

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Synthesis and characterization of novel biobased benzoxazines from cardbisphenol and the properties of their polymers

Received 23th Jun 2015,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shengfang Li,^{a,b*} and Shilin Yan^c

Two types of novel biobased benzoxazine monomers (named as CBB and CBF, respectively.) from cardbisphenol were synthesized by a solventless method. The chemical structure of the monomers was confirmed by FTIR, ¹H NMR and ¹³C NMR spectra, etc. FTIR and DSC showed that CBB and CBF were thermally initiated and polymerized via ring-opening polymerization. As a result, the thin polybenzoxazine (named as PCBB and PCBF, respectively.) films can be obtained. Dynamic mechanical analysis (DMA) indicated that the glass transition temperatures (*T_g*) of PCBB and PCBF were 94 °C and 121 °C, respectively. Thermogravimetric analysis (TGA) demonstrated that the thermal stability of PCBF was better than that of PCBB. Both PCBB and PCBF had low humidity absorption values.

1. Introduction

Nowadays, polybenzoxazines as a novel type of developed high performance phenolic resin have gained considerable attention over the past decade because they exhibit excellent properties, such as nearly zero shrinkage upon curing, high glass transition temperature, low water absorption, limited byproduct release upon curing and good flame retardancy[1-3]. Moreover, the benzoxazine chemistry synthesis offers a wide range of molecular design flexibility on benzoxazine monomers, which can be synthesized from a phenolic derivate, formaldehyde and a primary amine compound via the Mannich reaction [4-8]. These fascinating characteristics make polybenzoxazine resins a promising candidate in different application areas, for example, electronics, space-flight and aerospace [9].

Currently, synthesis of biobased benzoxazine from renewable resources i.e., eugenol, vanilline and urushiol has become a rapidly growing area, as these materials could potentially replace or partially replace environmentally and energy unfavorable petroleum-based materials[10-15]. Cardanol is an industrial yellow oil extracted from cashew shell liquid (CNSL), which is also a promising renewable phenol resource. So far, several research groups have reported synthesis of various benzoxazines (i.e., cardanol/ammonia, cardanol/aniline, cardanol/furfurylamine, cardanol/allylamine, cardanol/ethanolamine, cardanol/aromatic or aliphatic diamine) from cardanol to replace part of the petroleum-based phenolic compound [16-22]. However, almost all of these literatures only focused on synthesizing biobased benzoxazines

using monophenol as starting materials. Few literatures reported biobased benzoxazines using bisphenol derived from renewable resources as starting materials. Very recently, in our previous study, the cardanol-furfural phenolic resins were also used to prepare oligomeric benzoxazine precursors and the highly thermally stable polybenzoxazines could be obtained [23]. As we all know, cardbisphenol is a aliphatic-bridged bisphenol derived from cardanol, which has been used to prepare Mannich base [24]. However, to our best knowledge, biobased benzoxazines from cardbisphenol have never been reported up till now.

In this paper, we attempt to synthesize two types of novel biobased benzoxazine monomers (CBB and CBF) using the cardbisphenol, amine, furfurylamine and paraformaldehyde as starting raw materials as shown in Fig. 1. The thermally activated polymerization of CBB and CBF as well as the properties of the corresponding polybenzoxazines (PCBB and PCBF) was discussed in details.

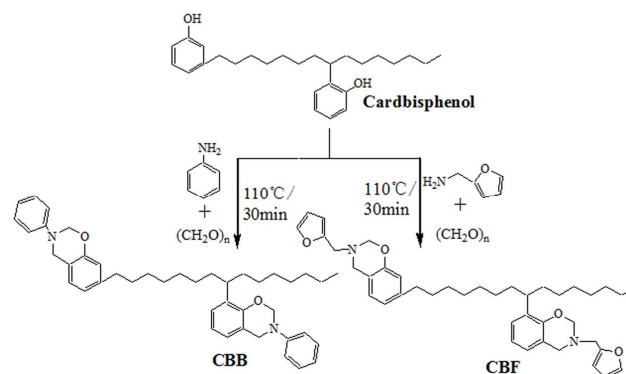


Fig.1 Synthesis of biobased benzoxazine monomers from cardbisphenol.

^a School of Chemistry and Chemical Engineering, Hubei Polytechnic University, Huangshi 435003, PR China, E-mail: lishengf_@163.com

^b Hubei Key Laboratory of Mine Environmental Pollution Control and Remediation, Hubei Polytechnic University, Huangshi 435003, PR China

^c Wuhan University of Technology, Wuhan 430070, PR China

2. Experimental

2.1. Materials

Cardanol was purchased from Shanghai Cashew Chemical Polymer Company (China). Phenol, paraformaldehyde (95%), furfurylamine, amine and chloroform were purchased from Shanghai First Reagent Company (China). Cardbisphenol prepared from distilled cardanol and phenol according to the modified method in the previous publication [25]. The yield was 65%. FTIR spectra (KBr), cm^{-1} : 685, 770, 825, 1170, 1485, 1510, 1610, 3350. ^1H NMR (CDCl_3 , 300MHz, δ ppm): 7.24-6.65 (m, 8H), 2.59-2.87 (m, H), 2.52 (t, 2H), 1.55-1.20 (m, 24H), 0.84 (s, 3H). All chemicals were AR grade and used without further purification.

