

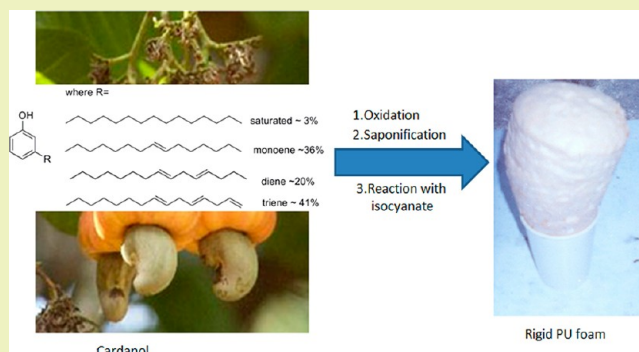
Rigid Polyurethane Foams from Cardanol: Synthesis, Structural Characterization, and Evaluation of Polyol and Foam Properties

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ABSTRACT: Global efforts to find renewable feedstocks for the chemical industry are aimed at replacing fossil reserves and a reduction in global warming by employing environmentally friendly technologies (green chemistry approaches) for specialty chemical manufacturing. Cardanol, obtained as a byproduct of the cashew processing industry, is an important renewable resource and a unique phenolic compound carrying a 15-carbon side chain in meta position with varying degrees of unsaturation. In this work, the synthesis of new biobased polyols for rigid polyurethane (PU) foams through oxidation of side chain unsaturation is reported using the environmentally benign reagent hydrogen peroxide. Polyols with hydroxyl values in the range of 350–400 mg KOH/g were prepared through epoxidation followed by hydrolysis and characterized for structure using IR, ¹H-NMR, ¹³C NMR, and mass spectroscopic techniques. The foaming characteristics were studied, and the polyols were successfully used in making rigid polyurethane foams with good physical and mechanical properties. The foams were characterized for density, compressive strength, morphology, and viscoelastic properties. The properties are compared with that of foams prepared using standard petroleum-based polyols.

KEYWORDS: Cardanol, *In situ* oxidation, Renewable polyols, Rigid PU foams, Morphology, Viscoelastic properties



INTRODUCTION

The Green Chemistry initiative, since its inception in 1991, has evolved many active programs to make polyols from renewable resources like vegetable oils as the feed-stock for value-added fine chemicals and polyurethane polymers.^{1–6} The utility of natural monomers and polymers, in-lieu of their structural diversity and complexity, to produce high value polymers after appropriate chemical modification methodologies has now been demonstrated.^{7–14} Vegetable oil derivatives useful in the preparation of polyurethanes, epoxies, etc. have been reported.^{15,16} Nonedible vegetable oils such as the rubber seed oil^{17,18} and cashew nut shell oil^{19,20} have also been explored as sustainable feed-stock for some important commercial polymers. Mainly, these efforts could be attributed to the plentiful availability of these oils as a byproduct of the farm industry or to replace petrochemicals with environmentally friendly renewable resources and provide value addition to existing agricultural products to benefit agriculture and industry.

Polyurethane chemistry is unique in terms of the versatile range of products that can be prepared using the same starting materials, namely, polyol and isocyanate, and the formulation can be tailored to make elastomers, adhesives, thermoplastics, or foams. Polyurethane foams constitute more than 60% of all polyurethane products. Rigid PU foams in the market are mainly prepared from sugar-based polyols and isocyanates. Foams based on PPO polyols are sensitive to hydrolysis and have moderate water absorption. Renewable resources as a

source of polyols in the preparation of PU foam has also been widely studied.^{15,16,21–23} The preparation of rigid foams using soy-based polyol has recently been reported by Tan et al.²¹ Other vegetable oils like castor oil and rosin were also used to synthesize polyester polyols either alone or as a blend to prepare rigid PU foams.^{22,23} The products displayed excellent strength and higher weight carrying capacity than other commercial packaging materials when used in thermal insulation and packaging. They are also easy to process and can be molded into complex shapes. Cardanol obtained from “Cashew Nut Shell Liquid” (CNSL) is a renewable resource of immense potential. It is the alkyl phenolic oil contained in the spongy mesocarp of the cashew nut shell (*Anacardium occidentale* L). Its composition, structure, and properties are well documented.^{24–29} The chemical modification of cardanol^{30,31} through reactions like allylation and regioselective cyclocarbonylation,³² reactions on hydrogenated cardanol, and preparation of phthalocyanines,³³ has been investigated. The porphyrin³¹ and fullerene³⁴ derivatives of cardanol have been reported to possess lower melting points and higher solubility than similar products without alkyl side chains. The side chain carries an average unsaturation of two double bonds per molecule, facilitating its use in the preparation of thermally curable compositions.²⁰

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The enzymatic method for epoxidation and subsequent oxidative polymerization of cardanol has been reported by Kim et al.³⁵ The preparation of Mannich-based polyols based on cardanol in combination with petroleum polyols to develop rigid foams has been recently reported by Petrovic et al.²³ However, to the best of the author's knowledge studies on per acid oxidation of cardanol has not been reported as a means to prepare polyols, except the patented process for the per acid oxidation of cardanol from our own group.³⁶ The peracid oxidation of olefins is one of the most applied oxidation methods used in the fine chemicals industry.^{37–44} These oxidants are generated in situ through reaction of a carboxylic acid with aqueous hydrogen peroxide. Advantages of using H₂O₂ as the oxidant are cited to be low cost, high active oxygen content, high oxidation potential, and the formation of only water as the reaction byproduct. The reactions can also be carried out using homogeneous or heterogeneous catalysts allowing for ease of separation and purification. In the present work, the peracid oxidation of cardanol is reported in detail as a means to synthesize polyols suitable in the manufacture of rigid foams. The synthesized polyols were evaluated in the preparation of rigid foams. The mechanical and viscoelastic properties etc. were measured and compared with those of commercial polyol-based rigid foams.

