

Synthesis of Novel Phosphorus-Containing Epoxy Hardeners and Thermal Stability and Flame-Retardant Properties of Cured Products

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Received 15 January 2011; accepted 14 May 2011

DOI 10.1002/app.34894

Published online 7 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Two novel flame-retardant curing agents for epoxy resins, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-containing 4-[(phenylamino)methyl]phenol (P-Ph) and DOPO-containing Mannich-type bases (P-DDS-Ph), were synthesized by the condensation of 4-hydroxybenzaldehyde with 4-aminophenol and DDS, respectively, followed by the addition of DOPO to the resulting imine linkage. Chemical structures of these materials were characterized with FTIR, $^1\text{H-NMR}$ spectra, $^{31}\text{P-NMR}$ spectra, and elemental analysis. The thermal properties and flame retardancy of *o*-cresol novolac epoxy resin (CNE) cured with different contents of the phosphorus-containing compounds were investigated by nonisothermal differential scanning calorimetry, thermog-

ravimetric analysis, and limiting oxygen index (LOI). The obtained results showed that more char was formed while containing lower contents of the phosphorus-containing compounds in the P-Ph/CNE and P-DDS-Ph/CNE indicating their excellent flame retardancy. Moreover, the P-DDS-Ph/CNE exhibited higher T_g (224°C) and better thermal stability ($T_{10\%}$, 330°C) than that of P-Ph/CNE. Therefore, the developed P-DDS-Ph/CNE may be potentially used as environmentally preferable products in electronic fields. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1219–1225, 2012

Key words: epoxy resins; phosphorus-containing; flame retardancy; thermal properties

INTRODUCTION

Epoxy resins have been widely used in advanced composite matrices, surface coating, and semiconductor encapsulation applications, owing to their solvent and chemical resistant, good mechanical and electrical properties, high tensile strength and modulus, low shrinkage in cure, and strong adherence to many substrates.^{1–6}

The common epoxy resin systems, however, cannot satisfy some applications which require high thermal and flame resistance. Traditionally, brominated compounds and antimonyoxide, serving as flame retardants, are imparted into the compounds for compensating its flammability. However, flame-retardant compounds containing bromine or chlorine will produce poisonous and corrosive smoke and may give supertoxic halogenated dibenzodioxins and dibenzofurans. To overcome these problems and to meet the new environmental regulations and standards, P-containing compounds have drawn

much attention and a wide variety of P-containing flame-retardant compounds had been studied.^{7–11} Incorporation of organophosphorus moiety into the epoxy thermosetting structure have been demonstrated to generate less toxic gas and smoke than halogen-containing compound and obtain superior flame retardance.

However, P-containing epoxy resin often shows unfavorable thermal resistance. Many researchers make efforts to develop a P-containing epoxy resin with both high flame retardancy and thermal properties. Among all P-containing organic compounds, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has attracted intensive attention due to its high flame retardant efficiency and thermal properties. Hence, various DOPO-based epoxy resins, curing agents, and additives have been reported.^{12–18} Liu^{19,20} and Ching et al.^{21,22} presented several DOPO-containing bisphenol and bisaniline compounds, and all of their cured epoxy composites showed excellent flame retardancy and good thermal properties. To our knowledge, the incorporation of aromatic group was advantageous to the thermal property.^{23,24} Thus, an epoxy resin which contains P and a high content of aromatic group together will be expected to provide not only excellent flame-retardant properties but also favorable thermal properties.

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Contract grant sponsor: National Science Foundation of China; contract grant number: J0830415.

In this article, two novel compounds (P-Ph and P-DDS-Ph) containing both P and a high content of aromatic group were synthesized through the electrophilic addition reaction of P(O)—H and C=N. The resulting compounds were used as curing agents for epoxy resin. The thermal and flame-retarding properties of the cured resins (P-Ph/CNE and P-DDS-Ph/CNE) were studied. The obtained products are expected to be qualified for encapsulants of electronic devices and other electronic applications.

