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Preparation and Characteristics of Reactive Blends of Phosphate-containing Maleimide and Epoxy

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 phenol-novolac type of epoxy so as to study their potential as reactive flame retardants. Thermal reaction of these blending systems had been discussed. Mechanical and thermal properties of blends had also been analysed. 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. Besides, the PMI with halogen atom may combine the flame retarding mechanism of gas-phase and solid-phase to promote their flame retardancy.

1 Introduction

Because of the stability of their molecular structure and the high reactivity of their unsaturated double bond, N-arylmaleimide monomers, such as N-phenyl-maleimide (PM), N-hydroxyphenylmaleimide (HPM), and halide-substituted N-hydroxyphenylmaleimide (XHPM) have been used to modify the thermal stability and flame retardancy of resins in recent years. 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 bromine-containing PM-oligomers to lower the dielectric constant of material [1], or to produce laminated boards with a low coefficient of expansion [2], and others have blended PM and PM-styrene copolymers with epoxy resins in order to promote the rigidity of these materials [3]. To improve their heat and solder resistance, some researchers have used PM polymers [4] or PM-co-styrene polymer [5] as a curing agent of epoxy resins, or have tried cyanates as curing agents

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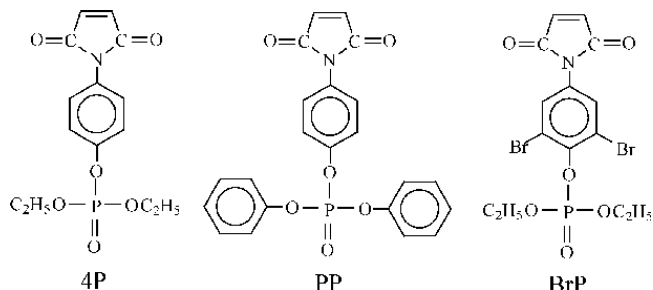
for PM/epoxy blends [6], while others have developed novel epoxy resins with PM segments [7, 8] or conversely, PM resins with epoxy segments [9, 10]. Also, some applications are emerging from further changes in the blend formulations, such as epoxies blended with PM polymers [11, 12], PM-styrene copolymers [13], or PM-diene copolymers [14]. To modify the flame retardancy, PM polymers and PM-styrene copolymers with good flame retardancy have been developed [15, 16]. Some PM-epoxy blends use a phosphorus-containing flame retardant (such as triphenyl phosphate) [17, 18]. Besides, many kinds of bismaleimide (BMI) resins blended with epoxy have also been widely studied in recent years [19 to 24].

We have already developed a series of phosphate-containing maleimide monomers that exhibit good flame resistance [25]. The copolymerization behaviour of these maleimides with styrene has been studied [26]. The present research was focused mainly on these novel phosphorus-containing maleimide monomers blended with a phenol-novolac type of epoxy resin, 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.

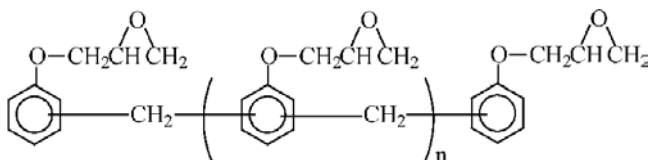
2 Experimental

2.1 Materials

Phosphate-containing maleimide monomers, 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 by a two-steps reaction [25]:



The epoxy resin was ESCN-195XL, a phenol-novolac type epoxy with an average epoxy equivalent 195. This was a commercial product obtained from Epolab Chemical Industries Inc.:



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

2.2 Preparation of Blending System

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.

2.3 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 1 Hz. 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 re-

tardancy was also studied by measuring the limiting oxygen index (LOI) using an oxygen index analyser (Stanton Redcraft) at an O_2/N_2 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.

3 Results and Discussion

3.1 Thermal Reaction of PMI with Diamine

Maleimide monomers can react with diamines by a nucleophilic addition (Michael addition) [27, 28], and so can be used to synthesize polyaspartimide copolymers [29, 30]. Figs. 1 to 3 show the DSC traces of some PMI/DDS systems. In the 4P/DDS system, as shown in Fig. 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 Fig. 2, the melting peak 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 Fig. 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.

