Synthesis and Properties of Silicon-Containing Bismaleimide Resins

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ABSTRACT: Two novel bismaleimide (BMI) monomers containing silicon atom in the structure, i.e., bis[4-(4-maleimidophenylcarbonyloxy)phenyl]dimethylsilane (BMI-SiE1) and bis[4-(4-maleimidophenyloxycarbonyl)phenyl]dimethylsilane (BMI-SiE2), were designed, synthesized, and polymerized with and without the use of diamine as comonomers to yield novel silicon-containing BMI resins. Both monomers obtained are readily soluble in organic solvents, such as chloroform and N, N-dimethylformamide. Differential scanning calorimetry and thermogravimetric analysis investigation of these two monomers indicated a high polymerization temperature ($T_p > 240°C$) and a good thermal and thermo-oxidative stability of cured BMI resins. The onset temperature for 5% weight loss was found to be above 450°C in nitrogen and above 400°C in the air. Polymerization of BMI-SiE1 and BMI-SiE2 with 4,4′-diaminodiphenylether (DPE) yielded a series of polyaspartimides that had good solubility and could be thermally cured at 250°C. TGA investigations of the cured diamine-modified BMI resins showed onset of degradation temperatures (T_ds) in the range of 344–360°C in nitrogen and 332–360°C in the air. Composites based on the cured diamine-modified BMI resins and glass cloth were prepared and characterized for their dynamic mechanical properties. All the composites showed high glass transition temperatures (e.g., >190°C) and high bending modulus in the range of 1000–2700 MPa. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 190–199, 2008

Key words: silicon-containing polymer; bismaleimide; thermal property; dynamic mechanical property; synthesis

INTRODUCTION

In the past 20 years, silicon-containing polymers have been extensively developed for various applications because of their good solubility, high thermal and thermo-oxidative stability, good flame retardancy, high moisture resistance, and good adhesion with semiconducting substrates.[1–3] Typical examples of such polymers include polyamides,[4] polyesters,[5] polyimides,[6] polyoxadiazoles,[7] polysulfones and polyketones,[8] epoxy resins,[9] and cyanate ester resins.[2] All of these polymers show improved processability and thermal stability and are promising candidates for wide applications ranging from aerospace to electronics. Introduction of silicon atoms into bismaleimide (BMI) resins may lead to a new type of high-performance polymeric materials. However, there are only a few literature references dealing with silicon-containing bismaleimide resins.[10,11]

BMI resins are an important type of thermoset polymeric materials characterized by their high glass transition temperatures and high modulus.[12,13] However, poor solubility of BMI monomers and BMI resins in common organic solvents and their inherent brittleness limits to a great extent their wide applications. To overcome these problems, effort has been made to develop novel BMI monomers containing flexible units; modification of BMI resins by using comonomers, such as the copolymerization of BMI monomers with diamines via the Michael addition reaction, has also been extensively explored to decrease the crosslinking density.[14,15] However, most of these methods suffer from an impaired thermal and thermo-oxidative stability that may result from the introduction of weak bonds.

In an effort to prepare high-performance BMI resins with good comprehensive properties, we have herein designed two novel BMI monomers containing silicon atom in the structure, in hoping that the introduction of flexible C—Si bonds may contribute to an improved solubility of the monomers and a high toughness of the resulting BMI resins. Meanwhile, the typical good thermal stability of BMI resins may be retained due to the good thermal and

thermo-oxidative stability of C—Si bond. In this article, the synthesis and properties of these silicon-containing bismaleimides (i.e., BMI-SiE1 and BMI-SiE2) will be presented in detail. Both of them exhibited a good solubility in common organic solvents and a high thermal and thermo-oxidative stability ($T_d >$ 450°C in N_2 and $T_d >$ 420°C in the air) after thermal curing. Copolymerization of these silicon-containing BMI monomers with a diamine (i.e., 4,4′-diaminodiphenylether) were carried out and compared with those derived from previously synthesized 1,3,4-oxadiazole-based BMI monomers.[16,17] Studies on the structure–property relationship of these thermally cured diamine-modified BMI resins will be presented.

EXPERIMENTAL

Materials

4-Maleimidobenzoic acid chloride, 4,4′-dicarboxyldiphenyldimethylsilane 5-tert-butyl-1,3-bis[5-(4-maleimidophenyl)-1,3,4-oxadiazole-2-yl]benzene (Buoxd), and 4,4′-bis[5-(4-maleimidophenyl)-1,3,4-oxadiazole-2-yl]diphenyldimethylsilane (Sioxd) were prepared according to the reported methods.[16] The molecular structures of Buoxd and Sioxd are shown in Chart 1. Tetrahydrofuran and toluene were dried over sodium and distilled. Pyridine and triethylamine were dried over potassium hydroxide and distilled. All other chemicals were purchased from Beijing Chemical Company (Beijing, China) and used as received.

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer using deuterated chloroform or dimethylsulfoxide-d_6 (DMSO-d_6) as the solvent with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm scale. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Magna 750 Fourier transform infrared spectrometer. Elemental analysis was recorded using an Elementar Vario EL instrument. Differential scan-
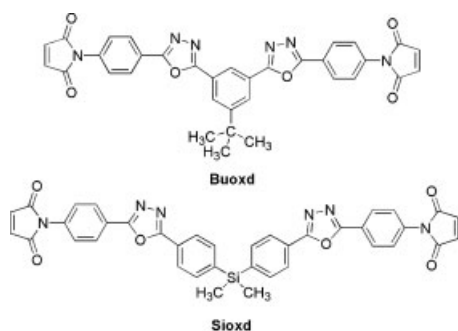

Chart 1. Molecular structures of Buoxd and Sioxd.

ning calorimetry (DSC) was carried out on a Thermal analysis (TA) DSC-2010 in nitrogen at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a TA TGA-DSC Q600 thermogravimetric analyzer at a heating rate of 10°C/min in nitrogen or in the air. Dynamic mechanical analysis (DMA) of composites comprising the cured diamine-modified BMI resins and glass cloth was performed on a NETZSCH DMA 242 C (NETZSCH, Selb, Germany) with a driving frequency of 1.0 Hz and a scanning rate of 3°C/min in nitrogen. The size of the specimen for DMA measurement was 8 mm × 5 mm × 0.5 mm for the single cantilever mode.