EXPERIMENTAL

Materials

4-Hydroxybenzaldehyde, 4-aminophenol, 4,4'-diaminodiphenylsulfone (DDS), methanol, and tetrahydrofuran (THF) were purchased from Shanghai Chemistry Reagent Company. DOPO was purchased from Synasia (Suzhou) Co. Ltd. The chemicals referred above were AR grade and used as received. A phenol formaldehyde novolac resin (PN) used as curing agent with a hydroxyl equivalent weight of about 126 g/equiv., and an *o*-cresol formaldehyde novolac epoxy (CNE, CTDCN-200, epoxy equivalent weight EEW = 207 g/equiv.) was kindly supplied by Baling Petrochemical Corp. of China.

Synthesis of DOPO-containing 4-[(phenylamino)methyl]phenol (P-Ph)

In a three-neck round-bottom flask equipped with a magnetic stirrer, 4-aminophenol (10.9 g, 0.1 mol), 4-hydroxybenzaldehyde (12.2 g, 0.1 mol), and methanol were placed. The resultant mixture was stirred for 5 h at 50°C under N₂ atmosphere. The product, 2-[(phenylimino)methyl]phenol, was precipitated by adding methanol (200 mL) and cooling the resulting solution with an ice/water bath. The solid was isolated by filtration and washed with cold methanol. Then, 2-[(phenylimino)methyl]phenol (10 g, 0.05 mol) and DOPO (21.6 g, 0.1 mol) were dissolved in THF (100 mL) at room temperature under N₂ atmosphere. The mixture was heated to 60°C and stirred for 12 h. The resulting white precipitate was filtered and washed several times with cold THF and then dried under a vacuum. Finally, the white power was labeled as P-Ph.

IR (KBr, cm⁻¹): 3456 (Ph—OH), 3309 (N—H), 1593, 1475 (P—Ph), 1232, 1198 (P=O), 1043 (P—O—C), 918 (P—O—Ph).

¹H-NMR (DMSO, ppm): 9.36 (OH, a); 8.40 (OH, b); 8.17–8.15 (H¹¹, H¹⁷); 8.02 (H¹⁴); 7.77 (H¹²); 7.56 (H¹³); 7.45 (H¹⁹); 7.32 (H¹⁸); 7.15–7.03 (H⁷); 7.01 (H²⁰); 6.67–6.64 (H⁸); 6.46–6.44 (H³); 6.37–6.35 (H²); 5.92 (NH); 4.77 (P—C—H).

³¹P-NMR (DMSO, ppm): 34.62.

Elem. Anal. Calcd.: C, 69.93%; H, 4.66%; N, 3.26%; P, 7.22%. Found: C, 69.31%; H, 4.64%; N, 3.37%; P, 7.08%.

Synthesis of DOPO-containing Mannich-type bases (P-DDS-Ph)

In a three-neck round-bottom flask equipped with a magnetic stirrer, DDS (24.8 g, 0.1 mol), 4-hydroxybenzaldehyde (24.4 g, 0.2 mol), and THF were placed. The mixture was stirred for 5 h at 50°C under N₂ atmosphere. Then, a solution of DOPO (86.4 g, 0.4 mol) in THF (150 mL) was added dropwise to the resultant mixture at room temperature for 1 h under N₂ atmosphere. The mixture was heated to 60°C and stirred for 12 h. The resulting white precipitate was filtered and washed several times with cold THF and then dried under a vacuum. Finally, the white power was labeled as P-DDS-Ph.

IR (KBr, cm⁻¹): 3367 (Ph—OH), 3294 (N—H), 1593, 1477 (P—Ph), 1232, 1198 (P=O), 1047 (P—O—C), 1007 (S=O), 928 (P—O—Ph).