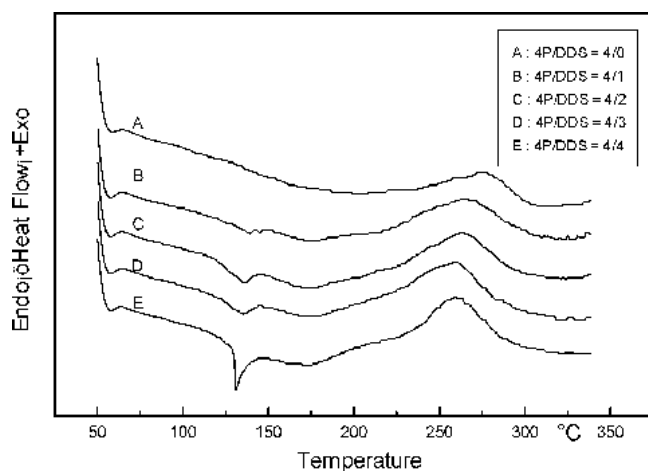


Fig. 1. DSC traces of 4P cured with various ratios of DDS at a heating rate of 10 °C/min in N_2

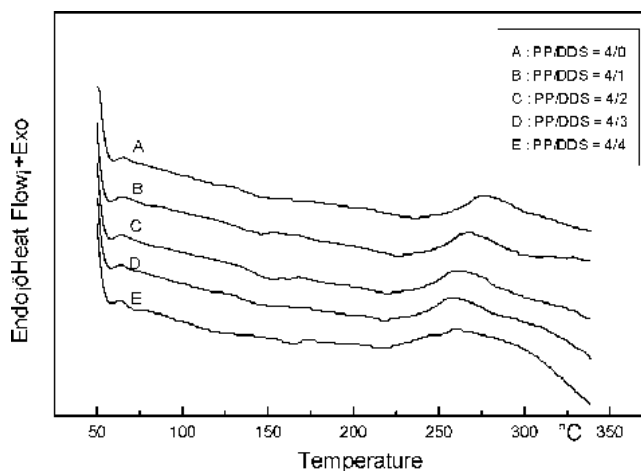


Fig. 2. DSC traces of PP cured with various ratios of DDS at a heating rate of 10 °C/min in N_2

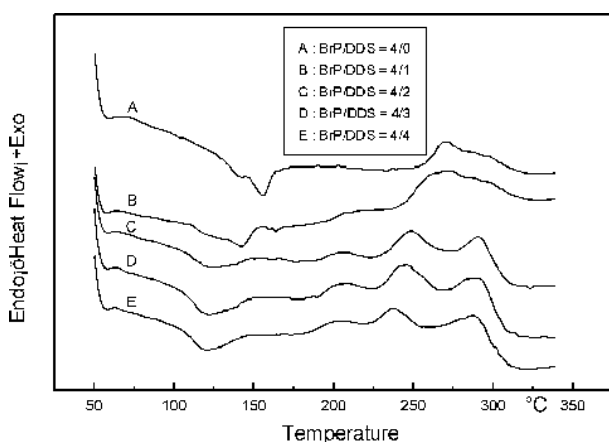


Fig. 3. DSC traces of BrP cured with various ratios of DDS at a heating rate of $10^{\circ}\text{C}/\text{min}$ in N_2

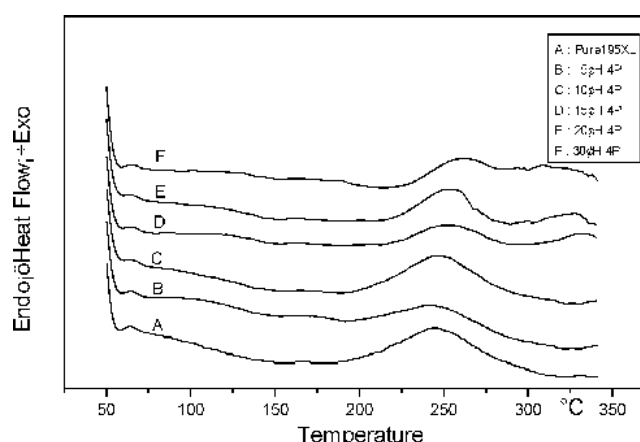


Fig. 4. DSC traces of 4P/195XL/DDS blending system at a heating rate of $10^{\circ}\text{C}/\text{min}$ in N_2

3.2 Curing Reaction of PMI/Epoxy/DDS Blends

Excess maleimide monomer can react with diamine to produce a crosslinkable resin [31]. Furthermore, there are some interactions between PMI and epoxy in addition to the crosslinking reaction [32, 33], such as alkylation of the nitrogen atom of DDS by the phosphate-group in the 4P- and BrP systems, and transesterification 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 complicated [31 to 35].

