

Phosphonate-Containing Bismaleimide Resins. II. Preparation and Characteristics of Reactive Blends of Phosphonate-Containing Bismaleimide and Epoxy

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Received 10 July 2003; accepted 14 November 2003

ABSTRACT: Two kinds of phosphonate-containing bismaleimide (BMI) monomers, phenyl-(4,4'-bismaleimidophenyl) phosphonate and ethyl-(4,4'-bismaleimido-phenyl) phosphonate, were synthesized and added through blending to two epoxy systems for the study of their applications as reactive flame retardants. The thermal behaviors of the BMI monomers in both kinds of epoxy systems, bisphenol and phenol–novolac, were similar. An increase in the BMI contents increased the storage modulus and glass-transition temperature but slightly reduced the mechanical strength of

the epoxy blends. The pyrolysis models of both BMI blends in the two epoxy systems were quite alike. Although the initial pyrolysis temperatures of all the blending systems gradually decreased as the phosphorous content increased, the flame retardancy of all the phosphonate-containing epoxy systems was promoted significantly by increasing contents of BMI. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2375–2386, 2004

Key words: flame retardance; blends; bismaleimide; epoxy

INTRODUCTION

The development and applications of bismaleimide (BMI) resins have been particularly interesting in recent years. Their quick development has been primarily due to the wide range of service temperatures between epoxy and polyimide. BMI resins with epoxy-like processing will not produce volatiles during the additional curing reaction; this enables a void-free structure. However, BMI resins still have some defects, such as high melting and curing temperatures, high brittleness, low adhesiveness, and high cost.^{1,2} The double bond of BMI monomers, activated by the presence of carbonyl groups, is excessively electron-depleted, and this can promote defects in BMI via various reactions. Epoxy resins can be introduced as plasticizers to improve the stiffness and processing of BMI resins, and the thermal stability and hygroscopic characteristics of epoxy can be improved via BMI resins. However, aromatic diamines, usually used as chain-extension agents of BMI, can also be curing agents of epoxy. Thus, BMI/epoxy/diamine resins, exhibiting, like BMI, high glass-transition temperatures (T_g 's), hygroscopic characteristics, and dimensional stability, can be improved in other characteristics, such as poor adhesiveness, high brittleness, and

high cost. Blends of BMI with epoxy have become one of the main streams of research on BMI modification.^{3–7}

In recent years, many kinds of BMI resins blended with epoxy have been widely studied. Some flexible segments, for example, have been introduced to promote the processing of BMI.⁸ Fluorine-containing segments have been introduced⁹ or cyanate esters have been blended^{10,11} to reduce the dielectric constant of BMI resins. For the modification of heat and solder resistance, BMI resins with higher thermal stability,¹² or amine-terminated BMI that can be used directly as a curing agent of epoxy,¹³ have been developed. For the modification of flame retardancy, phosphorous-containing BMI,^{14–17} blends of BMI with halogen-type epoxies¹⁸ or general epoxies with the addition of a general flame retardant (e.g., graphite)^{19,20} or a phosphorous-containing flame retardant (e.g., triphenylphosphate),^{21,22} and BMI/epoxy blends with a phosphorous-containing curing agent²³ have been widely studied.

We have developed two kinds of phosphonate-containing BMI monomers that exhibit good flame resistance.²⁴ This research mainly concerns these novel phosphorous-containing BMI monomers blended with two types of epoxy resins, examining the influence of the maleimide segments on the physical properties of general epoxy resins. The promoting effect of phosphorous-containing segments in flame retardancy has also been analyzed to confirm its practical value.

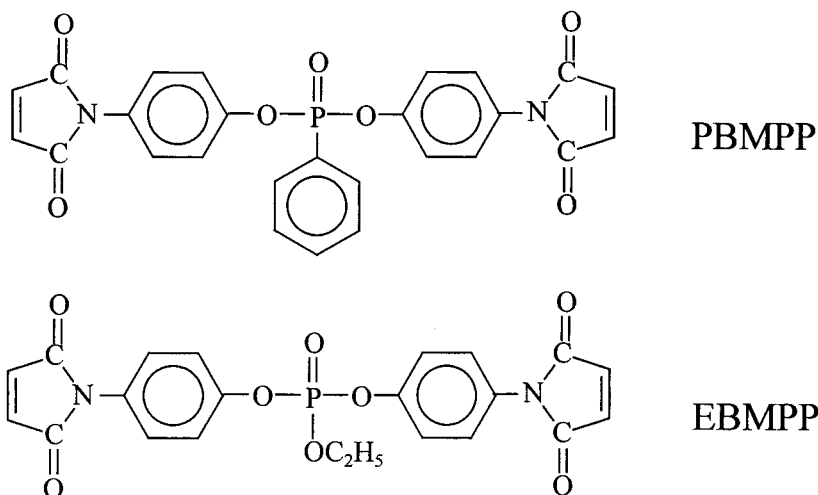
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EXPERIMENTAL

Materials

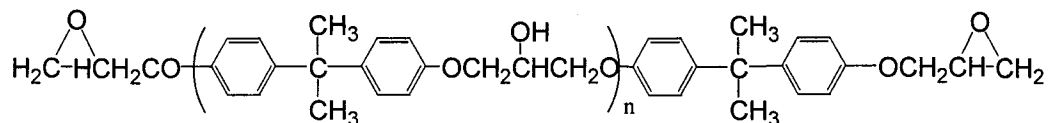
Two phosphonate-containing BMI monomers, phenyl-(4,4'-bismaleimidophenyl) phosphonate (PBMPP)

and ethyl-(4,4'-bismaleimido-phenyl) phosphonate (EBMPP), were synthesized by a two-step reaction:²⁴



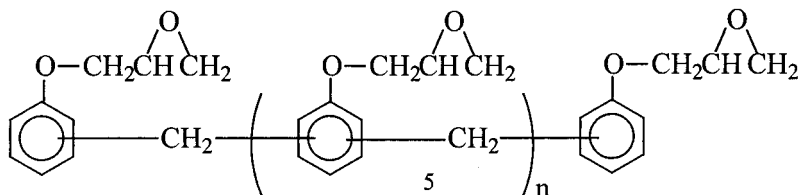
Two epoxy resins were used. Epon 828 (diglycidyl ether of bisphenol A with an epoxy equivalent of 190)

was obtained from Shell Chemical Co. (Akron, OH):



ESCN 195XL (a phenol-novolac type epoxy with an epoxy equivalent of 195) was obtained from Epolab

Chemical Industries, Inc. (Taoyuan, Taiwan):



Diaminodiphenyl sulfone (DDS) was obtained from TCI (Tokyo, Japan).

the molding device. The hardening periods of all the BMI-epoxy blend systems were determined with differential scanning calorimetry (DSC).