¹H-NMR (DMSO, ppm): 9.40 (OH); 8.12 (H¹⁰, H¹⁶); 7.8 (H¹³); 7.65 (H¹¹); 7.42 (H¹², H¹⁸); 7.32–7.24 (H⁶, H⁷); 7.15–7.13 (H¹⁷, H¹⁹); 6.69–6.63 (H², H³); 5.46 (N—H); 5.09 (P—C—H).

³¹P-NMR (DMSO, ppm): 34.09.

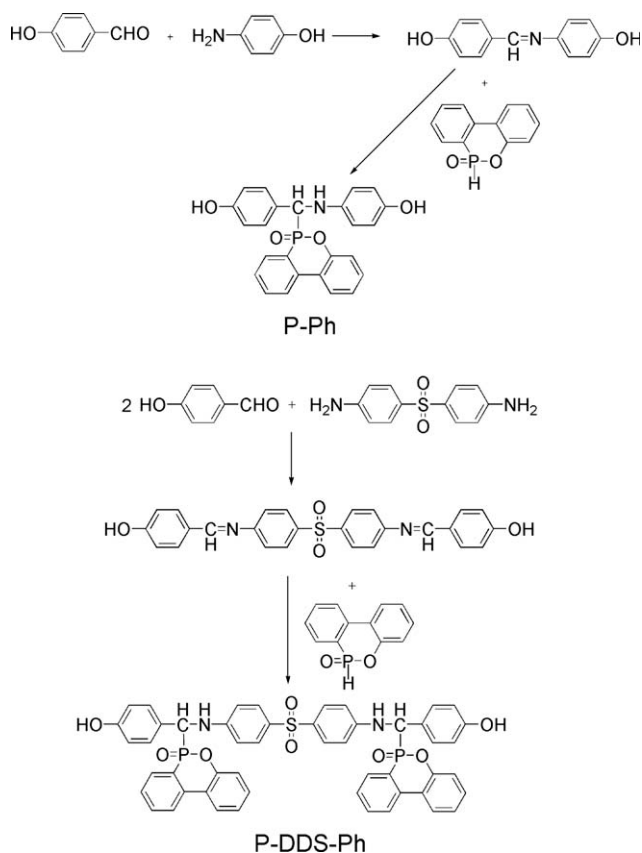
Elem. Anal. Calcd.: C, 67.56%; H, 4.28%; N, 3.15%; P, 6.98%. Found: C, 67.15%; H, 4.16%; N, 3.26%; P, 6.79%.

Curing procedure

The cured epoxy resins were obtained via thermally curing of P-Ph and P-DDS-Ph with CNE. The PN/CNE was used for preparing control sample. The curing agents consisted of P-Ph/PN and P-DDS-Ph/PN in various weight ratio (0/100, 25/75, 50/50, 75/25, 100/0) were prepared. The curing agents and CNE were mixed in a equivalent ratios of phenolic hydroxyl to epoxy as 1 : 1. Triphenylphosphine of 0.2 wt % was used as a curing accelerator. All samples were cured in a mold at 160°C for 1 h and then at 180°C for 2 h and further postcured at 200°C for 3 h.

Measurements

Fourier transform infrared (FTIR) spectra were obtained with a WQF-410 spectrophotometer (Beijing Second Optical Instrument Factory). Nuclear magnetic resonance (¹H-NMR) spectra and ³¹P-NMR spectra were obtained with a INOVA-400 (400 MHz) at 30°C by using DMSO-*d*₆ as solvent with tetramethylsilane (TMS) and H₃PO₄ as internal standards, respectively. Elemental analysis was performed with



Scheme 1 Synthetic route of P-Ph and P-DDS-Ph.

a Heraeus CHN-O rapid elementary analyzer with benzoic acid or 4-nitroaniline as a standard. DSC data and TGA data were obtained from 8 to 10 mg samples in a nitrogen atmosphere, at a heating rate of 5–20°C per minute using a STA-449C Thermogravimetric Analyzer. The LOI test was performed according to the testing procedure of ASTM D 2863-77 Oxygen Index Method with a test specimen bar of 10 cm in length, 6 mm in width, and 2.5 mm in thickness. Sample bars suspended vertically were ignited by a Bunsen burner. The flame was removed and the timer started. The concentration of oxygen must be raised if the specimen is extinguished before burning 3 min or 5 cm: continue to adjust oxygen content until limiting concentration is determined. The percentage of O₂ in the O₂–N₂ mixture just sufficient to sustain the flame was taken as the LOI.

