Development of a DOPO-Containing Melamine Epoxy Hardeners and Its Thermal and Flame-Retardant Properties of Cured Products

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ABSTRACT: In this study, a novel Schiff base of melamine used as flame-retardant curing agent for epoxy resins, was synthesized via condensation reaction of 4-hydroxybenzaldehyde with melamine, followed by the addition of 9,10-dihydro-9-oxa-10-phosphaphen-anthrene 10-oxide (DOPO) to the resulting imine linkage. The structure of DOPO-containing melamine Schiff base (P-MSB) was characterized by Fourier transformed infrared spectroscopy, [1]H-nuclear magnetic resonance (^{1}H-NMR) and ^{31}P-NMR. The compound (P-MSB) was used as a reactive flame retardant in o-cresol formaldehyde novolac epoxy resin (CNE) to prepare flame-retardant epoxy resins for electronic application. The thermal and flame-retardant properties of the epoxy resins cured by various equivalent ratios phenol formaldehyde novolac (PN) and P-MSB were investigated by the nonisothermal differential scanning calorimetry, the thermogravimetric analysis, and limiting oxygen index test. The obtained results showed that the cured epoxy resins possessed high T_g (165°C) and good thermal stability ($T_{5\%}$, 321°C). Moreover, the P-MSB/CNE systems exhibited higher limiting oxygen index (35) and more char was maintained in P-MSB/CNE systems than that in PN/CNE system and the effective synergism of phosphorus–nitrogen indicated their excellent flame retardancy. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Epoxy resins were widely used in various industrial fields such as coating, potting, adhesives, laminates, composites, and semiconductor encapsulation applications owing to their high adhesive properties to many substrates, low shrinkage in curing, good chemical and corrosion resistance, high tensile strength and modulus, good electrical properties, and excellent dimensional stability.[1–4] However, flammability is one of the main drawbacks of the epoxy resins and limits their applications,[5–8] and thus, the flame retardance of epoxy resins is an urgent problem and has attracted much attention. Traditionally, halogenated compounds are widely used as comonomers or additive in epoxy resins to obtain fire-retardant materials. Although flame-retardant epoxy resins containing bromine or chlorine can produce poisonous and corrosive smoke and may give super-toxic halogenated dibenzodioxins and dibenzofurans.

Recently, in consideration of environmental problems, halogen-free fire-retardant epoxy resins have received a great deal of attention.[9,10] Phosphorus-containing organic compounds or resins have been demonstrated as effective flame retardants for

epoxy resins and other polymer materials, attributed to their several advantages including high flame-retardant efficiency, low production of corrosive, and toxic gases in flames etc.[11–18] Compared with other phosphorous chemicals, 9, 10-dihydro-9-oxa-10-phosphaphen-anthrene 10-oxide (DOPO)-based compounds have relatively high thermal stability and flame-retarding efficiency. DOPO-containing resins developed in previous work[19,20] showed potential for curing with o-cresol formaldehyde novolac epoxy resin (CNE) resulting in epoxy resins with good thermal stability above 320°C and superior flame retardant.[19,20] Moreover, nitrogen compounds have also been known for their good flame-retardant properties combined with excellent thermal and chemical properties such as high thermal-oxidative resistance, low toxicity, etc.[21,22] Among nitrogen compounds, melamine and its salts are widely used as flame retardants.[23,24] When heated, melamine undergoes progressive condensation with the elimination of ammonia and formation of polymeric products named "melam," "melem," and "melon," which are more thermally stable than melamine itself. So, melamine compounds were used as effective flame retardants for epoxy resins.
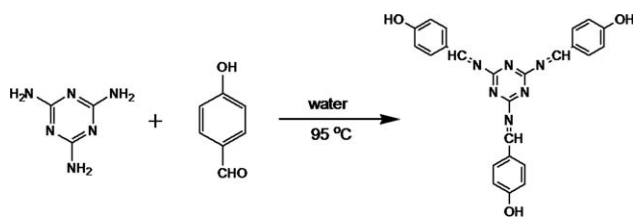
Scheme 1. Synthetic route of MSB.

