Synthesis and Characterization of New Benzoxazine-Based Phenolic Resins from Renewable Resources and the Properties of Their Polymers

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ABSTRACT: Two types of novel benzoxazine-based phenolic resins from phenol-furfural (PFB) and cardanol-furfural (CFB) resins had been synthesized and the highly thermally stable polybenzoxazines were obtained by the thermal cure of the corresponding benzoxazine-based phenolic resins. The chemical structure of benzoxazine-based phenolic resins derived from renewable resources was confirmed by Fourier transform infrared (FTIR), ^{1}H NMR, and gel permeation chromatography (GPC). FTIR spectrum and differential scanning calorimetry (DSC) showed that the monomers were thermally initiated and polymerized via ring-opening polymerization. Thermogravimetric analysis indicated that the incorporation of furan groups could enhance the char yield and thermal stability. However, the long alkyl side chain from cardanol could increase the toughness, while decreasing the char yield and thermal stability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2843–2848, 2011

Key words: benzoxazine; phenol; cardanol; furfural; performance enhancement

INTRODUCTION

In recent years, polybenzoxazines have been drawn much attention for their excellent properties, such as nearly zero shrinkage on curing, minimal moisture absorption, no byproduct release on curing and good thermal stability. Moreover, due to the aromatic polymer backbone and the extensive inter- and intramolecular hydrogen bonding, the physical, mechanical, and thermal properties of polybenzoxazines are excellent which is crucial for future applications in many areas such as spaceflight and aerospace.[1–6] Benzoxazine can be synthesized by using inexpensive and commercially available phenolic compounds, primary amines, and formaldehyde. Therefore, the chemistry of benzoxazine synthesis offers considerable molecular design flexibility. However, the major shortcomings of polybenzoxazines are their brittleness, their need for high curing temperature, and low degree of polymerization.[7–9] Thus, the studies on performance enhancement of polybenzoxazine mainly include copolymer, polymer alloys, fiber reinforced composites, and nanocomposite, etc. Another effective approach is that the polymerizable groups such as ethynyl, phenylethynyl, nitrile, propargyl, and maleimide are incorporated into benzoxazine monomer to improve the properties of the resulting polybenzoxazine.[10–13]

In addition, recent years have witnessed an increasing demand on natural products in industrial applications for environmental issues, waste disposal, and depletion of nonrenewable resources. Renewable resources provide a variety of new structures as thermosetting materials. Thermosetting resins are highly cross-linked polymers that are cured or set using heat, pressure, and light irradiation. This leads to high-performance materials for industry, with high modulus, strength, durability, and resistance toward thermal stress and chemical attacks, provided by their high cross-linking density. In this contribution, emphasis is made on a broad-brush approach of the opportunities and drawbacks in the use of renewable feedstock in the design of networks such as phenolics, unsaturated polyester, and polyurethane resins.[14] Several research groups have reported the synthesis of cardanol-based benzoxazine monomer using cardanol (a well-known renewable organic resource

and harmful by-product of the cashew industry) to replace part of the petroleum-based phenol.[15,16] The structure of the corresponding benzoxazine monomer and polymer was characterized.

In this study, we focus on the performance enhancement of polybenzoxazine by means of incorporation of furan and cardanol groups to benzoxazine-based phenolic resins. Phenolic raw materials used for the synthesis of PFB and CFB is based on agricultural renewable resources of cashew nut shell liquid (CNSL) and furfural. It is well known that furfural is also a renewable source and it is produced from vegetable waste like cane sugar, bagasse, rice hulls, maize cobs, and other such cellulosic waste materials. We expect that the heat stability of polybenzoxazine is enhanced due to the formation of linkages between Mannich bridges and aromatic furan groups during polymerization and the toughness of the cross-linked polybenzoxazine film is improved due to its internal plasticization of the side long alkyl substituent. Hence, we report the synthesis of benzoxazine-based phenolic resin using phenol-furfural (PFB) and cardanol-furfural (CFB) resins, aniline, and paraformaldehyde as raw materials. The characterization, thermal polymerization of PFB and CFB, and the properties of the corresponding polybenzoxazines are also discussed in detail.

