
Preparation and Characteristics of Reactive Blends of Phosphate-Containing Maleimide and Epoxy Resins

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SUMMARY

Three kinds of phosphate-containing maleimide (PMI) monomers, namely diethyl (4-(N-maleimido) phenyl) phosphate (4P) diphenyl (4-(N-maleimido) phenyl) phosphate (PP) and diethyl (2,6-dibromo-4-(N-maleimido)phenyl) phosphate (BrP), were synthesized and blended with a bisphenol type epoxy so as to study their potential as reactive flame retardants. It was expected that with an increase in the PMI content in the blending system, the Michael-addition reaction would take place more and easily. Increasing the PMI contents reduced the storage modulus, the T_g and the tensile strength, however good thermal stability was maintained. The flame retardancy of all the phosphate-containing epoxy systems was promoted significantly by increasing the PMI content.

INTRODUCTION

Because of the stability of their molecular structure and the high reactivity of their unsaturated double bond, N-arylmaleimide monomers, such as N-phenylmaleimide (PM), N-hydroxyphenylmaleimide (HPM), and halide-substituted N-hydroxyphenyl-maleimide (XHPM) have been used to modify the thermal stability and flame retardancy of resins. Some workers have modified the molecular structure of N-arylmaleimide monomers, and some have used blends of N-arylmaleimide monomers with various polymers. For example, some have used PM-oligomers to improve the toughness of polymers^{1,2}, or to produce laminated boards with a low coefficient of expansion³, and others have blended PM and PM-styrene copolymers with epoxy resins in order to promote the rigidity of these materials⁴. To improve their heat and solder resistance, some researchers have used PM polymers⁵ or PM-co-styrene polymers⁶ as curing agents for epoxy resins, or have tried cyanates as curing agents for PM/epoxy blends⁷, while others have developed novel epoxy resins with PM segments^{8,9} or conversely, PM resins with epoxy

segments^{10,11}. Also, some applications are emerging from further changes in the blend formulations, such as epoxies blended with PM polymers^{12,13}, PM-styrene copolymers¹⁴, or PM-diene copolymers¹⁵. To modify the flame retardancy, PM polymers and PM-styrene copolymers with good flame retardancy have been developed^{16,17}. Some PM-epoxy blends use a phosphorus-containing flame retardant (such as triphenyl phosphate)^{18,19}.

We have already developed a series of phosphate-containing maleimide monomers that exhibit good flame resistance²⁰. The copolymerization behaviour of these maleimides with styrene have been studied²¹. The present research was focused mainly on these novel phosphorus-containing maleimide monomers blended with epoxy resins, and was intended to elucidate the influence of maleimide segments on the physical properties of epoxy resins. The positive effect of phosphorus-containing segments in flame retardancy has also been analysed so as to confirm its practical value.

EXPERIMENTAL

Materials

Phosphate-containing maleimide monomers, diethyl (4-(N-maleimido) phenyl) phosphate (4P),

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diphenyl (4-(N-maleimido)phenyl)phosphate (PP), and diethyl (2,6-dibromo-4-(N-maleimido)phenyl)phosphate (BrP) were synthesized by a two-stage reaction²⁰ (Scheme 1).

The epoxy resin was Epon-828, the diglycidylether of bisphenol-A(DGEBA) with an average epoxy equivalent of 190 (Scheme 2). This was a commercial product obtained from the Shell Chemical Co.

Diaminodiphenyl sulfone (DDS) was obtained from Tokyo Kasei Kogyo Co., Ltd.(TCI).

Preparation of Blends

To compare different epoxy equivalents, the PMI monomers were mixed with epoxy resin and the curing agent DDS. The ratio of epoxy resin to DDS was about 1/2. The DDS was added theoretically to open all the maleimide double bonds and the epoxy rings. The mixture was then blended at 160 °C. Any air remaining in the blends was removed in a vacuum oven and the blends were then introduced into the moulding device. The hardening times of all the maleimide-epoxy blend systems were determined by DSC.

Instrumentation

The scanning curves of the PMI and related blending resins were produced using a TA-Instruments DSC10 (DSC) at a heating rate of 10 °C/min in nitrogen to determine the melting temperatures,