Synthesis

(4-Chlorophenoxy)trimethylsilane (C-1)

4-Chlorophenol (14.5 g, 0.11 mol), pyridine (16 mL, 0.20 mol), and anhydrous toluene (100 mL) were added to a 250-mL round-bottomed flask with stirring. Chlorotrimethylsilane (15 mL, 0.12 mol) was added dropwise to the stirring solution in an ice bath. After the addition, the reaction solution was warmed to room temperature and stirred for 8 h. The solution was then filtered and the filtrate was concentrated by rota-evaporation to yield a liquid residue, which was then vacuum-distilled to give the liquid product (20.0 g, 91% yield).

4,4′-Dihydrodiphenyldimethylsilane (C-2)

Sodium (4.6 g, 0.20 mol) and anhydrous toluene (100 mL) were put into a 500-mL three-necked round-bottomed flask equipped with a dropping funnel, a thermometer, and a reflux condenser. The apparatus was purged with argon. A uniform dispersion of the sodium as tiny beads in anhydrous toluene was achieved by heating the mixture to a temperature of 110°C under vigorous stirring, followed by cooling to 80°C. A solution of **C-1** (20.0 g, 0.10 mol) and dichlorodimethylsilane (6.0 mL, 50 mmol) in anhydrous toluene (20 mL) was prepared and added dropwise into the flask in 40 min. The reaction mixture was kept refluxing for 4 h. Upon cooling to room temperature, methanol (10 mL) was added slowly to the reaction solution to consume the excess amount of sodium. The solution was then washed with distilled water (3 × 100 mL) in a separatory funnel and concentrated to half of the volume by rota-evaporation. The residue solution was added to hydrochloric acid (1N, 15 mL) and stirred for 30 min. The organic layer was then separated, washed with distilled water, and dried over anhydrous magnesium sulfate. After removal of the solvent by rota-evaporation, the viscous liquid was stored at 0°C to give the crystalline product, which was further

purified by recrystallization from toluene (6.1 g, 50% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.489 [s, 6H, Si(CH_3)$_2$], 6.83 (d, J = 8.4 Hz, 4H, ArH), 7.39 (d, J = 8.6 Hz, 4H, ArH). Anal. Calcd. for C$_{14}$H$_{16}$O$_2$Si: C, 68.81; H, 6.60. Found: C, 68.75; H, 6.63. MS (EI): 244 (found).

N-(4-Hydroxyphenyl)maleimide (C-3)

This compound was synthesized according to the literature method.[11] IR (KBr, cm^{-1}): 3483 (v$_{O-H}$), 1703 (v$_{C=O}$ of maleimide). ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.07 (s, 1H, —OH), 6.85 (s, 2H, —CH=CH—), 6.90 (d, J = 9.0 Hz, 2H, ArH), 7.18 (d, J = 9.3 Hz, 2H, ArH). Anal. Calcd. for C$_{10}$H$_7$NO$_3$: C, 63.49; H, 3.73; N, 7.40. Found: C, 63.42; H, 3.80; N, 7.46.

4,4′-Diacylchroridediphenylsilane (C-4)

4,4′-Dicarboxyldiphenyldimethylsilane (30.0 g, 0.10 mol) was mixed with thionyl chloride (300 mL) in a 500-mL round-bottomed flask. The reaction mixture was heated slowly to a temperature of 80°C and stirred at the temperature for 1 h. After cooling down to room temperature, the excess thionyl chloride was removed by rota-evaporation to obtain a solid residue (33.7 g, 100% yield).

Bis[4-(4-maleimidophenylcarbonyloxy)phenyl] dimethylsilane (BMI-SiE1)

To an ice-cold solution of 4-maleimidobenzoic acid chloride (14.0 g, 60 mmol) in chloroform (200 mL) in a 500-mL round-bottomed flask, a solution of 4,4′-dihydrodiphenyldimethylsilane (6.1 g, 25 mmol) and triethylamine (9 mL, 62 mmol) was added dropwise in a mixture solvent of chloroform (100 mL) and N,N-dimethylformamide (10 mL). The reaction solution was then warmed to room temperature and stirred for 8 h. The solution was washed in a separatory funnel with distilled water (3 × 100 mL), dried over anhydrous magnesium sulfate, and rota-evaporated to give the yellow solid product. Recrystallization from DMF/ethanol (2 : 1, v/v) gave the pure BMI-SiE1 (12.0 g, 75% yield). IR (KBr, cm^{-1}): 1711 (v$_{C=O}$ of maleimide), 1603, 1511 (aromatic rings), 1144 (v$_{C-N-C}$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.59 [s, 6H, Si(CH$_3$)$_2$], 6.91 (s, 4H, —CH=CH—), 7.24 (d, J = 8.4 Hz, 4H, ArH), 7.60 (d, J = 9.0, 4H, ArH), 7.61 (d, J = 8.4 Hz, 4H, ArH), 8.32 (d, J = 9.0 Hz, 4H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$): −2.20, 121.36, 125.30, 128.46, 131.08, 134.45, 135.57, 135.67, 136.04, 151.84, 164.24, and 168.86. Anal. Calcd. for C$_{36}$H$_{26}$N$_2$O$_8$Si: C, 67.28; H, 4.08; N, 4.36. Found: C, 66.85; H, 4.23; N, 4.26. MS(EI): 642 (found).

