

## Constructing polyurethane foams of strong mechanical property and thermostability by two novel environment friendly bio-based polyols

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**Abstract**—Two novel cardanol-based polyols were synthesized and used to construct polyurethane (PU) foams. The cardanol-based polyols with high reactivity were obtained from the epoxidation of cardanol, followed by the ring opening reaction of epoxy group with diethanolamine (DEA). Subsequently, PU foams were synthesized by these cardanol-based polyols. Compared with petroleum-based (PEG) PU foams, these green cardanol-based PU foams exhibit better mechanical property and higher thermostability. Scanning electron microscopy (SEM) tests show that the cells of cardanol-based PU foams are monodisperse, with fairly uniform spherical shape and regular size.

Keywords: Bio-based Polyols, Polyurethane Foam, Cardanol, Mechanical Properties, Thermogravimetric Analysis (TGA)

### INTRODUCTION

Polyurethane (PU) foam is one of the most versatile materials in both industry and daily life, which is consumed above 12 million metric tons every year [1]. It is widely used in building construction, transportation, bedding, packaging and medical device industries because of superior insulation, excellent strength, lightweight, and high weight-carrying capacity [2,3]. However, PU foams have limited degradability when discarded after use, and consequently can be an environmental problem [4]. In addition, the rising environmental concerns and depletion of petroleum resources bring a new challenge to PU foam industries [5]. Huge efforts have been devoted in recent years to develop degradable PU foams from bio-renewable resources such as vegetable oils, lignin, chitosan, biopitch and so on [6-8].

Cashew nut shell liquid (CNSL) is a renewable natural resource obtained as a by-product of cashew nut and cashew apple production [9,10]. Cardanol is a natural alkylphenol obtained by vacuum distillation from CNSL [11-13]. It is a mixture of four *m*-alkylphenols differing by unsaturation degree of aliphatic chain, which contains about 3% saturated chains, 42% monoolefinic, 17% diolefinic, and 38% triolefinic chains (Fig. 1) [14]. Because of this versatile

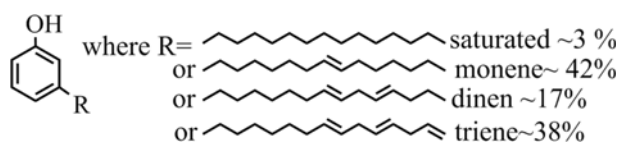


Fig. 1. Structure of cardanol.

chemical structure, cardanol can be used in manufacturing anti-corrosive mortars, synthetic resin, coatings, foundry oil and other bio-based polymers [15-18]. In recent years, researchers have studied the modification of the functional groups of hydroxyl and alkenyl for multifunctional applications. Greco reported the epoxidation of double bonds of alkenyl on the side chain of cardanol acetate and used as a plasticizer [14]. Jaillet studied the epoxy resins from commercial epoxidized cardanol and aromatic reactant, and the yield materials with good thermal and mechanical properties [19]. In most cases, more reactive bio-based polyols with higher hydroxyl values could be obtained through ring-opening reaction of epoxidized bio-resources. Thus, a series of polymers with more excellent properties could be obtained through this approach. However, to the best of our knowledge, the synthesis of cardanol-based polyols *via* ring-opening of epoxidized cardanols has never been reported in previous researches.

In this study, two green bio-based polyols were synthesized from cardanol through ring-opening reaction of epoxidized cardanols and used for the construction of PU foams. The procedure is as follows: First, epoxidized cardanols were obtained from epoxidation of the hydroxyl and double bonds of the side chain of cardanol. Subsequently, the epoxidized cardanols were employed as reactive feedstocks to synthesize the cardanol-based polyols through further ring-opening by diethanolamine (DEA). Then, the phenolic hydroxyl of cardanol was converted to an aliphatic hydroxyl (hydroxypropyl), which exhibits high reactivity with isocyanates [20]. In addition, the tertiary amine group of cardanol-based polyols could also be used as a catalyst for PU foaming reaction [21,22].