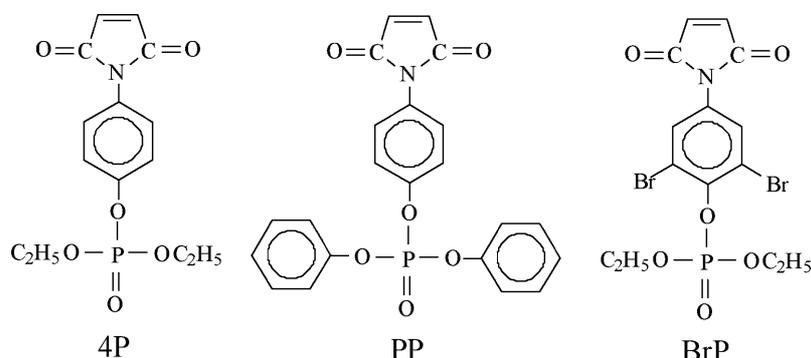
curing parameters and glass transition temperatures (T_g). The T_g s of the blends were also measured by a TA-Instrument DMA2980 (DMA) at a frequency of 1Hz. The thermal stability and flame retarding properties of the above resins were analysed by a TA-Instruments TGA 51 (TGA) at a heating rate of 20 °C/min in air and in nitrogen. The flame retardancy was also studied by measuring the limiting oxygen index (LOI) using an oxygen index analyser (Stanton Redcraft) at an O₂/N₂ flow rate of 20 L/min. The mechanical properties of the cured blends were measured by means of a Universal Testing Instrument (Instron 4469) in accordance with ASTM- D412-75.

RESULTS AND DISCUSSION

Thermal Reaction of PMI with Diamine

Maleimide monomers can react with diamines by a nucleophilic addition (Michael addition), and so can be used to synthesize polyaspartimide copolymers^{22,23}. Figures 1 to 3 show the DSC traces of some PMI/DDS systems. In the 4P/DDS system, as shown in Figure 1, the main exothermic peak of the reaction moved to a lower temperature with increasing amounts of DDS. The onset temperature of the reaction at about 180 °C was obviously lower than the self-polymerisation temperature of 4P. This indicated that the 4P monomer would undergo the Michael addition with DDS more easily. The PP/DDS system exhibited good miscibility between PP and DDS because both of them had the higher aromatic content. As shown in Figure 2, the melting peak

Scheme 1



Scheme 2

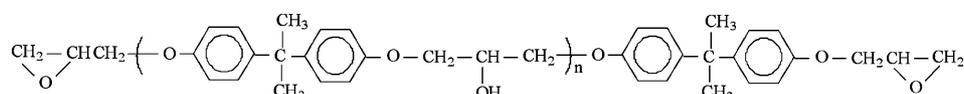
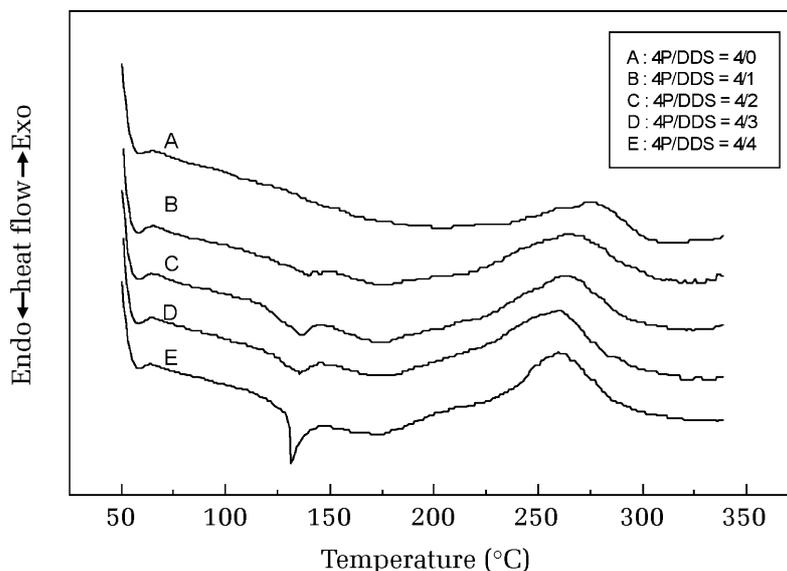
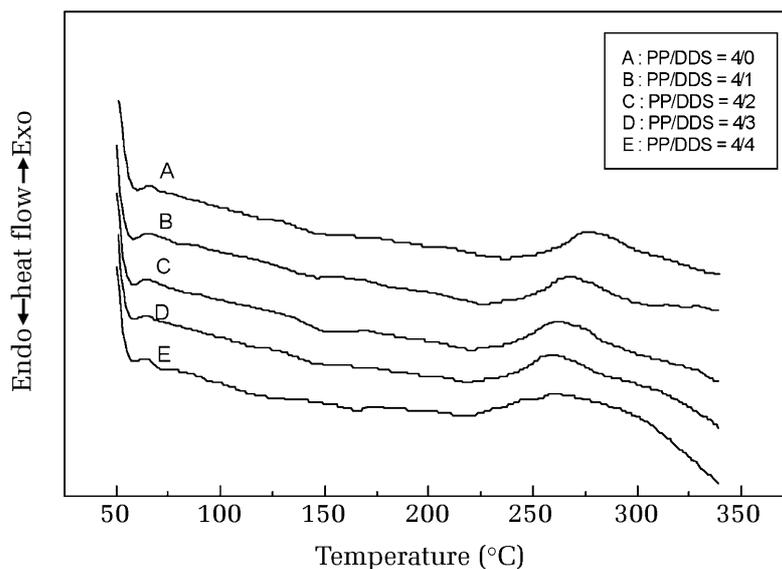


