

Synthesis and Characterization of Epoxy Film Cured with Phosphorous-Containing Phenolic Resin

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ABSTRACT: Through the electrophilic addition reaction of $-P(O)-H$ and $C=C$, a series of novel phosphorus-containing phenolic resins bearing maleimide (P-PMFs) were synthesized and used as curing agent for preparing high performance and flame retardancy epoxy resins. The structure of the resin was confirmed with FTIR and elemental analysis. Thermal properties and thermal degradation behaviors of the thermosetted resin was investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The epoxy resins exhibited high glass transition temperature (143–156°C), good

thermal stability ($>330^{\circ}C$) and retardation on thermal degradation rates. High char yields (700°C, 52.9%) and high limited oxygen indices (30.6–34.8) were observed, indicating the resins' good flame retardance for the P-PMFs/CNE cured resins. The developed resin may be used potentially as environmentally preferable products in electronic fields. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3813–3817, 2007

Key words: resins; phosphorus-containing; maleimide; flame retardance; thermal properties

INTRODUCTION

Because of the attractive characteristics of excellent moisture, high adhesion to many substrates, good chemical and corrosion resistance, and superior electrical properties,¹ epoxy resins were widely used in various industrial fields such as coating, potting, adhesives, laminates, and composites, etc. However, the developed surface mounting technology, lead-free soldering process, and other advanced electronic packaging techniques require materials being able to sustain high processing temperatures and providing excellent thermal and mechanical properties and good flame retardance for epoxy resins.² To achieve high flammability of the epoxy resins, brominated compounds and antimonyoxide are imparted into the encapsulant composition as flame retardants. The utilization of these halogenated and antimony compounds in polymeric materials is harmful to the environment and human health because toxic and corrosive gases are released as well as harmful endocrine disrupting chemicals.³ Therefore, the trend is toward using halogen-free flame retardants in polymers.^{4–6}

Halogen-free, flame-retardant epoxy resins have been obtained from the most effective reactive approach: incorporating phosphorus containing chemical units into the polymer backbone or side of oxiranes or curing agents.^{7–13} But, usually with the flame retardancy of ep-

oxy resins increased the original physical and mechanical properties and thermal stability are decreased.^{14,15} Polyimides and polybismaleimides, owing to their high degree of thermal stability, excellent mechanical properties, and chemical resistance are therefore utilized to toughen epoxy resin.^{16,17} However, polyimide materials are usually accompanied with the drawbacks of poor processibility, brittleness, and high cost. Therefore, modifications on epoxy resins and polyimides are widely investigated for providing materials with moderate cost and satisfied properties.²

In a previous study, epoxy resins modified by a maleimide-containing novolac (PMF) were demonstrated to show relatively high thermal stability and better mechanical properties. In this study, through the electrophilic addition reaction of $P(O)-H$ and $C=C$. A series of phosphorous-containing phenolic novolac were synthesized and used as curing agent for preparing high performance and flame retardancy epoxy resins. The synthesis, characterization, and curing reaction of the monomers and the thermal properties and flame retardancy of the resultant epoxy resins were investigated. The resulting epoxy resins are expected to be qualified for advanced applications in electrical and electronic industrials.

EXPERIMENTAL

Materials

4-Aminophenol, maleic anhydride, *p*-toluenesulfonic acid (*p*-TSA), formaldehyde supplied as a 34 wt %

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TABLE I
The Curing Conditions for the Epoxy Resins

Epoxy compositions	The initial temperature of the exothermic peak on DSC thermogram (°C)	Curing procedure		
		1st cure	2nd cure	3rd cure
P-PMF ₁ /CNE	118.3	120°C, 60 min	170°C, 120 min	200°C, 180 min
P-PMF ₂ /CNE	118.3	120°C, 60 min	170°C, 120 min	200°C, 180 min
P-PMF ₃ /CNE	151.6	–	170°C, 150 min	200°C, 180 min
PMF/CNE	109.3	120°C, 60 min	170°C, 120 min	200°C, 180 min
PN/CNE	140.3	–	170°C, 150 min	200°C, 180 min

aqueous solution, oxalic acid, phenol (Shanghai Chemicals). A phenol formaldehyde novolac resin used as curing agent with a hydroxyl equivalent weight of about 126 g/eq, and an *o*-cresol formaldehyde novolac epoxy CNE (CTDCN-200, epoxy equivalent weight EEW = 207 g/eq) were kindly supplied by BaLing Petrochemical of China. All solvents were reagent grade and used without further purification. 5,5-dimethyl-4-phenyl-2-oxy-1,3,2-dioxaphosphorinane phosphonate (DPODP) was prepared according to the literature.¹⁸

