

Synthesis and Properties of Novel Phosphorus-Containing Bismaleimide/Epoxy Resins

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ABSTRACT: A novel soluble phosphorus-containing bismaleimide (BMI) monomer, bis(3-maleimidophenyl)phenylphosphine oxide (BMIPO), was synthesized by the imidization of bis(3-aminophenyl) phenylphosphine oxide, in which its structural characterization was identified with ¹H-NMR, ¹³C-NMR, and Fourier transform infrared spectra. The BMIPO resin, with five-membered imide rings and high phenyl density, was an excellent flame retardant with a high glass-transition temperature (T_g), onset decomposition temperature, and limited oxygen index. In phosphorus-containing BMI/epoxy/4,4'-methylene dianiline (DDM)-cured resins, homogeneous products were obtained from all proportions without phase separation. Because of the higher reactivity of BMIPO/DDM relative to that of 4,4'-bismaleimidodiphenylmethane (BMIM)/DDM, the increase in the BMIPO/BMIM ratio in this blending resin increased the recrosslinking hazards of the postcuring stage and so lowered the T_g value and thermal stability. The thermal stability of the BMI/epoxy-cured system was lower than that of the epoxy-cured system because of the introduction of a phosphide group into BMIPO, whereas for the T_g value and flame retardancy, the former was significantly higher than the latter: the higher the BMIPO content in the blend, the higher the flame retardancy. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2080–2089, 2002; DOI 10.1002/app.10607

Key words: bismaleimide; phosphorus; flame retardance; blending; curing of epoxy

INTRODUCTION

Bismaleimide (BMI) resins, exhibiting excellent mechanical properties and high glass-transition temperatures (T_g 's) and possessing a processing ability similar to that of epoxy, have been widely used for applications in the electronic and infor-

mation sectors, printed circuit board (PCB), aerospace components, and high-quality composites. However, BMI resins still have some defects, such as high melting points (T_m 's) and curing temperatures, high brittleness, low adhesiveness, and high cost.^{1,2} For improving these defects, a blend of BMI with epoxy has become one of the main streams of research on BMI resins.^{3–6} In the BMI blending system, there are two processing problems to be considered.⁷ First, because BMI monomers are always crystalline solids with a value of T_m close to their curing temperature, they often incur partial curing during a hot blending process or an incomplete reaction during the curing pe-

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riod. Second, BMI tends to recrystallize from the blend system during aging. As a result, BMI blending resins often show inconsistent properties. To overcome the incongruence of the blending system, many studies^{8–10} have been made in which soft segments or phosphorus-containing groups have been introduced into BMI monomer to reduce T_m ^{8,9} or to promote the reactivity and solubility,¹⁰ respectively. Moreover, the flame retardancy of blending resins for the latter could be further promoted by the addition of phosphorus-containing BMI monomers, which are excellent flame-retarding agents.^{10–13} The introduction of phosphorus into BMI resins also reduces the thermal stability at the same time. Designing a rigid chain into the phosphorus-containing BMI backbone to promote its thermal stability became one of the major objectives of this study.

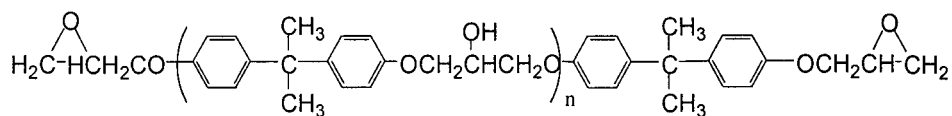
First, a novel phosphorus-containing BMI monomer with a rigid segment, bis(3-maleimidophenyl)phenylphosphine oxide (BMIPO), was synthesized by the nitration, reduction,^{14,15} and imidization of triphenylphosphine oxide (TPPO) to become a highly reactive monomer; its highly polar phosphide backbone increased the electron-withdrawing effect of double bonds and further improved blending processability. For a comparison of the reactivities of BMIPO and commercial

4,4'-bismaleimidodiphenylmethane (BMIM), they were self-cured and cured with diamine, respectively. The results, especially for the latter, provided data for analyzing the effects of blending different BMIPO/BMIM ratios into a bisphenol A-type epoxy [diglycidyl ether of bisphenol A (DGEBA)] resin. The thermal stability and flame retardancy of self-curing BMIPO and BMIPO blended into the DGEBA resin were also studied with thermogravimetric analysis (TGA) and limited oxygen index (LOI), respectively.

EXPERIMENTAL

Materials

Triphenylphosphine oxide (TPPO) and BMIM were obtained from Lancaster (Eastgate, England). Maleic anhydride, sodium acetate, and all other acids were obtained from Showa Chemical Co. (Tokyo, Japan). Ethyl acetate and all other solvents were obtained from Tedia Chemical Co. (Ohio). Tin chloride(II) was obtained from Riedel-Dehane Chemical Co. (Seelze, Germany). 4,4'-Methylene dianiline (DDM) and acetic anhydride were obtained from Aldrich Chemical Co. (Wisconsin). DGEBA (Epon 828) was obtained from Shell Chemical Co. (California).