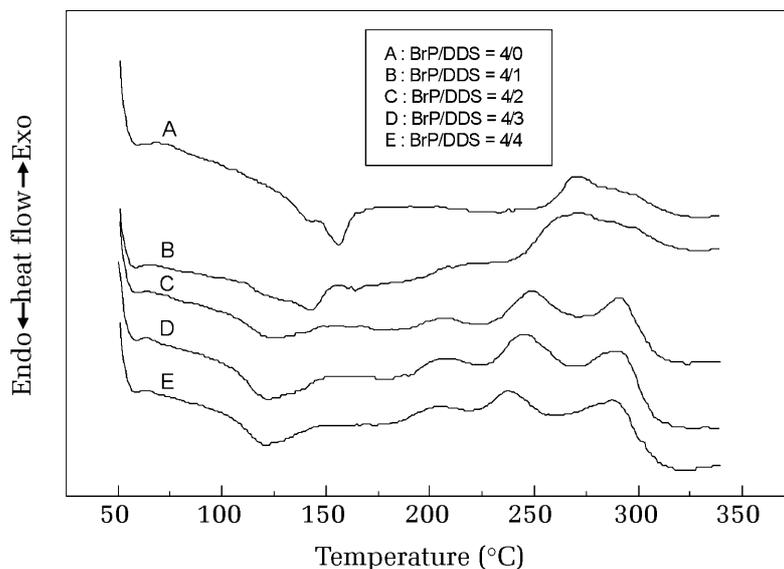
Figure 1. DSC traces of 4P cured with various ratios of DDS in N₂Figure 2. DSC traces of PP cured with various ratios of DDS in N₂

could hardly be detected. The Michael addition of PP to DDS and the self-polymerization of PP proceeded almost simultaneously. This might also be due to their good miscibility. In the BrP/DDS system, as shown in Figure 3, there was a eutectic phenomenon between BrP monomer and DDS, and, the eutectic point became progressively lower with increasing DDS content. When the ratio of BrP/DDS was close to 2, it exhibited a eutectic point at about 125 °C. Along with the eutectic effect, the self-polymerisation temperature of BrP monomer was

shifted from 270 °C to about 235 °C. The Michael addition reaction between BrP and DDS took place from about 190 °C. Since the thermal stability of the bromide was poor, there was also an exothermic peak associated with pyrolysis at about 285 °C.

Curing Reaction of PMI/Epoxy/DDS Blends

Excess maleimide monomer can react with diamine to produce a crosslinkable resin²⁴. Furthermore, there are some interactions between PMI and epoxy

Figure 3. DSC traces of BrP cured with various ratios of DDS in N₂

in addition to the crosslinking reaction²⁵⁻²⁶, such as alkylation of the nitrogen atom of DDS by the phosphate-group in the 4P- and BrP systems, and trans-esterification of the phenolic group by the epoxy group or the epoxy-derived OH-groups in the PP system. The reaction of PMI/Epoxy/DDS blends would be more complicated²⁴⁻²⁸.

The PMI/Epoxy/DDS blends were prepared by mixing PMI monomers with various amounts of epoxy and DDS. Figure 4 shows the DSC trace for the 4P/Epon828/DDS blending systems. The addition reaction between 4P and DDS, the self-polymerisation of 4P and the ring-opening reaction of the epoxy happened almost simultaneously. Therefore, there was only one exothermic peak in the first stage (at roughly 230 °C). Since the temperature of Michael addition of 4P monomer with DDS is lower, more 4P reacted with DDS while increasing the amount of 4P monomer in the blend. The temperature of the exothermic peak (T_{max1}) was also lower.

The thermal reactions of PP or BrP monomers with Epon828 were quite similar. All the data relating to the thermal reaction of the three systems are listed in Table 1. The addition reaction between PMI and DDS, the self-polymerization of PMI and the opening of the epoxy ring took place almost simultaneously. As shown in Table 1, two main exothermic peaks were respectively: (1) around 180 °C (T_{max1}) mainly associated with the addition reaction between PP with DDS (2) around 240 °C (T_{max2}) mainly associated

with the opening of the epoxy ring. The temperature of the addition reaction between the PMI and DDS in the epoxy-blending system was lower than that of the pure PP/DDS system. This might be due to the higher aromatic density of the PP-system, as mentioned previously. In Table 1, the temperature of the exothermic peak (T_{max1}) decreased on increasing the BrP contents. This might be due to the eutectic character of the BrP-system.

