

## Preparation and Properties of Cardanol-Based Polybenzoxazine/SiO<sub>2</sub> Hybrids by Sol-Gel Technique

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**ABSTRACT:** A new cardanol-based benzoxazine monomer containing a hydroxyl group (CBZ) was synthesized and characterized by FT-IR and <sup>1</sup>H NMR spectroscopy. The formation mechanism of cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrids from CBZ and tetraethoxysilane (TEOS) by sol-gel technique was investigated by FT-IR analysis. FT-IR and SEM confirmed that there were many SiO<sub>2</sub> particles formed and embedded in the cardanol-based polybenzoxazine. A phase separation occurred when the ratio (wt) of TEOS to CBZ was not less than 3 : 5. TGA results illuminated the thermal stability and char yield of cardanol-based polybenzoxazine could be enhanced due to the formation of SiO<sub>2</sub> particles in the polybenzoxazine matrix. Incorporation of SiO<sub>2</sub> could improve the surface de-wetting and anti-ultraviolet properties of the films. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4164–4171, 2013

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### INTRODUCTION

In recent years, organic–inorganic hybrids have attracted great interest because they display enhanced properties both in mechanics and calorifics.<sup>1</sup> In particular, the uniform dispersal of nano-SiO<sub>2</sub> in the polymers can improve the strength, abrasion-resistance, ageing resistance, and climate-resistance of polymer materials. Polybenzoxazines, a typical of polymer materials, have been actively studied due to their excellent properties, such as nearly zero shrinkage upon curing, minimal moisture absorption, no byproduct release upon curing and good thermal stability.<sup>2–4</sup> But the major shortcoming of polybenzoxazines is their brittleness and need for high curing temperature, which limits their application. Various efforts have been made to improve the properties of polybenzoxazines via the formation of copolymer, polymer alloys, fiber reinforced composites, nanocomposites, etc.<sup>5–8</sup>

Polybenzoxazine/clay hybrid nanocomposites have been prepared to enhance the thermomechanical properties of polybenzoxazines.<sup>9</sup> Du et al. reported that polybenzoxazine/trisilanol polyhedral oligomeric silsesquioxanes composites exhibited high weight residue at high temperature and improvements on the dynamic viscoelastic properties.<sup>10</sup> Yan et al. discussed the properties of surface-functionalized nano-SiO<sub>2</sub>/polybenzoxazine composites. They found that the resulting hybrids showed significant improvements in mechanical properties and thermal

stability.<sup>11</sup> Agag et al. also reported a polybenzoxazine-titania hybrid with improved thermal properties.<sup>12</sup> However, these organic–inorganic polybenzoxazine hybrids are mostly based on benzoxazines prepared from petroleum chemicals. Most of them focused on mechanical properties and thermal stability of hybrids. The surface and antiultraviolet properties of organic–inorganic polybenzoxazine hybrid films seldom have been reported. Several research groups have reported the synthesis of benzoxazine monomers using renewable organic resource to replace part of the petroleum-based phenol.<sup>13–15</sup> Very recently, in our previous study, novel benzoxazine-based phenolic resins from the renewable resources (i.e. cardanol and furfural) were prepared and the highly thermally stable polybenzoxazines with good flexibility could be obtained.<sup>16</sup>

In the present work, a new benzoxazine monomer containing a hydroxyl group (CBZ) based on cardanol was synthesized. The formation mechanism of cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrids from CBZ and TEOS was investigated. The morphologies, thermal, surface and anti-ultraviolet properties of the hybrids were also studied in detail.

### EXPERIMENTAL

#### Materials

Cardanol was purchased from Shanghai Cashew Chemical Polymer Company (China), which was recovered from the cashew

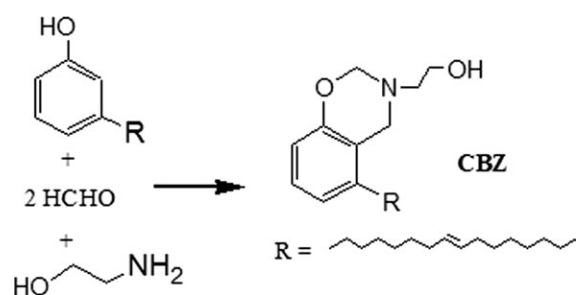
nut shell liquid by direct double vacuum distillation (5–10 mmHg) in the temperature range of 180 to 240°C, as reported by Bhunia et al.<sup>17</sup> Paraformaldehyde (95%), ethanolamine, ether, tetrahydrofuran (THF), and tetraethoxysilane (TEOS) were purchased from Shanghai First Reagent Company (China). All chemicals were AR grade and as-received.

### Measurements

The structure of the cured resin was analyzed using a FT-IR spectrometer. FT-IR spectra were obtained on a PerkinElmer-2 spectrometer (KBr pellet). <sup>1</sup>H-NMR measurement was carried out on a Bruker spectrometer at 300 MHz, CDCl<sub>3</sub> was used as a solvent. Differential scanning calorimetry (DSC) was measured with a heating rate of 10°C/min under N<sub>2</sub> atmosphere on Perkin-Elmer DSC6 apparatus. Dynamic scans of the samples were recorded. Thermogravimetric analyses (TGA) were performed on a DuPont 2000 thermogravimetric analyzer. Cured samples were weighed in the sample pan and then heated in the TGA furnace at a heating rate of 5°C/min. The resulting thermograms were recorded. Scanning electron microscopy of the fractured surfaces was performed using Hitachi ISI-SX-40 SEM. The fractured surfaces of the specimens were covered with gold vapor. The acceleration voltage was 20 kV. Antiuaviolet tests were evaluated by contact angle measurements before and after the irradiation of an ultraviolet lamp. Namely, various films were laid on a support under an ultraviolet lamp (30 w), where the distance between the support and the ultraviolet lamp was about 20 cm. After the irradiation, the contact angle of the film was conducted with a vide-based contact angle measurement device Data Physics OCA15 PLUS (Germany) by sessile drop method using 3 μL of distilled water. The imaging software used for the study was SCA20 (Germany).

