

ORIGINAL ARTICLE

Preparation and properties of bismaleimide resins modified with hydrogen silsesquioxane and dipropargyl ether and their composites

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A new type of modified bismaleimide (BMI) resins with good heat resistance and processing properties for advanced composites was developed. Modifiers hydrogen silsesquioxane (HSQ), dipropargyl ethers of bisphenol A, hexafluorobisphenol A, 4,4'-dihydroxydiphenyl ether and resorcinol were used to modify 4,4'-bismaleimidodiphenylmethane. The structure of the resins was verified by Fourier transform infrared spectrometry. The relationship between viscosity and temperature was used to characterize the processability of the resins. The curing behaviors of resins were investigated by a differential scanning calorimeter. The glass transition temperatures and thermal stabilities of cured resins were investigated by dynamic mechanical analysis and thermogravimetric analysis, respectively. The relationship between structures and properties of the resins was discussed, and the mechanical properties of the glass-fiber-fabric-reinforced composites were measured.

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INTRODUCTION

Thermosetting bismaleimide (BMI) resins have been widely used as a matrix for advanced composites in aerospace and astronautics. BMI resins possess excellent thermal and oxidative stability, as well as electrical and mechanical properties and a relatively low propensity for moisture absorption.^{1–3} However, unmodified BMI resins have some drawbacks, such as high melting points, high curing temperature and extreme brittleness. With the goal of increasing the toughness of BMI resins, a great deal of research has been carried out to modify them through homo- or copolymerization with such functionalized compounds as aromatic amines, epoxies, cyanates and allyphenols.⁴ However, to compromise between the heat resistance of modified BMI resins and the desirable mechanical properties, more effective methods are required.

Organic/inorganic hybrid materials have been widely regarded as among the most promising and rapidly emerging materials. Such hybrid materials often have good processability, toughness and thermally oxidative stability.^{5–8} Polyhedral oligomeric silsesquioxanes (POSS) contain capped functional groups and an inner inorganic framework consisting of Si and O atoms in the ratio of 1:1.5 ($\text{SiO}_{1.5}$)_n. POSS-containing materials have excellent thermal stability and high glass transition and decomposition temperatures. POSS with one or more covalently bonded reactive groups is suitable for polymerization, grafting, surface bonding, blending and other transformations to build organic/inorganic hybrid materials at the molecular level.^{9–13} POSS

functionalized with groups such as hydrogen,¹⁴ amine,¹⁵ vinyl,¹⁶ epoxy¹⁷ and isocyanate¹⁸ can be used as monomers or comonomers in typical polymerizations. One such POSS, hydrogen silsesquioxane (HSQ), has attracted increasing interest in scientific research and technological innovation.^{19–24}

A new kind of thermosetting resin with terminal propargyl groups has recently been developed as a high-performance polymer owing to its good processability, advantageous dielectric and mechanical properties and excellent thermal stability, whether in air or in a nitrogen atmosphere.^{25–30}

This paper presents new modified BMI resins prepared from BMI, HSQ and dipropargyl aryl ethers. We investigated the processability, mechanical properties and heat resistance of the resins and their composites.

EXPERIMENTAL PROCEDURE

Materials

4,4'-bismaleimidodiphenylmethane (hereafter referred to as BMI) was purchased from Hubei Honghu Chemical Company (Honghu, China). Pt-complex catalyst, dioxane and petroleum ether were purchased from Sinopharm Chemical Reagent (Shanghai, China). Glass fiber fabric (plain weave, 0.14-mm thick) was purchased from Hubei Feilihua Quartz Glass Co. Ltd (Jingzhou, China). HSQ, dipropargyl ethers of bisphenol A (DPBPA), dipropargyl ethers of hexafluorobisphenol A (DPBPF), dipropargyl ethers of 4,4'-dihydroxydiphenyl ether (DPBPE) and dipropargyl ethers of resorcinol (DPBPR) were synthesized in our laboratory.^{30–32}