Preparation of the blending system

For the comparison of different epoxy equivalents, the synthesized BMI monomers were mixed with epoxy and the curing agent DDS. DDS theoretically opened all the double bonds of BMI and the epoxy groups. The mixture was then blended homogeneously at 160°C. Bubbles in the blends were drawn out in a vacuum oven. Then, the blends were introduced into

Instrumentation

The scanning curves of the BMI and related blending resins were determined with a TA Instruments DSC10 instrument (New Castle, DE) at a heating rate of 10°C/min in N₂ for the analysis of the melting temperatures, curing parameters, and *T_g*'s. The *T_g* values of the blends were also measured with a TA Instruments DMA2980 instrument at a frequency of 1 Hz. The thermal stability

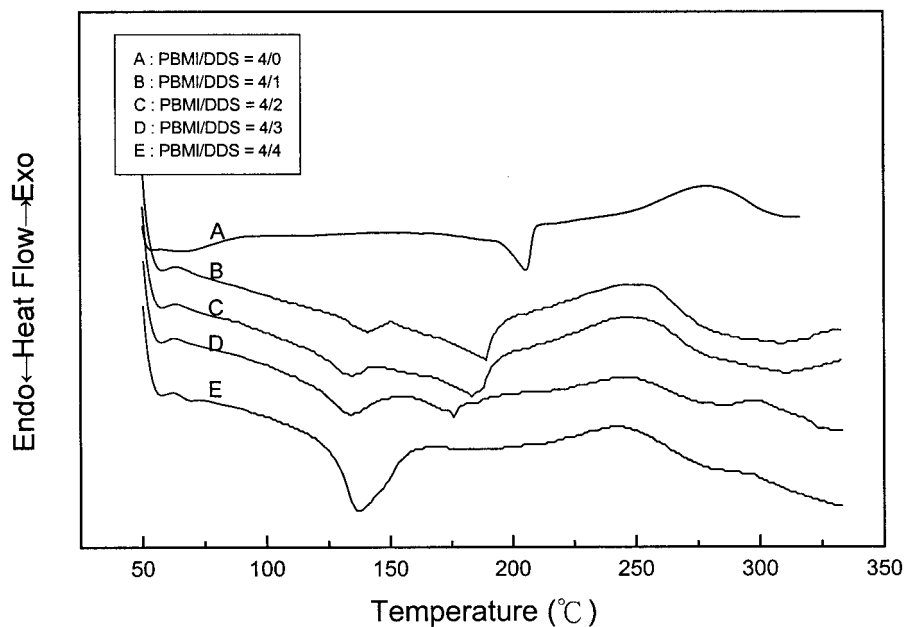


Figure 1 DSC traces of PBMPP cured with various equivalent ratios of DDS in nitrogen gas.

and flame-retarding properties of these resins were analyzed with a TA Instruments TGA 51 instrument at a heating rate of 20°C/min in air or N₂. The flame retardancy was also studied by the limiting oxygen index (LOI) with an oxygen index analyzer (Stanton Redcraft; Atlas Equipment Corp., Taipei, Taiwan) at an O₂/N₂ flow rate of 20 L/min. The mechanical properties of the cured blends were measured with an Instron 4469 universal testing instrument (Canton, MA) by the ASTM D 412-75 method.

RESULTS AND DISCUSSION

Thermal reaction of BMI with a diamine

The BMI monomer can react with a diamine via nucleophilic addition (Michael addition) to synthesize a polyaspartimide copolymer.^{25,26} Figures 1 and 2 show the DSC traces of the BMI/DDS systems. In the PBMPP/DDS system, as shown in Figure 1, there was a eutectic phenomenon between the BMI monomer and DDS: the melting point decreased as the DDS

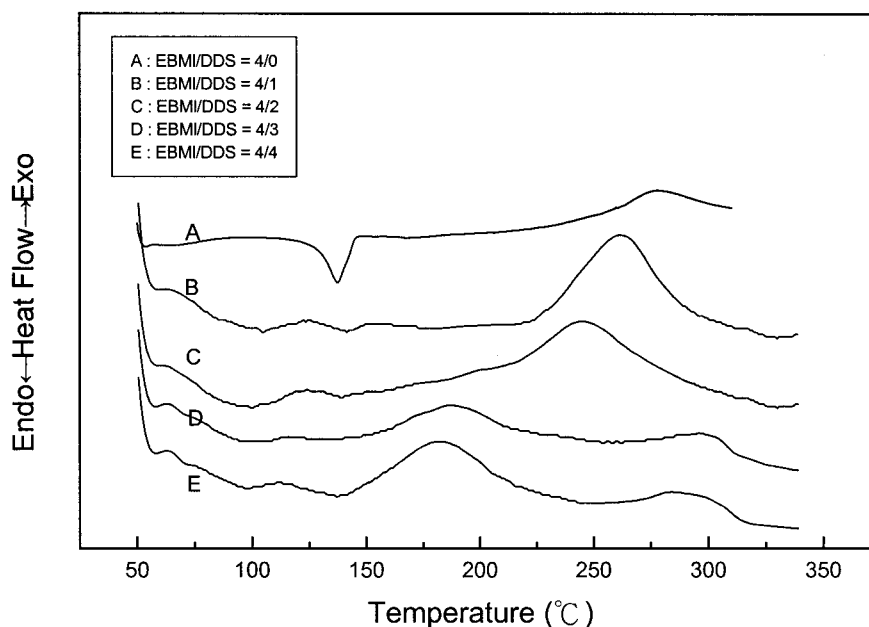


Figure 2 DSC traces of EBMPP cured with various equivalent ratios of DDS in nitrogen gas.

