

## SYNTHESIS AND CHARACTERIZATION OF MONOFUNCTIONAL BENZOXAZINE FROM CARDANOL

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Received: 30 December 2016; Accepted for publication: 3 March 2017

### ABSTRACT

A novel thermoplastic polybenzoxazine was synthesized based on agrochemical renewable cardanol—a by-product of cashew nut shell liquid (CNSL). A solventless synthesis of monofunctional benzoxazine monomer based on cardanol, aniline and paraformaldehyde was carried out. The liquid benzoxazine monomer was characterized by <sup>1</sup>HNMR and FTIR spectroscopy. Curing characteristics at different temperatures were studied and monitored by differential scanning calorimeter (DSC). The appearance of two exothermic peaks associated with reaction of double bonds of the aliphatic side-chain and ring opening polymerization of benzoxazine. High thermal stability of the polymer sample was confirmed by thermogravimetric analysis (TGA).

*Keywords:* benzoxazine, cardanol, cashew nut shell liquid, ring-opening polymerization.

### 1. INTRODUCTION

Polybenzoxazines (PBzs) appeared as attractive candidates over traditional phenolic polymers due to their superior properties. These include higher thermal stability, char yield, superior modulus properties, low water absorption, near zero volumetric shrinkage, and no release of byproducts during its thermal ring-opening polymerization. Another advantages of this polymer is the versatile molecular design flexibility of its monomer. Generally, benzoxazine can be readily synthesized from a phenolic compound, a primary amine and aldehydes [1, 2].

In recent years, the development of monomers and polymers starting from renewable resources has received significant consideration due to the increasing prices of petro-chemical products associated with growing environmental concerns. Renewable resources, generally known as biomass, refer to any material having recent biological origin, including plant

materials, agricultural crops, and even animal manure. Among these renewable resource materials, cardanol is considered as an important starting material bio-based benzoxazine synthesis purposes due to its unique structural features, abundant availability and low cost. Cardanol is a major constituent of the cashew nut shell liquid (CNSL) which is an agricultural by-product abundantly available in many parts of the world, particularly in ASEAN countries and Vietnam. Cardanol is a monohydroxyl phenol or a phenolic lipid having a long hydrocarbon chain ( $C_{15}H_{31-n}$ ,  $n = 0, 1, 2, 3$ ) at the meta position (Figure 1) [3].

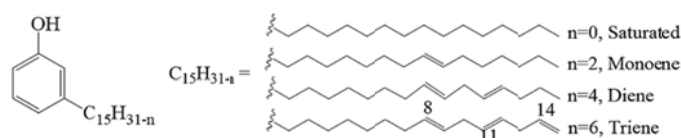


Figure 1. Molecular structure of cardanol.

Compared to conventional phenolic resins, cardanol based polymer may improve the flexibility due to the internal plasticization of the long chain, which provides a better processability. In addition, monofunctional benzoxazine with low viscosity can be further used as reactive diluent or blended with other neat resin for various applications such as structural composites, adhesives, and paints [4, 5].

Even though benzoxazines have been extensively studied in recent years, there has been very little research reported on synthesis and characterization of benzoxazines from Vietnam [6]. Herein, we would like to report a monofunctional benzoxazine prepared from cardanol, aniline and paraformaldehyde by solventless method. The monomer was characterized by <sup>1</sup>HNMR and FTIR spectroscopy. The curing behavior of benzoxazine monomer and thermal stability of the polymer will be described here.

## 2. MATERIALS AND METHODS

### 2.1. Materials

All reagents and solvents were used as received from commercial suppliers. Cardanol was procured from Son Chau Co., Ltd (Viet Nam). Cardanol was distilled at 230–240 °C under 2–4 mmHg. The characteristics of cardanol is given in Table 1. Aniline (99.5 %) and paraformaldehyde (95 %) were purchased from Merck. Chloroform (99 %), sodium hydroxide (97 %) and sodium sulfate (99 %) were obtained from Sigma-Aldrich. All reactions were carried out in oven-dried flask.

Table 1. Characteristics of cardanol used in this study.

