

Study on Oxirane Cleavage (Oxirane Ring Opening) of Epoxidized Cardanol by Methanol and Characterization of Polyols

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ABSTRACT

The impact of the main process variables (temperature, catalyst concentration, agitation, ratio of content, time of reaction) on the degradation of the oxirane ring of epoxidized cardanol by hydrogen active compound (methanol) when a homogeneous acid catalyst used, is analyzed in detail. Cashew Nut Shell Liquid (CNSL), an agricultural by-product abundantly available in tropical countries such as Vietnam, India, is one of the major and economical resources of naturally occurring phenols. Cardanol a by product of CNSL could be epoxidized by reacting carbon-carbon double bonds of long unsaturated chain with peracids via the Prileshajev-epoxidation process or the conventional process. This paper presents a simple and convenient method to oxirane ring opening of epoxidized cardanol by methanol with preservation of p-toluenesulfonic acid catalyst. The method uses mild reaction conditions: low temperature of 40°C – 50°C and low pressure (air pressure). The results shown that the oxirane ring opening of epoxidized cardanol efficiency reaches 76% at 50°C, stirring rates 1500 rpm, 6% p-toluenesulfonic acid catalyst and time of reaction 3h. The product of polyol cardanol is also characterized by FT-IR, ¹H-NMR and ¹³C-NMR.

KEYWORDS: epoxidized cardanol, oxirane ring opening, methanol, polyol cardanol, p-toluenesulfonic acid catalyst

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]. Most PUs is derived from petroleum resources. However, using fossil resources is causing increasingly prominent environmental issues. Therefore, using renewable monomers and PUs to replace traditional petrochemical-based monomers and PUs have attracted significant attention [2-4]. 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 [5]. Among all vegetable oils, cardanol is an agricultural by-product abundantly obtained from the complete distillation of Cashew Nut Shell Liquid (CNSL), and stands out for preparing cost effective materials [6-10]. Cardanol extracted from CNSL by via vacuum distillation is an agricultural byproduct considered very attractive

precursor to develop new materials to be used in eco-friendly process. Cardanol is unique since it contains a phenolic moiety with an unsaturated 15-carbon side chain having 1 to 3 double bonds. The long chain in the cardanol imparts flexibility due to internal plasticizing and the reactivity of the hydroxyl phenyl group of cardanol can be taken advantage of to develop a variety of structurally diverse functional molecules [11-14]. In recent years, there are many studies about the chemical modification of cardanol to diol or polyol compounds. For instance, 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 [15]. In this study, we report synthesis cardanol-based polyol (polyol cardanol) from epoxidized cardanol which is synthesized Vietnamese cardanol with methanol (Me) as a ring opener [16, 17].

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Experimental Materials

Epoxidizedcarrdanol (ECD) was synthesized by reaction of cardanol with glacial acetic acid and hydrogen peroxide using p-toluenesulfonic acid as a catalyst, toluene as a solvent [16]. The physico-chemical properties of the ECD are shown in Table 1.

Table 1: Physico-chemical properties of epoxidizedcarrdanol (ECD)

Parameters	Value
Viscosity (25 ⁰ C), Cps	30.34
Density (25 ⁰ C)	0.956
Hydroxyl value, mgKOH/g	150.7
Epoxy group content, %	21.45
Oxirane index, %	7.98
Iodine index, mg/g	30.78
Humidity, %	2.5
Ash, %	2.6

Methanol (99.5%) from Xilong (China); p-toluenesulfonic acid was obtained from Merck (Germany); solvent ether and toluene from Xilong (Chiana).

Methods

Synthesis of polyolcarrdanol (PCD)

In a four-necked a round-bottomed reaction flash equipped with a mechanical stirrer, thermometer sensor, and reflux condenser, epoxidizedcarrdanol (ECD), p-toluenesulfonic acid and toluene were charged. The mixture was heated to the desired temperature and time in a constant-temperature water bath. Methanol, was pre-warmed to the same temperature and then quickly added to the flask. After reaction was complete, the product is neutralized, washed with excess distilled water till neutral to litmus and dried over anhydrous sodium sulfate. Finally, toluene was removed by distillation under vacuum at 80⁰C for 2h to yield the product. The scheme of the idealized synthesis route of polyolcarrdanol based on epoxidizedcarrdanol are shown in Figure 1.