### Bis[4-(4-maleimidophenyloxycarbonyl)phenyl] dimethylsilane (BMI-SiE2)

To an ice-cold solution of 4,4′-diacylchroridediphenylsilane (26.9 g, 80 mmol) in tetrahydrofuran (200 mL) in a 1000-mL round-bottomed flask, a solution of N-(4-hydroxyphenyl)maleimide (34.0 g, 0.18 mol) and triethylamine (26 mL, 0.18 mol) was added dropwise in tetrahydrofuran (400 mL). After the addition, the reaction solution was warmed to room temperature and stirred for 8 h before being quenched by pouring into distilled water (2000 mL). The resulting yellow precipitate was collected by suction filtration, washed with distilled water, and dried in an oven at 80°C. Recrystallization from DMF/ethanol (2 : 1, v/v) gave the pure BMI-SiE1 (41.1, 80% yield). IR (KBr, cm^{-1}): 1712 (v$_{C=O}$ of maleimide), 1600, 1508 (aromatic rings), 1143 (v$_{C-N-C}$). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.66 [s, 6H, Si(CH$_3$)$_2$], 6.88 (s, 4H, —CH=CH—), 7.34 (d, J = 9.0 Hz, 4H, ArH), 7.45 (d, J = 9.0 Hz, 4H, ArH), 7.69 (d, J = 8.4 Hz, 4H, ArH), 8.19 (d, J = 8.4 Hz, 4H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$): −2.83, 122.36, 126.94, 128.79, 129.26, 129.97, 134.20, 134.29, 144.67, 150.03, 164.76, and 169.26. Anal. Calcd. for C$_{36}$H$_{26}$N$_2$O$_8$Si: C, 67.28; H, 4.08; N, 4.36. Found: C, 66.80; H, 4.23; N, 4.30. MS(EI): 642 (found).

Preparation of polyaspartimides and cured diamine-modified BMI resins

A general preparation procedure for the polyaspartimides is as follows: A mixture solution of BMI monomer (17 mmol) (e.g., Buoxd, Sioxd, BMI-SiE1 or BMI-SiE2), 4,4′-diaminodiphenylether (DPE) (17 mmol), and glacial acetic acid (0.1 mL) in m-cresol (40 mL) was heated to 100°C and stirred at the temperature for 10 h in argon. The reaction solution was poured into 500 mL of methanol with vigorous stirring. The precipitated polyaspartimide was collected by suction filtration, washed thoroughly with methanol (100 mL ×3), and dried at 60°C under vacuum for 8 h. The cured diamine-modified BMI resins were obtained by curing the polyaspartimides at 250°C for 1 h in an oven open to the air.

Preparation of cured diamine-modified BMI resin/ glass cloth composites

A general preparation procedure is described as follows: A polyaspartimide was dissolved in DMF at a concentration of 0.2 g/mL. A glass cloth of 8 mm × 5 mm × 0.5 mm was dipped into the solution and then vertically hung. The solvent was allowed to evaporate at 40°C in a dry box in the presence of concentrated sulfuric acid. The samples were cured in a closed steel mold at a high pressure at 250°C for 1 h. The weight percentage of the resin in the final
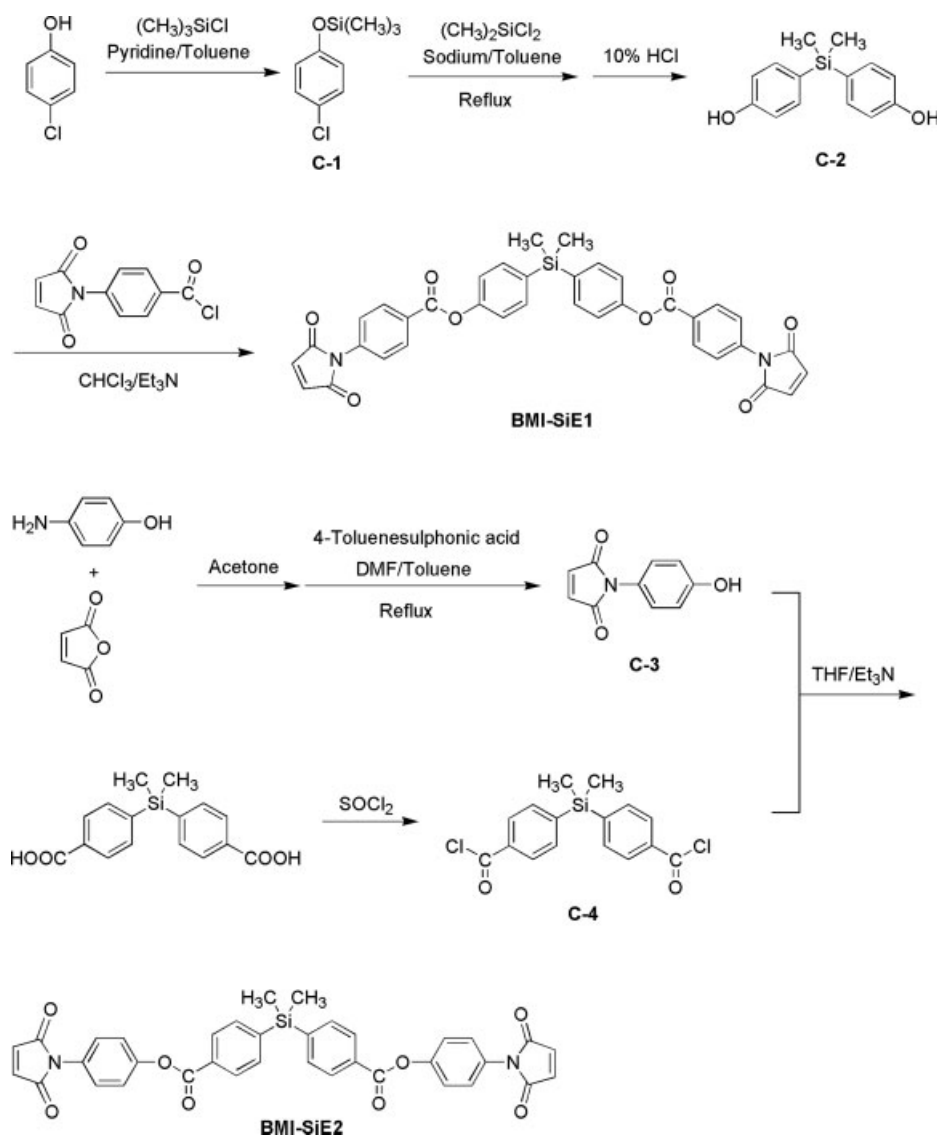
Scheme 1 Synthetic route for BMI monomers BMI-SiE1 and BMI-SiE2.

composite was determined to be around 50% by calculating the difference in the weights of the bare glass cloth and the composite.

