

Synthesis and properties of 1,3,4-oxadiazole-containing high-performance bismaleimide resins

Haoyu Tang^a, Naiheng Song^a, Zihong Gao^a, Xiaofang Chen^a, Xinghe Fan^{a,*},
Qian Xiang^b, Qifeng Zhou^{a,*}

^a Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^b State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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Abstract

Two novel bismaleimide (BMI) monomers containing 1,3,4-oxadiazole, i.e., 5-*tert*-butyl-1,3-di[5-(4-maleimidophenyl)-1,3,4-oxadiazole-2-yl]-benzene (Buoxd) and 4,4'-[5-(4-maleimidophenyl)-1,3,4-oxadiazole-2-yl]diphenyldimethylsilane (Sioxd), were designed, synthesized and copolymerized with 4,4'-bismaleimidodiphenylmethane (BMDM) to yield a new series of high-performance bismaleimide resins. Both monomers obtained are readily soluble in common organic solvents, such as dichloromethane and chloroform, enabling an easy solution processing. The thermal properties of the two monomers were carefully studied by the differential scanning calorimetry (DSC), optical microscopy and thermogravimetric analysis (TGA, simultaneous DSC). The BMI resins based on a mixture of Buoxd (or Sioxd) and BMDM in a weight ratio of 10% were prepared. DSC investigations showed that the thermal curing of the BMI resins could be accomplished at a lower temperature than the thermal curing temperatures of Buoxd and Sioxd, and the thermal processing window, i.e., the temperature range between the melting transition and thermal curing process, was over 26 °C. The thermal properties and thermal mechanical properties of the resulting BMI resins were investigated by DSC, thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). No glass transition temperature was found in the range of 50–350 °C, and very good thermal stability ($T_d > 490$ °C in nitrogen) and high thermo-oxidative stability ($T_d > 460$ °C in air) were revealed. Composites composed of the above BMI resins and glass cloth were also prepared, which showed high bending modulus (>1.6 GPa) at a very high temperature (e.g., 400 °C). © 2006 Elsevier Ltd. All rights reserved.

Keywords: High-performance polymer; 1,3,4-Oxadiazole; Bismaleimide

1. Introduction

Aromatic poly(1,3,4-oxadiazole) is a class of chemically resistant and thermally stable heterocyclic polymers having high glass transition temperatures (T_g) and melting temperatures (T_m). These polymers were studied as high temperature and flame resistant fibers or thermally stable films [1,2]. Many kinds of thermally stable polymers based on 1,3,4-oxadiazoles have been synthesized and studied, such as

polyamides [3,4], poly(arylene ether)s [5,6] and polyimides [7]. However, these polymers generally possess poor solubility and do not melt, and therefore are difficult to process. Much effort has been made to improve the processability of 1,3,4-oxadiazole-containing polymers, such as to find new solution system (nitromethane/Lewis acid [8]), and to modify the structures by introducing bulky substituents [9,10], by copolymerization [11] or by incorporation of flexible linkages in the backbone [12]. However, all these methods were found to be not so efficient in improving the processability.

Our group has taken another way to improve the processing features of 1,3,4-oxadiazole based polymers, that is to take advantage of the good processability of small molecules (or oligomers) that have functionalities enabling an in situ

* Corresponding authors. Tel.: +86 10 62772417; fax: +86 10 62751708.

E-mail addresses: fanxh@chem.pku.edu.cn (X. Fan), qfzhou@pku.edu.cn (Q. Zhou).

polymerization (or crosslinking) after forming the shape. In another word, we are interested in designing and synthesizing thermally polymerizable monomers containing 1,3,4-oxadiazoles moieties.

Many types of thermally reactive groups, such as acetylene [13], cyanate [14], benzoxazine [15], maleimide [16], are known. When a molecule contains two maleimide groups at the ends, it is called bismaleimide (BMI) that can be homopolymerized in situ by heating without addition of a free radical initiator [17,18] to produce thermosetting polyimides. Bismaleimide resins are known to have high temperature performance, high toughness and low cost. They have become one of the most important high-performance thermosetting engineering plastics that have found wide applications in both microelectronics and aerospace, such as in multilayer printed circuit boards, advanced composite for aerospace industries and structural adhesives [19–22]. To date, many types of bismaleimides have been synthesized and characterized, such as bismaleimides containing rigid rod amides and esters [23–25], polysiloxane [26], naphthalene [27,28], phosphorus [29,30] and epoxy backbone [31–33]. Bismaleimides containing one 1,3,4-oxadiazole moiety have also been reported. For example, Varma and Fohlen [34] synthesized a bismaleimide monomer (*p*-BMPO) containing one 1,3,4-oxadiazole and studied its thermal properties; Mehrabani and Pindur [35] used *p*-BMPO as a dienophile to synthesize a new biscarbazole, which is potentially useful as DNA ligands; Zhang and Jin [36] studied the fluorescence behavior of *p*-BMPO during copolymerization with 4,4'-diaminodiphenyl methane.

In this paper we report the synthesis and characterization of two novel bismaleimides (i.e., Buoxd and Sioxd) containing two 1,3,4-oxadiazole moieties in the structure. The preparation of BMI resins based on these monomers was also described. The thermal analysis (DSC, TGA and DMA) results showed that the resulting BMI resins and composites composed of the resins and glass cloth had very high thermal stability ($T_d > 490$ °C in nitrogen, >460 °C in air) and very high bending modulus (e.g., >1.6 GPa) even at high temperatures (e.g., 400 °C).

2. Experimental

2.1. Materials

5-*tert*-Butyl-isophthalic acid was purchased from Tokyo Chemical Industry and used as received. 4,4'-Bismaleimido-diphenylmethane (BMDM) was purchased from Yantai Hengxing Chemical Industrial Technologic Company and was purified by silica gel column chromatography. Toluene was dried over sodium and distilled. All other chemicals were purchased from Beijing Chemical Company and used directly.

2.2. Characterization

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometers using deuterated chloroform or dimethylsulfoxide- 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 scanning calorimetry (DSC) was recorded with a Thermal Analysis (TA) DSC-2010 in nitrogen. Thermogravimetric analysis (TGA) was performed on a TA TGA–DSC Q600 thermogravimetric analyzer at a heating rate of 10 °C/min in either nitrogen or air atmosphere. Dynamic mechanical analysis (DMA) of composites composed of 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 atmosphere. The size of the specimen for the DMA measurement was 8 mm \times 5 mm \times 0.5 mm for the single cantilever mode.