EXPERIMENTAL SECTION

Materials. Cardanol was obtained from m/s. Mercury Engineering, Hyderabad, India and purified by double vacuum distillation. The fraction distilling at 190–220 °C under a pressure of 0.01 mmHg was collected and stored in an amber colored bottle. Other chemicals such as hydrogen peroxide (30%), formic acid (85%), anhydrous Na₂SO₄, NaOH, and sodium acetate (AR, SD. Finechem, India) were used as received without any further purification. The solvents toluene, ethyl acetate, chloroform, methanol, acetone (SD. Finechem, India) were dried by standard methods. Polymeric MDI (Suprasec X2185, NCO = 22%, NCO/OH ratio used = 1.5) obtained from ICI polyurethanes, Belgium (presently Huntsman Polyurethanes, Belgium) was used as such. The base polyol used for comparison, also supplied by the sponsor of the project, had a hydroxyl value of 395 mg KOH/g and viscosity of 59 Poise at 25 °C. DABCO or 1,4-diazabicyclo[2.2.2]-octane catalyst and was obtained from Air Products. The surfactant TEGOSTAB B-8404 was procured from Degussa Corp. (Germany). The foaming agent ENOVATE 3000 was procured from Honeywell Technologies (India) through local suppliers.

Methods. All the products were characterized by spectroscopic methods and for physico-chemical characteristics. The hydroxyl value of the polyol was determined by pyridine-acetic anhydride method (ASTM-1957-86). The Viscosity was measured with a Brookfield viscometer using Spindle No.3 at 25 °C. Infrared spectra were recorded as thin films on a NICOLET FT-IR machine. The ¹H-NMR and ¹³C NMR measurements were carried out in CDCl₃ on a Varian 300 MHz machine using TMS as an internal standard. The mass spectra measurements were carried out on VG micromass 7070H instrument at 70 eV.

PREPARATION OF POLYOLS

Oxidation. The experimental procedure adopted for the oxidation was the same as reported originally.³⁶ In a typical experiment, cardanol was oxidized using performic acid according to the following recipe. A mixture of 7.82 g of formic acid (0.17 mol) and 50g of cardanol (0.17 mol) was taken together in a glass vessel, and the mixture under stirring was cooled to 0 °C. While stirring continued and maintaining the temperature, 38.5 g (0.34 mol) of 30% H₂O₂ was added dropwise from a pressure-equalizing funnel. The reaction was continued for 24 h under ambient conditions.

Saponification. The oxidation product formed was subjected to saponification with 10% sodium acetate solution. The reaction was continued for 4 h at 80 °C. Later, the product was neutralized, washed with excess water until neutral to litmus, and dried over anhydrous sodium sulfate. The product was analyzed by TLC, and the various fractions were collected on a silica gel column using toluene containing varying proportions of ethyl acetate as eluent. The product was isolated in near quantitative yield. This polyol is designated as Epol-112. Because the phenolic hydroxyl has a lower reactivity to isocyanates, a modified polyol, designated as Epol-112M, was also prepared through reaction of cardanol with epichlorohydrin under alkaline conditions.²⁰ The epoxide so obtained was later converted to aliphatic hydroxyl groups during saponification.

Preparation of Cup Foam. The suitability of the synthesized polyols in preparing rigid polyurethane foams was tested using the standard cup foam method (ASTM D7487-08). A brief description of the procedure used is as follows. The polyol was mixed with the other ingredients, viz. surfactant, catalyst, and water according to the following formulation.

Polyol	100 g
DABCO (1,4-diazabicyclo [2.2.2] octane)	2.8 g
Surfactant (TEGOSTAB B-8404)	1.5 g
Water	2.0 g

It was stirred well to homogenize and then conditioned in a constant temperature bath at 20 °C. Rigid foams were then prepared according to the formulation given below.

Polyol blend	100 g
Polymeric MDI (Suprasec X 2185)	135 g
Blowing agent (ENOVATE 3000)	35 g

The conditioned polyol blend, polymeric MDI (Suprasec X2185), and blowing agent (ENOVATE 3000) were weighed accurately into a paper cup, and the ingredients were mixed together with a high speed stirrer immediately. Simultaneously, a stopwatch was started. It was mixed effectively for 6 s at 2000 rpm moving the cup slightly in the vertical plane to ensure adequate mixing. Afterward, the cup was lowered so that the stirrer blade was just above the foam mix and excess mix was spun off the stirrer blade onto the inside cup walls. The container was then placed on a flat surface, and the foaming characteristics were noted using the stopwatch. The foam sample using commercial base polyol was also prepared under the same conditions for comparison.

Samples were cut after one week into specific shapes as per the test requirement, and the foam properties were then measured. These include density, morphology, and compressive strength. Scanning electron microscopy was performed on cut sections of the foam sample after coating the specimens with a thin layer of gold using a SEM Hitachi-S520 model from Japan.

Compressive Strength. The compressive strength of the rigid foams prepared was evaluated using a Shimadzu Universal Testing Machine (model AGS-10 kNG) as per the procedure (ASTM D 1621-73). The test was done at a cross head speed of 3 mm/min. The compressive strength was measured in the direction perpendicular to the direction of foam rise. Cylindrical test specimens with a diameter of 2.1 in. and height of 1.3 in. were used. Three specimens were tested for each sample. The compressive strength was taken as the stress value at 10% strain.

Dynamic Mechanical Properties. DMTA analysis was carried out on cut foam sections in the direction of foam rise with a dimension of 0.5 mm, 7 mm width, and 10 mm length. The test was performed in rectangular tension geometry at a

frequency of 1 Hz and an oscillating strain of 0.003%. The analysis was performed on a DMTA IV model from Rheometric Scientific Inc., U.K.

Free Rise Density. The free rise density of the foam was measured by cutting off the top portion of the foam at the top of the cup level as follows.

$$\begin{aligned} \text{Weight of the foam + cup} &= W_{fc} \text{ g} \\ \text{Weight of empty cup} &= W_c \text{ g} \\ \text{Cup volume} &= V \text{ mL} \\ \text{Free rise density} &= [(W_{fc} - W_c)/V] \\ &\quad \times 1000 \text{ kg/m}^3 \end{aligned}$$

RESULTS AND DISCUSSION

In the present work, oxidation of the side chain unsaturation of cardanol was achieved using performic acid, generated in situ from formic acid and H_2O_2 . The method is advantageous in that only one mol of hydrogen peroxide is required for each mole of the olefinic compound.^{24–26} Cardanol contains an average unsaturation of two double bonds in the side chain. Also the double bonds are not conjugated,^{24–26} as shown in Figure 1.

