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Novel thermosetting resins based on 4-(*N*-maleimidophenyl)glycidylether: II. Bismaleimides and polybismaleimides

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Abstract

Bismaleimides, having epoxy backbone linkages and various bridging groups, were prepared through reacting 4-(*N*-maleimidophenyl)glycidylether with various biphenol and silandiol compounds. The preparation route provided a convenient approach of introducing specific groups into the bridging groups of bismaleimides to alter their properties. The prepared bismaleimides in this study exhibited good oranosolubility, low melting points, and wide processing windows, further to indicate their excellent processability. The cured polymers were found having high glass transition temperatures above 210 °C and good thermal stability over 350 °C. The polybismaleimide having silicon group, which showed fairly good thermo-oxidative stability and low amount of volatiles, were suitably being considered as flame retardant for other polymeric materials.

Keywords: Bismaleimide; Thermosets; Thermal properties

1. Introduction

Bismaleimide resins (BMIs) are considered as thermosetting polyimides and can polymerize via multiple carbon–carbon bone formation without generating volatiles. The thermal curing characteristics of BMIs lead them being capable of being fabricated with epoxy-like conditions and result in cured resins having superior thermal and flame retardant properties over epoxy resins. The rapid development on the area of BMIs in recent years demonstrates the attractive properties and application potentials of BMIs [1–13].

On the other hand, the main drawbacks of BMIs are their brittleness, poor solubility in organic solvents, narrow processing windows (the temperature difference between the melting point of BMI monomer and its onset point of curing reaction), and high cost. Most of the research efforts on BMIs focused on improving the above-mentioned disadvantages [1]. To improve the brittleness of BMI resins some toughening agents such as diamines, dithiols, diallyl bisphenols, allylamine, and reactive elastomers were added into the curing formulations of BMI resins [14–17]. Incorporation of flexible ether groups and long phenoxy chains into the BMI monomer structures was another approach of increasing the toughness of BMI resins [2,5,6,10]. The former modification might reduce the glass transition temperatures and the thermal stability of the cured BMI resins [2,6,10]. The later approach would certainly increase the molecular weight of BMIs to increase the melting points and processing temperatures of the BMI monomers and reduce the crosslinking density of the cured BMI resins. Narrow processing windows of the BMIs were also encountered with these modifications.

Introduction of epoxy backbone between the maleimide ends could result in BMIs having improved toughness and less sacrifice in thermo-oxidative stability [3]. On the other hand, BMIs containing silicon linkages or phosphorus groups also attracted considerable attentions in improving the solubility, thermal stability, and processability of the BMIs [18–24]. In this study, with utilizing the previously synthesized 4-(*N*-maleimidophenyl)glycidylether (MPGE) [25], which possesses both oxirane ring and melaimide groups, and diol compounds, a convenient approach of

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obtaining BMIs having epoxy linkage backbones is developed. Moreover, this synthesis route provided a convenient way to introducing specific chemical groups into the BMI bridging linkages. Silicon- and phosphorus-containing BMI compounds were therefore prepared through using diol compounds having silicon or phosphorous groups. The properties of the obtained BMIs and their thermally cured products were characterized and discussed.

2. Experimental

2.1. Materials

Bisphenol-A, resorcinol, diphenylsilanediol (DPSD), 4,4-diaminodiphenylmethane (DDM), triphenylphosphine (TPP), and tin chloride dihydrate were purchased from Aldrich Chemical Co. and were used as received. DOPO-BQ was prepared in our laboratory according to the literature [24]. 4-(*N*-maleimidophenyl)glycidylether (MPGE) was synthesized in our laboratory according to the reported procedures [25]. The characterization data was showed as below. Melting point, 45–50 °C; epoxy equivalent weight = 254; FTIR (KBr, cm^{-1}): 715 (C=O bending), 912 (oxirane-ring), 1248, 1037 (Ph–O–CH_2), 1375 (C–N stretching), 1609 (C=C), 1715 (C=O symmetric stretching), 1781 (C=O asymmetric stretching), 3070 (C–H of imide group). ^1H NMR (300 MHz, DMSO-d_6, ppm): 2.72 (m, 1H); 2.87 (m, 1H); 3.68 (m, 1H); 4.13–4.26 (m, 2H); 6.87 (d, 2H); 7.24–7.46 (m, 4H).