RESULTS AND DISCUSSION

Synthesis and characterization of BMI monomers

Polymers containing silicon atoms in the structure have been extensively studied for their potential applications in both electronics and aerospace due to their good solubility, high thermo-oxidative stability, excellent toughness, and moisture resistance. In our study, silicon-containing BMI resins are of interest since the solubility and toughness of BMI resins might be improved by incorporating silicon atom in the molecular backbone. Thus, two new BMI monomers having a silicon atom in the structure (i.e.,

BMI-SiE1 and BMI-SiE2) were designed and synthesized. To improve the toughness of BMI resins, flexible ester bonds were also introduced into the structure. Considering that different orientation of ester bond may lead to different materials properties, BMI-SiE1 and BMI-SiE2 having opposite ester bond orientation were prepared. Scheme 1 illustrates the synthesis of BMI-SiE1 and BMI-SiE2. The chemical structures of BMI-SiE1 and BMI-SiE2 were confirmed by a combination of analytical techniques, i.e., IR, ^{1}H NMR, ^{13}C NMR, mass spectra, and elemental analysis. Figure 1 shows the ^{1}H NMR spectra of BMI-SiE1 and BMI-SiE2 in CDCl$_3$.

The solubility of BMI-SiE1 and BMI-SiE2 was tested in different solvents. As shown in Table I, both monomers were readily soluble in polar aprotic solvents, such as N-methyl-2-pyrrolidinone (NMP), dimethylsulphoxide (DMSO), and N, N-dimethylform-
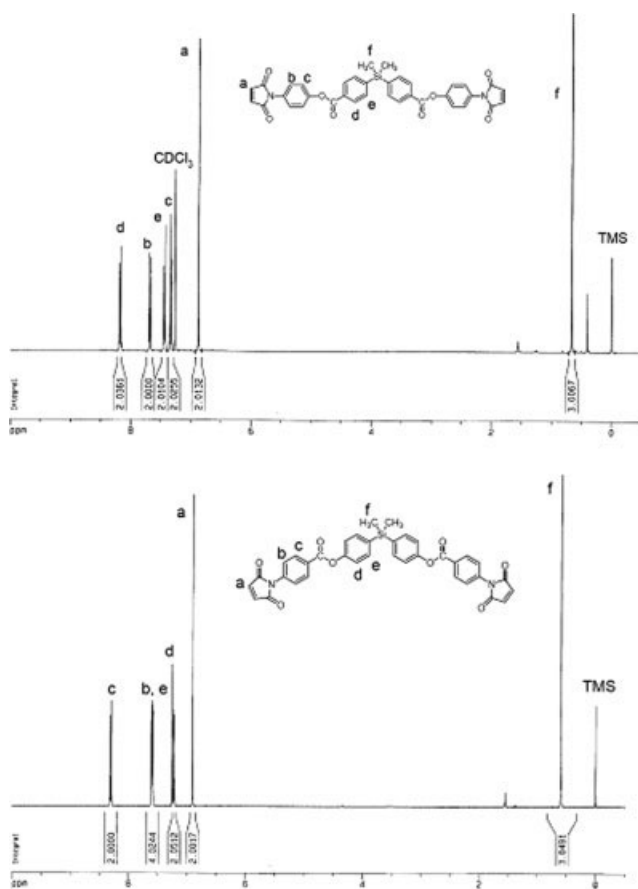
Figure 1 ¹H NMR spectra of BMI-SiE1 and BMI-SiE2 in CDCl₃.

amide (DMF), as well as less polar solvents such as chloroform and dichloromethane, indicating their good solution processability.

The thermal properties of BMI-SiE1 and BMI-SiE2 were investigated with DSC (Fig. 2 and Table II). BMI-SiE1 and BMI-SiE2 showed sharp endothermic melting transitions at 263 and 243°C, respectively, in their first DSC heating scans and broad exothermic transitions at 269 and 247°C, respectively, attributable to the polymerization reaction of maleimido groups.

To better understand the structure–property relationship of these two monomers, Buoxd and Sioxd (Chart 1) were used for comparison. Both Buoxd and Sioxd contain two 1,3,4-oxadiazole moieties in the

structure, but differ from each other in that the Buoxd has a wholly aromatic structure with a bulky *tert*-butyl group attached to the central phenyl ring, whereas Sioxd has a silicon atom in the center. Thermal properties of Buoxd and Sioxd have been reported in the previous publications (Table II).[16,17]

All the BMI monomers (BMI-SiE1 and BMI-SiE2, Buoxd and Sioxd) can be cured after the first heating scan (10°C/min to 350°C in nitrogen). No transition can be seen in the second heating scan from 50 to 350°C, indicating that the glass transition temperatures of all the cured BMI resins were above 350°C. TGA was used to study the thermal and thermo-oxidative stability of the cured BMI resins (Fig. 3). The onset decomposition temperature for 5% weight loss (T_d) was recorded (Table II). All the cured BMI resins (i.e., PBuoxd, PSioxd, PSiE1, and PSiE2) showed high thermal stability ($T_d > 450°C$ in nitrogen) and high thermo-oxidative stability ($T_d > 400°C$ in the air). It is interesting to see that although PSiE1 and PSiE2 have very similar molecular structures, PSiE2 showed a better thermal and thermo-oxidative stability. The T_d of PSiE2 is around 20°C higher than that of PSiE1 both in nitrogen and in the air. PSioxd showed lower T_d in the air than that of PSiE1 and PSiE2, indicating that the ester bond in these monomers is more thermo-oxidatively stable than 1,3,4-oxadiazole. Char yield (Y_c, at 700°C) is an important parameter of consideration for high performance materials. As shown in Table II, all the cured BMI resins showed a similar char yield at 700°C (around 45%) in nitrogen. However, for the TGA analysis of the thermo-oxidative stability in the air, PBuoxd that contains no silicon atom in the structure exhibited a zero char yield, whereas all the silicon-containing BMI resins (i.e., PSioxd, PSiE1, and PSiE2) showed a nonzero char yield in the range of 3–12%, which might be attributed to the formation of silica during the decomposition in the air.[18]