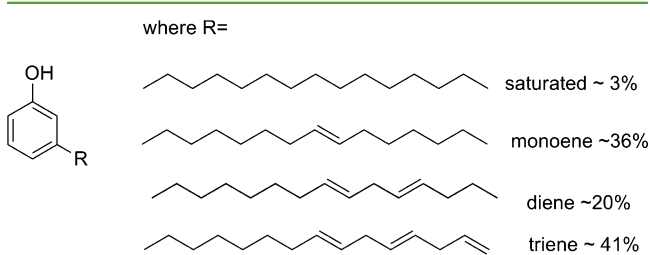


Figure 1. Structure of cardanol.

Synthesis and Characterization of Polyols. The performic acid oxidation of cardanol was carried out with a varying mole ratio of reactants. The molar ratio of cardanol: hydrogen peroxide: formic acid was found to influence the extent of conversion as well as the product viscosity. The details of the process have been disclosed in the patent application.³⁶ Since cardanol is a mixture of monoene, diene and triene all these constituents could undergo oxidation and different products could be formed depending upon the reaction conditions. This assumption has also been established through separation and analysis of the crude as well as column purified products. The general scheme of the reactions used for the preparation of the polyols from cardanol is given in scheme 1. A similar approach was also adopted by Z. Petrovic et al. in structural characterization to prepare polyols based on a Mannich-based reaction of cardanol.²³

As shown in Scheme 1, the epoxides initially formed as intermediates react with the excess organic acid present in the reaction medium to form the hydroxy-formoxy ester.⁴¹ The half ester formed when subjected to saponification gives the polyol. Accordingly, in Scheme 1, the tentative structures of possible reaction products formed during the oxidation process are shown. (Scheme 1, structures I–III and Ia–IIIa). As the final objective of the present work was to synthesize a polyol and its detailed structural characterization, no attempt was made to isolate the intermediate epoxide. As outlined in Scheme 1, the polyol preparation was carried out in two steps: first oxidation of cardanol, followed by saponification of the oxidized product. During the saponification, the epoxy-formoxy ester formed in the first step of the reaction will be converted to a polyol.

The IR spectrum of oxidized cardanol before and after saponification is shown in Figure 2. The main feature is that the unsaponified product shows the ester carbonyl absorption, arising from the reaction of epoxide with free acid at 1730 cm^{-1} (Scheme 1, structures IIa and IIIa). During saponification, the half ester group will be converted to the hydroxyl group. The band at 1600 cm^{-1} , common to both the starting material cardanol and the product, is attributed to the $\text{C}=\text{C}$ ring carbon of cardanol.

It is shown in Figure 2 that upon saponification the ester carbonyl at 1730 cm^{-1} disappeared. Further, the crude product after saponification was purified by column chromatography on a 60–120 mesh silica gel column. The eluent used was toluene containing a varying proportion of ethyl acetate. This will elute the epoxide and any unreacted cardanol. Finally, the column was washed with pure ethanol to elute the polyol. The three fractions were collected. The major fraction formed nearly 70%. A second fraction formed 15% and then unreacted cardanol, and a third fraction, which was a mixture of the upper and middle epoxide, was discarded. It is to be noted that the column purification and analysis was carried out mainly for structural characterization of the polyols; the foam preparation was carried out using the product without any column purification. The various components were further characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectroscopy for structure confirmation, and the main results are summarized below. The ^1H NMR spectral characteristics of the oxidized cardanol is summarized in Table 1 below with the possible group assignments.

The results presented in Table 1 confirm the presence of epoxide (I–III) as well as hydroxy-formoxy ester (Ia–IIIa) as outlined in Scheme 1. The upper spot that formed the minor component was analyzed and confirmed as that of cardanol. In Figure 3, the ^1H NMR of cardanol (Figure 3a) is compared with the saponified product, (middle fraction, Figure 3b and major fraction, Figure 3c), after column purification.

It is shown in Figure 3 that essentially the peaks at 4.9–5.4 ppm due to unsaturation (Figure 3a) in the side chain of cardanol disappeared in the oxidized product (Figure 3c), and peaks at 3.4 ppm due to H attached to secondary –OH appeared. The ^1H NMR of the second fraction given as Figure 3b has peaks at 2.9–3.1 ppm due to the epoxy group protons and also the secondary hydroxyl peaks at 3.4 ppm. This indicates the presence of structure carrying epoxy and hydroxyl groups. This observation was further confirmed by the ^{13}C NMR data presented in Table 2, along with the possible functional group assignments.

The spectral data thus supports the observation that during saponification the ester group undergoes conversion to the hydroxyl group to give the polyol. Here, essentially the transformation of half ester groups (structures Ia, IIa, and IIIa, Scheme 1) to hydroxyl group takes place. The FAB–mass spectrum (Figure 4) of the major fraction showed all the characteristic molecular ion peaks due to the presence of polyols from the monoene, diene, and triene. In other words, the spectral characterization as described above was helpful in identification of the presence of the various products formed during the oxidation of cardanol.

On the basis of this, the possible fragment ion structures are given in Scheme 2 along with the m/z values.

To assess the suitability of the polyol in rigid foam preparation, the hydroxyl value of the polyol was determined by the pyridine–acetic anhydride method and was reported in Table 3 along with other characteristics of all the polyols. It is

Scheme 1. Possible Reactions and Structures of Products Formed during the Performic Acid Oxidation of Cardanol