Characteristics of PMI/Epoxy/DDS Blends

Dynamic Mechanical Properties

The dynamic mechanical properties of specimens moulded from the PMI/Epoxy/DDS blends were measured in air. The DMA-traces for the PMI/Epon828 blends are shown in Figures 5~7. In all cases, the storage modulus (G') of the Epon828 resin system was reduced on adding PMI monomer. This is because the maleimide segments had a lower T_g (184 °C for 4P, 190 °C for PP, and 174 °C for BrP)¹⁹, but the T_g of the pure Epon828/DDS was 205.5 °C. The T_g s of the blends, therefore, decreased with increasing PMI content.

As mentioned previously, since the temperature of Michael addition of PMI monomer with DDS is lower, the blends will participate in the reaction more easily with increasing PMI content. This might also reduce the crosslink density and T_g of the blend.

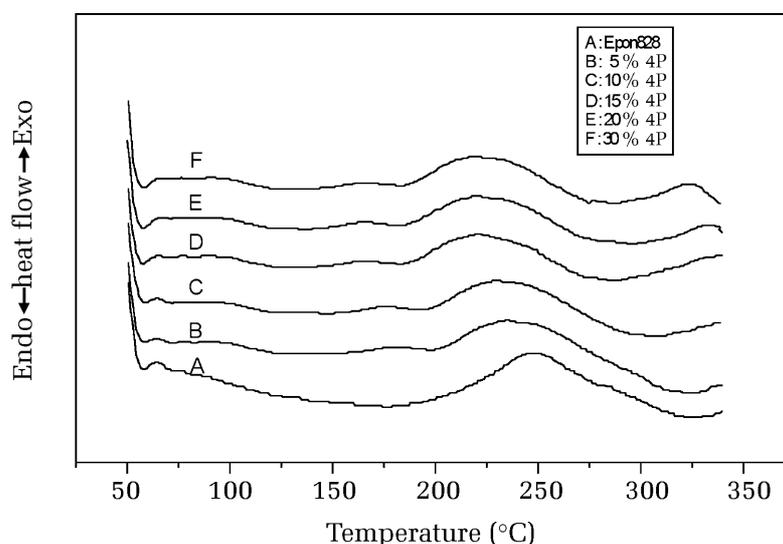
Figure 4. DSC traces of 4P/Epon828/DDS blending system in N₂

Table 1. Compositions and thermal reaction temperature of three PMI/Epon828 /DDS blending systems

PMI type	Epoxy ^a (eq.%)	PMI ^a (eq.%)	PMI (wt%)	P ^b (wt%)	T _{max1} °C	T _{max2} °C	T _c °C	T _g °C
4P	100	0	0	0	247	-	235	205.5
	95	5	6.3	0.60	234	-	225	211.2
	90	10	12.2	1.17	230	-	220	205.7
	85	15	17.9	1.71	222	-	210	204.7
	80	20	23.3	2.22	220	-	210	200.4
	70	30	33.3	3.18	219	-	210	165/201
PP	100	0	0	0	247	-	235	205.5
	95	5	8.0	0.59	201	245	235	200.9
	90	10	15.3	1.13	197	244	235	198.6
	85	15	22.1	1.62	198	245	235	196.2
	80	20	28.2	2.07	195	240	230	193.1
	70	30	39.4	2.90	191	242	230	190.0
BrP	100	0	0	0	247	-	235	205.5
	95	5	9.0	0.58	220	-	210	198.8
	90	10	17.2	1.10	211	-	200	194.2
	85	15	24.4	1.57	207	-	200	167/188
	80	20	31.1	1.99	208	-	200	167/187
	70	30	42.3	2.73	200	-	190	165/186

^aEquivalent ratio of PMI and epoxy when they were cured with DDS.

^bThe theoretical calculated weight ratio of P composition in blends.

T_{max} Exothermic peak temperature in the ith stage measured by DSC with a heating rate 10 °C/min.

T_c The cure temperature

T_g The glass transition temperature is analyzed by DMA at a heating rate of 5 °C/min in air