2.2. Equipment

Infrared spectra (FTIR) were obtained with a Perkin–Elmer 2000 FTIR. ^1H and ^{31}P NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer. Elemental analysis was performed with a Heraeus CHN–O rapid elementary analyzer with benzoic acid or 4-nitroaniline as a standard. The phosphorus contents of the chemicals were determined via phosphorus elemental analysis with a micro digestion apparatus with a spectrophotometer. DSC thermograms were recorded with a Thermal Analysis (TA) DSC-2900 in nitrogen. Thermogravimetric analysis (TGA) was performed by a TA TGA-2050 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere.

2.3. Preparation of bismaleimides

BMIs were prepared through reacting MPGE with various diol compounds. BMI-1, BMI-2 and BMI-3 were obtained with the same manner [26]. 0.02 mol of MPGE and 0.04 mol of diol dissolved in 15 mL diglyme were charged into a 50 mL round-bottom flask. Triphenylphosphine (TPP, 0.05 g) was added to the solution as a reaction promoter. The reaction solution was then heated to 140 °C for 5 h, and then cooled to room temperature. The solvent was removed out with a rotary evaporator. The product was then heated at 100 °C under vacuum for 3 h to give a solid product (yield: 100%).

The synthesis of BMI-4 was performed through the process similar to the above-mentioned manner. However, tin chloride dihydrate was used to replace TPP as the reaction promoter [27].

2.4. Preparation of cured maleimide resins

The BMI polymers were obtained from thermally curing the BMI monomers. The curing compositions (Table 1) were dissolved in certain amount of THF. The homogeneous solution was then poured into a Teflon-coated stainless plate and put in an oven. The curing conditions for the polymers were also listed in Table 1.

3. Results and discussion

3.1. Preparation and characterization of BMIs

The preparation of BMIs was carried out with the addition reaction between oxirane group and hydroxyl group (Fig. 1). All of the BMI compounds were obtained with good yields. It was noteworthy that tin chloride dihydrate was used as the reaction promoter for preparation of BMI-4, since in the previous work tin chloride dihydrate exhibited high efficiency on promoting the addition reaction between oxirane ring and silanol group [27]. The chemical structures of the BMIs were characterized with FTIR and the results were collected in Table 2. Taking BMI-1 as an example, the maleimido group showed significant absorption peaks at 715 cm^{-1} (C=O bending), 1394 cm^{-1} (C–N stretching), 1611 cm^{-1} (C=C), 1713 cm^{-1} (C=O symmetric stretching), and 1784 cm^{-1} (C=O asymmetric stretching). The disappearance of the absorption peak at about 912 cm^{-1} denoted the occurrence of addition reaction of the oxirane ring. Other absorption peaks at 3271 cm^{-1} (–CH–OH), 1531 cm^{-1} (phenyl ring), 1250 cm^{-1} (–C–O–C) further demonstrated the chemical structure of BMI-1. Besides the above-mentioned absorption peaks, some characteristic absorption peaks observed with the FTIR spectra of the BMI compounds further demonstrated the

Table 1
Preparation of BMI polymers

Polymer code	Polymerization composition (equivalent ratio)	Curing condition
PBMI-1	BMI-1	250 °C 2 h, 280 °C 2 h
PBMI-2	BMI-2	250 °C 2 h, 280 °C 2 h
PBMI-3	BMI-3	250 °C 2 h, 280 °C 2 h
PBMI-4	BMI-4	280 °C 2 h, 300 °C 2 h

