

Preparation of a Liquid Benzoxazine Based on Cardanol and the Thermal Stability of its Graphene Oxide Composites

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ABSTRACT: A novel liquid benzoxazine was synthesized by Mannich reaction of cardanol, paraformaldehyde, and allylamine. The benzoxazine structure was characterized by ¹H-NMR and FTIR. The liquid benzoxazine could dissolve easily in many solvents. The curing behavior of the benzoxazine was characterized by differential scanning calorimetry (DSC) and its curing temperature was about 233°C. A benzoxazine-functional silane coupling agent (BFSCa) was synthesized with paraformaldehyde, phenolphthalein, and aminopropyltriethoxysilane. Graphene oxide (GO) was also made via improved Hummer's method. Then benzoxazine/GO composites were prepared using BFSCa by solution blending and the curing behaviors of the composites were also characterized by IR, DSC, and thermogravimetric analysis. The minimum curing temperature and the highest 5% weight loss temperature for the composites was, respectively, 185 and 399.8°C. The SEM images of benzoxazine/GO composites demonstrated that BFSCa had improved the dispersion of GO in the benzoxazine and also enhanced the thermal decomposition temperature of the composites. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40353.

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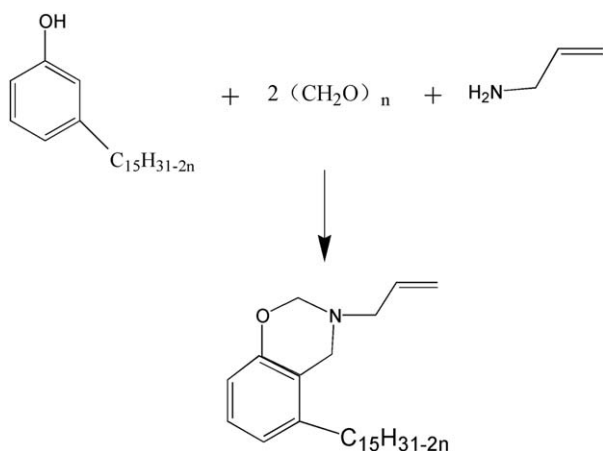
INTRODUCTION

Benzoxazine has attracted more and more attention these years due to a wide range of unique advantages,¹ such as no volatile release during cure and minimal cure shrinkage, thereby, leading to crack-free moldings, low water absorption,² no strong acid catalysts required for curing, usually has well thermal stability, which is demonstrated by T_g , degradation temperatures, and char yields. In view of these and other desirable properties, researchers have applied benzoxazine in many fields. Among the application, many disadvantages and certain drawbacks have appeared. For example, most benzoxazine are solid or very sticky at room temperature that potentially restrict its flow and diffusion in solvent, also restrict its application in composites.³ During the composite fabrication process,⁴ the viscosity of resin is an important factor, affecting the resin flow and wetting properties.⁵ Insofar, liquid resins are used prior in some composites due to easier handling.⁶

The application of benzoxazine is also restricted by materials.⁷ Benzoxazine is synthesized by Mannich condensation of phenol, formaldehyde, and primary amine. Different materials made various types of benzoxazine monomers with enormous properties.⁸ Various types of benzoxazine monomer can be synthesized

with various phenols and amines.⁹ Jin et al.¹⁰ have prepared bis(benzoxazine-maleimide)s from hydroxyphenylmaleimide, paraformaldehyde, and various diamines in a novel nonpolar high boiling point solvent. This benzoxazines with high purity and its properties have been studied. Wang¹¹ have synthesized 2,4,6-tri(4-hydroxyl-phenyl)-1,3,5-s-triazine (TP) with 4-cyanophenol as the material, and then converted TP into benzoxazine monomer-containing triazine via Mannich reaction. Long-term use of phenol not only constitutes a threat to human health but also aggravate the crises of petroleum.

Currently, polymers derived from renewable organic raw materials having attracted the attention of both academic and industrial research. Therein, the utilization of renewable resources have been advocated.¹² Cardanol is a byproduct of cashew nut tree, a major component of the cashew nut shell liquid and its levels close to 50%.¹³ It is found that cardanol and its polymers exhibit an excellent performance in chemical modification and polymerization into specialty polymers.¹⁴ Cardanol can react with formaldehyde under a variety of conditions to form thermosetting resins.^{15,16} Cardanol-formaldehyde resins have improved flexibility leading to better processability than conventional phenolic resins,¹⁷ which may be the internal plasticization



Scheme 1. Synthesis of benzoxazine based on cardanol (Bzc).

effect of the long chain.¹⁸ The long side chain employs a hydrophobic nature to the cardanol-formaldehyde resins,¹⁹ which would be better to water repellent and resistant to weathering.²⁰ A great deal of effort has been expended to use cardanol instead of phenol.^{21,22}

It was our endeavor to develop a liquid thermosetting system from cardanol, an agricultural renewable resource of cashew industry. In this study, we would like to report a novel liquid benzoxazine monomer prepared from cardanol, allylamine, and paraformaldehyde. The monomers were characterized by ¹H-NMR and FTIR spectroscopy. The thermal stability and curing behavior would be described here. The typical polybenzoxazine had high curing temperature (200°C or higher), which is the drawback of its application. Therein, to enhance performance of benzoxazine, graphene oxide (GO) was chosen as dispersion phase in Bzc. Benzoxazine-functional silane coupling agent (BFSca) was synthesized to improve the dispersion and compatibility between benzoxazine matrix as organic domain and GO as inorganic domain. The GO made in our lab was added in benzoxazine according to different proportions with the help of BFSca, and then Bzc/GO composites were prepared. The properties of these composites were characterized by SEM, FTIR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) in this article.

