

Thermal Properties of New Bismaleimide Resins Containing Hydrogen Silsesquioxane and Diallyl Bisphenol A

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Received 5 June 2009; accepted 2 February 2010

DOI 10.1002/app.32209

Published online 27 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Bismaleimide (BMI) resins modified with hydrogen silsesquioxane (HSQ) and diallyl bisphenol A (DABPA) (BMI-HSQ-DABPA resins) were prepared. DSC, FTIR, and TGA were used to characterize the curing behaviors, structures, and thermal properties of the BMI-HSQ-DABPA resins, respectively. The results showed that the glass transition temperatures and thermal stabilities of

the cured BMI-HSQ-DABPA resins increased with the rise of the contents of HSQ. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2932–2936, 2010

Key words: modified bismaleimide resin; hydrogen silsesquioxane; diallyl bisphenol A; thermal properties; high performance resin

INTRODUCTION

Organic/inorganic hybrid materials were widely regarded as one of the most promising and rapidly emerging materials. The properties of organic/inorganic hybrid materials derived from the polymeric and inorganic components to give good processability, toughness, and thermally oxidative stability.^{1–4} Polyhedral oligomeric silsesquioxanes (POSS) was a substance with an inner inorganic framework, made up of Si and O atoms in the ratio of 1 : 1.5 ($\text{SiO}_{1.5}$)_n, and organic functional groups capped. POSS materials had excellent thermal stability due to their inorganic structures, which contributes to their high glass transition and decomposition temperatures. POSS monomers with one or more covalently bonded reactive groups were suitable for polymerization, grafting, surface bonding, blending in molecular level.^{5–8} POSS substances functionalized with groups such as hydrogen,⁹ amine,^{10,11} vinyl,¹² epoxy,¹³ and isocyanate¹⁴ could be used as monomers or comonomers in a typical polymerization.

Hydrogen silsesquioxane (HSQ) as one of POSS monomers had been attracted increasing interest in scientific research and technological innovation.^{15–20}

HSQ could be used as Si/SiO₂ film precursor,²¹ negative resist,²² and low-k material.²³ Liu and Zheng²⁴ prepared the polybenzoxazine (PBA-a) nanocomposites containing HSQ in which the nanocomposites displayed higher glass transition temperatures (T_g) in comparison with the control PBA-a. The thermal stability and oxidation resistance of the PBA-a were improved by the introduction of HSQ.

Bismaleimide (BMI) resins modified with diallyl bisphenol A (BMI-DABPA) were widely used as matrices for advanced composites in aerospace and astronautics. BMI-DABPA resins possessed excellent thermal stability, electrical and mechanical properties, and relatively low propensity to moisture absorption. This explained why they dominated the polymer matrices for advanced composites. However, with the development of aerospace technology, new BMI resins with better performance could be required. Thus, some new approaches were developed to further modify BMI-DABPA resins. Boey et al.²⁵ reported the modification of BMI-DABPA resin using diaminodiphenylsulfone (DDS). The variation of the T_g of the cured BMI-DABPA-DDS resin with different cure temperatures was investigated. When the cure temperature was 220°C, the T_g approached to 250°C. Li et al.²⁶ reported the modification of BMI-DABPA resin using *N,N'*-diallyl-*p*-phenyl diamine (DPD). The cured BMI-DABPA-DPD resin displayed high mechanical properties and heat/wet resistance and was suitable for RTM molding. The T_g of the cured BMI-DABPA-DPD resin reached 285°C.

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Contract grant sponsor: National Basic Research Program of China; contract grant number: 513-006.

TABLE I
Formulation of BMI-HSQ-DABPA Resins

No.	Mass ratio of reagents [BMI] : [HSQ] : [DABPA]	Molar ratio of reagents [BMI] : [HSQ] : [DABPA]
a	54.8 : 1.0 : 44.2	64 : 1 : 60
b	55.8 : 2.1 : 42.1	32 : 1 : 28
c	58.2 : 4.3 : 37.5	16 : 1 : 12
d	63.3 : 9.4 : 27.3	8 : 1 : 4

In this article, we presented the synthesis of BMI resins modified by HSQ and DABPA and the investigation on the thermal properties of the cured resins. The BMI-HSQ-DABPA resins will be a good candidate as high performance matrix for advanced composites.

