



# Effect of structure on the properties of polyurethanes based on aromatic cardanol-based polyols prepared by thiol-ene coupling



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## ABSTRACT

Industrial-grade cardanol and 2-mercaptoethanol were reacted to generate hydroxyl-functionalized cardanol by UV, free-radical-initiated thiol-ene coupling between the double bond moieties of the cardanol long carbon side chain and thiol functional groups. The average hydroxyl number of the hydroxyl-functionalized cardanol was controlled by reaction time, with the hydroxyl values of this ranging within 168–201 mg KOH g<sup>-1</sup>. This cardanol was then used as a polyol to prepare cardanol-based polyurethane with hexamethylene diisocyanate and a NCO/OH ratio of 1. To compare the effect of cardanol-based polyols with the properties of cardanol-based polyurethane, cardanol modified with 10-undecylenate was used as a raw material to prepare cardanol-based polyols, including the long carbon chain of 10-undecylenate. All properties were examined, and data revealed that cardanol-based polyols including this long carbon chain can improve the hydrophobic and mechanic properties of the cardanol-based polyurethane.

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## 1. Introduction

Polyurethanes (PU) represent an important class of polymeric material. It has versatile properties and is suitable for foams, thermoplastic elastomers, adhesives, coatings, sealants, and fibers [1]. Conventional PU is prepared from the addition reaction between polyols and isocyanates. Most PUs are derived from petroleum resources. However, excessively using fossil resources is rapidly depleting it and causing increasingly prominent environmental issues. Therefore, using renewable monomers and PUs to replace traditional petrochemical-based monomers and PUs have attracted significant attention [2–6]. Vegetable oils are one of the cheapest and most abundant biological resources; they are a bio-renewable material that has many advantages such as low toxicity, inherent biodegradability, and high purity [7]. Vegetable oils are already widely used as raw materials for manufacturing PUs [8,9]. Although new vegetable oil-based PUs could replace or partially replace PUs produced from petroleum-derivatives in current markets, some properties such as lower toughness caused by the triglyceride

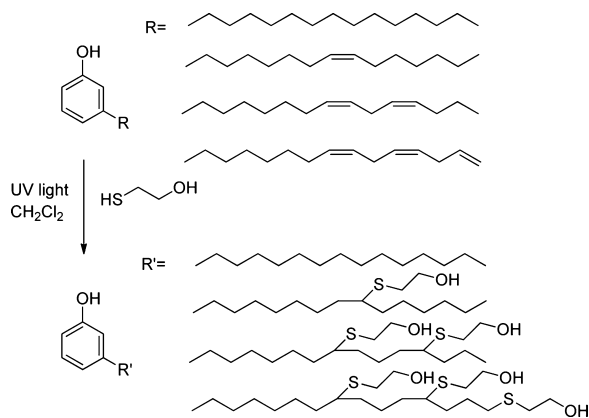
structure of the vegetable oil remain limited. Cardanol is an important renewable resource and a unique phenolic compound that carries a 15-carbon side chain in a Meta position with varying degrees of unsaturation; generally, cardanol-based polymer has wonderful hardness because of the rigid construction of benzene [10,11].

Cardanol extracted from cashew nut shell liquid is an agricultural byproduct of the cashew processing industry. Through the reactive functional group of the benzene ring, phenolic hydroxyl group, and unsaturated alkyl long-chain, cardanol has been modified as monomers and polymers and have been widely used in many applications [12,13], such as phenolic resins [14], epoxy resins [15], vinyl ester polymers [16], phenalkamine curing agents [17], benzoxazine resins [18], surfactants [19], PU foam [20], and PUs [21–26]. Cardanol is mainly modified as cardanol-based polyols to prepare bio-based PUs with isocyanates; and the phenolic hydroxyl group is the most commonly used modification site [18–26]. The coupling of benzene ring only prepares types of cardanol-based polyols [26]. All those cardanol-based polyols carry a 15-carbon side chain in a meta position as a hanging chain, which may affect some properties of polymers such as thermal and mechanical properties. Cardanol-based polyols were prepared by modifying the unsaturation sites on the 15-carbon side chain with a two-step procedure reported by Suresh of epoxidation, followed by hydrolysis [20]. Thiol-ene reaction proceeds between unsaturation with hydroxyl-functionalized thiols, which is a key step to synthesizing

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Scheme 1. CAP synthesis.

primary hydroxyl groups into vegetable oils and fatty acid chains for PU [27,28]. The side chain unsaturation of cardanol can also conduct thiol-ene coupling with hydroxyl-functionalized thiol to prepare cardanol-based polyols. However, cardanol-based polyols synthesized through thiol-ene coupling have not been applied in polyurethane. In fact, thiol-ene chemistry has been used for over 100 years and it proceeds via a free radical chain mechanism. Thiol-ene coupling is a green, practical, and atom-efficient methodology; it provides a new opportunity to modify vegetable oils and fatty acid derivatives and prepare functional monomers and polymers [28–30].

In the present work, the thiol-ene coupling of cardanol is reported in detail as a means to synthesizing aromatic polyols suitable for manufacturing PU. The synthesized polyols were evaluated in terms of their preparation of cardanol-based PU. The mechanical properties, thermal properties, etc. were measured, and the structure–activity relationship for cardanol-based polyols and PU was also discussed.