PU foams were constructed by using the above cardanol-based polyols. The properties of these foams were systematically investigated. To investigate the industry application of obtained polyols and foams, the most commonly used commercial polyether polyols (PEG) were used as a control. Compared with petroleum-based

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(PEG) PU foams, these green cardanol-based PU foams exhibit better mechanical property and higher thermal stability.

## EXPERIMENTAL

### 1. Materials

Cardanol (average molecular weight is 300 g/mol) was purchased from Zaozhuang Nate Biological Materials Co., Ltd. (Shandong, China). Epichlorohydrin (ECH) was supplied by Nanjing Haolifeng chemical Co., Ltd. (Nanjing, China). Polyarylpolyethylene isocyanate (PAPI) was obtained from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China), and the NCO group content was 30%. AK-8801, a silicone surfactant used to stabilize the foam, was a commercial product from Dymatic Shichuang Chemical Co., Ltd. (Nanjing, China). Benzyltriethylammonium chloride (BTEAC), diethanolamine (DEA), stannous octoate (STO), and other chemicals were of analytical grade and obtained commercially from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

### 2. Synthesis of Epoxidized Cardanols

Cardanol glycidyl ether (CGE) was synthesized by epoxidation of the hydroxyl of cardanol according to a one pot two steps reaction, which is illustrated in Scheme 1. At the first reaction step, 1-chloro-3-(3-alkylphenoxy) propan-2-ol was formed from the reaction between cardanol and ECH under the catalysis of BTEAC. After the addition of NaOH, 1-chloro-3-(3-alkylphenoxy) propan-2-ol reacted with NaOH and formed CGE. During this step, NaCl is the main byproduct and can be removed by washing with hot water. In a typical procedure, 175.0 g (0.67 mol) cardanol, 616.7 g (6.7 mol) ECH and 6.0 g catalyst (BTEAC, 0.03 mol) were added to a 2,000 mL four-necked glass flask equipped with a mechanical stirrer, a spherical condenser and a thermometer. The mixture was stirred for 4 h at 100 °C and then cooled to 70 °C. 28.0 g (0.70 mol) granular NaOH was added for 10 times in 2 h and reacted for another 4 h in 70 °C. When the reaction was completed, the crude product was washed with hot water several times to remove the

byproduct (NaCl) and then the organic phase was distilled under vacuum to recycle the ECH. CGE was obtained as reddish brown viscous liquid. IR,  $\nu$  (cm<sup>-1</sup>): 3013, =C-H; 2921-2856, -CH<sub>3</sub>, -CH<sub>2</sub>-; 1585-1449, -C=C-; 1261, Ar-O; 1169, -C-O-C; 908, characteristic absorption peak of epoxy unit. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 6.76-7.25 (Ar-H), 5.01-5.14, 5.31-5.45, 5.70-5.90 (=C-H), 3.92-4.25 (Ar-O-C-H), 3.35-3.41, 2.02-2.15 (C-H from the epoxy unit). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 153.1, 139.0, 131.3, 124.9, 123.9, 122.3, 121.4, 116.2, 109.6, 106.1, 63.5, 44.7, 30.7.