Synthesis of *N*-(4-hydroxy phenyl)maleimide

HPM was synthesized in two steps according to the reported procedure.² First the *N*-(4-hydroxyphenyl) maleamic acid (HPMAc) was prepared by the reaction of 4-amino phenol with maleic anhydride in acetone and give a yellow powder product. *p*-TSA was used for the cyclodehydration of HPMAc. The product was recrystallized from a mixed solvent of water-isopropanol (1 : 1 V/V) to give an orange crystalline needle product (yield: 58%). IR (KBr, cm⁻¹): 3481 (Ph—OH), 1705 (C=O, symmetrical stretching), 1396 (C—N stretching), 714 (C=O bending), 683 (C=C bending). Elemental analysis found % (calcd %) C: 63.51(63.49), H: 3.68 (3.70), N: 7.44 (7.41). mp: 183.2–184.1°C (lit. 189°C).

Synthesis of phenol formaldehyde bearing HPM

The PMF resins were synthesized by the copolymerization of phenol, HPM, and formaldehyde with oxalic acid as the catalyst according to the reported literature.¹⁹ A mixture of phenol (60 g, 0.638 mol), HPM (40 g, 0.212 mol), and oxalic acid (5 g) were heated in a two-necked flask fitted with a condenser and mechanical stirrer in a water bath at 75°C. A formaldehyde solution (56 mL, 34% formalin; phenol/formaldehyde 1 : 0.8) was added dropwise under mechanical agitation. After the addition, the contents were stirred at this temperature for 10 h. The resin was diluted with 200 mL of acetone and precipitated into a water-methanol (40% methanol) mixture. The polymer was puri-

fied by repeated precipitation with the same solvent-no solvent system. The filtered polymer was dried at 50°C under vacuum for 8 h. Yield: 70.94%. Softening point: 107.3°C. HEW (hydroxyl equivalent weight) = 143.3 (g/mol). IR (KBr, cm⁻¹): 3354 (—OH), 1771 (C=O asymmetrical stretching), 1704 (C=O symmetrical stretching), 1363 (C—N stretching), 688 (C=C bending). Elem. Anal. Calcd.: C, 73.536%; H, 4.911%; N, 2.745%. Found: C, 72.38%; H, 4.725%; N, 2.373%.

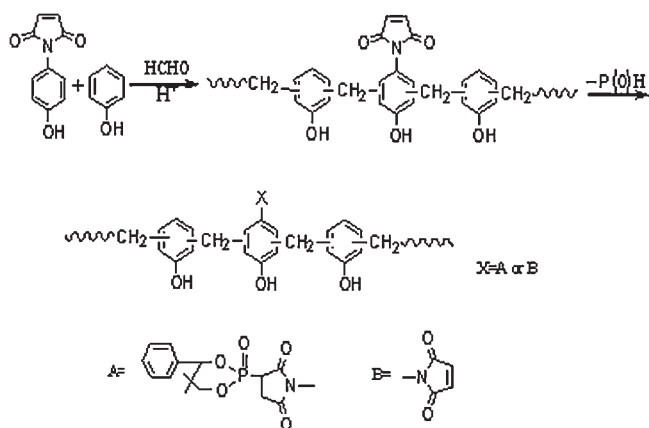
Preparation of phosphorous-containing PMF

Phosphorous-containing PMFs (P-PMFs, phosphorus content: 1.44, 2.27, and 3.05%) were synthesized through the electrophilic addition reaction of P(O)—H and C=C in varying proportions. A typical experiment, P—PMF₃ (the feeding ratio of P(O)—H and C=C is 1 : 1) with a phosphorus content of 3.05 w/w is discussed. A mixture of 11.49 g (0.0509 mol) of DPODP, 30 g (0.0509 mol C=C) PMF, 100 g of methylisobutyl ketone were heated in a three-necked flask fitted with a condenser and mechanical stirrer in a water bath at 80°C and maintained at that temperature for 20 h to ensure completion of the reaction. After the solvent was removed by evaporation under reduced temperature, the product then dried at 80°C under vacuum for 4 h and gave a brown color resin. HEW (hydroxyl equivalent weight) = 194.2 (g/mol). IR (KBr, cm⁻¹): 3340 (—OH), 1710 (C=O symmetrical stretching), 1363 (C—N stretching), 1216 (P=O st), 1162 (P—O—C ar st), 995 (P(V)). Elem. Anal. Calcd.: C, 69.35%; H, 5.295%; N, 1.716%; P, 3.799%. Found: C, 68.32%; H, 5.399%; N, 1.547%; P, 3.05%.