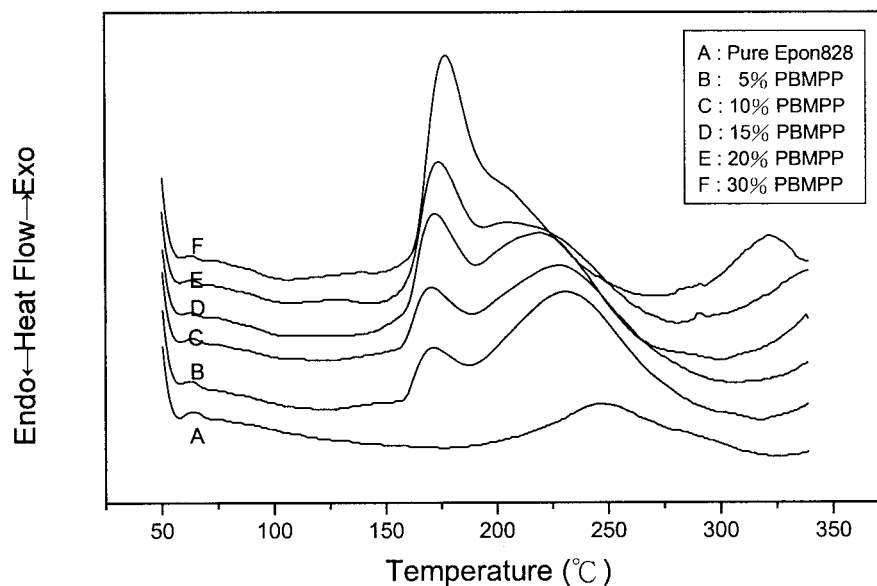


Figure 3 DSC traces of the PBMPPP/Epon 828/DDS blending system in nitrogen gas.

content increased. When the equivalent ratio of BMI to DDS was close to 1, it exhibited a eutectic point only at about 136°C. Because the secondary hydrogen within the amine groups of DDS could not react with BMI easily, there was an exothermal peak around 260°C due to the Michael addition of the primary hydrogen of the amine groups with BMI and the self-polymerization of PBMPPP when the DDS content was lower than 50%. For the eutectic effect, the self-polymerization temperature of the PBMPPP monomer was obviously shifted lower. The exothermal peak, due to the Michael addition of the secondary hydrogen of the

amine groups with BMI, appeared around 290°C when the DDS content was higher.

Figure 2 shows DSC traces of the EBMPP/DDS systems. The eutectic phenomenon between the EBMPP monomer and DDS was more obvious because their melting points were close. When the equivalent ratio of BMI to DDS was 4/3, it exhibited a full eutectic state, with a eutectic point around 102°C. For the eutectic effect, the exothermal peak due to the Michael addition of the primary hydrogen of the amine groups with BMI and the self-polymerization of EBMPP was obviously shifted to a lower point. The exothermal peak due to the

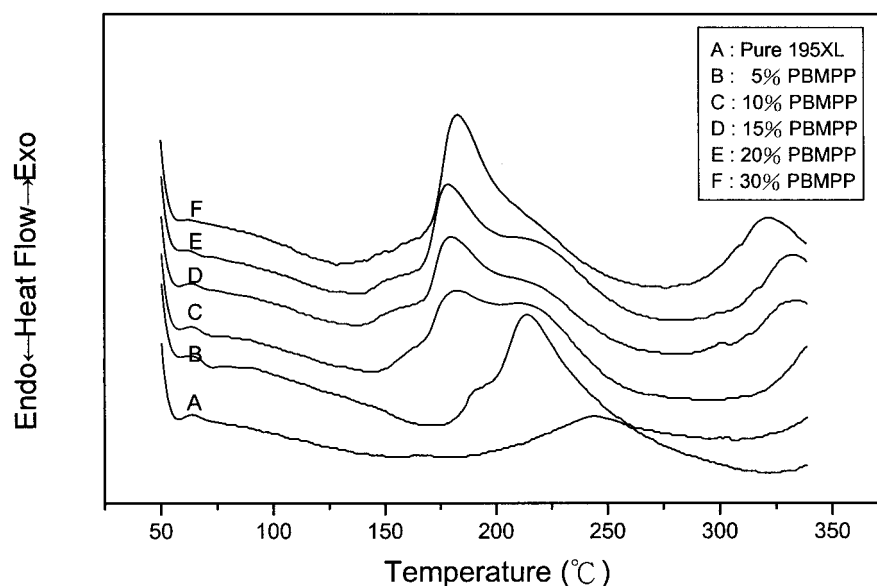


Figure 4 DSC traces of the PBMPPP/195XL/DDS blending system in nitrogen gas.

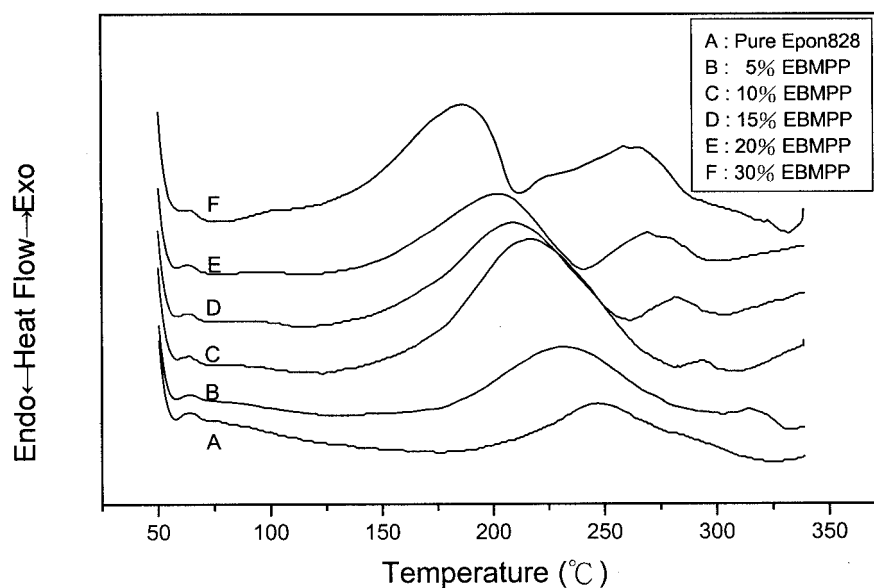


Figure 5 DSC traces of the EBMPP/Epon 828/DDS blending system in nitrogen gas.

