

Study of Surface-Functionalized Nano-SiO₂/Polybenzoxazine Composites

Chun Yan,¹ Xinyu Fan,¹ Juan Li,¹ Shirley Zhiqi Shen²

¹Ningbo Key Laboratory of Polymer Materials, Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, People's Republic of China

²CSIRO Material Science and Engineering, Highett, Victoria, Australia

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ABSTRACT: A series of the surface-functionalized nano-SiO₂/polybenzoxazine (PBOZ) composites was produced, and an attempt was made to improve the toughness of PBOZ material, without sacrificing other mechanical and thermal properties. A benzoxazine functional silane coupling agent was synthesized to modify the surface of nano-SiO₂ particles, which were then mixed with benzoxazine monomers to produce the nano-SiO₂-PBOZ nanocomposites. The notched impact strength and the bending strength of the nano-SiO₂-PBOZ nanocomposites increase 40% and 50%, respectively, only with the addition of 3 wt % nano-SiO₂. At the same load of nano-SiO₂, the nano-SiO₂-PBOZ nanocomposites exhibit the highest storage

modulus and glass-transition temperature by dynamic viscoelastic analysis. Moreover, the thermal stability of the SiO₂/PBOZ nanocomposites was enhanced, as explored by the thermogravimetric analysis. The 5% weight loss temperatures increased with the nano-SiO₂ content and were from 368°C (of the neat PBOZ) to 379°C or 405°C (of the neat PBOZ) to 426°C in air or nitrogen with additional 3 wt % nano-SiO₂. The weight residue of the same nanocomposite was as high as 50% in nitrogen at 800°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1525–1532, 2011

Key words: polybenzoxazine; nanosilicas; nanocomposite; mechanical properties; thermal stability

INTRODUCTION

Polybenzoxazine (PBOZ) has been developed as a novel phenolic resin, which is obtained from the ring-opening polymerization of corresponding benzoxazine (BOZ) monomers.^{1,2} BOZ monomers can be synthesized using inexpensive and commercially available phenols, formaldehyde, and primary amines either by using solution or solventless methods.^{3,4} PBOZ possess typical properties of traditional phenolic resins, such as the excellent thermal properties and flame retardance.⁵ They also have unique characteristics like near-zero shrinkage or expansion during polymerization^{6–8} and low water absorption,⁹ which overcome the flaws of traditional phenol resins. Therefore, PBOZ has had a lot of attentions from aerospace and electronic industries. However, the PBOZ thermoset is inherently brittle because of its low level of cross-linking density.⁶ Hence, the structural applications of PBOZ could be markedly nar-

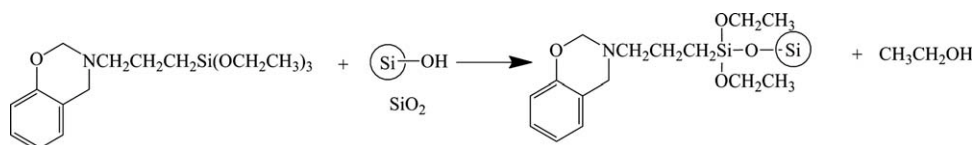
rowed. Various methods of toughening PBOZ have been reported. Amine-terminated butadiene acrylonitrile rubber¹⁰ and polyurethane^{11,12} were reported to be able to toughen PBOZ effectively. But the glass-transition temperatures decreased as rubber or polyurethane contents increased. Alloying of PBOZ with polyimide¹³ and poly(imide-siloxane)¹⁴ were effective in improving the brittleness of matrix and increasing the T_g and thermal degradation temperature without sacrificing the advantages of PBOZ.

Nanocomposites possess improved physical, mechanical, and thermal properties over the pristine polymer matrix as well known. The material properties of physically mixed inorganic-polymer composites depend on the content of the inorganic particles, their adhesion to the polymer matrix, the uniformity of particle dispersion, and some other factors.^{15–19} Numerous previous studies have reported that the resins modified with inorganic particles exhibited great improvements in their mechanical, thermal, and physicochemical properties compared with the pristine resin.^{18,20–23} However, there is no report on PBOZ toughening modified by nano-SiO₂ particles to our best knowledge. In this study, the nano-SiO₂ has been modified with a BOZ functional silane coupling agent to improve interface properties of SiO₂ and PBOZ in the nanocomposites. The effects of the modified nano-SiO₂ contents on the mechanical properties

Correspondence to: X. Fan (xinyu.fan@nimte.ac.cn).

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Scheme 1 Preparation of the modified nano-SiO₂ particles.

and fracture morphologies of the nanocomposites are also studied. Moreover, the dynamic viscoelastic analyses and the thermal stabilities of the SiO₂-PBOZ nanocomposites have been investigated as well.

EXPERIMENTAL

Materials

The nano-SiO₂ particles (particle size: ~ 10–15 nm) were obtained from Yuda Chemical Industry (Shaoying, China). Bifunctional BOZ was supplied by Sichuan University (Sichuan, China). A BOZ functional silane coupling agent, namely 3-triethoxysilyl-*n*-propyl-3,4-dihydro-2*H*-1,3-benzoxazine, was synthesized in-house according to a previous article by Ishida and Low.²⁴ Toluene and chloroform were from Sinopharm Chemical Reagent (Shanghai, China).