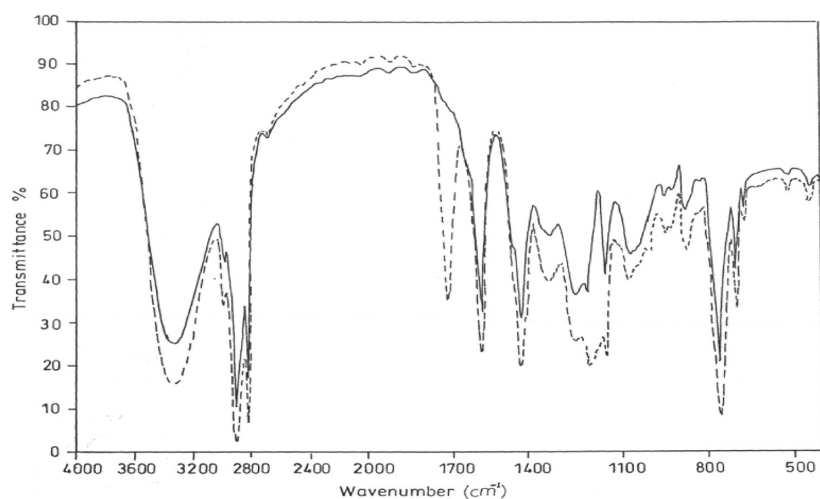
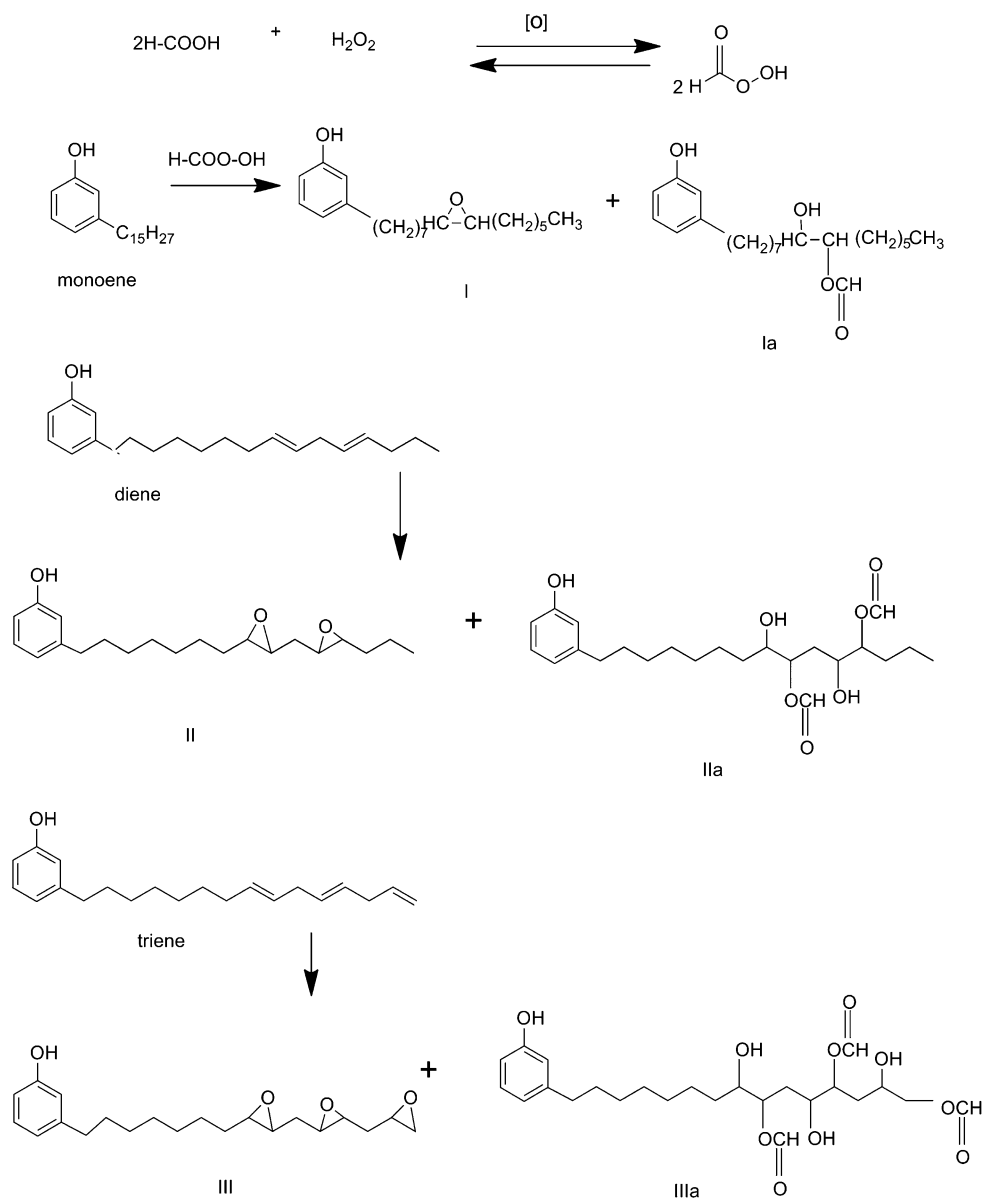
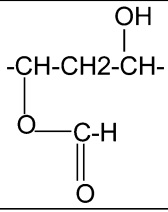
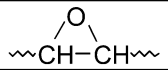
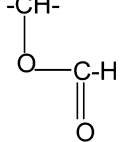
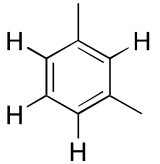


Figure 2. FT-IR spectrum of oxidized cardanol before (----) and after (—) saponification.

Table 1. $^1\text{H-NMR}$ Chemical Shifts of Protons Observed in the Structure of Oxidized Unsaponified Cardanol

Symbol	Chemical shift ppm	Proton type	Group assignment
a	0.9	methyl	$-\text{CH}_3$
b	1.30	methylene	$-(\text{CH}_2)-$
c	1.55	H β -to $-\text{OH}$	$-\text{CH}_2-\text{C}-\text{OH}$
d	1.60	H β -to $-\text{phenyl}$	$-\text{CH}_2-\text{C}-\text{Ar}$
e	1.7-1.8	H- β -to $-\text{OH}$ and ester function	
f	2.5	H- α to phenyl	$-\text{CH}_2-\text{Ar}$
g	2.9-3.2	internal 1,2-epoxide protons	
h	3.4-3.6	H- on carbon attached to ester group	
i	6.5-7.15	aromatic protons	
j	8.05	aldehyde proton	$-\text{CH}(=\text{O})\text{OR}$

shown that the characteristics are comparable to the standard base polyol and hence useful in the preparation of rigid foams.