EXPERIMENTAL

Materials

Cardanol was purchased from Shanghai Cashew Chemical Polymer (China). Paraformaldehyde (95%), aniline, phenol, toluene, tetrahydrofuran, ethylacetate, acetone, methylethylketone, chloroform, and dichloromethane were purchased from Shanghai First Reagent Company (China). All chemicals were AR grade and as-received.

Measurement

The structure of the cured resin was analyzed using a Fourier transform infrared (FTIR) spectrometer. FTIR spectra was obtained on a PerkinElmer-2 spectrometer (KBr pellet). ^{1}H NMR measurement was carried out on a Bruker spectrometer at 300 MHz, CDCl$_3$ was used as a solvent. Gel permeation chromatography (GPC) measurement was carried out on Waters ALC/GPC 150C instrument with a refractive index (RI) detector. Tetrahydrofuran was used as an eluent, and polystyrene was used as a standard. Differential scanning calorimetry (DSC) was measured with a heating rate of 10°C/min under N$_2$ 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.

Preparation of benzoxazine-based phenolic resins (PFB and CFB) (Fig. 1)

PFB and CFB resins were synthesized according to the method reported by Mishra et al.[17] Then, PFB was synthesized via a simple two-step reaction (Fig. 1). The first step was synthesis of 1, 3, 5-triphenylhexahydro-1, 3,5-triazine. The second step was synthesis of PFB using 1, 3, 5-triphenylhexahydro-1, 3, 5-triazine, formaldehyde, and PFB resin as raw materials through solventless method.[18] Namely, a mixture of as-synthesized PFB resin, 1, 3, 5-triphenylhexahydro-1, 3, 5-triazine, and formaldehyde with a mole ratio 3 : 1 : 3 was placed in a 500 mL flask and 30 mL of toluene was added. The mixture was stirred and heated at 100°C for 2 h. Then the toluene was removed at low pressure and the residual product was dissolved in ethylic ether, and washed three times with 3N NaOH and three times with water. Then, the organic phase was dried with MgSO$_4$ and the ethylic ether was removed at low pressure. The obtained compound was dried under a vacuum, and a fine brown powder obtained (yield 89%). As a result of GPC, M_n of PFB was 1520 and polydispersity index (PDI) was 1.15. CFB was also synthesized using the same method (yield 86%). As a result of GPC, M_n of CFB was 1500 and PDI was 1.20.

Preparation of polybenzoxazines

The polybenzoxazine was prepared according to the following method: about 40% by weight solution of PFB or CFB in butanone was placed over a glass plate. The solvent was evaporated at room temperature for 24 h. The samples were dried at room temperature overnight in vacuum to minimize any trace of solvent. Then the samples were step cured in a closed air-circulating oven for 1 h at 120, 150, 180, 200, 220, and 250°C, respectively. On completion of the curing, the samples (named as PPFB or PCFB) were allowed to freely cool to room temperature. Individual test samples were cut appropriate dimension to be applied for property evaluation.

RESULTS AND DISCUSSION

Preparation and characterization of PFB and CFB

PFB and CFB were prepared using PFB and CFB resins as raw material by a solventless method (Fig. 1). The yield of PFB and CFB were 89 and 86%, respectively. Both of PFB and CFB were brown powder
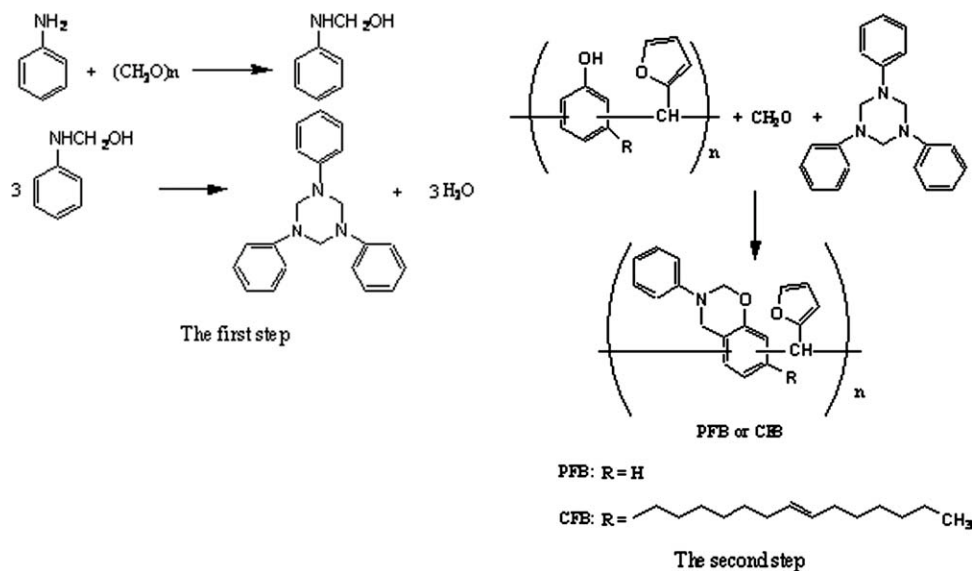
Figure 1 Synthesis of benzoxazine-based phenolic resin (PFB and CFB) a via simple two-step reaction.