2.3. Synthesis

2.3.1. Synthesis of 4-maleimido benzoic acid (C-2)

To a solution of *p*-aminobenzoic acid (87.2 g, 0.636 mol) in acetone (500 mL) was added dropwise a solution of maleic anhydride (63.7 g, 0.650 mol) in acetone (200 mL) in 1 h under stirring. After the addition, the reaction solution was stirred at room temperature for another 4 h. The resulting yellowish precipitate (C-1, Scheme 1) was collected by filtration, washed with acetone (500 mL) and dried in an oven at 80 °C overnight (68.0 g, 91% yield). C-1 (68.0 g) and sodium acetate (19.2 g) were added to acetic anhydride (250 mL) and the mixture was stirred at 80 °C for 10 h. The mixture was poured into 1500 mL of distilled water with stirring. The resulting light yellow precipitate was collected by suction filtration, washed thoroughly with distilled water and dried in an oven at 80 °C overnight. Recrystallization from DMF/H₂O (1/1, v/v) gave pure C-2 (44.1 g, 69% yield). IR (KBr, cm⁻¹): 3102 ($\nu_{\text{O-H}}$ of carboxylic acid), 1711 ($\nu_{\text{C=O}}$ of maleimide). ^1H NMR (300 MHz, DMSO- d_6): δ 7.24 (s, 2H, $-\text{CH}=\text{CH}-$), 7.51 (d, $J=8.4$ Hz, 2H, ArH), 8.06 (d, $J=9.3$ Hz, 2H, ArH), 13.13 (s, 1H, $-\text{COOH}$). Anal. Calcd. for C₁₁H₇NO₄: C, 60.83; H, 3.25; N, 6.45. Found: C, 60.68; H, 3.39; N, 6.29. MS (EI): 217 (found).

2.3.2. Synthesis of 4-maleimido benzoic acid chloride (C-3)

To a suspension of 4-maleimido benzoic acid (14.0 g, 64.5 mmol) in 1,2-dichloroethane (200 mL) in a 500 mL round-bottomed flask, thionyl chloride (38 mL) was added. The reaction mixture was heated slowly to a temperature of 80 °C and stirred at the temperature overnight. After cooling down to room temperature, 1,2-dichloroethane and the excess amount of thionyl chloride were removed by rota-evaporation. The residue was recrystallized from 1,2-dichloroethane to give the pure C-3 (9.2 g, 60% yield).

2.3.3. Synthesis of 4,4'-dimethyldiphenyldimethylsilane (C-4) and 4,4'-dicarboxyldiphenyldimethylsilane (C-5)

Sodium (4.6 g, 0.20 mol) and anhydrous toluene (100 mL) were put into a 500 mL three-neck round-bottomed flask equipped with a dropping funnel, a thermometer and a reflux

(6.0 g, 95% yield). IR (KBr, cm^{-1}): 2960 ($\nu_{\text{O-H}}$ of carboxylic acid), 1691 ($\nu_{\text{C=O}}$ of carboxylic acid). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 0.60 (s, 6H, $-\text{CH}_3$), 7.66 (d, $J = 8.0$ Hz, 4H, ArH), 7.93 (d, $J = 8.2$ Hz, 4H, ArH), 13.02 (s, 2H, $-\text{COOH}$). Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Si}$: C, 63.98; H, 5.37. Found: C, 63.75; H, 5.38. MS (EI): 300 (found).

2.3.4. Synthesis of 5-tert-butyl-isophthalic acid diethyl ester (**C-6a**) and 4,4'-dicarboxylesterdiphenyldimethylsilane (**C-6b**)

To a suspension solution of 5-tert-butyl-isophthalic acid (20.0 g, 90.0 mmol) in ethanol (200 mL) was added concentrated sulfuric acid (2 mL). The reaction mixture was heated slowly to 80 °C and refluxed overnight. Ethanol was removed by rota-evaporation and the liquid residue was poured into distilled water. The resulting white precipitate was collected by suction filtration, washed with distilled water and dried in an oven at 80 °C. Recrystallization from ethanol/ H_2O (4/1, v/v) gave the pure **C-6a** (21.3 g, 85% yield). IR (KBr, cm^{-1}): 1720 ($\nu_{\text{C=O}}$ of ester). ^1H NMR (300 MHz, CDCl_3): δ 1.38 [s, 9H, $-\text{C}(\text{CH}_3)_3$], 1.42–1.46 (t, $J = 7.2$, 7.2 Hz, 3H, $-\text{CH}_2\text{CH}_3$), 4.36–4.47 (q, $J = 7.0$, 7.0, 7.0 Hz, 2H, $-\text{CH}_2\text{CH}_3$), 8.26 (d, $J = 1.2$ Hz, 2H, ArH), 8.50 (s, 1H, ArH). Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_4$: C, 69.04; H, 7.97. Found: C, 69.17; H, 7.95. MS (EI): 278 (found).

C-6b was synthesized using the same method as described for **C-6a**. Yield: 80%. IR (KBr, cm^{-1}): 1719 ($\nu_{\text{C=O}}$ of ester). ^1H NMR (300 MHz, CDCl_3): δ 0.58 (s, 6H, $-\text{CH}_3$), 1.39 (t, $J = 7.2$, 7.2 Hz, 3H, $-\text{CH}_2\text{CH}_3$), 4.38 (q, $J = 7.2$, 7.2, 7.2 Hz, 2H, $-\text{CH}_2\text{CH}_3$), 7.57 (d, $J = 8.2$ Hz, 4H, ArH), 8.00 (d, $J = 8.0$ Hz, 4H, ArH). Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{Si}$: C, 67.38; H, 6.79. Found: C, 67.18; H, 6.84. MS (EI): 356 (found).

2.3.5. Synthesis of 5-tert-butyl-isophthalic dihydrazide (**C-7a**) and 4,4'-dihydrazidediphenyldimethylsilane (**C-7b**)

An aqueous solution of hydrazine monohydrate (85%, 200 mL) was added to a suspension of **C-6a** (12.0 g, 43.2 mmol) in ethanol (350 mL). The reaction mixture was refluxed for 17 h and then cooled to room temperature. Ethanol was removed by rota-evaporation. The white solid residue was then recrystallized from ethanol to give pure **C-7a** (7.9 g, 75% yield). IR (KBr, cm^{-1}): 1636 ($\nu_{\text{C=O}}$ of hydrazide). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 1.32 [s, 9H, $-\text{C}(\text{CH}_3)_3$], 4.53 (s, 4H, $-\text{NHNH}_2$), 7.95 (d, $J = 1.5$ Hz, 2H, ArH), 8.08 (s, 1H, ArH), 9.86 (s, 2H, $-\text{NHNH}_2$). Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_2$: C, 57.58; H, 7.25; N, 22.38. Found: C, 57.42; H, 7.34; N, 22.44. MS (EI): 250 (found).

