230/BE188	2.58	4.20	26.6	45
DCPPDA/BE188	2.77	4.51	53.0	91
PPDCD230/BE188	2.32	3.28	28.5	72
PPDCPDA/BE188	2.50	4.50	55.1	120
DCPD230/NPES-901	1.38	2.26	20.7	68
DCPPDA/NPES-901	3.18	3.12	36.8	94
PPDCD230/NPES-901	1.13	2.17	21.3	78
PPDCPDA/NPES-901	2.35	3.75	29.2	95
D230/GDP	4.83	1.34	36.4	64
EDA/GDP	5.23	1.37	39.4	60
PDA/GDP	4.80	1.67	36.2	79
DDM/GDP	4.90	1.27	37.0	82
DCPD230/GDP	5.44	2.26	30.6	61
DCPPDA/GDP	6.19	3.12	39.6	62
PPDCD230/GDP	5.31	2.17	31.5	55
PPDCPDA/GDP	5.96	3.75	37.5	65
D230/BE188/GDP(1:1)[a]	2.23	2.12	33.4	75
EDA/BE188/GDP(1:1)[a]	2.68	2.43	38.4	85
PDA/BE188/GDP(1:1)[a]	2.20	2.78	48.2	109
DDM/BE188/GDP(1:1)[a]	2.15	2.86	48.1	112
D230/BE188/GDP(1:2)[a]	2.71	2.47	32.3	59
EDA/BE188/GDP(1:2)[a]	3.25	2.08	38.7	93
PDA/BE188/GDP(1:2)[a]	2.86	2.43	47.4	101
DDM/BE188/GDP(1:2)[a]	2.95	1.88	45.4	109

BE188: diglycidyl ether of bisphenol-A(EEW = 188), NPES-901: diglycidyl ether of bisphenol-A(EEW = 500).

[a] The ratios of 1:1 and 1:2 are the weight ratios of BE188 and GDP.

$-(P(O)-O-Ph-O)_n-$ of GDP decreased rotational barrier and subsequently lowered the T_gs [15] despite of higher aromatic contents. Similar phenomenon was also observed for aliphatic D230 derivatives cured GDP and NPES-901 epoxy resins.

T_gs of the phosphorus-containing DCP-amines cured epoxy, which have the flexible –P–O– groups in the backbones, are lower than those of P–N and rigid P–Ph linkage, PPDC-amines cured epoxies, and phosphorus-free epoxy polymers. To enhance the T_gs of the cured phosphorus-containing epoxy, a commercially available epoxy BE-188 (EEW = 188) was used for curing formulation. Molar ratios of 1/1 and 1/2 (BE-188/GDP) were investigated. By incorporating BE-188 into the epoxy formulations, the crosslinking density enhanced due to the smaller EEW of BE-188. For the cured GDP, BE-188/GDP (1:1), BE-188/GDP (1:2) polymers, the T_g increased with increasing BE-188 content and decreased with increasing phosphorus contents.

3.3.2. Thermal stability of phosphorus-containing epoxy polymers

TGA thermograms of the aliphatic polyoxyalkyene amine D230 derivatives and aromatic amine PDA cured phosphorus-containing or phosphorus-free epoxy polymers are illustrated in Figs. 4 and 5. The degradation temperatures of the phosphorus-containing epoxy polymers (around 200–300 °C) are lower than those of

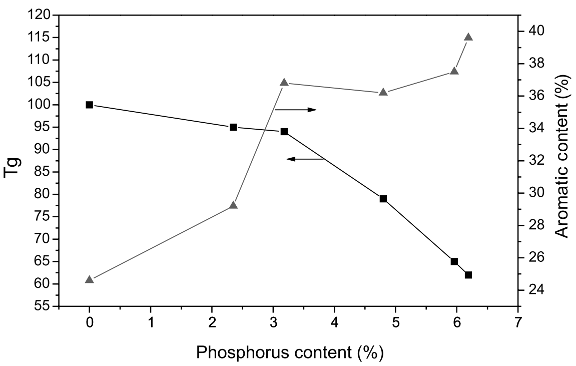


Fig. 3. T_gs of the PDA derivatives cured GDP and NPES-901 epoxy resins as a function of phosphorus and aromatic contents.