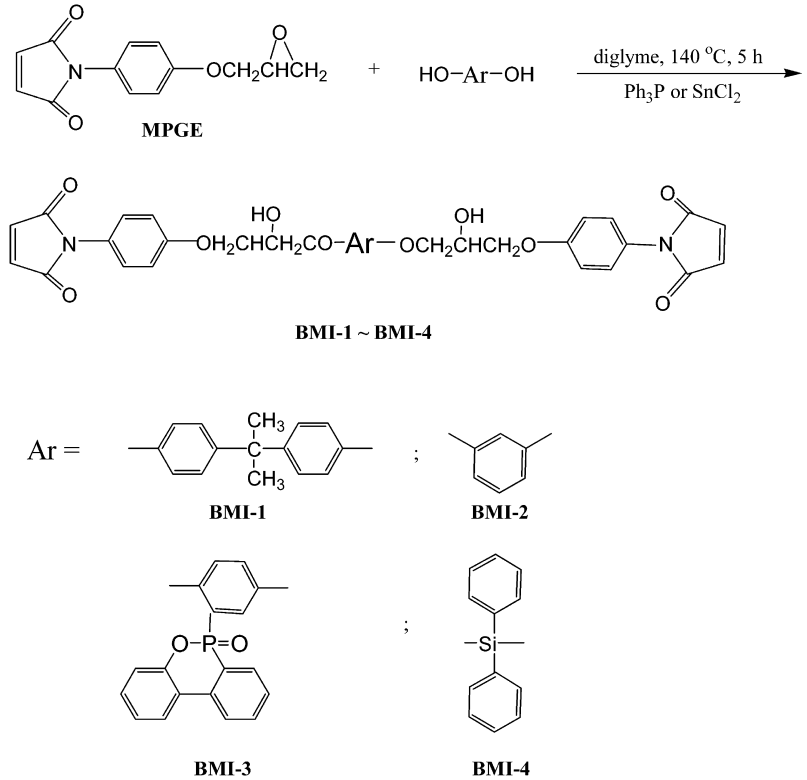

Fig. 1. Synthesis of BMI monomers.

chemical structures of respective BMIs. The characteristic absorption included peaks at 2971 cm^{-1} ($-CH_3$, BMI-1), 1478 cm^{-1} (P–Ph, BMI-3), 1202 cm^{-1} (P=O, BMI-3), and 1429 cm^{-1} (Si–Ph, BMI-4). Furthermore, the analytical data obtained from ^1H NMR analysis (Table 2) also showed reliable results to support the chemical structure of the BMI compounds and the success of preparation of them. BMI-3 was also characterized with ^{31}P NMR. A single peak at about $\delta = 22.6$ ppm implied BMI-3 containing the DOPO group and denoting the purity of the obtained product.

The processing properties of the BMI compounds were evaluated with observing their solubility in organic solvents and measuring their melting points and processing windows. Table 3 collected the experimental results of the solubility test on the BMI compounds. It is noteworthy that the BMIs showed good solubility not only in highly polar solvents like dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), but also in acetone, tetrahydrofuran (THF), and methylethylketone (MEK). Furthermore, BMI-4 exhibited a better solubility than the others, since it was also soluble in ethylacetate and hot chloroform. On the other hand, DOPO group was reported to show enhancement on the solubility of aromatic polyimides and polyamides owing to it possesses the polar P=O group, non-coplanar configuration, and bulky structure [28–30]. However, this effect was not observed with the BMI compound, since BMI-3 showed similar solubility with BMI-2 did. However, the good solubility of the BMI compounds indicated their wide processibility. Especially, since these low boiling point solvents (acetone, THF, and MEK) were widely used in the epoxy fabrication process, it was implied that the prepared BMI compounds could be processed with the current process for epoxy resins. On the other hand, the melting points (T_m, from microscopy with heating stage), the polymerization temperatures (T_p, from DSC measurements), and the processing windows ($T_p - T_m$) of the BMI compounds were measured and the results were collected in Table 4. The low melting points of these BMI compounds indicated their attractive processing properties under molten and solvent-free process. The extremely low T_m of BMI-4 (125 °C) was especially noteworthy. The relatively high T_p's of the prepared BMI compounds might be from the long length of the epoxy chain bridging the maleimide groups [18,22,23,31]. However, the electronic effect of the bridging groups also affected the reactivity of the maleimide polymerization, therefore, to illustrate the relative high T_p of BMI-3 [3] and BMI-4 [18]. The processing windows of the BMI compounds were extremely wide to bring certain convenience on processing these BMI resins.