Polyepoxide cardanol glycidyl ether (PCGE) was synthesized through further epoxidation of double bonds on the side chain of CGE [23-25]. In a typical procedure, 100 g CGE (0.28 mol), 20.0 g glacial acetic acid (0.28 mol) and 0.29 g H<sub>2</sub>SO<sub>4</sub> (0.003 mol) were mixed together in a four neck round bottom flask equipped with a mechanical stirrer, thermometer sensor and reflux condenser. Then, the mixture was heated to 60 °C under continuous stirring and 75.0 g (0.66 mol) of 30% H<sub>2</sub>O<sub>2</sub> was added dropwise from a pressure-equalizing funnel. When the reaction was completed, the crude product was washed with saturated sodium bicarbonate several times. Distilled water was then used to wash the product again. The remains of water were distilled under vacuum and PCGE was obtained. IR,  $\nu$  (cm<sup>-1</sup>): 3013, =C-H; 2926-2845, -CH<sub>3</sub>, -CH<sub>2</sub>-; 1585-1449, -C=C-; 1262, Ar-O; 1150, 1049, -C-O-C; 908, characteristic absorption peak of epoxy unit. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 6.62-7.22 (Ar-H), 5.73-5.94, 4.95-5.57 (=C-H), 4.02-4.25 (Ar-O-C-H), 2.80-3.05, 2.51-2.65 (C-H from the epoxy unit). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 158.3, 144.2, 129.1.3, 127.5, 120.9, 114.5, 110.7, 68.3, 56.9, 55.9, 55.3, 49.7, 44.3, 35.5.

### 3. Synthesis of Cardanol-based Polyols

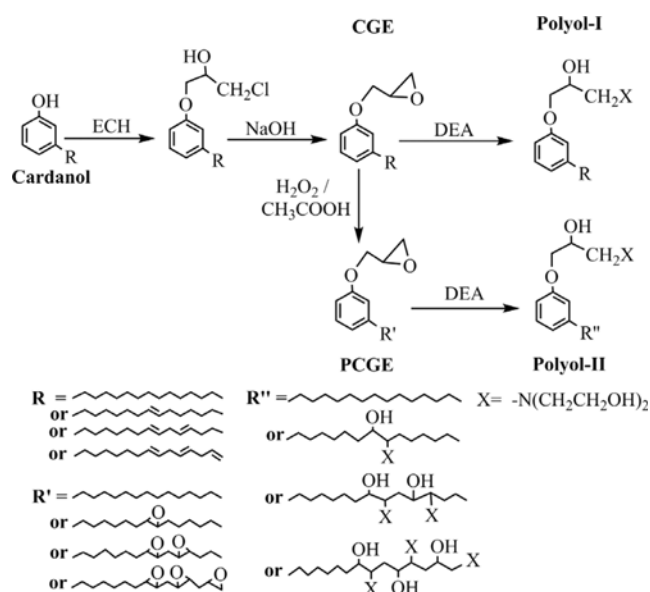
Cardanol-based polyols, which are named to be Polyol-I and Polyol-II, were derived from CGE and PCGE, respectively. Typically, epoxidized cardanol and DEA were mixed with a molar ratio of 1.2 to 1 in a flask. The reaction was carried out for 4 h at 90 °C to form a product with epoxy value less than 0.01 mol/100 g. Then, the reaction mixture was washed with hot water to remove the excess DEA. After the removal of remaining water by vacuum distillation, the final products were obtained (See Scheme 1).

Polyol-I, IR,  $\nu$  (cm<sup>-1</sup>): 3360, O-H; 3018, =C-H; 2925-2858, -CH<sub>3</sub>, -CH<sub>2</sub>-; 1585-1449, -C=C-; 1259, Ar-O; 1152, 1031, -C-O-C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 5.78-5.89 (Ar-H), 5.31-5.45, 4.98-5.09 (=C-H), 5.37 (-O-H from secondary hydroxyl), 4.15 (Ar-O-C-H), 3.92-4.01 (-O-H from primary hydroxyl), 3.74-3.80 (-C-H from tertiary carbon), 2.48-2.60 (N-C-H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 157.7, 143.6, 135.8, 129.3, 128.8, 128.3, 126.6, 120.2, 113.7, 110.5, 68.9, 66.5, 58.5, 56.5.