RESULTS AND DISCUSSION

Syntheses and characterizations

The reactive rigid heterocyclic ring structure containing phosphorus, P-Ph and P-DDS-Ph, were synthesized through the simple addition reaction between DOPO and Mannich-type bases according to Scheme 1.

The chemical structure of the obtained phosphorus-containing compounds P-Ph and P-DDS-Ph were identified by FTIR, ¹H-NMR, ³¹P-NMR, and elemental analysis. Figure 1 shows the FTIR spectra of DOPO, P-Ph, and P-DDS-Ph. The characteristic peaks were around 3300 cm⁻¹ (N–H), 1593 cm⁻¹, 1475 cm⁻¹ (P-Ph), 1232 cm⁻¹, 1198 cm⁻¹ (P=O), 1043 cm⁻¹ (P–O–C), 918 cm⁻¹ (P–O–Ph). The distinctive absorption at 2428 cm⁻¹ for P(O)–H stretching in DOPO disappeared. These characteristic peaks were consistent with the structure of P-Ph and P-DDS-Ph. Moreover, the distinctive absorption at 1007 cm⁻¹ for (S=O) stretching further confirmed the structure of P-DDS-Ph.

The structures of these compounds were also characterized by ¹H-NMR and ³¹P-NMR. Figure 2 shows (a) ¹H and (b) ³¹P-NMR spectra of the P-Ph, and the assignment of each peak was marked in Figure 2. As shown in Figure 2(a), the chemical shifts at 9.36 and 8.41 ppm represent the hydroxy groups OH^a and OH^b, respectively. The absorption peaks at 5.93 and 4.77 ppm were assigned to amino peak (N–H) and aliphatic hydrogen peak (P–C–H), respectively. The peaks between 6.35 and 8.20 ppm (16H) were assigned to benzene ring. Furthermore, P-Ph exhibits a single peak at 34.62 ppm in ³¹P-NMR spectra [Fig. 2(b)], indicating the cyclic DOPO structure in the obtained compound and a high purity.

Figure 3 shows (a) ¹H and (b) ³¹P-NMR spectra of the P-DDS-Ph. The peak at 9.40 ppm in Figure 3(a) represents only one kind of the hydroxy group (OH) which further confirmed the symmetrical chemical structure of P-DDS-Ph. Other analyses of ¹H and ³¹P-NMR spectra for P-DDS-Ph are similar to that of P-Ph.

All the results support that P-Ph and P-DDS-Ph were successfully synthesized via the simple addition reaction between DOPO and Mannich-type bases.

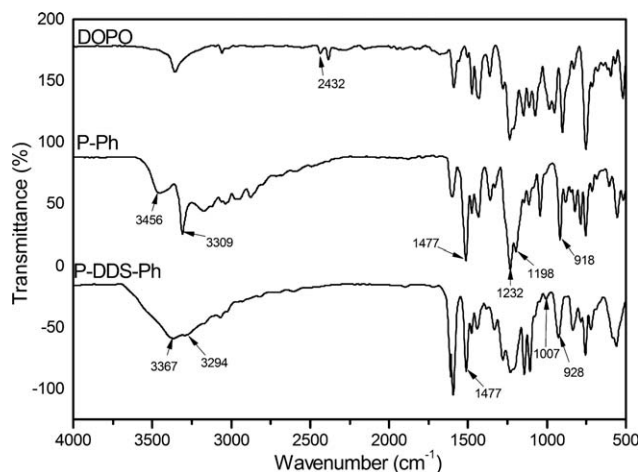


Figure 1 FTIR spectra of DOPO, P-Ph, and P-DDS-Ph.