A large number of articles[25–29] indicated that the flame-retardant efficiency significantly improved when phosphorus and nitrogen existed simultaneously in the curing system of epoxy resins. The phosphorus–nitrogen containing compounds mainly act as intumescent flame retardants resulting in a char layer in the condensed phase which can produce less toxic gas and smoke,[24–26] and the effect depends on the type of phosphorus and nitrogen products used. An effective intumescent flame retardant should comprise three basic elements, which are called dehydrating agent, char-forming agent, and foaming agent. Therefore, the phosphorus–nitrogen synergistic effect on flame retardancy is very interesting.

In this work, a novel intumescent flame retardant [DOPO-containing melamine Schiff base (P-MSB)] for epoxy resins containing both P and N was synthesized through the electrophilic addition reaction of P(O)—H and C=N. The synthesis, curing reaction of the monomers, the thermal properties, and flame retardancy of the resultant epoxy resins were investigated. The obtained products are expected to be qualified for encapsulants of electronic devices and other electronic applications.

EXPERIMENTAL

Materials

4-hydroxybenzaldhehyde, melamine, dimethylformamide (DMF) were purchased from the First Reagent Co. of Shanghai, China. 9,10-Dihydro-9-oxa-10-phosphaphen-anthrene 10-oxide (DOPO) was purchased from Synasia (Suzhou) Co. Ltd. The chemicals referred earlier were AR grade and used as received. A phenol formaldehyde novolac resin (PN) used as curing agent with a hydroxyl equivalent weight of $\sim$ 126 g/equiv, and a CNE (CTDCN-200, epoxy equivalent weight EEW = 207 g/equiv) was kindly supplied by Baling Petrochemical Corporation of China.

Synthesis of the MSB

Melamine (1.26 g, 0.01 mol) and 4-hydroxybenzaldhehyde (3.66 g, 0.03 mol) were mixed together in a 250-mL round-bottomed flask containing 100 mL water, which was fitted with condenser, thermometer, and magnetic stirrer. Reaction mixture was heated up to 95°C and melamine was solved at this temperature. The reaction was maintained for 5 h at 95°C under reflux (the reaction formula is shown in Scheme 1). Then cooled at room temperature and the product, MSB was slowly precipitated. The obtained solid was isolated by filtration, washed with hot water and then recrystal. Filtered, dried under vacuum at 60°C, the final products (pink powder, 3.7 g) was obtained (84% yield).

IR (KBr, cm^{-1}): 3340 (Ph–OH), 1670, 1635, 1549, 1454 (C=N), 1254, 1159, 1099 (C—N).

^{1}H-nuclear magnetic resonance (^{1}H-NMR) (DMSO, ppm): 9.79 (OH); 7.778 (H^{1}); 7.776 (H$^{1\prime}$), 7.757 (H$^{1\prime\prime}$); 6.945 (H^{2}); 6.942 (H$^{2\prime}$); 6.924 (H$^{2\prime\prime}$); 4.35 (N=CH).

Synthesis of P-MSB

MSB (1.76 g, 0.004 mol) and 9, 10-dihydro-9-oxa-10-phosphaphen-anthrene 10-oxide (DOPO) (2.59 g, 0.012 mol) were added to a 250-mL round-bottomed flask with 100 mL DMF, which was installed with condenser, thermometer, and magnetic stirrer, then reaction mixture was heated up to 120°C and stirred for 22 h under reflux (the reaction formula is shown in Scheme 2), finally, the mixture was cooled at room temperature and was slowly dropped into 300 mL cold water to precipitate the P-MSB. The obtained solid was filtered, washed with hot water to separate unreacted MSB from the condensation product. To minimize the byproduct, we can add excess of DOPO and increase reaction time. These obtained mixtures were purified using Combi Flash Chromatography and using 1 : 1 acetone/petroleum ether mixture as eluent. Then, it was dried in a vacuum desiccator.