The thermally-induced polymerization of the obtained BMI compounds could be observed with DSC exothermic peaks and the activation energies of the reactions were calculated from the DSC thermograms obtained at various heating rates. Two approaches proposed by Kissinger [32] and Ozawa [33], respectively, were employed for obtaining the activation energies of the BMI polymerization reactions (Table 5). All of the data ranging from 87.8–108.4 kJ/mol

Table 2
Characterization data of the BMI compounds

BMI	FTIR (cm^{-1})										^1H NMR (ppm)						Elemental analysis (%) found (calcd)		
	–OH	–C=C–	–C=O	Phenyl	C–N	–C–O–C–	–CH_3	P–Ph	P=O	Si–Ph	Aromatic protons	–C*H*=C*H*–	–OCH_2–	–CH_2C*H*(OH)–	–CH_3	DOPO	C	N	P
BMI-1	3271	1611	1713	1513	1394	1250	2071	–	–	–	6.9–7.9	6.7	3.7–4.1	3.1	1.6	–	71.02 (71.72)	4.88 (4.08)	–
BMI-2	3373	1605	1712	1513	1394	1250	–	–	–	–	7.0–7.8	6.9	3.7–4.1	3.1	–	–	66.12 (67.60)	4.78 (4.93)	–
BMI-3	3246	1608	1714	1513	1392	1250	–	1478	1202	–	6.9–7.8	6.6	3.7–4.1	3.2	–	22.6[a]	66.15 (67.52)	3.14 (3.58)	3.88 (3.96)
BMI-4	3380	1593	1717	1512	1375	1250	–	–	–	1429	7.2–7.6	6.9	3.7–4.1	2.5–2.8	–	–	66.03 (67.56)	4.47 (4.15)	–

[a] Chemical shift observed with absorption peak in ^{31}P NMR analysis.

(data from Kissinger's method) were reasonable to the polymerization reaction of bismaleimides.

3.2. Thermal properties of polybismaleimides

Polybismaleimides were prepared from thermally curing the BMI compounds (Table 1). The glass transition temperatures of these polymers evaluated with DSC were listed in Table 6. All of the polymers showed their T_g values between 205 and 215 °C, which were comparable with the T_g's of other cured epoxy-bismaleimides [5]. PBMI-4 showed the highest T_g among the prepared polymers. The high T_g of PBMI-4 might be correlated to its relatively high crosslinking density, since BMI-4 had the shortest chain length between the maleimide groups. The thermal degradation behavior and thermal stability of the polymers were studied with TGA (Fig. 2). The temperatures at 5% weight loss (T_d) of the polymers were considered as their initial thermal stability. For PBMI-1 and PBMI-2, T_d's around 347–360 °C were observed, respectively. The T_d values were comparable with other aromatic polybismaleimides [10]. The high T_d's of PBMI-1 and PBMI-2 also implied that incorporation of epoxy group into the bismaleimide linkages did not significantly alter the thermal stability of the cured BMI polymers. Moreover, PBMI-3 showed a relatively low T_d and PBMI-4 showed a highest one. The low T_d of PBMI-3 implied the thermal degradation of PBMI-3 might trigger at chemical bonds with low bond energies, rather than the epoxy-maleimide backbones. The pendent DOPO groups should be responsible to the low T_d of PBMI-3, since DOPO group possessed the thermally unstable P–O– linkage [26–28]. On the other hand, the high T_d of PBMI-4 should be mainly coming from its low weight loss rate, since from TGA thermograms (Fig. 2) PBMI-2 and PBMI-4 showed their initial weight loss at similar temperatures. However, the followed weight loss was retarded with the silicon groups to shift the T_d of PBMI-4 to a high temperature region. The retarded weight loss pattern of PBMI-4 was much obvious at high temperature region, to indicate incorporation of silicon group might level up the thermal stability of the degradation residual of polybismaleimides.