Figure 5. DMA traces of 4P/Epon828/DDS blending system

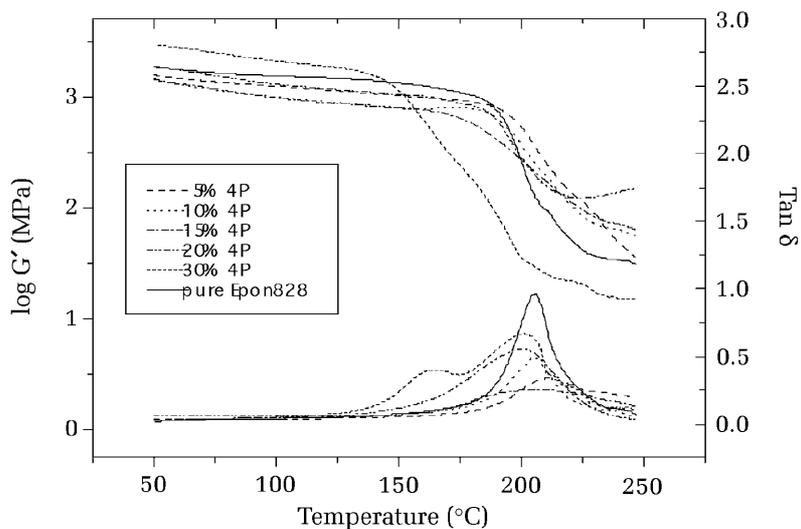


Figure 6. DMA traces of PP/Epon828/DDS blending system

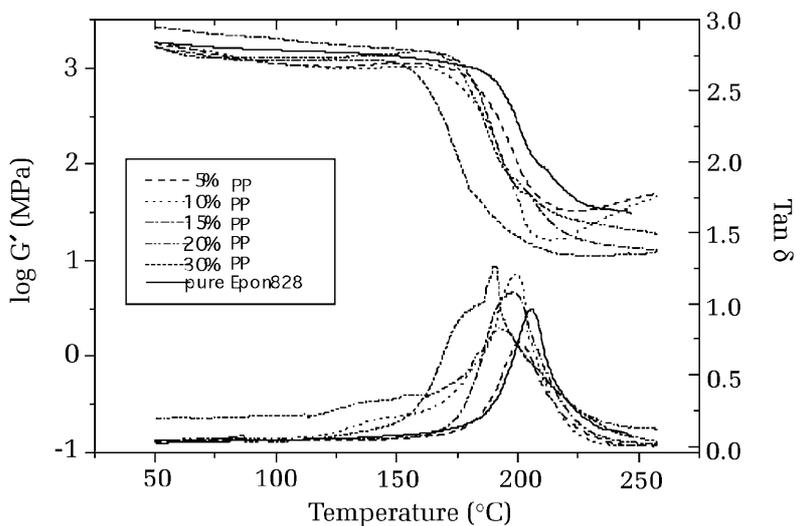
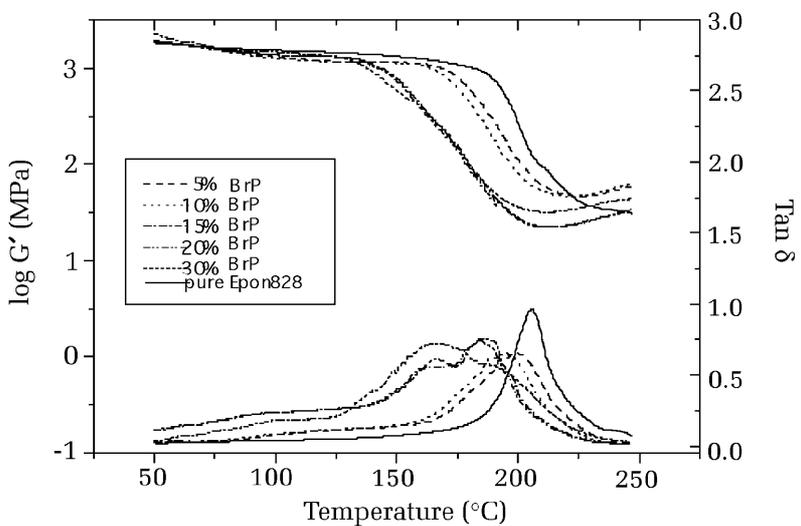


Figure 7. DMA traces of BrP/Epon828/DDS blending system



The storage modulus was also reduced by reason of the phase separation. There were, for example, two T_g s in the 4P-system with 30% 4P content, as shown in Figure 5. In addition, the bromine atoms with their high polarity could have caused partial incompatibility in the BrP/Epoxy/DDS system. The phase-separation phenomenon was more obvious in the BrP/Epoxy/DDS blends shown in Figure 7.

The T_g s of all the PMI/Epoxy/DDS blends measured by DMA are also listed in Table 1. The blends in the PP series showed a higher T_g than the others. This might be due to the higher concentration of benzene rings.

Tensile Properties

The tensile properties of the curing samples, such as their yield strength, Young's modulus and tensile strength were measured by the method of ASTM-D412-75. Table 2 shows the tensile properties of the PMI/epoxy/DDS blending system. The tensile strength of all the curing blends was reduced on

increasing the PMI content. This is mainly because adding PMI/DDS segments reduces the crosslinking density of the epoxy system. In the 4P-system with 5% of 4P, the elongation at break did not decrease, it increased, implying that this kind of PMI improved the toughness of the epoxy system at low addition levels.

The blends of the PP-system exhibited a higher tensile strength than the 4P ones because of their higher crosslink density. In the BrP/epoxy/DDS blends, phase-separation induces a storage stress at the interface during the specimen moulding process, when the content of BrP is higher. Obviously this might reduce their mechanical properties. Besides, the polar bromine atom might lower the strength of blends in the BrP-system for the side-chain effect.