Preparation and characterization of polyaspartimides

BMI resins modified by diamine compound, which were named as polyaspartimides, have been explored to improve the fracture toughness of BMI resins by decreasing the crosslinking density.[14,15]

TABLE I
Solubility of BMI-SiE1 and BMI-SiE2 in Different Solvents[a]

	Toluene	Acetone	DCM	Chloroform	DMAc	DMF	DMSO	NMP
BMI-SiE1	− −	− −	++	++	++	++	++	++
BMI-SiE2	− −	− −	++	++	++	++	++	++

DCM, dichloromethane; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulphoxide; NMP, *N*-methyl-2-pyrrolidinone.
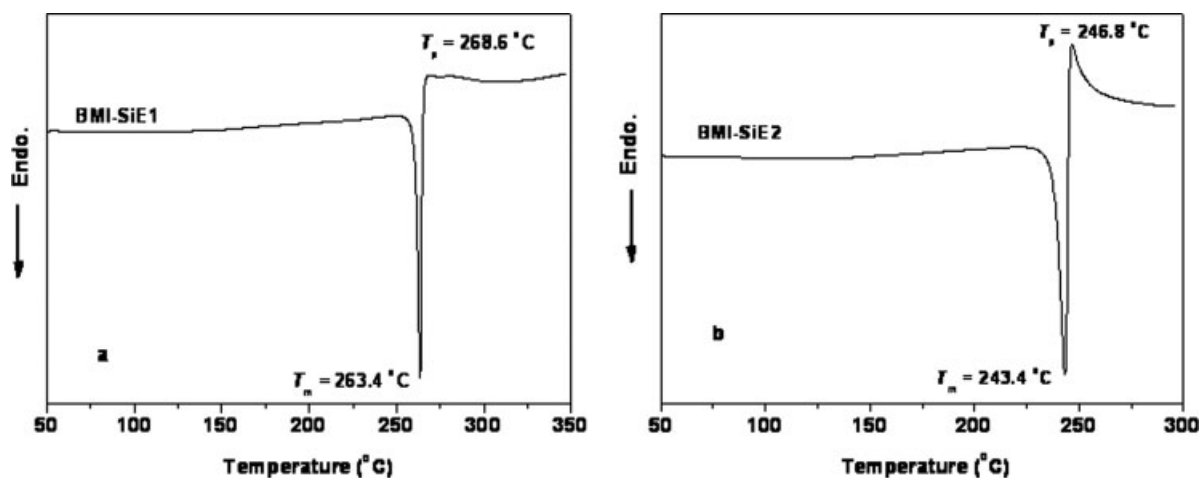[a] "++" = soluble (≥10 mg/mL); "− −" = insoluble.

Figure 2 DSC curves of BMI-SiE1 and BMI-SiE2 at a heating rate of 10°C/min in nitrogen.

Some of the polyaspartimides are already commercially available such as Kerimid (Rhone-Poulenc) and Compimide (Shell Chemical Company). In this work, the four BMI monomers, i.e., Buoxd, Sioxd, BMI-SiE1, and BMI-SiE2, were polymerized with 4,4'-diaminodiphenylether (DPE), respectively, via the Michael addition reaction to yield polyaspartimides, i.e., BuDPE, SiDPE, SiE1DPE, and SiE2DPE in the corresponding order (Scheme 2). A slightly acidic reaction medium (e.g., glacial acetic acid) was employed to facilitate protonation of intermediate species and to minimize reactions between the resulting imines and other maleimide units.[15]

The molecular structures of the resulting polyaspartimides, i.e., BuDPE, SiDPE, SiE1DPE, and SiE2DPE, were confirmed by ^{1}H NMR spectra as shown in Figure 4. Protons with chemical shifts in the range of 6.5–8.5 ppm are attributable to the aromatic rings. The primary and the secondary amine groups are observed at 4.8 ppm ($-NH_2$) and 6.0 ppm ($-NH-$), respectively. The peaks at 2.7 ppm ($-CH_2-$) and 3.3 ppm ($-CH-N-$) are attributable to the succinimide groups. The characteristic single peak for the maleimide groups at 7.2 ppm was observed for all the polyaspartimides, indicating that all the resulting polyaspartimides could be cured through homopolymerization of maleimide groups by heating. Furthermore, the number-average molecular weight (M_n) of the resulting polyaspartimides could be calculated using the ^{1}H NMR spectra by the following equations

$$\text{Int[maleim ido]}/\text{Int[side group]} = n_{male}/[n_{side}(n+1)];$$

$$M_n = X_n(n+1)$$

where Int[maleimido] and Int[side group] are the integral of peaks for protons of the maleimide groups and of the side groups (i.e., *tert*-butyl group and methyl group), respectively; n_{male} and n_{side} are the number of the protons of maleimide group and the side group, respectively, in the molecular structure;

TABLE II
Thermal Properties of BMI Monomers and Cured BMI Resins

Monomers	T_m (°C)[a]	T_p (°C)[b]	PBMI[c]	T_d (°C)[d]		Y_c (%)[e]	
				In N$_2$	In air	In N$_2$	In air
Buoxd	287.6	290.4	PBuoxd	453.8	400.6	46.0	0
Sioxd	263.1	280.7	PSioxd	461.5	415.6	48.9	11.5
BMI-SiE1	263.4	268.6	PSiE1	453.5	427.5	45.1	8.0
BMI-SiE2	243.4	246.8	PSiE2	475.8	444.5	49.7	3.0