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Characterization

Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet 550 spectrometer (Thermo Electron Scientific Instruments Corporation, Waltham, MA, USA), and the sample powder was pressed into a pellet with KBr. Hydrogen-1 nuclear magnetic resonance (^1H NMR) spectra were recorded on a AVANCE 500 (Bruker BioSpin GmbH, Rheinstetten, Germany) (500 MHz), C_6D_6 and dimethylsulfoxide- d_6 were used as solvents and chemical shifts were reported in p.p.m. Rheological behavior was traced on a RheoStress RS600 rheometer (Thermo Haake Corporation, Paramus, NJ, USA) with a heating rate of 2°C min^{-1} ; this was carried out on a plate with a shear rate of 0.1 s^{-1} in a temperature range from 50 to 220°C . Differential scanning calorimeter analyses were performed on a 200 PC modulated system (NETZSCH-Gerätebau GmbH, Selb, Germany) at a nitrogen flow rate of $15\text{ cm}^3\text{ min}^{-1}$ and a heating rate of $10^\circ\text{C min}^{-1}$ in a temperature range from 50 to 350°C . Dynamic mechanical analysis (DMA) was carried out on a DMA 242 analyzer (NETZSCH-Gerätebau GmbH) operating in the double-cantilever mode from 50 to 400°C at a frequency of 1 Hz with a programmed heating rate of 3°C min^{-1} . Thermogravimetric analysis (TGA) was conducted on a TGA/SDTA 851 analyzer (Mettler-Toledo (Schweiz) GmbH, Greifensee, Switzerland) under nitrogen with a heating rate of $10^\circ\text{C min}^{-1}$. The flexural test for the composites was carried out on a DXLL-5000 Tension Tester (D&G Machinery Equipment Co. Ltd, Shanghai, China) Tester according to China State Standard GB/T1449-2005.

Preparation of modified BMI resins

The BMI-HSQ-DPBPA resin was prepared from BMI and HSQ with DPBPA. HSQ (0.425 g, 1 mmol), BMI (11.467 g, 32 mmol) and dioxane (120 ml) were charged into a 250-ml three-necked round-bottom flask with a mechanical stirrer in the presence of a proper amount of Pt-complex catalyst. The mixture was heated to 90°C and maintained at this temperature for 8 h under N_2 . After cooling to room temperature, the mixture was precipitated in 600 ml of petroleum ether, and the precipitated BMI-HSQ was obtained by filtration. Then, BMI-HSQ (11.892 g) and DPBPA (8.523 g, 14.33 mmol) were added into a 100-ml three-necked flask and stirred at 160°C for 1 h, and the BMI-HSQ-DPBPA resin was obtained as a brown solid at ambient temperature, which was

soluble in common solvents such as dioxane and tetrahydrofuran. The schematic reaction for the preparation of the resin is shown in Figure 1. The preparations of other modified BMI resins were similar to that of the BMI-HSQ-DPBPA resin. The modified resins are referred to here as BMI-HSQ-DPBPF (from DPBPF), BMI-HSQ-DPBPE (from DPBPE) and BMI-HSQ-DPBPR (from DPBPR).

For all modified BMI resins, the molar ratio of the maleimide groups (MI) (in BMI) to hydrogen (H) (in HSQ) plus propargyl groups ($\text{C}\equiv\text{C}$) (in dipropargyl ether) was 1:1. Table 1 shows the formulation of modified BMI resins.

Preparation of cured modified BMI resins

The curing of modified resins was conducted in an oven under air. The curing cycles of BMI-HSQ-DPBPA, BMI-HSQ-DPBPE and BMI-HSQ-DPBPR resins were as follows: 2 h at 180°C , 2 h at 200°C , 2 h at 220°C and 5 h at 260°C , successively, and the curing cycle for BMI-HSQ-DPBPF resin was 2 h at 180°C , 2 h at 200°C , 2 h at 220°C and 5 h at 280°C . The cured resins (BMI-HSQ-DPBPA, BMI-HSQ-DPBPF, BMI-HSQ-DPBPE and BMI-HSQ-DPBPR) are referred to as c-BMI-HSQ-DPBPA, c-BMI-HSQ-DPBPF, c-BMI-HSQ-DPBPE and c-BMI-HSQ-DPBPR, respectively.

Preparation of glass-fiber-reinforced composite

The glass fabric was used as a reinforcing material for the composite. BMI-HSQ-DPBPA resin was weighed and dissolved in dioxane. The fabric was impregnated with the solution and dried in a vacuum oven at 60°C for 5 h. A prepreg with a resin content of about 37% was obtained and then pressed on a pressure machine under 5 MPa for 2 h at 180°C , 2 h at 200°C , 2 h at 220°C and 5 h at 260°C , successively.

RESULTS AND DISCUSSION

Preparation of BMI-HSQ and modified BMI resins

BMI-HSQ was examined by FT-IR, as shown in Figure 2. In the spectrum of BMI-HSQ, the Si-H absorption bands at 2296 cm^{-1} (stretching vibration) and 860 cm^{-1} (bending vibration) disappeared, which illustrates that Si-H groups in HSQ have reacted with $\text{C}=\text{C}$ in imide rings of BMI through an addition reaction.