EXPERIMENTAL

Materials

4,4'-Bismaleimidodiphenylmethane (BMI) was purchased from Hubei Honghu Chemical Company in China. Dioxane and petroleum ether were purchased from Sinopharm Chemical Reagent Co. HSQ and diallyl bisphenol A (DABPA) were synthesized in our laboratory.^{27,28}

Characterization

Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 550 spectrometer and the sample powder was pressed into a pellet with KBr. Dif-

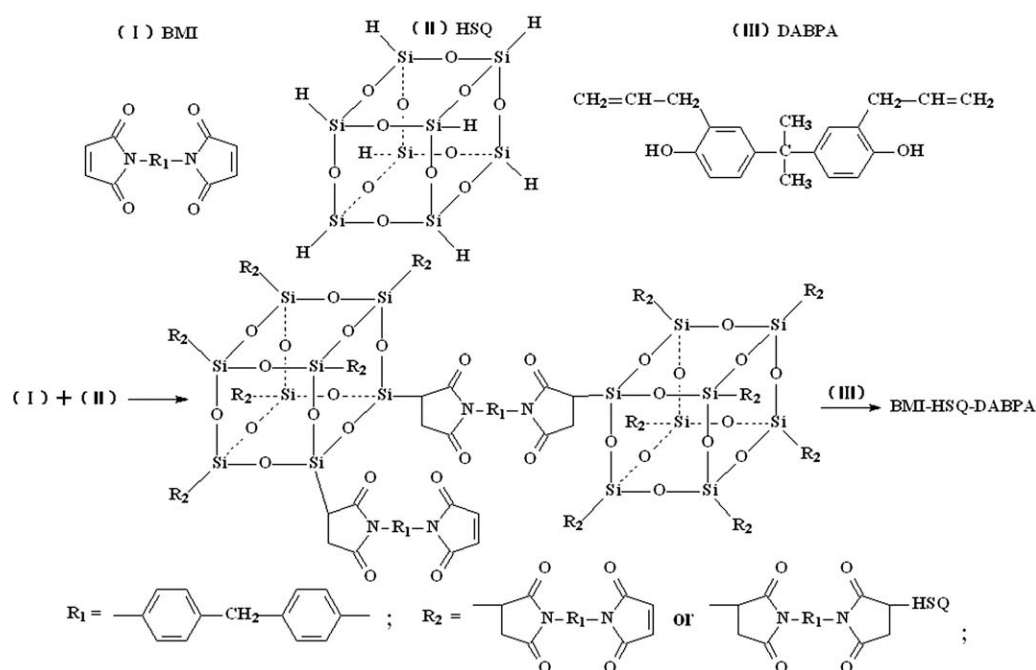
ferential scanning calorimeter (DSC) analyses were performed on a NETZSCH 200 PC modulated system at a flow rate of nitrogen gas of 15 cm³/min and the heating rate of 10°C/min or 20°C/min in the temperature range from 50°C to 350°C. Thermogravimetric analysis (TGA) was conducted on a METTLER TGA/SDTA 851 analyzer under nitrogen with the heating rate of 10°C/min.

Preparation of BMI-HSQ-DABPA resin

BMI (I) (5.48 g, 15.29 mmol), HSQ (II) (0.1 g, 0.24 mmol), and dioxane (60 mL) were charged into a 250-mL three-necked bottom flask with a mechanical stirrer in the presence of proper amount of catalyst Pt complex. The mixture was heated to 90°C and maintained at this temperature for 8 h under N₂. After cooled down to room temperature, the mixture was precipitated in 500 mL of petroleum ether and BMI-HSQ was obtained by filtration. BMI-HSQ (5.58 g) and DABPA (III) (4.42 g, 14.33 mmol) were added into a 100-mL three-necked flask and stirred at 120°C for 0.5 h, and the BMI-HSQ-DABPA resin (No. a) was obtained as brown solids at ambient.

Other resins (No. b–d) with various ratios of monomers, shown in Table I, were prepared in the similar way.

For all BMI-HSQ-DABPA resins, the molar ratio of maleimide groups (in BMI) to hydrogen plus allyl groups (in HSQ and DABPA, respectively) was kept at 1 : 1. The preparation procedure for BMI-HSQ-DABPA resins was shown in Scheme 1.