Tetrahydrofuran (THF) was distilled after dehydration with sodium. The other solvents were purified by conventional methods.

Synthesis

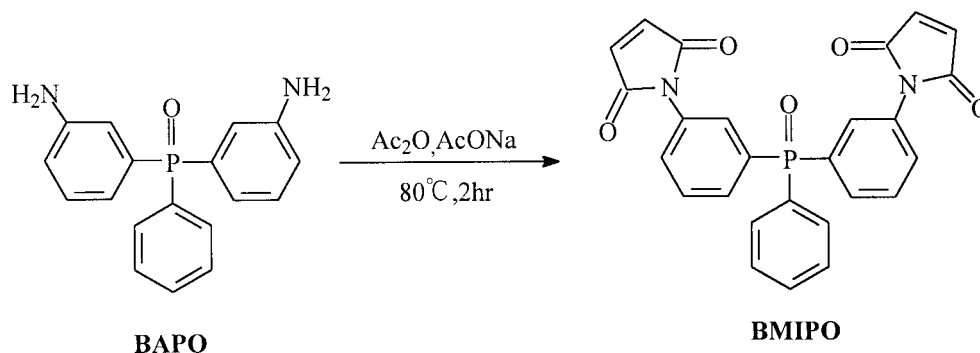
BMIPO

In a three-necked flask equipped with a Teflon stirrer and a thermometer and purged with nitrogen gas at a constant flow rate, the addition of 2 g of bis(3-aminophenyl) phenylphosphine oxide (BAPO), which was synthesized by the nitration and reduction^{14,15} of TPPO, and 1.5 g of maleic anhydride into 20 mL of THF provided a clear amic acid solution. The temperature of this solution was raised to 80°C, and 0.2 g of sodium acetate and 10 mL of acetic anhydride were added. After stirring at 80°C for about 2 h, this mixture was cooled and further poured into 2 L of

ice water to produce the precipitate. This precipitate was washed several times with deionized water and a 5% NaOH solution and then dried under reduced pressure.

Curing of the BMI/Epoxy/DDM Systems

Mixtures of BMIPO blended with commercial BMIM, according to equivalent proportions of 100/0, 75/25, 50/50, 25/75, and 0/100, were blended into Epon828 of the same equivalent, and the blending systems were further added to DDM of the same equivalent for curing. In this study, the curing temperature and time of the BMI/epoxy/DDM systems were decided by simulation of a dynamic scan at a heating rate of 10°C/min and of an isothermal scan by differential scanning calorimetry (DSC), respectively, to obtain two-stage curing processes. The curing temperature of the



Scheme 1. Synthesis of BMIPO.

blending resins during the first stage was carried out about 10°C below the peak of the dynamic DSC curve [i.e., the peak of the maximum weight-loss rate or exothermic peak temperature (T_{max})], whereas its curing time was decided by the isothermal DSC curve under the curing temperature. The postcuring cycle of the blending resins during the second stage, similar to the selected curing cycle during the first stage, was further carried out at 10°C below the exothermic ending temperature (T_f) for 10 min to obtain a completely cured resin.

Instrumentation

^{13}C - and ^1H -NMR spectra of all the synthesized monomers were measured with a Bruker AM400-NMR spectrometer (Massachusetts). In addition, a PerkinElmer 842 Fourier transform infrared (FTIR) reflection spectrophotometer (Massachusetts) and a Heraeus CHN-O rapid element analyzer (Germany) were used for analyses of the IR spectra and elemental analyses (C, H, N) of these monomers, respectively. The scanning curves of the BMIPO and relative blending resins with a TA Instruments DSC10 (Delaware) at a heating rate of 10°C/min in N_2 were used for analyzing T_m 's, curing temperatures, and T_g 's. The thermal stability and flame-retarding properties of the aforementioned resins were analyzed with a TA Instruments TGA 51 at a heating rate of 20°C/min in air or N_2 . The latter was also studied by LOI via data from an oxygen index analyzer (Atlas Electric Devices Co., Illinois) at an O_2/N_2 flow rate of 20 L/min.

RESULTS AND DISCUSSION

Characteristics of the BMIPO Resins

BMIPO was synthesized by the imidization route of BAPO shown in Scheme 1. The nitration and

subsequent reduction of TPPO, in accordance with the literature,^{14,15} were carefully controlled for the synthesis of a meta-type diamine compound (BAPO). Then, BAPO was imidized with maleic anhydride to obtain a soluble BMIPO monomer as a straw-yellow powder.