EXPERIMENTAL

Materials

Cardanol was kindly supplied by Shangdong Haobo Biological Material Co., China, $M = 304.52$; Graphite powder was kindly supplied by Hefei General Machinery Research Institute, China; Paraformaldehyde was purchased from Shanghai Chemical Reagents Company, China; Allylamine was bought from Tianjin chemical reagent factory, China; alcohol, NaOH, H₂SO₄, H₃PO₄, 30% H₂O₂, HCl, and KMnO₄ were bought from Sino-pharm Chemical Reagent Co., China; Phenolphthalein and aminopropyltriethoxysilane (98%) was bought from Aladdin Reagent Co., China.

All the reagents used throughout this study were used “as is” without any further purification.

Synthesis of Benzoxazine Based on Cardanol

1.5 mL allylamine and 1.2 g paraformaldehyde were placed in a 500 mL three-necked round flask equipped with magnetic stirrer, thermometer, reflux condenser, and 200 mL alcohol.²³ The mixture was pretreated in an ice bath for 1 h. Then 6 g cardanol was added dropwise into the flask. The temperature was raised to 95°C for about 10 h and the mixture becomes auratus at last. The crude of the reaction removed alcohol under vacuum. The product was dissolved in acetone and washed with 1 N NaOH, followed by distilled water in a separating funnel. The acetone phase was dried over Na₂SO₄ and the solvent was evaporated in a rotary evaporator. The synthesized route was shown in Scheme 1. A maroon liquid benzoxazine was isolated.

Preparation of BFSca Based on Phenolphthalein

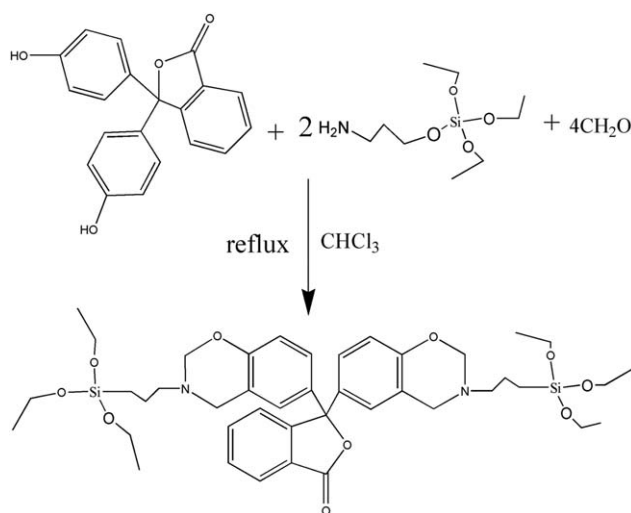
Paraformaldehyde, phenolphthalein, and aminopropyltriethoxysilane took reaction in 4 : 1 : 2 molar ratio.²⁴ Paraformaldehyde and phenolphthalein were placed in a 500 mL three-necked round flask equipped with magnetic stirrer, thermometer, reflux condenser, and 200 mL chloroform. The mixture was pretreated for 1 h. Then aminopropyltriethoxysilane was added and the temperature was raised to 100°C for about 24 h. The purification procedure was the same as above. The synthesized route was shown in Scheme 2. A yellow particle, BFSca was obtained.

Preparation of GO via Improved Hummer's Method

The oxidized graphite was made in our lab via improved Hummer's method,²⁵ a 9 : 1 mixture of concentrated H₂SO₄/H₃PO₄ was added to a mixture of graphite powder and KMnO₄, stirred for 10 min, then heated to 50°C and continued stirred for 12 h. The reaction was stopped by ice bath then 30 wt % H₂O₂ was added. The mixture was washed with water to neutral. 30 wt % HCl was added into the obtained solid and continued washing with water and filtered to neutral. Then, GO was obtained by the ultrasonication and centrifugation of the oxidized graphite.²⁶

Preparation of Bzc/GO Composites

Bzc/GO composites were prepared in alcohol by solution blending.²⁷ Combined benzoxazine with 1, 2, and 4 wt % GO and same proportions of BFSca at elevated temperature, followed by



Scheme 2. Synthesis of BFSca.

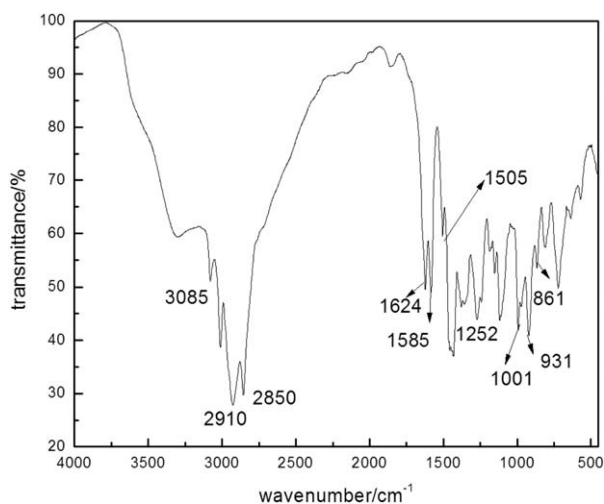


Figure 1. FTIR spectra of Bzc.

stirring at 80°C for 1 h. The mixtures were then placed in a vacuum oven for 2 days at 80°C to remove alcohol.