Characteristic	Test Method	Values
Water Content (by vol/mass) (%)	ASTM D 95–13e1	0.1
Relative Density at 25 °C (g/cm <sup>3</sup> )	ASTM D 4052–11	0.9363
Kinematic Viscosity at 25 °C (mm <sup>2</sup> /s)	ASTM D 445–12	51.47
Acid Number (mg KOH/g)	ASTM D 664–11a	0.8
Hydroxyl Value (mg KOH/g)	ASTM D 1957–86	184.8
Non-volatile Content (by mass) (%)	ASTM D 1353–13	99.5

## **2.2 Synthesis of cardanol based benzoxazine monomer (C-Bz)**

Cardanol based benzoxazine was synthesized by a method adopted from earlier report [7]. Cardanol (10 g, 0.033 mol) was heated to 50 °C in a 100 mL three-necked round flask equipped with magnetic stirrer and thermometer. Then paraformaldehyde (1.98 g, 0.066 mol) and aniline (3 mL, 0.033 mol) were added drop wise under vacuum environment. The temperature was gradually raised to 80 °C and kept at this temperature for 5 h. The starting of reaction indicated by evolution of water and the color changing. The reaction color changed from yellow to orange or maroon.

The reaction mixture was then cooled at room temperature and dissolved in chloroform. The product was washed three times with 2 N NaOH followed by washing with distilled water in a separating funnel. The organic phase was dried over sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) and filtered to give a red oil. The solvent was removed under reduced pressure and then dried at 60 °C for 12 h under vacuum to obtain the final product which is monomer benzoxazine with a yield of 73 %.

## **2.3 Polymerization of cardanol based benzoxazines**

To prepare samples for thermal characterization, benzoxazine CA—a monomer was dropped on the separate aluminum plates, put in an oven and heated simultaneously at different temperatures (160 °C, 180 °C, 220 °C) for 2 h.

## **2.4 Measurements**

### *2.4.1. Structural characterization*

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Bruker Tensor37 spectrophotometer with a resolution from 4000–400 cm<sup>-1</sup> in the absorbance and transmittance modes. The test was done at Institute of Chemical Technology, Vietnam Academy of Science and Technology (VAST), Ho Chi Minh City.

<sup>1</sup>H (500 MHz) nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance AM500 FT-NMR spectrometer with Fourier transform and CDCl<sub>3</sub> as solvent. The chemical shift is given relative to tetra methyl silane (TMS). The NMR measurements and analysis were performed at Center for Applied Spectroscopy, Institute of Chemistry, Vietnam Academy of Science and Technology (VAST), Hanoi.

High Performance Liquid Chromatography (HPLC) analysis of cardanol was done on Agilent 1200 Series coupled to MS detector, micrOTOF-QII Bruker (Agilent, USA) at Central Laboratory for Analysis, University of Science–VNUHCM. A column (C18, 150 mm × 4 mm, 5 μm) was used and the mobile phase was acetonitrile/water/acetic acid (80:20:1) at a flow rate of 1.80 mL/min. Absorbance was monitored at 280 nm.

### *2.4.2. Thermal characterization*

Differential scanning calorimetric (DSC) studies were carried out on a Mettler Toledo thermal analyzer using N<sub>2</sub> as a purge gas, heated from room temperature to 300 °C at scanning rate of 10 °C/min.

The thermal stability of polymer was studied by thermogravimetric analysis (TGA) using a TGA Q500 instrument. The thermograms were obtained at a temperature rate of 10 °C/min from 25 °C to 800 °C under nitrogen environment.

DSC and TGA measurements were carried out at Central Laboratory for Analysis, University of Science–VNUHCM.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural characterization of cardanol based benzoxazine

Cardanol is a monophenol compound with a C<sub>15</sub> unsaturated side chain at the m-position. Cardanol used in this work is a mixture of monoene (15 %), diene (15 %) and triene (47 %), and unidentified product (the rest, not isolated) as determined by HPLC (Figure 2). The material was used for benzoxazine synthesis without any further purification since we would like to ensure the viability of large scale commercial applications.