Preparation of modified nano-SiO₂ particles

67.8 g (0.2 mol) of the BOZ functional silane coupling agent and 20 g of the nano-SiO₂ were added to 150 mL toluene and kept stirring at 100°C for 15 h, as shown in Scheme 1. The modified nano-SiO₂ was then separated by centrifugal filtering, washed with toluene, and dried at 60°C in vacuum for 24 h consequently.

Preparation of SiO₂/PBOZ nanocomposites

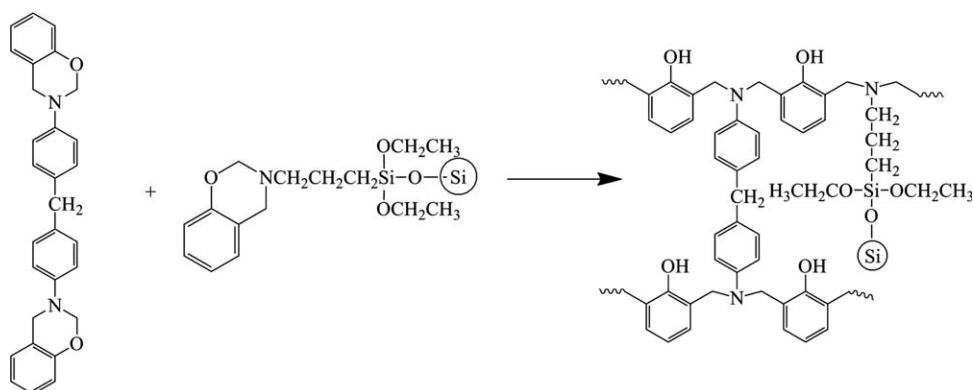
The designated amounts of modified nano-SiO₂ of 0, 1, 2, 3, 4, and 5 wt % and BOZ were dispersed into chloroform in a ultrasonic bath for 2 h. The solvent was then evaporated using a rotary evaporator, and, finally, the mixture was vacuum-dried at 80°C for

12 h. The mixture was placed in a stainless steel mold (cavity dimensions: 80 mm × 10 mm × 8.0 mm) and was degassed at 0.01 atm at 120°C for 1 h, and then was hold at 180°C for 2 h, 200°C for 2 h, and 220°C for 2 h in an air-circulating oven, respectively. The ring-opening polymerization of BOZ monomers and with the modified nano-SiO₂ is shown in Scheme 2. The obtained nanocomposites were treated by a buffing machine, and the thickness of the sample was 4.0 mm. The same procedure was also used for the preparation of a PBOZ sample as a comparison.

Characteristics and properties measurements

The nano-SiO₂ before and after modification were tested by Fourier transform infrared (FTIR) spectroscopy at a resolution of 4 cm⁻¹ with 32 scans using a Thermo-Fisher Nicolet 6700 FTIR. All samples were prepared as KBr pellets. ²⁹Si-nuclear magnetic resonance spectroscopy was also used for the same fine powder samples on a Bruker DSX-400WB.

Differential scanning calorimetry (DSC) was conducted on a Mettler Toledo DSC1 at a heating rate of 10°C/min over a temperature range of 50–350°C under a nitrogen flowing atmosphere for the cure kinetic study. Dynamic mechanical analysis (DMA) of the SiO₂-PBOZ nanocomposites and PBOZ was performed on a Mettler Toledo Star^e System DMA/SDTA861^e instrument. The rectangular specimens of 80 mm × 10 mm × 4.0 mm were tested using the three-point bending mode over a temperature range of 30–300°C. The heating rate and dynamic frequency were 5°C/min and 1.0 Hz, respectively. Thermogravimetric analyses (TGA) on the nanocomposites



Scheme 2 Ring-opening polymerization of BOZ monomer and modified nano-SiO₂.

was carried out on a Mettler Toledo TGA/DSC1, with a heating rate of 10°C/min over a temperature range of 50–800°C under either nitrogen or air flow at a rate of 30 mL/min.

Bending strengths were carried out on specimens with a dimension of 10 mm wide and 4.0 mm thickness and 80 mm length using Instron 5567 universal testing machine according to Chinese national standard GB 9341-2000. The notched impact strength was determined by an izod impact-testing machine (XJ-50Z, Chende, PRC) according to Chinese national standard GB 1843-1996. Transmission electron microscopy (TEM) (FEI Tecnai F20) was used to examine the microstructure of the nanocomposites at an acceleration voltage of 200 kV. The specimens were cut to about 100-nm-thick films using a diamond knife of a Leica Ultracut UCT ultramicrotome. The morphologies of the fracture surfaces were observed by a scanning electron microscope (FE-SEM S-4800, Hitachi, Japan) after gold sputtered.