Thermal Curing of the Benzoxazine and Its Composites

The Bzc and Bzc/GO composites were heated in a stainless rectangular mold with a stepwise cure in an air-circulating oven. The step profile was as follows: 100°C for 2 h, 200°C for 2 h, 220°C for 1 h and 250°C for 1 h.

Instruments

SEM observations were conducted on a FEI Sirion200 system with an accelerating voltage of 3 kV. X-ray diffraction (XRD) was carried out by a powder diffractometer (Rigaku, D-MAX2500-PC) with Cu radiation. FTIR spectra were collected in transmission mode on spectrophotometer (Thermo Nicolet, Nicolet-6700) with KBr as reference. The curing characteristics were studied by DSC using METTLER 821e/400 instrument (Zurich, Switzerland) in the temperature range of 25–300°C at a heating rate of 10°C min⁻¹ in nitrogen atmosphere. TGA was conducted on TGA Q5000 (New Castle, DE) at a heating rate of 10°C min⁻¹ in nitrogen atmosphere. The gas flow rate was 100 mL min⁻¹. ¹H-NMR spectra were recorded in DMSO-*d*₆ on a VNMRH800 instrument (Newport, VA). Water bath ultrasonication was performed with a KQ-100E sonicator (100 W).

RESULTS AND DISCUSSION

Characterizations of Bzc

The chemical structures of Bzc were confirmed by FTIR and ¹H-NMR. The infrared spectrum of Bzc was shown in Figure 1. There were significant bands, respectively, at 1252 cm⁻¹ (asymmetric stretching of C—O—C), 1001 cm⁻¹ (symmetric stretching of C—O—C), and at 861 cm⁻¹ (trisubstituted benzene ring). The band at 931 cm⁻¹ was typical of benzoxazine ring structure. Characteristic absorption bands assigned to allyl group appeared at 3085 cm⁻¹ (stretching of =C—H) and at 1624 cm⁻¹ (stretching of C=C).²⁸

The ¹H-NMR spectrum of Bzc was shown in Figure 2.²⁹ NMR was performed in DMSO-*d*₆, and the chemical shift was calibrated by setting the chemical shift of DMSO-*d*₆ as 2.47 ppm. The two multi-

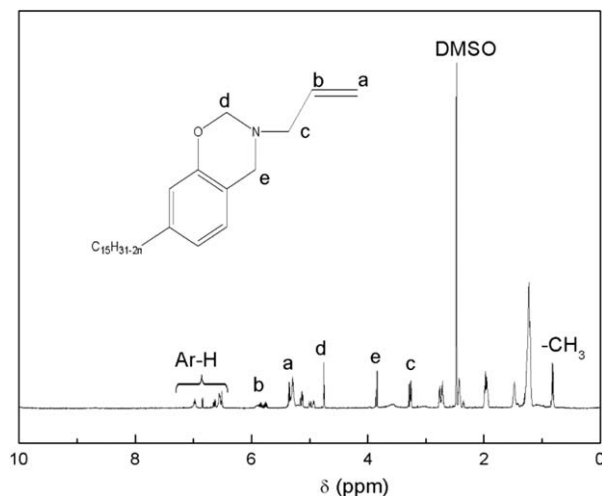


Figure 2. ¹H-NMR spectrum of the Bzc.

plets at 5.24 and 5.83 ppm were typical for the protons of =CH₂ and =CH— in allyl group, respectively. The protons of —CH₂— of allyl group showed a doublet at 3.26 ppm. The characteristic protons of oxazine ring appeared at 3.84 and 4.76 ppm assigned to —Ar—CH₂—N— and —O—CH₂—N—, respectively. The aromatic protons appeared as multiplet at 6.50–6.95 ppm. The other characteristic protons of cardanol's side chain were observed at 0.82 ppm assigned to —CH₃, 1.24–1.48 ppm assigned to aliphatic CH₂ protons, 1.96–2.42 ppm (m, CH₂CH=), 2.72–2.76 ppm (m, CH₂(CH=)₂). As reported in the literature, there would be three olefin groups in the cardanol's long side chain, which created multiple peaks between 4.92 and 5.16 ppm.

IR spectra after each cure stage of Bzc are shown in Figure 3. Characteristic absorption bands assigned to allyl group appeared at 3085 cm⁻¹ (stretching of =C—H) and at 1624 cm⁻¹ (stretching of C=C), which began to decrease at 110°C, and disappeared at 220°C, demonstrated that allyl group reacted.

The absorption at 931 cm⁻¹ was typical of benzoxazine ring structure, which also disappeared at 250°C, suggesting the completion of ring-opening of benzoxazine to afford polybenzoxazine.