Michael addition of the secondary hydrogen of the amine groups with BMI appeared around 290°C when the DDS content was higher.

Curing reaction of the BMI/epoxy/DDS blends

Excess BMI monomer can react with a diamine to produce a crosslinking resin.²⁷ Furthermore, the reaction system of BMI/epoxy/DDS blends would be more complicated.²⁷⁻³⁰ The BMI/epoxy/DDS blends were prepared through the mixing of BMI monomers with various ratios of epoxy and the curing agent

DDS. Figures 3 and 4 show DSC traces of the PBMPP/Epon 828/DDS and PBMPP/195XL/DDS blending systems, respectively. The thermal reactions of the PBMPP monomer with the two types of epoxy were quite alike. There were two exothermic peaks around 170°C (T_{max1}) due to the Michael addition of BMI with DDS and the self-polymerization of PBMPP and around 230°C (T_{max2}) due to the ring-opening reaction of the epoxy. T_{max2} increased as the epoxy content increased, and this indicated that more of the secondary amine joined the ring-opening reaction of the epoxy. Besides, the secondary amine reacted with

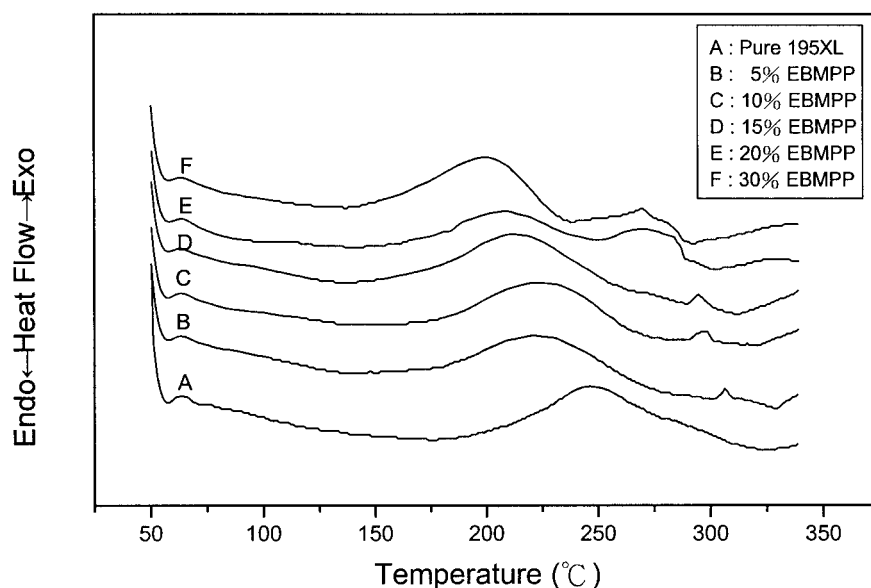


Figure 6 DSC traces of the EBMPP/195XL/DDS blending system in nitrogen gas.

TABLE I
Compositions and Thermal Reaction Temperatures of the PBMPP/Epoxy/DDS Blending System

Epoxy type	Epoxy (eq %) ^a	PBMPP (eq %) ^a	PBMPP (wt %)	P (wt %) ^b	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	T_c (°C)	T_g (°C)
Epon 828	100	0	0	0	247	—	235	205.5
	95	5	9.3	0.59	172	230	220	223.2
	90	10	17.3	1.11	170	228	215	221.2
	85	15	24.4	1.56	172	219	210	220.0
	80	20	30.6	1.96	173	205	195	218.3
	70	30	41.2	2.64	177	204	195	215.7
195XL	100	0	0	0	244	—	235	246.0
	95	5	9.1	0.56	190	214	205	245.4
	90	10	17.0	1.05	182	210	200	246.5
	85	15	24.0	1.49	179	209	200	246.4
	80	20	30.2	1.88	178	207	195	243.1
	70	30	40.8	2.53	182	206	195	245.7

$T_{\max i}$ = exothermic peak temperature in the i th stage as measured by DSC at a heating rate of 10°C/min; T_c = temperature selected for the blends to cure. T_g = was analyzed by DMA at a heating rate of 5°C/min in air.

^a Equality ratio of BMI and epoxy when they were cured with the equality ratio of DDS.

^b The theoretical calculation weight ratio of the P composition in the blends.

PBMPP via Michael addition at a higher temperature only when the epoxy content was lower. The Michael addition of the blend with 30% BMI, for example, appeared around 320°C ($T_{\max 3}$).

Figures 5 and 6 show DSC traces of the EBMPP/Epon 828/DDS and EBMPP/195XL/DDS blending systems, respectively. The thermal reactions of the EBMPP monomer with the two types of epoxy were alike. In comparison with the PBMPP/epoxy/DDS blending systems, the addition reaction of EBMPP with DDS, the self-polymerization of EBMPP, and the ring-opening reaction of epoxy happened almost simultaneously, and this was attributed to the lower eutectic point of BMI/DDS. Therefore, only one exothermal peak appeared during the first stage. At the same time, $T_{\max 1}$ increased as the epoxy content in-

creased, and this indicated that more of the secondary amine joined the ring-opening reaction of the epoxy. Besides, the secondary amine reacted with EBMPP via Michael addition at a higher temperature ($T_{\max 2}$) only when the epoxy content was lower. The Michael addition happened more easily and $T_{\max 2}$ was reduced as the EBMPP content increased. $T_{\max 2}$ of the blend with 30% EBMPP, for example, appeared around 260°C. All the data for the thermal reactions of the blending systems are listed in Tables I and II.