The PMI/Epoxy/DDS blends were prepared by mixing PMI monomers with various amounts of epoxy and DDS. Fig. 4 shows the DSC trace for the 4P/Epoxy/DDS blending systems.

The addition reaction between 4P and DDS, the self-polymerization 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 250°C). Since the ESCN-195XL is a multifunctional epoxy, it is more difficult for 4P to react with DDS or itself in such a circumstance with a higher crosslinking density as increasing the 4P monomer. The temperature of exothermal peak ($T_{\text{max}1}$) is therefore higher.

The thermal reactions of PP or BrP monomers with ESCN-195XL 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 Type	Epoxy ¹ eq.%	PMI ¹ eq.%	PMI wt%	P ² wt%	$T_{\text{max}1}$ °C	$T_{\text{max}2}$ °C	T_c ³ °C	T_g ⁴ °C
4P	100	0	0	0	244	–	235	246.0
	95	5	6.2	0.59	242	–	230	237.0
	90	10	12.0	1.15	245	–	235	227.7
	85	15	17.5	1.68	252	–	240	209.0
	80	20	23.0	2.19	253	–	240	202.8
	70	30	32.9	3.14	262	–	250	208/223
PP	100	0	0	0	244	–	235	246.0
	95	5	7.8	0.58	201	246	235	240.1
	90	10	15.1	1.11	200	245	235	230.7
	85	15	21.7	1.60	202	245	235	217.0
	80	20	27.8	2.05	198	246	235	194.5
	70	30	38.9	2.87	191	247	235	160/208
BrP	100	0	0	0	244	–	235	246.0
	95	5	8.5	0.56	232	–	220	228.8
	90	10	16.1	1.05	230	–	220	221.6
	85	15	22.8	1.49	215	–	205	209.1
	80	20	28.9	1.88	210	–	200	187.1
	70	30	39.3	2.53	208	–	200	184.2

1 Equality ratio of PMI and epoxy when they were cured with equality ratio of DDS.

2 The theoretical calculation weight ratio of P composition in blends.

3 The temperature selected for blends to cure.

4 The glass transition temperature is analyzed by DMA at a heating rate of $5^{\circ}\text{C}/\text{min}$ in air $T_{\text{max}i}$: exothermic peak temperature in the i^{th} stage measured by DSC with a heating rate $10^{\circ}\text{C}/\text{min}$.

Table 1. Compositions and thermal reaction temperature of PMI/epoxy/DDS blending system

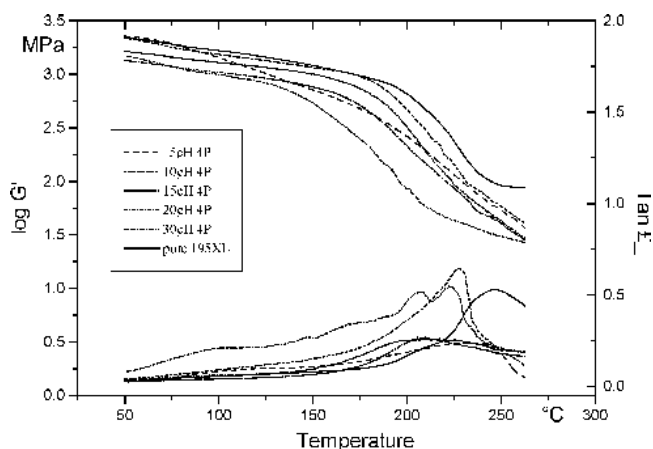


Fig. 5. DMA traces of 4P/195XL/DDS blending system measured at a frequency of 1 Hz