2.2. Measurements

FTIR spectrum was obtained on a PerkinElmer-2 spectrometer (KBr pellet). ^1H (300 MHz) and ^{13}C (100.5 MHz) nuclear magnetic resonance (NMR) spectra were obtained with a Bruker spectrometer with Fourier transform, with CDCl_3 as a solvent, and TMS as an internal standard. Elemental analysis was performed with a VARIO EL III rapid elemental analyzer. DSC was measured with a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere on Perkin-Elmer DSC6 apparatus. Dynamic scans of the samples were recorded. 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 $5^\circ\text{C}/\text{min}$ under N_2 atmosphere. The resulting thermograms were recorded. Scanning electron microscopy (SEM) 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. The T_g of the polybenzoxazine film was measured with a dynamic mechanical analyzer (DMA, Thermal Analysis DMA-Q800). The applied static force and dynamic force were 0.11 and 0.10 N, respectively. The heating rate was $5^\circ\text{C}/\text{min}$ and the frequency was 1 Hz. The peak temperature of the $\tan \delta$ plot was taken as T_g of the sample. Humidity absorption of cured samples were conditioned under vacuum at 90°C for 20 h before being placed in air (79% and 29% relative humidity (RH)). All these experiments were conducted at room temperature. Then, the humidity absorption content (HA) of the cured samples was calculated according to formula (1) as follows [26]:

$$\text{HA} (\%) = (W_t - W_0) \times 100\% / W_0 \quad (1)$$

Where the W_0 and W_t represent the sample weights before and after (dry sample) humidity absorption, respectively. Humidity absorption content was measured for 5 samples of each material group and the average values were recorded.

2.3. Synthesis of biobased benzoxazine monomers from cardbisphenol

CBB was prepared by the previous reported solventless method [27]. Namely, a mixture of cardbisphenol, aniline and paraformaldehyde with a mole ratio of 1: 2: 4 was added into a flask and stirred at 110°C for 30 min. The product was

dissolved in dichloromethane. The resulting solution was filtered and washed with deionized water and the solvent was removed by rotary evaporation at reduced pressure. The product (CBB) was dried at reduced pressure and room temperature to provide a brown yellow powder. The yield was 85%. m.p.: 58°C . Anal. $\text{C}_{43}\text{H}_{54}\text{O}_2\text{N}_2$; C 81.90%; H 8.57%; N 4.44%; found: C 82.21%; H 8.12%; N 4.03%. FTIR spectra (KBr), cm^{-1} : 753, 807, 897, 960, 991, 1031, 1076, 1115, 1144, 1241, 1372, 1431, 1457, 1497, 1601, 2853, 2925, 3026. ^1H NMR (CDCl_3 , 300MHz, δ ppm): 7.25-6.63 (m, 9H), 5.34 (s, 4H), 4.60 (s, 4H), 2.50-2.49 (d, 2H), 1.96 (m, 4H), 1.55 (s, 2H), 1.28-1.25 (d, 20H), 0.87 (t, 3H). ^{13}C NMR (CDCl_3 , δ ppm): 14, 22, 25, 27, 29, 31, 32, 34, 35, 48, 50, 79, 107, 108, 110, 115, 116, 119, 120, 121, 127, 129, 142, 152 and 153.

CBF was also synthesized using cardbisphenol, furfurylamine and paraformaldehyde as raw materials by the same method. The yield was 84%. m.p.: 55°C . Anal. $\text{C}_{41}\text{H}_{54}\text{O}_4\text{N}_2$; C 77.12%; H 8.46%; N 4.39%; found: C 77.63%; H 8.22%; N 4.12%. FTIR spectra (KBr), cm^{-1} : 753, 809, 867, 885, 938, 968, 995, 1012, 1076, 1121, 1149, 1240, 1361, 1430, 1458, 1503, 1578, 2854, 2927. ^1H NMR (CDCl_3 , 300MHz, δ ppm): 7.41 (d, 2H), 7.35-6.64 (m, 6H), 6.33 (d, 2H), 6.14 (d, 2H), 5.19 (s, 4H), 4.89 (s, 4H), 4.76 (s, 4H), 2.52 (d, 4H), 1.95 (d, 4H), 1.58 (s, 18H), 1.21 (s, 2H), 0.85 (s, 3H). ^{13}C NMR (CDCl_3 , δ ppm): 14, 22, 25, 27, 29, 31, 32, 34, 35, 36, 37, 40, 50, 79, 116, 117, 118, 120, 121, 126, 128, 129, 143, 148 and 154.