### Synthesis of CBZ

As shown in Figure 1, cardanol-based benzoxazine monomer containing a hydroxyl group (CBZ) was synthesized by a solventless process adapted from earlier work.<sup>18</sup> Freshly distilled cardanol (0.4 g, 0.1 mol) and 6 g (0.2 mol) paraformaldehyde were weighed in a round bottom flask and placed over a magnetic stirrer. Ethanolamine (6.1 g, 0.1 mol) was added drop wise into the flask. The temperature was raised to 80 to 90°C and the heating continued for about half an hour. The mixture becomes homogeneous and turns into brown color. Then the temperature was raised to 130–135°C and the heating continued for another 20 to 30 min. It was then cooled and the product



**Figure 1.** Synthesis of benzoxazine monomer containing a hydroxyl group based on cardanol (CBZ).

**Table I.** The Feed Composition of PCBZ and Cardanol-Based Polybenzoxazine/SiO<sub>2</sub> Hybrids

Sample code	CBZ (g)	TEOS (g)	0.3 M HCl (aqueous, mL)
PCBZ	5	0	0
PCBZT1	5	1	0.35
PCBZT2	5	3	1.05
PCBZT3	5	5	1.75

was dissolved in ether solvent. The solids were filtered out and the solution was washed three times with a 1% NaOH solution followed by distilled water in a separating funnel. The ether phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated in a rotary evaporator. Yield: 48%. IR (liquid film on KBr) cm<sup>-1</sup>: 3388, 2933, 2844, 1647, 1625, 1568, 1444, 1342, 1244, 1172, 1120, 1028, 937, 810, 709. <sup>1</sup>H NMR (CDCl<sub>3</sub>) ppm: 7.18–6.61 (aromatic protons), 5.19 and 4.79 (-O-CH<sub>2</sub>-N- and Ar-CH<sub>2</sub>-N-), 4.92 and 5.13 (vinyl double bond), 2.75 (-CH<sub>2</sub>-Ar-), 2.57 (-OH).

### Preparation of Cardanol-Based Polybenzoxazine/SiO<sub>2</sub> Hybrid Films

To synthesize cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films, some experimental methods have been adopted. For the polybenzoxazine (PCBZ) film, CBZ was dissolved in THF and the solution was poured in a silane coated glass plate and cured at 120°C (2 h), 160°C (2 h), 180°C (2 h), 200°C (2 h), and 220°C (2 h) to get a transparent PCBZ film. For the cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films, the experiment was performed by using 1 : 5, 3 : 5, and 5 : 5 (w/w) of TEOS to CBZ, respectively with stoichiometric quantity of the dilute HCl (0.3 M) for hydrolysis of TEOS. TEOS was dissolved in THF and the exact equivalent of the dilute acid was added with continuous stirring for 30 min followed by the addition of 1 equivalent of CBZ dissolved in THF and mixed well to get a clear solution and then stirred for 1 h at 35°C. Then the mixed solution was poured in a silane coated glass plate and left for 24 h at room temperature. Finally, all the samples were heated gradually to 120°C, and cured at 120°C (2 h), 160°C (2 h), 180°C (2 h), 200°C (2 h), and 220°C (2 h), respectively. The brown films were obtained. The feed composition of PCBZ and cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films is given in Table I.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of CBZ

In order to obtain cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films, a new benzoxazine monomer containing a hydroxyl group based on cardanol (CBZ) was synthesized using cardanol, paraformaldehyde and ethanolamine as raw materials by a solventless method (Figure 1). The chemical structure of CBZ was further confirmed by FT-IR and <sup>1</sup>H NMR spectroscopy. Figure 2 shows the FT-IR spectra of CBZ. The characteristic absorptions of the benzoxazine structure appeared at 1244 cm<sup>-1</sup> (asymmetric stretching of C-O-C), 1172 cm<sup>-1</sup> (symmetric stretching of C-O-C), and at ~937 cm<sup>-1</sup> (trisubstituted benzene ring). The antisymmetric and symmetric C-N-C stretching was observed at 1028 to 1120 cm<sup>-1</sup> and 810 to 709 cm<sup>-1</sup>, respectively.