IR (KBr, cm^{-1}): 3329 (N—H), 3180 (Ph—OH), 1562, 1477 (P—Ph), 1230, 1203 (P=O), 1049 (P—O—C), 928 (P—O—Ph).

^{1}H-NMR (DMSO, ppm): 9.26 (OH); 8.17-8.11 (H^{6}, H$^{6\prime}$); 7.86-7.73 (H^{2}, H$^{2\prime}$); 7.58-7.42 (H^{3}, H$^{3\prime}$); 7.30-7.22 (H^{4}, H$^{4\prime}$); 6.92-6.89 (H^{1}, H$^{1\prime}$); 6.57 (H^{5}); 6.55 (H$^{5\prime}$); 3.52 (N-H); 3.33 (C-H). ^{31}P-NMR (DMSO, ppm): 36.84.

Curing Procedure

The cured epoxy resins were obtained via thermally curing of CNE with various equivalent ratios curing agents of P-MSB and PN (0/100, 25/75, 50/50, 75/25, 100/0). The PN/CNE system without phosphorus–nitrogen was used for preparing control sample. The curing agents and CNE were mixed in equivalent ratios of phenolic hydroxyl to epoxy as 1 : 1. Triphenylphosphine of 0.2 wt % was used as a curing accelerator. All samples were thermally cured in a mold at 150°C for 1 h, followed by 180°C for 2 h, and further postcured at 210°C for 3 h to obtain cured specimens.

Measurements

Fourier transform infrared (FTIR) spectra were obtained with a WQF-410 spectrophotometer (Beijing Second Optical Instrument Factory). ^{1}H-NMR spectra and ^{31}P-NMR spectra were recorded on an INOVA-400 instrument (Siemens Company of German) with tetramethylsilane (TMS) and H$_3$PO$_4$ as internal standards, respectively, and DMSO-d_6 as solvent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted with a NETZSCH STA 449C at a
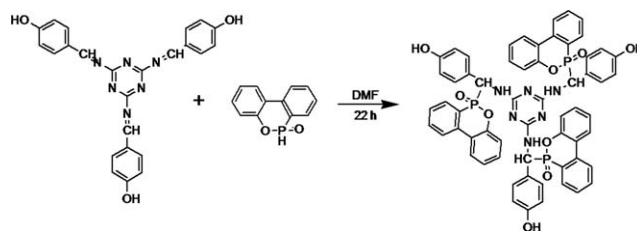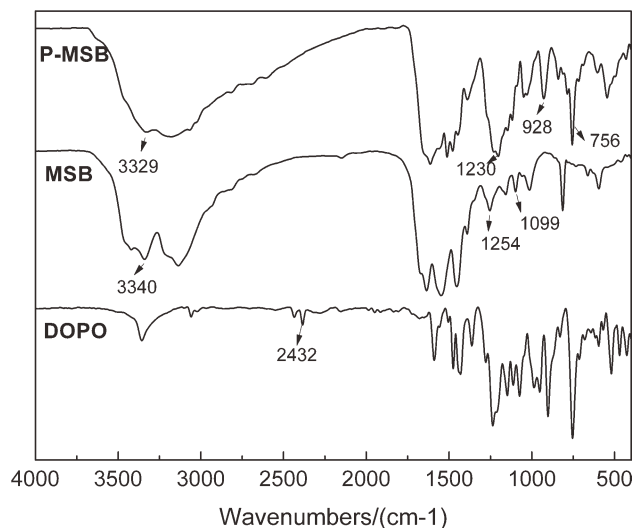

Scheme 2. Synthetic route of P-MSB.

Figure 1. FTIR spectra of DOPO, MSB, and P-MSB.

heating rate of 10°C /min under nitrogen atmosphere. The limiting oxygen index (LOI) was determined with an Atlas LOI chamber according to the ASTM standard method with a test specimen bar of 10 cm in length, 6 mm in width, and 3 mm in thickness. The percentage in the O_2–N_2 mixture, deemed sufficient to sustain the flame, was taken as the LOI. Scanning electronic micrograph (SEM) and observed on a FEI QUANTA-2000 (FEI, USA) to investigate the residues of the P-MSB/CNE system, which were obtained after LOI test.