Scheme 1 Synthesis of BMI-HSQ-DABPA resins.

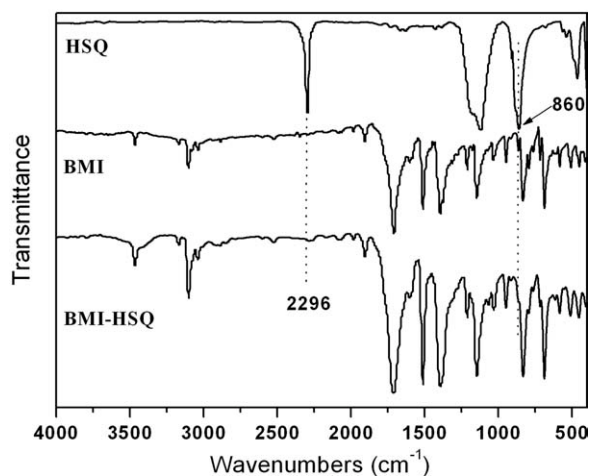


Figure 1 FTIR spectra of HSQ, BMI, and BMI-HSQ.

RESULTS AND DISCUSSION

Characterization of BMI-HSQ and BMI-HSQ-DABPA resin

The BMI-HSQ was examined by FTIR, as shown in Figure 1. In the spectrum for BMI-HSQ, the Si-H absorption bands at 2296 cm^{-1} (stretching vibration) and 860 cm^{-1} (bending vibration) disappeared, which illustrated that Si-H groups in HSQ had reacted with C=C in imide rings of BMI through addition reaction.

Figure 2 presented the FTIR spectra of the BMI-HSQ-DABPA resin (No. b). The characteristic bands at 3075 and 1149 cm^{-1} were attributed to the absorption of =C-H and C-N-C in imide ring, respectively. The characteristic band at 920 cm^{-1} was assigned to allyl groups.^{29,30}

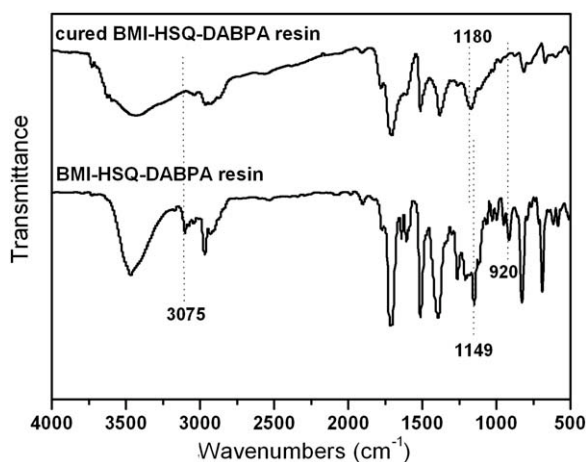


Figure 2 FTIR spectra of BMI-HSQ-DABPA and cured BMI-HSQ-DABPA resins (No. b).

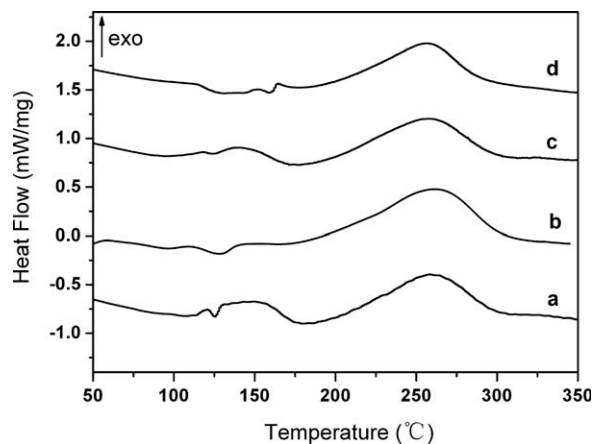


Figure 3 DSC trace of BMI-HSQ-DABPA resins with various ratios.