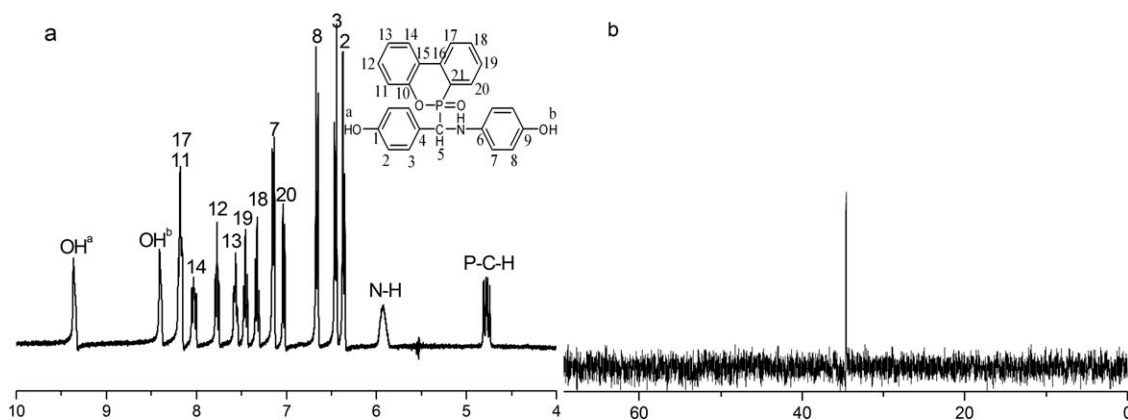


Figure 2 The ^1H and ^{31}P -NMR spectra of P-Ph.

Curing reactions of P-Ph and P-DDS-Ph on epoxies

The curing reactions of CNE with P-Ph and P-DDS-Ph were studied with DSC. Figure 4 showed the dynamic heating curves of P-Ph/CNE at various heating rates of 5, 10, 15, and 20 $^{\circ}\text{C}/\text{min}$. As expected in the samples, the peak temperature increased with increasing heating rate.

The activation energy of the P-Ph/CNE was determined from DSC studies. It was stimulated by the method of Kissinger.²⁵ The governing equation was shown as follows:

$$-\ln(\beta/T_p^2) = E_k/RT_p - \ln AR/E_k \quad (1)$$

where E_k is the activation energy; β is the heating rate; R is the ideal gas constant, and T_p is the peak temperature of the DSC thermogram. Hence, the activation energy of the P-Ph/CNE was obtained from the slopes of the plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ [eq. (1)]. The calculated activation energy of the P-Ph/CNE (64.7 kJ/mol) was lower than the activation energy of P-DDS-Ph/CNE (86.1 kJ/mol) with the same analysis method. It implied that P-DDS-Ph had lower reactivity toward epoxy groups than P-Ph.

The low reactivity of P-DDS-Ph toward epoxy might be because of the effect of steric hindrance owing to incorporation of more bulky DOPO groups into the P-DDS-Ph.

Thermal properties

The cured polymers were prepared according to the curing procedures determined from DSC. Moreover, the epoxy resin CNE cured with PN used as control for evaluating their application potential in the encapsulation of microelectronic devices. The compositions and thermal properties of the cured epoxy resins are shown in Table I. The glass transition temperatures (T_g s) of these cured epoxy resins are noteworthy. The T_g s of the (P-Ph/CNE)s and (P-DDS-Ph/CNE)s were found to be higher than that of the control and increased with more phosphorus contents in the resins. It has been reported that incorporating the bulky DOPO group into the epoxy would decrease the crosslinking density of the cured epoxy, therefore, decreasing the T_g s of the polymers.^{2,7} The uncommon result might be understood by the rigidity of the DOPO groups and the high content of