Yield: 75%. mp: 198.8°C. FTIR (KBr, ν , cm^{-1}): 1716 (C=O), 1380 (C—N—C), 824 (C=C), 1182 (P=O), 1426 (P—Ph). ^1H -NMR (DMSO, δ , ppm): 7.62 (1H, m, 4'-H), 7.48–7.59 (5H, m, 2'',3'',4'',5'',6''-H), 6.82 (2H, s, —CO—CH=CH—CO—), 6.80 (1H, d, 6'-H), 6.75 (1H, d, 2'-H), 6.59 (1H, m, 5'-H). ^{13}C -NMR (DMSO, δ , ppm): 116.3 (2'-C), 118.5 (4'-C), 116.7 (6'-C), 131.5 (3'-C), 128.1–129 (2'',3'',5'',6''-C), 131.8 (4''-C), 152.4 (1'-C—N—), 135.6 (—CO—CH=CH—CO—), 169.9 (2-C=O), 132.5–134.1 (5',1''-C—P=O). ELEM. ANAL. Calcd.: C, 66.7%; H, 3.7%; N, 5.9%. Found: C, 66.8%; H, 4.0%; N, 5.3%.

Self-Curing of the BMI Resins

Figure 1 shows self-curing curves of BMIPO and commercial BMIM monomers analyzed by DSC. The values of T_m , the exothermic starting temperature (T_i), T_{max} , and T_f for the BMI monomers are given in Table I. Each of the two BMI monomers had a sharp melting endothermic peak (199 and 160°C for BMIPO and BMIM, respectively) during the heating process. Therefore, T_m of BMIPO was about 39°C higher than that of BMIM, indicating that the higher molecular weight and phenyl density of the former increased its intermolecular attraction. BMIPO and BMIM analyzed by DSC, as shown in Figure 1, generated exothermic peaks of the curing reaction within the ranges 210–330 and 170–280°C, respectively. The results from a DSC comparison of these self-cured resins indicated that the introduction of the triphenyl phosphide group into the studied BMI backbone was unable to change the fact of the

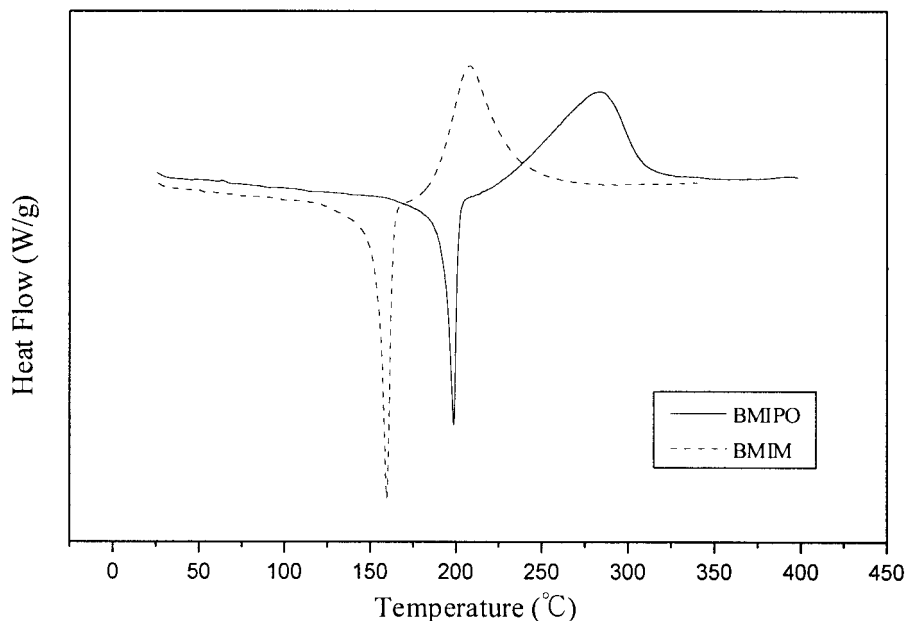


Figure 1 DSC traces of two kinds of BMI resins by self-curing.

curing reaction starting near T_m . In addition, the self-curing temperature and conversion rate of BMIPO were apparently higher than those of BMIM because of the greater number of phenyl rings and higher electron-withdrawing effects of the former; this is similar to the explanation of Melissaris and Mikroyannidis⁸ for a BMI study.

The aforementioned BMI monomers were self-cured by the heating processes listed in Table I. Each of the two BMI self-cured resins analyzed by DSC, as shown in Figure 2, had a single T_g (243 and 225°C for BMIPO and BMIM, respectively). The T_g value of the former was higher than that of the latter because of the higher rigid structure and intermolecular attraction of the former.

