

Polybenzoxazine Containing Polysilsesquioxane: Preparation and Thermal Properties

Yonghong Liu, Weian Zhang, Yan Chen, Sixun Zheng

College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, People's Republic of China

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ABSTRACT: Benzoxazine bearing trimethoxysilane (BA-b) was successfully synthesized via Mannich condensation among phenol, paraformaldehyde, and γ -aminopropyltrimethoxysilane. The hydrolysis and condensation of the BA-b catalyzed by hydrochloric acid can afford a soluble polysilsesquioxane bearing benzoxazine groups (denoted PSSQ-b). By initiating the cocuring reaction of PSSQ-b with difunctional benzoxazine of bisphenol A (BA-a), the inorganic–organic hybrids of polybenzoxazine with polysilsesquioxane were pre-

pared. The hybrids displayed enhanced T_g 's in comparison with the control polybenzoxazine. In terms of initial decomposition temperature (T_d) and char and ceramic yields, the hybrids exhibited improved thermal stability as shown by thermogravimetric analysis (TGA). © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 927–936, 2006

Key words: benzoxazine trimethoxysilane; inorganic–organic hybrids; thermal properties

INTRODUCTION

Incorporating inorganic or organometallic segments to polymers to afford improved properties continues to be a driving force for the development of new materials.^{1–7} During the past decades, considerable attention has been focused on the syntheses of crosslinked glass-like matrices composed of Si–O–Si linkages via sol–gel process. Hydrolysis and subsequent condensation of tri- or tetraalkoxysilanes can result in a variety of silsesquioxane structures ranging from oligosilsesquioxanes⁸ to polysilsesquioxane networks, depending on the reaction conditions employed.^{1–3} The sol–gel process of alkoxysilanes with various functionalities also makes it possible to tailor the structure and properties of inorganic–organic hybrids. Generally, densely crosslinked silica (SiO₂) structures can be obtained via the hydrolysis and condensation of tetrafunctional alkoxysilanes, whereas the hydrolysis and condensation of trifunctional alkoxysilanes affords soluble branched polysilsesquioxanes with the general formula of RSiO_{3/2}.⁴ One of important purposes to employ sol–gel process is to prepare branched (or ladder-like) low-molecular-weight polysilsesquioxanes bearing functional (e.g., polymerizable) groups. The copolymerization of organic mono-

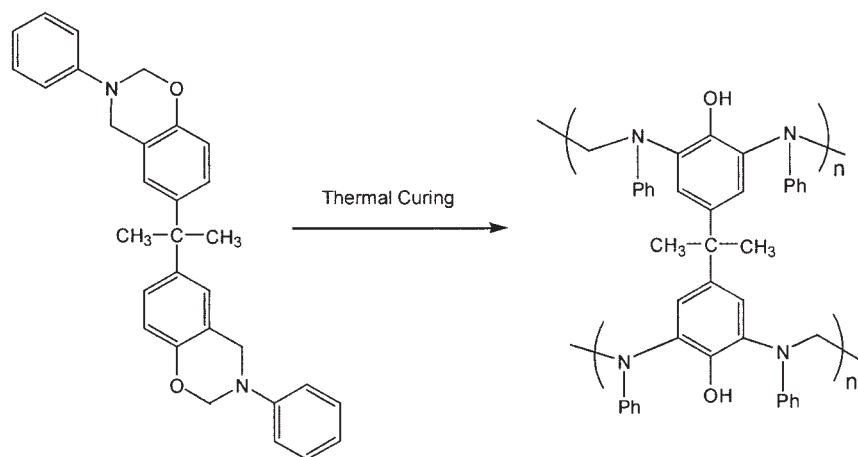
mers with the low-molecular-weight polysilsesquioxanes bearing polymerizable groups can lead to the formation of the organic–inorganic hybrids. The diversity of organic functional groups in polysilsesquioxane can provide ones with tremendous space for maneuver and control the microstructure and properties of the inorganic–organic hybrids. In recent years, there has been considerable interest in the preparation of organic–inorganic hybrids by means of epoxy-functionalized polysilsesquioxanes via the hydrolysis and condensation of 3-glycidoxypropyltrimethoxysilane.^{6–12} More recently, Crivello et al.¹³ reported a novel series of cationically polymerizable epoxy-functionalized organic–inorganic hybrid resin.

Polybenzoxazines (PBA-a) are a class of attractive phenolic resins, which can be used as the matrices of high-performance composites due to its superior mechanical properties and high-temperature stability. Without curing agent, the direct thermal curing of benzoxazine monomers can afford the thermosetting polybenzoxazine (PBA-a) (Scheme 1). Furthermore, PBA-a possesses excellent processability through a very wide range of molecular design flexibility.^{14–16} The potential applications of PBA-a motivate to prepare the materials with improved properties. It is expected that incorporating polysilsesquioxane segments to PBA-a could significantly improve their properties such as superior heat, radiation, and fire resistance, which makes them suitable for more extensive applications, e.g., in protecting coatings, thermal insulating materials, and optoelectronic devices. Agag and Takeichi¹⁷ have first reported the preparation of polybenzoxazine–silica hybrids via sol–gel process.

Correspondence to: S. Zheng (szheng@sjtu.edu.cn).

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Scheme 1 Thermal polymerization of BA-a

The silica component was formed in situ via sol-gel process of the physical mixtures of benzoxazine with tetraethoxysilane. It was reported that the incorporation of silica into polybenzoxazine matrix has a noticeable effect on the thermal and mechanical properties. In the hybrid materials, no chemical covalent bonds were formed between silica and PBA-a matrix, and thus the phase separation could occur at a considerable scale. It is proposed that the formation of chemical bonds between PBA-a matrix and inorganic component could optimize the dispersion of inorganic component in organic matrix by improving the inter-component adhesion, and thus the properties of materials will be further improved.