the phosphorus-free counterparts (around 300–350 °C). The temperatures at 5% weight loss for all materials are listed in Table 2. Introducing the phosphorus-containing functional groups into the backbones would reduce the thermal stability of the resulted epoxy polymers. The depressed thermal stability of the phosphorus-containing epoxy polymers might possibly result from the decomposition of the P–O–C bonds [15,27]. However, the weight losses of the phosphorus-containing epoxy polymers at high temperatures region are less than those of the phosphorus-free ones. The extents of weight loss at high temperatures are usually proportional to the phosphorus contents of epoxy polymers. This is due to the fact that the decomposition of the phosphorus-containing functional groups at relatively lower temperatures forms a phosphorus-rich layer to protect the residues from heat. This plays an important role for phosphorylated materials in fire resistance via the condensed–phase [11–13,28]. Phosphorus-free epoxy polymers prepared by amine/BE-188 and amine/NPES-901 exhibited different thermal degradation behavior as shown in Figs. 4 and 5. Based on the data of 5% weight loss temperatures of those materials in Table 2, the cured NPES-901 polymers were more stable than the cured BE-188 polymers in nitrogen, whereas the cured BE-188 polymers were more thermally stable in air. The cured BE-188 epoxy polymers possess higher nitrogen and aromatic contents (2.85–3.74% and 30.9–50.8%, respectively) than NPES-901 (nitrogen content: 1.27–1.67% and aromatic content: 25.1–26.7%). Yet the cured BE-188 epoxy polymers were less stable in nitrogen. It is important to note that the only difference between the above-mentioned two cured epoxy polymers is the longer bisphenol-A (BPA) chain in NPES-901. The cured NPES-901 epoxy polymers displayed better thermal stability in nitrogen despite having lower nitrogen and aromatic contents. This indicates backbone structure and molecular weight are the overwhelming factor for thermal stability in nitrogen [29]. While undergoing thermal oxidation in air, the amine structures could be the most important factor in acting as scavengers for radicals under oxidative condition [29]. Therefore, the cured BE-188 epoxy polymers were more thermally stable in air.

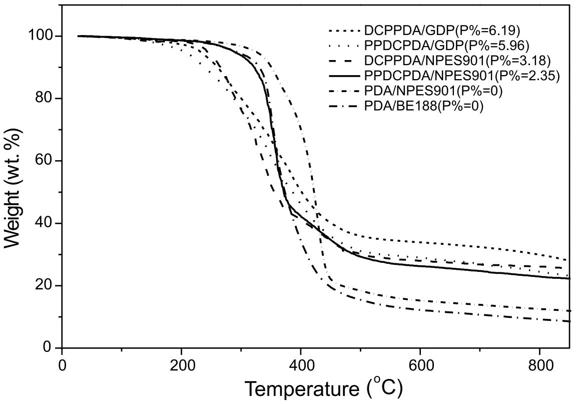


Fig. 4. TGA thermograms of the PDA derivatives cured phosphorus-containing epoxy resins in nitrogen.

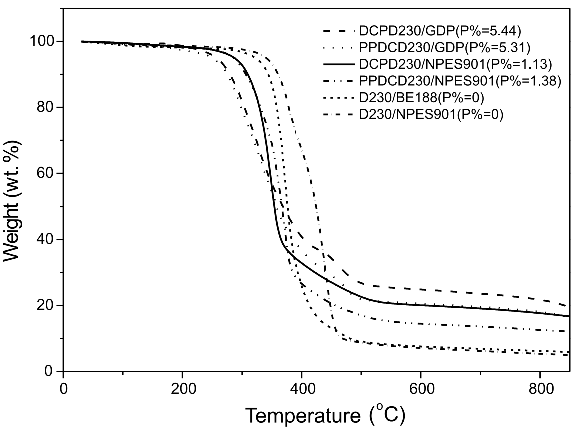


Fig. 5. TGA thermograms of the D230 derivatives cured phosphorus-containing epoxy resins in nitrogen.