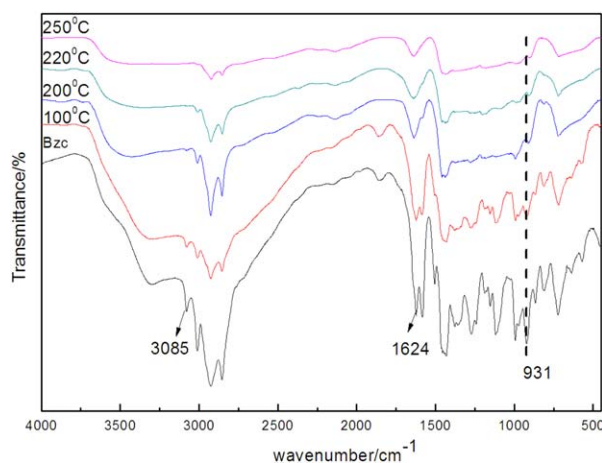


Figure 3. IR spectra of Bzc after different temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

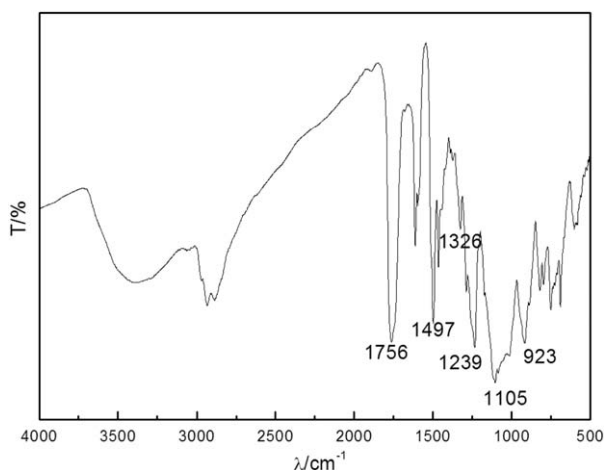


Figure 4. IR spectra of BFSca.

Preparation of BFSca

BFSca had been synthesized to increase the adhesion between GO and benzoxazine matrix. The FTIR spectrum of BFSca has been shown in Figure 4. The characteristic absorption bands of benzoxazine structure were observed at 1497, 1326, and 1239 cm^{-1} due to disubstituted benzene ring, CH_2 wagging, and asymmetric stretching of $\text{C}-\text{O}-\text{C}$, respectively. Furthermore, the characteristic absorption peak of $\text{C}=\text{O}$ in phenolphthalein was observed at 1756 cm^{-1} ; there were significant bands at 1105 cm^{-1} (stretching of $\text{Si}-\text{O}-\text{Si}$); and the band at 923 cm^{-1} was typical of benzoxazine ring structure. All these confirmed the structure of BFSca.

Characterizations of GO Made by Improved Hummer's Method

The infrared spectra of graphite oxide and graphite powder were shown in Figure 5. The above curve was spectrum of graphite oxide, $\text{O}-\text{H}$ stretching vibration in intercalated water was 3578 cm^{-1} , a weak band at 3120 cm^{-1} might be $\text{O}-\text{H}$ coupling stretching vibration in carboxyl group, $\text{C}-\text{C}$ stretching vibration at 1620 cm^{-1} was characterize of unoxidized graphite, which was manifested in the

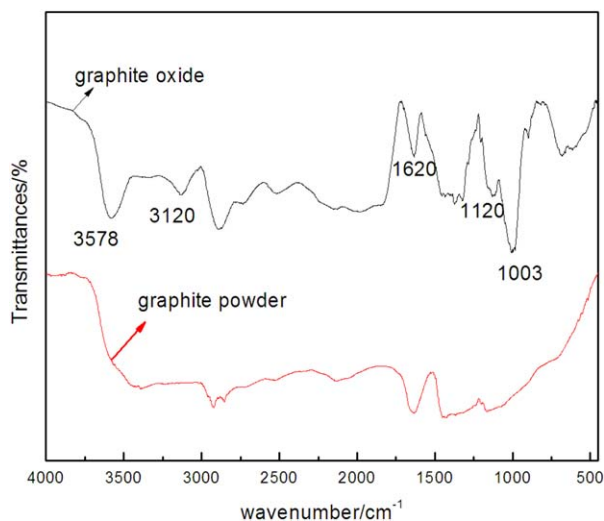


Figure 5. IR spectra of graphite powder and graphite oxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

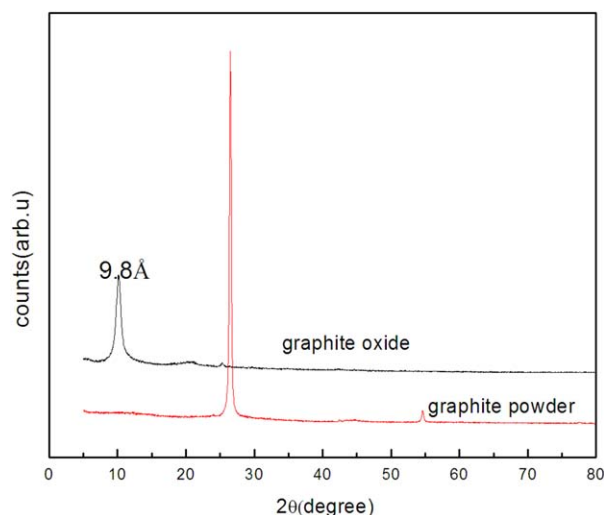


Figure 6. XRD spectra of graphite powder and graphite oxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spectrum of graphite powder. $\text{C}-\text{O}$ stretching vibrations were shown at 1120 cm^{-1} and a sharp band at 1003 cm^{-1} .