In this work, we first present the synthesis of benzoxazinotrimethoxysilane, a benzoxazine-functionalized trimethoxysilane, which was further used to prepare in situ a branched (or ladder-like) low-molecular-weight polysilsesquioxanes bearing benzoxazine groups via hydrolysis and condensation in the mixtures with difunctional benzoxazine resin (e.g., BA-a). By initiating the thermal curing of the mixture, the PBA-a hybrids containing polysilsesquioxane were prepared. To our knowledge, there were no precedent reports on the preparation of PBA-a hybrids by incorporating benzoxazine-functionalized polysilsesquioxanes. The purpose of this work, therefore, is to characterize the structure of the inorganic-organic hybrids by means of Fourier transform infrared (FTIR), and ^{29}Si solid-state nuclear magnetic resonance spectroscopy (NMR). The thermal properties of the PBA-a hybrids will be addressed based on the results of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Bisphenol A, phenol, aniline, 3-aminopropyltrimethoxysilane (APTMS), and formaldehyde solution

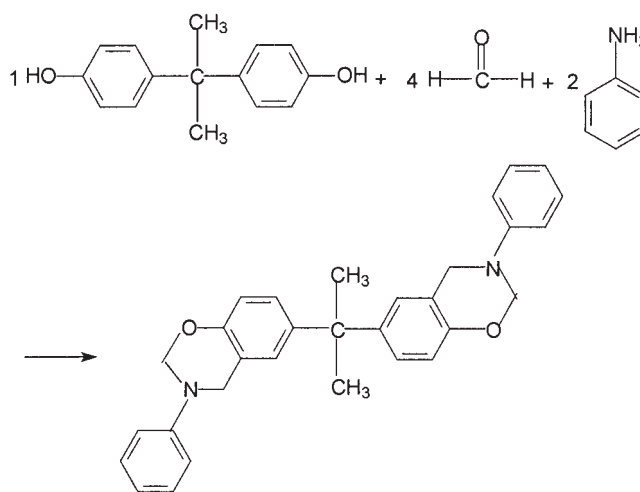
(~40% in water) were purchased from Shanghai Reagent Co., Shanghai, China, and were used as received. Paraformaldehyde was obtained from Sigma-Aldrich Co. The solvents such as chloroform, tetrahydrofuran, 1,4-dioxane were of analytically pure grade, obtained from commercial resource. Prior to use, chloroform was purified by distillation over calcium hydride (CaH_2).

Synthesis of difunctional benzoxazine (BA-a)

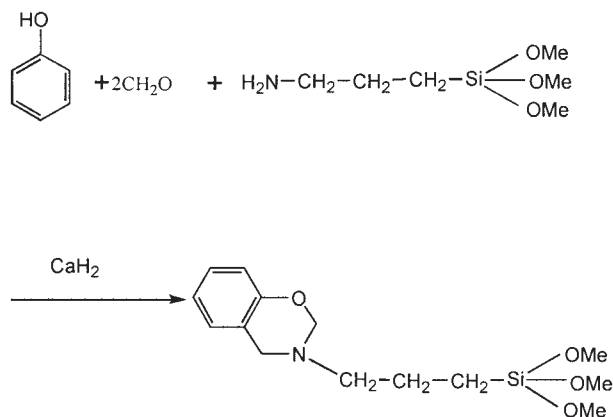
The difunctional benzoxazine based on bisphenol A (BA-a) was synthesized and purified according to the procedure described elsewhere.^{14,18,19} The Mannich condensation among bisphenol A, formaldehyde solution, and aniline was employed to prepare BA-a as shown in Scheme 2.

Synthesis of 3-(trimethoxysilyl)-*n*-propyl-1,3-dihydro-2*h*-1,3-benzoxazine (BA-b)

The benzoxazine-functionalized trimethoxysilane (BA-b) was synthesized by a modification of the method



Scheme 2 Synthesis of difunctional benzoxazine (BA-a)



Scheme 3 Synthesis of benzoxazine (BA-b)

available in the literature²⁰ (Scheme 3). In a typical experiment, a suspension of paraformaldehyde (1.21 g, 0.04 mol with respect of formaldehyde) in 25 mL chloroform was charged to a 100 mL three-neck flask in a nitrogen atmosphere and 2.0 g calcium hydride (CaH_2) was added to the system. The mixture was heated up to 65°C and then the 3.58 g (0.02 mol) of γ -aminopropyltrimethoxysilane was added to the system with vigorous stirring. The above reactive system was heated up to 85°C. At this temperature, 1.88 g (0.02 mol) of phenol was added and the reaction was conducted for 3 h. The solid residues were filtered out. The solvent together with other volatile impurities was distilled out under decreased pressure to afford the transparent and viscous liquid (4.88 g, yield: 82%). FTIR (cm^{-1}) with KBr windows: 1087 (methoxy groups); 926 (oxazine ring); 1334 (C—N); 1257, 1032 (Ar—O—C); 819 (1,2-disubstituted benzene ring), 1228 (C—O—C). ^1H NMR (chloroform-*d*, ppm): 3.58 (Si—O— CH_3 , 9H), 0.67 ($-\text{CH}_2-\text{Si}$, 2H), 1.66 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$, 2H), 2.73 (N— CH_2-CH_2 , 2H), 3.98 (Ph— CH_2-N , 2H), 4.82 (O— CH_2-N , 2H), 6.75–7.26 (aromatic ring, 4H).