For phosphorus-containing epoxy polymers, PPDC-amines cured BPA-type polymers exhibits more thermally stable than DCP-amines cured BPA-type polymers during early period of the degrading process. This is due to the higher phosphorus content and the presence of P–O–C linkages in DCP-amines. On the other hand, the polymers based on phosphorus-containing epoxy GDP and phosphorus-containing amine were observed to be less thermally stable than the compositions mentioned above. Furthermore, by incorporating BE-188 into the epoxy formulations, the crosslinking density was enhanced. Because of higher crosslinking density, this series show comparable thermal stability as the

Table 2
Thermal properties of the cured epoxy polymers

Materials	P (%)	Aromatic (%)	TGA in N_2		TGA in air		LOI	(OI)*m*
			5% loss (°C)	850 °C residue (%)	5% loss (°C)	850 °C residue (%)		
D230/BE188	0	30.9	322	1.9	282	0	18	–
EDA/BE188	0	37.4	326	3.0	303	0	19	–
PDA/BE188	0	50.8	292	8.5	274	0	21	–
DDM/BE188	0	47.9	355	18.9	360	0	23	–
D230/NPES-901	0	24.6	340	5.4	248	0	18	–
EDA/NPES-901	0	26.7	337	6.2	239	0	19	–
PDA/NPES-901	0	24.6	324	12.5	263	0	22	–
DDM/NPES-901	0	25.1	355	13.3	286	0	23	–
DCPD230/BE188	2.58	26.6	215	13.9	172	0	23	15.5
DCPPDA/BE188	2.77	53.0	206	28.8	253	14.4	28	17.0
PPDCD230/BE188	2.32	28.5	250	6.50	211	2.9	21	14.8
PPDCPDA/BE188	2.50	55.1	291	24.6	287	4.6	27	15.9
DCPD230/NPES-901	1.38	20.7	286	17.7	288	0	23	11.6
DCPPDA/NPES-901	3.18	36.8	243	25.3	245	3.8	27	17.6
PPDCD230/NPES-901	1.13	21.3	286	12.6	280	0	22	10.5
PPDCPDA/NPES-901	2.35	29.2	288	21.3	298	1.2	26	15.3
D230/GDP	4.83	36.4	241	16.6	248	7.0	28	21.8
EDA/GDP	5.23	39.4	224	17.2	239	12.2	28	22.7
PDA/GDP	4.80	36.2	283	26.8	263	18.2	30	22.5
DDM/GDP	4.90	37.0	262	25.3	286	13.6	31	22.6
DCPD230/GDP	5.44	30.6	257	21.8	262	8.3	30	23.3
DCPPDA/GDP	6.19	39.6	232	29.9	236	12.0	32	25.5
PPDCD230/GDP	5.31	31.5	250	18.1	239	12.4	29	22.8
PPDCPDA/GDP	5.96	37.5	205	22.6	205	13.4	30	24.4
D230/BE188/GDP(1:1)[a]	2.23	33.4	254	10.3	243	0	23	14.6
EDA/BE188/GDP(1:1)[a]	2.68	38.4	275	14.6	272	0	22	16.0
PDA/BE188/GDP(1:1)[a]	2.20	48.2	281	24.6	273	0	25	14.8
DDM/BE188/GDP(1:1)[a]	2.15	48.1	297	20.6	292	0	26	14.7
D230/BE188/GDP(1:2)[a]	2.71	32.3	257	12.3	220	0	22	16.0
EDA/BE188/GDP(1:2)[a]	3.25	38.7	256	13.4	228	4.3	25	17.8
PDA/BE188/GDP(1:2)[a]	2.86	47.4	296	24.8	286	0	26	17.3
DDM/BE188/GDP(1:2)[a]	2.95	45.4	297	23.1	304	0.2	27	17.7

BE188: diglycidyl ether of bisphenol-A(EEW = 188), NPES-901: diglycidyl ether of bisphenol-A(EEW = 500).

[a] The ratios of 1:1 and 1:2 are the weight ratios of BE188 and GDP.

epoxy polymers based on all phosphorus-containing components (Fig. 6 and Table 2).

Besides the decomposition temperature and the weight retention in TGA, the residual weight (char yield) at high temperatures would reveal another aspect of the thermal characteristics. As shown in Table 2, all of the phosphorus-containing polymers resulted in relatively high char yields than the phosphorus-free ones in nitrogen. As mentioned previously, the high char yields of the phosphorus-containing epoxy polymers result from the decomposition pattern of the phosphorus groups, and formation of the phosphorus-rich layer.