Thermal Properties

Figure 8 shows the TGA traces for the decomposition of the 4P/Epon828/DDS blending system. The onset

Table 2. Tensile properties^a of three PMI/Epon828/DDS blending systems

PMI Type	Epoxy (eq.%)	PMI (eq.%)	Breaking Stress (MPa)	Breaking Strain (%)	Yield Stress (MPa)	Modulus (MPa)
4P	100	0	34.3	4.9	31.4	2304.6
	95	5	29.4	5.5	29.4	2069.2
	90	10	22.6	5.0	21.6	1961.3
	85	15	14.7	3.9	14.7	1902.5
	80	20	8.8	3.4	7.8	1667.1
	70	30	2.9	2.2	2.9	1412.2
PP	100	0	34.3	4.9	31.4	2304.6
	95	5	31.4	4.5	29.4	2108.4
	90	10	23.5	4.1	21.6	1980.9
	85	15	16.7	3.2	16.7	1922.1
	80	20	8.8	2.8	7.8	1686.7
	70	30	3.9	2.1	3.9	1471.0
BrP	100	0	34.3	4.9	31.4	2304.6
	95	5	26.5	4	25.5	1980.9
	90	10	19.6	3.6	18.6	1833.8
	85	15	13.7	3.1	11.8	1706.4
	80	20	6.9	2.6	6.9	1559.3
	70	30	2.0	1.9	2.0	1294.5

^aAccording to the test method of ASTM-D412-75 with a sample size 50×12.7×1.25 mm

temperature of pyrolysis ($T_{5\%}$) of the blending system decreased as the phosphorus content increased, whether in nitrogen or in air. This is primarily because of the lower bond energy of phosphorus-containing segments. It can also be deduced from Figure 8(a) that all the thermal-cracking curves of the blends in nitrogen relate to one-stage pyrolysis. Moreover, the pyrolysis rate slowed down as the amount of 4P in the blend was increased. The thermal-cracking curves of the blends in air, as shown in Figure 8(b), relate to two-stage pyrolysis because of oxidation at high temperatures.

The TGA traces of PP/Epon828/DDS and BrP/Epon828/DDS blend systems are shown in Figures 9 and 10, respectively. The pyrolysis conditions of

the PP or BrP blends were mostly similar to those for the 4P-system. The $T_{5\%}$ of the blends decreased with increasing phosphorus content. Since the density of benzene rings in the PP-system was higher, these blends exhibited better thermal stability.

The thermal properties of all the PMI/epoxy blends are listed in Table 3. The PP-system exhibited a higher $T_{5\%}$ than the 4P-system. On the other hand, the BrP-system exhibited a lower $T_{5\%}$ because of its high bromine content.

Flame Retardancy

The flame retardancy of all the cured blends was improved by increasing the amount of PMI. The