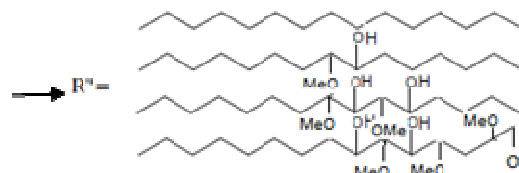
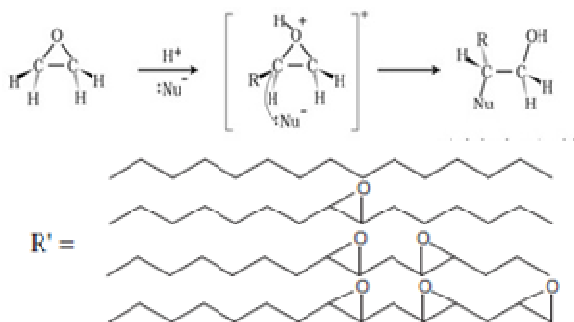


Fig.1: Scheme of the idealized synthesis route of polyolcarrdanol based on epoxidizedcarrdanol

Characterization of the compounds

The density was determined by Erichsen Pycnometer Model 290 according to the standard ISO 2611. The viscosity of the compounds was determined at room temperature with a Brookfield RVT viscometer. The hydroxyl values were determined according to the standard ASTM D1957-86. The epoxy group content was determined by the direct titration of the compounds with HBr according to the standard method for oils and fats [18]. The Iodine index was determined according to the standard ASTM D5768-02 (Wijs method). Fourier transform infrared (FT-IR) spectroscopy was performed on a FT/IR Affinity-IS (Shimadzu-Japan) spectrometer using NaCl plate at 23⁰C ± 1⁰C. The sample was scanned from 4000 to 400 cm⁻¹. Proton and carbon NMR (¹H-NMR and ¹³C-NMR) spectra of compounds in deuteated chloroform (CDCl₃) were recorded with a Bruker 400 MHz spectrometer (Bruker, Rheinstetten Germany) at room temperature.

Results and discussion

Synthesis of the polyolcarrdanol

The effect of temperature on the oxirane ring opening reaction of the epoxidizedcarrdanol

The oxirane ring opening reaction of the ECD was carried out over a temperature range of 40⁰C to 70⁰C with a step change of 10⁰C. Molar ratio of the components ECD/Methanol = 1/10. Catalyst is p-toluenesulfonic acid with content 6% w/w. The stirring rates of 1500 rpm and time of reaction is from 0.5h to 3.5h. The conversion efficiency of the oxirane ring opening reaction of ECD is calculated based on the amount of hydroxyl group formed in the reaction. The results are shown in Figure 2.

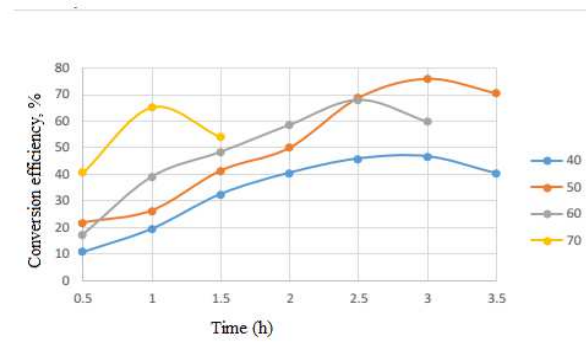


Fig.2: Effect of temperature on the oxirane ring opening reaction of ECD

The results in Fig.2 show that the conversion efficiency (CE) of the oxirane ring opening reaction of ECD is lowest at 40°C and highest at 50°C. The CE of the reaction increases when raising the temperature, but temperature increases to high the CE decreases. This can happen because when temperature high, methanol easy volatile and polyol group formed is unstable and easy to decompose. Thatwhy, 50°C is the temperature chosen for the oxirane ring opening reaction of ECD.

The effect of catalyst content on the oxirane ring opening reaction of ECD

Catalyst is p-toluenesulfonic acid with content change from 2%, 4%, 6% and 8% w/w. The reaction was carried out at 50°C. Other conditions of oxirane ring opening reaction are kept the same as in the above. The analysis results are shown in Figure 3.