[a] Melting transition temperature determined from the first DSC heating scan in nitrogen with a heating rate of 10°C/min.
[b] Exothermic polymerization temperature determined from the first DSC heating scan in nitrogen with a heating rate of 10°C/min.
[c] The cured BMI resins.
[d] The 5% weight loss temperature determined from TGA at a heating rate of 10°C/min.
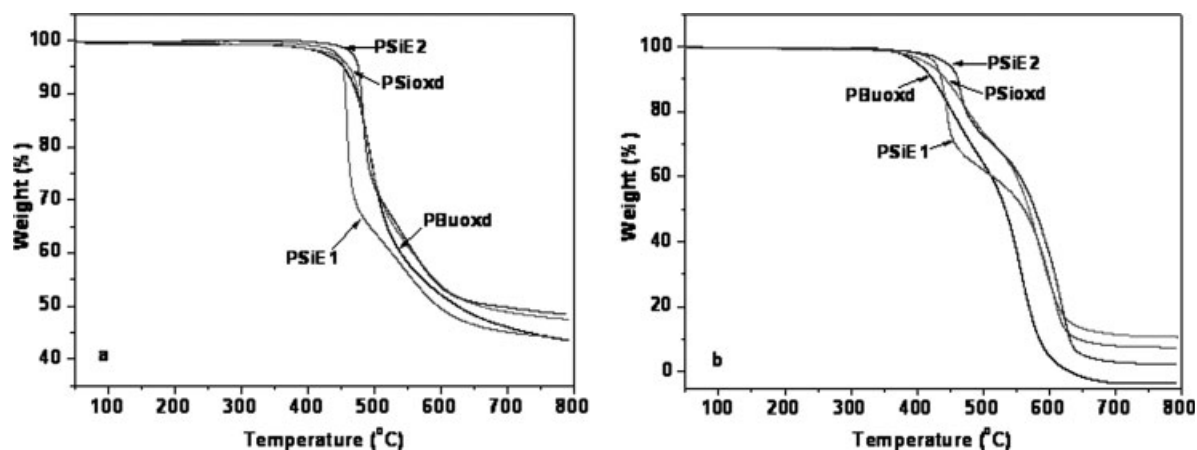[e] Char yield at 700°C determined from the TGA analysis.

Figure 3 TGA curves of cured BMI resins at a heating rate of 10°C/min in nitrogen (a) and in the air (b).

X_n is the molecular weight of the repeat unit and n is the number of repeat unit. Thus, the average molecular weight (M_n) of polyaspartimides can be calculated to be 1686 ($n = 1.07$), 1916 ($n = 1.15$), 2198 ($n = 1.61$), and 1970 ($n = 1.34$) for BuDPE, SiDPE, SiE1DPE, and SiE2DPE, respectively.

Properties of cured diamine-modified BMI resins and their composites

Polyaspartimides were cured at 250°C for 1 h to yield the cured diamine-modified BMI resins, i.e.,

PBuDPE, PSiDPE, PSiE1DPE, and PSiE2DPE. Thermal and thermo-oxidative stability of the cured diamine-modified BMI resins was first studied by TGA in nitrogen [Fig. 5(a)] and in the air [Fig. 5(b)], respectively, and the onset temperatures for 5% weight loss (T_d) were recorded. As shown in Table III, all the cured diamine-modified BMI resins displayed a T_d in the range of 340–360°C in nitrogen and in the range of 330–360°C in the air, which was lower than the corresponding values of the cured BMI resins that were not modified using diamines (i.e., PBuoxd, PSioxd, PSiE1, and PSiE2), indicating
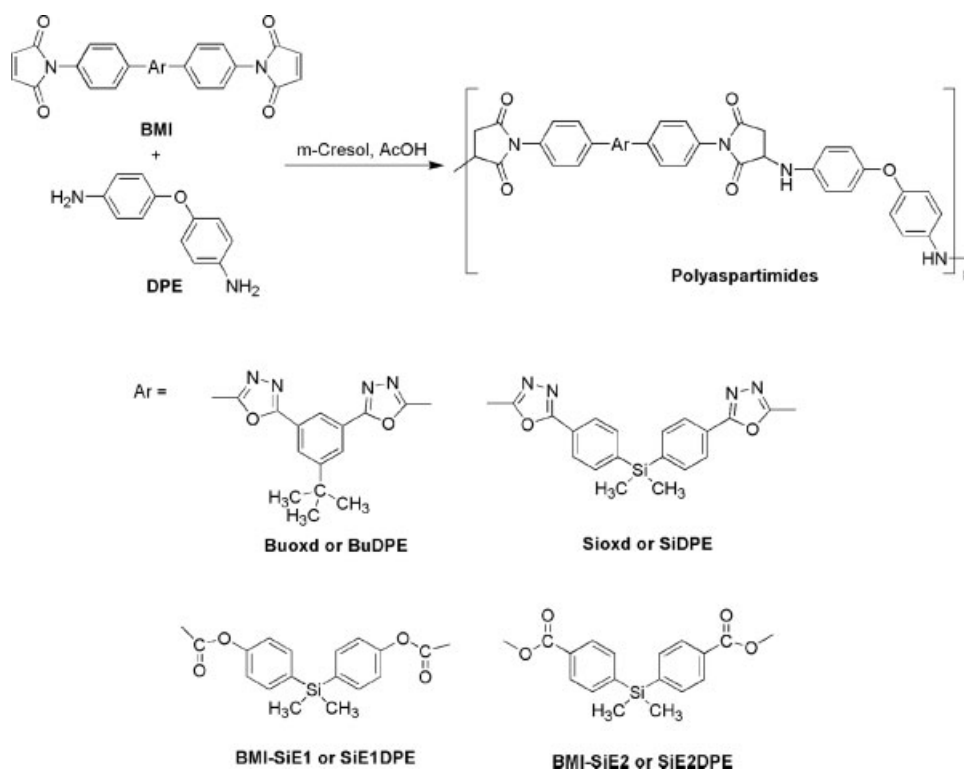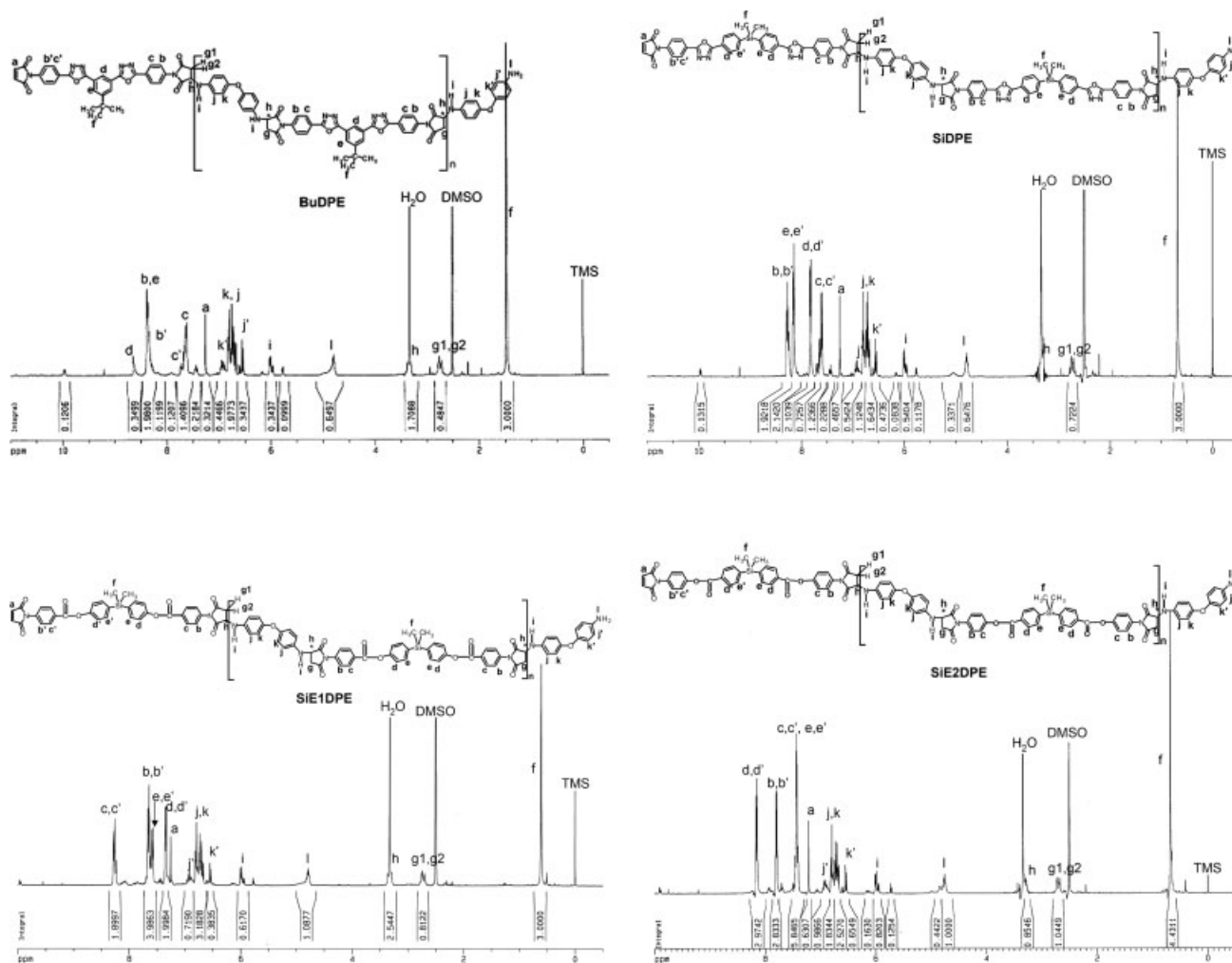