TGA traces of BMIPO and BMIM self-cured resins measured at a heating rate of 20°C/min in air and nitrogen, respectively, are shown in Figure 3. The decomposition process of all the aforementioned BMI resins was a two-stage or one-

stage reaction in air or nitrogen, respectively. The thermal degradations and oxidation reactions for the resins apparently occurred during the first and second stages, respectively. The onset decomposition temperature [(i.e., temperature of 5% weight loss ($T_{5\%}$)), T_{\max} , and char yield of solid residue for the resins are given in Table II. In nitrogen, $T_{5\%}$ and the solid char yield at 800°C for the BMIPO resin reached 435°C and 60%, respectively. In air, $T_{5\%}$ for the BMIPO resin dropped only marginally, even under the effect of oxidation at high temperatures. Therefore, BMIPO had better thermal stability and flame-retarding properties. In a comparison of the $T_{5\%}$ values of BMIPO and BMIM in Table II, the former (>420°C) was still lower than the latter (>520°C), either in air or in nitrogen. Besides, the temperature difference between $T_{5\%}$ and T_{\max} over 50°C and the char yield of solid residue over 45% for the former were higher than those for the latter.

Table I Thermal Properties of BMIPO and BMIM by Self-Curing

Monomer	T_m^a (°C)	T_i^a (°C)	T_{\max}^a (°C)	T_f^a (°C)	T_g^b (°C)
BMIPO	199	210	284	328	243
BMIM	160	169	208	280	225

^a Measured for two kinds of BMI resins by DSC at a heating rate of 10°C/min.

^b BMIPO-cured resin (cured at 270°C for 30 min and post cured at 320°C for 10 min and BMIM-cured resin (cured at 200°C for 30 min and post cured at 270°C for 10 min) were measured by DSC at a heating rate of 10°C/min.

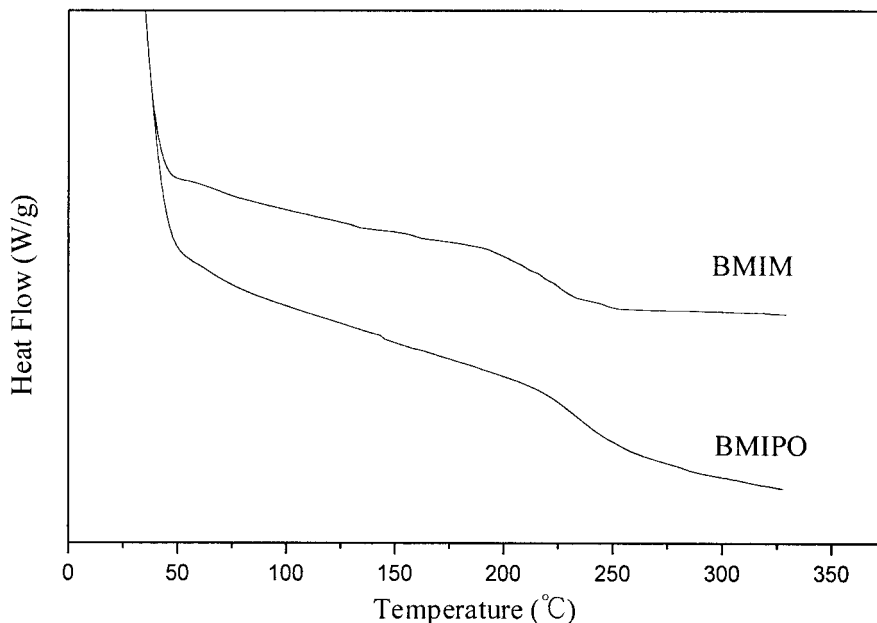


Figure 2 DSC traces of two kinds of BMI-cured resins.

The results of the moderate thermal stability and excellent flame retardancy for the former relative to the latter indicated that the introduction of the triphenylphosphide group into the BMIPO backbone synergized the effect of both the low bond energy and the highly rigid and polar segment. The higher LOI value of BMIPO (ca. 53) relative to that of BMIM (ca. 43), as listed in Table II, could make the former an excellent flame retardant.

Reaction Activities of the BMI Resins with DDM

The electron-withdrawing effect of the carbonyl group within the BMI backbone increased its unsaturated double bonds attacked by diamine or other nucleophilic reagents easily. The DSC traces of BMI/DDM cured resins are shown in Figure 4. The results of the lower T_m and exothermic peak of BMIPO relative to BMIM reacting with DDM apparently indicated that the higher