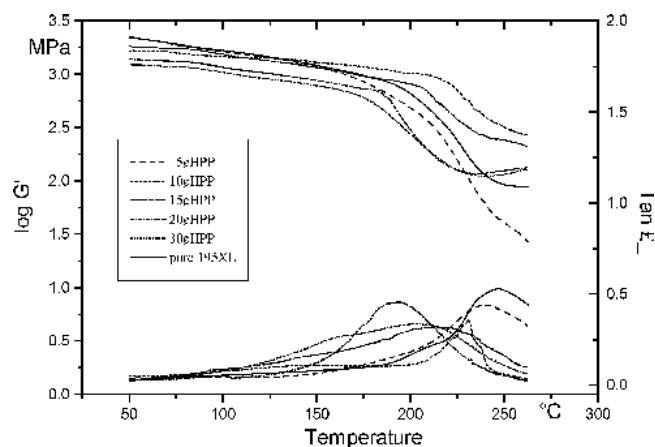


Fig. 6. DMA traces of PP/195XL/DDS blending system measured at a frequency of 1 Hz

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.

3.3 Characteristics of PMI/Epoxy/DDS Blends

3.3.1 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/195XL blends are shown in Figs. 5 to 7. In all cases, the storage modulus (G') of the 195XL 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) [25], but the T_g of the pure 195XL/DDS is 205.5 °C. The T_g s of the blends, therefore, decreased with increasing PMI content.

PMI type	Epoxy eq.%	PMI eq.%	Breaking stress MPa	Breaking strain %	Yield stress MPa	Modulus MPa
4P	100	0	52.9	5.2	51.9	2626.4
	95	5	42.1	5.6	41.2	2332.4
	90	10	33.3	5.2	33.3	2097.2
	85	15	26.5	4.5	27.4	1979.6
	80	20	20.6	3.2	19.6	1862.0
	70	30	15.7	2.5	14.7	1587.6
PP	100	0	52.9	5.2	51.9	2626.4
	95	5	45.1	4.6	44.1	2548.0
	90	10	35.3	3.2	35.3	2273.6
	85	15	29.4	2.5	28.4	2136.4
	80	20	24.5	2.2	23.5	2048.2
	70	30	18.6	1.5	18.6	1607.2
BrP	100	0	52.9	5.2	51.9	2626.4
	95	5	37.2	4.2	36.3	2097.2
	90	10	28.4	3.8	27.4	1999.2
	85	15	19.6	3.3	19.6	1852.2
	80	20	13.7	2.7	13.7	1734.6
	70	30	8.8	2.1	8.8	1391.6

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

Table 2. Mechanical properties¹ of PMI/epoxy/DDS blending system

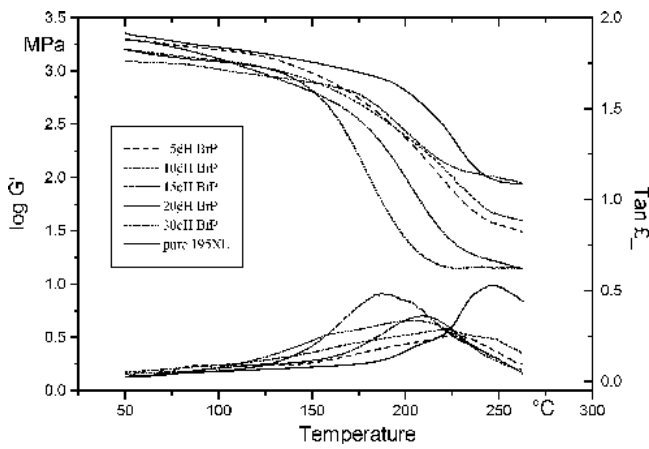


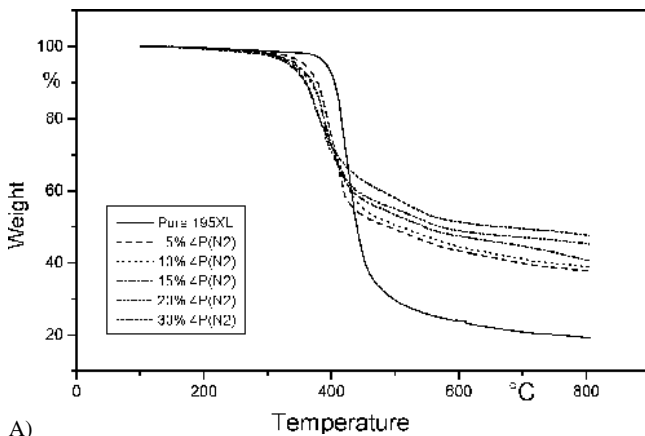
Fig. 7. DMA traces of BrP/Epon828/DDS blending system measured at a frequency of 1 Hz