Figure 8. TGA traces of 4P/Epon828/DDS blending system

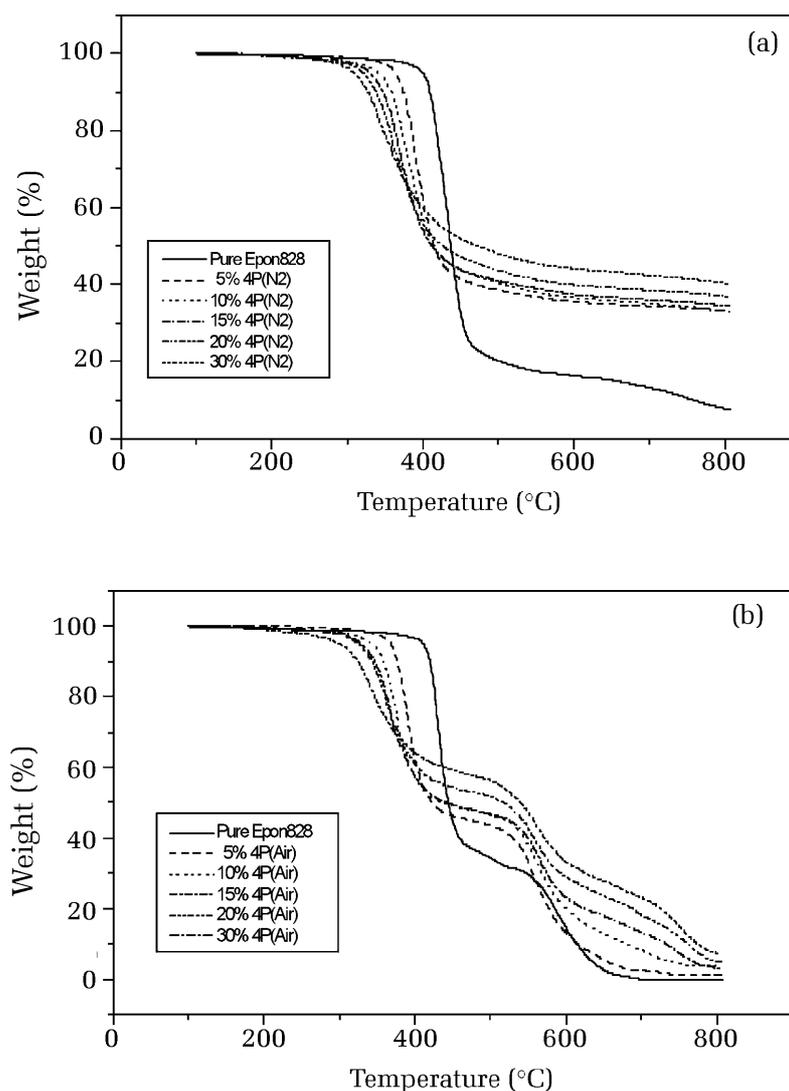
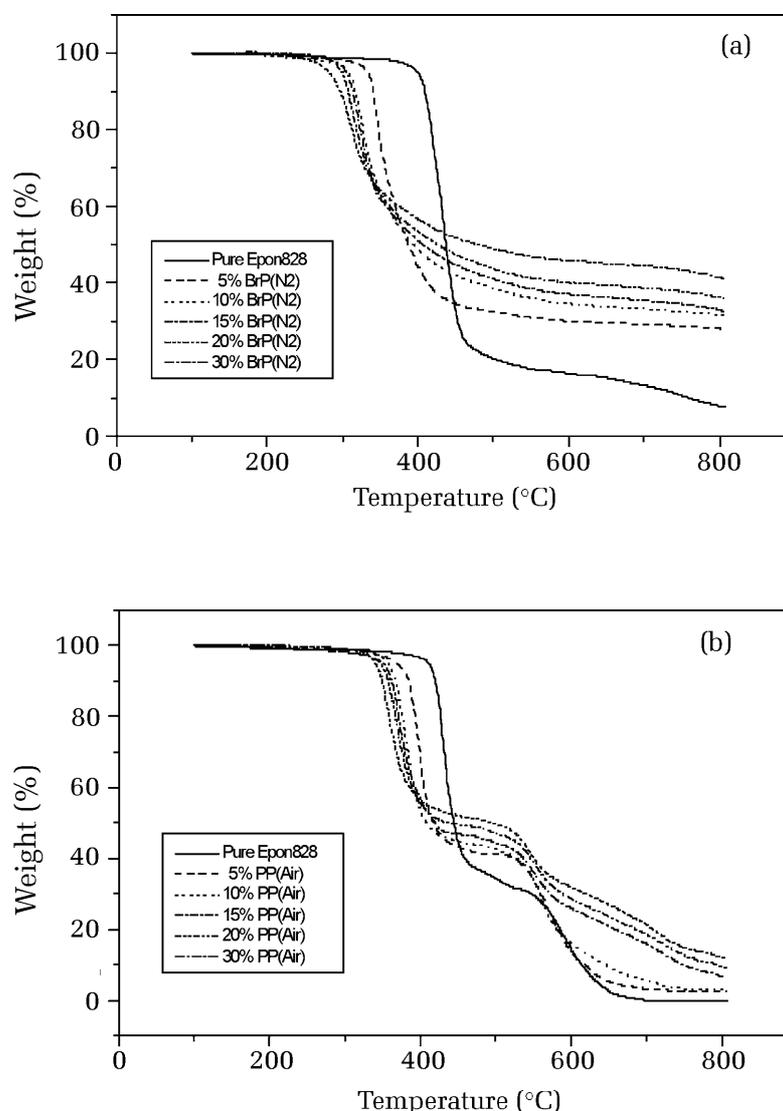