3.3.3. Flame retardant properties of phosphorus-containing epoxy polymers

Flame retardant properties of a polymer can be predicted from its char yield at temperatures higher than 700 °C [10–19]. A relationship between char yield ratio (CR%) at 850 °C under nitrogen, and LOI has been reported [24]. As shown in Table 2, the residual weights for all the phosphorus-containing epoxy polymers were increased with increasing phosphorus and aromatic contents in nitrogen at temperatures up to 850 °C. However, this trend was not so distinct in air due to the complicated thermal oxidation. Most phosphorus-con-

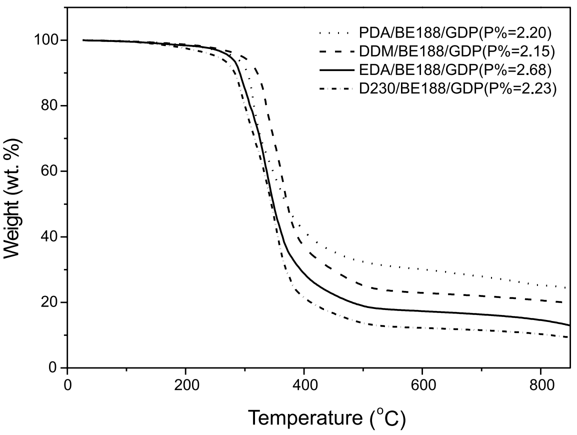


Fig. 6. TGA thermograms of the phosphorus-containing BE188/GDP cured epoxy polymers in nitrogen.

taining epoxy polymers (phosphorus contents = 1.13–6.19%) possessed char yields higher than 10% in nitrogen. Moreover, higher char yields were also obtained for the epoxy polymers with higher phosphorus and aromatic contents when in air. However, high char yields were not available for the polymers with relatively low phosphorus contents, and high aromatic contents when in air (Table 2). In air, phosphorus functional group played an important role upon raising the amount of char yield despite low aromatic contents (Table 2). It has been reported that high char yields and larger LOI values are indicative of better flame-retardant properties [24,25]. LOI values for all of the epoxy polymers are shown in Table 2. The phosphorus-free epoxy polymers exhibited LOI values of 18–23, whereas the LOI values of the phosphorus-containing ones were leveled up to 23–28 for DCP-amines/commercial epoxy, and to 21–27 for PPDC-amines/commercial epoxy. Moreover, the phosphorus-containing epoxy GDP cured with commercial amines possessed the values of 28–31. It is important to note that larger LOI values could be obtained for the phosphorus-containing polymers with high aromatic contents. This is possibly due to the char formation of phenyl groups [25]. Furthermore, polymers with high phosphorus contents resulted in high LOI values. For example, the cured DCP-amines/GDP and PPDC-amines/GDP epoxy polymers containing higher phosphorus contents (5.31–6.19%) exhibited the largest LOI values of 30–32 and 29–30, respectively. This indicates that high phosphorus contents result in better flame retardant properties.

It has been reported that the calculated LOI value, i.e. (OI)*m* of polyphosphate could be evaluated as follows [11]:

$$(\mathrm{OI})m = 3.0\ (\text{temperature of 50\% weight loss}/10)^{1/3} \times (\text{phosphorus content})^{1/2}$$

The (OI)*m* values were calculated for phosphorus-containing epoxy resins based on phosphorus contents and TGA data (Table 2). Compared with the measured LOI values in Table 2, the values of (OI)*m* were much lower (10.5–25.5). However, similar pattern was also observed in terms of the flame-retardant properties dependent on different compositions. Fig. 7 shows the curves of LOI/(OI)*m* as a function of phosphorus contents, indicating that the ratio of LOI/(OI)*m* approaches unity at high phosphorus contents. While phosphorus content is low, aromatic groups as the predominant factor for flame retardation, would hinder the degradation of polymers. Consequently, the temperature of 50% weight loss is higher than that of aliphatic ones. However, for the polymers with higher P contents, the aromatic groups along with phosphorus functional groups exert influence on the flame retardation simultaneously. This leads to reduction of the LOI/(OI)*m*

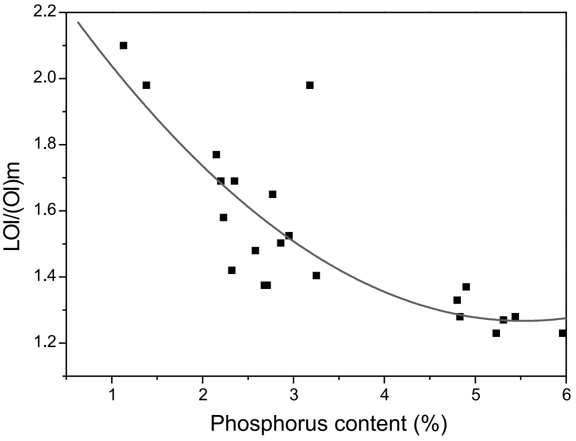


Fig. 7. LOI/(OI)*m* vs phosphorus content (%).