Polyol-II, IR,  $\nu$  (cm<sup>-1</sup>): 3366, O-H; 3018, =C-H; 2918-2858, -CH<sub>3</sub>, -CH<sub>2</sub>-; 1585-1449, -C=C-; 1259, Ar-O; 1152, 1031, -C-O-C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 6.68-7.16 (Ar-H), 4.95-5.23, 5.49-5.91 (=C-H), 5.33 (-O-H from secondary hydroxyl), 4.05-4.18 (Ar-O-C-H), 3.83-4.00 (-O-H from primary hydroxyl), 3.52-3.83 (HO-C-H), 2.56-2.79 (N-C-H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 158.4, 144.3, 128.8, 120.8, 114.6, 110.9, 69.5, 66.9, 58.8, 58.3, 57.1, 55.9, 55.4, 35.8.

### 4. Synthesis of Cardanol-based PU Foams

The foam formulations used to synthesize cardanol-based PU foams and the control foam are shown in Table 1. The polyols, cata-



Scheme 1. The preparation of cardanol-based polyols.

**Table 1. Formulations for prepared PU foam**

Samples	Polyols		Catalysts (pph)	Surfactant (pph)	Blowing agent (pph)	PAPI	
	Components						(pph)
PEG-foam	*Blends of PEG and glycerol (OH value, 405.3 mg/g)		100	0.5	2.5	1	Index×1.05
Foam-I	Polyol-I (OH value, 362.10 mg/g)		100	0.5	2.5	1	Index×1.05
Foam-II	Polyol-II (OH value, 553.20 mg/g)		100	0.5	2.5	1	Index×1.05

Note: pph=Parts per hundred parts of polyol by mass. The PEG (Mn=600 g/mol) and glycerol were mixed in weight ratio of 1 : 1

lysts (STO), surfactant (AK-8801), and blowing agent (distilled water) were added into a 250 mL circular plastic cup and premixed thoroughly at ambient temperature. Then PAPI was added quickly into the mixture and mixed with a high speed mixer (3,000 rpm) for 10 s. The mixture was poured immediately into a cubic paper container (100×100×100 mm<sup>3</sup>) and allowed to rise freely at room temperature. After one week, the properties of the foams were measured. For simplicity, cardanol-based PU foams produced from Polyol-I and Polyol-II were designated as Foam-I and Foam-II, respectively. The reference foam was synthesized from polyols mixture consisting of the polyethylene glycol (PEG, Mn=600 g/mol) and glycerol with the weight ratio of 1 : 1.5.

## 5. Characterization

### 5-1. Characterization of Cardanol-based Polyols

The epoxy group content (the mol amount of epoxy groups contained in 100 g resin) of epoxidized cardanols was determined in accordance with GB/T 12008.7-2010. The hydroxyl value and acid value of cardanol and cardanol-based polyols were determined according to the Chinese national standards (GB/T 12008.3-89 and GB12008.5-89). Their viscosities were determined in accordance with GB/T 12008.7-2010.

### 5-2. Fourier Transform Infrared Spectroscopy

FTIR spectra were obtained from a Nicolet IS10 spectrometer (Nicolet, USA) using ATR attenuated total reflectance (ATR) mode. All spectra were obtained at a resolution of 2 cm<sup>-1</sup> and a number of 32 scans.

### 5-3. NMR Spectroscopic Analysis

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a NMR spectrometer (Bruker, Germany, 300 MHz), using tetramethylsilane as an internal and deuterated chloroform (CDCl<sub>3</sub>) as solvent.

### 5-4. Mechanical Tests

The compressive strength of the prepared PU foams was tested according to related China national standard (GB/T 8813-2008). Foams were cut with a bench saw into cubes of 50 mm<sup>3</sup>. The compressive strength was measured by Electronic Universal Testing Machine (XJZ-50, Shenzhen, China). The impact testing was carried out on a simply supported impact machine tester (XJY-5, Chengde, China). Foams were cut into specimen size of 120 mm<sup>3</sup>×15 mm<sup>3</sup>×10 mm<sup>3</sup> according to related China national standards (GB/T 1043-1993). The tensile testing was carried out according to related China national standard (GB/T 9464-1988) using an Electronic Universal Testing Machine (XJZ-50, Shenzhen, China). Mechanical properties reported in our paper are an average of five samples per foam.