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. The storage modulus was also reduced by reason of the phase separation. This would cause inconformity in their physical properties. There were, for example, two T_g s in the

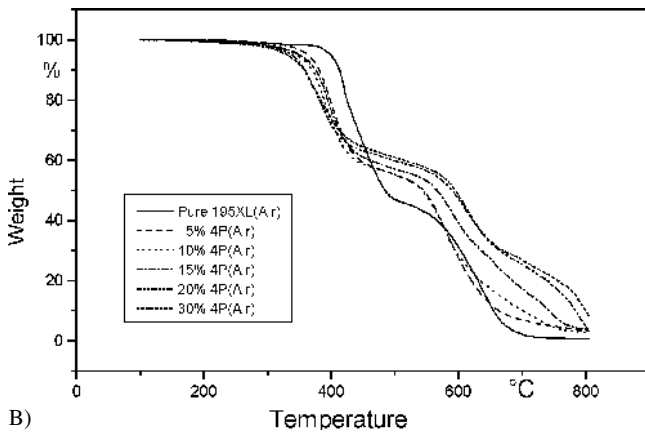
4P- and PP-system with 30 % PMI content, as shown in Fig. 5. and Fig. 6. In addition, the blends of PP series got a higher T_g than the others. This might due to their higher phenyl density. The T_g s of all the PMI/Epoxy/DDS systems measured by DMA-method are also listed in Table 1.

3.3.2 Mechanical Properties

The mechanical 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. As comparing to the 3 PMI-systems, 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.

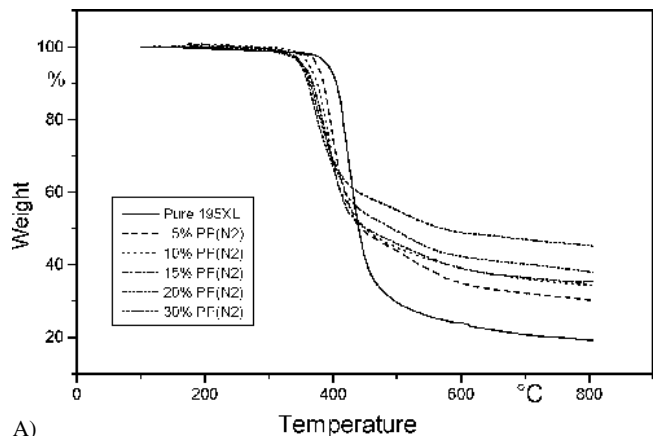


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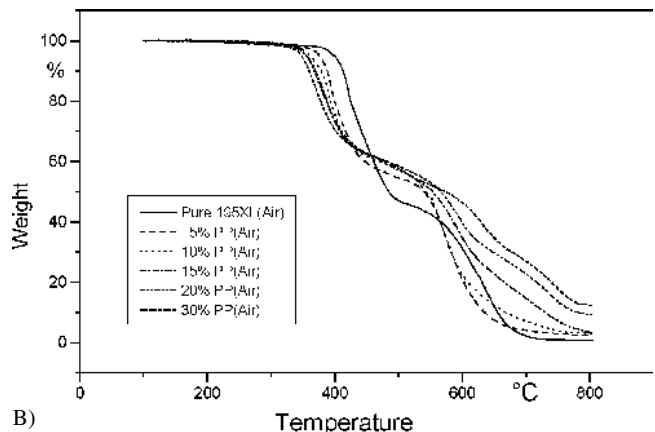


B)

Fig. 8. TGA traces of 4P/195XL/DDS blending system at a heating rate of 20 °C/min, (A) in N_2 and (B) in air



A)



B)

Fig. 9. TGA traces of PP/195XL/DDS blending system at a heating rate of 20 °C/min, (A) in N_2 and (B) in air