The change of interlayer spacing of the lattice structure was usually detected by XRD. The XRD patterns of graphite powder and graphite oxide were shown in Figure 6. For the raw material, graphite powder showed a peak at (002) plane (characteristic peak at $2\theta = 26.5^\circ$); after oxidation, it showed a peak at a relatively low angle, $2\theta = 9.8^\circ$.

All these results suggested that graphite powder was oxidized successfully.

Preparation of Bzc/GO Composites and Their Thermal Stability

Same proportions of GO and BFSca were added into benzoxazine monomer and got the Bzc/GO composites.³⁰ The structures of benzoxazine monomer and its composites were demonstrated by FTIR according to Figure 7.³¹

When 1 wt % GO and 1 wt % BFSca was mixed and added into benzoxazine monomer, the IR spectra have changed greatly. Characteristic absorption at 931 cm^{-1} assigned to benzoxazine ring structure decreased, which may be due to GO, and benzoxazine reacted with the help of BFSca. Due to increase in the amount of GO and BFSca, the IR spectra appeared to have many characteristic absorption of BFSca. The peaks at 1624, 1446, and 1120 cm^{-1} all appeared in the Bzc/GO composites with the amount of 2 wt % GO and 2 wt % BFSca, and 4 wt % GO and 4 wt % BFSca. These absorption spectra strengthened in the last composite. The peak at 1624 cm^{-1} may be due to amide stretch vibration, and the peaks at 1446 cm^{-1} and around 1200 cm^{-1} may be due to $\text{Si}-\text{C}$ vibration; significant bands at 1120 cm^{-1} may be typical of $\text{Si}-\text{O}-\text{Si}$ structure.

The thermal behavior of this novel liquid benzoxazine monomer and its composites was also analyzed by DSC in N_2 atmosphere at a heating rate of 10 $^\circ\text{C min}^{-1}$. The thermal degradation behavior of polybenzoxazine and its composites copolymers was

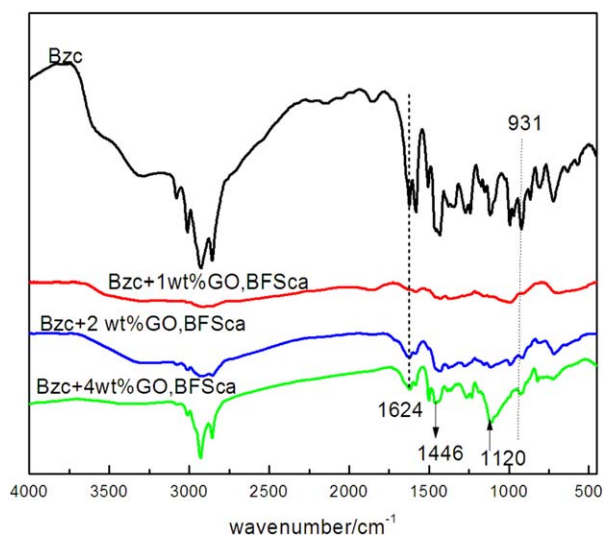


Figure 7. IR spectra of Bzc/GO composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

analyzed by TGA in N_2 atmosphere at a heating rate of $10^\circ C \text{ min}^{-1}$. All these results are shown in Figures 8 and 9.

The Bzc/GO composites had ideal curing behavior, which was demonstrated in Figure 8. The exothermal peak temperature of benzoxazine monomer was $233^\circ C$ during curing in N_2 atmosphere. The exothermal peak became ahead in Bzc/GO composites, when 1 wt % GO and 1 wt % BFSca were added; the onset of reaction temperature was $225^\circ C$; however, the curing behavior became endothermic and the endothermic peak temperature was $248^\circ C$. The cure direction changed due to the benzoxazine that was to be inserted in the layer structure of GO, which needed energy, so the curing behavior became endothermic. As 2 wt % GO and 2 wt % BFSca were added into benzoxazine, the curing curve became more flat; the exothermal peak temperature was $227^\circ C$. When 4 wt % GO and 4 wt % BFSca were added into benzoxazine, the curing curve became sharper than others; there were two peaks among the whole cure pro-

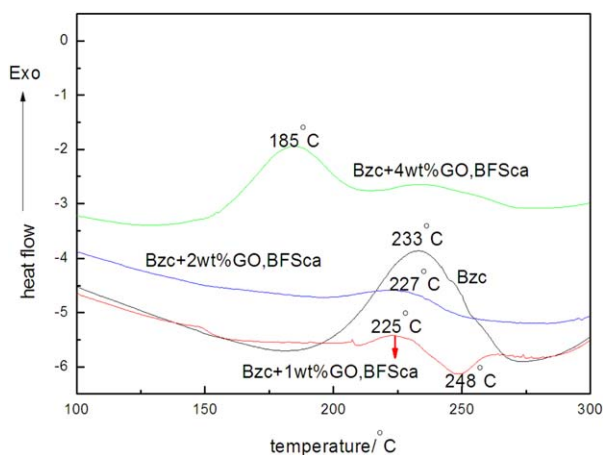


Figure 8. DSC curve of Bzc and its composites in different ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