### 5-5. Scanning Electron Microscopy

The morphology of cell structure was observed using a scanning electron microscope (SEM, S-3400N, Hitachi Company, Japan)

**Table 2. General properties of cardanol-based polyols**

Components	Viscosity at 25 °C (mPa·s)	Hydroxyl value (mg/g)	Acid value (mg/g)	Water content (%)
Cardanol	30	200.80	3.00	0.47
Polyol-I	4795	362.10	0.06	0.13
Polyol-II	5879	553.20	0.05	0.21

operating at 15 kV. Foam was cut perpendicular to the foam rise direction with a razor blade and cut into rectangular slices (10 mm<sup>3</sup>×10 mm<sup>3</sup>×2 mm<sup>3</sup>) [26]. The fractured surface was coated with gold before observation and subsequently mounted on a custom-built SEM holder.

### 5-6. Thermogravimetric Analysis

Thermal stability was studied by using a thermogravimetric analyzer (TGA409PC, Netzsch Company, Germany). A sample weighing about 3-5 mg was heated from 35 °C to 800 °C under nitrogen at 20 °C·min<sup>-1</sup>.

## RESULT AND DISCUSSION

### 1. General Properties of Cardanol-based Polyols

Table 2 shows the comparison of the main physical parameters of cardanol and synthesized cardanol-based polyols (Polyol-I and Polyol-II). According to Table 2, the acid value and the water content of Polyol-I and Polyol-II are similar to those of cardanol. The viscosities of the obtained cardanol-based polyols are higher than that of cardanol, but note that cardanol-based polyols are still suitable to make rigid foams because their viscosity was lower than 6,000 mPa·s, which is a commonly accepted upper limit used in the PU industry [27]. Also from Table 2, the hydroxyl value of cardanol is only 200.80 mg·g<sup>-1</sup>, which is lower than the hydroxyl value requirement (300-600 mg·g<sup>-1</sup>) for PU foaming preparation [28]. In addition, the phenolic hydroxyl of cardanol has low reactivity to isocyanate [20], so cardanol is not suitable for direct preparation of PU foams. Through our synthesis method, the phenolic hydroxyl of cardanol was converted to an aliphatic hydroxyl (hydroxy-propyl), which is of good reactivity with isocyanates. The hydroxyl values of cardanol-based polyols increased to 362.10 mg·g<sup>-1</sup> and 553.20 mg·g<sup>-1</sup>, indicating that the obtained cardanol-based polyols are well suitable for the preparation of PU foams.

### 2. FTIR Spectroscopic Analysis

During the foaming process, we used FTIR to determine the change of groups in this reaction system, and the results are shown in Fig.