Preparation of polybenzoxazine containing polysilsesquioxane

The desired amount of BA-a and BA-b were mixed and dissolved in tetrahydrofuran (THF) with the concentration less than 10 wt %. Deionized water [H_2O]/[BA-b] = 6 : 1 (mol)] and 0.01M HCl [$[\text{HCl}]/[\text{H}_2\text{O}] = 0.3 : 1(\text{mol})$] were charged to the mixtures. The hydrolysis and condensation was carried out for 3 h at room temperature with continuous stirring until homogeneous solutions were attained. The solutions were cast onto Petri dishes, and the majority of solvent was evaporated at room temperature and the residual solvent was removed by drying *in vacuo* at 60°C for 2 h. The films were further cured at 180°C for 4 h and the

cured hybrids were obtained with the concentration of BA-b up to 90 wt %.

Measurement and techniques

Fourier transform infrared spectroscopy

The FTIR measurements were conducted on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer at room temperature (25°C). The samples of hybrids were granulated and the powder was mixed with KBr pellets to press into the small flakes. The specimens were sufficiently thin to be within a range where the Beer-Lambert law is obeyed. In all cases, 64 scans at a resolution of 2 cm^{-1} were used to record the spectra.

Nuclear magnetic resonance spectroscopy

The NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 27°C. The BA-b was dissolved with deuterated chloroform and the ^1H NMR spectrum was recorded with tetramethylsilane (TMS) as the external reference. The solid-state NMR experiment was also carried out. The high-resolution ^{29}Si NMR spectra were obtained using the cross polarization (CP) /magic angle spinning (MAS) together with the high-power dipolar decoupling (DD) technique. The 90°-pulse width of 4.6 μs was employed with free induction decay signal accumulation, and the CP Hartmann-Hahn contact time was set at 3.5 ms for all the experiments. The rate of MAS was 4.0 kHz for measuring the spectra. The Hartmann-Hahn CP matching and DD field was 57 kHz. The time of recycle delay was set to be 10.0 s for the signal accumulation. The chemical shifts of all ^{29}Si spectra were determined by taking the silicon of solid Q_8M_8 relative to TMS as an external reference standard.

Differential scanning calorimetry

The calorimetric measurement was performed on a Perkin-Elmer Pyris-1 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with standard Indium. All the samples (about 10 mg in weight) were heated from 20 to 250°C and the DSC curves were recorded at a heating rate of 20°C/min. The glass transition temperature was taken as the midpoint of the capacity change.

Thermogravimetric analysis

A Perkin-Elmer thermal gravimetric analyzer (TGA-7) was used to investigate the thermal stability of the hybrids. The samples (about 10 mg) were heated under N_2 atmosphere from ambient temperature to 800°C at the heating rate of 20°C/min in all cases. The

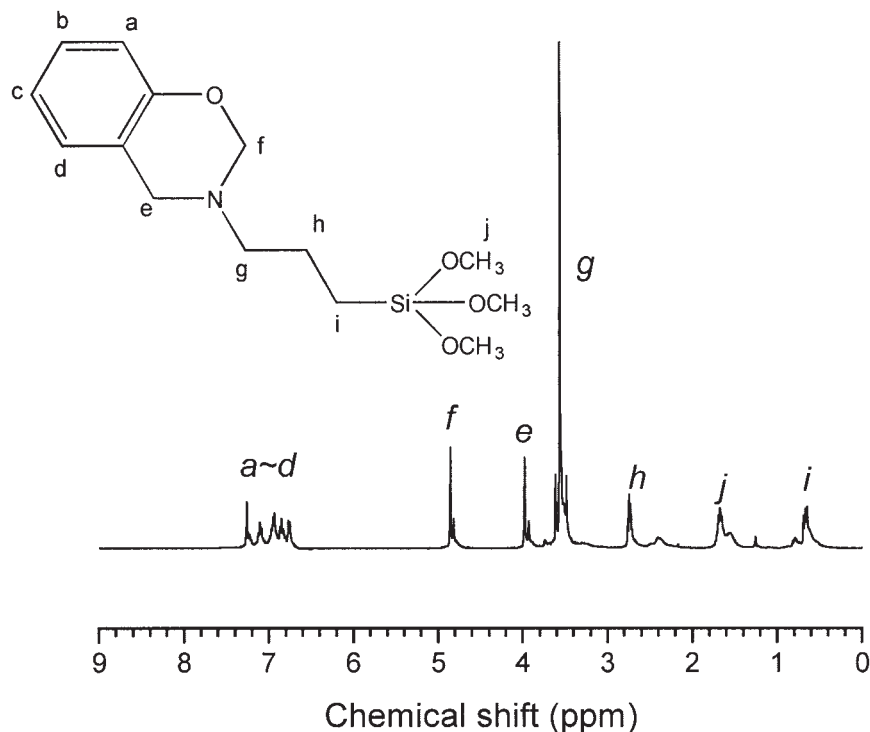


Figure 1 ^1H NMR spectrum of BA-b.

thermal degradation temperature was taken as the onset temperature at which 5 wt % of weight loss occurs.