Characteristics of the BMI/epoxy/DDS blends

Dynamic mechanical properties

The dynamic mechanical properties of the slices molded from the BMI/epoxy/DDS blends were mea-

TABLE II
Compositions and Thermal Reaction Temperatures of the EBMPP/Epoxy/DDS Blending System

Epoxy type	Epoxy (eq %) ^a	EBMPP (eq %) ^a	EBMPP (wt %)	P (wt %) ^b	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	T_c (°C)	T_g (°C)
Epon 828	100	0	0	0	247	—	235	205.5
	95	5	8.7	0.59	231	312	220	224.1
	90	10	16.4	1.11	219	290	210	223.3
	85	15	23.1	1.58	210	281	200	222.7
	80	20	29.2	1.99	205	275	195	220.4
	70	30	39.7	2.70	186	267	180	215.4
195XL	100	0	0	0	244	—	235	246.0
	95	5	8.5	0.57	222	305	210	240.6
	90	10	16.4	1.07	211	298	200	243.6
	85	15	22.8	1.51	208	296	200	242.0
	80	20	28.9	1.91	206	270	200	241.5
	70	30	39.3	2.60	200	267	195	240.2

$T_{\max i}$ = exothermic peak temperature in the i th stage as measured by DSC at a heating rate of 10°C/min. T_c = temperature selected for the blends to cure. T_g = was analyzed by DMA at a heating rate of 5°C/min in air.

^a Equality ratio of BMI and epoxy when they were cured with the equality ratio of DDS.

^b The theoretical calculation weight ratio of the P composition in the blends.

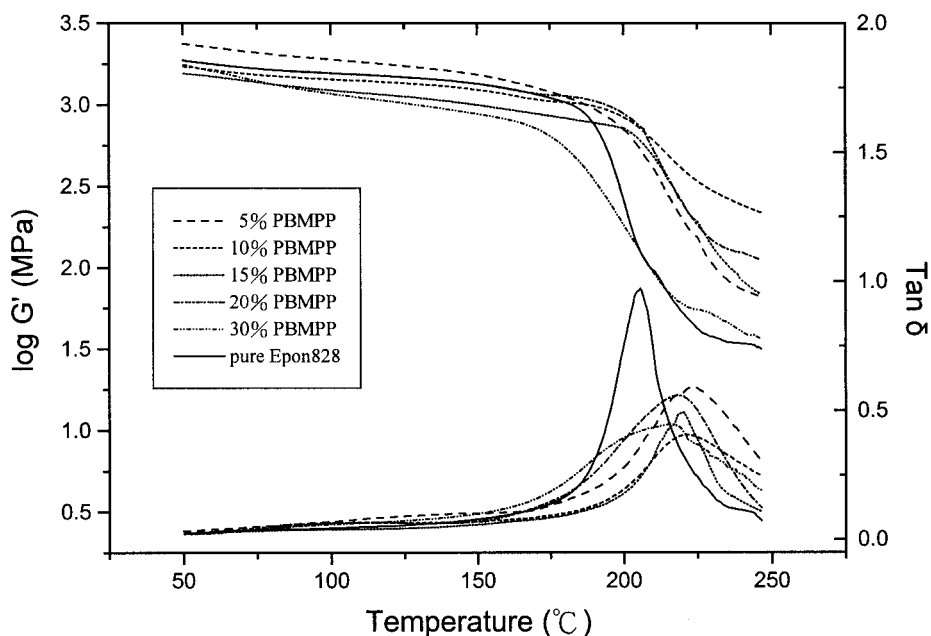


Figure 7 DMA traces of the PBMPPEpon 828/DDS blending system.

sured at air pressure. The dynamic mechanical analysis (DMA) traces of the BMI/Epon 828 blends are shown in Figures 7 and 8. The storage modulus (G') and T_g of the Epon 828 system were promoted by the blending of the BMI monomer. This was attributed to the higher T_g of the BMI segments (256°C for PBMPPE and 252°C for EBMPP).²⁴ However, the T_g 's of the blends decreased slightly as the BMI contents increased. Because the addition-reaction temperature of the BMI monomer with DDS was lower, the blends

were expected to undergo the Michael addition reaction more easily when the BMI contents were increased. This could also reduce the crosslinking density and T_g of the blend system. Besides, PBMPPE with a higher phenyl density also had a lower value of G' because of phase separation. Therefore, there was a trend of the second T_g developing at a lower temperature, as shown in the $\tan \delta$ curve of Figure 7.

The T_g 's of the BMI/epoxy/DDS systems measured by the DMA method are also listed in Tables I and II.

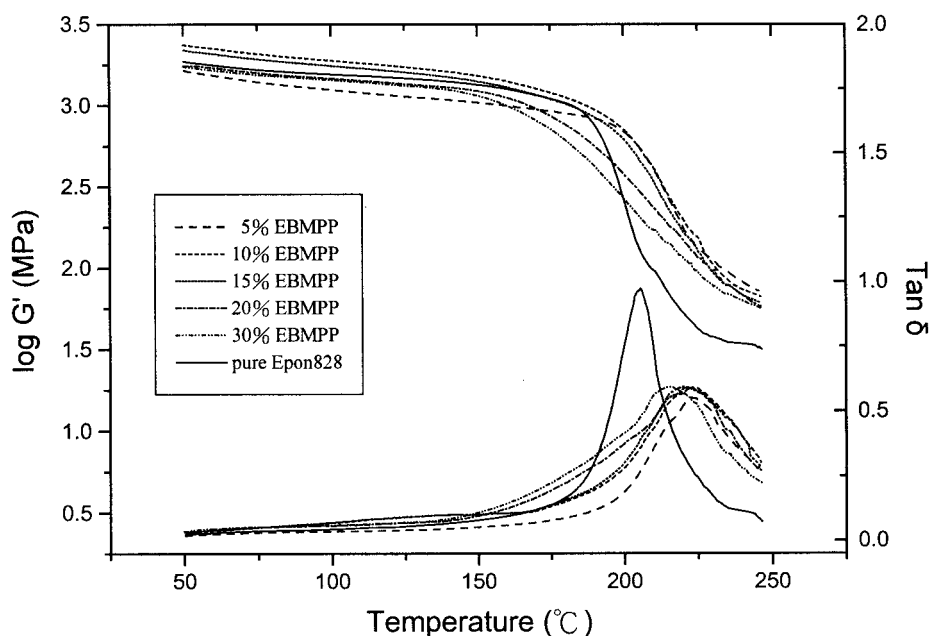


Figure 8 DMA traces of the EBMPP/Epon 828/DDS blending system.