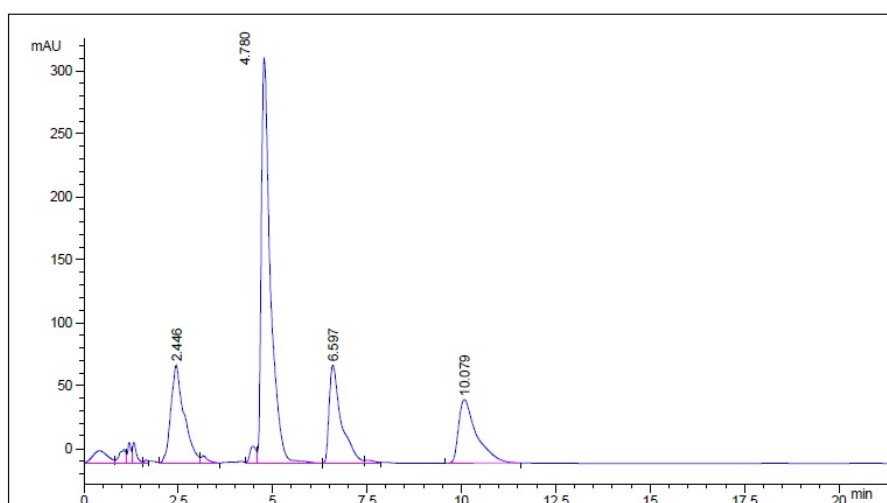


Figure 2. HPLC chromatogram of cardanol (peak at retention time 4.7, 6.5 and 10.7 minutes are due to cardanol triene, diene, and monoene component).

According to Tyman et al. cardanol that has unsaturated triene bonds is easily polymerized, while the unsaturated binding of monoene and diene are more stable [7]. The content of unsaturated triene of the cardanol in this study was 47 % and higher than that of the cardanol used in other works which is always below 39 % [8, 9], indicating that the carbon chains in this cardanol are readily available for polymerization/oligomerization by thermal.

A monomer was obtained under solvent free conditions from cardanol, paraformaldehyde and aniline in molar ratio of 1:2:1 as shown on Figure 3.

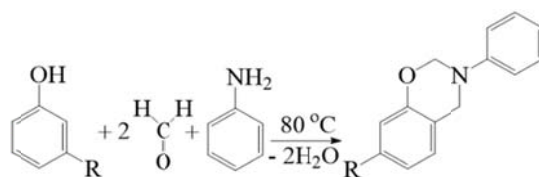


Figure 3. Synthetic scheme of cardanol based benzoxazine (C-Bz).

The structure of the monomer was confirmed by FTIR and  $^1\text{H}$  NMR spectroscopy. FTIR spectra of pure cardanol and C-Bz monomer is displayed in Figure 4. The FTIR spectrum of C-Bz shows significant absorption bands of the benzoxazine due to the asymmetric and symmetric stretching of Ar-O-C group at 1241 and 1031  $\text{cm}^{-1}$ , respectively. The spectrum also shows a band at 1498  $\text{cm}^{-1}$  due to tri-substituted benzene ring. C-H stretching of benzene ring appears at 3008  $\text{cm}^{-1}$  and the bands at 2924 and 2852  $\text{cm}^{-1}$  are attributed to the asymmetric and symmetric stretching of  $\text{CH}_2$  of oxazine ring as well as aliphatic side chain of cardanol. The band due to the phenolic OH of cardanol around 3344  $\text{cm}^{-1}$  is absent, suggesting a complete conversion of the hydroxyl group of cardanol to oxazine ring. Moreover, the absence of the characteristic absorption bands of aniline due to the asymmetric and symmetric NH stretching (3442 and 3360  $\text{cm}^{-1}$ , respectively), NH bending (1619  $\text{cm}^{-1}$ ), and C-N stretching (1281  $\text{cm}^{-1}$ ) confirm the absence of unreacted aniline in the C-Bz monomer [9, 10].