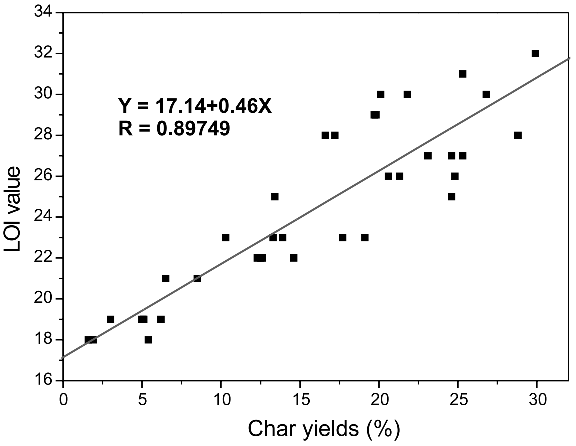


Fig. 8. LOI values vs char yields (%).

Table 3
The linear relationships of char yields vs. LOI values with different phosphorus-containing structures

	Phosphorus in epoxy monomer		Phosphorus in curing agent	
	Aromatic structure	Aliphatic structure	Aromatic structure	Aliphatic structure
	LOI = 23.68 + 0.27CR		LOI = 16.96 + 0.43CR	
LOI = 17.14 + 0.46CR $R = 0.89749$	LOI = 24.50 + 0.24CR	LOI = 21.41 + 0.40CR	LOI = 18.78 + 0.38CR	LOI = 16.90 + 0.44CR

ratio to nearly unity. With high phosphorus and aromatic contents, the above-mentioned equation can be applied to this epoxy polymer system.

It has been reported that LOI values could be calculated via a linear relationship with char residue as follows: LOI = 17.5 + 0.4CR [23,30]. As shown in Fig. 8, the experimental linear relationship of the cured epoxy system can be represented by LOI = 17.14 + 0.46CR. This experimental equation is almost coincidental to the one from literature. It is noteworthy that the locations of phosphorus functional groups in epoxy polymers influence the relationship between LOI and CR as shown in Table 3. The LOI value equals y intercept while CR is decreased to zero (i.e. complete burning out). The intercept is 23.68 when the phosphorus function group is located in epoxy monomers, whereas the intercept is 16.96 when phosphorus function group is located in curing agents. This indicates that the epoxy monomers have greater influence on flame retardant properties of the polymers than the curing agents in this study. The intercept values of the GDP cured with respective aromatic and aliphatic curing agents are 24.50 and 21.41, respectively. Moreover, the intercept values (18.78) of the commercial epoxy monomers cured with aromatic curing agents are larger than those of the commercial epoxy monomers cured with aliphatic ones (16.90). This implies that aromatic groups exert greater effect in influencing thermal stability and flame retardant properties.

4. Conclusions

Families of phosphorus-containing diamines and a glycidyl ether were successfully synthesized and used to prepared epoxy polymers. These products were characterized using FTIR, NMR, EA, and amine titration, etc. Compared with phosphorus-free epoxy polymer systems, the higher reactivity of epoxy GDP and lower reactivity of curing agents attributed to the electron-withdrawing effects of phosphorus-functionalities. The combination of soft –P–O– linkage, polyoxyalkyene, and hard aromatic groups in the amines or epoxy resin rendered the epoxy polymers with tunable flexibility. Thermal analyses and LOI measurements showed that the resultant epoxy polymers had a pronounced improvement in flame-retardant property, but with slightly reduced thermal stability during early period of the degrading process. A high phosphorus content of 6.19% for the cured epoxy polymers based on phosphorus-containing components led to excellent flame retardancy, demonstrated by the high char yield of nearly 30% at 850 °C under nitrogen, and large LOI value of 32. Furthermore, it was found that aromatic contents in the phosphorus-containing polymers significantly enhanced their LOI and CR values, as well as the thermal stability. It is also important to note that the factors contributing to the mechanical and thermal properties were illustrated by the structural versatility of epoxy polymers in this work. The balance between hard and soft segments in the curing agents or epoxy monomers allows one to develop epoxy polymer networks with desirable properties.

Acknowledgements

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