RESULTS AND DISCUSSION

Synthesis of BA-b

Mannich condensation can be employed to synthesize a variety of benzoxazine monomers.^{14,18,19} Ishida et al.²⁰ reported the synthesis of BA-b via Mannich condensation among phenol, formaldehyde, and γ -aminopropyltriethoxysilane as depicted in Scheme 2. In the synthesis, the water molecules produced can be automatically separated from the product phase when the nonpolar solvent was used, since the benzoxazine portion of the product is insoluble in water; therefore, the triethoxyl groups of the silane were protected. However, we noted that the literature method was not applicable to the synthesis of BA-b when γ -aminopropyltrimethoxysilane (APT MOS) was used as the reactant, which could be due to the higher activity of trimethoxysilane portion in APT MOS in the reaction of hydrolysis. Our experiments showed that the extensive hydrolysis of trimethoxysilane induced by the portion of water molecules occurred. To overcome the problem, we added a desired amount of calcium hydride (CaH_2) to the system to consume the water molecules produced during Mannich condensation. The experimental results indicate that this exercise

was quite efficient to suppress the undesired hydrolysis reaction. It is noted that either excessive CaH_2 or the $\text{Ca}(\text{OH})_2$ produced from the reaction of CaH_2 with the water molecules existed in the reactive system in the form of precipitates, which did not affect the reaction in the organic phase and can easily be isolated.

Shown in Figure 1 is the ^1H NMR spectrum of the as-synthesized product together with the assignment of its resonance signals. The BA-b was characterized by the resonance at 0.67, 1.66, 2.73, and 3.58 ppm, which indicates the presence of APT MOS moiety. The resonance of APT MOS moiety together with Mannich bridge portion of the product indicates that no dimer (or oligomer) of benzoxazine was produced by means of the synthetic technique with modification. The FTIR spectrum of the product is shown in Figure 2. The BA-b is characterized by the bands at 1087 and 926 cm^{-1} , respectively. The former is ascribed to the stretching vibration of Si-O bonds in trimethoxysilane, whereas the latter to that of oxazine ring. The fact that no stretching vibration band in the range of 3200–4000 cm^{-1} was observed in the FTIR spectrum further indicates that no dimers or oligomers were formed in the synthesis.

Preparation of inorganic-organic hybrids

The hydrolysis and condensation of trifunctional BA-b catalyzed by hydrochloric acid will afford soluble oli-

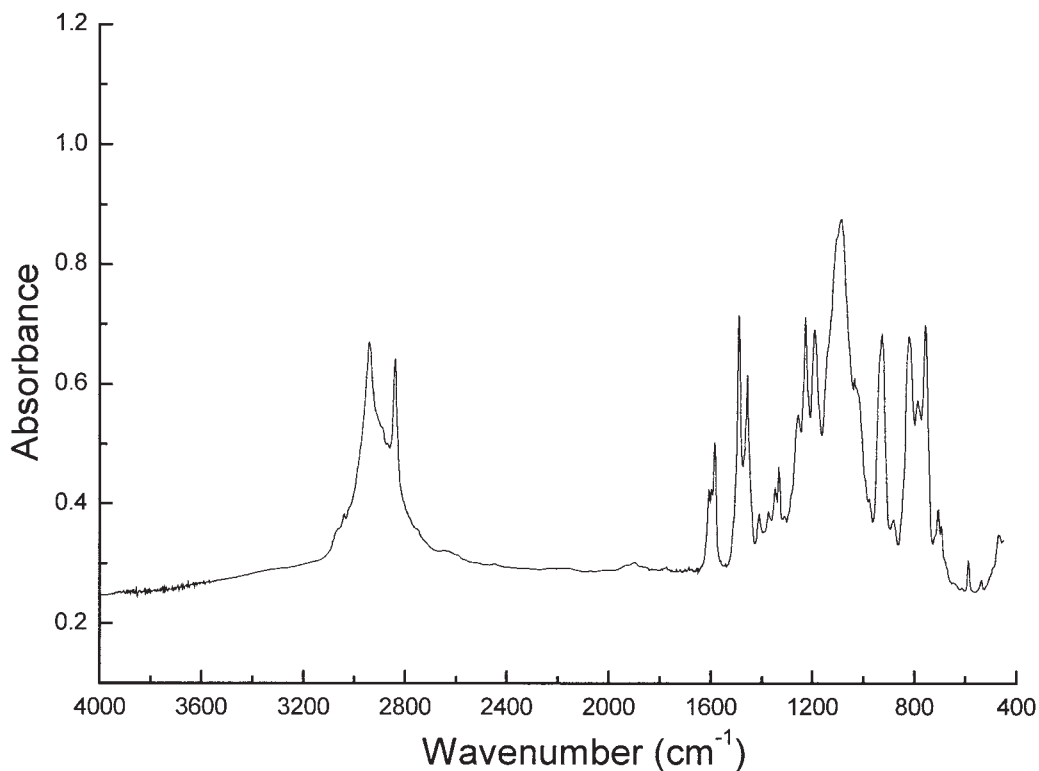
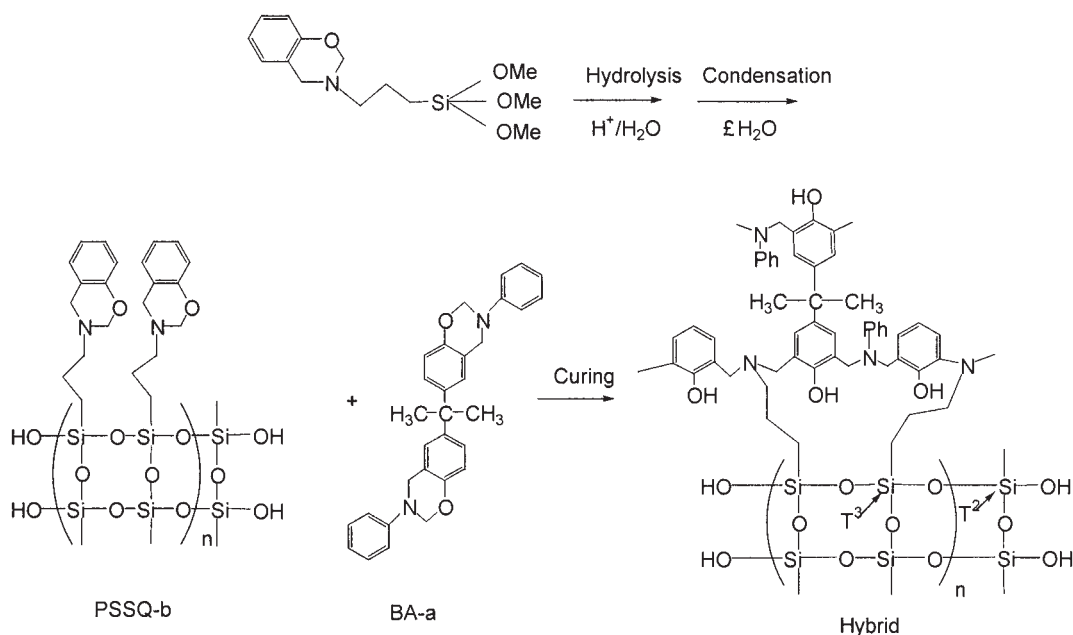