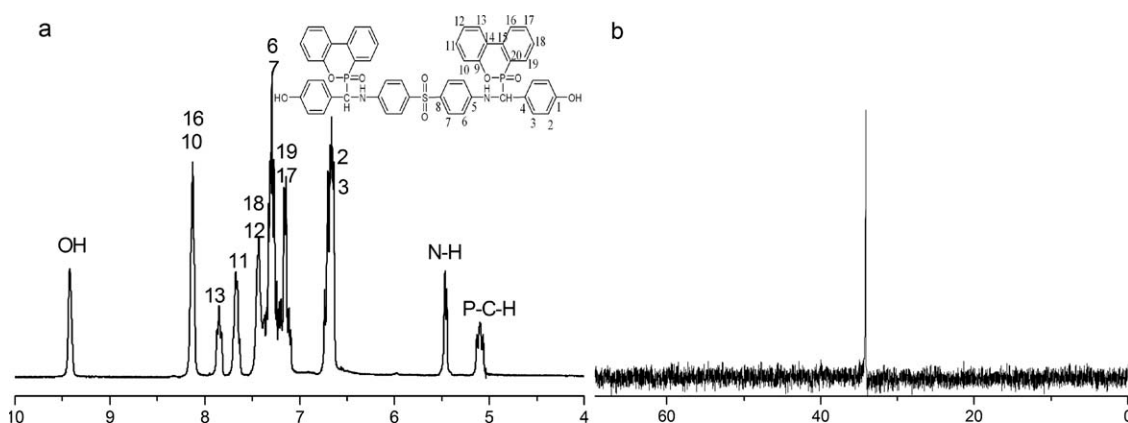


Figure 3 The ^1H and ^{31}P -NMR spectra of P-DDS-Ph.

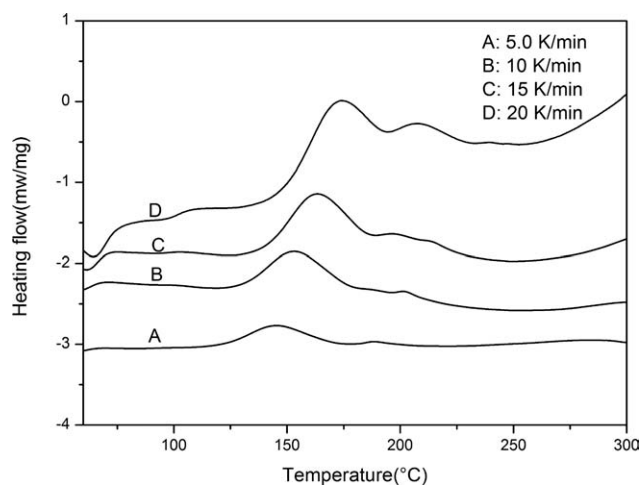


Figure 4 DSC thermograms of epoxy curing at various heating rates for P-Ph/CNE.

aromatic group. Both of them, therefore, contribute to level up the T_g s of the resultant resins. Additionally, (P-DDS-Ph/CNE)s exhibit higher T_g s (184–224°C) than that of the (P-Ph/CNE)s (165–180°C) which may be attributed to more incorporation of bulky DOPO groups. This rigid structure may increase the difficulty of chain rotation and constrain the thermal movement of polymer backbone, and thus lead to higher T_g .

Thermogravimetric analysis (TGA) is the most favored technique for rapid evaluation in comparing and ranking the thermal properties of various compounds. The thermal behavior of cured epoxy resins comprising P-Ph and P-DDS-Ph were investigated by TGA in N_2 . Figure 5 shows the thermogravimetric traces of the control CNE resins, P-Ph resins, and P-DDS-Ph resins. The temperature of 10% weight loss ($T_{10\%}$), the maximum decomposition rate temperature, and char yield at 700°C were summarized in Table I. According to Table I, the results show

that CNE cured with P-Ph and P-DDS-Ph have higher char yield than that of the control CNE resins. Moreover, the residual chars increased when P-containing curing agent increased in P-Ph/CNE and P-DDS-Ph/CNE.