The other P-PMFs, P-PMF₁, and P-PMF₂ (with phosphorus contents of 1.44 and 2.27% w/w, respectively), were synthesized in a procedure similar to that described for P-PMF₃.

Preparation of cured resins

The cured epoxy resins were obtained via thermally curing of P-PMFs with CNE. The phosphorus-free PMF/CNE and HPM-free phenolic novolac/epoxy



Scheme 1 Synthetic route of P-PMFs.

(PN/CNE) were also used for preparing control samples. To obtain a highly crosslinked polymer with good thermal stability, one epoxy equivalent weight of the epoxy resins was cured with one functional equivalent weight of the novolac curing agents.²⁰ The curing cycles were determined from differential scanning calorimetry (DSC) tracing of the respective epoxy/curing agent compositions (Table I).

Instrumental analysis and measurements

IR spectra were recorded with an infrared spectrophotometer (WQF-410). Elemental analyses were performed using a Heraeus CHN—O—S-Rapid elemental analyzer. Melting points were determined in a polarizing microscope (Laboratory Devices MELTEMP II), spectrophotometer. DSC thermograms were recorded with a thermal analysis (TA) at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a STA-449C Thermo gravimetric analyzer at a heating rate of 20°C/min under nitrogen or air atmosphere. The LOI was determined with an Atlas limiting oxygen index chamber according to the ASTM standard method. The percentage of O₂ in the O₂—N₂ mixture just sufficient to sustain the flame was taken as the LOI.

RESULTS AND DISCUSSION

Preparation of phosphorous-containing PMF

P-PMF resins with different proportions of DPODP were synthesized by the electrophilic addition reaction of P(O)—H and C=C (Scheme 1). The occurrence of the above-mentioned reaction was monitored by FTIR. (Fig. 1). Let us take P-PMF₃ as an example—the characteristic peaks were 1710 cm⁻¹ (C=O, symmetrical stretching), 1363 cm⁻¹ (C—N—C, stretching), 1216 cm⁻¹ (P=O), 1162 cm⁻¹, 995 cm⁻¹ (P—O—C), 748 cm⁻¹ (P—C). A broad bond was observed at

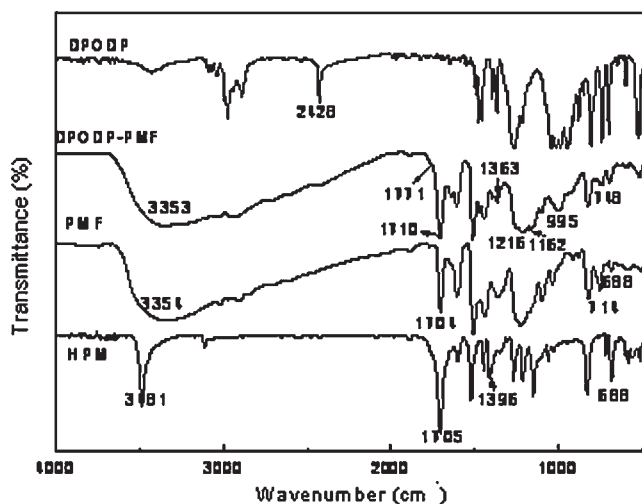


Figure 1 FTIR spectra of PMF and P-PMF.

3354cm⁻¹ that was due to the absorption for various kinds of hydroxyl. The distinctive absorption at 2428cm⁻¹ for —P(O)—H stretching in DPODP and 688cm⁻¹ for C=C in PMF disappeared. These characteristic peaks were consistent with the structure of P-PMF₃.