TABLE III
Mechanical Properties^a of the PBMPP/Epoxy/DDS Blending System

Epoxy type	Epoxy (eq %)	BMI (eq %)	Breaking load (kgf)	Breaking stress (kgf/mm ²)	Breaking strain (%)	Yield stress (kgf/mm ²)	Modulus (kgf/mm ²)
Epon 828	100	0	84	3.5	4.9	3.2	235
	95	5	80	3.3	4.7	3	224
	90	10	82	3.4	4.4	3.1	229
	85	15	79	3.2	4.2	2.9	224
	80	20	74	3	3.9	2.7	209
	70	30	68	2.8	3.7	2.5	191
195XL	100	0	92	5.4	5.2	5.3	268
	95	5	81	4.7	4.6	4.7	237
	90	10	78	4.5	4.4	4.5	227
	85	15	77	4.4	4.2	4.4	224
	80	20	76	4.4	4	4.3	223
	70	30	71	4.1	3.8	4.1	209

^a According to the ASTM D 412-75 test method with a sample size 50 × 12.7 × 1.25 mm.

G' of the phenol–novolac type of epoxy (ESCN 195XL) could also be promoted by the blending of the BMI monomer. However, the T_g 's of the blends were not affected significantly by PBMPP or EBMPP. The phenol–novolac type of epoxy with a more rigid structure exhibited a higher T_g (246°C). In addition, the blends of the PBMPP series had higher G' and T_g values than the EBMPP series. This might be related to their higher phenyl density, which induced better compatibility with the epoxy resin.

Mechanical properties

The mechanical properties of the curing samples, such as the yield strength, Young's modulus, and breaking strength, were measured with the ASTM D 412-75 method. Table III shows the mechanical properties of the PBMPP/epoxy/DDS blending system. The mechanical strength of all the curing blends probably

decreased as the BMI contents increased. This was primarily related to the brittleness of BMI and the addition of BMI/DDS segments, which reduced the crosslinking density of the epoxy system. On the contrary, the stiffness of BMI could be promoted efficiently with increases in the epoxy contents. In the PBMPP system with 10% BMI, the blend had the best mechanical properties. Table IV shows the mechanical properties of the EBMPP/epoxy/DDS blending system. The mechanical strength of all the curing blends also probably decreased as the EBMPP contents increased.

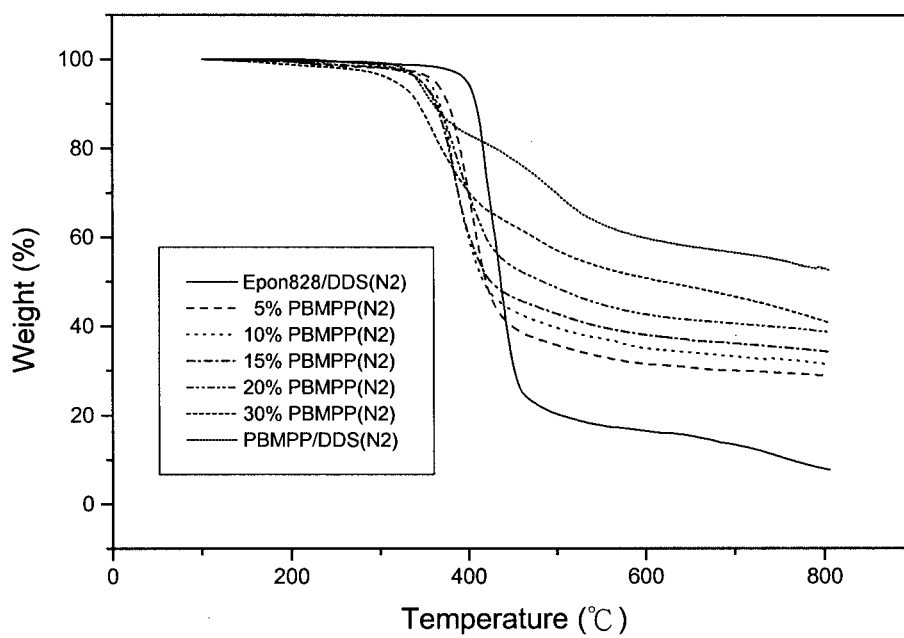
Thermal properties

Figure 9 shows the decomposition traces of the PBMPP/Epon 828/DDS blending system analyzed by thermogravimetric analysis (TGA). The onset temperature ($T_{5\%}$) of the blending system decreased as the