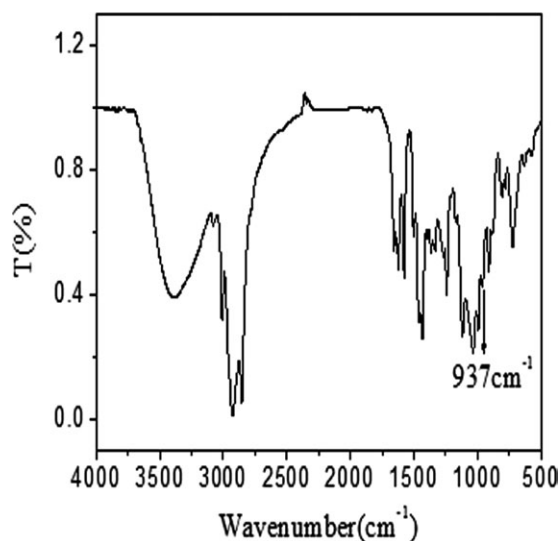


Figure 2. FT-IR spectrum of CBZ.

Meanwhile the characteristic absorptions at  $3388\text{ cm}^{-1}$  belonged to the functional hydroxyl group and  $2933, 2844\text{ cm}^{-1}$  (C-H stretching),  $1647, 1586\text{ cm}^{-1}$  (aromatic ring) and  $1625, 770\text{ cm}^{-1}$  (C = C),  $1444, 1342\text{ cm}^{-1}$  ( $-\text{CH}_3$ ) belonged to the long alkyl side-chain of cardanol.

As shown in Figure 3, the characteristic protons of oxazine ring appeared at 5.19 and 4.79 ppm assigned to  $-\text{O}-\text{CH}_2-\text{N}-$  and  $\text{Ar}-\text{CH}_2-\text{N}-$ , respectively. The absorption peaks at 6.61 to 7.18 ppm were assigned to the absorption peaks of aromatic protons. The broad signal at 2.75 ppm may be assigned to the  $-\text{CH}_2-\text{Ar}-$  and at  $\sim 5.0\text{ ppm}$  be assigned to the  $-\text{CH}=\text{CH}-$  in the long alkyl side-chain of cardanol. In addition, the absorption peak assigned to the functional hydroxyl groups was observed at 2.57 ppm.

#### Preparation and Formation Mechanism of Cardanol-Based Polybenzoxazine/SiO<sub>2</sub> Hybrids

It is well known that the sol-gel process is a promising method for preparing various organic-inorganic hybrid materials at the molecular level. A three-dimensional cross-linked SiO<sub>2</sub> structure using TEOS as precursor can be developed *in situ* with a polymer matrix. The process mainly involved in the hydrolysis and condensation as follows (Figure 4).

Polybenzoxazine is a new type of phenolic resin. Ghosh et al.<sup>2</sup> and Ning and Ishida<sup>3</sup> have synthesized many types of benzoxazines and studied the cure kinetics, molecular structure, and mechanical properties. They illustrated that one character of polybenzoxazine was that the benzoxazine ring was stable at low temperature, but the ring-opening reaction occurred at high temperature, and the tertiary amine groups were produced (Figure 5).

Based on the chemistry of benzoxazine and TEOS, cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films were successfully prepared by the sol-gel processing of TEOS in the presence of CBZ. Namely, firstly, CBZ, water, HCl, and TEOS were mixed in the THF, and were stirred at room temperature for a period of time. Then, the mixed solution was poured in a silane-coated glass plate and left for 24 h at room temperature. When the THF was volatilized completely, a brown membrane was obtained. In order to understand the reaction during the information of the brown membrane, we also investigated the reaction of TEOS, H<sub>2</sub>O, and HCl without CBZ at room temperature for 24 h. As a consequence, a transparent membrane was obtained after the reaction of TEOS and H<sub>2</sub>O catalyzed by HCl in the absence of CBZ. This meant that the process in the current experiment had involved in the hydrolysis of TEOS and the following condensation of Si-OH at room temperature. Figure 6 shows FT-IR spectra of TEOS, the membrane from the reaction of TEOS and H<sub>2</sub>O catalyzed by HCl in the absence or presence of CBZ at room temperature for 24 h, the membrane from the reaction of TEOS and H<sub>2</sub>O catalyzed by HCl in the presence of CBZ cured at 120°C (2 h), 160°C (2 h), and the other at 120°C (2 h), 160°C (2 h), 180°C (2 h).

From Figures 6(a,b), it can be seen that the bands at 656, 1296, 2976, and 2891  $\text{cm}^{-1}$  from  $-\text{Si}-\text{O}-\text{C}_2\text{H}_5$  almost completely disappeared. A new peak appeared at 3455  $\text{cm}^{-1}$  from Si-OH. In addition, for the brown membrane (in the presence of CBZ), a new peak appeared at 3449  $\text{cm}^{-1}$  assigned to Si-OH. Furthermore, there is an obvious intensive adsorption at 937  $\text{cm}^{-1}$  [Figure 6(c)]. This indicated that HCl had catalyzed the hydrolysis of TEOS and the following condensation of Si-OH, but had not catalyzed the ring-opening polymerization of CBZ at room temperature.