Curing reactions of epoxy compositions

The curing reactions of P-PMFs with epoxies were studied with DSC. The epoxies based on CNE were utilized in the investigation. Figure 2 shows the typical DSC thermogram of P-PMF1/CNE. The exothermic peak denotes the proceeding of the curing reaction between P-PMF1 and CNE. The reactivity of P-PMF1 toward the epoxy could be read from the start point of the exothermic peak.²¹ Furthermore, the cur-

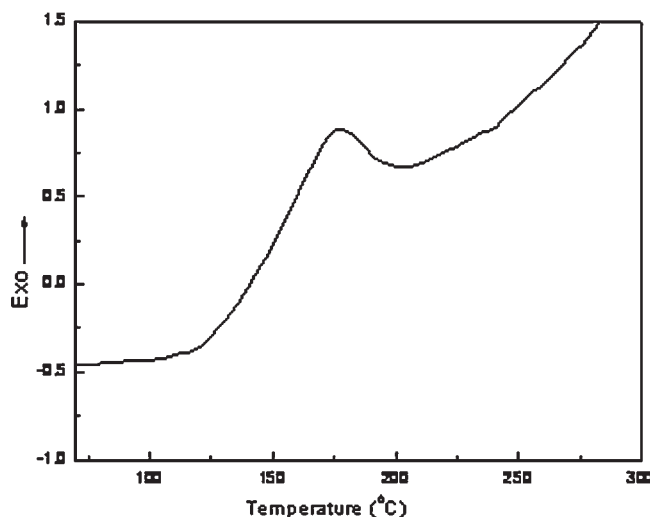


Figure 2 DSC of P-PMF1/CNE.

TABLE II
Thermal Properties of Cured Epoxy Resin

Sample	P (%)	T_g , °C	Temperature of weight loss				Rapid weight loss temp (T_r , °C)				Char yield (%)		
			5%		10%		Step I		Step II		700°C		
			Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂	LOI
PN/CNE	0	143	372	358	393	383	418	419	469	–	9.1	29.4	23.4
PMF/CNE	0	174	391	384	409	408	426	429	642	–	0.5	37.8	29.5
P-PMF ₁ /CNE	0.49	156.2	347	332	367	366	385	395	670	543	29.7	51.2	30.6
P-PMF ₂ /CNE	1.05	154	341	332	362	361	380	398	700	537	34.0	52.9	33.7
P-PMF ₃ /CNE	1.48	143.5	330	340	360	363	390	400	768	488	37.9	49.8	34.8

Step II of rapid rate was not found.

ing procedures for preparing epoxy resins based on various compositions were also determined from the DSC exothermic peaks, and the results were shown in Table I. Because of the existence of reactive group C=C, the initial temperatures of the exothermic peaks of PMF/CNE, P-PMF₁/CNE and P-PMF₂/CNE were lower than those of PMF₃/CNE and PN/CNE. The lower reactivity of P-PMF₃ toward epoxy than the PN/CNE system might be because of the effect of steric hindrance owing to the incorporation of the bulky HPM-DPODP group onto the P-PMF novolac.

Thermal properties of the cured epoxy resins

The cured polymers were prepared according to the curing procedures determined from DSC (Table I). Moreover, the epoxy resins with PN and PMF used as control were also prepared 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 II. The glass transition temperatures (T_g s) of these cured

epoxy resins are noteworthy. The T_g s of the P-PMF-cured epoxy resins were found to be lower than that of the PMF-cured epoxy resins and decreased with increasing phosphorus contents in the resins. The result might be understood by the steric effect of the bulky DPODP group in P-PMFs and the decrease of the contents of C=C, and therefore the crosslinking density of the cured epoxy is decreased, consequently lowering the T_g of the polymer. In other aspects, though the P-PMF-cured epoxy resins exhibit lower T_g s (143.5–156.2°C) than the PMF-cured resins, the T_g s of the phosphorus-containing epoxy resins are comparable to PN-systems and are still as high to reach the requirements for electronic applications.

TGA is the most favored technique for rapid evaluations in comparing and ranking the thermal stability of various polymers. Typical TGA thermograms of the cured epoxy resins measured in nitrogen and in air are shown in Figures 3 and 4 respectively. The thermal stability of the phosphorus-containing resins was lower than the control ones and decreased with the increasing of phosphorus contents in the resins. Phosphorus groups that decomposed at relatively low tem-

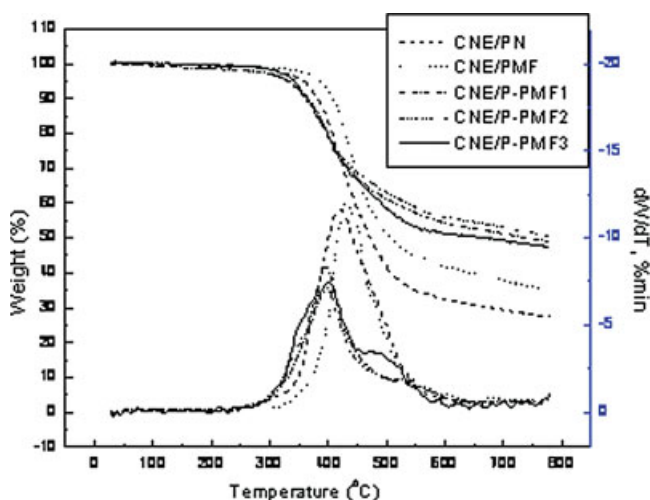


Figure 3 TGA thermograms of cured epoxy resins in N₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