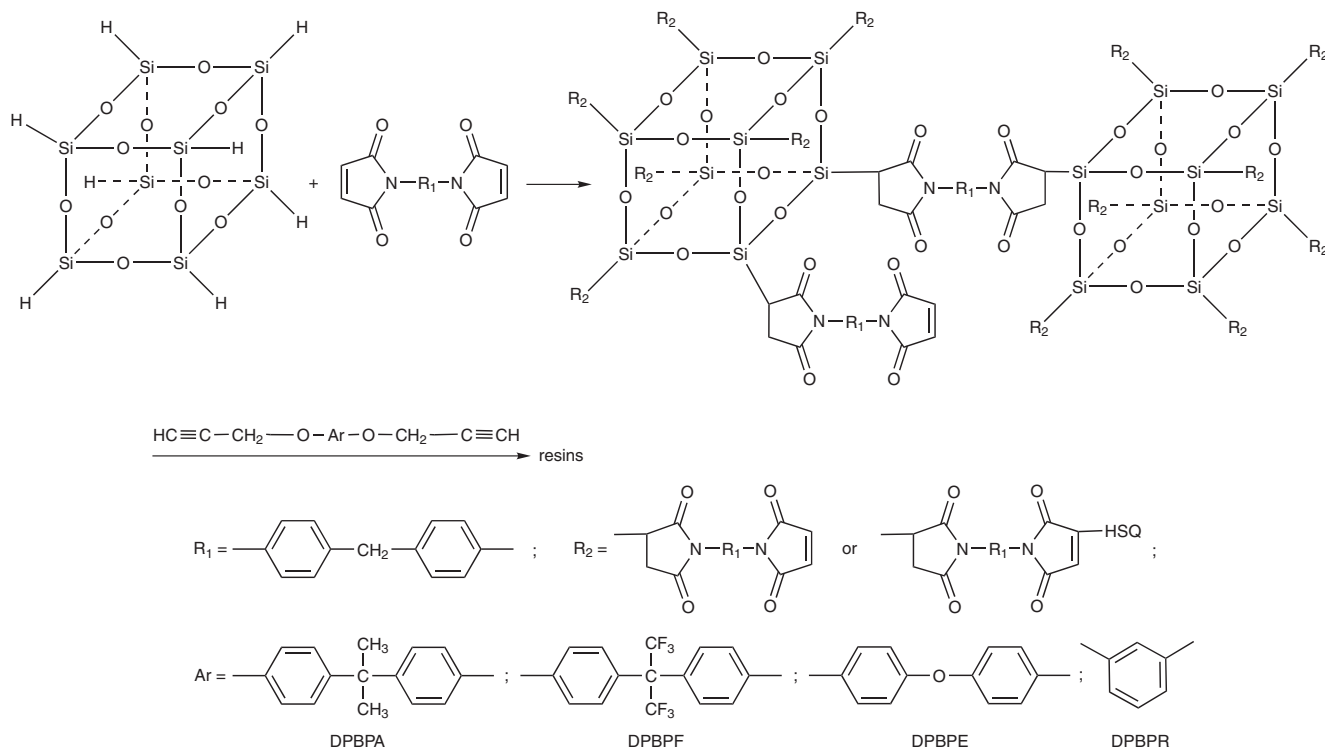


Figure 1 Preparation of modified BMI resins.

Table 1 Formulation of various modified BMI resins

Resin	Mass ratio of reagents (BMI):(HSQ):(DPBPA)	Molar ratio of reagents (BMI):(HSQ):(DPBPA)	Molar ratio of groups (MI):(H):(C=C)
BMI-HSQ-DPBPA	56.2:2.1:41.7	32:1:28	64:8:56
BMI-HSQ-DPBPF	48.9:1.8:49.3	32:1:28	64:8:56
BMI-HSQ-DPBPE	58.2:2.2:39.6	32:1:28	64:8:56
BMI-HSQ-DPBPR	67.0:2.5:30.5	32:1:28	64:8:56

Abbreviations: BMI, bismaleimide; DPBPA, dipropargyl ethers of bisphenol A; DPBPE, dipropargyl ethers of 4,4'-dihydroxydiphenyl ether; DPBPF, dipropargyl ethers of hexafluorobisphenol A; DPBPR, dipropargyl ethers of resorcinol; HSQ, hydrogen silsesquioxane.

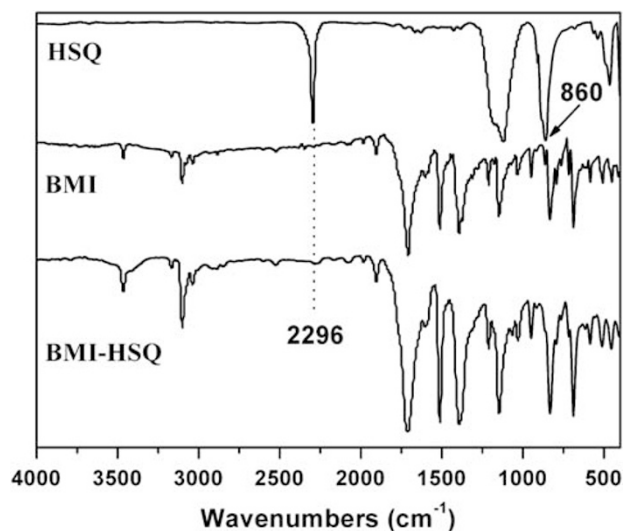


Figure 2 FT-IR spectra of HSQ, BMI and BMI-HSQ.