and showed a good solvency. The solubility of two types of benzoxazine-based phenolic resin in several organic solvents at 3.0% (w/v) is shown in Table I. From Table I, it can be seen that both of PFB and CFB were soluble in common solvents such as toluene, tetrahydrofuran, ethylacetate, acetone, butanone, chloroform, and dichloromethane, indicating their good processing properties in solution processes.

The chemical structure of the obtained PFB and CFB was further confirmed by FTIR and ^{1}H NMR spectra. As shown in Figure 2, the characteristic absorption band of benzoxazine for both PFB and CFB appeared at 935 cm^{-1}. The bands at around 1229 and 1017 cm^{-1} were assigned to asymmetric stretching of C—O—C and the band at 1328 cm^{-1} was assigned to wagging of CH$_2$. In addition, the bands at around 1465 and 1496 cm^{-1} were assigned

to multisubstituted benzene ring and the furan groups in both of the benzoxazine-based phenolic resins were observed with the absorption peaks at 1571, 972, and 925 cm^{-1}.

As shown in Figure 3, the characteristic protons of oxazine ring appeared at 5.21 and 4.84 ppm. And the absorption peaks at 6.74–7.39 ppm were assigned to the absorption peaks of aromatic protons. Furthermore, the furan ring was characterized with absorption peaks at 5.51–6.28 ppm (—CH=CH—), 7.45 ppm (—O—CH=) for PFB, and 5.71–5.82 ppm (—CH=CH—), 7.27 ppm (—O—CH=) for CFB.[8] Moreover, for CFB, the broad signal at 2.52 ppm could be assigned to the —CH$_2$—Ar— and at 2.0 ppm be assigned to the —CH$_2$=CH— in the long alkyl side-chain. It should be noted that some peaks area in the ^{1}H NMR spectra of CFB maybe not proportioned to their number because that CFB was

TABLE I
The Solubility of PFB and CFB

Solvent	Solubility	
	PFB	CFB
Methanol	±	−
Alcohol	±	−
n-Hexane	±	±
Xylene	+	+
Toluene	+	+
Chloroform	+	+
Dichloromethane	+	+
Acetone	±	+
Tetrahydrofuran	+	+
Dimethyl formamide	+	+
Dimethylsulphoxide	+	+

Note: +Soluble at room temperature; ±Soluble on heating at 70°C; − Insoluble.
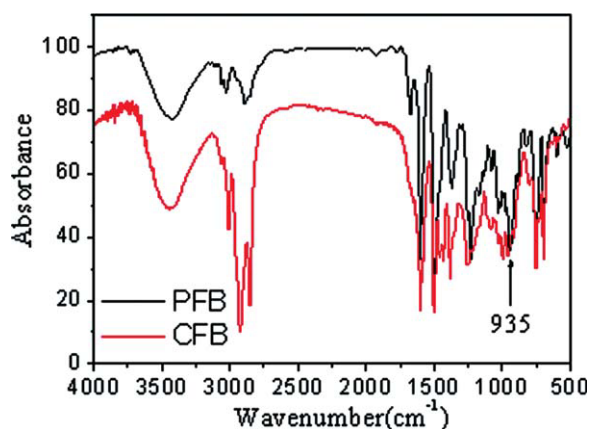
Figure 2 FTIR spectra of PFB (a) and CFB (b) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