Figure 2 FTIR spectrum of BA-b.

gomerics polysilsesquioxane bearing benzoxazine (denoted PSSQ-b). It is seen that all the mixtures composed of BA-a and PSSQ-b were homogeneous and transparent, indicative of the miscibility of both components. The miscibility can be ascribed mainly to the

entropy contribution because the molecular weights of all the components are rather low. The mixture of BA-a and PSSQ-b was thermally cured at 180°C for 4 h and the inorganic–organic hybrids involving polybenzoxazine and polysilsesquioxane were formed in situ



Scheme 4 Preparation of polybenzoxazine hybrids containing polysilsesquioxane

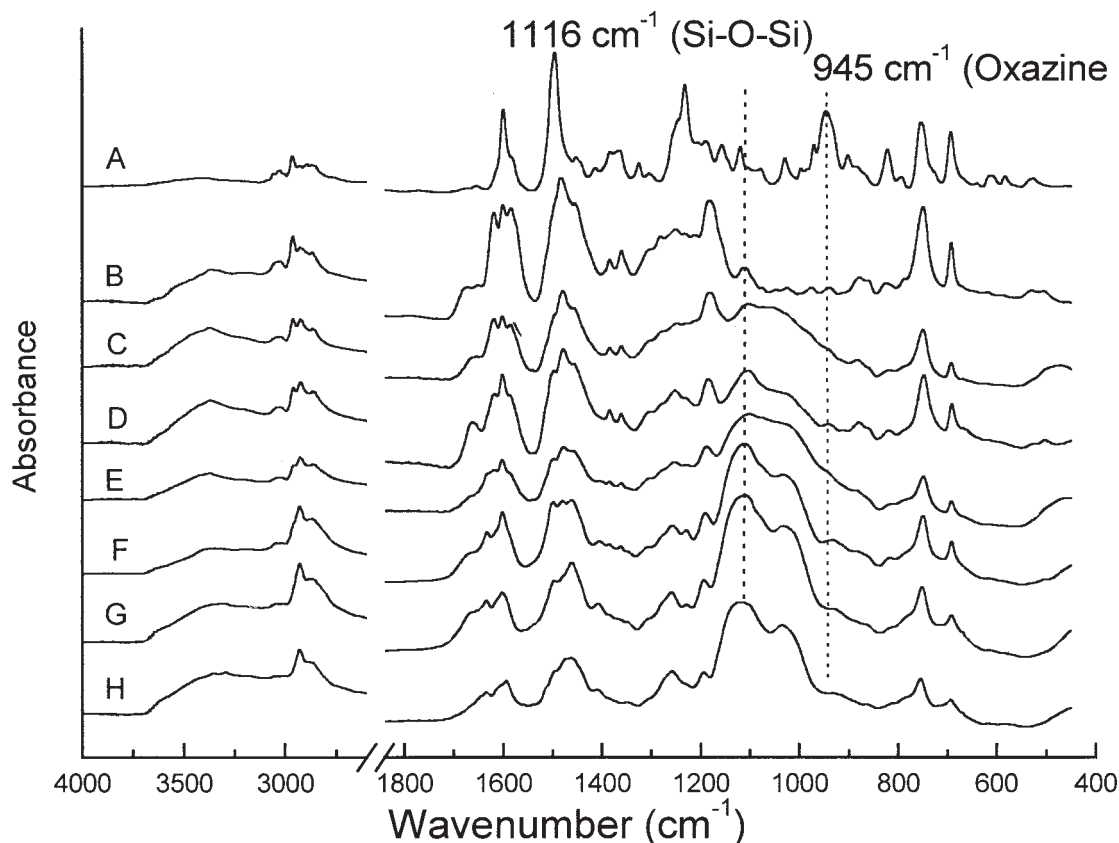


Figure 3 FTIR spectra of BA-a, PBA-a, and the hybrids: (A) BA-a; (B) PBA-a; (C) the hybrids containing 7.9; (D) 24.7; (E) 43.2; (F) 64.2; (G) 87.3; and (H) 100 wt % of PSSQ.

as shown in Scheme 4. It is noted that all the PBA-a hybrids containing polysilsesquioxane were transparent, suggesting that the hybrids are homogenous, i.e., no phase separation occurred at the scale more than the wavelength of visible light. This observation is in marked contrast to the case when silica (SiO_2) was physically mixed with polybenzoxazine.¹⁷ It is proposed that the formation of chemical bonding between PBA-a and polysilsesquioxane via ring-opening polymerization of benzoxazine groups effectively suppresses the phase separation at the considerable scale.