RESULTS AND DISCUSSION

Syntheses and Characterizations
Schiff base of melamine was synthesized via many methods,[30,31] but all of them involved complex procedure and organic solvent. The method described here was a simple process, with high yield (84%). Importantly, to meet the requirement of the industrialization and the environmental friendly the organic solvent was replaced with water. The reactive rigid heterocyclic ring structure containing phosphorus and P-MSB was synthesized through the simple addition reaction between DOPO and Schiff bases of melamine.

The chemical structure of MSB and the obtained phosphorus-containing compound P-MSB were confirmed by FTIR. Figure 1 shows the FTIR spectra of DOPO, MSB, and P-MSB. The characteristic peaks were found at around 3180 cm^{-1} (O—H), 1562 cm^{-1}, 1477 cm^{-1} (P—C), 1230 cm^{-1}, 1203 cm^{-1} (P=O), 1049 cm^{-1} (P—O—C), 928 cm^{-1} (P—O—Ph). However, the distinctive absorption at 2432 cm^{-1} for P (O)—H stretching in DOPO disappeared. The results demonstrated that the reaction of DOPO and MSB successfully.

The structure of MSB was characterized by ^{1}H-NMR, and P-MSB was characterized by ^{1}H-NMR and ^{31}P-NMR. Figure 2 shows ^{1}H spectra of the MSB, and the assignment of each peak was marked in Figure 2. The single absorption peak $\delta = 9.79$ ppm and single $\delta = 6.05$ ppm correspond to three phenolic –OH groups and three –N=C—H groups, respectively. The peaks between 7.77–7.75 ppm (6 H) and 6.94–6.92 ppm (6 H) were

assigned to benzene ring. As show in Figure 3, the absorption peak $\delta = 9.26$, $\delta = 3.52$, $\delta = 3.33$ ppm in Figure 3(a) represents only one kind of the phenolic –OH groups, –N—H groups, and –C—H groups, respectively, which confirmed the symmetrical chemical structure of P-MSB. The peak between 8.17-8.11 ppm, 7.58-7.42 ppm, 7.30-7.22 ppm, and 6.57-6.55 ppm represents four kinds ^{1}H of benzene ring of DOPO. Other analyses of ^{1}H are similar to that of MSB. Furthermore, P-MSB exhibits a single peak at 36.84 ppm in ^{31}P-NMR spectra [Figure 3(b)].

All the results supported the conclusion that P-MSB was successfully synthesized via the simple addition reaction between DOPO and Schiff bases of melamine, and indicated the symmetrical structure and a high purity in the obtained compound.

Curing Reactions of P-MSB on Epoxies
The curing reactions of CNE with P-MSB were studied with DSC. Figure 4 shows the dynamic heating curves of P-MSB/CNE at various heating rates of 2.5, 5, 10, 15, and 20°C/min. As expected in the samples, the DSC curves shift to higher peak temperature at higher heating rate.

The activation energy of the P-Ph/CNE can be determined by the method of Kissinger without a precise knowledge of the reaction mechanism.[32,33] The governing equation was shown as follows:

$$\frac{d[\ln(\beta/T_p{}^2)]}{d(1/T_p)} = -E/R \qquad (1)$$

where E is the activation energy (kJ/mol); β is the heating rate (K/min); R is the ideal gas constant, 8.314 J/(mol K); and T_p is the peak temperature of the DSC thermogram (K). The fitting straight line of the plots of ln $(\beta/T_p{}^2)$ versus $1/T_p$ was curved (Figure 5) and the linear regression equation was $y = 8.86$–$8.44x$. Therefore, the activation energy of the P-Ph/CNE was obtained from the slope of the line as a value of 70.17 kJ/mol calculated by eq. (1).