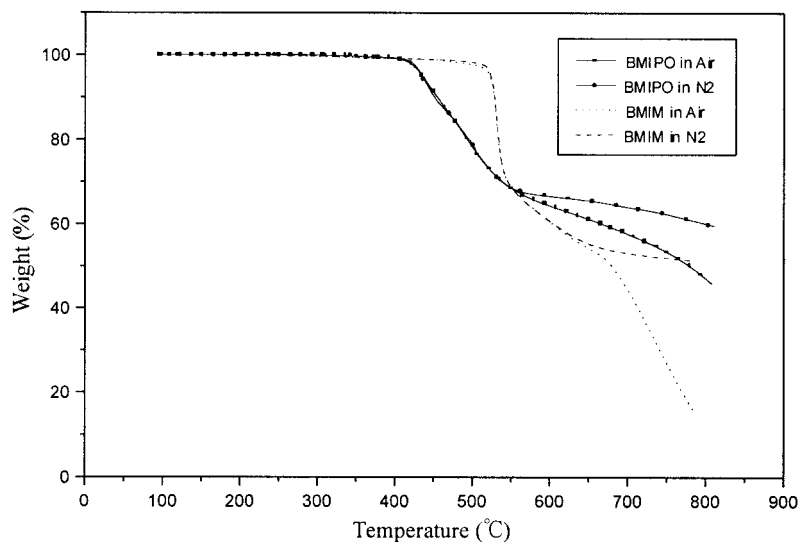


Figure 3 TGA traces of two kinds of BMI-cured resins.

Table II Thermal Decomposition Properties of BMIPO- and BMIM-Cured Resin

Cured Resin	$T_{5\%}$ (°C)		T_{\max} (°C)		Char Yield at 800°C(%)		LOI
	N ₂	Air	N ₂	Air	N ₂	Air	
BMIPO	435.8	435.1	497.3	490.7	60	47	53
BMIM	524.2	522.3	530.8	530.8	51	15	45

The thermal decomposition property was analyzed by TGA at a heating rate of 20°C/min in N₂ or in air.

polar and electron-withdrawing effect of the phosphide group for the former could increase its solubility and reactivity with DDM. In a comparison of the solubility and reactivity of BMIPO, BMIM, and epoxy resins with DDM, the solubility via the T_m values, curing rates, and conversion efficiencies of these studied resins were in the order BMIPO > epoxy > BMIM, indicating that the processing of the former was best of all.

Curing of the BMI/Epoxy/DDM Resins

The DSC traces of the BMI/epoxy (Epon828)/DDM blending system cured at a heating rate of 10°C/min under a nitrogen atmosphere are shown in Figure 5. T_i , T_{\max} , and T_f for the BMI blending system are given in Table III. There was a two-stage exothermic reaction for each of the aforementioned blending resins, as shown in Figure 5

and listed in Table III. As the BMIPO/BMIM ratio increased in this blending resin, its two exothermic peaks also shifted toward a low temperature as a result of the higher reactivity of BMIPO relative to that of BMIM. The curing conditions for the BMI blending resins were carried out at 110°C for an hour and then, for postcuring, at 230°C for 30 min. The curing conditions for pure epoxy/DDM resin, however, were preformed at 110°C for an hour before postcuring at 170°C for 30 min. The T_g values of the BMI/epoxy-cured or pure epoxy-cured resins measured by DSC are shown in Figure 6 and listed in Table III. On the basis of Table III, the addition of BMI to the blending systems would increase T_g about 30°C higher than that of the Epon828 epoxy resin. This BMI/epoxy blending system possessed not only good processing ability and adhesiveness of epoxy

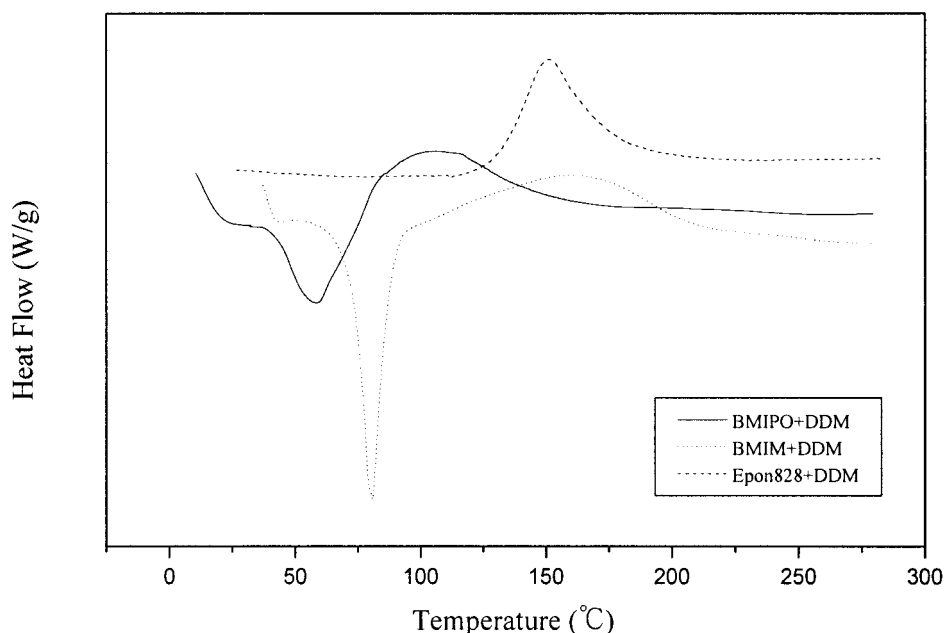


Figure 4 DSC traces of the BMIPO, BMIM, and epoxy resins reacting with DDM.