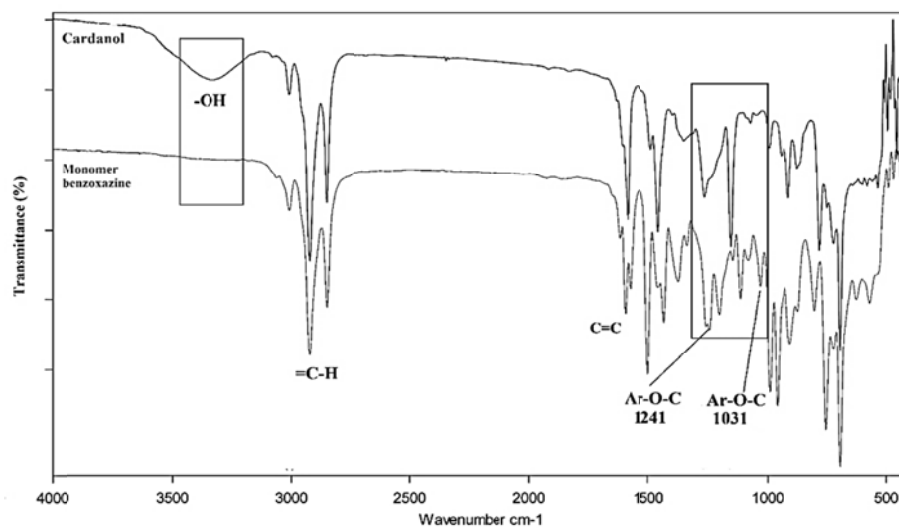


Figure 4. FTIR spectra of cardanol and cardanol based benzoxazine (C-Bz).

The  $^1\text{H}$  NMR spectra gave further support to C-Bz chemical structure (Figure 5). It can be seen that the  $^1\text{H}$  NMR spectrum of the C-Bz presents not only the specific signals of the benzoxazine ring, but also chemical shifts that belong to the aromatic signals and the aliphatic chain of cardanol. The two signals at 4.58 ppm (a) and 5.3 ppm (b) correspond to nitrogen bonded methylene protons ( $\text{Ar-CH}_2\text{-N-}$ , and  $\text{-O-CH}_2\text{-N-}$ ) respectively. The aromatic protons were observed as multiplet in position at 6.63–7.26 ppm. The peaks observed at 0.90, 1.29, 1.55, 2.05 and 2.80 ppm, are attributed to the long alkyl chain of cardanol [2, 9].

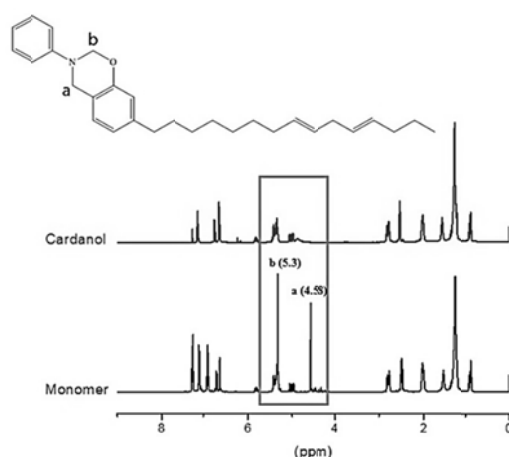


Figure 5.  $^1\text{H}$  NMR spectra of cardanol and cardanol based benzoxazine monomer (C-Bz).

### 3.2. Thermal characterization of cardanol based benzoxazine

Figure 6 displays the DSC thermograms of the C-Bz monomer and its polymer. The exothermic transition observed was characterized by determining onset curing temperature ( $T_o$ ), temperature of exothermic peak ( $T_p$ ) and heat of curing reaction ( $\Delta H$ ) from the area under the curve. The curing characteristics ( $T_o$ ,  $T_p$  and  $\Delta H$ ) of C-Bz monomer and cardanol based benzoxazines after heating at different temperatures are summarized in Table 2.