To examine the degree of curing reaction, we measured the infrared spectra of the cured hybrids. Shown in Figure 3 are the FTIR spectra of BA-a, PBA-b, and the hybrids containing PSSQ-b up to 100 wt %. The benzoxazine ring is characterized by the stretching vibration band at 945 cm^{-1} . It is noted that under the present condition, the curing reaction of the difunctional benzoxazine (BA-a) was quite complete, which was evidenced by the disappearance of the oxazine band. The similar results were also found for the PBA-a hybrids containing polysilsesquioxane, indicating that the curing reactions in the hybrids were performed to completion.

The ^{29}Si CP/MAS NMR spectroscopy was used to quantitatively investigate the degree of condensation

for trimethoxysilane in the hybrids in terms of the abundance of the T^2 and T^3 silicon nuclei (see Scheme 4). Figure 4 presents the ^{29}Si NMR spectra of the hybrids. For the hybrid prepared from the pure BA-b, the sharp resonance at -65.4 ppm is attributed to silicon atoms in completely condensed trimethoxysilane (*viz.* T^3 structure) and the weak remnant resonance at low field (*viz.* -55.6 ppm) is responsible for those of incompletely condensed silane (*viz.* T^2 structure), which was in a good agreement with the literature values.²¹

It is seen that for the hybrids prepared from BA-a/BA-b (90/10 and 70/30) mixtures, the amount of the incompletely condensed structure (i.e., T^2) is much higher than that from BA-b. The content of T^2 structure increased with increasing the content of PBA-a. In the composite system, the hydrolysis of BA-b affords a great number of silanol hydroxyls, which are highly reactive and tend to self-condense to form polysilsesquioxane linkage, especially at the elevated temperature.²² In the oligomeric PSSQ-b, the terminal silanol hydroxyls were easily condensed to completion due to the high concentration. However, after the miscible component BA-a, which could act as the diluent or spacer of PSSQ-b, was added to the system, the incomplete condensation among the silanol hydroxyls will

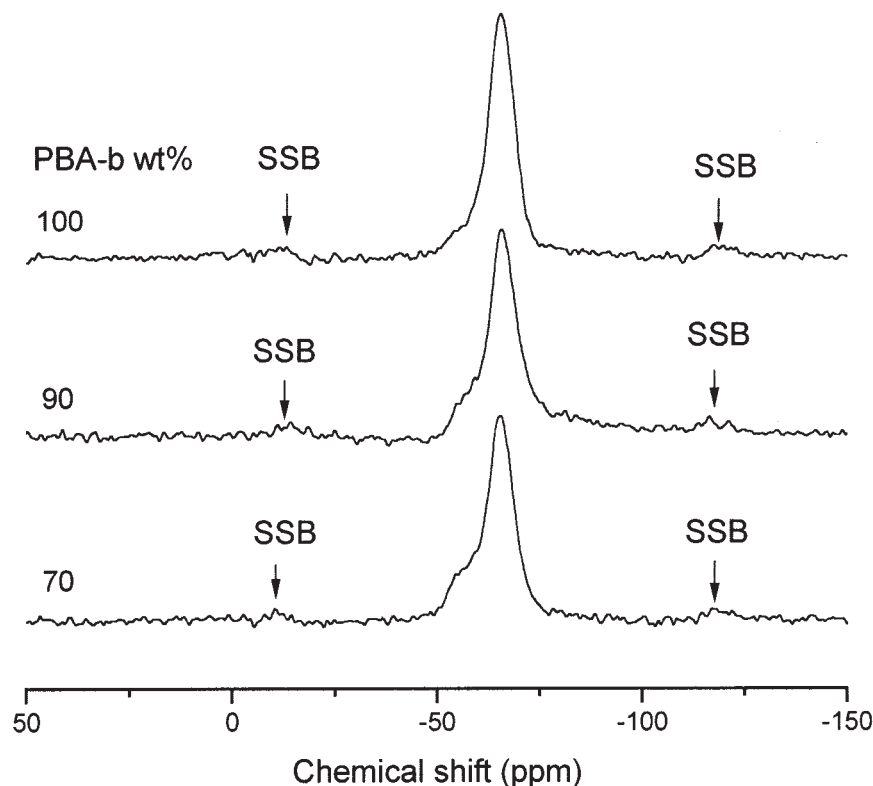


Figure 4 ^{29}Si CP/MAS NMR Spectra of the hybrids.

occur. With the curing reaction proceeding at elevated temperature, the systems underwent a series of structural changes, such as chain growth, branching, gelation, and vitrification. The formation of crosslinked PBA-a will inhibit the condensation of silanol hydroxyls of PSSQ-b. Therefore, the higher the concentration of BA-a, the more is the incompletely condensed moieties as shown in Figure 4. The solid ^{29}Si NMR spectroscopic result also suggests that polysilsesquioxane moiety could be homogeneously dispersed into the PBA-a matrix on the segmental scale.

Thermal properties

Glass transition behavior

All the hybrids were homogeneous and transparent, implying that no phase separation occurred at the scale exceeding the wavelength of visible light. The polysilsesquioxane-containing polybenzoxazine hybrids were subjected to thermal analysis. The DSC curves of the hybrids are presented in Figure 5. The control PBA-a displayed a glass transition temperature (T_g) at about 163°C .²³ For the cured PSSQ-b, the glass transition occurred at 213°C , which is much higher than that of the control PBA-a. For all other hybrids, all the DSC thermograms displayed single glass transition temperatures (T_g 's) in the experimental temperature range (20 – 250°C). The single glass

transition behavior indicates that the hybrids are homogeneous. It is seen that the T_g 's of the hybrids increase with increasing the concentration of PSSQ-b (Fig. 6). The enhancement in T_g for the hybrids is ascribed to the reinforcement of polysilsesquioxane structure. The change in T_g 's could suggest that the motions of polymer chains were disturbed by polysilsesquioxane moieties on the segmental level, i.e., at the scale of 20 – 30 nm in terms of T_g feature^{24,25} for the hybrids.