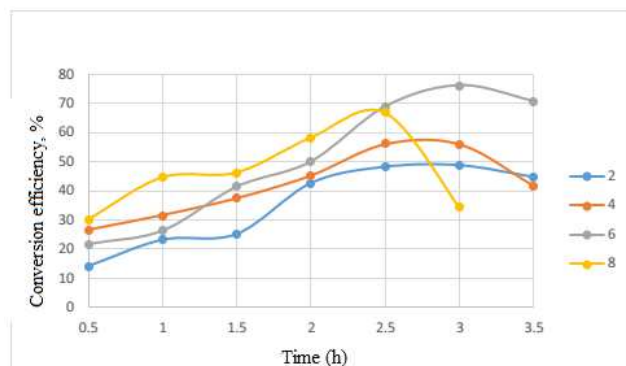


Fig.3: The effect of catalyst content on the oxirane ring opening reaction of ECD

The results in Figure 3 show that the CE of the reaction is lowest with catalyst was 2%, the highest with catalyst was 6%. When the catalyst increases, the CE of the reaction increases. However, when the catalyst is too high, the CE decreases. Because p-toluenesulfonic acid is a strong acid, it easily causes side reactions to create esters. Therefore, 6% p-toluenesulfonic acid is optimal content for the oxirane ring opening reaction of ECD

The effect of the initial component ratio on oxirane ring opening reaction of ECD

The molar ratio of the initial components to the oxirane ring opening reaction of ECD is changed as follows: ECD/methanol = 1/6; 1/8; 1/10; and 1/12 at 50°C and catalyst content 6% p-toluenesulfonic acid. The results are shown in Figure 4.

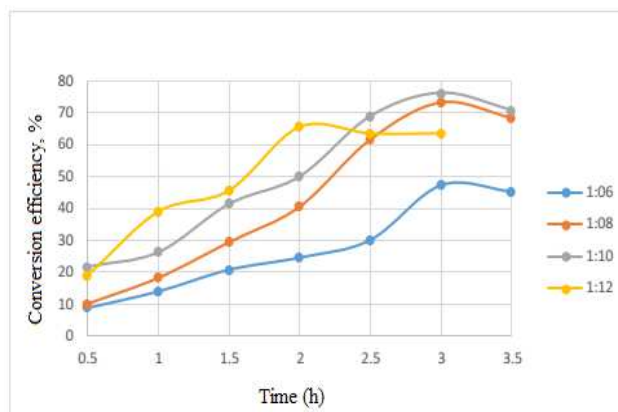


Fig.4: Effect of the initial component ratio on oxirane ring opening reaction of ECD

The results in Fig.4 show that the CE of oxirane ring opening reaction of ECD is lowest at molar ratio ECD/methanol = 1/6 and highest at ECD/methanol = 1/10. When increasing methanol, the reaction efficiency increases. However, if it continues to increase, the efficiency will clearly decrease. This may be because the amount of methanol has reached saturation or side reactions may have occurred. Thus, the molar ratio ECD/methanol = 1/10 is optimal for the oxirane ring opening reaction of ECD under the investigated conditions.

The effect of the stirring rate on the oxirane ring opening reaction of ECD

The stirring rate in the oxirane ring opening reaction of ECD is changed as follows: 1200 rpm; 1500 rpm; 1800 rpm and 2100 rpm. The temperature of the oxirane ring opening reaction of ECD is 50°C and catalyst of 6% p-toluenesulfonic acid. The molar ratio of ECD/methanol = 1/10. The analysis results are shown in Figure 5.

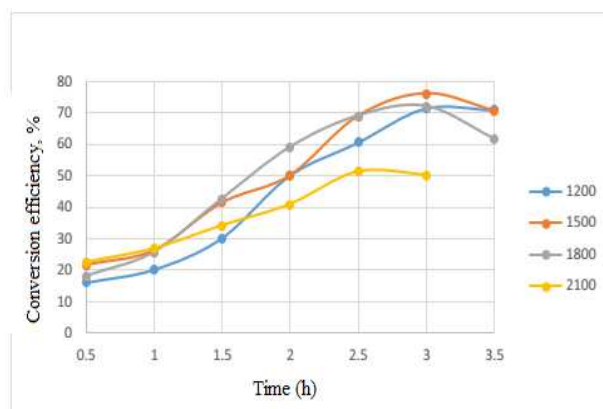


Fig.5: The effect of the stirring rate on the oxirane ring opening reaction of ECD

The results in Fig.5 show that the CE of the oxirane ring opening reaction is lowest when the stirring speed is 2100 rpm, the highest when the stirring speed is 1500 rpm. When the stirring speed is increased, the reaction efficiency increases.

