

Rapeseed Oil as Feedstock for High Functionality Polyol Synthesis

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ABSTRACT: In this study, polyols with high average functionality were synthesized from a renewable resource, rapeseed oil, as raw material for rigid PU foam production. A well-known method of rapeseed oil fatty acid double bond epoxidation was used to introduce oxirane rings into rapeseed oil structure. The temperature influence on epoxidation reaction conversion rate was studied by volumetric and FTIR spectra analysis. After epoxidation of rapeseed oil, an oxirane ring-opening reaction was carried out to obtain high functionality polyols. Diethylene glycol, a conventional oxirane ring-opening reagent, was compared to amine-based polyfunctional alcohols, diethanolamine and triethanolamine. The introduction of tertiary amine groups into the polyol structure provided catalytical properties for obtained polyols, which will allow a reduction of the amount of catalysts in polyurethane foam formulations. Hydroxyl value, acid value, moisture content, viscosity and density of synthesized polyols were determined, and their structure and average functionality were analyzed by FTIR and MALDI-TOF spectroscopy and GPC analysis. Also, the main characteristics of rigid PU foam obtained from synthesized polyols were determined.

KEYWORDS: Vegetable oil, polyols, renewable raw materials, polyurethane foams

1 INTRODUCTION

Renewable resources for polymer production have been widely studied in the past decade. The main driving force behind these investigations is to push forward a replacement for petrochemical materials and the introduction of sustainable solutions which are motivated by new government regulations and market demands. This article describes a study by the Latvian State Institute of Wood Chemistry (IWC) on the development of catalytically active, high functionality polyols for rigid polyurethane (PU) foam production.

Several biobased polyols have been developed for PU material production and their production technology has been up-scaled to industrial scale. The main feedstock for biobased polyol production is different natural oils, like soybean oil, palm oil, sunflower oil, corn oil, linseed oil, olive oil, castor oil and others, as well as an oil of animal origin—fish oil [1, 2]. The global plant oil production over the last 40 years has

shown a steady increase from about 23 million metric tonnes (MMT) in 1967 to 129 MMT in 2007. While soybean, today's second largest oil crop, has shown an increase in oil production from 5 MMT in 1967 to 36 MMT in 2007. It can be considered as primary feedstock for biobased polyol and PU production. Palm oil production has risen from 2 MMT in 1967 (then the 6th largest) to become the largest oil crop in 2007 with 39 MMT, but it is used mainly in general food consumption. Rapeseed (*Brassica napus*) is the third largest oil crop with 12% of the world plant oil market and is used for food applications as well as feedstocks, mainly for biodiesel production [3].

PU materials are obtained in the reaction between hydroxyl groups and isocyanate groups. All natural oils, except castor oil, have to be chemically modified before they can be used for PU material production as they do not contain hydroxyl groups. A generic triglyceride structure of natural oils can be seen in Figure 1 [4–6]. Two approaches for polyol synthesis from vegetable oils can be distinguished, modification of double bonds in unsaturated fatty acids and transesterification of triglyceride backbone [7]. Most frequently, epoxidation and ring-opening reaction with haloacids and alcohols is used to functionalize

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unsaturated fatty acids. Also, ozonolysis of double bonds can be used to obtain biobased polyols [7, 8], as well as other methods. Narine *et al.* reported that PU elastomers obtained from rapeseed oil by ozonolysis and hydrogenation-based technology showed poor performance due to the structure of polyols. The polyols had a high content of mono-ol and low content triols and diols. Mono-ols act as chain terminator when the polymer is crosslinked with isocyanates [9].

Another approach to obtain polyol with primary hydroxyl groups is to carry out transesterification of ester bonds of glycerol backbone using different polyfunctional alcohols. A transesterification of fatty acid ester can be carried out using glycerol, as seen in Figure 2, but several drawbacks have been reported like low selectivity towards monoglyceride products, separation of monoglyceride from other reaction products is an energy-intensive process, and neutralization of homogenous phase catalysts requires a high-temperature process [10–12]. The main application of such fatty acid monoglycerides is as nonionic surfactant used as emulsifiers in the food, detergent and cosmetics industries. Nevertheless, their application as a polyol for PU material production has been reported [7, 13–15]. Unfortunately, rigid PU foams

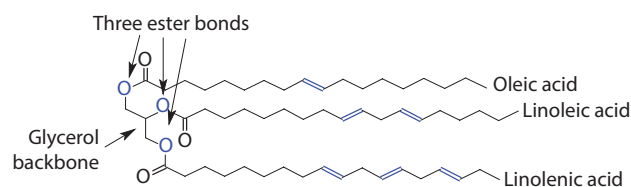


Figure 1 The generic structure of vegetable oil containing oleic, linoleic and linolenic acid chains [4–6].