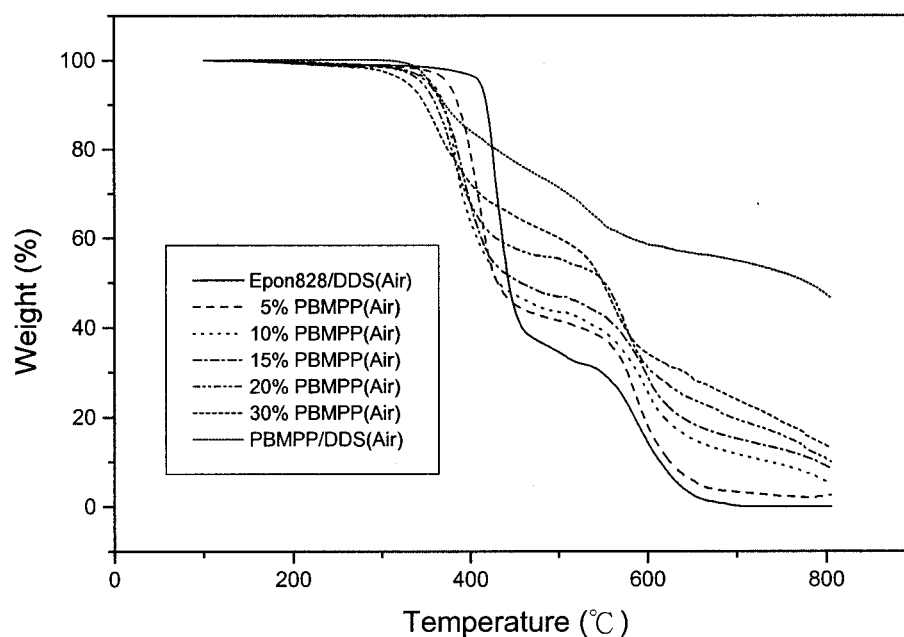
TABLE IV
Mechanical Properties^a of the EBMPP/epoxy/DDS Blending System

Epoxy type	Epoxy (eq %)	BMI (eq %)	Breaking load (kgf)	Breaking stress (kgf/mm ²)	Breaking strain (%)	Yield stress (kgf/mm ²)	Modulus (kgf/mm ²)
Epon 828	100	0	84	3.5	4.9	3.2	235
	95	5	82	3.5	4.7	3.2	231
	90	10	81	3.4	4.6	3.1	229
	85	15	81	3.4	4.5	3	230
	80	20	73	3	4.2	2.7	205
	70	30	67	2.8	3.9	2.6	192
195XL	100	0	92	5.4	5.2	5.3	268
	95	5	80	4.5	4.4	4.5	227
	90	10	78	4.4	4.3	4.4	224
	85	15	77	4.4	4.1	4.4	224
	80	20	72	4.1	3.9	4.1	210
	70	30	67	3.9	3.7	3.8	195

^a According to the ASTM D 412-75 test method with a sample size 50 × 12.7 × 1.25 mm.



(a)

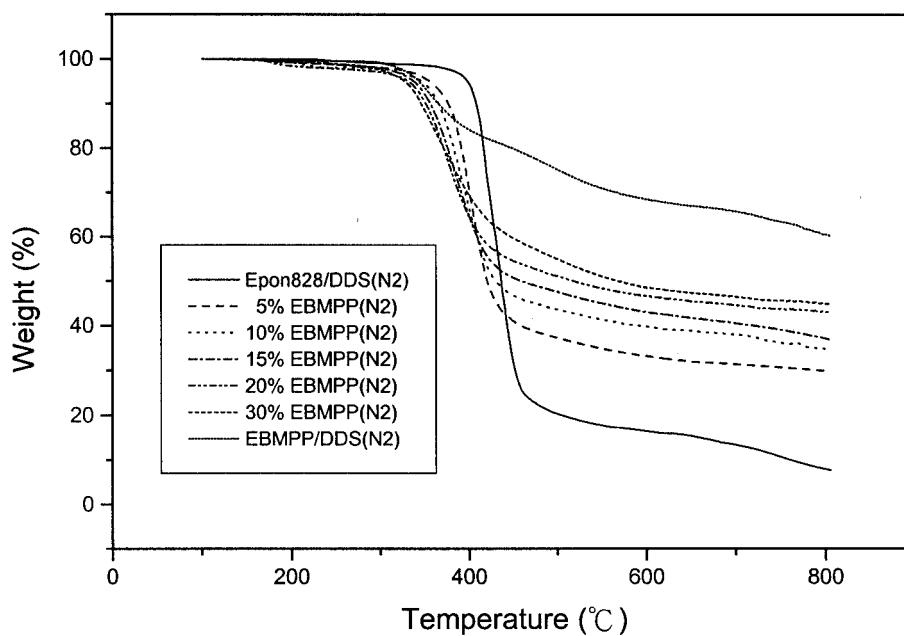


(b)

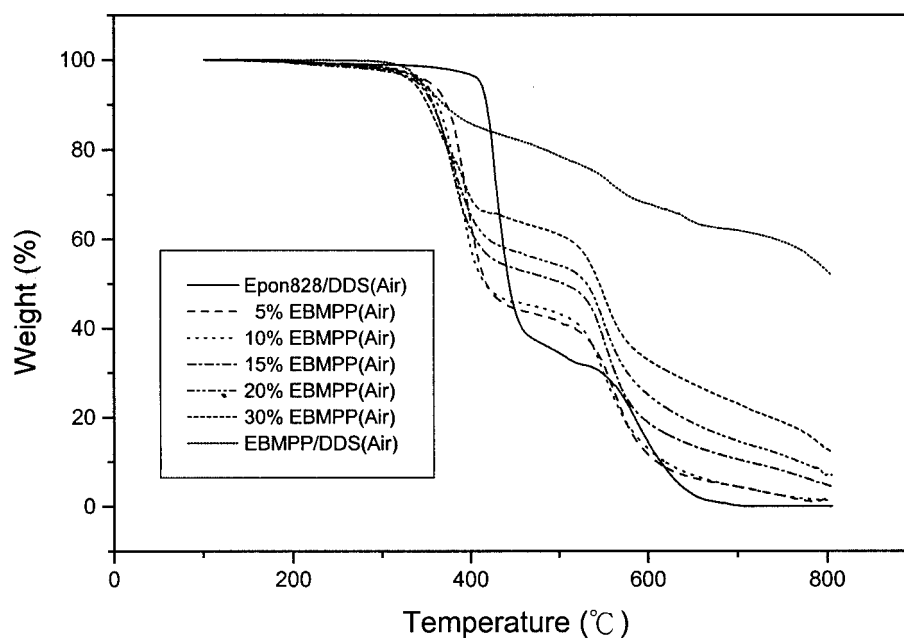
Figure 9 TGA traces of the PBMPP/Epon 828/DDS blending system: (a) in nitrogen gas and (b) in air.