Figure 3 displays the ^1H NMR spectra of HSQ, BMI and BMI-HSQ. The ^1H NMR spectrum of HSQ showed a single peak at 4.2 p.p.m., assigned to Si-H, indicating that all hydrogen atoms were in the same chemical environment in the molecule. This confirmed the chemical structure of HSQ.

The ^1H NMR spectrum of BMI showed four proton environments: H_a , H_b , H_c and H_d (see Figure 3). In the spectrum of BMI-HSQ, the Si-H peak at 4.2 p.p.m. disappeared, whereas two distinct peaks at 2.1 and 2.8 p.p.m. appeared, belonging to the hydrosilylation products of BMI and HSQ.

Figure 4 shows the FT-IR spectra of the series of modified BMI resins. All modified resins possessing several identical groups displayed similar absorptions. The absorption peaks at 3285 cm^{-1} and 2122 cm^{-1} belonged to the stretching vibrations of $\equiv\text{C-H}$ and $\text{C}\equiv\text{C}$, respectively, and the vibration of C-H of the benzene ring appeared at 3101 and 3041 cm^{-1} . The peak at 1715 cm^{-1} was attributed to C=O in the maleimide ring. The absorption peaks at 1149 and 1181 cm^{-1} belonged to the C-N-C groups of maleimide and succinimide, respectively. The absorptions of the Ar-O-C band were located in the ranges of $1026\text{--}1046$, $1206\text{--}1223$ and $1248\text{--}1298\text{ cm}^{-1}$, and the benzene skeleton vibration was located at $1453\text{--}1610\text{ cm}^{-1}$.

Rheological behavior of modified BMI resins

The viscosity of a resin is important for its processing. A resin viscosity of $0.2\text{--}0.3\text{ Pa s}$ is believed to give the best overall processability for

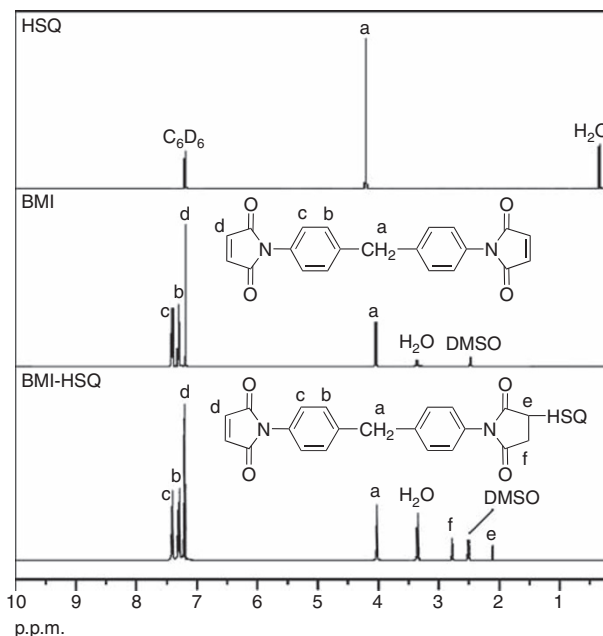


Figure 3 ^1H NMR spectra of HSQ, BMI and BMI-HSQ.

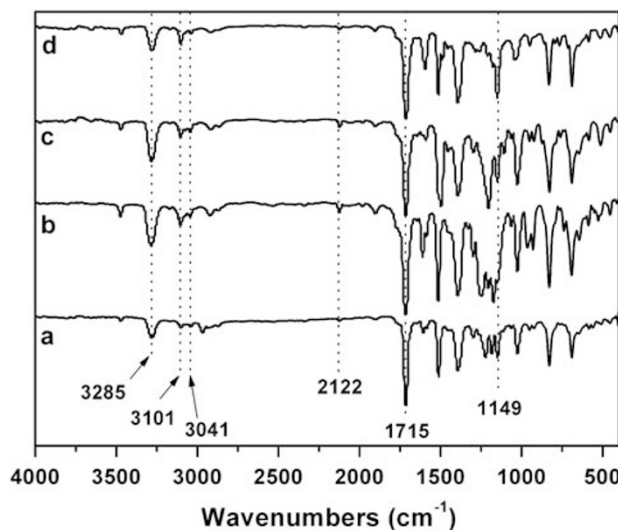


Figure 4 FT-IR spectra of modified BMI resins (a: BMI-HSQ-DPBPA; b: BMI-HSQ-DPBPF; c: BMI-HSQ-DPBPE; d: BMI-HSQ-DPBPR).