Thermal Properties
The glass transition temperature (T_g) is an important parameter for application of epoxy resin thermosets. The T_g of the PN/CNE as control sample and the epoxy resins cured with P-MSB had been measured by DSC at a heating rate of 10°C/min. The compositions and thermal properties of the cured epoxy resins
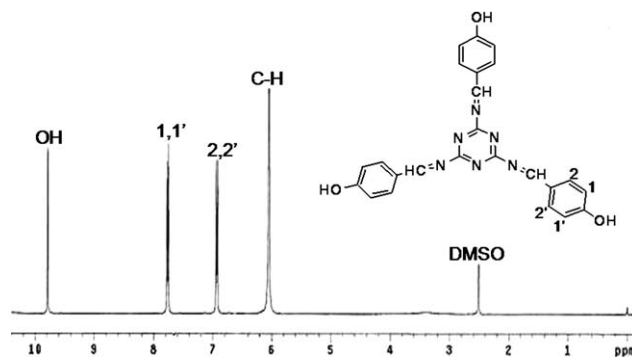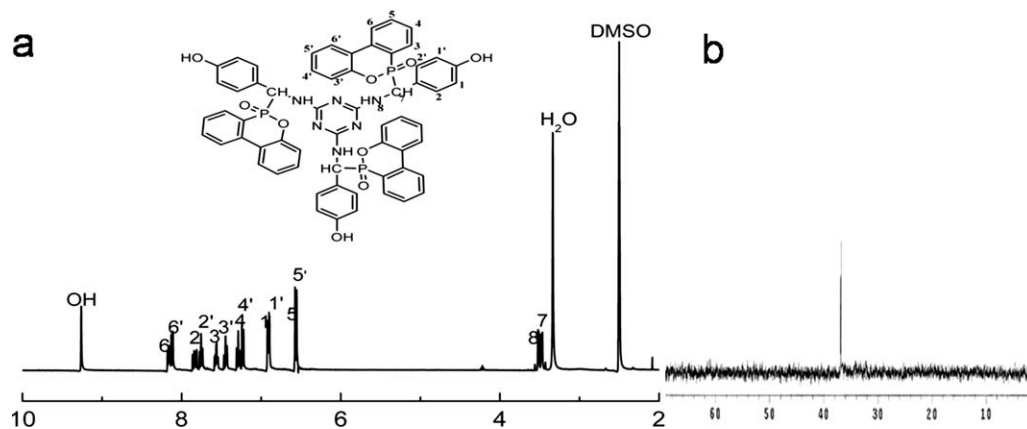

Figure 2. ^{1}H spectra of MSB.

Figure 3. (a) ^{1}H and (b) ^{31}P-NMR spectra of P-MSB.

were shown in Table I. The T_gs of the (P-MSB/CNE)s were found to be higher than that of the control and decreased with more P-MSB content in the resins. As usual, the curing compositions provide a rigid melamine ring and a high reactive functionality with epoxy to the curing system, consequently increasing the resins' T_g.[8,23] However, the T_gs of P-MSB in epoxy resin thermosets decreased with the increasing of the additive added, it was attributed to the incorporation of bulky DOPO group into the epoxy which increase the rotational barrier and decrease the crosslinking density of the cured epoxy resins.[25,26] Above all, it is noteworthy that these phosphorus–nitrogen containing epoxy thermosets had T_gs above 165°C. The results showed T_g relatively higher than that of only DOPO-containing cured epoxy resins in the reported result.[7,9]

Thermal stabilities of the curing agents consisted of P-MSB/PN in various weight ratio cured with CNE were evaluated by TGA under nitrogen with a temperature range from the room temperature to 800°C. The cured polymers were prepared according to the curing procedures determined from DSC. Figure 6 shows the thermogravimetric traces of the control CNE resins and P-

MSB resins. The temperature of 5% weight loss ($T_{5\%}$), the maximum decomposition rate temperature and char yield at 800°C were summarized in Table I, in which the corresponding data from the epoxy resin with PN used as control was also listed.

As shown in Table I, the decomposition temperature of 5% weight loss for P-MSB/CNE was 321°C. The char yields at 800°C for P-MSB-cured epoxy resins was 27% in N_2. The developed P-MSB/CNE reached the requirements for application in advanced electronics.