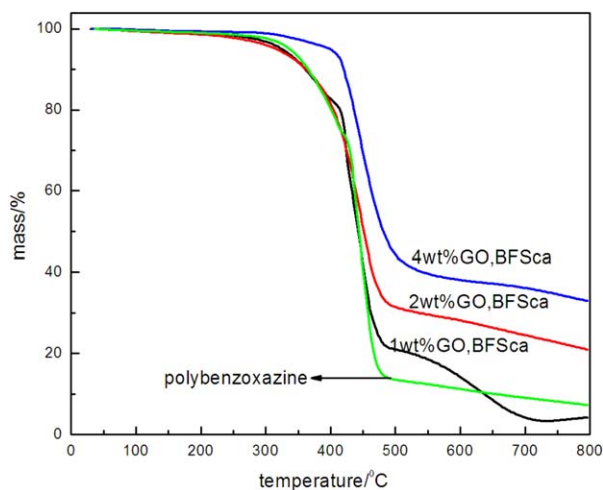


Figure 9. TGA trace of polybenzoxazine and its composites in different ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

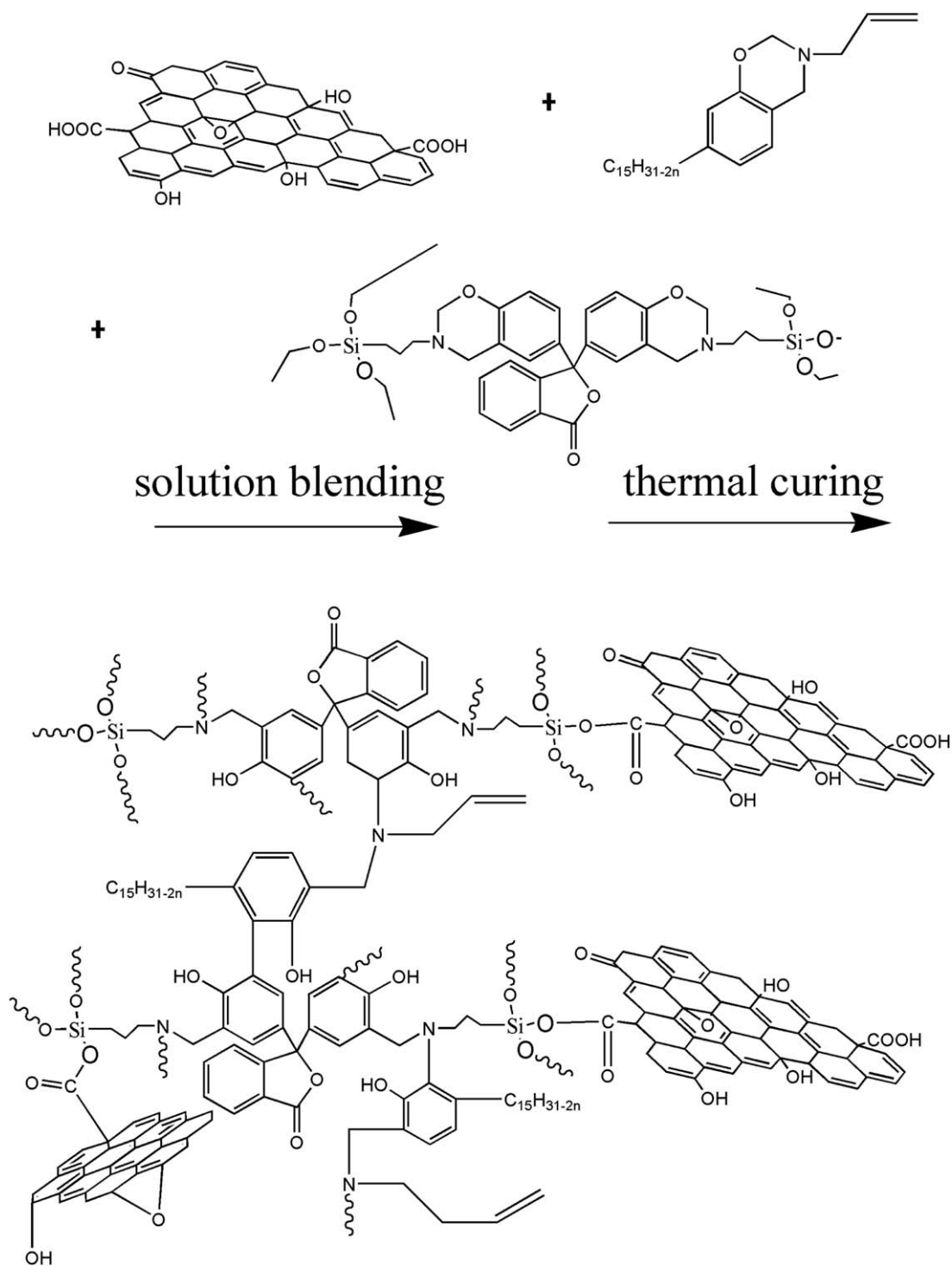
cess, the first exothermal peak temperature was $185^\circ C$. The curing temperature decreased down than pure benzoxazine-based polymer, which might be due to the acidic nature of the silanol groups of silica and an acid catalyst was used to accelerate the ring-opening polymerization of benzoxazine, so the curing temperature decreased.