RESULTS AND DISCUSSION

Characterization of modified nano-SiO₂ particles

The FTIR spectra of unmodified and modified nano-SiO₂ are shown in Figure 1. It is evident that the peak intensity at 3440 cm⁻¹ corresponding to -OH group²⁵ significantly decreases after the modification with BOZ functional silane. The characteristic absorptions of the modified nano-SiO₂ at 2934–2978 cm⁻¹ (stretching vibration of CH₂) and at 1457–1489 cm⁻¹ (bending vibration of CH₂) are observed, which indicate that the BOZ functional silane has been coupled onto the nano-SiO₂ surface.²⁶ The characteristic peaks of BOZ at 940 cm⁻¹ and Si-OH at 955 cm⁻¹ overlap. Figure 2 displays the solid-state ²⁹Si-nuclear magnetic resonance spectroscopy spec-

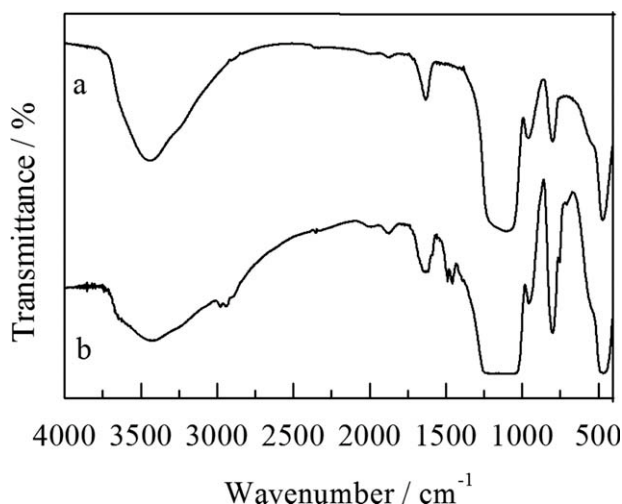


Figure 1 FTIR spectra of (a) unmodified nano-SiO₂ and (b) modified nano-SiO₂.

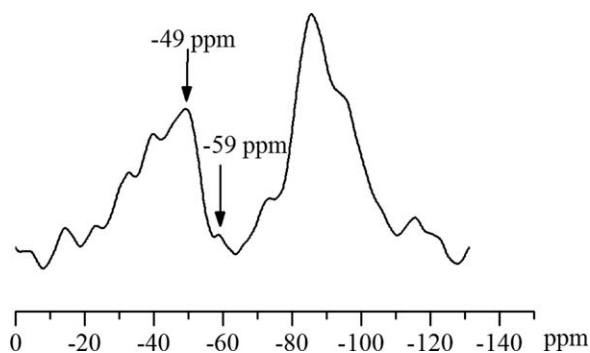


Figure 2 Solid-state ²⁹Si-nuclear magnetic resonance spectroscopy spectrum of modified nano-SiO₂ particle.

trum of the modified nano-SiO₂ particles. In the spectrum, the chemical shift of mono- and disubstituted siloxanes appear at -49 and -59 ppm, respectively.²⁷ It can be seen from the spectrum that the mono-substituted BOZ functional silane is dominant. Thus, one nano-SiO₂ particle can covalently link many BOZ functional silane molecules. Therefore, the BOZ functional silane on the surface of nano-SiO₂ will provide covalent bonding to PBOZ when oxazine ring-opening polymerization occurs.

Curing behavior of the SiO₂/PBOZ nanocomposites

The curing behavior of the SiO₂/PBOZ nanocomposites was studied by DSC and FTIR and was similar to each other with different nano-SiO₂ contents. So, only the result with 4 wt % of nano-SiO₂ content is discussed in details as an example. Figure 3 shows the DSC curves of the SiO₂/PBOZ nanocomposites with 4 wt % of nano-SiO₂ after heated at various temperatures for 2 h. A SiO₂/BOZ mixture without any heat treatment has an exotherm peak with an onset at 208°C and a maximum at 237°C corresponding to the ring-opening polymerization of BOZ. The cure enthalpy was calculated to be 263 J/g. After being heated at 180°C for 2 h, both the cure enthalpy and the onset temperature of the SiO₂/PBOZ nanocomposite decreased. The reason is that part of the BOZ monomers have been ring-opening polymerized and the phenolic hydroxyl groups have been obtained, which decrease the further ring-opening polymerization temperature. The cure enthalpy reduced to 133 J/g. After being heated at 200°C for 2 h, the cure enthalpy was only 37 J/g. It shows that most of BOZ monomers have been ring-opening polymerized and the residual oxazine ring opening occurs at a higher temperature with a maximum of 241°C. The exothermic peak disappears completely after being heated at 220°C for 2 h.

The curing behavior was also monitored by FTIR spectra (Fig. 4). The characteristic absorption bands for the BOZ structure at 933 cm⁻¹ (trisubstituted