We also investigated the FT-IR spectras of the CBZ before and after curing at 120°C (2 h), 160°C (2 h), 180°C (2 h),

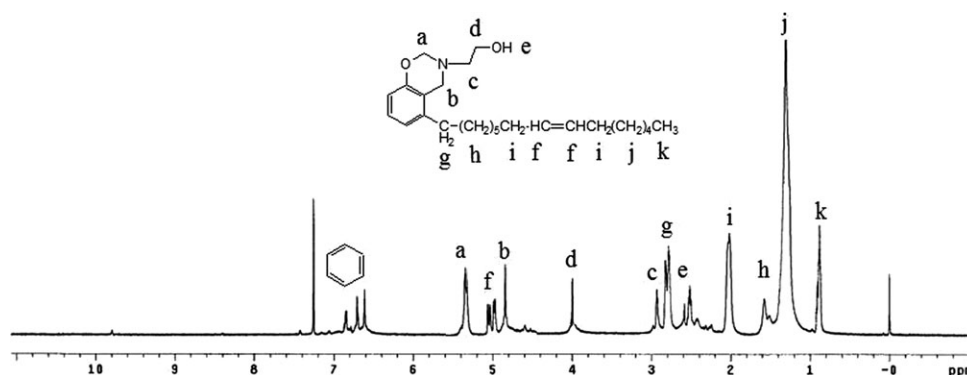
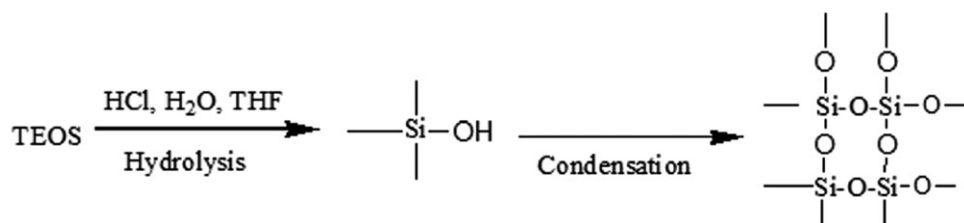


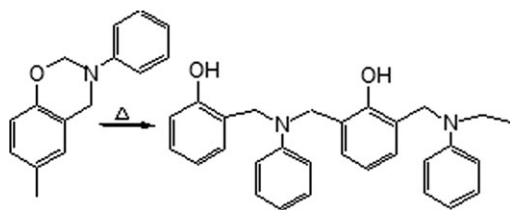
Figure 3. <sup>1</sup>H NMR spectrum of CBZ.



**Figure 4.** The hydrolysis and condensation reactions involved in the sol-gel process using TEOS as precursor.

200°C (2 h), and 220°C (2 h). It was found that the adsorption at  $937\text{ cm}^{-1}$  completely disappeared after curing procedure. This phenomenon confirmed that the ring-opening reaction of CBZ only occurred at high temperature [120°C (2 h), 160°C (2 h), 180°C (2 h), 200°C (2 h), and 220°C (2 h)] (Figures 7 and 8).

Comparing with the FT-IR spectra of the membrane from the reaction of TEOS and  $\text{H}_2\text{O}$  catalyzed by HCl in the absence or presence of CBZ (Figure 6), for that with CBZ, the peak of Si-OH was shifted from  $3455$  to  $3449\text{ cm}^{-1}$ . This indicated that the hydrogen bonding existed between the  $-\text{CH}_2\text{CH}_2-\text{OH}$  groups of CBZ and  $-\text{Si}-\text{OH}$  groups of TEOS precursor during the curing process. As shown in Figure 8, the FT-IR spectra of the membrane from the reaction of TEOS and  $\text{H}_2\text{O}$  catalyzed by HCl in the absence or presence of CBZ (5 g TEOS/1 g  $\text{H}_2\text{O}$ /0.35 mL HCl) at room temperature for 24 h and the corresponding membrane cured at 120°C (2 h), 160°C (2 h), and the other at 120°C (2 h), 160°C (2 h), 180°C (2 h), it was found that the intensive adsorption at around  $3450\text{ cm}^{-1}$  obviously decreased after cured at high temperature. This may be attributed to the further condensation of Si-OH. In the present sol-gel procedure, HCl was mainly used to catalyze the hydrolysis reaction of TEOS and the following condensation of Si-OH. After the hydrolysis reaction of TEOS and the following condensation reactions of Si-OH for 24 h, most of HCl volatilized and a little remained in the film. Whether or not the residual HCl catalyze the ring-opening reaction of CBZ, CBZ would polymerize at elevating temperature. Figure 9 represents FT-IR spectra of PCBZ and cardanol-based polybenzoxazine/ $\text{SiO}_2$  hybrids. Compared with the FT-IR spectroscopy of CBZ, for all samples (PCBZ, PCBZT1, PCBZT2, and PCBZT3), the peaks at  $937\text{ cm}^{-1}$  disappeared and the new absorption peak appeared at  $1461\text{ cm}^{-1}$  due to the tetra substituted benzene ring, which confirmed the ring-opening polymerization of CBZ.<sup>5–8</sup> In addition, the absorption peak at  $1084\text{ cm}^{-1}$  confirmed the formation of  $-\text{Si}-\text{O}-\text{Si}-$  linkage due to the hydrolysis reaction of TEOS and the following condensation reactions of Si-OH. The intensity of the absorption peak at  $1084\text{ cm}^{-1}$  increased with the increase in the ratio of TEOS to CBZ. It illuminated there