Scheme 2 Synthesis of polyaspartimides.

Figure 4 ^{1}H NMR spectra of polyaspartimides in DMSO-d_6.

that the modification by using 4,4′-diaminodiphenyl-ether (DPE) reduced the thermal and thermo-oxidative stability of the cured BMI resins. Furthermore, although PSiE1DPE and PSiE2DPE have the similar molecular structures, the latter is more thermally stable both in nitrogen and in the air. Char yields (Y_c, at 700°C) of the resulting diamine-modified BMI resins are shown in Table III. All of them showed a
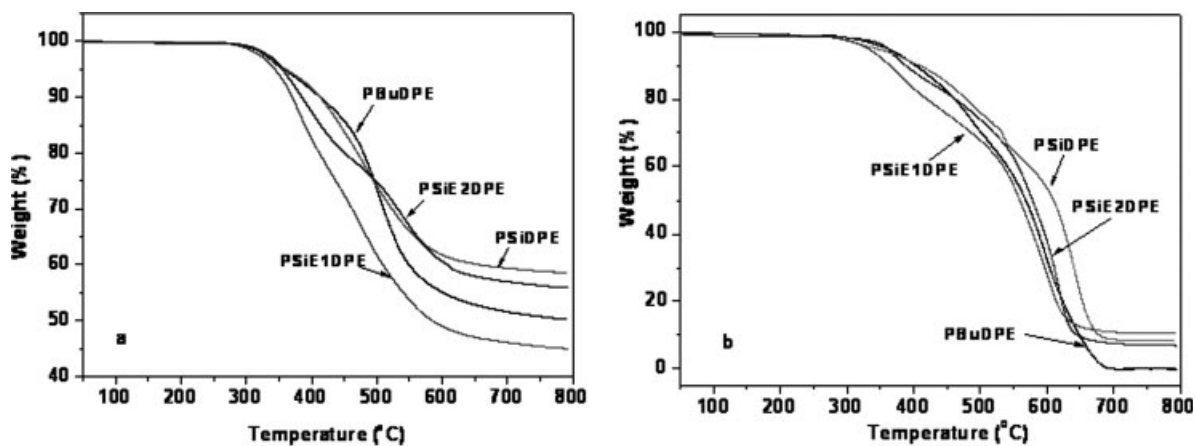

Figure 5 TGA curves of cured diamine-modified BMI resins at a heating rate of 10°C/min in nitrogen (a) and in the air (b).