RTM. It is generally considered that a high injection and molding pressure is required when viscosity is higher than 0.5 Pa s . However, problems such as fiber displacement may occur in the mold cavity at a high injection pressure. Viscosity of the BMI-HSQ-DPBPA resin was measured by a rheometer. The viscosity response to temperature ramping at a heating rate of $2\text{ }^\circ\text{C min}^{-1}$ is shown in Figure 5. It can be seen that viscosity decreased dramatically as temperature increased. At temperatures above $81\text{ }^\circ\text{C}$, the viscosity of the resin was below 1 Pa s . The viscosity of the resin measured at 107 and $117\text{ }^\circ\text{C}$ was 0.3 and 0.2 Pa s , respectively, which is suitable for the RTM process. At temperatures higher than $196\text{ }^\circ\text{C}$, viscosity increased rapidly, which indicates that curing reactions occur at temperatures above $196\text{ }^\circ\text{C}$ and that gelation occurs thereafter. The results showed that the BMI-HSQ-

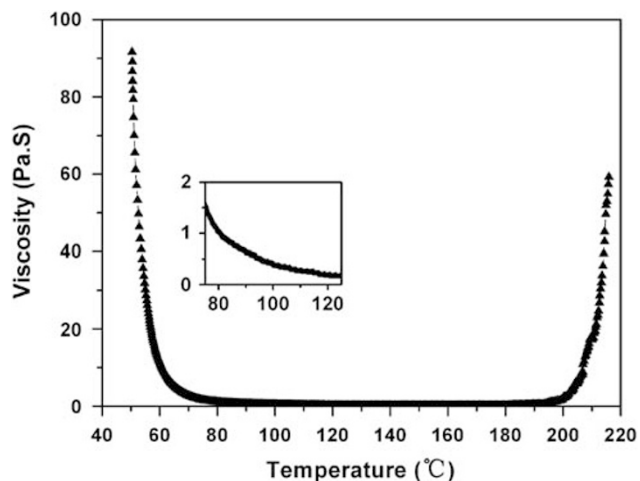


Figure 5 Viscosity-temperature curve of BMI-HSQ-DPBPA resin.

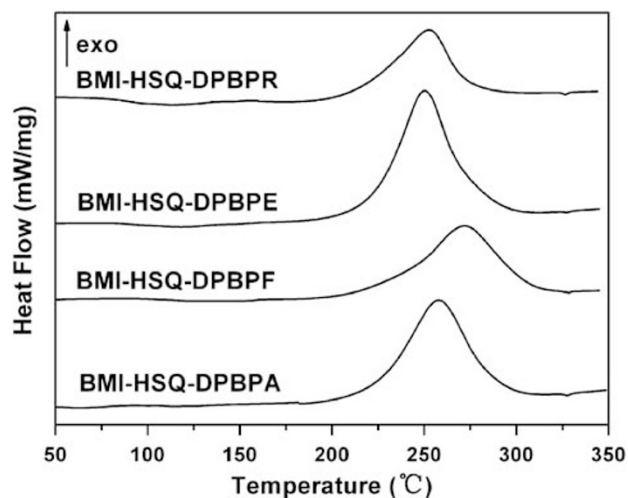


Figure 6 DSC traces of modified BMI resins.

DPBPA resin had a relatively low viscosity at temperatures between 81 and 196 °C, thus allowing a wide processing window.

The curing reaction of modified BMI resins

Figure 6 presents differential scanning calorimeter traces of modified BMI resins at a heating rate of 10 °C min⁻¹. It was observed that modified BMI resins showed a unimodal reaction exotherm because of their thermopolymerization. No melting endotherm appears in Figure 5, implying that modified BMI resins were noncrystalline. All modified resins showed a single wide exothermic peak, which indicates that curing reactions occurred and would facilitate the processing of resins to some extent. Table 2 listed the onset temperature (T_i), top temperature (T_p) and end temperature (T_f) of the curing exothermic peaks of the resins, which were determined mainly by curing reactivity and followed the trend of BMI-HSQ-DPBPR < BMI-HSQ-DPBPE < BMI-HSQ-DPBPA < BMI-HSQ-DPBPF.