2.4. Preparation of biobased polybenzoxazines

The biobased polybenzoxazines were prepared by thermally polymerization according to the following method: about 40% by weight solution of CBB or CBF in tetrahydrofuran solution was placed over a glass plate. After most of the solvent was removed under ambient atmosphere at 60°C , the glass plate was placed into a vacuum oven at 60°C for 24 h to remove the residual solvent. After that, the vacuum oven was subjected to a step curing procedure as follows: 120°C (2h), 150°C (2h), 180°C (2h), 200°C (2h), 230°C (2h), respectively. Upon completion of the curing, the samples (named as PCBB or PCBF) were allowed to freely cool to room temperature and cut appropriate dimension to be applied for property evaluation.

3. Results and discussion

3.1. Preparation and Characterization of the biobased benzoxazine monomers

Cardbisphenol based benzoxazine monomers (CBB and CBF) were synthesized by the condensation reaction of cardbisphenol with paraformaldehyde and aniline or furfurylamine as shown in Fig. 1. The yield of CBB and CBF were 85% and 84%, respectively. Both of them were brown yellow powder at room temperature and showed a good solvency in common solvents.

The structure of CBB and CBF was confirmed by FTIR, ^1H NMR and ^{13}C NMR spectral methods. Fig. 2 shows the FTIR spectra of CBB and CBF, respectively. The typical absorption band of benzoxazine ring for CBB appeared at 942 cm^{-1} , whereas for CBF appeared at 938 cm^{-1} . For both CBB and CBF,

other characteristic absorption bands can be also observed at 1012-1121 cm^{-1} (symmetric stretching of C-O-C), about 1240 cm^{-1} (asymmetric stretching of C-O-C), about 1144 cm^{-1} (symmetric stretching vibrations of C-N-C) and about 1361 cm^{-1} (wagging of CH_2). In addition, the absorption peaks at 1490-1601 cm^{-1} was assigned to the trisubstituted benzene groups. The characteristic absorption bands at about 2927 cm^{-1} ($-\text{CH}_2-$) and about 2854 cm^{-1} ($-\text{CH}_3$) were assigned to the aliphatic alkyl chain from carbisphenol. Furthermore, the characteristic absorption peaks of furan rings in CBF was found at 1578, 968, and 753 cm^{-1} . Another characteristic absorption peak of furan ring at 938 cm^{-1} overlapped with the absorption band of benzoxazine ring [23].

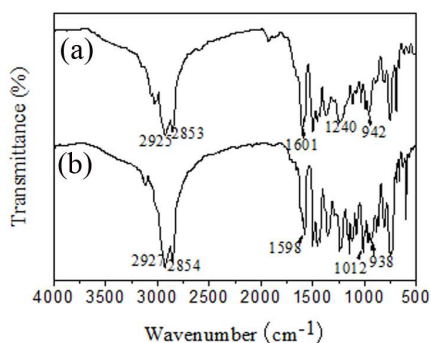


Fig. 2 FTIR spectra of CBB (a) and CBF (b), respectively.

Fig. 3 shows the ^1H NMR spectra of carbisphenol, CBB and CBF, respectively. Comparing with Figs. 3(a), (b) and (c), it was very clear that both CBB and CBF had the same characteristic protons of aliphatic alkyl chain appeared at 2.52, 1.95, 1.58, 1.21 and 0.85 ppm as well as carbisphenol, respectively. The aromatic ring protons appeared as multiplets between 6.63 and 7.35 ppm. Furthermore, for CBB, the characteristic protons of oxazine ring appeared at 5.34 and 4.60 ppm ($-\text{O}-\text{CH}_2-\text{N}-$ and $\text{Ar}-\text{CH}_2-\text{N}-$), respectively (Fig. 3(b)). However, for CBF, the characteristic protons of oxazine ring appeared at 5.19 and 4.89 ppm ($-\text{O}-\text{CH}_2-\text{N}-$ and $\text{Ar}-\text{CH}_2-\text{N}-$), respectively (Fig. 3(c)) [1-3]. In addition, for CBF, the protons of the furan ring gave peaks at 6.2, 6.3, and 7.4 ppm, while the methylene group connecting the oxazine ring and the furan ring resonated at 4.76 ppm [23, 28].