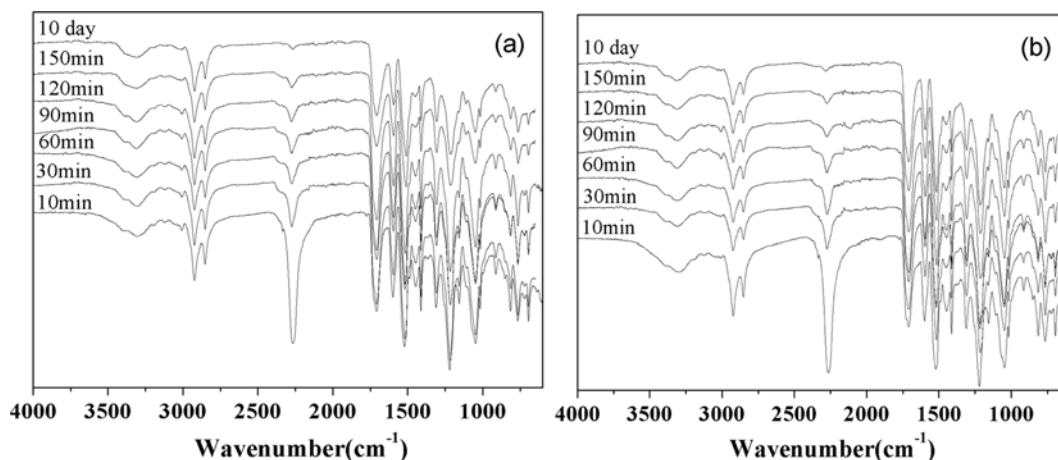


Fig. 2. FTIR spectra for cardanol-based PU foams at different reaction times; Foam-I (a), Foam-II (b).

2. From Fig. 2, the absorption bands changed considerably during the polymerization of cardanol-based polyols, indicating that the complex foaming process involves the generation and disappearance of chemical groups [29]. The band assigned at  $2,270\text{ cm}^{-1}$  is attributed to the stretching vibration of isocyanate group [30]. This absorption band decays rapidly with reaction time and nearly disappears after 10 days, which implies that the isocyanate groups of PAPI have totally reacted with water and the hydroxyl groups of cardanol-based polyols. The broad absorption band between  $3,100\text{ cm}^{-1}$  and  $3,600\text{ cm}^{-1}$  decreases to a constant value as the reaction proceeds [31]. The broad band contains overlapping absorption of hydroxyl groups and the N-H bonds of urethane groups. The cluster assigned at  $2,870\text{ cm}^{-1}$  corresponds to the stretching region of C-H bond [32]. The absorption peaks from  $1,600\text{ cm}^{-1}$  to  $1,800\text{ cm}^{-1}$  correspond to the stretching vibration of carbonyl group. Moreover, a relative increase of peak intensity is observed with the procedure of the polymerization reaction. Initial peak intensity is attributed to the original carbonyl group of PAPI. During the course of polymerization, other types of carbonyl groups appear, which corresponds to the formation of the urethane group [33]. The peak at  $1,600\text{ cm}^{-1}$  corresponds to vibration absorption of aromatic ring [34]. The bands at  $1,530$ ,  $1,220$ , and  $1,213\text{ cm}^{-1}$  can be attributed to N-H, C-N, and C-O of urethane linkages [35].

### 3. Mechanical Property of Cardanol-based PU Foams

Fig. 3 shows that the mechanical performance of cardanol-based PU foams is better than that of PEG-based foam, for several reasons: (1) the benzene ring on cardanol, cardanol-based PU foams exhibits stronger mechanical properties than PEG-based foam [36]. (2) The  $C_{15}$  side chain on cardanol can also play a crucial role in the good mechanical properties of cardanol-based PU foams. Without aliphatic side chain, the generated foam will be too rigid to be potentially applied to substitute PEG in industry [37]. Fig. 3 also

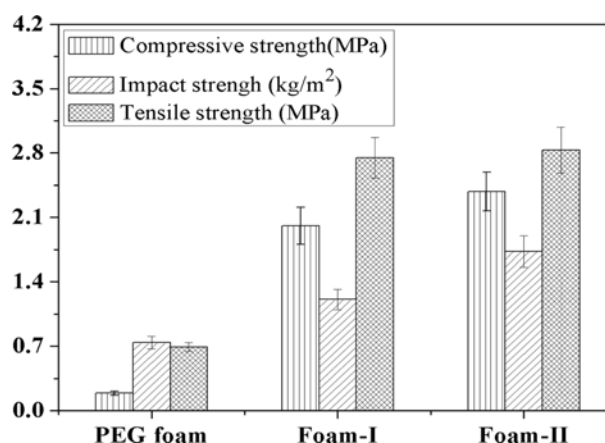


Fig. 3. Mechanical performances of PEG-based and cardanol-based PU foams.

shows that the compressive strength of the Foam-II is better than the Foam-I, which may be due to the higher cross-linking density of Foam-II [37]. To confirm the above hypothesis, the crosslinking density of foams was further calculated according to the method reported by Lan and coworkers [38], listed in Table 3. Table 3 shows that Foam-I has greater equilibrium swelling than Foam-II, which allows for the qualitative conclusion that the crosslink density is likely to be less in the former than in the latter, given that the overall composition of the two foams is nearly identical. From the formulations shown in Table 1, the Foam-II system contains a slightly higher concentration of reactive groups than the Foam-I system, which makes the crosslink density of the Foam-II greater than that of the Foam-I. The above results further demonstrate that the molecular structure and reactivity of polyols have important effects on the properties of PU foams.