Figure 7 presents the pathways proposed for the reaction of BMI and dipropargyl ether. In the thermopolymerization of propargyl ether and BMI, partial propargyl ether was initially subjected to chromene rearrangement and Claisen rearrangement (A); subsequently, copolymerization and autopolymerization occurred between the double bonds from the chromenes and/or maleimide rings of BMI

Table 2 DSC analysis results of modified BMI resins

Resin	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (Jg ⁻¹)
BMI-HSQ-DPBPA	226	258	287	493
BMI-HSQ-DPBPF	234	272	308	403
BMI-HSQ-DPBPE	224	250	275	563
BMI-HSQ-DPBPR	215	252	272	305

Abbreviations: BMI, bismaleimide; DPBPA, dipropargyl ethers of bisphenol A; DPBPE, dipropargyl ethers of 4,4'-dihydroxydiphenyl ether; DPBPF, dipropargyl ethers of hexafluorobisphenol A; DPBPR, dipropargyl ethers of resorcinol; DSC, differential scanning calorimeter; HSQ, hydrogen silsesquioxane; T_i , end temperature; T_o , onset temperature; T_p , top temperature.

(B), and then a simultaneous Diels-Alder reaction took place between the acetylenic bonds of propargyl ether and the double bonds of maleimide rings (C).^{30,33,34}

Figure 8 displays the infrared spectra of the cured modified BMI resins. After curing, the absorption peak at 1149 cm⁻¹ assigned to C-N-C groups shifted to 1180 cm⁻¹ and broadened, with the peak intensity increasing. The above results indicate that the BMI participated in crosslinking reactions.

The characteristic absorptions at 3285 and 2122 cm⁻¹ due to \equiv C-H and C \equiv C vibrations of dipropargyl ethers disappeared, suggesting the complete consumption of dipropargyl ethers. The absorption band associated with Ar-O-C decreased, which indicates that propargyl ether groups were converted into cyclic ether or other structures. A broad absorption was noted in the region of 3300-3600 cm⁻¹, representing OH groups in the cured resin, owing to the fact that phenolic OH groups were formed by the Claisen rearrangement of the structure of propargyl ether in the thermopolymerization process.

Thermal properties of cured modified BMI resins

Glass transition temperatures (T_g) of cured modified BMI resins were detected by DMA. Generally, the damping peak of $\tan \delta$ was identified as T_g in a DMA curve because a large decrease in modulus occurred at this point. The DMA curves of cured modified resins are shown in Figure 9, and DMA and TGA analysis results are tabulated in Table 2.

The order of T_g for the cured resins was BMI-HSQ-DPBPE < BMI-HSQ-DPBPA < BMI-HSQ-DPBPF < BMI-HSQ-DPBPR. The T_g s of the former three were close to one another, having values of 337, 344 and 352 °C, respectively. By comparison, the cured BMI-HSQ-DPBPR resin possessed the highest T_g , 421 °C, which was derived from the highest curing density.

The T_g of the c-BMI-HSQ-DPBPA resin (344 °C) was higher than that of the cured BMI-DPBPA resin (320 °C).³⁰ The cage structure of POSS would hinder the segment motion of the modified resins. For that reason, the addition of HSQ increases the T_g of the cured resin.

Thermal stability of cured modified BMI resins

The thermal stability of cured modified BMI resins was analyzed by TGA. The results are given in Figure 9 and Table 3. As shown in Figure 10, the T_{d5} of the cured modified resins increased as follows: c-BMI-HSQ-DPBPA < c-BMI-HSQ-DPBPE < c-BMI-HSQ-DPBPR < c-BMI-HSQ-DPBPF. The thermal stability of each resin was determined by the specific structure of the applied bisphenol derivative and the crosslinked network. As for the bisphenol structures, the moieties of C(CF₃)₂ in hexafluorobisphenol A possessed higher heat resistance than did the C(CH₃)₂ groups in bisphenol A because of the higher bond energy of C-F. Thus, the thermal stability of the c-BMI-HSQ-DPBPF resin was superior to that of the c-BMI-HSQ-DPBPA resin.