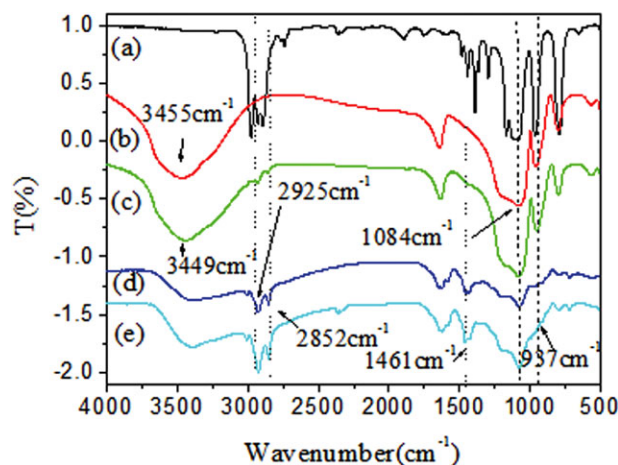


**Figure 5.** Ring-opening reaction of a benzoxazine ring.

were more  $\text{SiO}_2$  particles formed by the hydrolysis reaction and the following condensation reactions of Si-OH, and embedded in the PCBZ matrix. Furthermore, PCBZ showed the peak at around  $3400\text{ cm}^{-1}$ , which is characteristic of the phenolic hydroxyl group. However, this band in PCBZ1, PCBZ2, and PCBZ3 was shifted to  $3391$ ,  $3382$ , and  $3365\text{ cm}^{-1}$ , respectively. This may be attributed to the hydrogen bonding interactions between cardanol-based polybenzoxazine and  $\text{SiO}_2$  particles from hydrolysis reaction and the following condensation reactions of Si-OH. Figure 10 demonstrates the preparation process and possible reaction involved in the preparation of cardanol-based polybenzoxazine/ $\text{SiO}_2$  hybrids. The preparation process of cardanol-based polybenzoxazine/ $\text{SiO}_2$  hybrids mainly included the hydrolysis and the following condensation reactions of TEOS at room temperature, further condensation reactions of Si-OH and the ring-opening reaction of CBZ at high temperature.

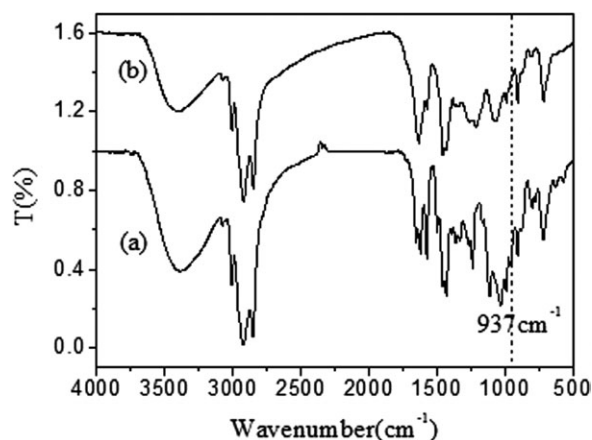
#### Morphological Studies

The homogeneous hybrid films were only obtained through step by step curing reaction. We found that for PCBZ, PCBZT1, and PCBZT2, the flexibility of the films increased with the increase of the content of TEOS. However, for PCBZT3, the film became relatively brittle (Figure 11). We also observed that the obtained neat PCBZ film was yellow color and highly transparent while



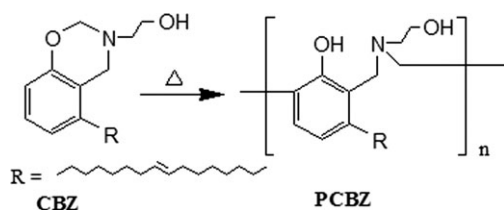
**Figure 6.** FT-IR spectras of TEOS (a), the membrane from the reaction of TEOS and  $\text{H}_2\text{O}$  catalyzed by HCl in the absence (b) or presence of CBZ(c) at room temperature for 24 h, the membrane from the reaction of TEOS and  $\text{H}_2\text{O}$  catalyzed by HCl in the presence of CBZ cured at 120°C (2 h), 160°C (2 h) (d); and at 120°C (2 h), 160°C (2 h), 180°C (2 h) (e). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



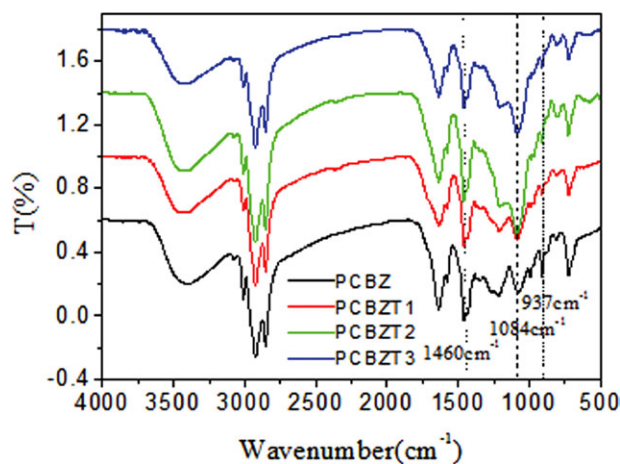


**Figure 7.** FT-IR spectra of the CBZ before (a) and after (b) curing at 120°C (2 h), 160°C (2 h), 180°C (2 h), 200°C (2 h), and 220°C (2 h).

all cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films were deep brown. PCBZT1 was transparent and PCBZT2 samples were translucent. However, PCBZT3 sample became less transparent or translucent. It seemed that at high TEOS ratio, the resulting films were opaque. These different optic properties maybe resulted from different inner microstructures of hybrids. Therefore, the morphologies of PCBZ and cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films are investigated by SEM (Figure 12). For PCBZ, the fracture surface of polymeric film was very smooth due to the single neat composition. However, for PCBZT1, PCBZT2, and PCBZT3, the fracture surface of cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films became less smooth gradually with the increase in the ratio of TEOS and CBZ. For PCBZT1 and PCBZT2, it can be clearly seen that there were many quasi-spherical micron-size SiO<sub>2</sub> particles (the average diameter: 0.1–0.8 μm), suggesting that the spherical phases correspond to polysilsesquioxanes from the hydrolysis reaction of TEOS and the following condensation reactions of Si-OH, embedded equably in the polymeric PZBZ medium. However, for PCBZT3, many rod-like crystals were observed in the polymeric matrix. Ardhyana et al.<sup>19</sup> reported polybenzoxazine-polydimethylsiloxane (PBa-PDMS) hybrids prepared by *in situ* ring-opening polymerization of benzoxazine (Ba) and the sol-gel process of diethoxydimethylsilane (DEDMS). They also found hybrid with 7 ca. 25 wt % PDMS content, macroscopic phase separation occurred and the film became brittle. Hernandez-Padron et al.<sup>20</sup> also prepared a phenolic-formaldehydic resin (PFR) modified by the incorporation of carboxylic end groups (MPFR). The study results showed the hybrid SiO<sub>2</sub>-MPFR material was transparent when there was a homogeneous distribution



**Figure 8.** Ring-opening reaction of CBZ.

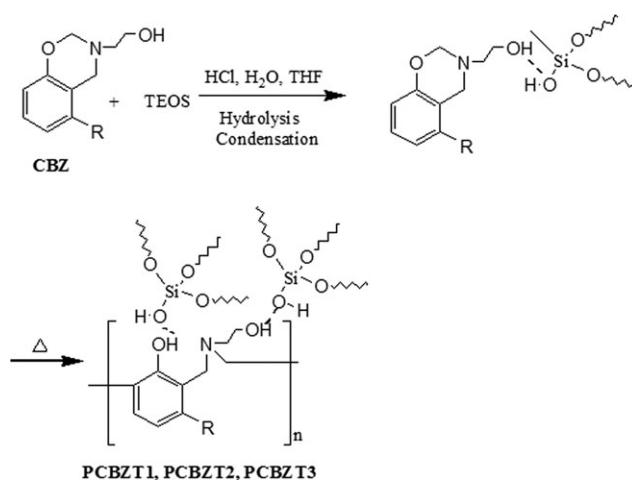


**Figure 9.** FT-IR spectra of PCBZ, PCBZT1, PCBZT2, and PCBZT3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

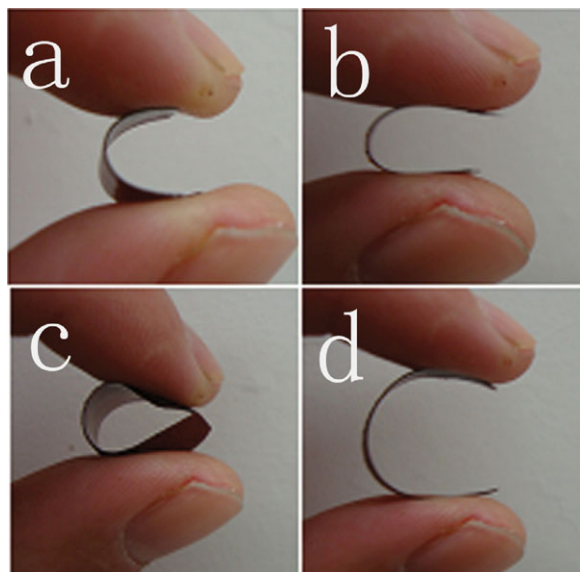
of micrometric silica aggregates, whereas it can become less transparent or transparency when some phase segregation arises between SiO<sub>2</sub> and MPFR matrix. Therefore, in the current experiment, it could be believed that the less transparent or transparency and rod-like crystals of PCBZT3 maybe result from the phase separation at a high content of TEOS in the hybrid system when the ratio of TEOS to CBZ was not less than 3 : 5.

#### Thermal Stability of Cardanol-Based Polybenzoxazine/SiO<sub>2</sub> Hybrids

The thermal stability of PCBZ and cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrids was evaluated by TGA. Figure 13 shows the TGA curves of PCBZ and cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films and the results are listed in Table II. All four samples showed similar decomposition curves, but the difference was that the 5% and 10% mass loss temperatures of PCBZT1 (357°C and 402°C, respectively) and PCBZT2 (356°C and 399°C, respectively) were higher than that of the neat PCBZ matrix (334°C and 376°C, respectively). Furthermore, the char yield at 800°C of PCBZ, PCBZT1, and PCBZT2 were 21.1%,

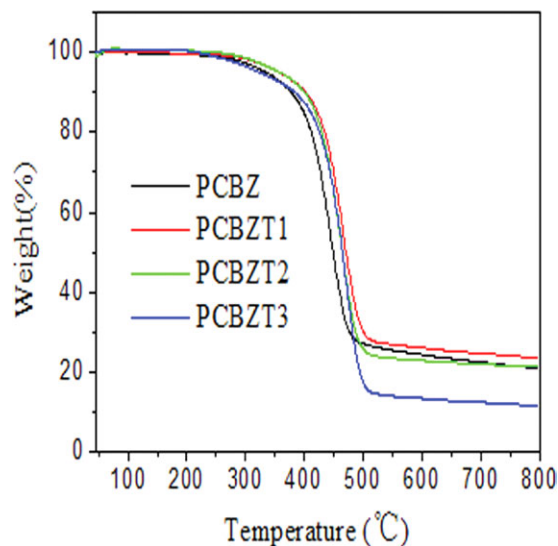


**Figure 10.** Schematic representation of preparation cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrids.



**Figure 11.** Photographs of the bending PCBZ (a), PCBZT1 (b), PCBZT2 (c), and PCBZT3 (d). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