Table 3. The results of equilibrium solvent uptake experiment

Samples	Original mass (g)	Swollen mass (g)	Final dry mass (kg/m <sup>2</sup> )	Volume fraction of polymer in swollen network ( $\phi$ )	Swelling (%)
Foam-I	0.078	0.126	0.073	0.543	67.95
Foam-II	0.080	0.127	0.076	0.575	63.75

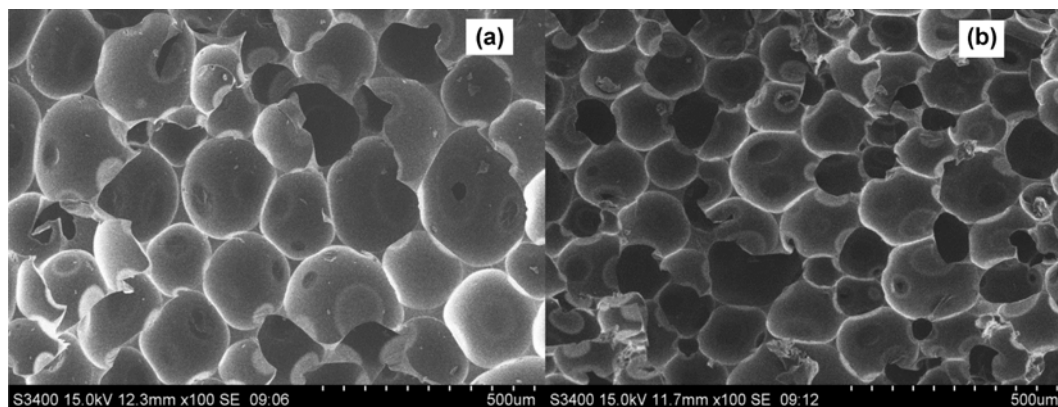


Fig. 4. SEM images of cardanol-based PU foams; Foam-I (a), Foam-II (b).

#### 4. Morphological Structures of Cardanol-based PU Foams

For further insight into the structure of cardanol-based PU foams, the microstructure of the fracture surfaces for rigid PU foams was characterized. As shown in the SEM image (Fig. 4), the cell of cardanol-based PU foams is of fairly uniform spherical shape, and the cell size is regular. Moreover, the cell size of Foam-II is smaller than Foam-I, which can be attributed to the crosslinking speed of polyols and isocyanate in the initial foaming stage. Although they have similar functional groups, Polyol-II has more OH groups. As a result, the viscosity increase of Polyol II is faster and the average cell size is smaller [39].

#### 5. Thermogravimetric Analysis

To probe the thermal stability of the obtained foams, TG and its derivative thermogram (DTG) curves of the samples under  $N_2$  atmosphere were obtained. As demonstrated in Fig. 5, the DTG curves indicate three stages of thermal decomposition of PEG-based PU

foam. Meanwhile, cardanol-based PU foams have only two states of thermal decomposition. It is widely accepted that the thermal stability of PU foams depends mainly on the equilibrium between polymerization and de-polymerization of functional groups or linkages presented in the polymer chains. Equilibrium is a complex process consisting of many physical and chemical phenomena [36, 40,41]. The weight loss degradation of cardanol-based PU foams between 275 °C and 320 °C can be attributed to the decomposition of labile urethane groups [42]. Meanwhile, the degradation observed from 320 °C to 575 °C results from chain scission of isocyanurate and cardanol [40,43-45].