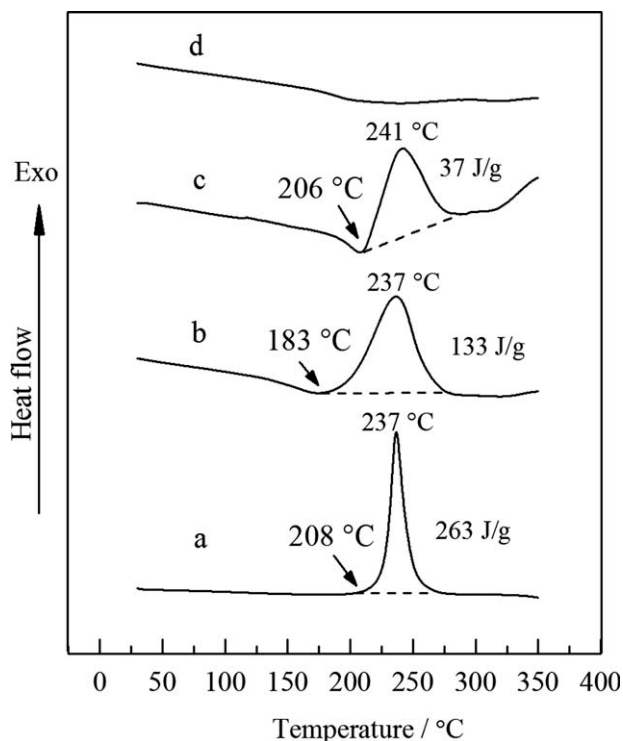


Figure 3 DSC curves of the SiO₂/PBOZ nanocomposites (a) without heat treatment; (b) cured at 180°C for 2 h; (c) cured at 200°C for 2 h; and (d) cured at 220°C for 2 h.

benzene ring), 1225 cm⁻¹ (asymmetric stretching of C-O-C), and 1336 cm⁻¹ (CH₂ wagging) decrease after heated at various temperatures and disappear after heated at 220°C for 2 h.² It suggested that the ring-opening polymerization of BOZ form PBOZ has been completed. In the meanwhile, a new peak at 3432 cm⁻¹ emerges, and the intensity of this peak increases with the heating temperatures. It is because that the ring-opening reaction of BOZ generates the phenolic hydroxyl groups. The amount of the phenolic hydroxyl groups increase with the heating temperatures and reaches the maximums when all oxazine rings have opened.

In summary, the SiO₂/PBOZ nanocomposites can be cured completely after heated at 220°C for 2 h. The FTIR results also confirm that BOZ have completely cross-linked to form the polymer according to the disappearing characteristic absorption bands of BOZ rings.

Mechanical properties of the SiO₂/PBOZ nanocomposites

Table I summarizes the results of impact and bending tests and also lists the contents of modified nano-SiO₂ particles in each case. Both the notched impact strength and the bending strength increase with the nano-SiO₂ contents first and reached the maximums of 2.68 kJ/m² and 151.4 MPa, respec-

tively, when the nano-SiO₂ content is 3 wt %. Both strengths decrease with further increases in the nano-SiO₂ contents. The modified nano-SiO₂ particles are bonded with the PBOZ matrix by chemical bonding, which forms an organic-inorganic hybrid interpenetrating network. When the nanocomposites were impacted, much more microcracks were formed and much more energies were absorbed accordingly than PBOZ without modified nano-SiO₂ particles. Thus, the nano-SiO₂ particles can enhance the toughneses of the SiO₂/PBOZ nanocomposites. However, when excess of the nano-SiO₂ particles are present, particle aggregations occurred, and the microcracks would be easily developed into macroscopic cracks, which decrease the impact strength of the nanocomposites. The 3 wt % of nano-SiO₂ may be just before the critical amount for the nanoparticles becoming agglomerates. When the nano-SiO₂ content reaches 3 wt %, the SiO₂/PBOZ nanocomposites show the highest values of both impact strength and bending strength. When the nano-SiO₂ content is more than 3 wt %, particle aggregates occur, which will be confirmed by the TEM photos in the next section, and cause decrease in the mechanical strengths.

Microstructure of the nanocomposite

The microstructures of the SiO₂/PBOZ nanocomposites containing different amounts of the nano-SiO₂ were investigated by TEM and scanning electron microscopy. The dispersions of the nano-SiO₂ of the nanocomposites observed by TEM are shown in Figure 5. With the increase in the nano-SiO₂

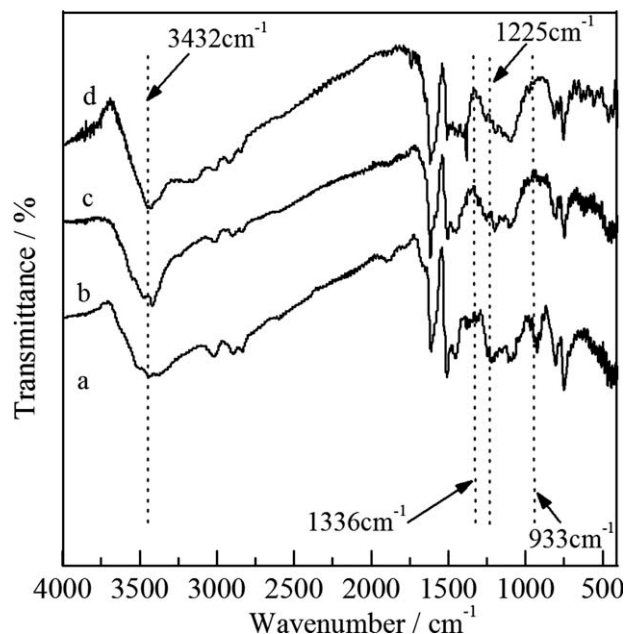


Figure 4 FTIR spectra of the SiO₂/PBOZ nanocomposite (a) without heat treatment; (b) cured at 180°C for 2 h; (c) cured at 200°C for 2 h; and (d) cured at 220°C for 2 h.