Preparation and Evaluation of Rigid Foams. Two different polyols were prepared in the present work, designated as Epol-112 and Epol-112M. The petroleum-based polyol was designated as the base polyol (BP). In the case of Epol-112, only the unsaturation in the side chain was converted to hydroxyl groups, while in the second case (Epol-112M) the phenolic $-\text{OH}$ was also converted to aliphatic hydroxyl groups using the procedure reported earlier.²⁰ For this, cardanol was first reacted with epichlorohydrin, and the epoxide obtained was subsequently hydrolyzed to hydroxyl groups. The suitability of the synthesized polyols in the preparation of the rigid foam was tested using the reaction of polyisocyanate with the hydroxyl group of polyol coreactant and the blowing agent. Rigid polyurethane foams are characterized by a closed cell structure and high compressive strength, which are commonly produced from a highly branched short chain polyol and isocyanate. Ideally, the average molecular weight between cross links is 400–700 g/mol for rigid polyurethane foams. The choice of isocyanate used is normally limited, and thus the variation between cross links is primarily controlled by the poly hydroxyl compound. Polyol variations that can affect the foam

include molecular weight, molecular weight distribution, and the ratio of primary to secondary hydroxyls.²² The foaming kinetics of the different polyols is tabulated in Table 4.

It is shown in Table 4 that the cardanol-based polyols react faster in comparison to the petroleum polyols. This is also indicated by the shorter end of rise time and tack free time. During the cream time, the isocyanate reacts with the water and polyol. The exact reason for the faster reactivity is not clear, though it is known that secondary hydroxyl groups react slower compared to the primary. One of the possible reasons for the enhanced reactivity of the cardanol-based polyol may be due to its better miscibility with MDI resulting from its aromatic–aliphatic character, compared to polyether or vegetable oil-based polyols that are nonaromatic. The $-\text{OH}$ groups are also less shielded compared to the triglyceride oil-based polyols. These polyols are also of lower molecular weight. A typical photograph of the cup foam prepared from Epol-112M is shown in Figure 5.

Rigid Foam Characteristics. The cardanol-based foams were comparable to base polyol foam in appearance, color, and shrinkage. The properties like density, compressive strength, and dynamic mechanical properties were also measured as discussed below.

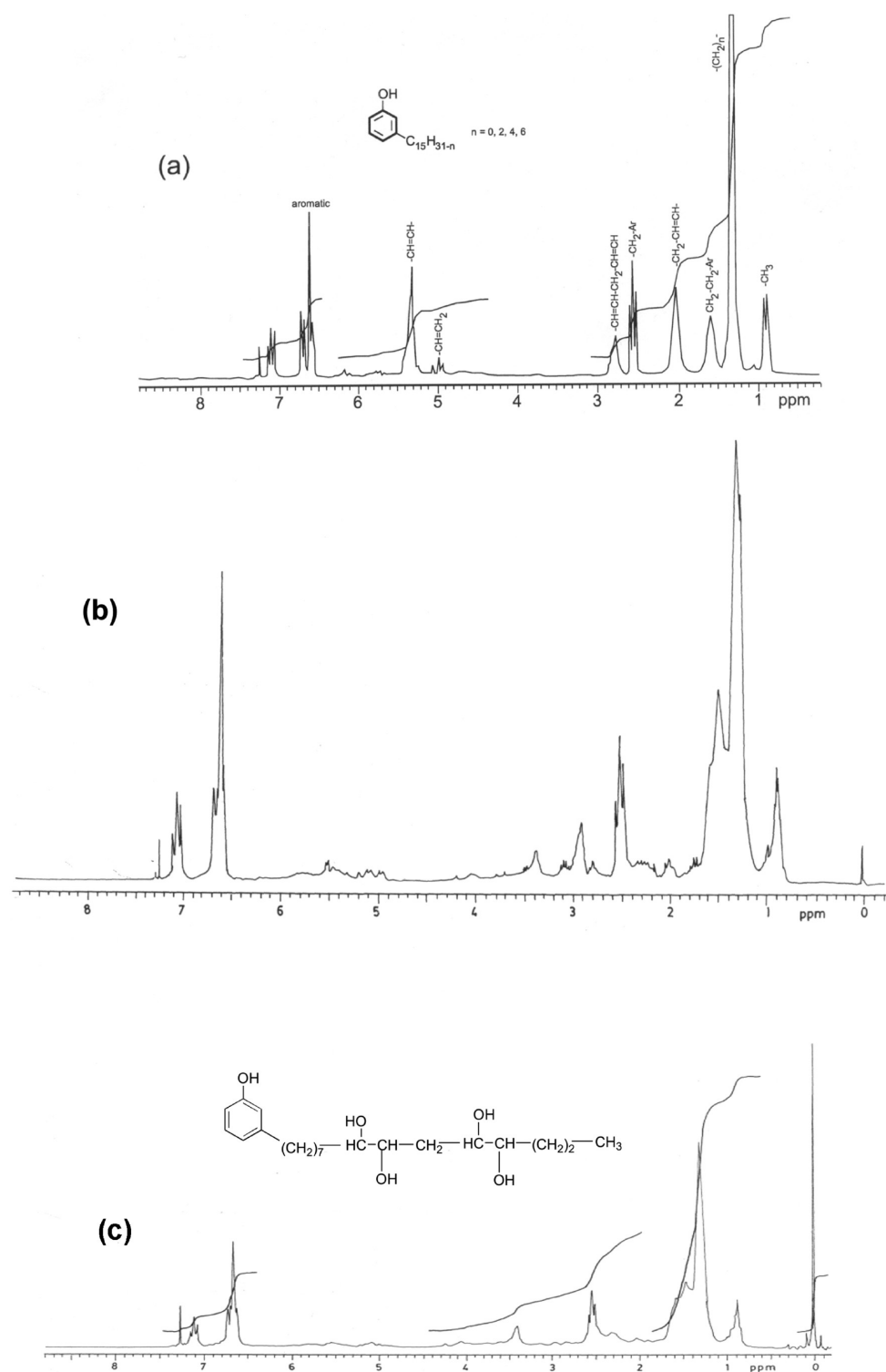


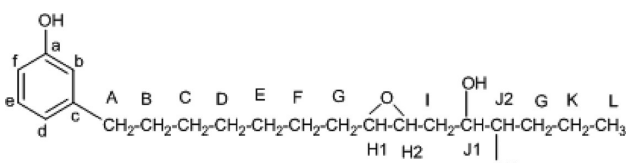
Figure 3. ^1H NMR spectrum of (a) column-purified cardanol (upper fraction), (b) epoxide (middle fraction), and (c) product after saponification (major fraction).