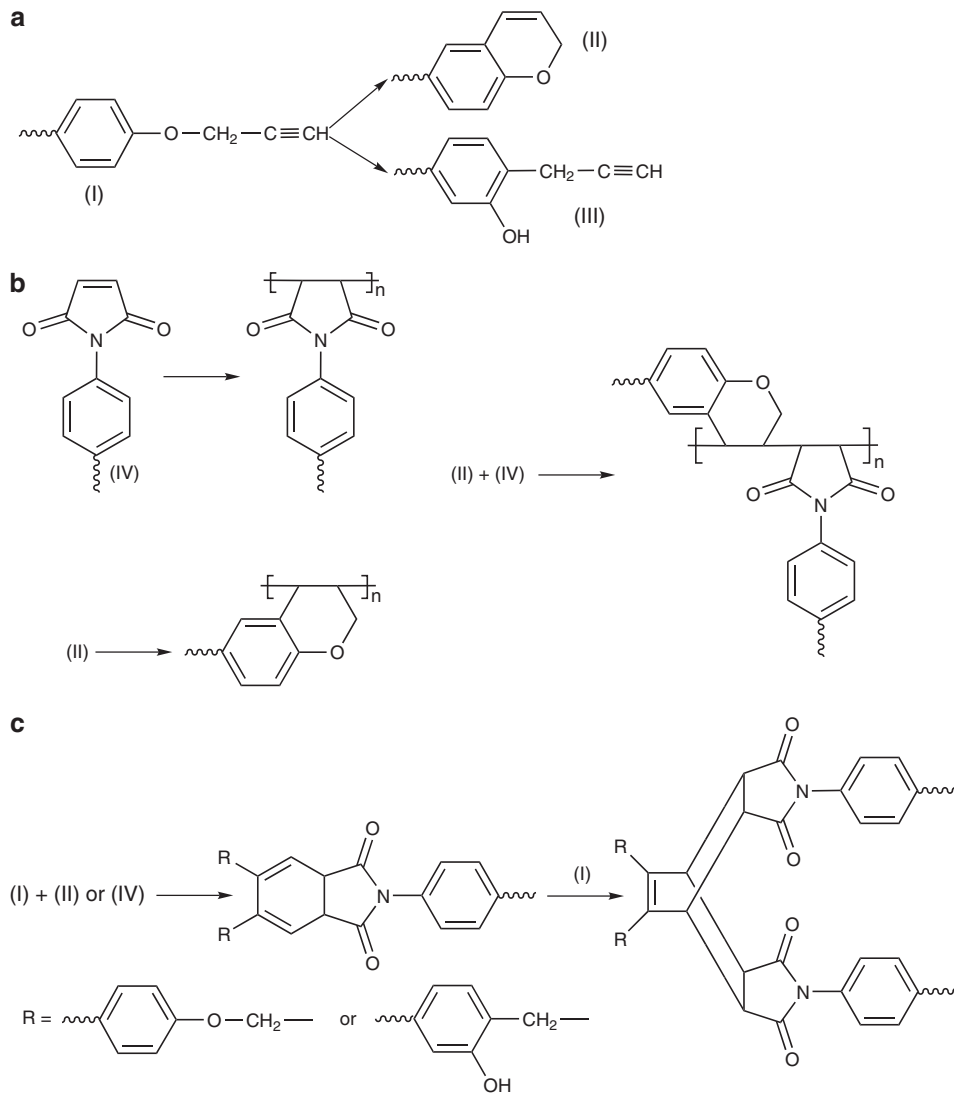


Figure 7 Pathways proposed for the reactions between BMI and dipropargyl ether.

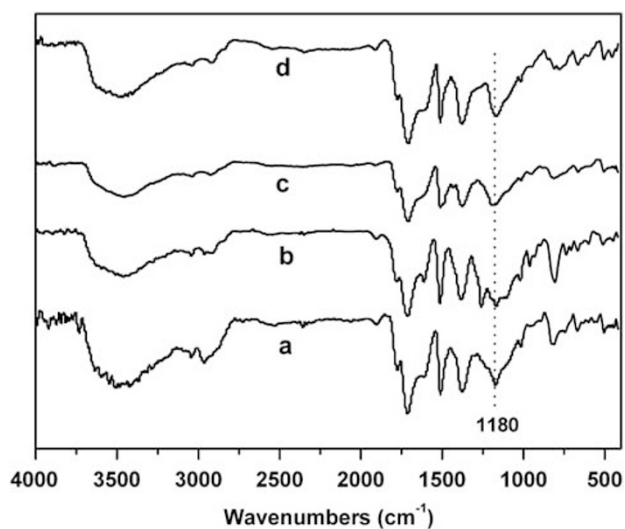


Figure 8 FT-IR spectra of cured modified BMI resins (a: c-BMI-HSQ-DPBPA; b: c-BMI-HSQ-DPBPF; c: c-BMI-HSQ-DPBPE; d: c-BMI-HSQ-DPBPR.)