TABLE I
Mechanical Properties of the SiO₂/PBOZ
Nanocomposites

Nano-SiO ₂ content (wt %)	Impact strength (kJ/m ²)	Bending strength (MPa)	Bending modulus (GPa)
0	1.92 ± 0.13	98.1 ± 2.3	4.52 ± 0.08
1	2.23 ± 0.36	120.8 ± 9.1	4.57 ± 0.05
2	2.25 ± 0.24	133.6 ± 4.7	4.96 ± 0.05
3	2.68 ± 0.20	151.4 ± 14.9	4.99 ± 0.06
4	2.61 ± 0.31	118.7 ± 9.1	4.91 ± 0.07
5	2.58 ± 0.21	117.5 ± 8.7	4.89 ± 0.08

contents, nanoparticles become agglomerates very obviously when the loading is more than 3 wt %. When the loading is less than 3 wt %, nanoparticles appear well dispersed in the matrix. This observation confirms that the impact strength and bending

strength decrease after nano-SiO₂ particles is more than 3 wt % because of the particle agglomerates.

The morphologies of the impact fracture surface of the SiO₂/PBOZ nanocomposites, observed by scanning electron microscopy, are shown in Figure 6(b–f). They are quite different from that of the pristine PBOZ, shown in Figure 6(a). The fracture surface of the pristine PBOZ is very smooth with uniform crack direction, which reveals the characteristic of a brittle fracture. However, the fracture surfaces of the SiO₂/PBOZ nanocomposites appear rougher and more irregular. The fracture stripes increase and some of them divert to different directions. The internal stress of nanocomposites is dispersed, and the propagating cracks are arrested. Thus, the toughness of the nanocomposites is enhanced. Therein, the morphologies in Figure 6(d) show these phenomena the

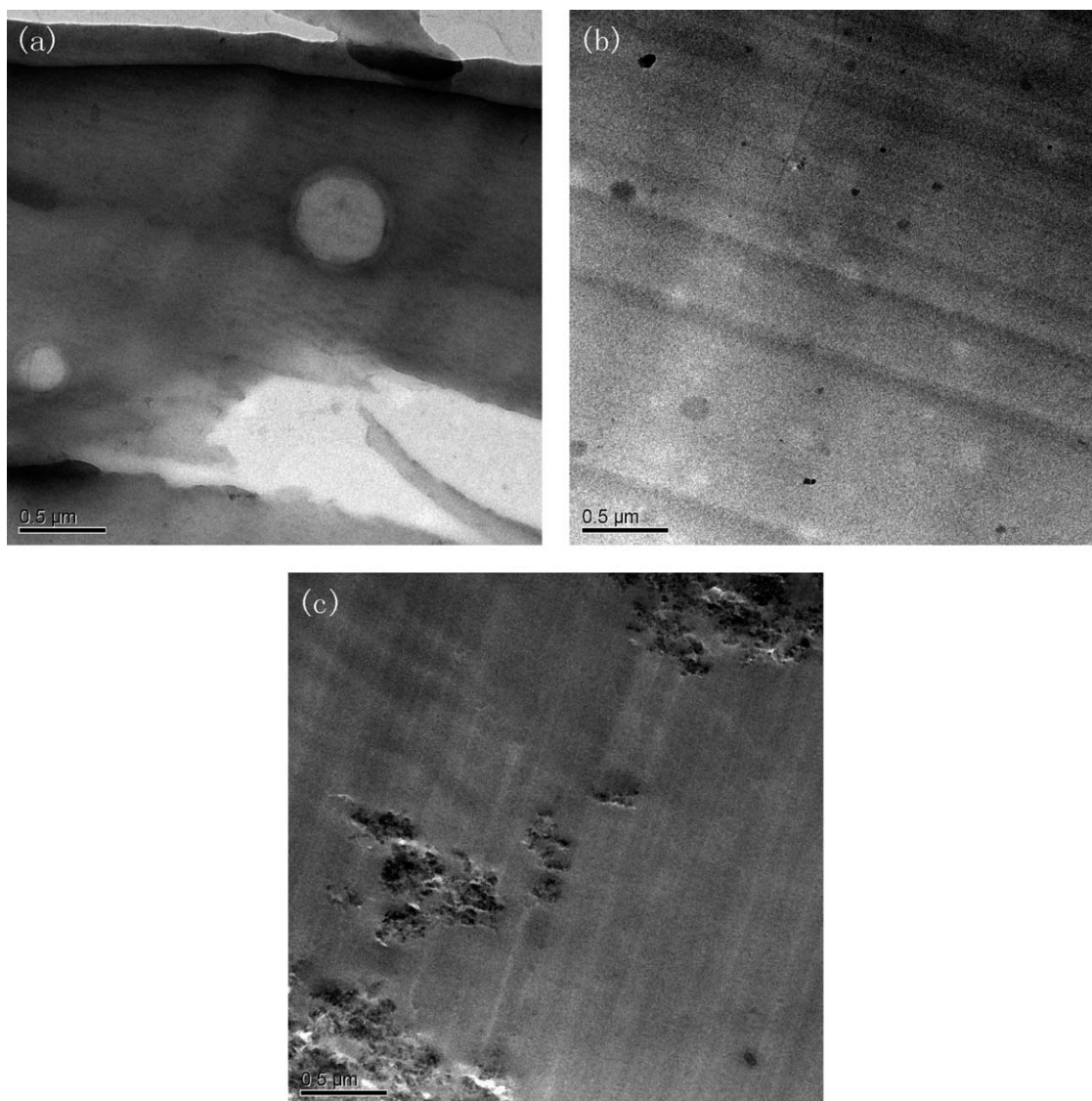


Figure 5 TEM images of the SiO₂/PBOZ nanocomposites with (a) 1 wt % nano-SiO₂; (b) 3 wt % nano-SiO₂; and (c) 4 wt % nano-SiO₂.