Compressive Strength. In Figure 6, typical stress–strain plots of the foam samples obtained from the compressive test are compared. It is shown that the compressive strength of the foams prepared from cardanol (Epol-112) and the base polyol are nearly the same. Foams prepared from Epol-112M showed an increased compressive strength value. The foam prepared from base polyol starts deforming at about 80 kPa. The foam prepared from cardanol starts deforming at 105 kPa, whereas

the in Epol-112M, foam starts deforming above 120 kPa. It has been reported that a smaller cell size improves the compressive strength.²¹ The morphology studies have shown that foams based on Epol-112 have smaller cell structures than base polyol foams, and Epol-112M has both small and large cells.

However, the final shape of the cup foam was found to be slightly different from that of the base polyol and Epol-112. Because no major variation in hydroxyl value was noticed, the

Table 2. ^{13}C -Chemical Shifts of Carbon Atoms in the Saponified and Oxidized Cardanol along with Possible Group Assignments



symbol	chemical shift (ppm)	proton type	group assignment
a	155.9		aromatic
b	115		
c	144		
d	121		
e	130		
f	113		
A	37	aliphatic	
B	32		
C	30		
D	30		
E	30		
F	31		
G	33		
H1	58	epoxy	epoxy
H2	54		
I	30		
J1,J2	74		2°alcohol
K,L	22,14		aliphatic

improved compressive strength of the cardanol-based foams may be due to the uniform cell structure and rigidity of the foams.

Dynamical Mechanical Properties. To assess the damping characteristics and modulus properties of the foam, cut sections were analyzed using the dynamic mechanical thermal analyzer. Typical thermograms showing variation in viscoelastic properties are shown in Figures 7 and 8.

In Figure 7, the storage modulus of all the foam samples are compared, which shows the highest modulus for the foam prepared using Epol-112M and the least for Epol-112. The $\tan \delta$ behavior of the foams is compared in Figure 8. The glass transition temperature increases from 147 °C for the BP foam to 173 °C for the Epol-112M, which may be due to the higher hydroxyl value of 397 mg KOH/g for this polyol. In comparison, Epol-112 displayed two T_g 's at 112 and 141 °C, attributed to the different phenolic hydroxyl and aliphatic hydroxyl in the pure cardanol-based polyol. In the DMTA results, the heterogeneous nature of the SBOP (soybean oil-based) polyol was found to produce multiple peaks or a broadening of the damping peak.²¹ Glass transition temperature typically increases as the $-\text{OH}$ number increases. The foam based on Epol-112M also possess excellent damping characteristics as indicated by the higher $\tan \delta$ magnitude. In comparison, both the base polyol and Epol-112 displayed lower values and hence a low damping feature. The damping was found to extend over a temperature range of 90 °C for Epol-112M but only 60 °C for the base polyol and Epol-112 foams. Figure 7 shows that cardanol-based foams display better modulus retention after 200 °C, where as that of the base polyol foam decayed to a lower value, which may be due to the increased aromatic content.

Recent studies on cardanol-based polyols, though obtained by a different route, show the significance of cardanol-based polyols in the preparation of rigid PU foams. Ionescu et al.²³

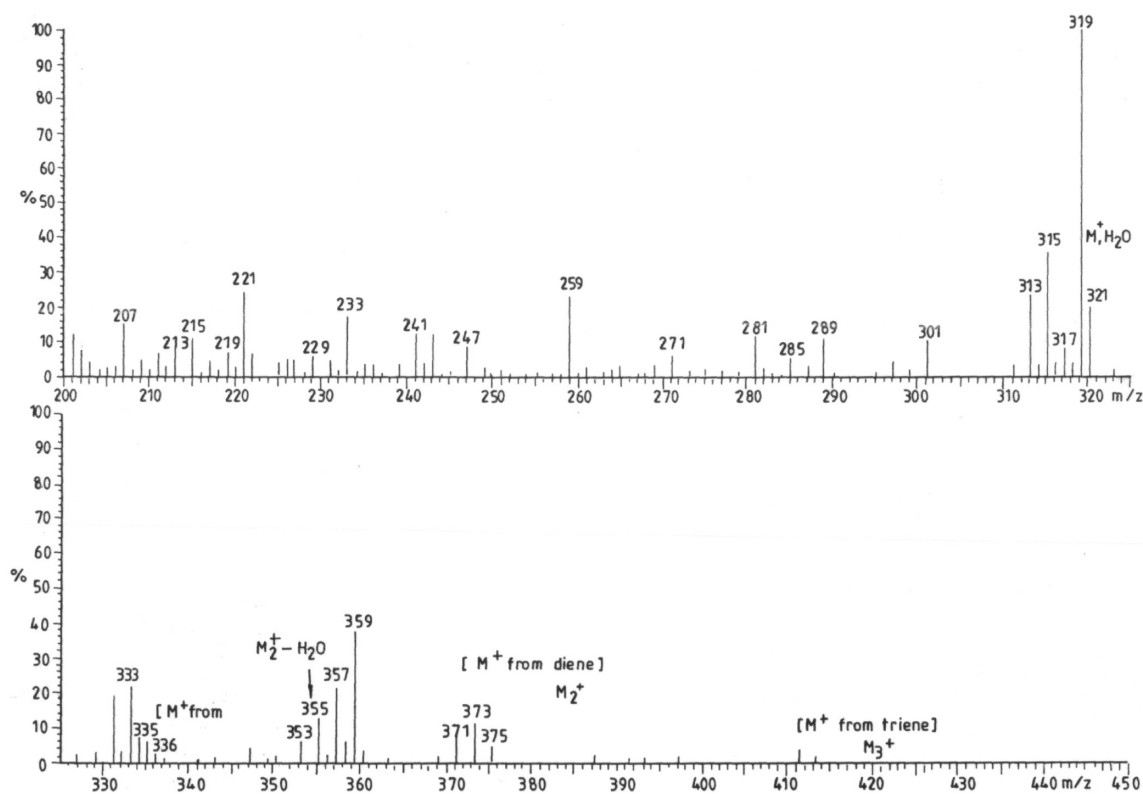


Figure 4. FAB-mass spectrum of oxidized cardanol after saponification and column purification. (Scheme 2 for possible molecular ion structures formed during the fragmentation process).