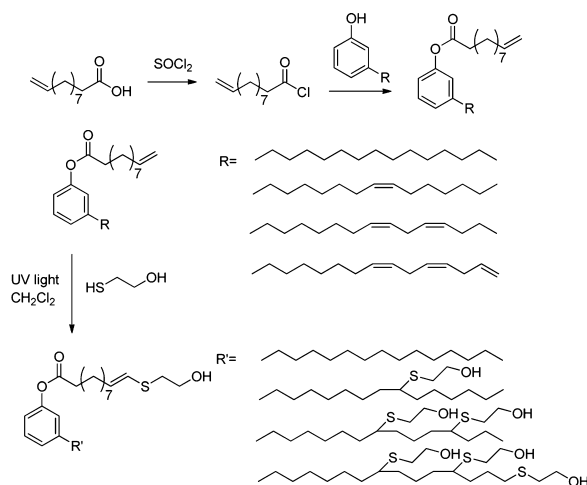
## 2. Experimental

### 2.1. Materials

Cardanol (CA) and hexamethylene diisocyanate (HDI) are industrial products. Acetic anhydride and 2-mercaptoethanol (ME) were obtained from Xiya Reagent, China. Dichloromethane (DCM) and *N,N*-dimethyl formamide (DMF) were obtained from Beijing Chemical Works. 2-Hydroxy-2-methylpropiophenone (UV1173) was obtained from Jiuri Chemical of China; and 10-undecylenic acid (95% purity), ditinbutyldilaurate (DBTDL), triethylamine, pyridine, and thionyl chloride were purchased from Aladdin China. All the materials were used without any further purification. The water used in this study was deionized and doubly distilled.

### 2.2. Preparation of cardanol-based polyols (CAP)

Scheme 1 shows the method used to prepare cardanol-based polyols. CA (8.0 g, 0.027 mol), ME (9.4 g, 0.120 mol), and UV1173 (0.35 g) were dissolved in DCM (25 mL) in a single necked flask. The reaction mixture was stirred at room temperature through UV light irradiation ( $1700 \mu\text{W cm}^{-2}$ , 365 nm) for 15 h. The reaction was monitored using proton nuclear magnetic resonance ( $^1\text{H NMR}$ ) spectroscopy based on the decrease or absence of double-bond proton peaks. The cooled mixture was washed with water to ensure that the ME is completely removed. Then, the DCM phase was dried over magnesium sulfate and evaporated until dry. The brown cardanol-based polyols (CAP1) liquid with an average hydroxyl functionality of 2.2 was obtained with 81% yield.



Scheme 2. UCAP synthesis.

CAP2 and CAP3 were prepared with the same procedure by controlling the reaction time, when we prolonged the reaction time to 22 h, CAP2 with an average hydroxyl functionality of 2.5 was obtained with 83% yield, and CAP3 with an average hydroxyl functionality of 3.3 was obtained with 78% yield through UV light irradiation for 50 h. Detailed information about CAP is shown in Table 1.

### 2.3. Preparation of 10-undecylenate modified cardanol-based polyols (UCAP)

Scheme 2 shows the schematic of UCAP synthesis. 10-Undecenoic acid (8.0 g, 43.4 mmol) was dissolved in thionyl chloride (29.2 mL, 330 mmol) in a single necked flask. The mixture was stirred under reflux conditions for 1.5 h. Then, thionyl chloride was evaporated, and dry DCM was added. The solution was rotated before the above operations were repeated four times, and 10-undecenoyl chloride was obtained in the form of brown oil. 10-Undecenoyl chloride (8.8 g, 43.4 mmol) was added dropwise to the solution composed by CA (10.1 g, 33.5 mmol), triethylamine (4.4 g, 43.4 mmol) and dry DCM (50 mL) at  $0^\circ\text{C}$ . Then, the reaction mixture was allowed to reach room temperature and stirred for 24 h. Subsequently, the solution was washed with 10 wt% NaOH solution ( $2 \times 100 \text{ mL}$ ), and brine ( $3 \times 100 \text{ mL}$ ), after which the organic layer was dried with anhydrous magnesium sulfate. The resulting clear solution was evaporated. Silica gel flash chromatography using petroleum ether/ethyl acetate (8/1, v/v) as eluent was used for further purification. The 10-undecylenate modified cardanol (UCA) of pale brown liquid was obtained with 91% yield.

UCA (5.0 g, 0.010 mol), ME (6.5 g, 0.083 mol), and UV1173 (0.23 g) were dissolved in DCM (25 mL) in a single necked flask. The reaction mixture was stirred at  $40^\circ\text{C}$  through UV light irradiation ( $1700 \mu\text{W cm}^{-2}$ , 365 nm) for 45 h. The reaction was monitored via  $^1\text{H NMR}$  spectroscopy and the absence of double bond proton peaks was monitored. The cooled mixture was washed with water to ensure ME is completely removed. Then, the DCM phase was dried over magnesium sulfate and evaporated until dryness. The brown liquid of 10-undecylenate modified cardanol based polyols (UCAP) with an average hydroxyl functionality of 3.3 was obtained with 75% yield.

### 2.4. Cardanol-based polyurethane (CPU) and films preparation

The CPU and films were prepared using the formulations in Table 2. The CPU was synthesized in a three-necked, round-bottom flask equipped with a magnetic stirrer, a condenser, and a nitrogen

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