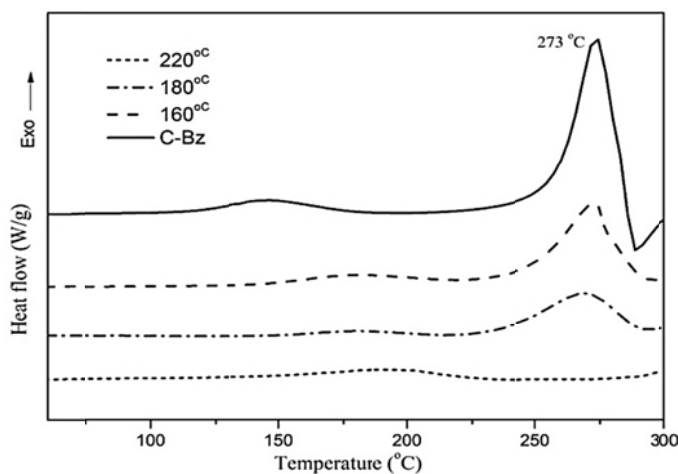


Figure 6. DSC thermograms of cardanol based benzoxazines at different polymerization temperatures.

Table 2. Summary of values of the DSC thermograms of the benzoxazines.

Sample	Peak 1			Peak 2		
	$T_o$ (°C)	$T_p$ (°C)	$\Delta H$ (J.g $^{-1}$ )	$T_o$ (°C)	$T_p$ (°C)	$\Delta H$ (J.g $^{-1}$ )
C-Bz	126.4	145.6	17.6	258.5	273.8	121.2
M160	129.1	179.8	14.3	248.9	273.6	86.1
M180	158.7	180.3	6.4	244.8	266.8	46.7
M220	148.4	193.9	20.8	–	–	–

Typically, the thermogram of C-Bz reveals two exotherm peaks. The lower exotherm peak may be due to the reaction took place through unsaturation of side chain, both from internal double bond (monoene, diene) and vinyl bond (triene). This reaction could lead to the increase in viscosity of the benzoxazine monomer [3]. According to Rodrigues et al. cardanol could be thermal oligomerized at 140 °C and the dimer was the main oligomer formed. The two possible dimerization reactions are presented in Figure 7: (I) obtained from internal double bond loss, taking the monoene as example, and (II) from vinyl loss in triene. It can be seen that decrease in  $\Delta H$  values of this process was not significant because the oligomerization was slow [11]. Interestingly, this phenomenon was not observed from other reports [8, 9].

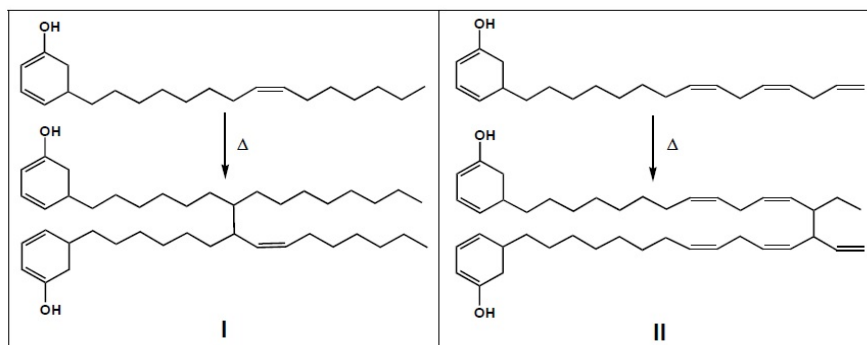


Figure 7. Dimerisation reaction of cardanol from: (I) internal double bond loss (monoene) and (II) vinyl loss in triene.

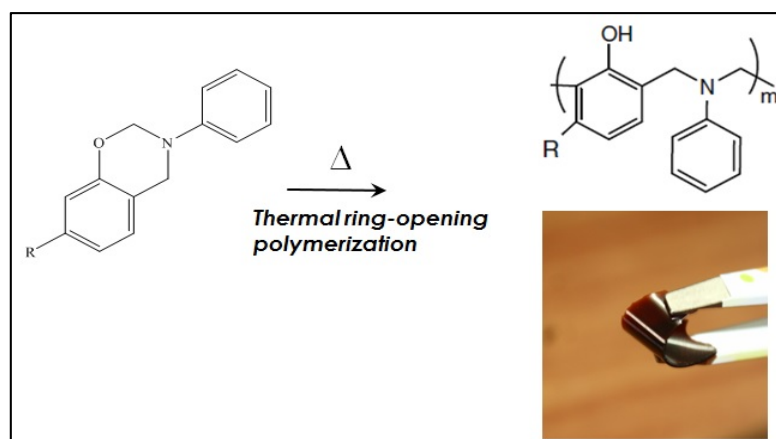


Figure 8. Polymerization of cardanol based benzoxazine.