Scheme 2. Structures of Different Molecular Ion Peaks and Possible Fragmentation Pattern of Molecular Ions Observed in the FAB–Mass Spectrum

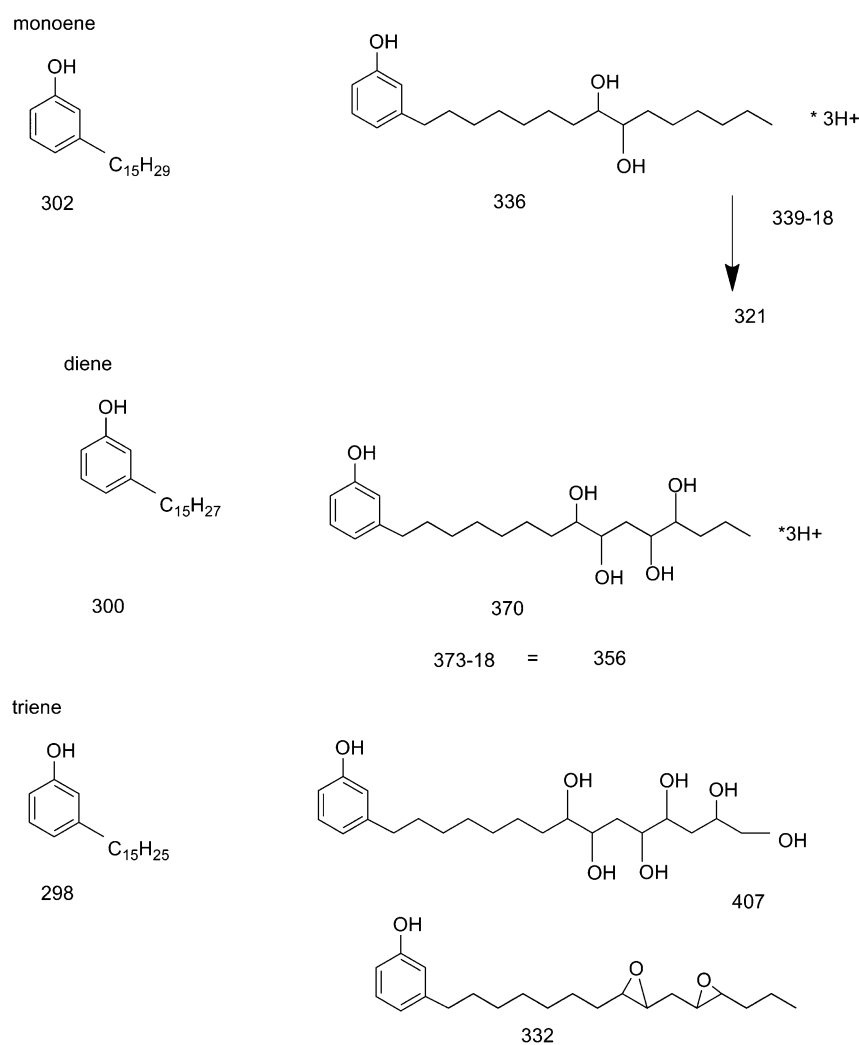


Table 3. Physico–Chemical Characteristics of the Polyol Synthesized in the Present Work

polyol sample	hydroxyl value (mgKOH/g)	acid value (mgKOH/g)	viscosity ^a poise at 25 °C
base polyol	395	0.5	59
Epol1112	370	1.5	84
Epol1112M	397	1.2	105

^aDetermined with a Brookfield viscometer, spindle No. 3 at 25 °C.

Table 4. Foaming Kinetics of Rigid Foam Formulations in Comparison with Standard Base Polyol Formulation

polyol	isocyanate	cream time (sec)	string time (sec)	end of rise time (sec)	tack free time (sec)	foam density (kg/m ³)
base polyol	Suprasec X2185	16	90	126	171	24.02
Epol-112	-do-	10	65	110	159	19.80
Epol-112M	-do-	14	68	105	162	26.59

have reported the synthesis of a series of biobased Mannich polyols starting from cardanol through the oxazolidine group. Polyols with functionality ranging from 3–5 and hydroxyl values ranging from 350–436 mg KOH/g were synthesized.



Figure 5. Photograph of cup foam prepared from cardanol-based polyol (Epol-112M).

The foams prepared based on Mannich polyols were of low density. Using a blend of cardanol polyols with commercial sucrose polyols, the foams displayed excellent compressive

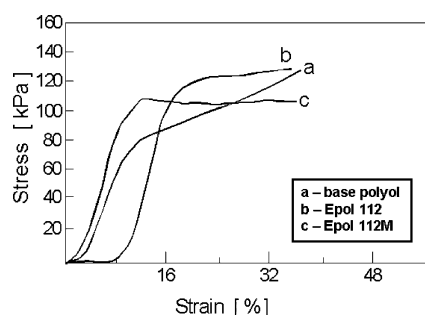


Figure 6. Stress–strain plots showing the compressive behavior of the foams.

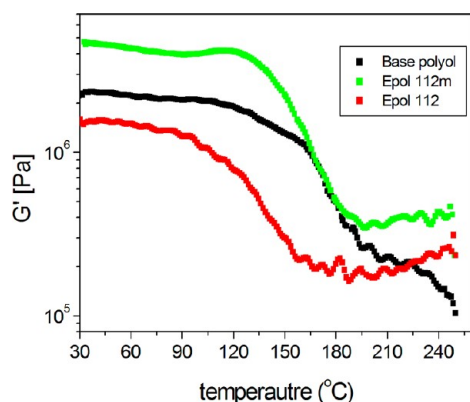


Figure 7. DMTA spectrum of rigid PU foams prepared using the cardanol-based polyol showing variation in storage modulus as a function of temperature.