The temperatures at 5%, 10% and 50% of foams weight loss and the residue content at 650 °C are summarized in Table 4. The results show that cardanol-based PU foams have higher decomposition temperatures at 5%, 10% and 50% weight loss than PEG-based PU foams, which implies that cardanol-based PU foams have better

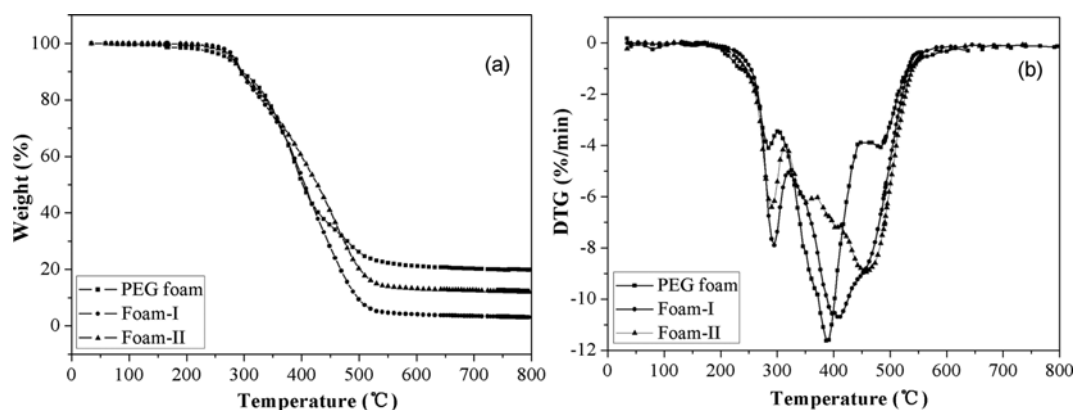


Fig. 5. TG and DTG curves of cardanol-based PU foams in  $N_2$  atmosphere.

Table 4. Thermal characters of PEG-based and cardanol-based PU foams

Samples	Degradation temperatures (°C)			Residual weight at 650 °C	DTG peak temperatures (°C)	
	$T_{5\%}$	$T_{10\%}$	$T_{50\%}$		$T_{1max}$	$T_{2max}$
PEG-foam	265.6	269.1	396.9	20.6	283.8	389.1
Foam-I	283.9	295.5	404.8	3.7	295.6	409.0
Foam-II	278.8	293.6	427.7	12.9	291.0	456.0

thermal stability. Additionally, the data in Table 4 also indicate that the decomposition temperatures at 5%, 10% for Foam-I are very similar to that of Foam-II. However, the decomposition of Foam-I occurs at 404 °C with 50% weight loss, which is lower than that of Foam-II. The residues of Foam-I and Foam-II at 650 °C are 14% and 49%, respectively. The above results imply that Foam-II has higher decomposition temperature, which may be attributed to the higher crosslinking matrix of Foam-II, as well as the higher hydroxyl value of Polyol-II.

## CONCLUSIONS

Green cardanol-based polyols were successfully synthesized and used for constructing bio-based PU foams. The properties between cardanol-based PU foams and PEG-based PU foam were compared. The results show that cardanol-based PU foams have stronger mechanical properties because of the unique structure and higher reactivity of cardanol-based polyols. SEM images show that the cell of cardanol-based PU foams is of fairly uniform spherical shape with regular cell size. Due to the combination of the hard aromatic structure and long flexible alkyl chain of cardanol, cardanol-based PU foams exhibit excellent thermal stability. The current research extends the synthetic strategy and methodic versatility for further development of cardanol-based polyols and foams. These materials will have bright application prospects in PU industry.

## ASSOCIATED CONTENT

**Supporting Information** The NMR data of CGE, PCGE and cardanol-based polyols.

## ACKNOWLEDGEMENTS

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## SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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