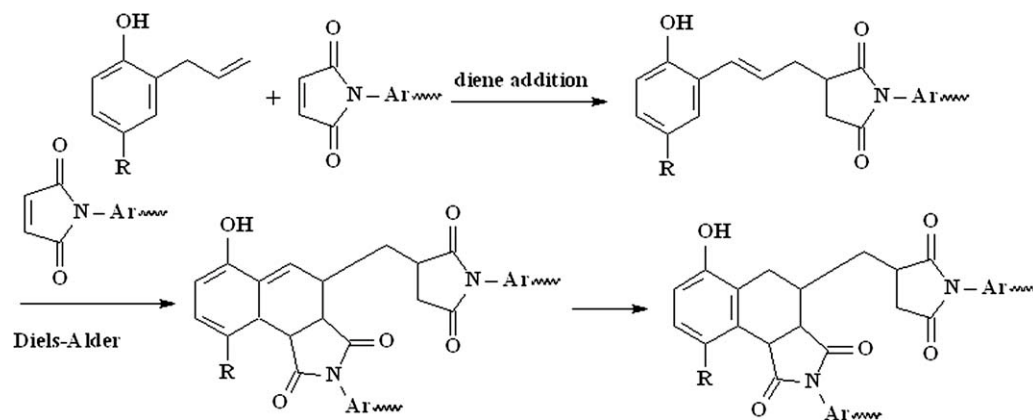
The curing behaviors of the BMI-HSQ-DABPA resin

Figure 3 presented DSC traces of the BMI-HSQ-DABPA resins at the heating rate of $10^\circ\text{C}/\text{min}$. The DSC analysis results of the second peak were tabulated in Table II. Two exothermic peaks appeared in the ranges of $130\text{--}170^\circ\text{C}$ and $190\text{--}290^\circ\text{C}$, which resulted from the diene-addition and Diels-Alder reaction between DABPA and BMI-HSQ, respectively. The curing reactions for BMI-HSQ-DABPA resins were similar to those for BMI-DABPA resins (see Scheme 2).^{30,31} According to the results, the curing cycle of BMI-HSQ-DABPA resins was determined in several steps as follows: $180^\circ\text{C}/2\text{ h} + 200^\circ\text{C}/2\text{ h} + 220^\circ\text{C}/2\text{ h} + 250^\circ\text{C}/5\text{ h}$.

The cured BMI-HSQ-DABPA resin (No. b) was examined by FTIR, as shown in Figure 2. The stretching vibration peak at 3075 and 920 cm^{-1} almost disappeared in the spectrum of cured BMI-HSQ-DABPA resin. The absorption peak at 1149 cm^{-1} assigned for C-N-C groups disappeared, and another peak at 1180 cm^{-1} became wide, with the peak intensity increasing. Those facts indicated that the reaction between C=C in the imide rings of BMI and the allyl groups in DABPA occurred during the curing of the resins.

TABLE II
DSC Analysis Results of BMI-HSQ-DABPA Resins

No.	T_i ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	H (J/g)
a	189	258	294	182
b	192	262	303	185
c	197	253	284	142
d	199	256	287	127



Scheme 2 The curing reaction process of BMI and DABPA.

Properties of the cured BMI-HSQ-DABPA resins

The influences of the HSQ component on the glass transition temperatures (T_g) of the cured BMI-HSQ-DABPA resins were investigated by DSC. The DSC analysis (in N_2 , $20^\circ\text{C}/\text{min}$) results were shown in Figure 4 and Table III. The addition of HSQ increased the T_g of the cured resins obviously. The T_g of the cured BMI-DABPA was 304°C . As shown in Table III, the T_g of the cured modified resins enhanced with the increment of HSQ contents. The No. d possessed the highest T_g at 323°C .

The aforementioned results were derived from two factors. First, HSQ could hinder the polymer chain motions due to its rigid cage structure. Thus, the T_g of the cured BMI-HSQ-DABPA resins was increased with the increment of the HSQ contents. Second, the flexible isopropylidene structure in DABPA could enhance the motion of the polymer chains. The T_g of the cured BMI-HSQ-DABPA resins would increase when the DABPA loadings reduced.

The thermal properties of the cured BMI-HSQ-DABPA resins was better than those of the cured

BMI-DABPA resin and other modified BMI-DABPA resins, such as cured BMI-DABPA-DDS resin (T_g : 250°C) and cured BMI-DABPA-DPD resin (T_g : 285°C).^{25,26} The BMI-HSQ-DABPA resins would be a good candidate as a high performance matrix for advanced composites.