However, when the stirring speed increases too high, the efficiency decreases. This may happen because the reaction system here is heterogeneous with ECD and toluene being the hydrophobic phases, and p-toluenesulfonic acid and methanol being the hydrophilic phases, thus uniform dispersion of the substances in the reaction system is essential because the reaction will take place on the phase interface. With different stirring speeds, different contact capabilities and phase contact times lead to different reaction efficiencies. Thus, the stirring rate of 1500 rpm is the optimal stirring speed for the oxirane ring opening reaction of ECD with the investigated conditions.

The effect of the time on the oxirane ring opening reaction of ECD.

The time in the oxirane ring opening reaction of ECD is changed as follows: 0.5h; 1h; 1.5h; 2h; 2.5h; 3h and 3.5h. the temperature of the reaction is 50°C and catalyst of 6% p-toluenesulfonic acid. The stirring rate of the reaction is 1500 rpm. The molar ratio of the initial components as follows: ECD/methanol = 1/10. The results are shown in Figure 6.

The results in Fig.6 show that the CE of oxirane ring opening reaction of CE increases gradually over time. The highest CE when reaction time is 3h. The CE of the reaction decreases when continuing the reaction. This may happen because as the reaction continues to prolong, a side reaction occurs that hinders the process of opening the ring of the epoxy group to create a hydroxyl group. Therefore, the reaction time of 3h is the optimal time for the oxirane ring opening reaction of ECD.

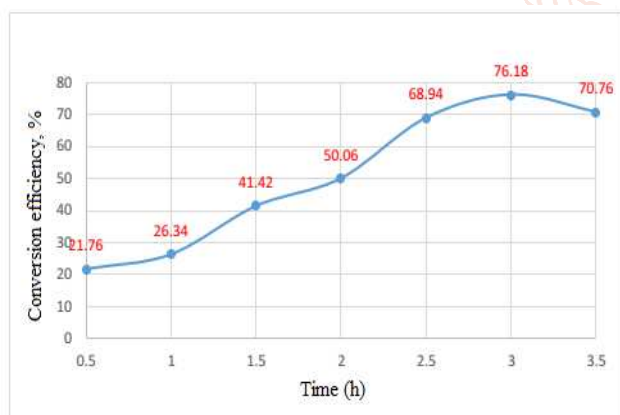


Fig.6: Effect of the time on oxirane ring opening reaction of ECD

Thus, the optimal conditions for the oxirane ring opening reaction of ECD (synthesis polyolcardanol (PCD)) as follows:

- The initial component molar ratio of the oxirane ring opening reaction of ECD: ECD/methanol = 1/10.

- The temperature of the reaction: 50°C.
- The catalyst content of the reaction: 6% p-toluenesulfonic acid.
- The stirring speed of the reaction: 1500 rpm.
- The time of the reaction: 3h.

The conversion efficiency of the oxirane ring opening reaction of ECD with above is 76.18%.

The characterization of the polyolcardanol (PCD)

The physico-chemical properties of the PCD synthesized according to the above conditions are shown in Table 2

Table 2: Physico-chemical properties of the polyolcardanol (PCD)

Parameters	Value
Viscosity (25°C), Cps	22.18
Density (25°C)	0.938
Hydroxyl value, mgKOH/g	334.9
Epoxy group content, %	2.15
Oxirane index, %	0.8
Iot index, mg/g	10.15
Humidity, %	1.3
Ash, %	0.85

FT-IR technique was employed first to study the structure of the epoxidizedcardanol (ECD) and polyolcardanol (PCD). The spectra of ECD and PCD are depicted in Figure 7.

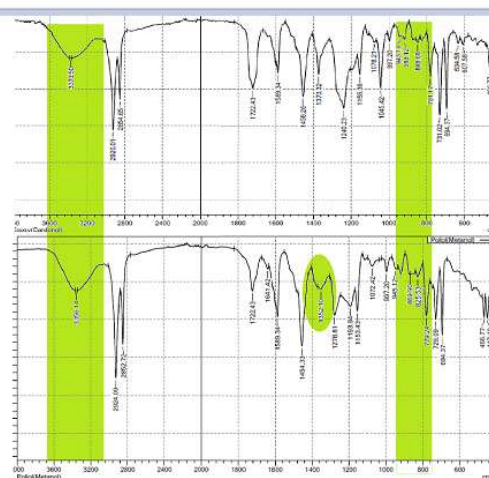


Fig.7: The spectra of ECD and PCD

Observing the infrared spectra of ECD and PCD, it was found that both peaks of the OH group appeared at 3356 cm⁻¹, showing the presence of the phenol hydroxyl group of cardanol, however, at PCD, the peak area expanded due to resonance of the OH group in the PCD chain. The typical peak of the epoxy group at 848 cm⁻¹ and 918 cm⁻¹ of ECD have almost disappeared in the spectrum of PCD. In addition, on the spectrum of PCD, peak 1352 cm⁻¹

appears, representing the OH group attached to the hydrocarbon branch chain.