contents of phosphorus increased under nitrogen or air pressure. This was primarily attributed to the lower chain energy of the phosphorus-containing segments. Also, Figure 9(a) shows that all the cracking curves of the blends in N_2 were one-stage pyrolysis

curves and that the pyrolysis rate slowed as the adding ratio of PBMPP was gradually increased. The cracking curves of the blends in air, as shown in Figure 9(b), were two-stage pyrolysis curves. The first stage was due to the pyrolysis of the unstable phos-



(a)



(b)

Figure 10 TGA traces of the EBMPP/Epon 828/DDS blending system: (a) in nitrogen gas and (b) in air.

phorus-containing segments and diamine segments, especially for the secondary amine groups (HN—C). The second stage was the pyrolysis of the stable five-member ring and imide groups, which could also be catalyzed by oxygen in air.³¹ The thermal stability of

the blends via the index $T_{5\%}$ in air was obviously higher than that in the nitrogen atmosphere. This might be related to oxidation in air, which would induce an oxidized protective layer and, therefore, improve the thermal stability of the blends.³²

TABLE V
Thermal Properties^a of the PBMPP/Epoxy/DDS Blending System

Epoxy type	Epoxy (eq %)	BMI (eq %)	P (wt %)	$T_{5\%}$ (°C) ^b		Cha at 800°C (wt %) ^b		LOI ^b
				Air	N ₂	Air	N ₂	
Epon 828	100	0	0	411	399	0	7.9	25
	95	5	0.59	374	363	2.4	29.0	29
	90	10	1.11	358	356	5.6	31.6	30
	85	15	1.56	353	348	9.0	34.4	32
	80	20	1.96	345	347	10.7	38.9	33
	70	30	2.64	328	317	13.6	41.2	35
195XL	0	100	4.97	355	344	47.5	53.0	42
	100	0	0	399	392	0	19.2	27
	95	5	0.56	355	357	2.4	41.8	32
	90	10	1.05	351	365	4.2	42.5	33
	85	15	1.49	363	353	5.3	43.8	34
	80	20	1.88	353	356	5.7	46.8	34
	70	30	2.53	342	344	15.8	49.2	37
	0	100	4.97	355	344	47.5	53.0	42

^a thermal properties were analyzed by TGA at a heating rate of 20°C/min in N₂ or in air.

^b LOI was analyzed with an LOI chamber at an O₂/N₂ flow rate of 20 L/min.

The TGA traces of the EBMPP/Epon 828/DDS blending system are shown in Figure 10. All the data for the thermal properties of these blends are also listed in Tables V and VI. The pyrolysis conditions of the EBMPP blends were mostly like those of the PBMPP system. The $T_{5\%}$ values of the blends decreased as the phosphorus contents increased. Because the phenyl density of the PBMPP system was higher, these blends exhibited better thermal stability. The PBMPP system exhibited a higher $T_{5\%}$ value than the EBMPP system; the data are listed in Tables V and VI.

According to the data measured by TGA, the pyrolysis model of the BMI blends in the epoxy system of

the phenol–novolac type was very like that of the system of the bisphenol A type. The PBMPP/195XL/DDS blends had the highest thermal stability of the systems because the higher phenyl density of PBMPP and epoxy could induce good compatibility.

Flame retardancy

The flame retardancy of all the curing blends was probably improved as the BMI contents increased. The decomposition reactions of all the phosphonate-containing blends were initialized mainly by the scission of phosphonate ester side chains with lower bond

TABLE VI
Thermal Properties^a of the EBMPP/Epoxy/DDS Blending System

Epoxy type	Epoxy (eq %)	BMI (eq %)	P (wt %)	$T_{5\%}$ (°C) ^b		Char at 800°C (wt %) ^b		LOI ^b
				Air	N ₂	Air	N ₂	
Epon 828	100	0	0	411	399	0	7.9	25
	95	5	0.59	354	356	1.4	29.9	30
	90	10	1.11	348	347	1.6	34.8	30
	85	15	1.58	340	338	4.8	37.1	33
	80	20	1.99	343	332	7	43	35
	70	30	2.70	335	328	12.8	44.9	38
195XL	0	100	5.24	344	344	53	60.6	45
	100	0	0	399	392	0	19.2	27
	95	5	0.57	366	368	0	39.7	31
	90	10	1.07	363	359	2.6	42.9	33
	85	15	1.51	350	360	5	46.2	35
	80	20	1.91	355	357	9.2	48.8	37
	70	30	2.60	350	349	20.4	52.5	39
	0	100	5.24	344	344	53	60.6	45

^a thermal properties were analyzed by TGA at a heating rate of 20°C/min in N₂ or in air.

^b LOI was analyzed with an LOI chamber at an O₂/N₂ flow rate of 20 L/min.

energy, and they produced further scission of the maleimide main chain along with carbonization, forming high char yields of solid residues. This was confirmed by the TGA traces and LOI data listed in Tables V and VI. The pyrolysis rate slowed as the adding ratio of BMI was gradually increased. The char yield also obviously increased under nitrogen or air pressure. The LOI values of all the blend types also increased gradually as the BMI contents increased, and the trend mostly agreed with the char yields measured by TGA.³³ The LOI values of all the blend types were increased by about 10 as the BMI concentration reached 30%. The LOI of the EBMPP system with a higher percentage of phosphorus was higher than the LOI of the PBMPP system. The epoxy system of the phenol–novolac type with a more rigid structure also had a higher LOI value than the bisphenol A type epoxy system.

CONCLUSIONS

Two kinds of phosphonate-containing BMI monomers were applied to some blending systems of epoxy. Although the mechanical strength of the BMI/epoxy blends was reduced, they still had good thermal stability and exhibited very good flame resistance. The conditions of the thermal reactions and the blend formulations of these systems can be used as a reference for the blending of normal resins in industry.

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