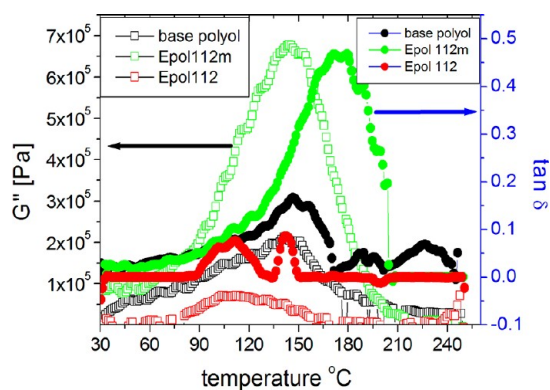


Figure 8. Variation of loss modulus (G'') and $\tan \delta$ of the rigid foams prepared using cardanol-based polyol and petroleum-based polyol.

strength and flame retardancy. They have reported enhanced reactivity with isocyanate by conversion of the phenolic hydroxyl to aliphatic hydroxyls.²³ Because the phenolic hydroxyl reacts with isocyanate very slowly, the methodology used was propoxylation of Mannich-based product to prepare the polyol. The prepared polyols were reported to be very useful in spray foams due to the fast reactivity of the polyols, and a typical cream time of 2 s and end of rise time of 59–62 s was reported.

Foam Density and Morphology. The densities of the various foams prepared are tabulated in Table 4. The density is also an indicator of cell size. The density of Epol-112M and base polyol foam was nearly comparable. In Epol-112, the density was significantly lower, indicating a less dense open cell

structure. A similar observation correlating foam density to cell size was also observed by S. Tan et al.²¹ in soy-based rigid foams. Similarly Veronese et al.²² studied polyols developed from soybean oil through peracid oxidation and transesterification of castor oil with glycerol and/or triethanol amine. In these systems, the number and position of the hydroxyl group in the molecular structure of each oil is different. However, foams with higher density were obtained ($50 \pm 1 \text{ kg/m}^3$). It was shown that the mechanical response is directly influenced by the chemical structures and functionality of the polyol. In the present work, the comparable density of Epol-112M and base polyol also suggest similarity of cell size. The density variation also followed a similar trend as the compressive strength, with the foams displaying higher density displaying higher strength.

The foam density can also depend on the type of surfactant. Tan et al., while studying the replacement of petroleum-based polyols in the formulation of rigid foams, observed that soy polyols produce smaller cell size.²¹ This was attributed to the higher viscosity of the soy-based polyol (SBOP) that can reduce the cell drainage by gravity of the initial foaming stage leading to smaller average cell size. The increased compressive strength was attributed to the smaller (decreased) cell size. These observations are further revealed from the morphological studies of the prepared foams. Scanning electron microscopy (SEM) was used for the morphological characterization of the

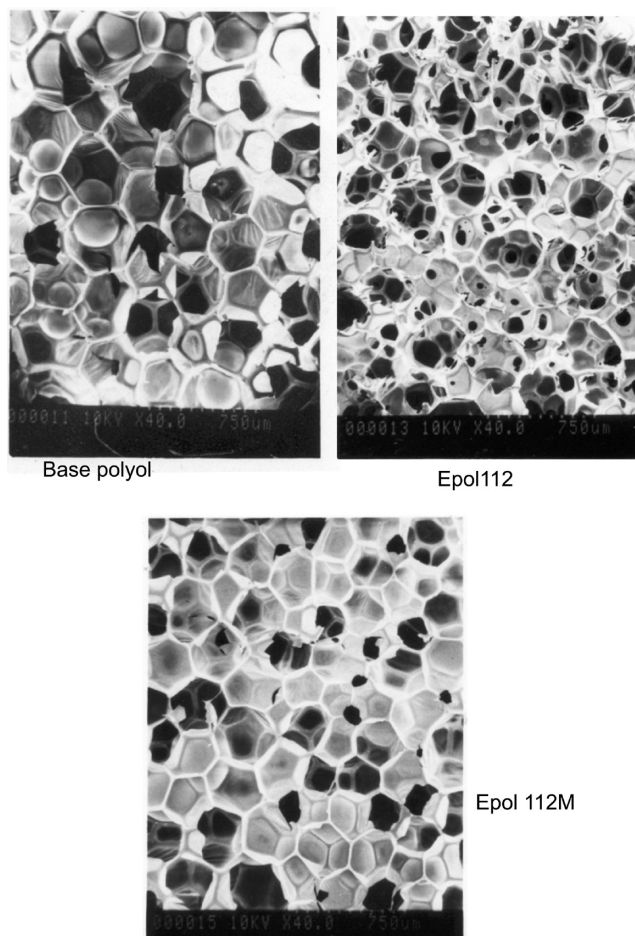


Figure 9. Scanning electron micrographs of the cut sections of the cup foams showing the cell morphology.

foams. Typical SEM photographs of the cut section of the foams were taken to study the cell structure and are shown in Figure 9.

It is shown that rigid foam prepared from Epol-112M has a regular cell structure comparable to the base polyol foam and also contains smaller cells. This could be the reason for the improved compressive strength and marginally higher density compared to the base polyol. The foams prepared from Epol-112 had a very fine cell structure with no clear cell geometries.

CONCLUSIONS

In this work, the preparation and properties of rigid foams using polyols developed from cardanol, a renewable organic resource obtained as a byproduct of the cashew industry, are reported. The oxidation reaction was studied with emphasis on the detailed structural characterization of the reaction products formed from cardanol and properties of the rigid foams prepared. The reaction proceeds with the formation of an epoxy intermediate that reacts with the excess organic acid present in the reaction medium to give a formoxy-hydroxy ester. The half ester so formed on saponification gives the polyol. This observation was confirmed using IR and NMR analysis before and after the saponification. The mass spectrum of the column-purified product shows the presence of a poly hydroxy compound arising from the monoene, diene, or triene present in cardanol. Considering the fact that cardanol contains a varying degree of unsaturation, the detailed structural characterization studies as presented here are important to the development of environment friendly processes for a sustainable chemical industry utilizing this renewable resource. The peracid oxidation could be used as a one pot process for the simultaneous epoxidation and hydroxylation of cardanol. Foams were also prepared after conversion of the phenolic hydroxyl group into aliphatic hydroxyl groups. In this case, the foams displayed good compressive strength, and analysis of morphology by SEM show uniform cell structure in the case of foams prepared using modified cardanol.

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Notes

The authors declare no competing financial interest.

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