According to Table I, For the CNE cured with various weight ratios of P-MSB and PN, the 5% weight loss temperatures of the control sample was 346°C and the P-MSB-D-cured system decreased to 321°C which was close to that of the control CNE resin. It indicated almost the same thermal stability of the P-MSB-cured epoxy resins as the P-free PN-cured resin. It is known that the phosphorus-containing epoxy resins were relatively lower thermal stability than phosphorus-free resins because the phosphorous group degraded at relatively low temperatures.[5–7] The differences were attributed to the
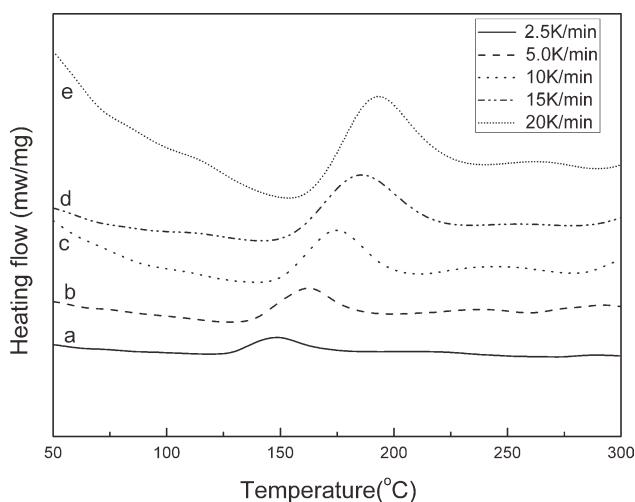

Figure 4. DSC thermogram of epoxy curing at various heating rates for P-MSB/CNE.
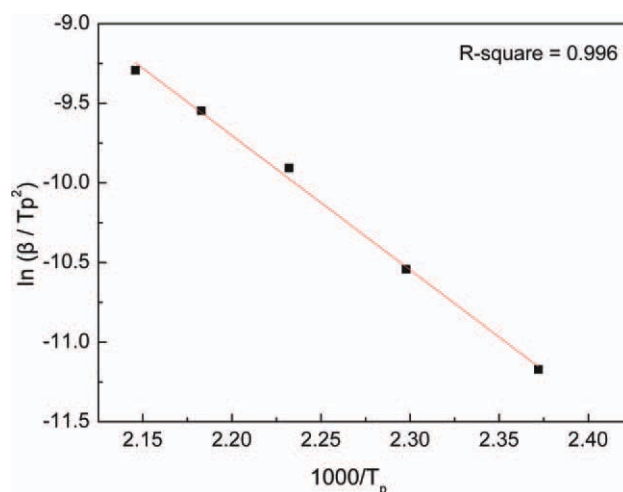

Figure 5. Plots of ln (β/T_p^2) versus $1/T_p$ for calculating the activation energies by Kissinger method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

Sample P-MSB/PN (wt %)	P (%)	N (%)	T_g (°C)	N₂ atmosphere		Char yield at 800°C %	LOI
				$T_{5\%}$	T_{max}		
Control	0/100	0	0	143	346	406	24.2	22
P-MSB-A	25/75	1.31	1.19	180.6	328	398	32.1	34
P-MSB-B	50/50	2.03	1.83	179.6	327	394	29.2	33
P-MSB-C	75/25	3.49	3.15	178.3	314	378	27.5	34
P-MSB-D	100/0	5.44	4.91	165.5	321	381	27	35

$T_{5\%}$: decomposition temperature at 5% of weight loss. T_{max}: decomposition temperature at maximum decomposition rate.

incorporation of N-containing moiety in P-MSB. N-containing epoxy resins usually show superior heat resistance.[28]

From the traces of the TGA and the DTGA, it exhibited a major mass loss via a single largely decrease of approximately 56 wt % from 350°C to 500°C, and then the rate of mass loss decreased very slowly. It can also be seen that the weight loss rates of the P-containing resins were lower than the control ones and the temperature of maximum decomposition rate decreased when P-containing curing agent increased in P-MSB/CNE.[8–14] This phenomenon played an important role in improving the flame retardancy of the resins. When ignited, the phosphorous group degraded at first and the decomposition of phosphate group formed a phosphorus-rich residue to prevent further decomposition of the resins matrix and resulted in a high char yield.