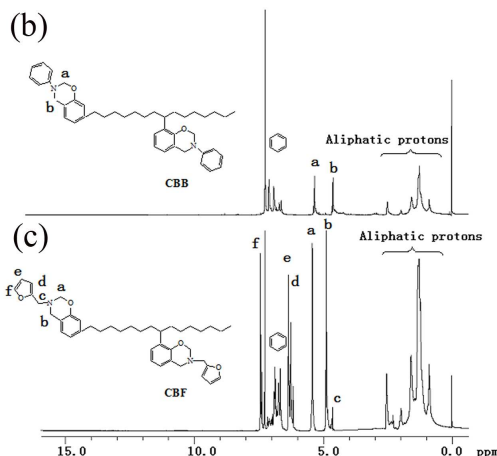
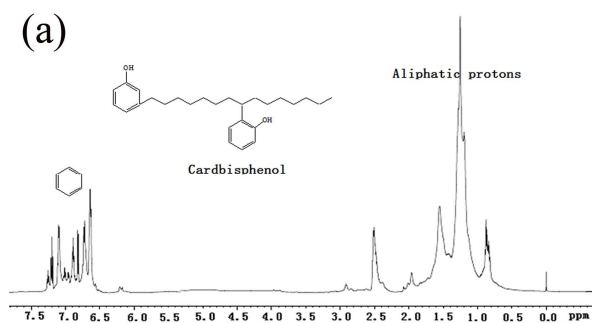


Fig. 3 ^1H NMR spectra of carbisphenol (a), CBB (b) and CBF (c), respectively.

Fig. 4 shows the ^{13}C NMR spectra of CBB and CBF, respectively. As shown in Fig.4, the characteristic carbon resonances of the oxazine ring were found at 50 and 79 ppm for $\text{Ar}-\text{CH}_2-\text{N}$ and $\text{N}-\text{CH}_2-\text{O}$, respectively. The peak at 48 and 152 ppm was attributed to the methylene group carbons connecting the oxazine ring and the furan ring. In addition, the peaks at 108, 110 and 142 ppm were assigned to the furan ring carbons.

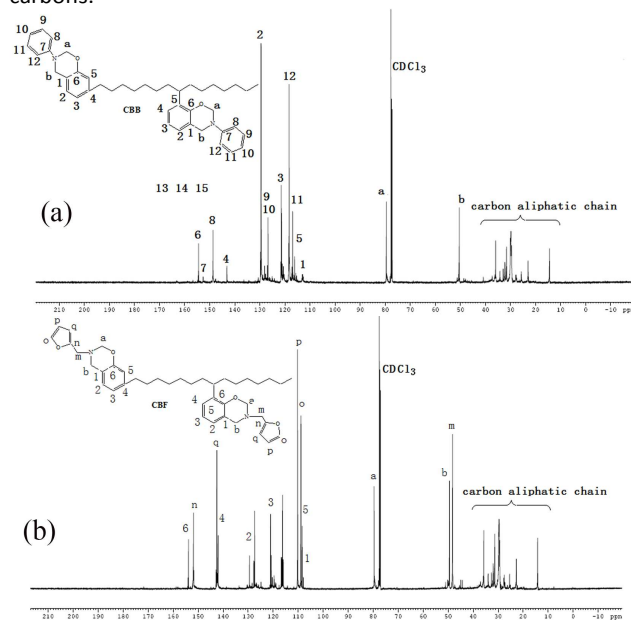


Fig. 4 ^{13}C NMR spectra of CBB (a) and CBF (b), respectively.

3.2. Thermally activated polymerization of the bio-based benzoxazine monomers

Thermally activated polymerization of CBB and CBF was investigated by FTIR and DSC methods. Figs. 5a and b show the FTIR spectra of CBB and CBF after curing at different temperature. Comparing with the FTIR spectra of monomers in

Fig. 2, for both CBB and CBF, the intensity of characteristic peaks at 942 or 938 cm^{-1} assigned to benzoxazine ring decreased significantly to a considerable extent when the curing temperature was elevated from 180 $^{\circ}\text{C}$ to 220 $^{\circ}\text{C}$. At the same time, the intensity of absorption peak at 3401 or 3408 cm^{-1} assigned to $-\text{OH}$ increased markedly as the curing reaction advanced. All the results suggested that the ring opening reaction of oxazine ring had occurred in both CBB and CBF when the temperature was elevated gradually [3, 5]. Additionally, the absorption of furan ring at 1578 cm^{-1} became broad after polymerization, indicating the formation of disubstituted furan ring. Formation of disubstituted furan rings in polymerization indicated that furan ring participated in the polymerization reactions [28].

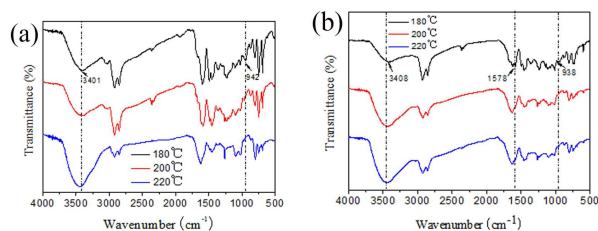


Fig. 5 FTIR spectra of CBB (a) and CBF (b) after thermally polymerization at different temperature.