TGA of the polybenzoxazine and its composites were conducted under a nitrogen atmosphere and the thermogram of cured samples was shown in Figure 9. The thermal stabilities of these samples were compared by considering the 5% weight loss temperature (T_5), the 10% weight loss temperature (T_{10}). All these results were listed in Table I.

The table reflected that the efficient role of the BFSca as coupling agent on the interface between polybenzoxazine matrix and GO sheets to produce chemical hybridization, which was significant, and hence, increased thermal stability of the composites. The polybenzoxazine based on cardanol begun to lose weight from $337.8^\circ C$ with a peak decomposition temperature of $441.8^\circ C$ and the char yield was 7.25%. When 1 wt % GO and 1 wt % BFSca were added, the TG curve became two stages, the 5% weight loss temperature was $325.8^\circ C$ with a peak decomposition temperature of $424.9^\circ C$ and the char yield was 4.2%. These data, all decreased than pure polybenzoxazine based on cardanol, which consistent with the results in DSC. The cause for temperature decrease might be due to benzoxazine inserted

Table I. Decomposition Temperatures of Polybenzoxazine and the Composites

S. no.	Sample Bzc : GO : BFSca(g)	$T_5(^{\circ}C)$	$T_{10(^{\circ}C)}$
1	100 : 0 : 0	337.8	365.5
2	100 : 1 : 1	325.8	361.5
3	100 : 2 : 2	316.8	362.5
4	100 : 4 : 4	399.8	419.9



Scheme 3. Mechanism of polybenzoxazine and GO react with the help of BFSca.

into the laminated structure of GO, so it is decomposed quickly at the end. When 2 wt % GO and 2 wt % BFSca were added, the composites began to decompose at 316.8°C with a peak decomposition temperature of 449.1°C and the char yield was 21%. 4 wt % GO and 4 wt % BFSca were added, the TG curve became smoother than polybenzoxazine, the 5% weight loss temperature was 399.8°C with a peak decomposition temperature of 446.6°C and the char yield was 32.9%.

The above results show that GO had great effect on the thermal stability of benzoxazine, and had multiple oxygen-containing functional groups, such as hydroxyls and epoxides in the basal plane and carboxyl groups at plane edges; these characteristic structures could easily lead GO to react with benzoxazine based on cardanol with the help of BFSca.

Scheme 3 showed the mechanism of polybenzoxazine and GO react with the help of BFSca. To observing the FTIR spectra of

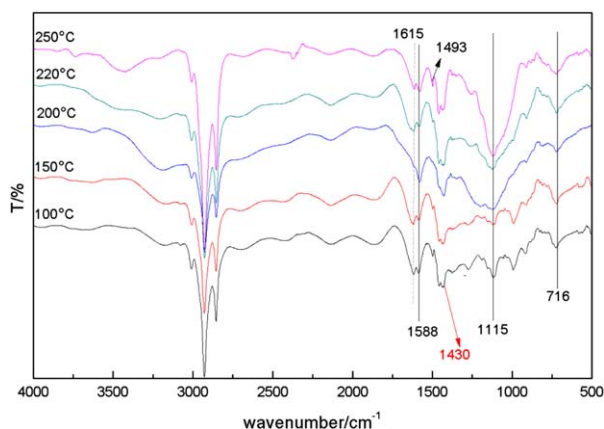


Figure 10. IR spectra of polymerization after various temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites after each cure stage as to confirm the mechanism of polymerization. The composites were gradually cured at 100, 150, 200, and 220°C for 2 h each and 250°C for 1 h. The polymerization of the sample (benzoxazine mixed with 4 wt % GO and 4 wt % BFSca) was chosen as a representative example and has been studied by FTIR spectra. The results were shown in Figure 10. The benzene rings in the benzoxazine monomer were trisubstituted. As the temperature increased, the ring-opening

polymerization preceded, the oxazine ring of benzoxazine molecule opened and the benzene ring changed to the tetrasubstituted. Insofar, a new absorption band appeared at 1493 cm^{-1} due to the tetrasubstituted benzene ring. The silanol groups of BFSca bonded to COOH of GO and so the structure of $-\text{C}=\text{O}-\text{O}-\text{Si}-$ was formed with characteristic strong absorption falling at 1588 cm^{-1} due to the asymmetric stretch; the symmetric stretch absorption was weaker and appeared at 1430 cm^{-1} . When the molecule contains two or more carbonyl groups that can mechanically couple, the carbonyl absorption is split, as shown near 1430 cm^{-1} . The absorption at 716 and 1115 cm^{-1} were due to $-\text{Si}-\text{O}-\text{CH}_2\text{CH}_2-$ and $-\text{O}-\text{Si}-\text{O}$ vibrations. N-substituted amides showed a strong band at 1615 cm^{-1} . Also, the aldehydes in cardanol's side chain had distinctive CH absorption near 2858 and 2930 cm^{-1} . These are all kept in the whole reaction. The broad OH absorption centered at 3200 cm^{-1} and stretched to 3439 cm^{-1} with increased temperature. All these data indicated the formation of polybenzoxazine network. These are also demonstrated from the following SEM images.