C-7b was synthesized using the same method as described for **C-7a**. Yield 85%. IR (KBr, cm^{-1}): 1672 ($\nu_{\text{C=O}}$ of hydrazide). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 0.57 (s, 6H, $-\text{CH}_3$), 4.50 (s, 4H, $-\text{NHNH}_2$), 7.59 (d, $J = 8.1$ Hz, 4H, ArH), 7.80 (d, $J = 8.1$ Hz, 4H, ArH), 9.80 (s, 2H, $-\text{NHNH}_2$). Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2\text{Si}$: C, 58.51; H, 6.14; N, 17.06. Found: C, 58.24; H, 6.06; N, 16.92. MS (EI): 328 (found).

2.3.6. Synthesis of 5-tert-butyl-1,3-di[5-(4-maleimidophenyl)-1,3,4-oxadiazole-2-yl]benzene (Buoxd) and 4,4'-[5-(4-maleimidophenyl)-1,3,4-oxadiazole-2-yl]diphenyldimethylsilane (Sioxd)

In a 250 mL flask, a solution of *N*-methyl-2-pyrrolidinone (NMP, 100 mL) containing LiCl (10.0 g) and **C-7a** (12.5 g, 50.0 mmol) was prepared and cooled in an ice bath. To the stirred solution, a solution of **C-3** (25.8 g, 110 mmol) in NMP (100 mL) was added in one shot. The reaction mixture was stirred at 0 °C for 2 h and then allowed to warm up to room temperature and stirred overnight. The reaction solution was poured into stirring distilled water (2000 mL) and the resulting yellow precipitate was collected by filtration, washed with distilled water and dried in an oven at 80 °C. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 1.41 [s, 9H, $-\text{C}(\text{CH}_3)_3$], 7.25 (s, 4H, $-\text{CH}=\text{CH}-$), 7.55 (d, $J = 8.7$ Hz, 4H, ArH), 8.05 (d, $J = 6.9$ Hz, 4H, ArH), 8.18 (d, $J = 1.5$ Hz, 2H, ArH), 8.34 (s, 1H, ArH), 10.74 (d, $J = 17.6$ Hz, 4H, $-\text{NHNH}-$).

In a 100 mL flask, dry **C-8a** (10.0 g, 15.4 mmol) was dissolved in polyphosphoric acid (PPA, 200 g) by stirring and heating to a temperature of 150 °C. The mixture was then cooled to 120 °C and stirred for 8 h. After cooling down to room temperature, the reaction mixture was poured portionwise into stirring distilled water (2000 mL). The yellow solid precipitate was filtered and washed thoroughly with distilled water. The dried product was subjected to silica gel column chromatography (EtOAc/ CHCl_3 , 1/4, v/v) to give pure Buoxd (4.6 g, yield 50%). IR (KBr, cm^{-1}): 1717 ($\nu_{\text{C=O}}$ of maleimide), 1613 ($\nu_{\text{C=N}}$ of 1,3,4-oxadiazole). ^1H NMR (400 MHz, CDCl_3): δ 1.50 [s, 9H, $-\text{C}(\text{CH}_3)_3$], 6.93 (s, 4H, $-\text{CH}=\text{CH}-$), 7.66 (d, $J = 8.6$ Hz, 4H, ArH), 8.31 (d, $J = 8.6$ Hz, 4H, ArH), 8.39 (d, $J = 1.4$ Hz, 2H, ArH), 8.66 (s, 1H, ArH). ^{13}C NMR (100 MHz, CDCl_3): δ 31.18, 35.34, 122.52, 122.74, 124.76, 126.03, 127.31, 127.90, 134.49, 134.59, 153.90, 164.26, 164.28, 168.94. Anal. Calcd. for $\text{C}_{34}\text{H}_{24}\text{N}_6\text{O}_4$: C, 66.66; H, 3.95; N, 13.72. Found: C, 66.14; H, 3.99; N, 13.64. MS (MALDI-TOF): 613 (found).

C-8b was synthesized using the same method as described for **C-8a**. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 0.64 (s, 6H, $-\text{CH}_3$), 7.25 (s, 4H, $-\text{CH}=\text{CH}-$), 7.53 (d, $J = 8.4$ Hz, 4H, ArH), 7.71 (d, $J = 7.8$ Hz, 4H, ArH), 7.94 (d, $J = 8.1$ Hz, 4H, ArH), 8.03 (d, $J = 8.7$ Hz, 4H, ArH), 10.62 (d, $J = 11.7$ Hz, 4H, $-\text{NHNH}-$).

In a 100 mL flask, **C-8b** (10.0 g, 13.8 mmol) was dissolved in 40 mL of thionyl chloride. The solution was refluxed overnight and then cooled to room temperature. The excess amount of thionyl chloride was removed by rota-evaporation, and the resulting yellow solid was subjected to purification by silica gel column chromatography (EtOAc/ CHCl_3 , 1/4, v/v) to give pure Sioxd (4.6 g, yield 45%). IR (KBr, cm^{-1}): 1718 ($\nu_{\text{C=O}}$ of maleimide), 1609 ($\nu_{\text{C=N}}$ of 1,3,4-oxadiazole). ^1H NMR (400 MHz, CDCl_3): δ 0.67 (s, 6H, $-\text{CH}_3$), 6.91 (s, 4H, $-\text{CH}=\text{CH}-$), 7.62 (d, $J = 8.7$ Hz, 4H, ArH), 7.71 (d, $J = 8.1$ Hz, 4H, ArH), 8.14 (d, $J = 8.1$ Hz, 4H, ArH), 8.24 (d, $J = 8.7$ Hz, 4H, ArH). ^{13}C NMR (100 MHz, CDCl_3): δ -2.72, 122.91, 124.49, 125.95, 126.17, 127.70, 134.38, 134.43, 134.79, 142.44, 163.93, 164.74, 168.91. Anal. Calcd.

for $C_{38}H_{26}N_6O_6Si$: C, 66.08; H, 3.79; N, 12.17. Found: C, 66.10; H, 3.79; N, 12.23. MS (MALDI-TOF): 691 (found).

2.4. Preparation of the BMI resins

A general preparation procedure for the resins based on BMI monomer mixtures is as follows: a mixture of two BMI monomers, i.e., the Buoxd/BMDM (1/9, wt/wt) or Sioxd/BMDM (1/9, wt/wt) was dissolved in chloroform to give a homogeneous solution. Upon removal of the chloroform by rota-evaporation, the resulting solid residue was finely grounded and then put into a Teflon-coated metal mould. The curing was carried out in an oven open to air and the heating profile is as follows: 200 °C for 4 h, 250 °C for 2 h and 280 °C for 0.5 h. The characterizations of the BMI resins obtained are shown in Table 3.