Fig. 6 shows the DSC thermograms of CBB and CBF with the results summarized in Table 1. The endothermic peaks centered around 55–58 $^{\circ}\text{C}$ were attributed to the melting point of the benzoxazine monomers. Then an exothermic behavior observed at high temperature region associated to the ring-opening polymerization of oxazine rings. The onset polymerization temperatures of CBB and CBF were 214 $^{\circ}\text{C}$ and 219 $^{\circ}\text{C}$, respectively, which were comparable to the polymerization temperatures of other benzoxazine monomers [1–3]. The exothermic maxima were observed at 242 $^{\circ}\text{C}$ and 253 $^{\circ}\text{C}$ for CBB and CBF, respectively. The temperature difference between melting point and onset of polymerization is often defined as the processing window. According to the calculation, it was found the processing window for CBB and CBF was 156 $^{\circ}\text{C}$ and 164 $^{\circ}\text{C}$, respectively. This indicated both CBB and CBF had wide processing windows, which were beneficial to some resin transfer molding process.

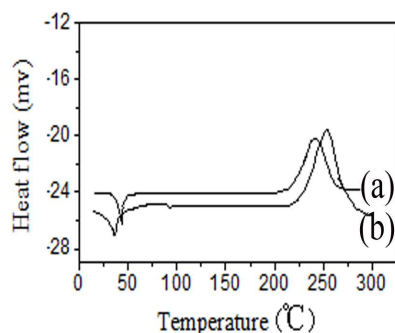


Fig. 6 DSC curves of CBB (a) and CBF (b), respectively.

Table 1 DSC datas of CBB and CBF, respectively.

Sample	T_m ($^{\circ}\text{C}$)	T_{onset} ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	$T_{\text{processing window}}$ ($^{\circ}\text{C}$)	$\Delta H/\text{Jg}^{-1}$
CBB	58	214	242	156	83.6
CBF	55	219	253	164	112.3

The reaction enthalpies of polymerizations of CBB and CBF were found as 83.6 and 112.3 J/g, respectively. In other words, the exothermic enthalpy of CBF was much higher than that of CBB. The main reason may be that, for CBF, the additional reaction of furan ring in molecular backbone as stated above could increase the exothermic enthalpy [28].

3.3. Thermal properties of the biobased polybenzoxazines

The thermal stability of the biobased polybenzoxazines is further studied by TGA (Fig. 7). The results are summarized in Table 2. Fig. 7 indicated that the thermal properties of two biobased polybenzoxazines at high temperature range (especially above 400 $^{\circ}\text{C}$) were very similar. However, the thermal properties of two polybenzoxazines were obvious different when the temperature is in the range from 200 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$. From Table 2, it can be seen that the 5% and 10% weight loss temperature (T_5 and T_{10}) of PCBB were 304 $^{\circ}\text{C}$ and 348 $^{\circ}\text{C}$, Whereas T_5 and T_{10} of PCBF were 356 $^{\circ}\text{C}$ and 374 $^{\circ}\text{C}$, respectively. Moreover, the char yields of PCBB and PCBF at 800 $^{\circ}\text{C}$ were 21.74% and 22.50%, respectively. Obviously, the thermal stability of PCBF was superior to that of PCBB. This may be attributed to the fact that the additional reaction of furan ring in the molecular backbone of CBF could increase the crosslink density of the polybenzoxazine. Similar results were also reported previously [23, 28].

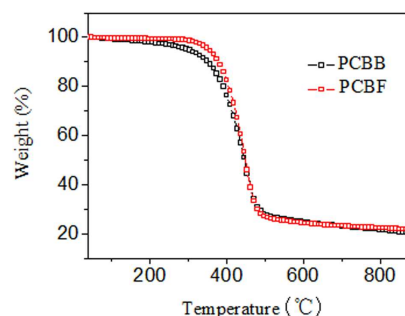


Fig. 7 TGA curves of the biobased polybenzoxazines under nitrogen atmosphere.

Table 2 TGA results of the biobased polybenzoxazines.

Sample	T_5 ($^{\circ}\text{C}$)	T_{10} ($^{\circ}\text{C}$)	Char yield (800 $^{\circ}\text{C}$)
PCBB	304	348	21.74%
PCBF	356	374	22.50%

3.4. Film-forming abilities of the biobased polybenzoxazines

It is very known that the high brittleness and the difficulties in preparing thin films are mainly disadvantages associated with conventional bisphenol-A based polybenzoxazine [1].

RSC Advances

Thus, we attempted to prepare a thin polybenzoxazine film by thermally polymerization of the as-synthesized biobased benzoxazines to overcome the shortcomings of bisphenol-A based benzoxazine. As a result, for both CBB and CBF, we found a brown yellow and transparent thin polybenzoxazine film could be obtained easily according to a step curing process. There were no bubbles and cracks on the surface of polybenzoxazine films, exhibiting good film-forming abilities. In addition, these obtained polybenzoxazine films were flexible in some degree due to the introduction long aliphatic chain alky groups in cardbisphenol, which can overcome the brittleness brought by the highly rigid aromatic backbone in the conventional bisphenol-A based polybenzoxazine. They can be bent as shown Fig.8. However, the flexibility of PCBF film reduced comparing with that of PCBB because of higher crosslink density resulted from the additional reaction of furan rings as stated above.