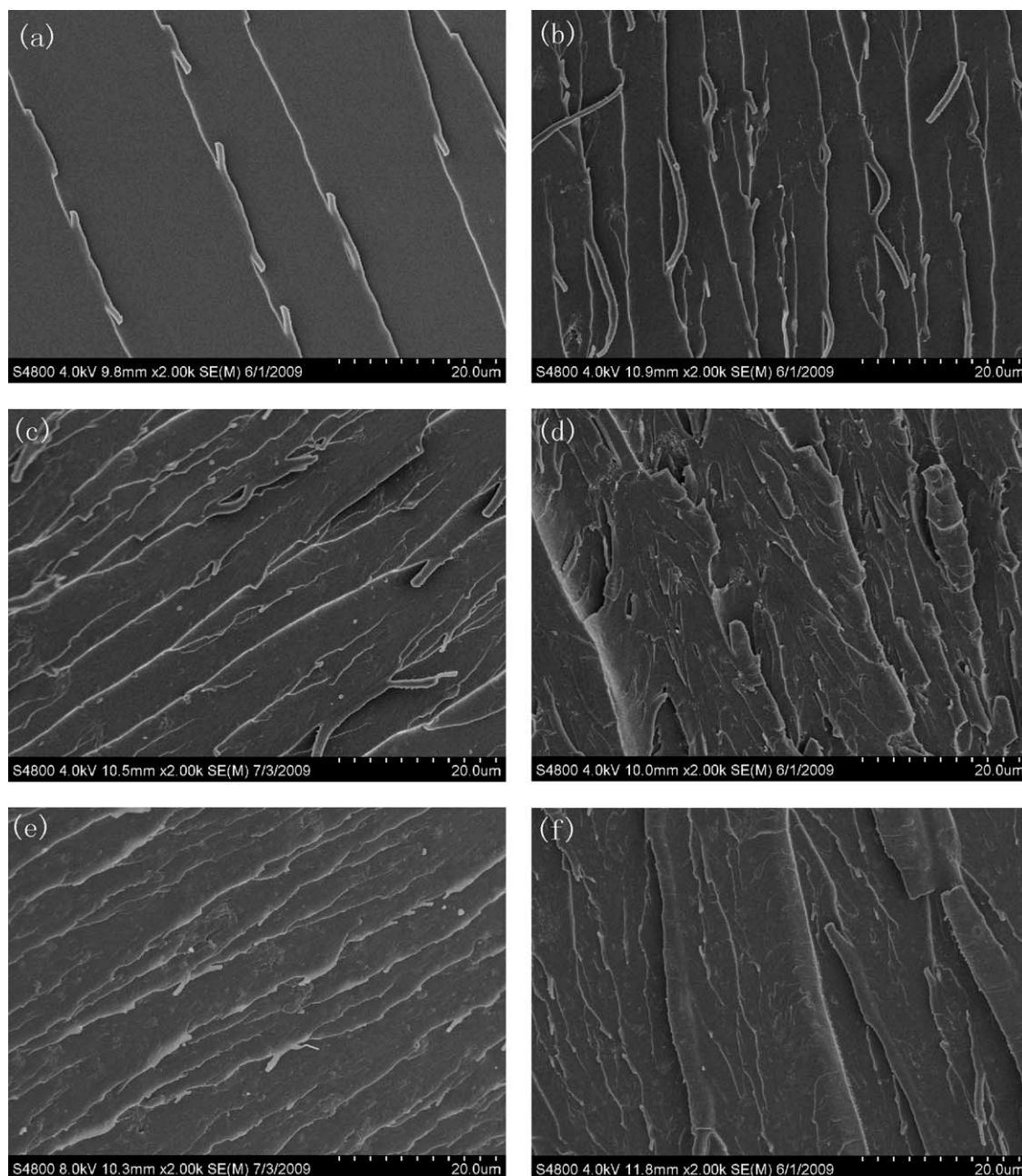


Figure 6 Scanning electron microscopy micrographs of the fracture surfaces of the SiO₂/PBOZ nanocomposites with (a) 0 wt % nano-SiO₂; (b) 1 wt % nano-SiO₂; (c) 2 wt % nano-SiO₂; (d) 3 wt % nano-SiO₂; (e) 4 wt % nano-SiO₂; and (f) 5 wt % nano-SiO₂.

most, matching the 3 wt % nano-SiO₂ samples, which have the best mechanical results.