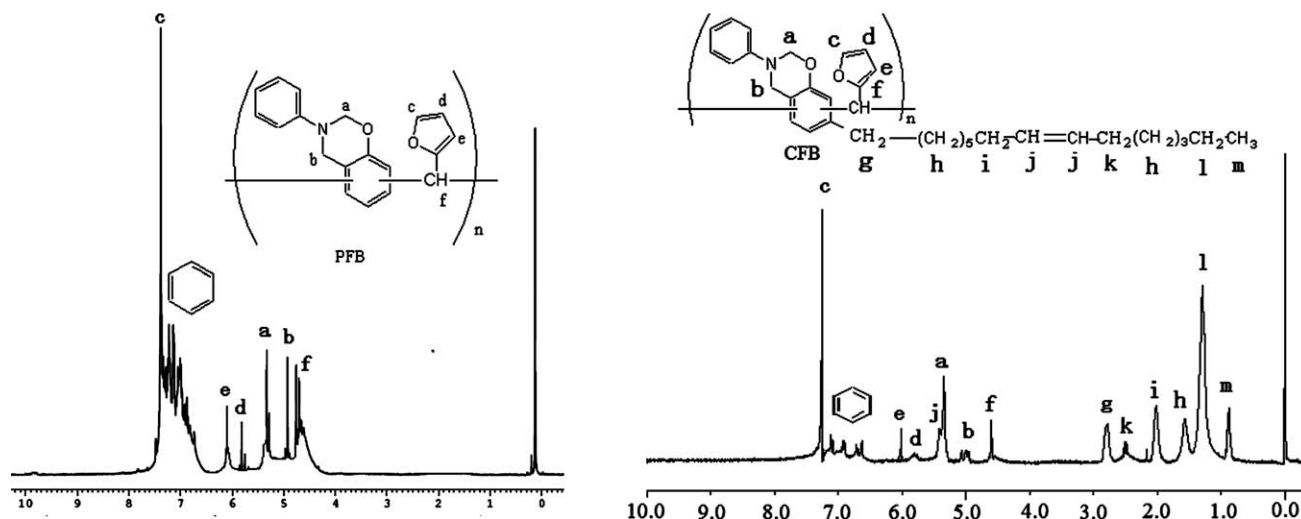**Figure 3** ^{1}H NMR spectra of PFB and CFB.

synthesized based on polymer system (CFB resin). Thus, the peak area in ^{1}H NMR spectra of CFB may be not accurate like benzoxazine monomers synthesized based on small organic molecules. In addition, little impurity may have effect on the results of peak. However, the main characteristic peaks area of "^{1}H" such as a, b, c, d, e, f, g, and j in Figure 3 were proportioned to their number approximately.

Thermally polymerization of PFB and CFB

The curing reactions of PFB and CFB were further confirmed by FTIR analysis. Figures 2 and 4 show the FTIR spectra of PFB and CFB before and after the polymerization, respectively. As a result, the absorption at 935 cm^{-1} assigned to trisubstituted benzene ring attached with benzoxazine ring disappeared. It suggested that the ring opening reaction of benzoxazine have occurred in both PFB and CFB. Moreover, as shown in Figure 4, for CFB, the disappearance of the peak at 1620 cm^{-1} was due to the polymerization of the double bond at high temperature.