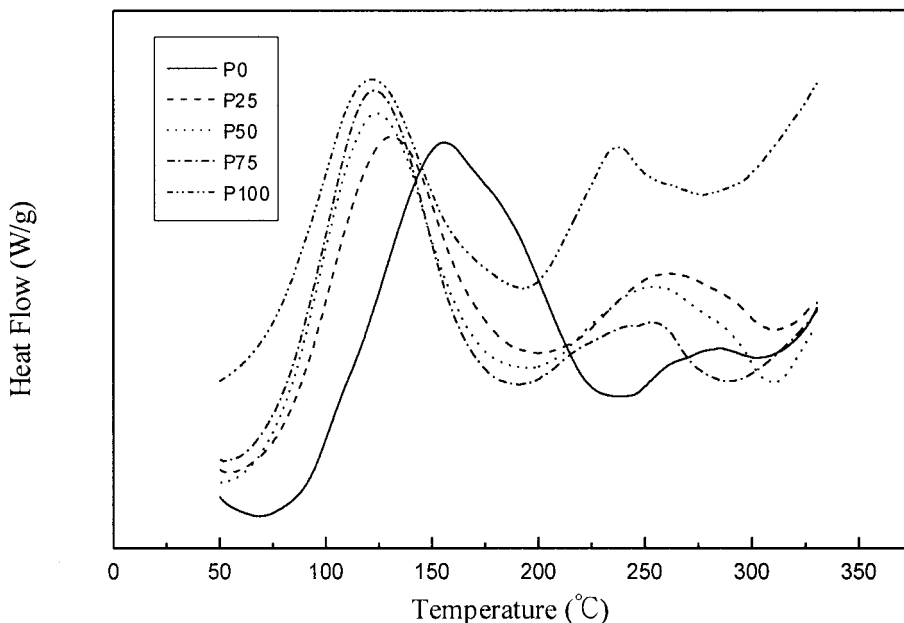


Figure 5 DSC traces of BMI/epoxy resins reacting with DDM.

but also a high T_g value of BMI. As shown in Figure 4, the higher reactivity and solubility of BMIPO/DDM relative to those of BMIM/DDM indicated that increasing the BMIPO content in this blending resin suppressed the recrosslinking degree of the postcuring stage. Therefore, the increasing BMIPO/BMIM ratio reduced T_g for this blending resin. Although BMIPO had a high phenyl density, the increasing BMIPO content in the blending system did not change this result. All of

the BMI blending resins exhibited single T_g 's within 174.8–192.4°C. This phenomenon indicated that they still maintained a homogeneous phase after curing.

Figure 7(a,b) shows the decomposition traces of the cured BMI blending resins analyzed by TGA in air or nitrogen, respectively. $T_{5\%}$, T_{\max} , the maximum weight-loss rate (V_{\max}), and the char yield of solid residue for the aforementioned resins are given in Table IV. As shown in Figure 7(a),

Table III Thermal Properties of BMI/Epoxy Resins Reacting with DDM

Sample	Composition ^a (Epon828/BMIPO/BMIM)	T_i^b (°C)	T_{\max}^b (°C)	T_f^b (°C)	T_g^c (°C)	LOI
E100	4/0/0	75.8	149.1	183.4	144.1	25
P100	4/4/0	50.8	121.7	194.0	174.8	40
		195.1	237.6	275.6		
P75	4/3/1	51.3	123.2	186.3	178.2	36
		196.8	253.6	289.5		
P50	4/2/2	52.6	124.5	190.7	180.4	32
		200.2	254.1	310.2		
P25	4/1/3	56.8	131.1	199.7	182.2	30
		203.7	262.5	310.7		
P0	4/0/4	72.2	156.6	233.6	192.4	28
		243.8	278.5	305.8		

^a The ratio of blending BMI/epoxy with DDM was same equivalent.

^b Measured for BMI/epoxy/DDM resins by DSC at a heating rate of 10°C/min.

^c Measured for BMI/epoxy-cured resin was by DSC at a heating rate of 10°C/min.