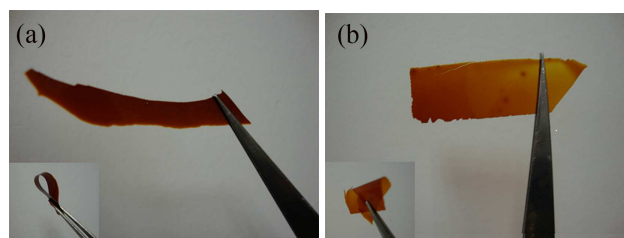


Fig. 8 Thin film photographs of the biobased polybenzoxazines before and after bending. (a) PCBB and (b) PCBF, respectively.

The fractured surfaces of the obtained biobased polybenzoxazine films are further investigated by SEM. As a result, for both PCBB and PCBF, the fibrous patterns and plastic deformations could be observed. These fibrous patterns and plastic deformations can absorb energy upon impacting due to the introduction of the aliphatic alkyl chain of cardbisphenol, indicating a tough fractured surface (Fig.9 (a)-(d)) [29].

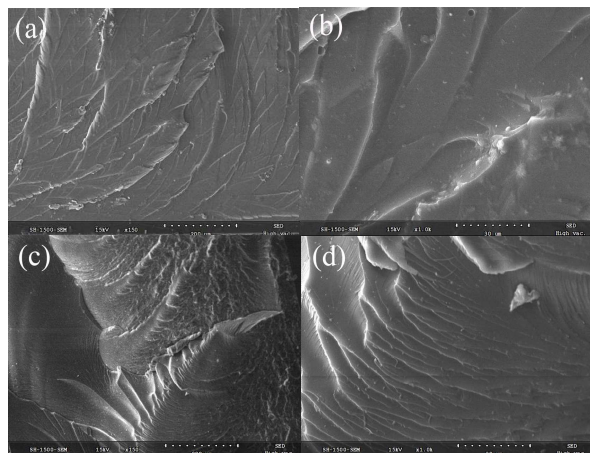


Fig. 9 SEM photographs of the fractured surfaces of the polybenzoxazines. (a) PCBB; (b) PCBB; (c) PCBF; (d) PCBF. The

magnification was $\times 150$ for a and c; and $\times 1000$ for b and d, respectively.

3.5. Mechanical properties of the biobased polybenzoxazines

DMA was performed to study the thermomechanical properties of PCBB and PCBF. As seen in Fig. 10, the storage modulus (E') of PCBB and PCBF at room temperature were 7.25, 2.94 GPa, respectively. The E' value for PCBF started to decrease at about 93°C , whereas for PCBB at about 58°C . Comparing the decreasing slope of the E' value from glassy state to rubbery plateau, it was found that the decreasing slope of PCBF was much lower than that of PCBB. This demonstrated that PCBF had higher mechanic performance than that of PCBB.

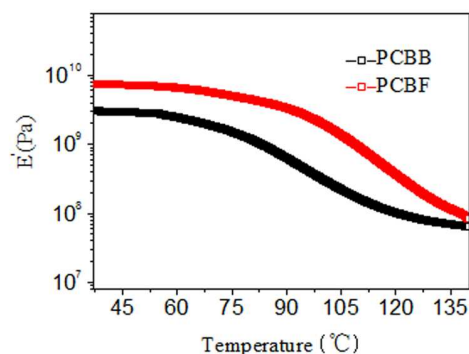


Fig. 10 Storage modulus of the biobased polybenzoxazines.

T_g was determined from the peak maximum of the $\tan\delta$ curve. Fig. 11 shows the $\tan\delta$ curves for the biobased polybenzoxazines. In general, a flexible polybenzoxazine shows a low T_g due to the poor thermal stability. Mele et al. reported that the polybenzoxazine prepared from cardanol, formaldehyde and ammonia exhibited a T_g of 36°C [16]. Patton et al. synthesized a series of aliphatic-bridged bisphenol-based benzoxazines by varying the length of the aliphatic-bridged bisphenol used in the monomer synthesis. They found that the T_g s of the resulting polybenzoxazines were in a range from 66°C to 101°C [30, 31]. Agag et al. reported that T_g s of the polybenzoxazines containing pendent aliphatic chains were in a range from 81°C to 92°C [32]. Interestingly, the result of $\tan\delta$ curves showed that T_g s of PCBB and PCBF were 94°C and 121°C , respectively (Fig.11). This meant that the T_g s of the present cardbisphenol based polybenzoxazines were relatively higher than those flexible cardanol based mono-functional polybenzoxazines, other flexible aliphatic-bridged bisphenol based polybenzoxazines or the flexible polybenzoxazines containing pendent aliphatic chains reported previously [16, 30-32].