3.3. Thermal degradation and stability

The degradation patterns of the polymers read from TGA thermograms were also noteworthy. The one-stage weight loss in nitrogen and two-stage pattern in air of the polymers were just similar with the degradation patterns of other polymers. However, the weight loss of PBMI-3 and PBMI-4 were retarded at high temperatures, especially under heating in air. This weight loss behavior correspondingly resulted in high char yields of these two polymers. The specific behavior of PBMI-3 degradation was correlated to the condensed-phase mechanism of char formation and flame retardation, which was widely

Table 3
The solubility of the BMI compounds

BMI	Acetone	Toluene	THF	Ethylacetate	Ethanol	MEK	Chloroform	DMSO	DMAc	DMF	NMP
BMI-1	◎	X	◎	△	△	◎	X	◎	◎	◎	◎
BMI-2	◎	X	◎	X	△	◎	X	◎	◎	◎	◎
BMI-3	◎	X	◎	X	△	◎	X	◎	◎	◎	◎
BMI-4	◎	X	◎	◎	△	◎	△	◎	◎	◎	◎

◎: Soluble; △: soluble under heating; X: unsoluble.

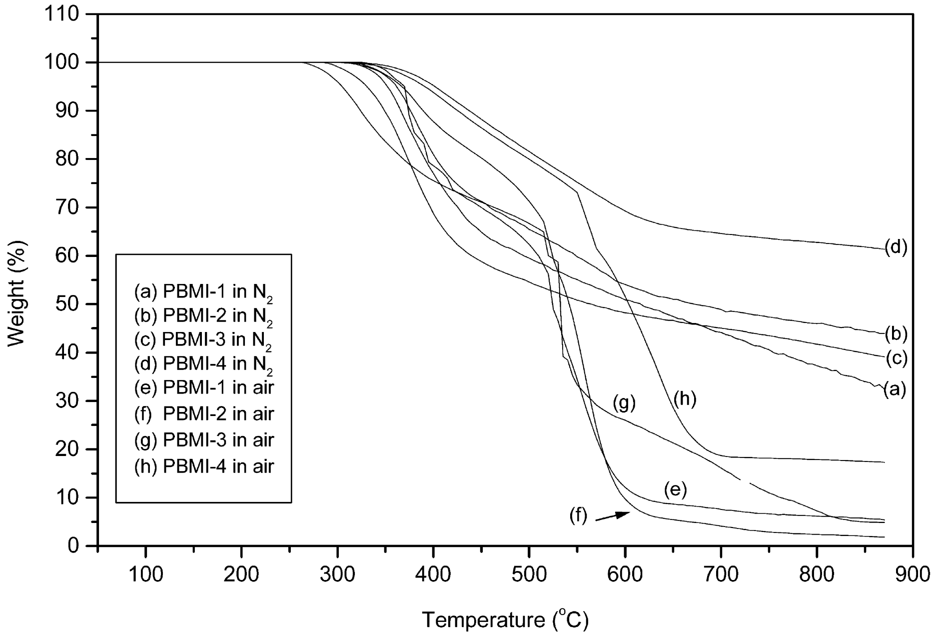

Fig. 2. TGA thermograms of the PBMI polymers.

observed with phosphorus-containing polymers [34–36]. The extremely high thermal-stability of the degraded residual of PBMI-4 was observed with that there was almost no weight loss occurring at temperatures above 700 °C. The incorporated silicon groups contributed to the high thermal stability of residual through formation of a silica protecting-layer, which was thermally stable and extraordinary heat-resistant, on the residual surface to avoid further thermal degradation of the residual [29, 37–39].

Since using T_d could only provide initial decomposition temperature of the PBMI polymers, another parameter of integral procedure decomposition temperature (IPDT) [40] was utilized. IPDT can provide information about the amounts of volatile parts of polymeric materials as well as the polymers' inherent thermal stability. From Table 6 it was read PBMI-3 exhibited a relatively high IPDT than the phosphorus-free PBMI-1 and PBMI-2, to confirm the phosphorus in PBMI-3 reduced the amount of released volatiles under heating. The especially high IPDT of PBMI-4 fingered the excellent thermal stability of PBMI-4. Moreover, high IPDT also corresponded to containing less amount of volatile. Basing on the condensed-phase mechanism of flame retardation, a high IPDT value of a polymer has also been correlated to good flame retardance [26,39]. It can be reasonably inferred PBMI-4 is extremely flame retardant. The flame retardance of these maleimide resins was read from measuring their LOI values, and the

Table 4
Thermal properties of the BMI compounds

BMI	T_m (°C)	T_p (°C)	Processing window (T_p–T_m, °C)
BMI-1	160	217	57
BMI-2	150	265	115
BMI-3	180	235	55
BMI-4	125	295	170