All the results mention above showed that CNE cured with various weight ratios of P-MSB/PN had higher char yield than that of the control PN/CNE resin. A similar result was also seen in the reported result, in which a P-containing curing agent cured epoxy showing relatively low char yield.[11,18] However, the residual chars decreased when N-containing curing agent increased in P-MSB/CNE, it means that more additive P-MSB added into CNE may not bring more remarkable flame-retardant behavior of P-MSB epoxy resins. But some studies in the published literature,[23] it was attributed to that the decomposition of

melamine in an open system mostly generated gas (e.g., NH₃) above 250°C, left little residue and resulted in low char yield.

Above all, the thermal stability and the flame-retardant behaviors were very complicated when phosphorus and nitrogen existed simultaneously in the curing system of epoxy resin.[25,26] Therefore, the flame-retardant behaviors will be further discussed by other characterization later.

Flammability

LOI was defined as the minimum fraction of oxygen in an oxygen-nitrogen mixture that is required to support downward combustion of the specimen after ignition.[10] The flame-retardant properties of the obtained epoxy resins were examined by measuring the LOI of the resins. The LOI values of all cured epoxy resins were presented in Table I. A significant increase in LOI could be observed when P-MSB was utilized in the epoxy curing compositions (Table I). LOI value of the resultant epoxy resins was drastically increased from 22 to 35 for PN/P-MSB/CNE systems. It could be concluded from the results that the epoxy resins with phosphorus–nitrogen improved the flame-retardant property.

According to Table I, the phosphorus–nitrogen-cured systems had much higher LOI than that of only phosphorus-containing cured systems reported in early.[17,18] But, it showed almost the
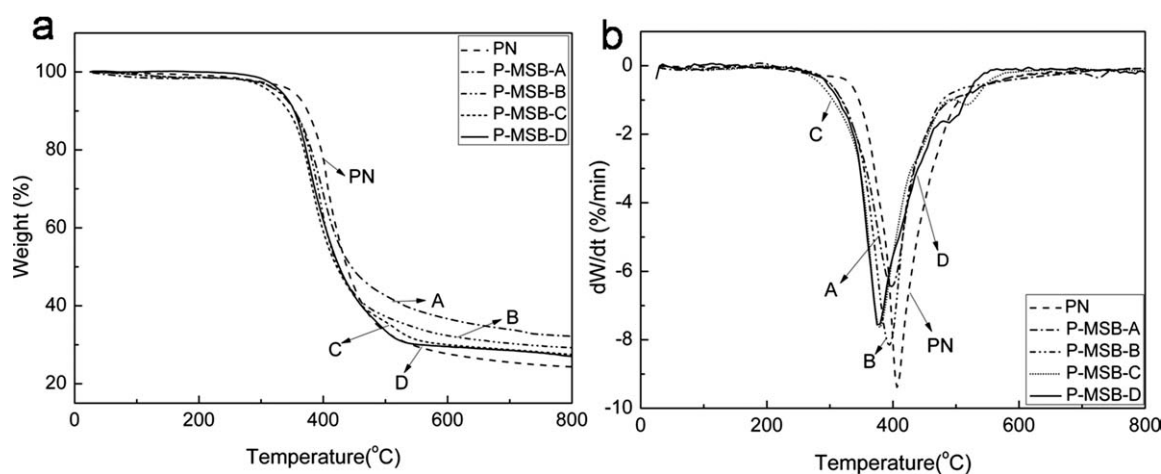