In order to better understand the above phenomenon, crosslink density $\rho(E')$ can be estimated from the rubbery plateau storage modulus at $T_g + 40^\circ\text{C}$ according to the theory of rubbery elasticity (equation (2)) as follows [33-36]:

$$\rho(E') = E' / 3\phi RT \quad (2)$$

Where Φ is the front factor, T is the absolute temperature, R is the gas constant, and E' is the storage modulus of the sample at temperature T . It should be noted that the equation (2) typically apply only to lightly crosslinked system. Therefore, the values should be taken as qualitative comparisons. As a result, assuming that Φ was equal to 1, the values of $\rho(E')$ of PCBB and PCBF were calculated as 6.9×10^3 and 8.3×10^3 mol/m³, respectively. This suggested that crosslink density of PCBF was higher than that of PCBB. This high crosslink density may be attributed to the additional reaction of furan ring in CBF as mentioned above. Thus, the motions of polybenzoxazine chain were restricted by the highly crosslink structure [37]. So, PCBF exhibited a relatively high T_g .

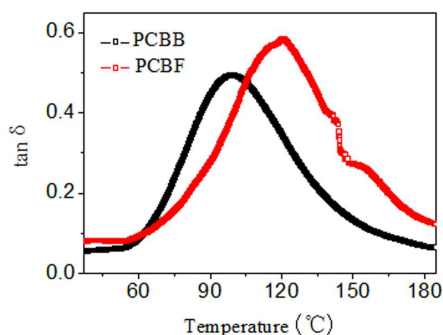


Fig. 11 Tan δ of the biobased polybenzoxazines.

3.5. Humidity adsorption of the biobased polybenzoxazines

The humidity absorption contents of the biobased polybenzoxazines are shown in Fig. 12. As shown in Figs. 12a and b, although the values of HA increased slightly with an increase in time, both PCBB and PCBF exhibited low humidity absorption values at room temperature. For PCBF and PCBB, When RH = 29%, HA < 0.52%, 0.46%, respectively. Whereas when RH = 79%, HA < 0.77%, 0.52%, respectively. The low humidity absorption abilities of PCBB and PCBF were mainly attributed to the introduction of the long hydrophobic aliphatic chain alkyl groups in cardbisphenol. Moreover, PCBF showed lower humidity absorption ability than that of PCBB due to the higher crosslink density.

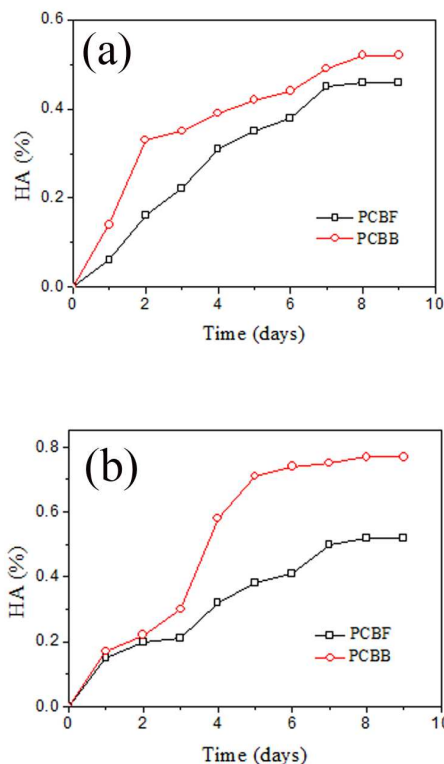


Fig. 12 HA of the biobased polybenzoxazines at room temperature. (a). RH = 29%; (b). RH = 79%.

4. Conclusions

In this paper, two types of biobased benzoxazine monomers (CBB and CBF) with good film-forming abilities have been successfully synthesized from cardbisphenol. The structures of the monomers were supported by FTIR, ¹H NMR and ¹³C NMR spectra. The thin polybenzoxazine films can be obtained easily by ring-opening polymerization of corresponding biobased benzoxazine monomers. SEM of the fractured surface of the obtained biobased polybenzoxazine films indicated a tough fractured surface. Moreover, TGA and DMA showed that the thermal and mechanical properties of PCBF were higher than that of PCBB because that the additional reaction of furan rings in PCBF could increase the crosslink density of the cured sample. The HA values of two polybenzoxazines were very low at high or low relative humidity. This new class of biobased polybenzoxazines has a potential for use in thin films devices, membranes and coatings applications where improved flexibility and thermomechanical properties.

Acknowledgements

The project sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, Hubei provincial Science & Technology Department

RSC Advances

(2013CFB040), Hubei Polytechnic University (13xj01A; 2012101), China.