Figure 9. TGA traces of PP/Epon828/DDS blending system

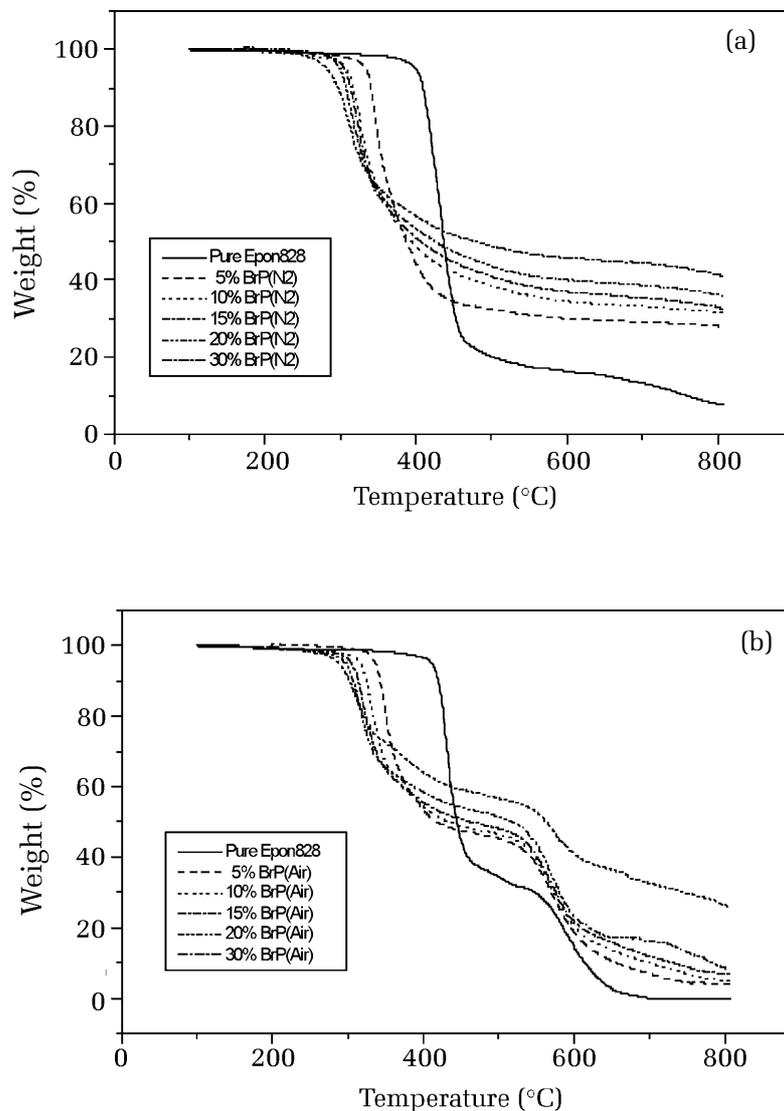


decomposition reaction of all the phosphate-containing blends should be initiated mainly by scission of the phosphate ester side chains because of their lower bond energy, and then scission of the maleimide main-chain^{19,29} along with carbonization to form a char. This could be confirmed from the TGA traces and the LOI data in Table 3.

The pyrolysis rate was slowed down as the proportion of PMI was gradually increased. The char yield was also promoted whether in nitrogen or in air. Along with the increase in the proportion

of PMI, the LOI value of all the various blends also increased gradually, and the trend was generally consistent with the char yield measured by TGA³⁰, increasing by about 15 as the PMI addition level reached 30%. The LOI of the 4P-system with its higher phosphorus content was higher than could be obtained with the PP-system. Besides, although the bromine-containing BrP-system exhibited a lower char yield at 800 °C, this kind of blend gave a higher LOI value because of the synergic effect of the phosphorus-bromine in respect of flame retardancy. When the proportion of BrP, for example, increased to 30%, the value of LOI was elevated to

Figure 10. TGA traces of BrP/Epon828/DDS blending system



about 45. These experimental data show that the three kinds of PMI monomer impart very good fire resistance when used as reactive flame retardants in epoxy blends.

CONCLUSIONS

Three kinds of phosphate-containing maleimide monomer were synthesized and blended with a

bisphenol type epoxy. Although the tensile strength of the PMI/Epoxy blends was adversely affected, they still maintained good thermal stability, and in particular they had a very good flame resistance. The reaction conditions and the blend formulations evaluated can be used as references for the industrial blending of resins.

PMI Type	Epoxy (eq.%)	PMI (eq.%)	P (wt%)	T _{5%} ^b (°C)		Char at 800°C ^b (wt%)		LOI ^b
				Air	N ₂	Air	N ₂	
4P	100	0	0	411	399	0	7.9	25
	95	5	0.60	369	364	1.4	33.1	32
	90	10	1.17	343	342	3.8	33.4	33
	85	15	1.71	328	330	3.2	34.6	35
	80	20	2.22	325	321	5.0	37.0	37
	70	30	3.18	300	310	7.4	40.4	41
PP	100	0	0	411	399	0	7.9	25
	95	5	0.59	370	376	2.6	31.4	31
	90	10	1.13	357	359	2.9	32.6	32
	85	15	1.62	352	353	6.8	34.4	35
	80	20	2.07	348	348	9.5	35.6	36
	70	30	2.90	341	344	12.0	38.4	40
BrP	100	0	0	411	399	0	7.9	25
	95	5	0.58	338	333	4.0	28.0	36
	90	10	1.10	316	308	5.0	31.6	38
	85	15	1.57	306	306	6.8	33.0	40
	80	20	1.99	297	300	8.5	36.2	42
	70	30	2.73	287	282	26.4	41.4	45

^a: Thermal properties are analyzed by TGA at a heating rate of 20°C /min in N₂ or in air.
^b: LOI are analyzed by LOI chamber at a O₂/N₂ flow rate of 20 l/min.

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