Table 5
The activation energies of the polymerization reactions of the BMI compounds

BMI	Kissinger's method		Ozawa's method	
	Ea (kJ/mol)	*R*	Ea (kJ/mol)	*R*
BMI-1	87.8	0.9966	94.0	0.9984
BMI-2	108.4	0.9962	111.9	0.9968
BMI-3	105.6	0.9984	109.3	0.9987
BMI-4	103.2	0.9993	107.3	0.9994

Table 6
Thermal characterization data of polybismaleimides

Polymer code	T_g (°C)	TGA analytical data				IPDT (°C)		LOI
		T_d[a] (°C)		Char at 700 °C (%)		In N_2	In air	
		In N_2	In air	In N_2	In air			
PBMI-1	205	347	367	43.1	7.6	1121	563	38.0
PBMI-2	205	362	364	48.9	3.8	1133	551	39.5
PBMI-3	209	320	300	43.9	15.3	1311	556	48.0
PBMI-4	215	401	391	64.6	18.5	2628	814	>50.0

[a] Temperature at 5% weight loss.

results were collected in Table 6. The LOI values of PBMI-1 and PBMI-2 were similar to those of previously reported epoxy-maleimide resins [25,26]. The relatively high LOI value of PBMI-3 was considered from the phosphorus group, which was widely known as flame retardant groups to polymeric materials through a condensed-phase mechanism. Moreover, this high LOI value of about 48.0 might also derived from the phosphorus–nitrogen synergistic effect on flame retardation [25]. In addition, the extremely high LOI value of PBMI-4 (>50.0) was noteworthy. Silicon played a synergistic effect on flame retardation with phosphorus has been observed [37,38], owing to the silicon groups formed a protecting layer with highly thermo-oxidative stability. The high LOI value of PBMI-4 could be correlated to the similar synergistic effect of silicon–nitrogen, since the nitrogen-containing maleimide groups also formed a lot of char under heating. On the other hand, since polybismaimides is inherently flame retardant, it might be meaningless to improve the flame retardant property of PBMI polymers. Nevertheless, PBMI-4 could be considered as an efficient agent for improving the flammability of other polymers like epoxy resins [41], especially for the halogen-free and phosphorus-free materials. This will be verified in future investigation.

In addition, the PBMI polymers were also examined by isothermal gravimetric analysis (IGA) [10] at 300 and 400 °C, respectively. In Fig. 3, the weight loss of the PBMI polymers at 300 °C was shown. It can be seen that all of the PBMI polymers, excepting PBMI-3 heated in nitrogen, maintained more than 90% weight after 5 h and then almost levelled off. The relatively poor stability of PBMI-3 is reasonable, since PBMI-3 showed significant weight loss at about 300 °C in TGA heating scan. Furthermore, the stability of PBMI-3 heated in air was obviously better than which heated in nitrogen. This behavior was unusual for general polymers, however, was coincident with the result from TGA thermograms. As it can be seen in Fig. 2, after initially decomposition the weight loss rate of PBMI-3 in air (curve g) was much smaller than that in nitrogen (curve c), to indicate the residual of PBMI-3 formed in air was much thermally stable than that in nitrogen. Same result was also observed with PBMI-3 IGA traces at 400 °C (Fig. 4). For PBMI-3 heated in nitrogen at 400 °C (Fig. 4, curve -▲-), the sample rapidly lost about 45% of weight in first