References

- N. Ghosh, B. Kiskan and Y. Yagci, *Prog. Polym. Sci.*, 2007, **32**, 1344-1391.
- R.S. Kumar, M. Ariraman and M. Alagar, *RSC Adv.*, 2014, **4**, 19127-19136.
- M.Zhang, Z. Tan, H. Ma, J. Qiu and C. Liu, *RSC Adv.*, 2014, **4**, 53505-53513.
- S. Li, W. Huang, X.Liu, X. Yu and W. Xiao, *Polym. Adv. Technol.*, 2010, **21**, 229-234.
- S. Li and M. Tao, *J. Therm. Analysis. Calorim.*, 2013, **113**, 633-639.
- K. Sethuraman and M. Alagar, *RSC Adv.*, 2015, **5**, 9607-9617.
- M. G.Mohamed, C.H. Hsiao, F. Luo, L. Dai and S.W. Kuo, *RSC Adv.*, 2015, **5**, 45201-45212.
- J.Liu, C. Scott, S. Winroth, J. Maia and H. Ishida, *RSC Adv.*, 2015, **5**, 16785-16791.
- S. Rajesh Kumar, J. Dhanasekaran and S. Krishna Mohan, *RSC Adv.*, 2015, **5**, 3709-3719.
- G. Lligadas, A. Tüzün, J.C. Ronda, M. Galià and V. Cádiz, *Polym. Chem.*, 2014, **5**, 6636-6644.
- P. Thirukumaran, A. Shakila and S. Muthusamy, *RSC Adv.*, 2014, **4**, 7959-7966.
- H. Xu, Z Lu and G. Zhang, *RSC Adv.*, 2012, **2**, 2768-2772.
- H. Xu, W. Zhang, Z Lu and G. Zhang, *RSC Adv.*, 2013, **3**, 3677-3682.
- N.K. Sini, J. Bijwe and I.K. Varma, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **43**, 5267-5282.
- A. Van, K. Chiou and H. Ishida, *Polymer*, 2014, **55**, 1443-1451.
- E. Calò, A. Maffezzoli, G. Mele, F. Martina, S.E. Mazzetto, A. Tarzia and C. Stifani, *Green Chem.*, 2007, **9**, 754-759.
- B. Lochab, I. Varma and J. Bijwe, *J. Therm. Anal. Calorim.*, 2010, **102**, 769-774.
- B. Lochab, I. Varma and J. Bijwe, *J. Therm. Anal. Calorim.*, 2012, **107**, 661-668.
- B.S. Rao and A. Palanisamy, *Prog. Org. Coat.*, 2012, **74**, 427-434.
- B.S. Rao and A. Palanisamy, *React. Funct. Polym.*, 2011, **71**, 148-154.
- S. Li, T. Zou, L. Feng, X. Liu and M. Tao, *J. Appl. Polym. Sci.*, 2013, **128**, 4164-4171.
- P. Thirukumaran, P. A.Shakila and M. Sarojadevi, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2790-2801.
- S. Li, S. Yan, J. Yu and B. Yu, *J. Appl. Polym. Sci.*, 2011, **122**, 2843-2848.
- M. Ramasri, G.S. S. Rao, P.S. Sampathkumaran and M.M. Shirsalkar, *J. Appl. Polym. Sci.*, 1990, **39**, 1993-2004.
- M. Ramasri, G.S. S. Rao, P.S. Sampathkumaran and M.M. Shirsalkar, *Ind. J. Chem.*, 1987, **26(B)**, 683-684.
- M. Zhang, Z. Tan, S. Hu, J. Qiu and C. Liu, *RSC Adv.*, 2014, **4**, 44234-44243.
- C. Wang, C. Zhao, J. Sun, S. Huang, X. Liu and T. Endo, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 2016-2023.
- Y.L. Liu and C.I. Chou, *J. Polym. Sci. Part A: Polym. Chem.*, 2005, **43**, 5267-5282.
- I. Hamerton, L.T. Mcnamara, B.J. Howlin, P.A. Smith, P. Cross and S. Ward, *Macromolecules*, 2014, **47**, 1946-1958.
- A.D. Baranek, L.L. Kendrick, C.A. Tretbar and D.L. Patton, *Polymer*, 2013, **54**, 5553-5559.
- A.D. Baranek, L.L. Kendrick, C.A. J. Narayanan, G.E. Tyson, S. Wand and D.L. Patton, *Polym. Chem.*, 2012, **3**, 2892-2900.
- T. Agag, A. Akelah, A. Rehab and S. Mostafa, *Polym. Int.*, 2012, **61**, 124-128.
- P.J. Flory, *Polymer*, 1970, **20**, 1317-1320.
- H. Ishida and D.J. Allen, *Polymer*, 1996, **37**, 4487-4495.
- X. Li, Y. Xia, W. Xu, Q. Ran and Y. Gu, *Polym. Chem.*, 2012, **3**, 1629-1633.
- S.H. Hsiao and H.Y. Chang, *J. Polym. Sci., Part A: Polym. Chem.*, 1996, **34**, 1421-1431.
- H. Ishida and D. J. Allen, *J. Polym. Sci., Part B: Polym. Phys.*, 1996, **34**, 1019-1030.

Graphical Abstract