Thermal stability

TGA was applied to evaluate the thermal stability of the polysilsesquioxane-containing polybenzoxazine hybrids. Shown in Figure 7 are the TGA curves of control PBA-a, the cured PSSQ-b and their composites, recorded in nitrogen atmosphere. For the pure PBA-a, the initial decomposition that was defined as 5% of mass loss occurs at about 310°C and the char yield at 800°C is 19 wt %. For the cured PSSQ-b, the initial decomposition temperature is 330°C , which was higher than that of the pure PBA-a. Nonetheless, the summation of char and ceramic yield is about 63 wt %, which is much higher than that of PBA-a due to the presence of polysilsesquioxane structure. Comparison of the thermal stabilities shows that the PBA-b is more stable than PBA-a. For the PSSQ-containing hybrids,

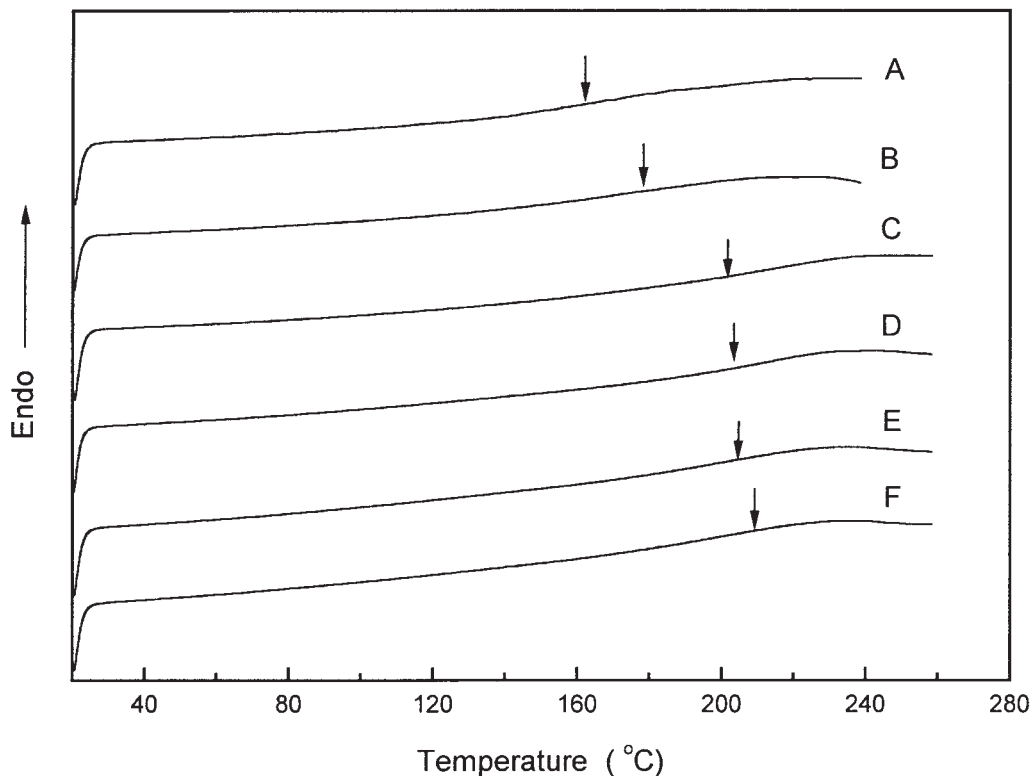


Figure 5 DSC curves of PBA-a hybrids containing polysilsesquioxane. (A) PBA-a; (B) hybrids containing 7.9; (C) 24.7; (D) 43.2; (E) 64.2; (F) 87.3; and (F) 100 wt % of PSSQ.

the initial decomposition temperatures and the summation of char and ceramic yield significantly increased with increasing the concentration of PSSQ-b. In terms of the thermogravimetric results, the thermal stability of hybrids was significantly enhanced with incorporating the inorganic component. In the cured PSSQ-b and its composites with PBA-a, the polysilsesquioxane participated in the formation of the crosslinked network, i.e., the polysilsesquioxane moieties were anchored onto the organic matrix via the curing reaction of benzoxazine rings. It is plausible to propose that mass loss from segmental decomposition via gaseous fragments could be suppressed by well-dispersed polysilsesquioxane at the segmental level. The similar results were also founded in fully exfoliated polymer-clay nanocomposites^{26,27} and polyhedral oligomeric silsesquioxanes containing hybrids.^{28–30}

CONCLUSIONS

The benzoxazine bearing trimethoxysilane (BA-b) was successfully synthesized via Mannich condensation among phenol, paraformaldehyde, and APTMOS. To overcome the problem that the water molecules produced during the condensation extensively hydrolyzed the alkoxy silane groups, calcium hydride

(CaH₂) was added to the system to eliminate the water molecules. The synthesis can be taken as a modification of the method previously reported. The as-synthesized BA-b was mixed with desired amount of benzoxazine of bisphenol A (BA-a) using the cosolvent THF. Prior to solution casting, a small amount of deionized water together with a catalytic amount of hydrochloric acid was added to the system to afford the polysilsesquioxane bearing benzoxazine groups (PSSQ-b). The homogeneous inorganic-organic hybrids comprised of polybenzoxazine and polysilsesquioxane were prepared via cocuring reaction of BA-a and PSSQ-b at the elevated temperature. FTIR spectroscopy indicates the cocuring reaction was performed to completion. DSC showed that the polybenzoxazine prepared from BA-b displayed a higher glass transition temperature (T_g) than PBA-a; the inorganic-organic hybrids containing polysilsesquioxane displayed enhanced T_g 's. TGA indicates that the hybrids exhibited improved thermal stability in terms of initial decomposition temperature (T_d) and the summation of char and ceramic yields. The improvement of thermal properties is attributed to incorporation of polysilsesquioxane moiety via chemical anchor, which could reinforce the organic matrix and thermally insulate the release of gaseous fragments during thermal decomposition.