$^1\text{H-NMR}$ spectra of ECD and PCD are displayed in Figure 8.

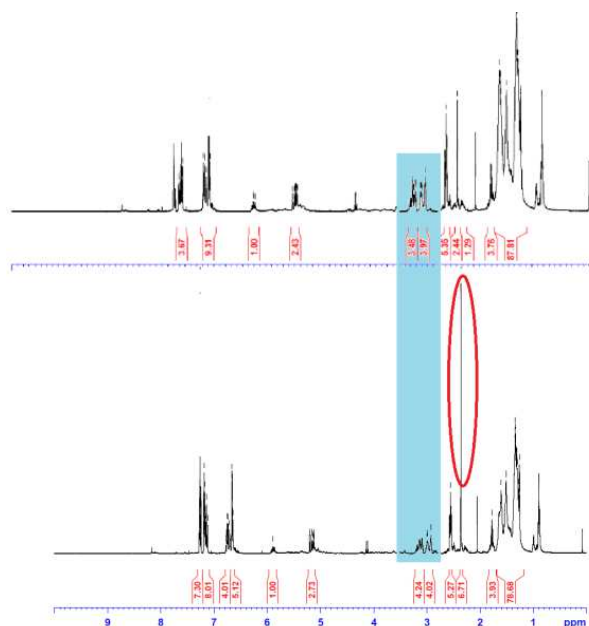


Fig.8: $^1\text{H-NMR}$ spectra of ECD and PCD

In both ECD and PCD spectra in Fig.8, a peak at 5.2 ppm representing the phenolic hydroxyl group is still observed. The peaks at 2.9 - 3.2 ppm are clearly shown in the ECD spectrum, but in the PCD spectrum these peaks have decreased a lot, meaning that there is a ring opening of the epoxy group to transform into an OH group. In the PCD spectrum, the peak at 2.2 - 2.5 was clearly observed, showing the appearance of the OH group attached to the straight chain hydrocarbon branch of PCD.

$^{13}\text{C-NMR}$ spectra of ECD and PCD are shown in Figure 9.

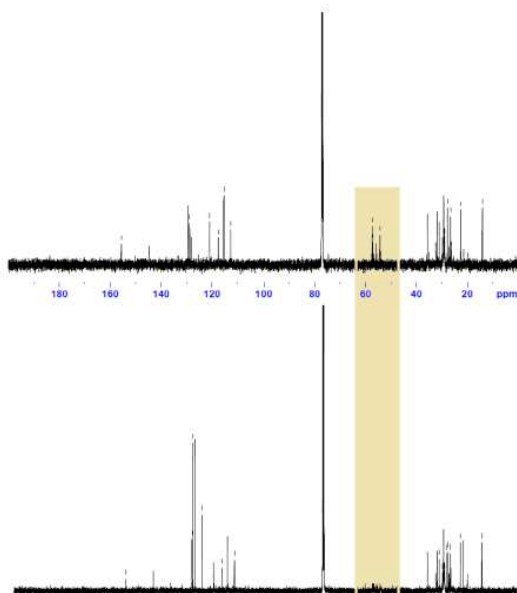


Fig.9: $^{13}\text{C-NMR}$ of ECD and PCD

Observing on the graph of Figure 9, we see that the peaks in region 55.5 – 54.7 ppm present in the ECD spectrum have almost disappeared from the PCD spectrum. Thus, it can be seen that the epoxy groups present at ECD have transformed into OH groups of PCD.

Conclusion

In this study, the polyolcardanol (PCD) was synthesized by oxirane ring opening reaction of the epoxydizedcardanol (ECD) with methanol as a switching component. The reaction occurs under the following conditions: initial component molar ratio ECD/methanol = 1/10; temperature 50°C; 6% catalyst p-toluenesulfonic acid; stirring speed 1500 rpm and time of reaction 3h. The conversion efficiency of the oxirane ring opening reaction of ECD is 76.18%. The analysis of FT-IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of ECD and PCD showed that the epoxy groups in ECD have almost disappeared in the spectrum of PCD and the spectrum of PCD, peak 1352 cm^{-1} appears, representing the OH group attached to the hydrocarbon branch chain.

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