2.5. Preparation of the composites composed of the cured BMI resins and glass cloth

A general preparation procedure is described as follows: BMI monomer mixtures were 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 mould at a high pressure by the following heating profile: 200 °C for 4 h, 250 °C for 2 h and 280 °C for 0.5 h. The weight percentage of the resin in the final composite was determined to be around 24% by calculating the difference in the weights of the bare glass cloth and the composites.

3. Results and discussion

3.1. Synthesis and properties of BMI monomers

The BMI monomers containing 1,3,4-oxadiazole (i.e., Buoxd and Sioxd) were designed and synthesized for producing novel type of BMI resins with improved properties. Both monomers contain two 1,3,4-oxadiazole units in the structure, but they differ from each other in that the Buoxd has a wholly aromatic structure with a bulky *tert*-butyl group attached on the center phenyl ring, while Sioxd has a silicon atom in the center. The synthesis of Buoxd and Sioxd is illustrated in Scheme 1. First, 4-aminobenzoic acid reacted with maleic anhydride in acetone at room temperature to afford an amic acid intermediate which was subjected to imidization in the presence of acetic anhydride and then treated with thionyl chloride to afford 4-maleimido benzoic acid chloride (C-3). On the other hand, 5-*tert*-butyl-isophthalic acid was esterified and subsequently reacted with hydrazine monohydrate to yield 5-*tert*-butyl-isophthalic dihydrazide (C-7a). The reaction between C-7a and C-3 afforded the intermediate C-8a, which was dehydrated in polyphosphoric acid to give the final product Buoxd at an overall yield of 50%. 4,4'-Dicarboxyldiphenyldimethylsilane (C-5) was prepared in two steps:

1-chloro-4-methylbenzene and dichlorodimethylsilane were coupled in toluene to afford 4,4'-dimethyldiphenyldimethylsilane (C-4) which was then oxidized by $KMnO_4$ /pyridine system to yield the C-5. The total yield of this two-step reaction was above 90%. C-5 was esterified with ethanol in the presence of sulfuric acid and subsequently reacted with hydrazine monohydrate to yield 4,4'-dihydrazidediphenyldimethylsilane (C-7b). Then, the dihydrazide C-7b reacted with C-3 in the LiCl/NMP system to afford the precursor C-8b, which was dehydrated in thionyl chloride to yield Sioxd at an overall yield of 45%.

The chemical structures of Buoxd and Sioxd were confirmed by a combination of analytical techniques, i.e., IR, 1H NMR, ^{13}C NMR, MALDI-TOF and elemental analysis. Fig. 1 shows the 1H NMR spectra of Buoxd and Sioxd in $CDCl_3$. The characteristic peaks for the maleimide group at 6.93 ppm for Buoxd and 6.91 ppm for Sioxd were observed. The singlet peak at 1.50 ppm is associated with the protons of the *tert*-butyl group in Buoxd while the singlet peak at 0.67 ppm is attributable to the protons of the methyl group connected to the silicon atom in Sioxd. The integral of each proton agrees well with the expected structures. The monomers were further characterized by MALDI-TOF mass spectroscopy, which also gave the exact molecular weight of 613 and 619 for Buoxd and Sioxd, respectively.

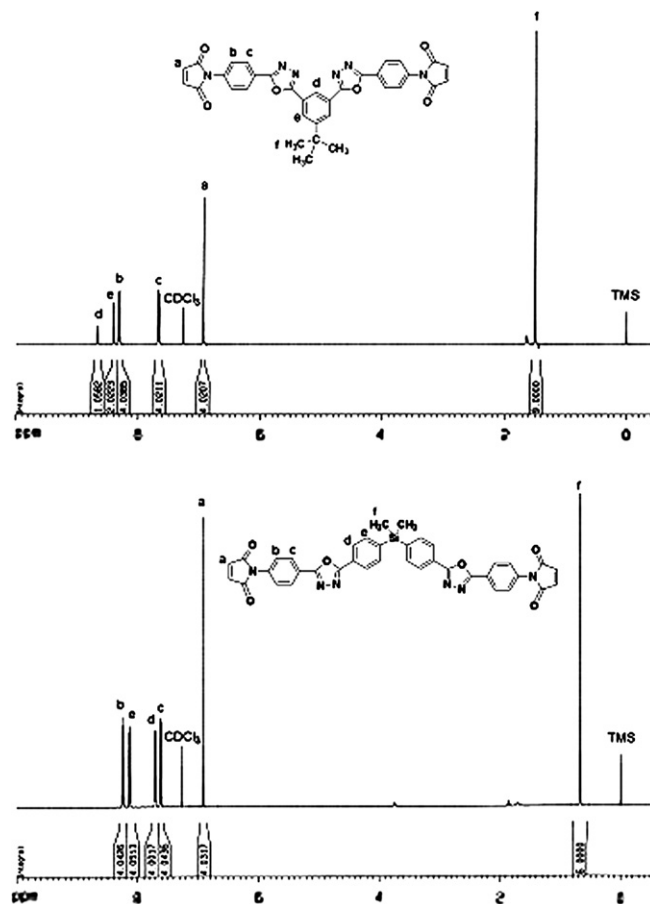


Fig. 1. 1H NMR spectra of Buoxd and Sioxd in $CDCl_3$.

Table 1
The solubility of BMI monomers

	Toluene	Acetone	DCM	Chloroform	THF	DMF	DMSO	NMP
Buoxd	–	–	++	++	+	++	++	++
Sioxd	–	–	++	++	+	++	++	++

'++' = soluble (≥ 10 mg/mL), '+' = soluble under heating, '–' = insoluble. DCM = dichloromethane, THF = tetrahydrofuran, DMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide, NMP = *N*-methyl-2-pyrrolidinone.

The solubility of Buoxd and Sioxd was tested in different solvents. As shown in Table 1, both Buoxd and Sioxd are readily soluble not only in polar aprotic solvents, such as NMP, DMSO and DMF, but also in less polar solvents such as chloroform and DCM, indicating their good solution processability.