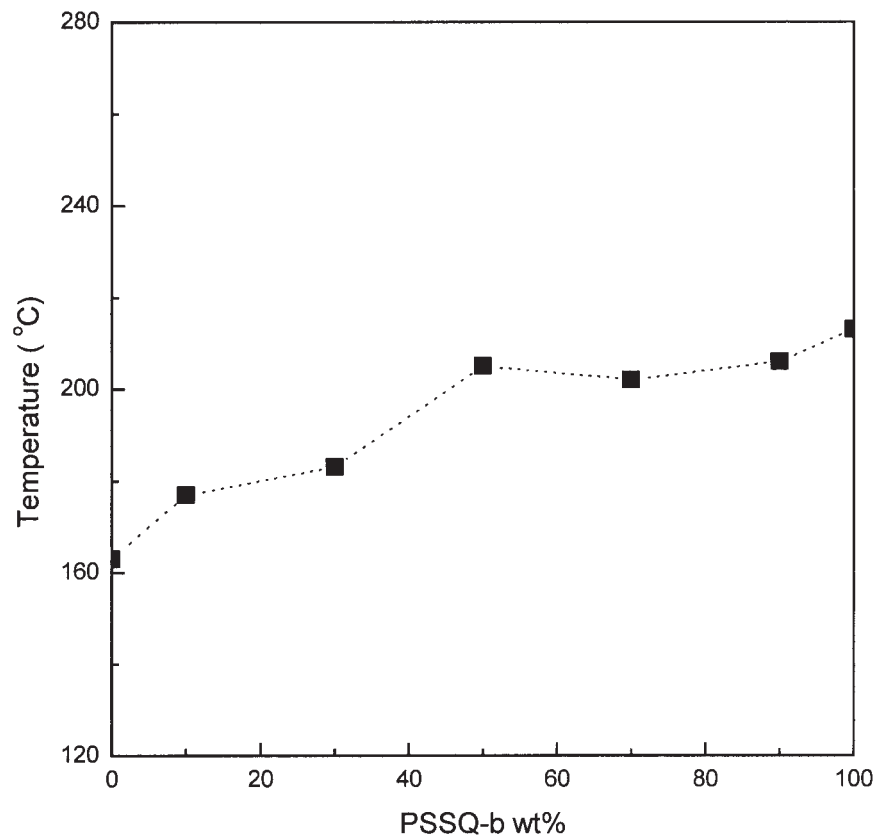


Figure 6 Plot of T_g 's as functions of PSSQ-b concentration for PBA-a hybrids containing polysilsesquioxane.

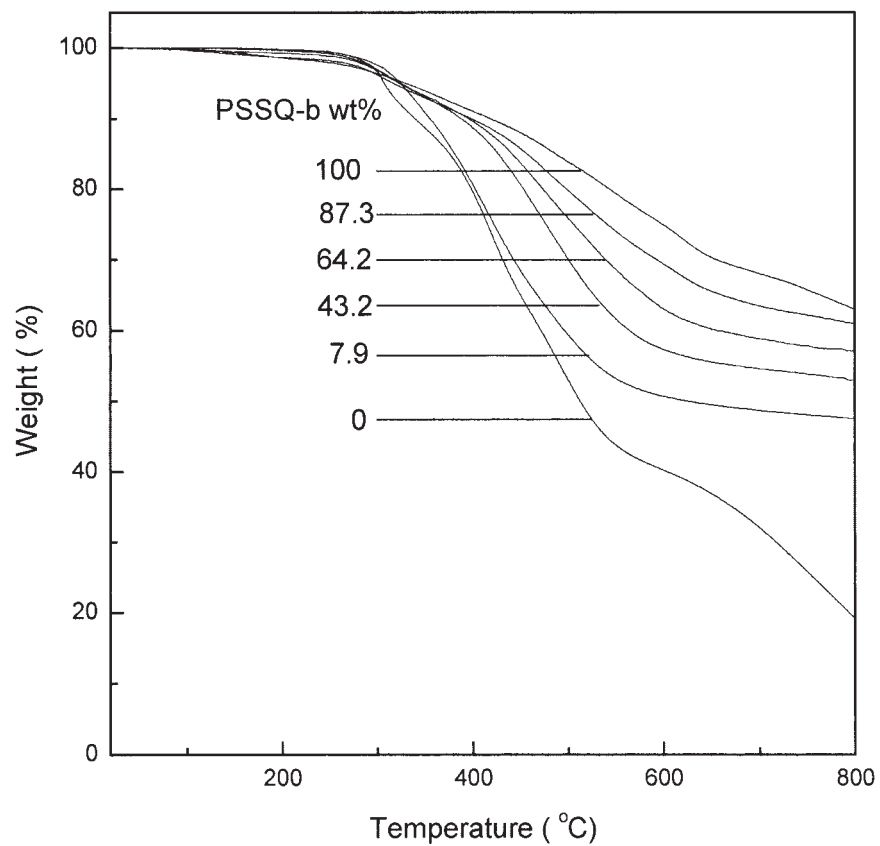


Figure 7 TGA curves for PBA-a hybrids containing polysilsesquioxane.

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