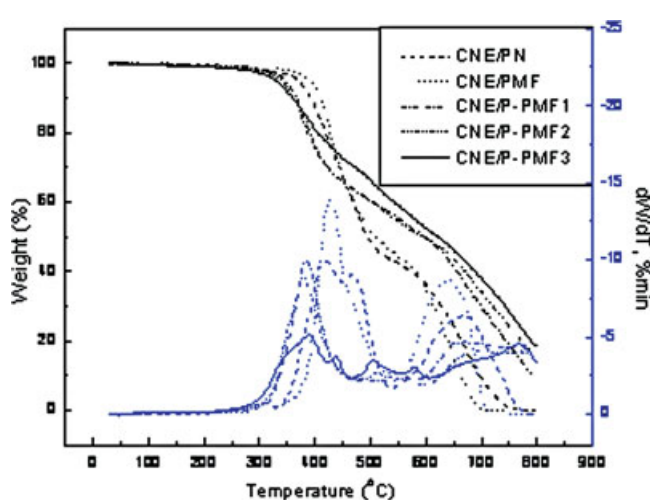


Figure 4 TGA thermograms of cured epoxy resins in Air. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

peratures were reported to have key roles in enhancing polymer char formation and flame retardancy.^{5,22}

For thermal stability analysis at high temperatures in air, although the first rapid-weight-loss temperatures of the control CNE resins were 418 and 426°C for PN-cured resins and PMF-cured resins respectively, slightly higher than the temperatures of P-PMFs/CNE, unlike the one-stage rapid weight loss of the control CNE resins, the P-PMFs/CNE epoxy resins exhibited a second stage of rapid weight loss at a higher temperature. From the traces of the TGA, it also can be seen that the weight loss rates of the phosphorus-containing resins were lower than the control ones. This phenomenon played an important role in improving the flame retardancy of the resins. When ignited, the phosphorus-containing groups first decomposed around 400°C and then formed a phosphorus-rich residue that prevented further decomposition of the epoxy resin by raising the second decomposition temperature to a higher level; this resulted in high char yields.

The char formation of the cured epoxy resins was notably enhanced with the incorporation of DPODP group into the curing compositions (Table II). The char yields increased with increasing phosphorus contents of the resins. The enhancement of the char formation was especially dominant when samples were heated in air. It can be seen the char yields at 700°C for phosphorus-containing resins are greatly higher than that of the control resins, with only 0.5% of the phosphorus content the char yields at 700°C in N₂ was 51.2% and in air was 29.7%.

Flame retardancy

Increasing the char formation can limit the production of combustible gases, decrease the exothermicity of pyrolysis reactions, and inhibit the thermal conductivity of burning materials,²³ thereby leveling up the flame retardance of the resins through a condensed-phase mechanism.²⁴ A cured epoxy resin with a high phosphorus content is expected to have a high char residue on pyrolysis, and the char residue on pyrolysis is linearly proportional to the oxygen index for halogen-free polymers and, consequently, limits the flammability of the material.²³ Here, the residual char increased with the phosphorus content, indicating that the flame retardancy increased with the phosphorus content.

The flame-retardant properties of the obtained epoxy resins were examined with LOI measurements (Table II). When the DPODP group was introduced into the curing compositions, LOI values of the resultant epoxy resins were significantly increased from 29.5 to 34.8 for P-PMF series resins with the P% 0.49, 1.05, and 1.48% respectively. The improvement with

phosphorus of the flame-retardant properties of the epoxy resins was demonstrated.

CONCLUSIONS

The phosphorus-containing novolac P-PMFs were successfully synthesized and used as curing agents with *o*-cresol novolac-type epoxies. The cured epoxy resins were found to have high glass transition temperatures, excellent thermal stability and good flame retardant properties. The synthesized P-PMF is therefore suitable to be used as a reactive flame retardant in the epoxy systems for application in green electrical/electronic materials. However, any effort to characterize the new flame retardant phenolic novolac in comparison between some well-known phosphorus-containing systems such as DOPO ones and some commercial phosphorus epoxy resin has not been made and will be the main direction of our future work.

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