The polymerization behaviors of PFB and CFB were studied with DSC at heating rate of 10°C/min under a nitrogen atmosphere from room temperature to 320°C. Figure 5 shows the DSC thermograms of PFB and CFB and the characteristic parameters are listed in Table II. As seen in Figure 5, a sharp endothermic peak centered at 151°C and 49°C may be attributed to the melting points of PFB and CFB, respectively. Then an exothermic behavior observed at high temperature region was associated with the ring-opening polymerization of oxazine rings. The onset polymerization temperatures of PFB and CFB were 198°C and 225°C, respectively. This was comparable with the polymerization temperatures of other benzoxazine compounds. The temperature difference

between melting point and onset polymerization temperature is often defined to the processing window of the benzoxazine resin. For PFB, the processing window temperature was 47°C, while for CFB, was 176°C. The wide processing window of CFB indicated its good property in processing than that of PFB.
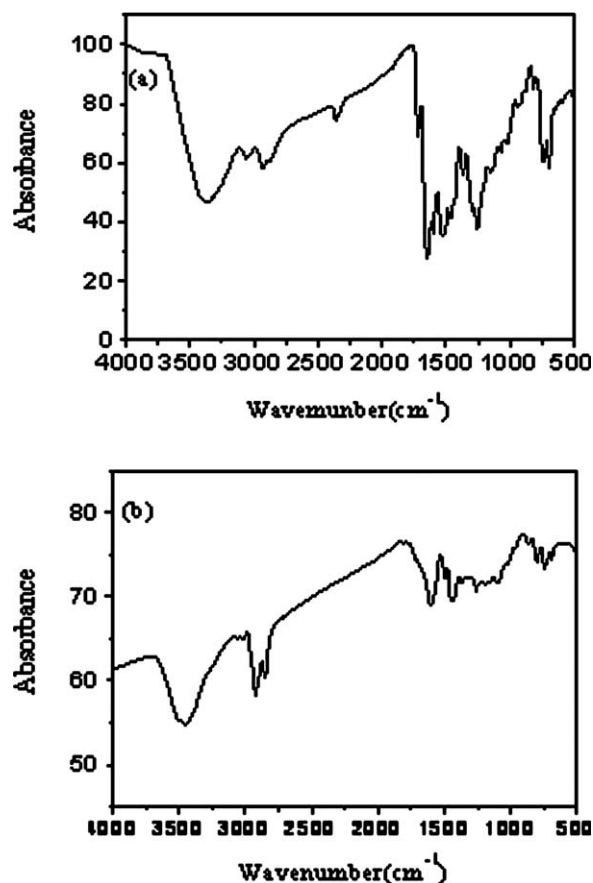

Figure 4 FTIR spectra of PFB (a) and CFB (b) after polymerization at 120°C (1h) + 150°C (1h) +180°C (1h) +200°C (1h) + 220°C + 250°C (1h).
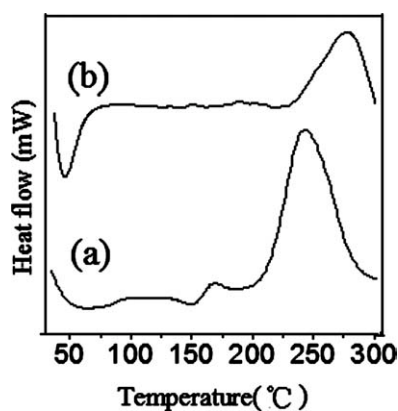
Figure 5 DSC profile of PFB (a) and CFB (b).

As it can be seen in Figure 5, PFB exhibited an exothermic peak centered at 241°C, and a relatively broad peak centered at 275°C was observed for CFB. As mentioned earlier, the polymerization temperatures of both PFB and CFB were 198°C and 225°C, respectively. After initial polymerization, CFB maybe met steric hindrance in polymerization due to the side long alkyl substituent, so as to shift the exothermic peak to a high temperature and broadened the exothermic peak. The reaction enthalpies of polymerizations of PFB and CFB were 92 and 85 J/g, respectively. In previous research, the thermal behavior of benzoxazine-base *p*-cresol was also investigated by Espinosa et al. They found that curing exotherm of benzoxazine-base *p*-cresol with a peak located at 272°C.[5] These results illustrated that the temperature of polymerization reaction of PFB was much lower than that of benzoxazine-base *p*-cresol, which could be attributed to the introduction of furan ring groups into the benzoxazine-based phenolic resin.

Properties of polybenzoxazine from PFB and CFB

TGA was used to evaluate the thermal stability of polybenzoxazine cured from PFB and CFB (PPFB and PCFB). Figure 6 shows the TGA curves for PFB and CFB after curing and the results are summarized in Table III.