The thermal properties of Buoxd and Sioxd were investigated with DSC. As shown in Fig. 2a, the first heating scan of Buoxd showed two endothermic peaks at 266 °C and 288 °C, respectively, and two exothermic peaks at 269 °C and 290 °C, respectively. This is very different from most other BMI monomers [27–30] that exhibit only one endothermic peak corresponding to the melting transition, and one

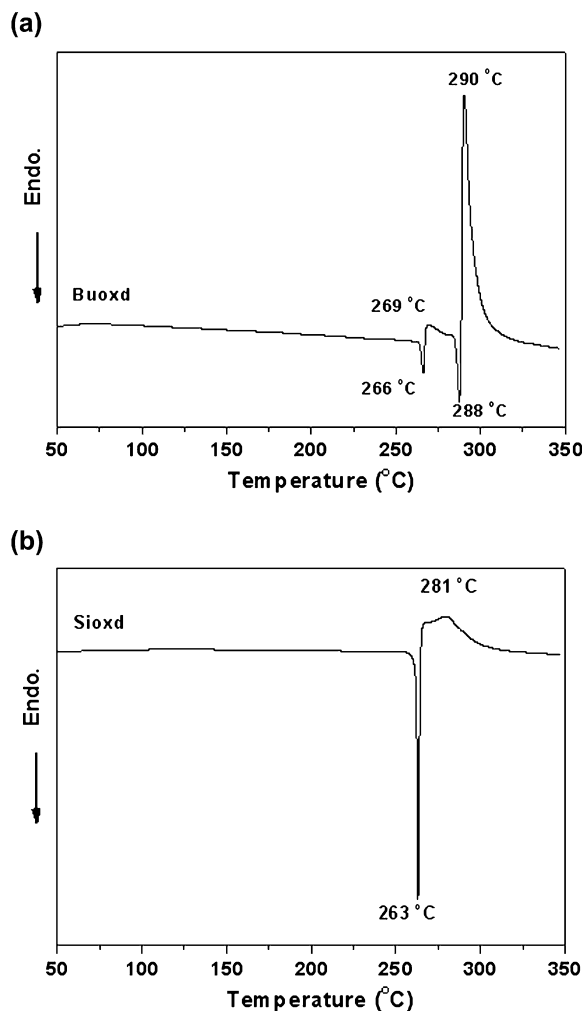


Fig. 2. DSC curves of Buoxd and Sioxd at a heating rate of 10 °C/min in nitrogen.

exothermic peak corresponding to the curing process in the DSC heating scan. Since both the melting and curing processes are critical for the preparation of BMI resins, the nature of the double endothermic/exothermic transitions of Buoxd was carefully studied using optical microscopy and TGA–DSC. First, under the optical microscope, Buoxd showed no distinct melting behavior until the temperature reached the second endothermic transition temperature of 288 °C. TGA–DSC was used to correlate the thermal transitions with any weight loss. Two comparative experiments were thus carried out: (1) a Buoxd specimen was heated (the first heating) at a rate of 10 °C/min to the first exothermic transition temperature of 269 °C, kept at the temperature for 30 min, and then heated to 300 °C at a rate of 10 °C/min, followed by cooling down to 180 °C and then heated (the second heating) up again to 400 °C at a rate of 10 °C/min (Fig. 3a); (2) a Buoxd specimen was heated at a rate of 10 °C/min to 269 °C, kept

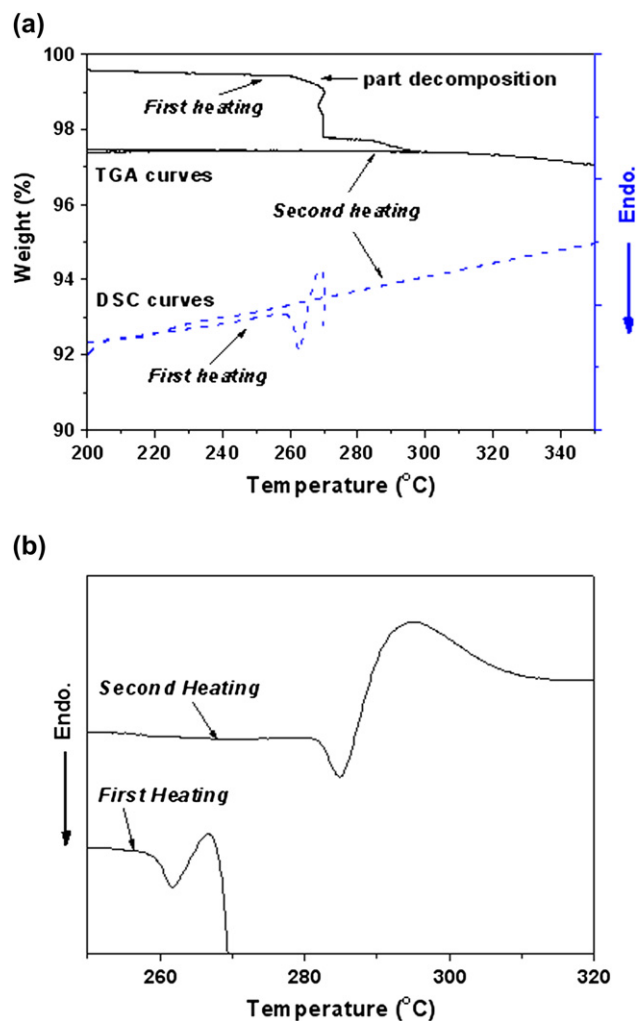


Fig. 3. TGA–DSC curves of Buoxd: (a) the Buoxd specimen was heated (first heating) at a rate of 10 °C/min to 269 °C, kept at the temperature for 30 min, then heated to 300 °C (10 °C/min), followed by cooling down to 180 °C and then heated (second heating) again to 400 °C (10 °C/min) (Fig. 4a). (b) The Buoxd specimen was heated (first heating) at a rate of 10 °C/min to 269 °C, kept for 30 min at 269 °C, cooled down to 180 °C and then heated (second heating) again to 400 °C (10 °C/min).

for 30 min at 269 °C, cooled down to 180 °C and then heated up again to 400 °C at a rate of 10 °C/min (Fig. 3b).

In Fig. 3a, the solid lines are TGA curves and the dashed lines are DSC curves. From the first TGA heating curve, a small weight loss of about 1% can be seen at the first endothermic transition temperature of 266 °C. However, no further weight loss was observed when the sample was heated at higher temperatures. The origin of the small weight loss observed at around 266 °C is still not understandable to us at the current stage. IR investigations showed no significant difference in the structures between samples with and without heating history, except for the changes in the ν_{C-N-C} of the maleimide groups, and the possibility of a small amount of solvent trapped in the sample, which might contribute to the weight loss, was excluded due to the good purity of Buoxd, as evidenced by its NMR spectrum, as well as the good reproducibility of the same weight loss peak for samples having different thermal history. No glass transition and any other transitions was observable in the second heating scan once the sample was heated to 400 °C, indicating the completeness of curing process. To determine which exothermic transition should be accounted for the curing of Buoxd, IR spectroscopy was used to investigate the structural change for samples that were treated at 269 °C and 290 °C. As shown in Fig. 4, Buoxd-P1 was the sample that Buoxd was isothermal at 269 °C for 30 min then cooled down to 50 °C; Buoxd-P2 was the sample that Buoxd was isothermal at 290 °C for 30 min then cooled down to 50 °C. They exhibited different IR spectrum. However, both exhibited a decreased absorption at 1150 cm^{-1} , which is attributable to the ν_{C-N-C} of maleimide, and an increased absorption at 1180 cm^{-1} , which is attributable to the ν_{C-N-C} of succinimide, indicating that both the first and the second exothermic transitions of Buoxd in the first DSC heating scan should be correlated to the curing process of Buoxd. Study on the reaction mechanism corresponding to each exothermic transition is undergoing in our group.