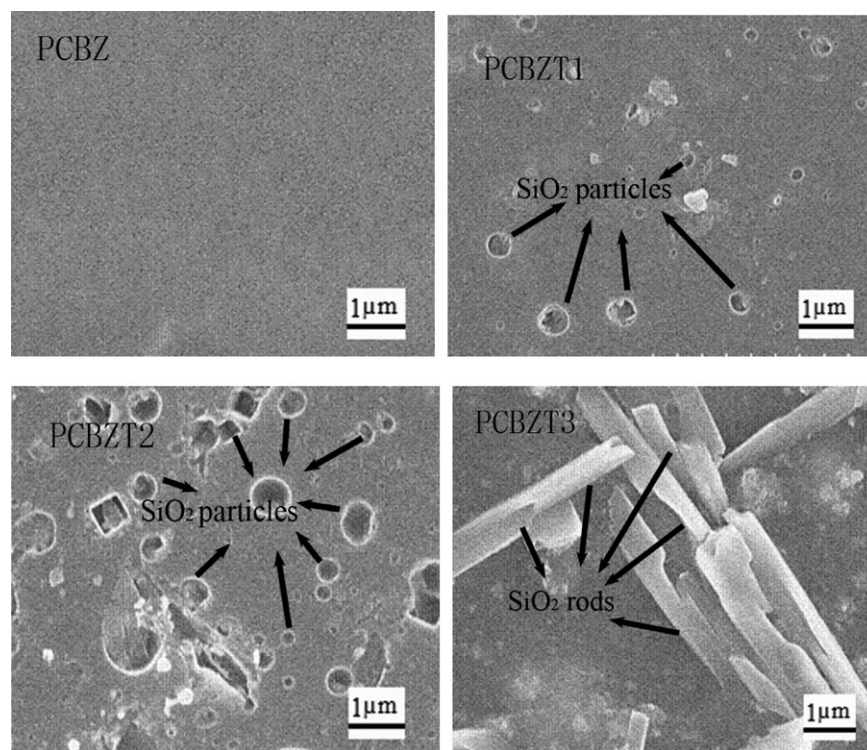
23.6%, and 21.4%, respectively. The increasing char residue of hybrids also resulted from more inorganic SiO<sub>2</sub> particles in the polybenzoxazine matrix. However, for PCBZT3, a decreased char yield at 800°C mainly resulted from the phase separation, which may cause a relatively bad interaction between PCBZ and SiO<sub>2</sub> particles. Maybe the associated little air bubble in the cured products display decreased char yield.



**Figure 13.** TGA thermograms of PCBZ (a), PCBZT1 (b), PCBZT2 (c), and PCBZT3 (d) under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### Surface and Antiuaviolet Properties of Cardanol-Based Polybenzoxazine/SiO<sub>2</sub> Hybrids

Polybenzoxazine is a kind of materials with good hydrophobicity. Although the present PCBZ possessed a long pendent alkyl side-chain, it showed low water contact angle (68°) (Figure 14), which was much lower than that of conventional BA-a (*bis*(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane) film (105.5°).<sup>21</sup> The water contact angle of PCBZ and cardanol-based



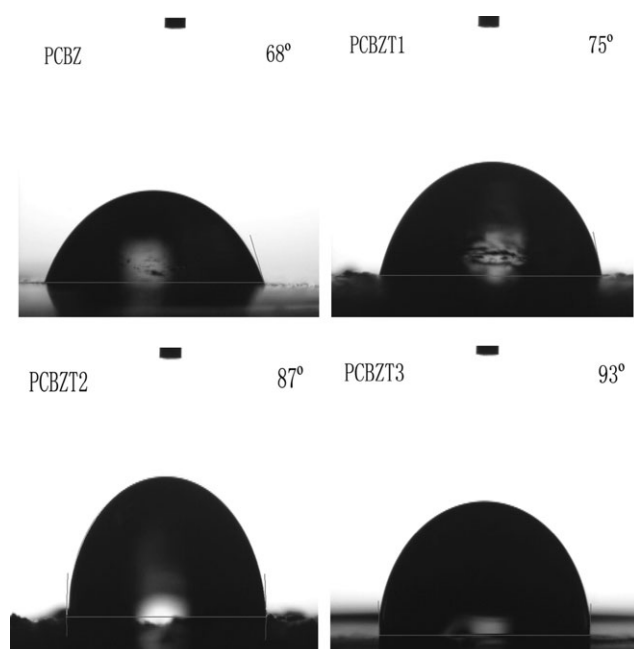
**Figure 12.** SEM images of PCBZ (a), PCBZT1 (b), PCBZT2 (c), and PCBZT3 (d).