For the CNE cured with various weight ratios of P-DDS-Ph and PN, their 10% weight loss temperatures were around 300°C and the P-DDS-Ph-D cured system even reached 330°C which is close to that of the control CNE resin. It indicated almost the same thermal stability of the P-DDS-Ph cured epoxy resins as the P-free PN cured resins. It is known that the phosphorus-containing epoxy resins have relatively lower thermal stability because the phosphorous group degraded at relatively low temperatures.^{26–29} The differences were attributed to incorporation of a high content of aromatic group in P-DDS-Ph. Thermal stability of the epoxy resins can be enhanced by a high content of aromatic group.^{23,24} In another words, the P-DDS-Ph/CNE has good thermal stability.

On the other hand, 10% weight loss temperatures of the CNE cured with various weight ratios of P-Ph/PN were much lower than that of the control CNE resin. It indicated that the P-Ph cured epoxy resins are not as thermally stable as the phosphorus-free PN-cured resins. The poor thermal stability of the phosphorus-containing epoxy resins due to not only the DOPO degrading at relatively low temperatures but also the molecular weight of the P-Ph. The molecular weight is one of the key factors of the thermal property for cured epoxy resins.

Like most P-containing compounds,^{30,31} the CNE epoxy resins cured with phosphorus-containing P-Ph and P-DDS-Ph showed quite complicated weight loss behavior. From the traces of the DTGA, at the region of temperatures higher than 400°C, it also can be seen that the weight loss rates of the P-containing resins were lower than the control. This

TABLE I
Thermal Analysis Data and LOI Values of the Cured Epoxy Resins

Sample	P (%)	T_g (°C)	N_2 atmosphere		Char yield at 700°C (%)	LOI	
			$T_{10\%}$	T_{max}			
P-Ph/PN (wt %)							
Control	0/100	0	143	353	403	25.0	22
P-Ph-A	25/75	2.9	165	215	409	25.0	22
P-Ph-B	50/50	3.1	170	195	402	25.6	22
P-Ph-C	75/25	3.2	174	193	391	26.4	23
P-Ph-D	100/0	3.6	180	206	379	28.3	26
P-DDS-Ph /PN (wt %)							
P-DDS-Ph-A	25/75	3.0	184	299	397	29.2	27
P-DDS-Ph-B	50/50	3.4	194	289	396	30.7	28
P-DDS-Ph-C	75/25	3.9	207	277	394	32.0	30
P-DDS-Ph-D	100/0	4.7	224	330	386	36.2	33

$T_{10\%}$: decomposition temperature at 10% of weight loss.

T_{max} : decomposition temperature at maximum decomposition rate.