Viscoelastic properties of the SiO₂/PBOZ nanocomposites

The effect of the nano-SiO₂ contents on the storage modulus (E') of the SiO₂/PBOZ nanocomposites was investigated by DMA, shown in Figure 7. The addition of nano-SiO₂ causes an increase in the storage modulus (E'). When nano-SiO₂ content is 3 wt %, the E' of the nanocomposite at 50°C reached

5.8 GPa, which was 23% higher than that of the pristine PBOZ (4.7 GPa). The chemical bonding between PBOZ and nano-SiO₂ because of the surface modifications contributes to the increase in the interface adhesion between the PBOZ matrix and nano-SiO₂ particles. Thus, the motion of PBOZ chains around nano-SiO₂ was restricted and resulted in higher E' apart from the rigid particle affect. In addition, the higher storage modulus keeps constant up to a higher temperature than that of the pristine PBOZ, increasing soft point of the nanocomposites. However, the E' decreases when more than 3 wt %

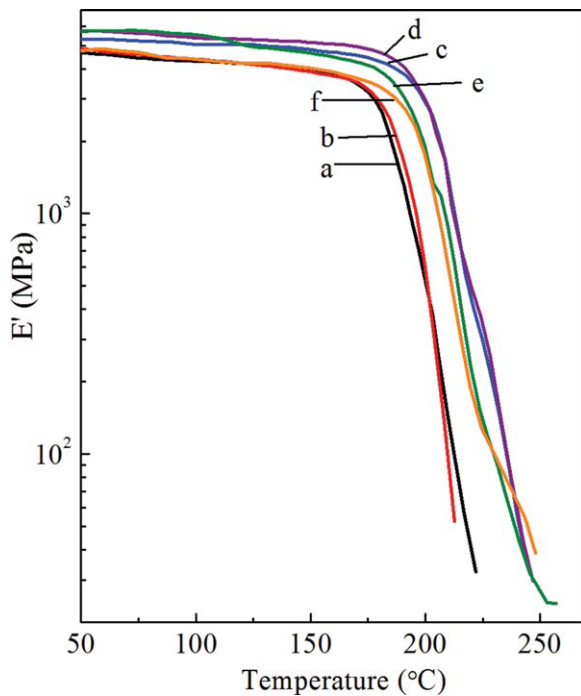


Figure 7 DMA of the SiO₂/PBOZ nanocomposites with different nano-SiO₂ contents: (a) 0 wt %; (b) 1 wt %; (c) 2 wt %; (d) 3 wt %; (e) 4 wt %; and (f) 5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nano-SiO₂ presents because of the nano-SiO₂ particle aggregations.

The effect of the nano-SiO₂ contents on the glass-transition temperature (T_g) of the PBOZ/SiO₂ nanocomposites is shown in Figure 8 clearly. The glass-transition temperatures were obtained from either the maximum of loss factor ($\tan \delta$) or loss

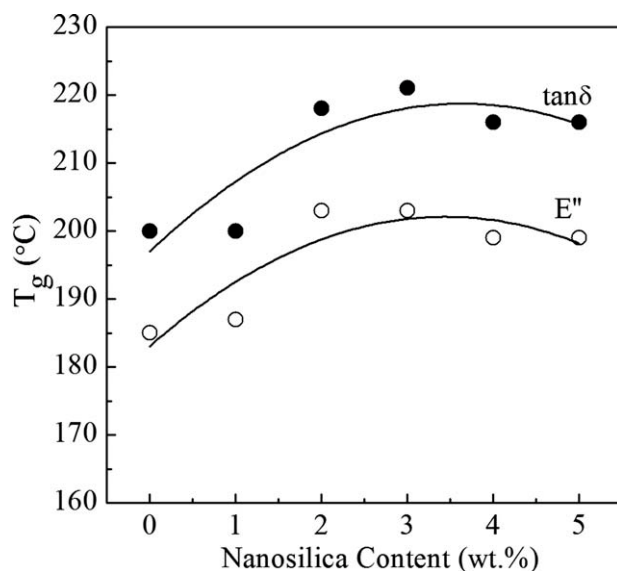


Figure 8 The effect of the nano-SiO₂ contents on the T_g of the SiO₂/PBOZ nanocomposites.

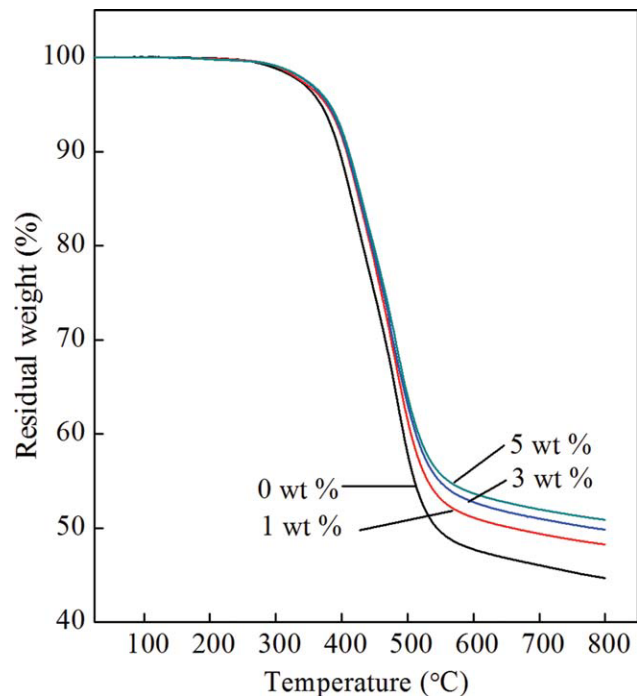


Figure 9 TGA curves of the SiO₂/PBOZ nanocomposites with nano-SiO₂ content of 0, 1, 3, and 5 wt % in nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modulus (E''), respectively. Although the values of T_g from $\tan \delta$ are higher than those from E'' , the same trend of T_g is observed. The glass-transition temperatures of the nanocomposites are higher than