PMI Type	Epoxy eq.%	PMI eq.%	P wt%	T _{5%} ¹ (°C)		Char at 800 °C ¹ (wt%)		LOI ²
				Air	N ₂	Air	N ₂	
4P	100	0	0	399	392	0	19.2	27
	95	5	0.59	363	358	3.3	37.8	33
	90	10	1.15	345	340	2.9	39.0	35
	85	15	1.68	351	344	3.8	40.8	37
	80	20	2.19	338	337	5.2	45.3	39
	70	30	3.14	330	333	10.2	47.7	42
PP	100	0	0	399	392	0	19.2	27
	95	5	0.58	376	375	2.4	30.3	31
	90	10	1.11	362	362	3.0	34.5	34
	85	15	1.60	356	354	3.4	35.3	36
	80	20	2.05	356	353	9.3	38.1	38
	70	30	2.87	347	349	12.3	45.3	42
BrP	100	0	0	399	392	0	19.2	27
	95	5	0.56	330	344	3.6	43.9	36
	90	10	1.05	321	327	3.5	44.2	38
	85	15	1.49	306	318	6.0	45.1	41
	80	20	1.88	302	301	8.4	47.7	43
	70	30	2.53	295	288	9.6	54.0	46

1 Thermal properties are analyzed by TGA at a heating rate of 20 °C/min in N₂ or in air.

2 LOI are analyzed by LOI chamber at a O₂/N₂ flow rate of 20 l/min.

Table 3. Thermal properties of PMI/epoxy/DDS blending system

3.3.3 Thermal Properties

Figs. 8 to 10 show the decomposition traces of PMI/195XL/DDS blending system analyzed by TGA. The onset 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 Fig. 8A 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 Fig. 8B, relate to two-stage pyrolysis because of oxidation at high temperatures.

The TGA traces of PP/195XL/DDS and BrP/195XL/DDS blend systems are shown in Fig. 9 and Fig. 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.

3.3.4 Flame Retardancy

The flame retardancy of all the cured blends was improved by increasing the amount of PMI. The decomposition reaction of all the phosphate-containing blends should be initiated mainly by scission of the phosphate ester side chains because of their

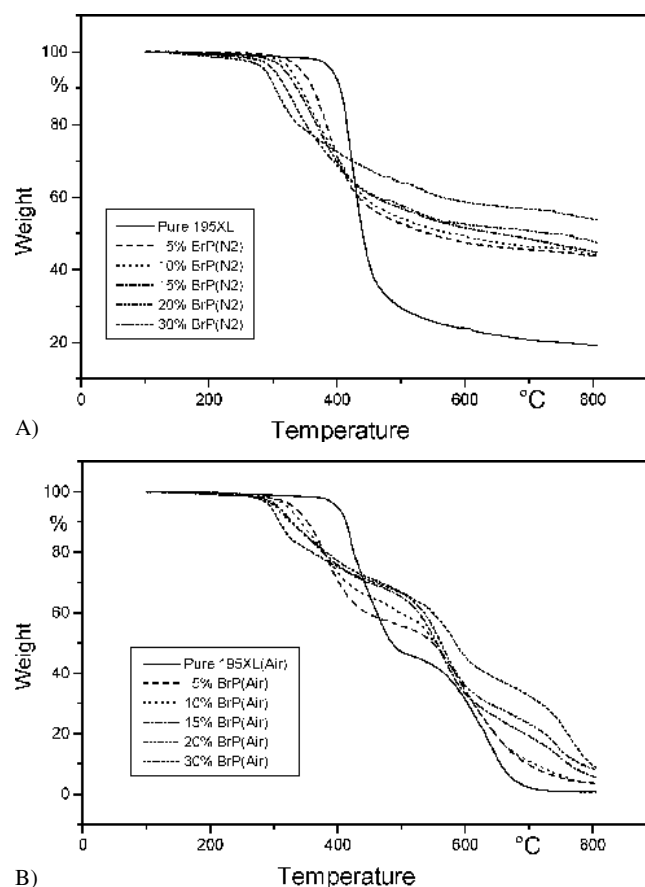


Fig. 10. TGA traces of BrP/195XL/DDS blending system at a heating rate of 20 °C/min, (A) in N₂ and (B) in air

lower bond energy, and then scission of the maleimide main-chain [25, 36] 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 TGA [37], 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 about 46. 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.

4 Conclusions

Three kinds of phosphate-containing maleimide monomer were synthesized and blended with a phenol-novolac 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 pyrolysis rate was slowed down and the flame resistance of blends promoted as the proportion of PMI was gradually increased. The PMI with bromine atom promoted flame retardancy due to the synergy effect of P/Br. The reaction conditions and the blend formulations evaluated can be used as references for the industrial blending of resins.

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