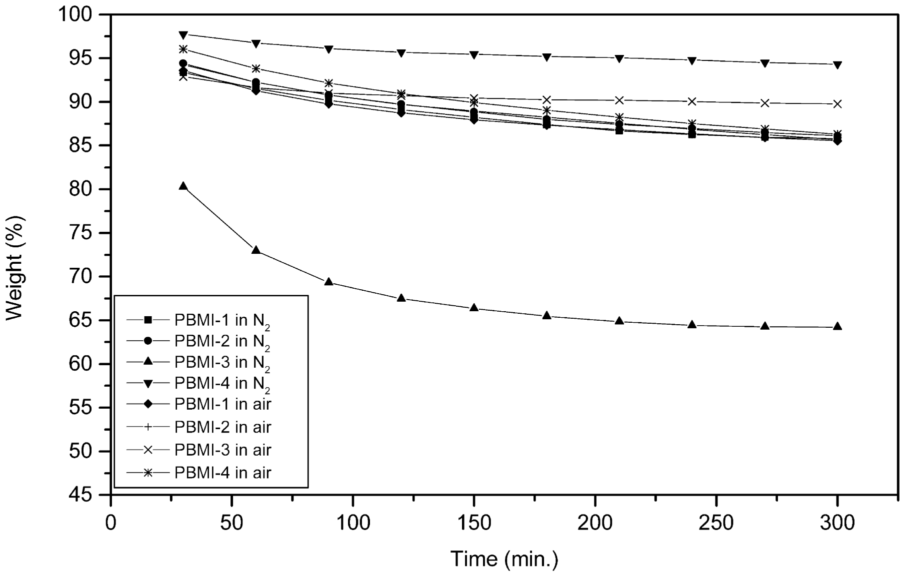

Fig. 3. Isothermal gravimetric traces of PBMI polymers at 300 °C.

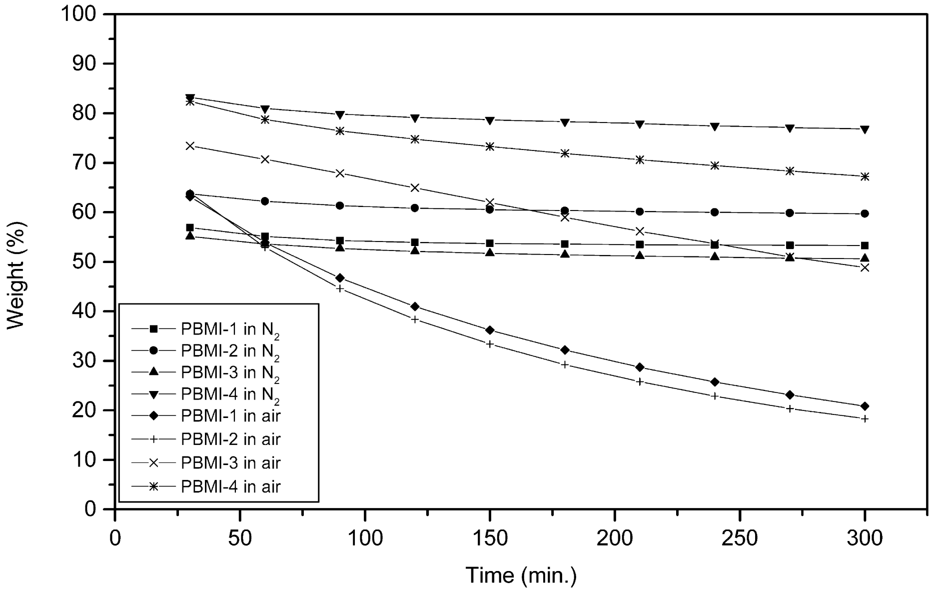

Fig. 4. Isothermal gravimetric traces of PBMI polymers at 400 °C.

0.5 h. While being heated in air (Fig. 4, curve -X-), the weight loss of PBMI-3 in the first 0.5 h was only about 25%, and in the next 4.5 h the weight loss gradually increased to 45%. Furthermore, it can be seen that incorporation of phosphorus and silicon groups into the PBMI polymers significantly increased the thermally oxidative stability of the polymers, and the effect of silicon group was especially dominant.

4. Conclusion

Through using 4-(*N*-maleimidophenyl)glycidylether as a raw material, bismaleimides containing epoxy groups as the bridge were obtained through the oxirane addition reaction with phenol and silanoxyl groups. The synthesis route provided much convenience of introducing various specific bridge structures into the bismaleimide backbones and very high product yields. The obtained bismaleimides exhibited good oragnosolubility, low melting points, and wide processing windows to indicate their good processability. The cured polymers also showed high glass transition temperatures above 210 °C and high thermal stability over 350 °C. The polymers having silicon group had extremely high thermally-oxidative stability and low amount of volatiles while being heated, and could be considered as flame retardant for other polymeric materials.

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