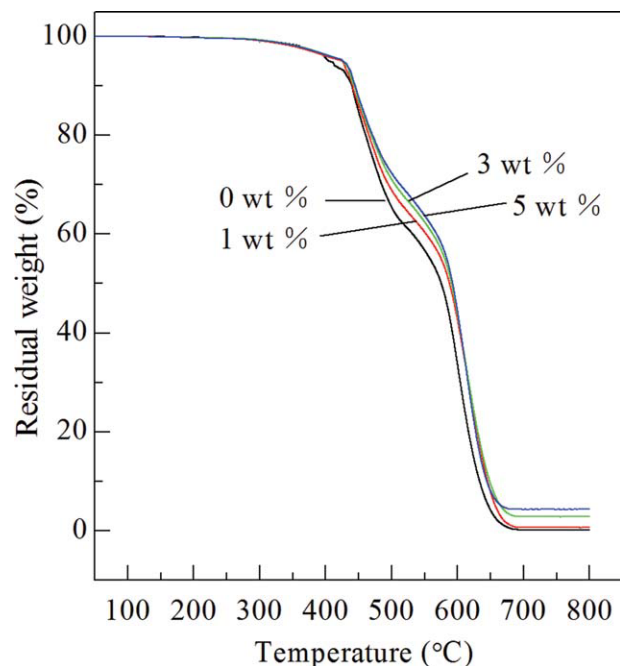


Figure 10 TGA curves of the SiO₂/PBOZ nanocomposites with nano-SiO₂ content of 0, 1, 3, and 5 wt % in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Degradation Temperatures and Residual Weights of the
SiO₂/PBOZ Nanocomposites

Nano-SiO ₂ content (wt %)	T ₅ (°C) in N ₂	T ₁₀ (°C) in N ₂	T ₅ (°C) in air	T ₁₀ (°C) in air	Weight residue in N ₂ at 800°C (%)
0	368	397	405	440	45
1	377	407	425	441	48
3	379	408	426	444	50
5	382	411	426	445	51

that of the pristine PBOZ. The T_g increases with the increase in the nano-SiO₂ contents until it reaches a maximum when nano-SiO₂ content is 3 wt %, then decreases when nano-SiO₂ content further increases. The aggregation of nano-SiO₂ in composites becomes evident after 3 wt % load, hence leads to the decrease of T_g . This phenomenon relies on the other competing fact, namely the interfacial bonding of nano-SiO₂ and the PBOZ matrix, which obviously prevails over the aggregation of nano-SiO₂ before 3 wt % load.

Thermal stabilities of the SiO₂/PBOZ nanocomposites

TGA of the SiO₂/PBOZ nanocomposites in nitrogen and air is shown in Figures 9 and 10, respectively. The 5% and 10% weight loss temperatures increase with increasing nano-SiO₂ contents, and the 5% and 10% weight loss temperatures in air of 426°C and 465°C are higher than those in nitrogen of 382°C and 411°C, respectively. The cross-linking reaction in air may possibly result in the higher degradation temperatures. The residual weight in nitrogen and the temperature at 5% and 10% weight loss for the PBOZ/SiO₂ nanocomposites with various nano-SiO₂ contents are summarized in Table II. The residual weight increases with the nano-SiO₂ contents. But the residual weights in nitrogen are much higher than those in air, which indicates that the thermal stability of the PBOZ/SiO₂ nanocomposites in nitrogen is much better than that in air at higher temperatures. The weight residue is as high as 51% in nitrogen at 800°C when nano-SiO₂ content is 5 wt %.

CONCLUSIONS

A series of the SiO₂/PBOZ nanocomposites has been successfully prepared by benzoazine functional silane modifying nano-SiO₂. The BOZ functional silane-modified nano-SiO₂ may have covalent bonding to PBOZ matrix because of the ring-opening polymerization of oxazine rings both in the matrix and on the surfaces of the modified nano-SiO₂. Therefore, the SiO₂/PBOZ nanocomposites exhibit significant improvements in mechanical properties and

thermal stability compared with the pristine PBOZ. The SiO₂/PBOZ nanocomposite with 3 wt % nano-SiO₂ content exhibits the best mechanical properties in terms of impact strengths (toughness) and bending strengths. Dynamic viscoelastic analysis shows that the nanocomposites have the highest storage modulus and highest glass-transition temperature also at the 3 wt % nano-SiO₂ content. Moreover, the glass-transition temperatures of nanocomposite increase about 20°C compared with the pristine PBOZ with 3 wt % nano-SiO₂. The 5% and 10% weight loss temperatures in air of 426°C and 465°C are higher than those in nitrogen of 382°C and 411°C, respectively, and the weight residue is as high as 51% in nitrogen at 800°C when the nano-SiO₂ content is 5 wt %. With 3 wt % nano-SiO₂ content, the SiO₂-PBOZ nanocomposites exhibit the best improved mechanical and thermal properties apart from enhanced toughness.

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