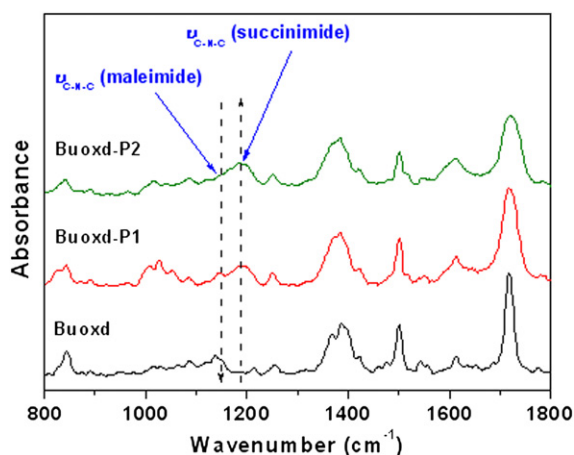


Fig. 4. FTIR spectra of Buoxd monomer and Buoxd treated at different temperatures (Buoxd-P1 and Buoxd-P2). Buoxd-P1 was the sample that Buoxd was isothermal at 269 °C for 30 min then cooled down to 50 °C; Buoxd-P2 was the sample that Buoxd was isothermal at 290 °C for 30 min then cooled down to 50 °C.

In comparison, for samples that were pre-heated to the first exothermic transition temperature (269 °C) and treated at that temperature for 30 min, the second endothermic transition at 288 °C and the second exothermic transition at 290 °C were still observable in the second heating scan as shown in Fig. 3b, suggesting that the second exothermic transition may be mainly responsible for the curing of Buoxd.

From Fig. 2b, it can be seen that Sioxd had only one endothermic transition at 261 °C in its first DSC heating scan, which can be attributed to the melting transition, and one major exothermic transition at 281 °C, which is attributable to the curing process.

The activation energies (E_a) of the thermal curing of Buoxd and Sioxd were calculated by using Ozawa equation and Kissinger equation [37,38]:

$$\text{Kissinger equation: } d \left[\ln \left(\beta / T_p^2 \right) \right] / d(1/T_p) = -E_a/R$$

$$\text{Ozawa equation: } d(\log \beta) / d(1/T_p) = -0.4567 E_a/R$$

where β is the heating rate, T_p is the exothermic transition temperature, R is the gas constant and E_a is the activation energy of thermal curing. A series of DSC studies with different β values were carried out for the estimation of E_a from the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ and from the plot of $\log \beta$ versus $1/T_p$.

Based on the DSC results obtained at different heating rates (Table 2), the kinetic plots of Buoxd and Sioxd based on the Kissinger equation and Ozawa equation were drawn. As shown in Fig. 5, the E_a values of the first curing process of Buoxd were calculated to be 1173 kJ/mol and 1124 kJ/mol according to the Kissinger equation and Ozawa equation, respectively, while the E_a of the second curing process of Buoxd were 713 kJ/mol and 687 kJ/mol, respectively. The E_a values calculated by the two equations are comparable, indicating the validity of the results. However, in comparison with E_a values (about 100 kJ/mol) of other reported bismaleimides [29], the magnitudes of the activation energies of Buoxd are unusually high, which cannot be interpreted very well yet except that Buoxd has a more extensively conjugated wholly aromatic structure in comparison with other BMI monomers. The E_a of the thermal curing of Sioxd was found to be 167 kJ/mol according to both Kissinger equation and Ozawa equation, which is very much comparable with E_a values of typical bismaleimides reported.

Table 2
The DSC analysis of Buoxd and Sioxd monomers at different heating rates

Heating rate β (°C/min)	Buoxd		Sioxd
	T_{p1}^a (°C)	T_{p2}^b (°C)	T_p^c (°C)
2.5	265.8	287.0	264.8
5	267.5	288.3	270.9
10	269.0	290.4	280.2
15	269.6	292.6	288.8
20	270.0	294.4	293.7

^a The first exothermic transition temperature of Buoxd.

^b The second exothermic transition temperature of Buoxd.

^c The exothermic transition temperature of Sioxd.