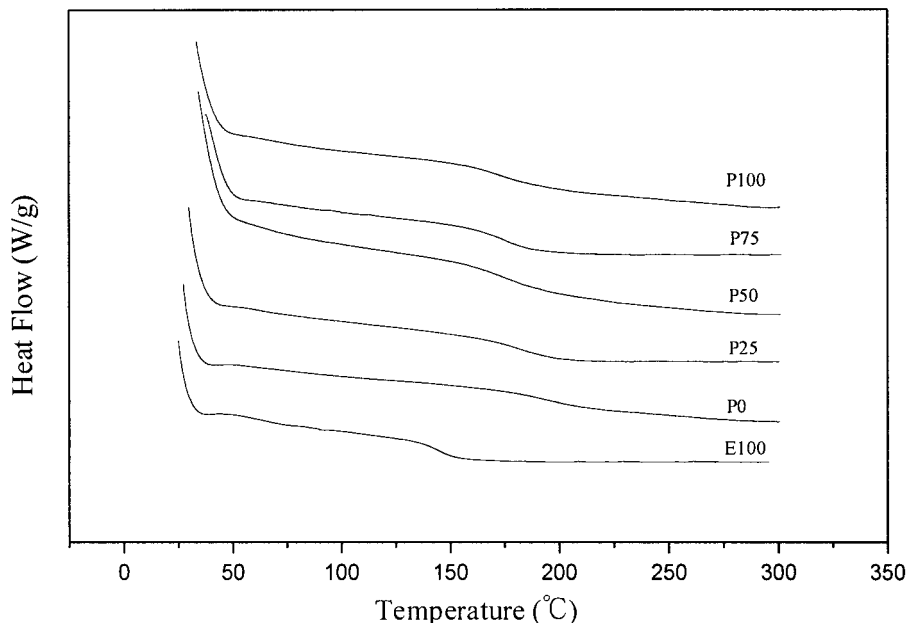


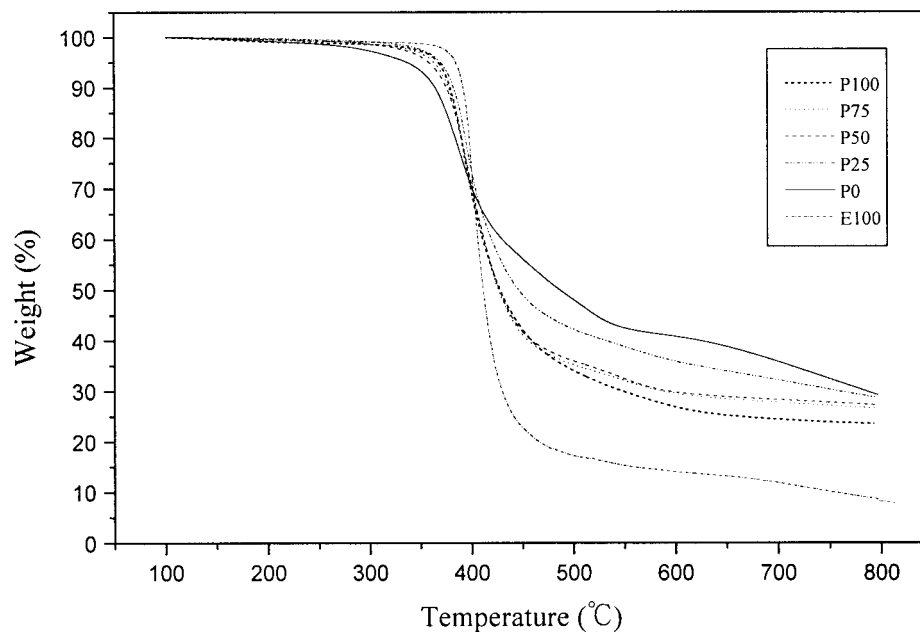
Figure 6 DSC traces of BMI/epoxy/DDM-cured resins.

thermal decomposition for E100 and P0 (i.e., the non-phosphorous system) showed a one-stage process in nitrogen. The curing of the phosphorus-containing blending system was also similar to a one-stage decomposition. With the BMIPO content increasing in this blending system, $T_{5\%}$ for this cured resin shifted toward a low temperature, from 420 to 409°C, but its char yield apparently increased from 8.2 to 27%, as listed in Table IV. This implied that the addition of BMIPO to this blending system caused poor recrosslinking density of the postcuring stage, lowering the thermal stability. In nitrogen, although $T_{5\%}$ for the BMI/epoxy system was lower than that for the pure epoxy system, the V_{\max} values of the former were lower than those of the latter, and the char yield at 800°C was over 15% higher than that of the non-BMI system via E100. Therefore, the addition of BMIPO/BMIM to this blending system could improve the thermal stability and fire retardancy. In air, when the aforementioned cured resins were heated, as shown in Figure 7(b), the oxidation reaction occurred during the second, high-temperature stage. Therefore, the decomposition of all the cured resins was a two-stage process. As the BMIPO content increased in the cured resins, they decomposed in air and maintained their thermal stability, indicating that the blending system in the oxidation environment had better antioxidation scission. Similar to the aforementioned conditions, the V_{\max} values of the