SEM images of Bzc/GO, benzoxazine, and GO were shown in Figure 11. Typical wrinkled GO structure could be clearly seen in the SEM images; indicated GO was successfully prepared from graphite powder via improved Hummer's method. The image of benzoxazine synthesized with cardanol showed many hollow structures and irregular shapes. When 1 wt % GO and 1

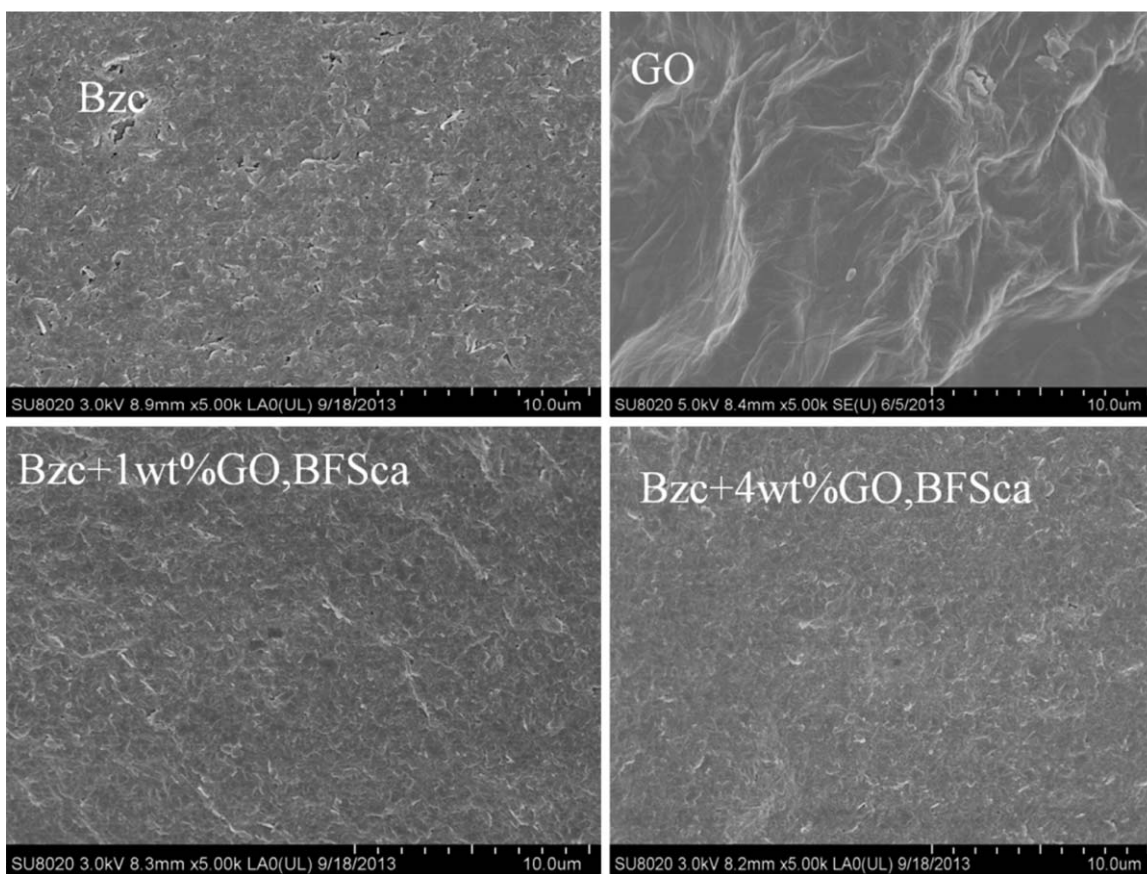


Figure 11. SEM images of fracture for the Bzc and BzcGO composites.

wt % BFSca were added to benzoxazine, the structures changed and the hollow disappeared, and a wrinkled structure appeared; however, the color of this composite changed a little. When 4 wt % GO and 4 wt % BFSca were added to benzoxazine, the structures and the color changed. Their appearance was fairly uniform with a certain degree of wrinkled structures and a light color, which might demonstrate that the mechanical strength of benzoxazine was enhanced, and the composites became more malleable than pure benzoxazine monomer.

CONCLUSIONS

A novel liquid benzoxazine based on cardanol was prepared. The benzoxazine/GO composites were also made using BFSca by solution blending. The properties of the benzoxazine were greatly influenced by the presence of GO and BFSca. Introduction of 4 wt % GO and 4 wt % BFSca were proved as the most effective addition. The curing temperature of the benzoxazine was dramatically reduced from 233 to 185°C; the highest 5% weight loss temperature for the composites was 399.8°C. The TGA and SEM were utilized to reveal that Bzc/GO composites had great thermal stability and uniform structure. The formation of polymerization network was manifested to observe the curing behavior of Bzc/GO composites.

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