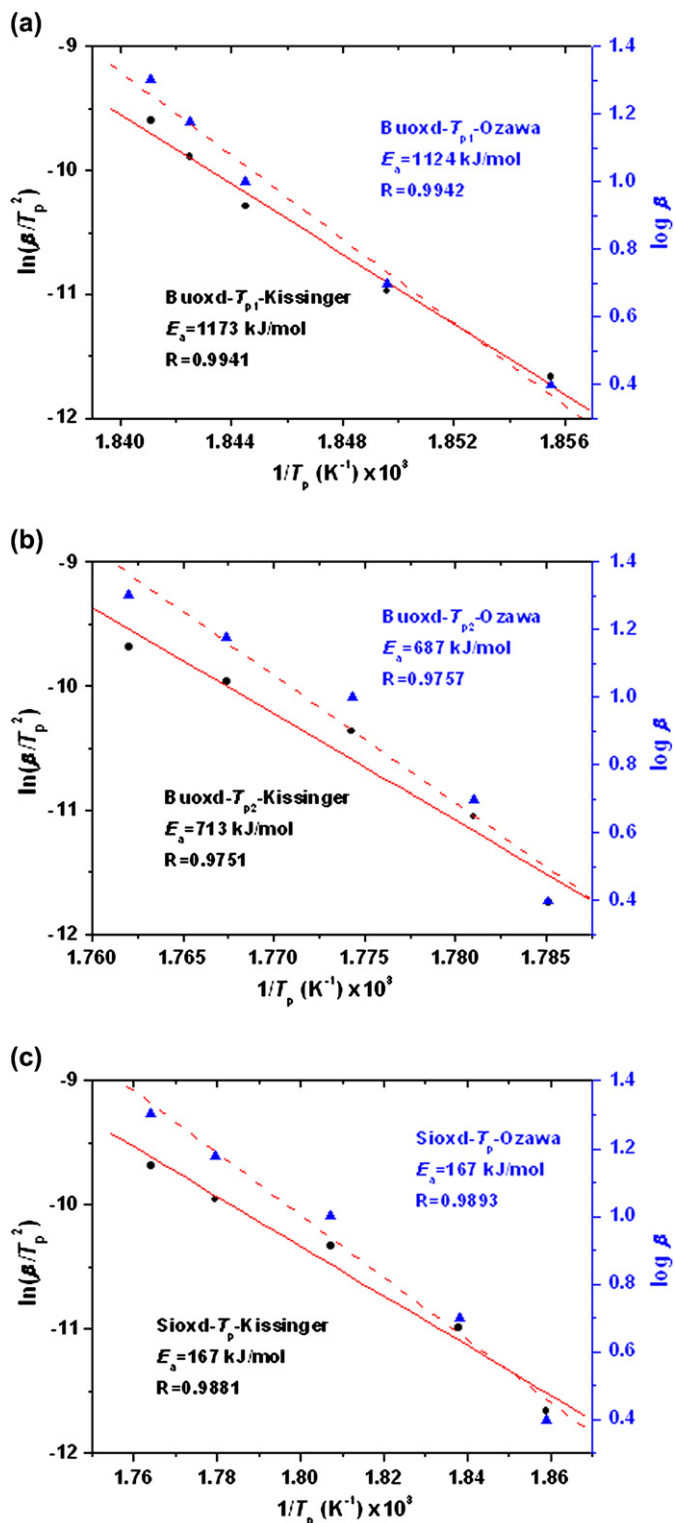


Fig. 5. Kinetic plots of Buoxd and Sioxd based on Kissinger equation (solid line) and Ozawa equation (dash line). The E_a of the (a) first curing process of Buoxd, (b) second curing process of Buoxd, and (c) curing process of Sioxd.

3.2. BMI resins based on Buoxd/Sioxd and BMDM

Both Buoxd and Sioxd were found to undergo a rapid thermal curing upon melting at high temperatures, which is

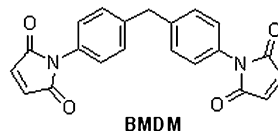


Chart 1. The molecular structure of BMDM.

generally not required for practical use due to the narrow processing window. Since mixtures of BMI monomers have been successfully employed to decrease the melting and curing temperature [39,40], preparations of BMI monomer mixtures based on Buoxd/BMDM and Sioxd/BMDM was carried out in our study. BMDM was chosen as the co-monomer due to its low melting temperature (T_m , 161 °C) and low thermal curing temperature (T_p , 249 °C). And also, it is a commercially available and has been extensively used for the preparation of high-performance BMI resins. The molecular structure of BMDM is shown in Chart 1.

DSC studies were thus carried out to study the thermal properties of the BMI monomer mixtures, i.e., Buoxd/BMDM (1/9, wt/wt, Bu10) and Sioxd/BMDM (1/9, wt/wt, Si10). From Fig. 6a, the sharp melting transitions at 157 °C and 160 °C and broad exothermic transitions at 273 °C and 274 °C attributable to the thermal curing of Bu10 and Si10, respectively, can be observed. The initial curing temperatures (T_i) of Bu10 and Si10, noted as the low onset temperatures of the exothermic transition were found to be the same at 186 °C. The processing window (i.e., $T_i - T_m$) of Bu10 and Si10 was thus 29 °C and 26 °C, respectively, as shown in Table 3. These results showed that the processing properties of Buoxd and Sioxd could be improved by using mixtures of them with BMDM.

3.3. Thermal properties of cured BMI resins (PBu10 and PSi10)

The glass transition temperature (T_g) is one of the most important parameters of high-performance polymers. For thermoset materials, the T_g is mainly determined by polymer structures and crosslinking density. Fig. 6b shows the DSC scans of the cured BMI resins, i.e., PBu10 based on Bu10 and PSi10 based on Si10. No obvious glass transition was observed for both PBu10 and PSi10 in the temperature range from 50 °C to 350 °C, indicating that the movement of polymer chains was restricted by the formation of highly crosslinking networks. The absence of exothermic transitions in the DSC scans indicates that Buoxd and Sioxd participated in the curing process of BMDM at the relatively lower temperatures than the curing temperatures of pure Buoxd and Sioxd.

The thermal stability and thermo-oxidative stability of PBu10 and PSi10 were investigated by TGA (Fig. 7). The onset temperatures for 5% weight loss (T_d) were found to be above 490 °C in nitrogen and above 460 °C in air (Table 4) for both PBu10 and PSi10. Similar to the degradation patterns of other BMI resins, the degradation of PBu10 and PSi10 experienced a one-stage weight loss in nitrogen and a two-stage

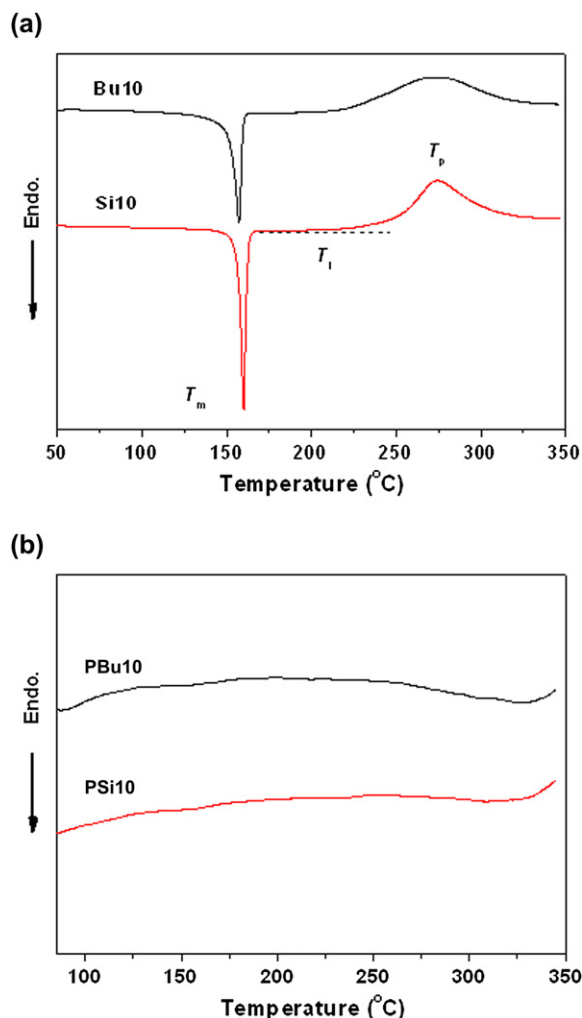


Fig. 6. DSC curves of BMI resins (Bu10 and Si10) and cured BMI resins (PBu10 and PSi10) at a rate of 10 °C/min in nitrogen. T_m stands for the melting transition temperature, T_i for the initial curing temperature and T_p for the exothermic transition temperature.