**Table II.** The Thermal Properties of PCBZ and Cardanol-Based Polybenzoxazine/SiO<sub>2</sub> Hybrids

Sample code	CBZ : TEOS (w/w)	Temp. at 5 wt % loss (°C)	Temp. at 10 wt % loss (°C)	Char yield (%) (800°C)
PCBZ	5:0	334	376	21.1
PCBZT1	5:1	357	402	23.6
PCBZT2	5:3	356	399	21.4
PCBZT3	5:5	324	383	11.7

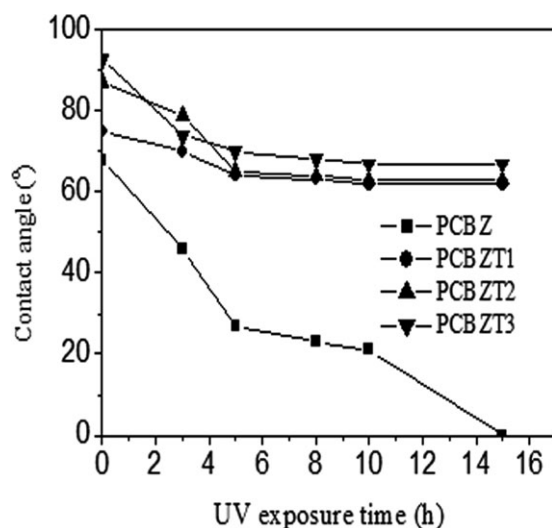
polybenzoxazine/SiO<sub>2</sub> hybrid films depended on the strength of intra- and intermolecular hydrogen bonding in the polybenzoxazine. Wang et al reported that enhanced intramolecular hydrogen bonding leads to a decrease in the surface free energy and an increase in the water contact angle, whereas increasing the fraction of intermolecular hydrogen bonding leads to the opposite effect.<sup>22</sup> On one hand, CBZ is a type of single functional benzoxazine monomer while BA-a is a type of two functional benzoxazine monomer. The crosslinking methods of them are different. On the other hand, the structure and steric interference of them are also different. The steric interference of cardanol groups in CBZ may hinder the formation of the intermolecular hydrogen bonding. So it is very difficult to compare the intra- and intermolecular hydrogen bonding of BA-a polybenzoxazine and PCBZ.

As shown in Figure 14, the contact angle for PCBZ was 68°, while for PCBZT1, PCBZT2 and PCBZT3, were 75°, 87°, and 93°, respectively. This indicated that the water contact angle of cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films increased with the increase in the ratio of TEOS and CBZ. That is to say,

**Figure 14.** Water contact angles for PCBZ, PCBZT1, PCBZT2, and PCBZT3 films.

the present cardanol-based polybenzoxazine/SiO<sub>2</sub> films showed improved surface de-wetting properties with the increase in the ratio of TEOS to CBZ. This may be attributed to the fact that high silica content in the cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid with the increase in the ratio of TEOS and CBZ. Thus, more -Si-OH groups involved in the intramolecular hydrogen bonding in the hybrid system. More intramolecular hydrogen bondings led to an increase in the water contact angle of the hybrid surface.

UV radiation has sufficient energy to disrupt and break the chemical bonds or hydrogen bonding of organic molecules through photochemical reactions. Thus, the surface properties (hydrophilicity or hydrophobicity) could be changed by the UV radiation. Macko and Ishida determined that a photo-oxidation reaction occurred in bisphenol A-based polybenzoxazine upon irradiation in air at room temperature. They found that the intramolecular hydrogen bonding in bisphenol A-based polybenzoxazine decreased after UV radiation.<sup>23</sup> Since the photo-oxidation reaction induced by UV radiation can break the intramolecular hydrogen bonding of polybenzoxazines, we anticipated that the water contact angle of cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films would be strongly affected by their length of UV exposure. The UV exposure time and water contact angles of cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrid films are shown in Figure 15. For PCBZ, the water contact angle decreased rapidly upon increasing the UV exposure time, from 68° to 0° after 15 h of UV exposure. However, for PCBZT1, PCBZT2, and PCBZT3, the water contact angle decreased from 75°, 87°, and 93° to 62°, 63°, and 67°, respectively. This indicated that incorporation of SiO<sub>2</sub> particles into PCBZ could cause a considerable reduction of the decrease in water contact angle during UV radiation. In other words, the antiultraviolet properties could be improved by adding TEOS to PCBZ. With the ratio of CBZ to TEOS increased gradually from 1 : 5 to 5 : 5, the decrease in the water contact angle of the films exposed to UV radiation became slow gradually. Among the three

**Figure 15.** Water contact angles for PCBZ, PCBZT1, PCBZT2, and PCBZT3 films with different UV exposure times.



samples, PCBZT3 had the best antiultraviolet property, with a highest water contact angle (67°) after 15 h of UV exposure.

## CONCLUSIONS

In this work, new cardanol-based polybenzoxazine/SiO<sub>2</sub> hybrids were successfully synthesized by the sol-gel procedure. The formation mechanism of hybrids involved in the polymerization of CBZ, the hydrolysis reaction of TEOS and the following condensation of Si-OH and the interaction between cardanol-based polybenzoxazine and SiO<sub>2</sub> particles from hydrolysis reaction and the following condensation of Si-OH. The morphological, thermal, optical and surface properties of these hybrid films strongly depended on the ratio of TEOS to CBZ. The differences in TGA results and water contact angle may be due to differences in content of silica in the materials. The polybenzoxazines/SiO<sub>2</sub> hybrid films showed improved surface de-wetting and antiultraviolet properties with an increase in the ratio of CBZ to TEOS.

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