From Table III, it can be seen that both of the polybenzoxazines showed fairly good thermal stability. They were approximately stable up to 380°C in air
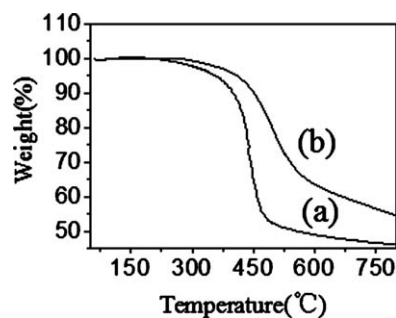

Figure 6 TGA thermograms of polybenzoxazines under nitrogen atmosphere: PCFB (a) and PPFB (b).

or nitrogen. Above 380°C, the degradation occurred and the thermal degradation mainly included amine evaporation, phenol and furan ring decomposition. For PPFB, the 5 and 10% weight loss temperatures (Td5 and Td10) were 432°C and 461°C, whereas for PCFB, Td5 and Td10 increased to 383°C and 415°C, respectively. However, in the same conditions, the 5% weight loss temperatures for polybenzoxazine cured from commercial monofunctional and bifunctional benzoxazine were 342°C and 310°C, respectively.[1] Obviously, the thermal stability of PPFB was superior than those of the typical polybenzoxazine cured from commercial monofunctional and bifunctional benzoxazine. Moreover, the char yields of PPFB and PCFB at 800°C were 52.5% and 46.2%, respectively, which were the same as the results of Td5 and Td10. These results indicated that furan group incorporation had a significant effect on improving the thermal stability and char yield of polybenzoxazines due to the formation of linkages between Mannich bridges and aromatic furan groups during polymerization. Similar results were also previous reported.[8] Furthermore, the thermal stability and char yield of PPFB were higher than that of PCFB. This may be attributed to the fact that there were the side long alkyl moieties in PCFB comparing with PPFB, which decreased the thermal stability of PCFB.

In addition, the obtained polybenzoxazine films from PPFB and PCFB were characterized by a DSC scan (not shown in the Figures). It was found that the glass transition temperature (T_g) of PPFB and PCFB were 250 and 80°C, respectively. In the same conditions, the T_g of PCFB was also much higher

TABLE II
DSC Characteristics of PFB and CFB

Feature temperature (°C)	PFB	CFB
Melting peak	151	49
Start cure temperature	198	225
Peak temperature	241	275
Stop temperature	313	315
Exothermic enthalpy (J/g)	92	85

TABLE III
Thermal Resistance of PPFB and PCFB
Measured by TGA

Resin sample	Temperature at 5 wt % loss (°C)	Temperature at 10 wt% loss (°C)	Char yield (%) (800°C)
PPFB	432	461	52.5
PCFB	383	415	46.2
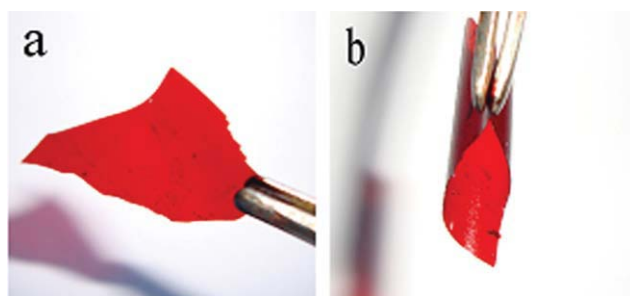
Figure 7 Tin film photographs of PCFB (a) before bending; (b) after bending [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

than that of polybenzoxazine prepared from cardanol, ammonia, and formaldehyde ($T_g = 36°$C).[15] This was accordant with earlier report.[8] Liu and Chou also reported synthesis of benzoxazine containing furan groups to enhance the glass transition temperature and the thermal stability of the corresponding polybenzoxazine. They also pointed out that the densities of furan-containing polybenzoxazine were larger than that of their aniline-based analogues.[8]