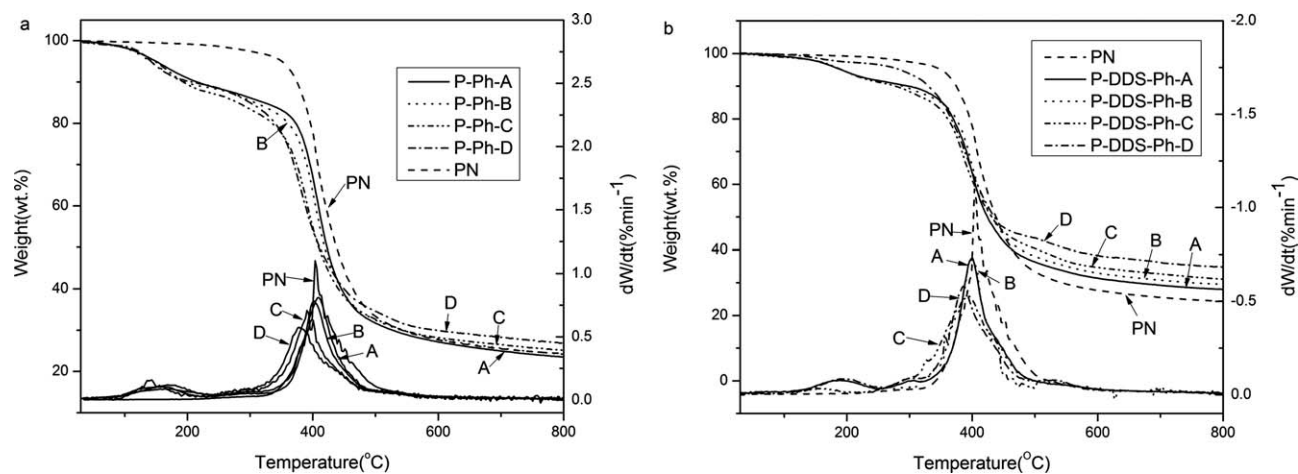


Figure 5 TGA thermograms and DTGA thermograms of the cured epoxy resins in N_2 .

phenomenon played an important role in improving the flame retardancy of the resins. When ignited, the decomposition of phosphate group forms a phosphorus-rich residue to prevent further decomposition of the resins matrix and resulted in a high char yield.^{19,32} In any case, the epoxy resins cured with P-Ph and P-DDS-Ph exhibited higher char yields than the control.

As shown in Table I, the char yields at 700°C for P-Ph and P-DDS-Ph cured epoxy resins are 28.3% and 36.2% in N_2 , respectively. The decomposition temperature of 10% weight loss for P-Ph/CNE and P-DDS-Ph/CNE are 206 and 330°C, respectively. Obviously, P-DDS-Ph/CNE exhibited higher char yields and better thermal stability than that of P-Ph/CNE.

Above all, the developed P-DDS-Ph/CNE reached the requirements for application in advanced electronics.

Flammability

The flame-retardant properties of the obtained epoxy resins were examined by measuring the LOI of the resins. LOI is defined as the minimum fraction of oxygen in an oxygen–nitrogen mixture that is required to support downward combustion of the specimen after ignition. The LOI values of all cured epoxy resins were presented in Table I. A significant increase in LOI could be observed when P-Ph and P-DDS-Ph were utilized in the epoxy curing compositions (Table I). LOI values of the resultant epoxy resins were drastically increased from 22 to 26 for P-Ph/CNE with the P% 2.9, 3.1, 3.2, 3.6% and from 27 to 33 for P-DDS-Ph/CNE with the P% 3.0, 3.4, 3.9, 4.7%, respectively. The improvement of the flame-retardant properties of the epoxy resins with phosphorus was demonstrated. Moreover, we have found

that P-DDS-Ph have higher flame-retardant efficiency. P% of the P-Ph/CNE was 3.6, the LOI was 26. Meanwhile, the LOI of P-DDS-Ph/CNE reached to 27 only with the P% = 3.0. The phenomenon may be due to the increasing aromatic group. The LOI values for the phosphorus-containing epoxy polymers were increased with increasing aromatic contents in nitrogen.^{33,34} Furthermore, a material with a LOI value of 26 or above was rated as a flame-retardant material. Thus, incorporating 0.80% of P-DDS-Ph into the epoxy resin would render these epoxies as flame-retardant polymers.

CONCLUSIONS

Two novel flame-retardant curing agents, P-Ph and P-DDS-Ph, were successfully synthesized and used as curing agents for *o*-cresol formaldehyde novolac epoxies. Comparing with P-Ph/CNE, the P-DDS-Ph cured resins have better flame retardant properties. The LOI values of P-DDS-Ph/CNE reach up to 33. The P-DDS-Ph cured resins also exhibited more favorable thermal properties. The T_g of P-DDS-Ph/CNE is high up to 224°C, its $T_{10\%}$ reach to 330°C which is near to the control PN/CNE. The synthesized P-DDS-Ph is therefore suitable to be used as a reactive flame retardant in the epoxy systems for application in green electrical/electronic materials.

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