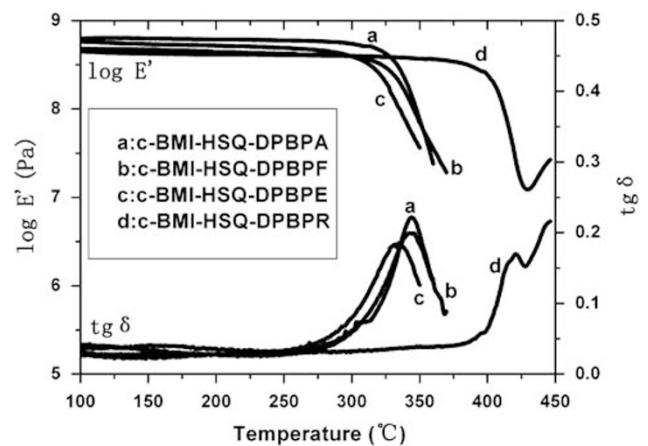
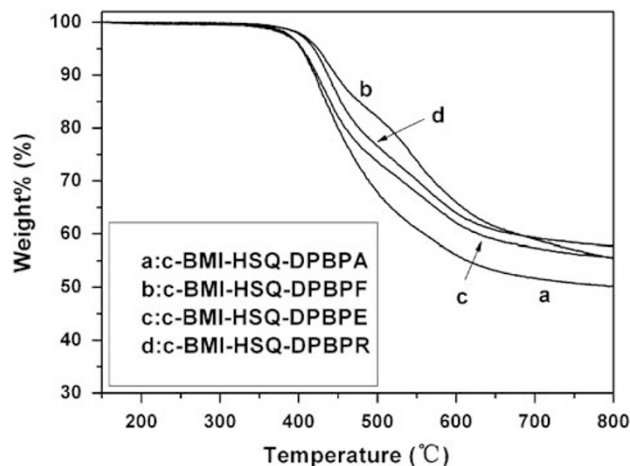


Figure 9 DMA curves of cured modified BMI resins.

Table 3 DMA and TGA analysis results of cured modified BMI resins

Resin	T_g ($^{\circ}\text{C}$)	T_{d5} ($^{\circ}\text{C}$)	Y_r (%)
c-BMI-HSQ-DPBPA	344	403	50
c-BMI-HSQ-DPBPF	344	424	55
c-BMI-HSQ-DPBPE	337	405	56
c-BMI-HSQ-DPBPR	421	419	58

Abbreviations: BMI, bismaleimide; DMA, dynamic mechanical analysis; DPBPA, dipropargyl ethers of bisphenol A; DPBPE, dipropargyl ethers of 4,4'-dihydroxydiphenyl ether; DPBPF, dipropargyl ethers of hexafluorobisphenol A; DPBPR, dipropargyl ethers of resorcinol; HSQ, hydrogen silsesquioxane; TGA, thermogravimetric analysis; T_{d5} , the temperature at 5% weight loss; T_g , glass transition temperature; Y_r , the residue yield.

**Figure 10** TGA curves of cured modified BMI resins.**Table 4** Properties of glass-fiber-reinforced BMI-HSQ-DPBPA composites*

Measuring temperature	RT	250 $^{\circ}\text{C}$	Retention at 250 $^{\circ}\text{C}$ (%)
Flexural strength (MPa)	497	363	73
Flexural modulus (GPa)	20.7	20.3	98
Laminar shear strength (MPa)	31.7		

Abbreviations: BMI, bismaleimide; DPBPA, dipropargyl ethers of bisphenol A; HSQ, hydrogen silsesquioxane; RT, room temperature.

*Resin content in composites was about 30 weight %.

Mechanical properties of glass-fiber-reinforced composite

Table 4 lists the properties of the glass-fabric-reinforced BMI-HSQ-DPBPA composite. As shown, the composite exhibited excellent mechanical properties. The flexural strength of BMI-HSQ-DPBPA composites was 497 and 363 MPa at room temperature and at 250 $^{\circ}\text{C}$, respectively. Thus, the retentions of flexural strength and modulus for BMI-HSQ-DPBPA composites at 250 $^{\circ}\text{C}$ were 73 and 98%, respectively. The laminar shear strength of BMI-HSQ-DPBPA composites was 31.7 MPa. Therefore, modified BMI resins are expected to be used for the matrix of advanced composites.

CONCLUSIONS

A series of BMI resins modified with HSQ, DPBPA, DPBPF, DPBPE and DPBPR were prepared. The resins exhibited excellent processability, especially the BMI-HSQ-DPBPA resin, which had a low viscosity of 0.2–0.3 Pa s at temperatures between 81 and 196 $^{\circ}\text{C}$. The

cured resins showed high heat resistance, with T_g above 330 $^{\circ}\text{C}$ and T_{d5} of 400 $^{\circ}\text{C}$. The c-BMI-HSQ-DPBPR resin possessed the highest T_g , 421 $^{\circ}\text{C}$, and the c-BMI-HSQ-DPBPF resin possessed the highest T_{d5} , 424 $^{\circ}\text{C}$. The glass-fiber-reinforced BMI-HSQ-DPBPA resin composites possessed good mechanical properties. The modified BMI resins would be good candidates for a high-performance matrix for advanced composites.

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