TABLE III
Thermal Properties of Cured Diamine-Modified BMI Resins

PBMIDPE	$T_g{}^a$ (°C)	$T^{d,b}$ (°C)		$Y^{e,c}$ (%)	
		In N$_2$	In air	In N$_2$	In air
PBuDPE	302.3	357.0	359.8	51.6	0
PSiDPE	>350	360.0	343.6	59.4	8.8
PSiE1DPE	193.9	343.5	331.5	46.4	10.9
PSiE2DPE	206.6	355.4	360.3	57.0	7.6

[a] Melting transition temperature determined from the first DSC heating scan in nitrogen with a heating rate of 10 °C/min.
[b] Exothermic polymerization temperature determined from the first DSC heating scan in nitrogen with a heating rate of 10 °C/min.
[c] The cured BMI resins.
[d] The 5% weight loss temperature determined from TGA at a heating rate of 10 °C/min.
[e] Char yield at 700 °C determined from the TGA analysis.

char yield in the range of 46–59% in nitrogen and 0–11% in the air at 700°C. All the silicon-containing BMI resins (i.e., PSiDPE, PSiE1DPE, and PSiE2DPE) showed nonzero char yield in the air, which might contribute to a good flame retardancy.[18]

DMA was used to study the dynamic mechanical properties of composites derived from the cured diamine-modified BMI resins and glass cloth (Fig. 6). The composites were prepared by dipping a glass cloth of 8 mm × 5 mm × 0.5 mm into a DMF solution of the polyaspartimides at a concentration of 0.2 g/mL, followed by drying the composites in a dry box at 40°C in the presence of sulfuric acid. The samples were cured in a closed steel mold at a high pressure at 250°C for 1 h. Composites exhibited good bending modulus at 50°C (E' = 1000–2700 MPa) and high modulus retentions (e.g., >90%) at 150°C (for composites based on PSiE1DPE and PSiE2DPE) or at 250°C (for composites based on PBuDPE and PSiDPE).

The glass transition temperatures (T_g) of the resulting composites were defined by the tanδ peak temperatures (Fig. 6 and Table III). It is known that T_g values of thermoset materials are typically determined by two main factors: the molecular structure and the crosslinking density. In this study, as described earlier, all the resulting polyaspartimides have similar molecular weight ($M_n \approx 2000$) and number of repeat unit [n = 1.0(1.6)]. Therefore, a similar crosslinking density should be expected for cured diamine-modified BMI resins derived from these polyaspartimides. As a result, the T_g values may be mainly determined by the molecular structures of the cured diamine-modified BMI resins. In comparison, composites based on PSiE1DPE and PSiE2DPE showed much lower T_g values at 194 and 207°C, respectively, than those of composites based on PBuDPE (302°C) and PSiDPE (>400°C), indicating that 1,3,4-oxadiazole moieties contributed more to
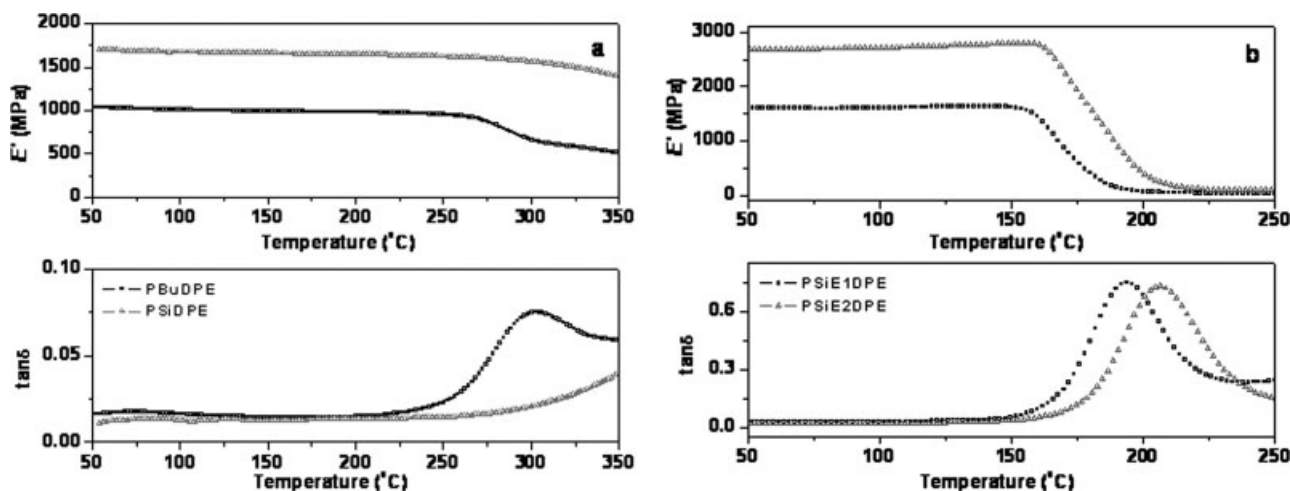

Figure 6 DMA curves of BMI composites composed of cured diamine-modified BMI resins and glass cloth at a heating rate of 3°C/min in nitrogen with a single cantilever mode.

the molecular rigidity while silicon and ester bond increased the flexibility of the molecular structure.

CONCLUSIONS

Two novel BMI monomers (i.e., BMI-SiE1 and BMI-SiE2) containing silicon were prepared and polymerized with and without the use of 4,4′-diaminodiphenylether (DPE) as comonomer. Both monomers have good solubility in common organic solvents, high melting temperatures ($T_m > 243°C$), and high polymerization temperatures ($T_p > 247°C$). TGA investigations showed high thermal stability ($T_d > 450°C$ in nitrogen) and high thermo-oxidative stability ($T_d > 400°C$ in the air) for the thermally cured BMI resins. Copolymerization of BMI-SiE1 and BMI-SiE2 with DPE via the Michael addition reaction yielded polyaspartimides. Thermal curing of these polyaspartimides at 250°C for 1 h led to the formation of cured diamine-modified BMI resins. TGA investigations showed that all the cured diamine-modified BMI resins displayed lower T_d (340–360°C in nitrogen and 330–360°C in the air) than those of the cured BMI resins derived directly from BMI-SiE1 and BMI-SiE2.

Composites of the cured diamine-modified BMI resins and glass cloth were prepared and showed high bending modulus (1000–2700 MPa).

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