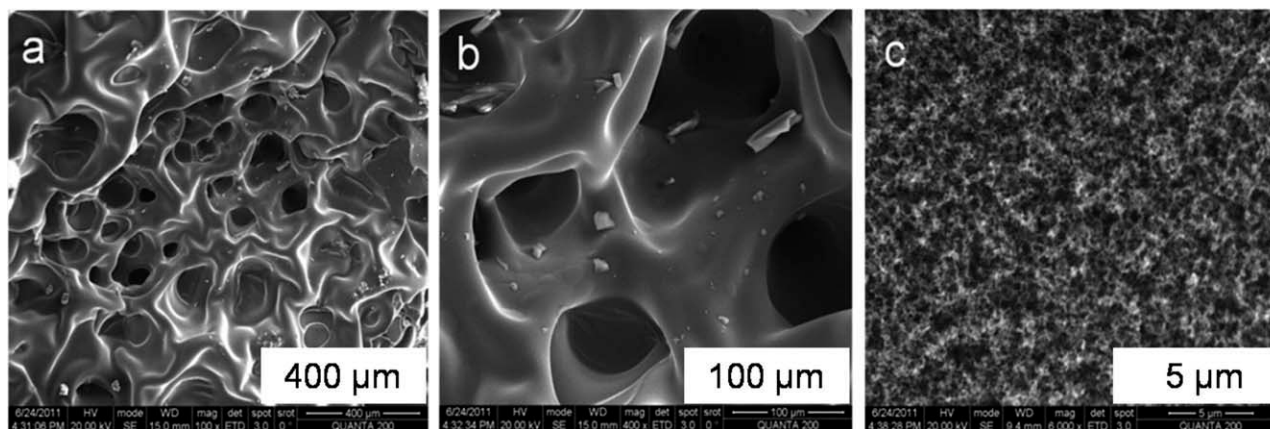**Figure 6.** TGA and DTGA thermograms of the cured epoxy resins in N2.

Figure 7. SEM morphologies of the residues of P-MSB-cured epoxy resins.

same LOI values of the P-MSB-cured epoxy resins systems with different phosphorus and nitrogen containing but the ratio of P/N in the cured systems of P-MSB/CNE were the same. The conclusion was conformed with the reported literature,[22] the LOI value increased with the increase of the ratio of P/N. It indicates that the effective synergism of phosphorus and nitrogen elements influence the flame-retardant properties of the epoxy resins mainly depends on the ratio of P/N. The reasons of this phenomenon will continue to be studied in our future work. Generally, materials with LOI values higher than 26 would show self-extinguishing behavior and were considered to be highly flame retardant. Thus, the obtained curing agent P-MSB both containing phosphorus and nitrogen for epoxy resins may be used potentially as efficient flame-retardant and green materials in electronic fields.

Morphology of the Residue
The morphology of the residue of the cured epoxy resins after LOI burned was investigated by SEM. Figure 7 shows SEM for the inner (a, b), outer (c) surface of the char for P-MSB/CNE composite. The images showed that the inner char had much porous as well as the outer surface. However, the inner pore path was much larger than the outer pore, the reason is the fact that swelled honeycomb structure was formed for the generation of H_2O, NH_3, etc., in the process of combustion and heat of the skeleton structure of melamine, and then delivered from the outer surface slowly leading to the formation of narrow pores on the surface of the residue of the cured epoxy resins. The formation of efficient intumescent chars for P-MSB/CNE composites can prevent heat transfer between the flame zone and the resins, and thus protect the underlying materials from further burning and pyrolysis. Thus the thermosets containing P-MSB obtained excellent flame retardancy.

CONCLUSIONS
A novel DOPO-containing Schiff base of melamine for curing agent, P-MSB, was successfully synthesized through a two-step reaction, and characterized by FTIR, ^{1}H-NMR and ^{31}P-NMR. Comparing with PN/CNE resin, the P-MSB-cured CNE systems had better flame-retardant property, LOI value of P-MSB/CNE was high up to 35. The P-MSB cured system also exhibited excellent T_g (165°C) and thermal stability, its $T_{5\%}$ reached up to 321°C. In summary, the synergistic effect of phosphorus and nitrogen in the P-MSB/CNE systems provided excellent flame retardancy as well as good thermal stability. The synthesized P-MSB in this study has potential applications as a reactive flame retardant in the epoxy systems in electric and electronic fields in consideration of the environment and human health.

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