It is well known that the opening of oxazine ring occurred at very high temperature ( $\geq 200$  °C), thus the peak observed at 273 °C is attributed to the polymerization temperature of the cardanol based benzoxazine. The opening of the oxazine ring at higher temperature indicates a greater stability of the ring, due to increased strength of C–O bond [1, 2]. In this case, cardanol-based benzoxazine exhibits higher curing temperature than traditional benzoxazines because of their unique molecular structure. As expected, a progressive decrease in  $T_o$  and  $T_p$  values with increasing polymerization temperature was found. It was also observed that the polymerization was completed at 220 °C. The increase in  $\Delta H$  value of peak 1 for this sample implies that the

reaction of long alkyl side chain may be competed with the ring-opening polymerization. Figure 8 illustrates the thermal ring-opening polymerization of C-Bz monomer.

Thermal stability of cured benzoxazines (M220) was studied by TGA. A typical TGA and DTG trace is shown in Figure 9. Cardanol based benzoxazines possess relatively good thermal stability. From the TGA curve, there was no weight loss observed below 200 °C which indicates that the cured sample have nearly zero moisture content or low molecular weight compounds. There are four-stage weight loss processes caused by the degradation of molecule structures. The degradation at first stage could be related to the decomposing of phenolic moiety. The main weight loss (72 %) could be attributed to the degradation of the side chain of the cardanol moiety and of the Mannich bridges in the polymer. Finally, the degradation of the aromatic ring occurred at the temperature above 500 °C [12].

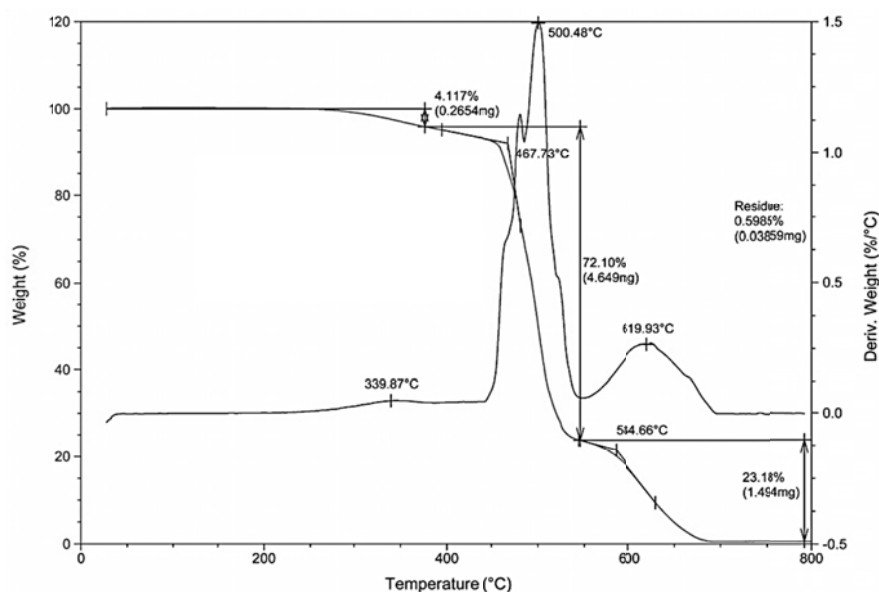


Figure 9. TGA thermograms of cardanol based benzoxazine polymer.

#### 4. CONCLUSIONS

In this paper we described the successful synthesis and characterization of a monofunctional benzoxazine monomer from cardanol, a by-product of cashew industry by a solventless method. The monomer structure were confirmed by the FTIR and <sup>1</sup>H NMR spectroscopy. DSC results indicates that the long alkyl chain substituent at the meta position in C-Bz also involved in the curing process and lead to higher polymerization temperature compared to the conventional benzoxazines. The polymer is flexible and shows a good thermal stability.

**Acknowledgements.** The authors would like to thank AUN/SEED Net for their financial support through Research Grant for Alumni (CRA).



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