TGA (in N_2 , $10^\circ\text{C}/\text{min}$) was adopted to investigate the stabilities of the cured BMI-DABPA and BMI-HSQ-DABPA resins. The results were presented in Figure 5 and Table III. The decomposition curves had only one step, as shown in Figure 5, which demonstrated that the HSQ was integrated into the crosslinking network in the form of chemical dispersion.

The stabilities of the cured resins were improved by the addition of HSQ. With increasing in the content of HSQ, the temperature at 5 wt % loss (T_{d5}) and residue yield (Y_r) of cured BMI-HSQ-DABPA resins increased. Especially T_{d5} and Y_c of resin d reached 422°C and 50.7%, respectively, as compared with that of the 393°C and 32.3% of the cured BMI-DABPA resin (curve o in Fig. 5). The thermal stabilities of the modified resins could be contributed by the introduction of HSQ into the crosslinking network. Eight functional groups in one HSQ molecule would take part in crosslinking reactions to largely enhance the crosslinking density of the cured resins. Moreover, the excellent heat-resistant Si—O—Si inorganic framework further contributes

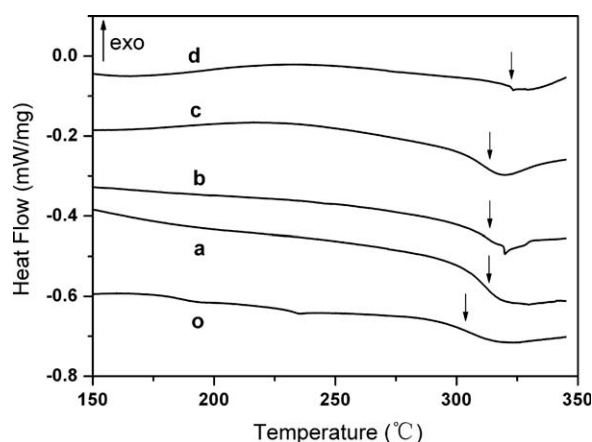


Figure 4 DSC curves of the cured BMI-HSQ-DABPA resins with various ratios.

TABLE III
DSC and TGA Analysis Results of the Cured BMI-HSQ-DABPA Resins

No.	T_g ($^\circ\text{C}$)	T_{d5} ($^\circ\text{C}$)	Y_r (%)
o (BMI-DABPA)	304	393	32.3
a	313	388	33.0
b	313	397	37.0
c	313	410	41.9
d	323	422	50.7

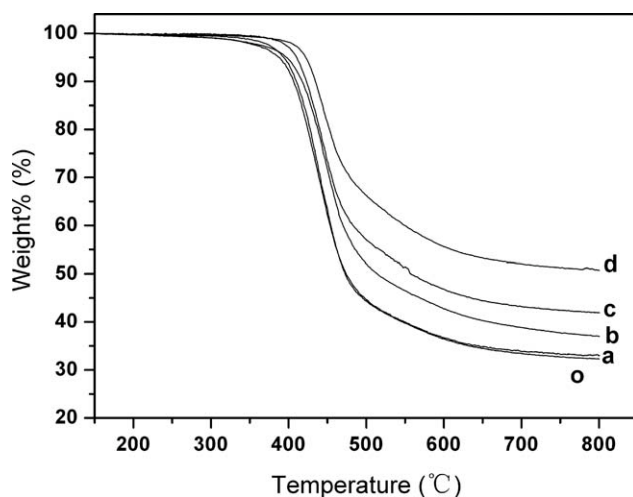


Figure 5 TGA curves of the cured BMI-HSQ-DABPA resins (in N_2) with various ratios.

to the stabilities of the modified polymer. Conclusively, high crosslinking density and inorganic components were the main reason that the cured BMI-HSQ-DABPA resins exhibited outstanding thermostability.

CONCLUSIONS

A series of modified BMI resins, BMI-HSQ-DABPA resins, containing different contents of HSQ were prepared. The curing behaviors of the BMI-HSQ-DABPA resins were investigated by DSC and FTIR. The DSC of the cured BMI-HSQ-DABPA resins showed high T_g and a rise of T_g from 304°C to 323°C, with the increment of HSQ content. The TGA results of the cured BMI-HSQ-DABPA implied an increment of the decomposition of T_{d5} from 393°C to 422°C and residue yield Y_r from 32.3% to 50.7% due to the addition of HSQ.

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