As high-performance thermosetting materials, one of major shortcomings of polybenzoxazines is its brittleness. In general, polymers containing furans also have brittle characters because of their high rigidity of molecular chain. Thus, the obtained polybenzoxazine film from PPFB was very difficult to be bent. However, the obtained polybenzoxazine film from PCFB was very flexible and it can be bent easily (see Fig. 7), indicating its excellent toughness. The excellent toughness of PCFB film may be attributed to the induction of soft long side alkyl group in the backbone chain. In addition, in our experiments, we also found that the polybenzoxazine film from PPFB and PCFB showed excellent chemical resistance and none of the polybenzoxazine films were soluble in the solvents such as NMP, DMF, toluene, acetone, ethanol, methanol, etc. Water absorption of the prepared polybenzoxazine film from PCFB is only 0.62%. Low water absorption may be owing to high cross-link density of network of PCFB and the long hydrophobic side alkyl group from cardanol.

CONCLUSIONS

In this work, new benzoxazine-based phenolic resins (PFB and CFB) were synthesized from renewable organic resources and successively polymerized to produce the corresponding polybenzoxazine. PFB and CFB were characterized by FTIR, ^{1}H NMR, DSC, and GPC. DSC indicated that the polymerization temperature of PFB was much lower than that of benzoxazine-base *p*-cresol, which could be attributed to the introduction of furan ring groups into the benzoxazine-based phenolic resin. While CFB met steric hindrance in polymerization due to the side long alkyl substituent, so as to shift the exothermic peak to a high temperature and broadened the exothermic peak. The TGA results demonstrated that the heat stability of polybenzoxazine could be enhanced due to the formation of linkages between Mannich bridges and aromatic furan groups during polymerization. Moreover, the toughness of the cross-linked polybenzoxazine film may be improved due to its internal plasticization of the side long alkyl substituent. Further studies on the degradation mechanism of polymer and the mechanical properties of polybenzoxazine films are in progress.

References

1. Ghosh, N. N.; Kiskan, B.; Yagci, Y. Prog Polym Sci 2007, 32, 1344.
2. Li, S.; Wang, L. J Appl Polym Sci 2006, 99, 1359.
3. Li, S.; Huang, H.; Liu, X.; Yu, X.; Xiao, W. Polym Adv Technol 2010, 21, 229.
4. Wang, C. F.; Chiou, S. F.; Ko, F. H.; Chou, C. T.; Lin, H. C.; Huang, C. F.; Chang, F. C. Macromol Rapid Commun 2006, 27, 333.
5. Espinosa, M. A.; Cádiz, V.; Galià, M. J Appl Polym Sci 2003, 90, 470.
6. Kiskan, B.; Yagci, Y.; Ishida, H. J Polym Sci Part A: Polym Chem 2008, 46, 414.
7. Liu, Y. L.; Chang, C. Y.; Hsu, C. Y.; Tseng, M. C.; Chou, C. J Polym Sci Part A: Polym Chem 2010, 48, 4020.
8. Liu, Y. L.; Yu, J. M.; Chou, C. J Polym Sci Part A: Polym Chem 2005, 43, 5267.
9. Agag, T.; Takeichi, T. J Polym Sci Part A: Polym Chem 2006, 45, 1878.
10. Kiskan, B.; Yagci, Y. Polymer 2008, 49, 2455.
11. Brunovska, Z.; Ishida, H. J Appl Polym Sci 1999, 73, 2937.
12. Agag, T.; Takeichi, T. Macromolecules 2001, 34, 7252.
13. Gacal, B.; Cianga, L.; Agag, T.; Takeichi, T.; Yagci, Y. J Polym Sci Part A: Polym Chem 2007, 45, 2774.
14. Suresh, K. I.; Kishanprasad, V. S. Ind Eng Chem Res 2005, 44, 4504.
15. Calo, E.; Maffezzoli, A.; Mele, G.; Martina, F.; Mazzetto, S. E.; Tarzia, A.; Stifani, C. Green Chem 2007, 9, 754.
16. Lochab, B.; Varma, I. K.; Bijwe, J. J Therm Anal Calorim 2010, 102, 769.
17. Mishra, D. K.; Mishra, B. K.; Lenka, S.; Nayak, P. L. Polym Eng Sci 1996, 36, 1047.
18. Ishida, H.; US Pat 1996, 5,543,516.