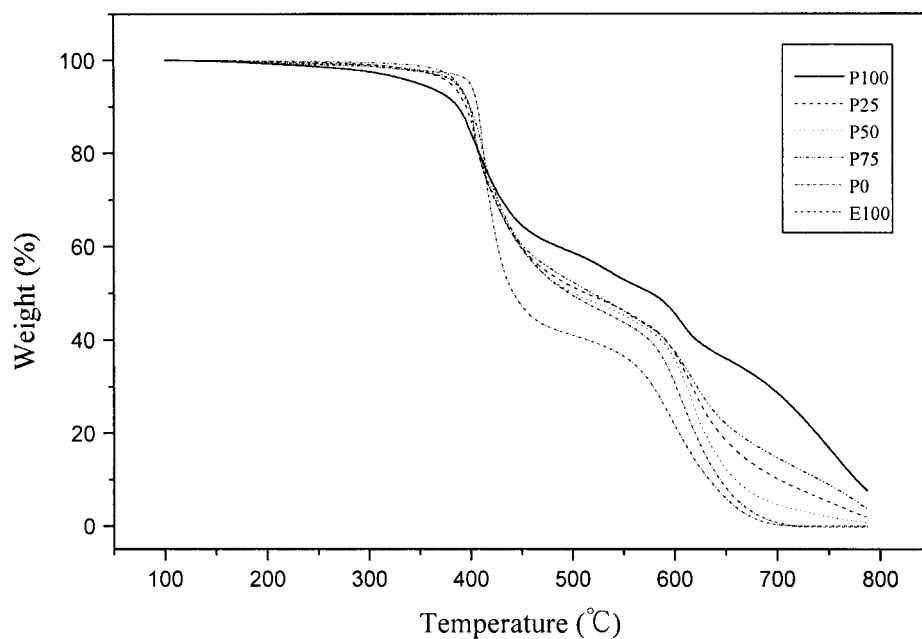
two stages for the blending system became lower, and T_{\max} during the second-stage and the char yield of solid residue increased from 594 to 750°C and from 0 to 15.73%, respectively (as listed in Table IV). The results indicated again that the addition of BMIPO to the blending system could promote its antioxidation effect via flame retardancy in air. From the results of fire retardancy testing (as given in Table III), the LOI of P100 was about 12 times higher than that of P0, proving that the flame retardancy of BMIPO was higher than that of BMIM.

CONCLUSIONS

A novel soluble BMIPO monomer was synthesized by an imidizing route of BAPO with maleic anhydride. Comparing the BMIPO and commercial BMIM self-cured resins, we found the order of both T_g and flame retardancy to be BMIPO > BMIM. The solubility and reactivity of BMIPO/DDM were higher than those of BMIM/DDM because of the higher polar and electron-withdrawing effect of the phosphide group in the backbone of the former. In the BMI/epoxy (Epon828) blending system, there was a single T_g for each composition without phase separation. Because of the higher reactivity of BMIPO/DDM relative to that of BMIM/DDM, the increase in the BMIPO content in the blending system reduced the value of



(a)



(b)

Figure 7 TGA traces of BMI/epoxy/DDM-cured resins: (a) in nitrogen and (b) in air.

T_g and the thermal stability. However, for BMIPO blended into epoxy resin, the T_g , char yield, and LOI values were apparently higher

than those for pure epoxy resin. This proved that BMIPO could become an excellent flame retardant.

Table IV Thermal Decomposition Properties of BMI/Epoxy-Cured Resins

Sample	P (wt %)	$T_{5\%}$ (°C)		Stage 1				Stage 2			Char yield (800°C)	
		Air	N ₂	Air		N ₂		Air		N ₂	Air	N ₂
				T_{\max}	V_{\max}	T_{\max}	V_{\max}	T_{\max}	V_{\max}			
E100	0	396	404	412	3.16	418	0.80	594	0.42	—	0.0	8.2
P100	2.21	381	357	396	0.57	409	0.10	750	0.26	—	15.7	29.1
P75	1.71	382	378	400	0.67	411	0.33	616	0.37	—	12.3	28.7
P50	1.09	382	384	402	1.00	413	0.39	614	0.46	—	7.7	27.2
P25	0.05	383	389	403	1.16	413	0.41	614	0.61	—	1.8	26.5
P0	0	383	390	404	1.31	420	0.29	605	0.56	—	0.0	23.5

The thermal decomposition property was analyzed by TGA at a heating rate of 20°C/min in N₂ or in air.

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