Table 3
Thermal properties of BMI resins based on mixtures of Buoxd and Sioxd with BMDM

Composition (wt/wt)	Code	T_m^a (°C)	T_i^b (°C)	T_p^c (°C)	$T_i - T_m^d$ (°C)	
BMDM/Buoxd	100/0	BMDM	161.0	199.0	248.7	38.0
	90/10	Bu10	157.2	186.4	273.2	29.2
	0/100	Buoxd	287.6	— ^c	269.0,	—
				290.4		
BMDM/Sioxd	90/10	Si10	159.9	186.3	274.4	26.4
	0/100	Sioxd	263.1	—	280.7	—

^a The melting transition temperature.

^b The initial curing temperature.

^c The exothermic transition temperature.

^d The processing window.

^e Polymerized immediately after melting.

pattern in air. Char yields (Y_c) of PBu10 and PSi10 at 700 °C were 58% and 57%, respectively, in nitrogen and 17% and 7%, respectively, in air.

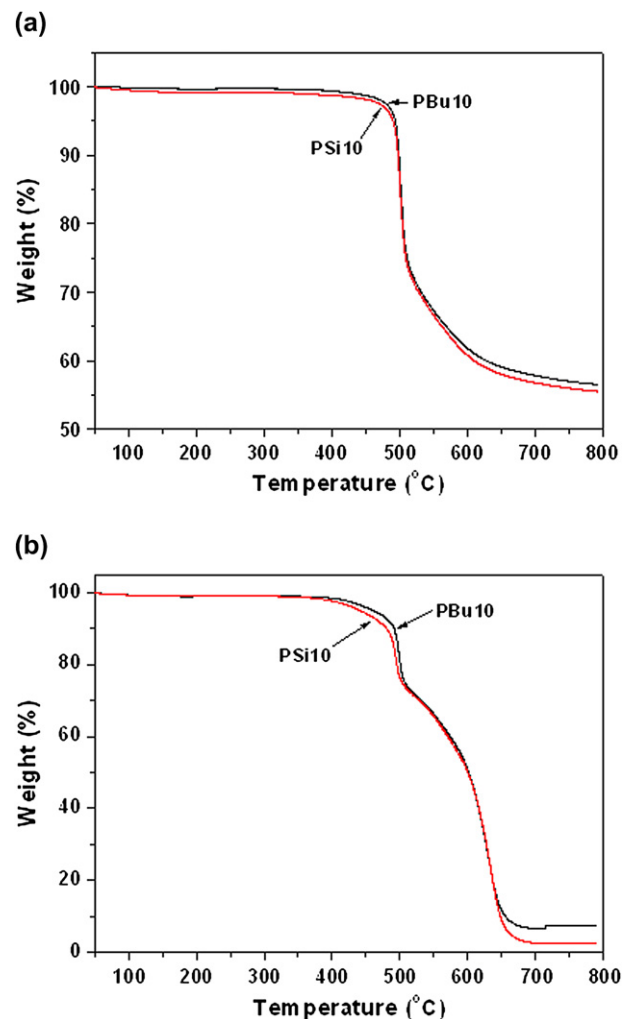


Fig. 7. TGA curves of cured BMI resins (PBu10 and PSi10) at a rate of 10 °C/min (a) in nitrogen and (b) in air.

Table 4

TGA analysis of cured BMI resins based on mixtures of Buoxd and Sioxd with BMDM

PBMI	T_d^a (°C)		Y_c^b (%)	
	In N ₂	In air	In N ₂	In air
PBu10	493.1	461.8	57.8	16.6
PSi10	490.0	460.5	56.8	6.7

^a Temperature at 5% weight loss.

^b Char yield at 700 °C.

3.4. The dynamic mechanical properties of the composites composed of PBu10 and PSi10 with glass cloth

BMI resins have been widely used as high-performance materials for advanced composites that have high thermal stability, high toughness and high chemical resistance [18,25,29]. In our study, the thermal mechanical properties of composites composed of PBu10 or PSi10 with glass cloth were investigated by DMA (Fig. 8). All the composite samples exhibited high bending modulus both at room temperature (1.8 GPa for composite based on PBu10 and 3.5 GPa for composite

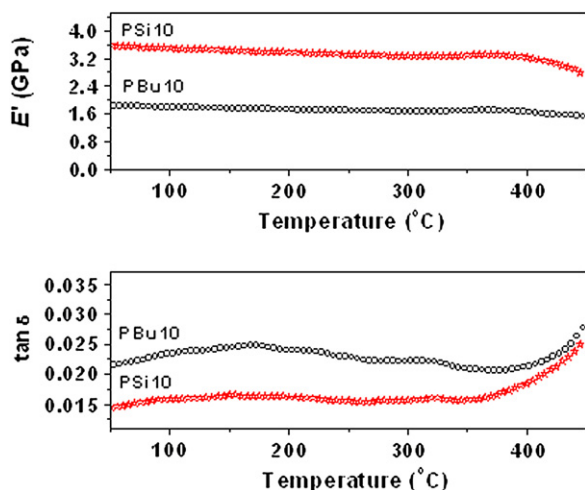


Fig. 8. DMA of the composites composed of cured BMI resins (PBu10 and PSi10) and glass cloth at a rate of 3 °C/min in nitrogen, single cantilever mode.

based on PSi10) and at 400 °C (1.6 GPa for composite based on PBu10 and 3.2 GPa for composite based on PSi10). Above 400 °C, the modulus started to decrease, however, even at a temperature as high as 450 °C, the modulus retained above 1 GPa. Generally, a peak in the $\tan \delta$ curve corresponds to the glass transition. No peak in $\tan \delta$ curve was observed up to 450 °C, indicating the excellent thermal stability of the resulting composites.

4. Conclusion

Two new bismaleimide monomers (i.e., Buoxd and Sioxd) containing 1,3,4-oxadiazole moieties and having good solubility and high melting temperatures were designed and synthesized. DSC investigations revealed that Buoxd had two exothermic transitions, both related to the thermal curing of Buoxd, and unusually high activation energies (e.g., 1100 kJ/mol and 700 kJ/mol to the first and second exothermic transition, respectively), whereas Sioxd had only one exothermic transition, corresponding to the thermal curing of Sioxd, and an activation energy on the level of 160 kJ/mol. BMI resins based on Buoxd and Sioxd with BMDM were prepared by blending Buoxd and Sioxd with BMDM at a 10% weight ratio. The processing properties of the BMI resins were improved by blending. DSC, TGA and DMA investigations showed that the cured BMI resins had no distinct glass transition temperature up to 400 °C, and had high thermal stability ($T_d > 490$ °C, in nitrogen) and high thermo-oxidative property ($T_d > 460$ °C, in air). Composites composed of the glass cloth and BMI resins based on the mixtures of Buoxd (or Sioxd) and BMDM were also prepared, which showed high bending modulus (e.g., >1.6 GPa) in the temperature range of 35–400 °C.

Acknowledgements

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