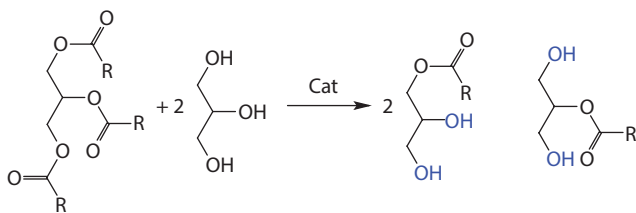


Figure 2 Overall simplified scheme of fatty glycerolysis [11].

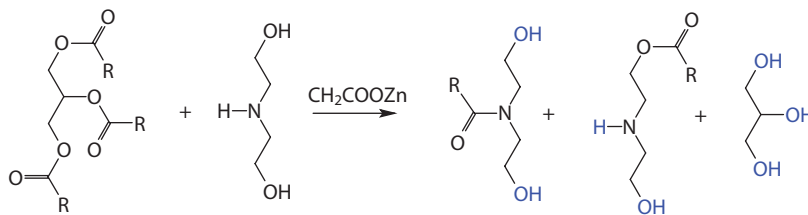


Figure 4 Idealized natural oil transamidization with diethanolamine in the presence of zinc acetate as a catalyst [6, 27].

obtained from palm oil polyol which was obtained in transesterification process with glycerol showed a comprehensive decrease in mechanical and thermal properties [16].

Also, other reagents, like pentaerythritol [17] and triethanolamine (TEA) [5], have been used to obtain polyols via transesterification process, the latter of which is seen in Figure 3. Polyols obtained in rapeseed oil transesterification reaction with TEA showed potential to be used in rigid polyisocyanurate (PIR) foams as their flammability and mechanical characteristic improved with the increase of isocyanate index [18, 19]. Replacement of petrochemical polyether-based polyols with rapeseed oil-based polyols showed a beneficial influence on the heat-insulating properties and significantly reduced water absorption [20]. Such polyols were used not only for the production of rigid PU foams but also for the development of spray-applied coatings [21]. Castor oil, which is a natural oil that already has hydroxyl groups in its structure, was also transesterified with TEA to increase polyol's hydroxyl value. Such polyol was used to obtain rigid PU foams with properties comparable to commercial polyol [22].

Natural oil triglyceride transesterification has been used in conjunction with hydroxylation of unsaturated acids. In the first step, hydrogen peroxide with formic or acetic acid was used to introduce epoxide rings which were hydroxylated *in situ* to obtain polyols. After that, separation of excess water and acid residue alcoholysis of hydroxylated natural oil with TEA was performed at 150 °C in the presence of LiOH catalyst. Using this method, rapeseed oil and tung oil were used to prepare polyols with increased hydroxyl value from which polyol rigid PU foams were obtained

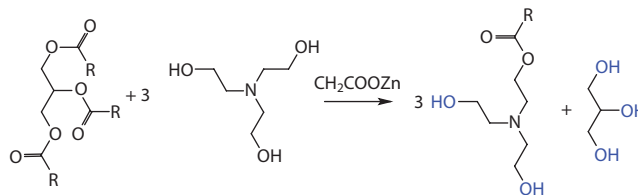


Figure 3 Idealized natural oil transesterification with triethanolamine in the presence of zinc acetate catalyst [6, 23].

with comparable characteristics to commercially used materials [24, 25].

In a similar method to TEA, the diethanolamine (DEA) can be used to obtain polyols from rapeseed oil and other natural oils, as seen in Figure 4. Such polyols have been successfully used for PU coating and rigid PU foam development [26]. Rigid PU foams from linseed oil polyols obtained in transamidization with DEA showed low dimensional stability properties which limit their application on an industrial scale [27]. Similar polyols have been reported in phthalic anhydride resin coating application [28] as well as in polyesteramide resins [29]. Rapeseed oil was used to obtain polyols in transamidization with DEA and rigid PU foams were developed with comparable characteristics to commercial formulations [6, 30]. In the transamidization reaction of rapeseed oil, two types of products are obtained; tertiary amide of rapeseed fatty acids and fatty acid ester. The equilibrium shifts to the fatty acid diethanolamide side after polyol synthesis, which was confirmed by Stirna *et al.* [5].

Currently, the most common way to obtain polyols from natural oils is by using epoxidation of double bonds and epoxy ring opening with diols. This process has already been up-scaled to industrial production and several commercial products are available on the market like Cargill BiOH® [31], Lupranol® Balance 50 [32], Novocard XFN resins [33], etc. The majority of these products have been used for the production of flexible PU foams. They are not used for rigid PU foam production, most likely due to their relatively high price and low profit margins. Also, secondary hydroxyl groups in their structure are less reactive, which limits their application in rigid PU foams, especially for spray-foam formulations [1]. Thus, alternative polyols with higher functionality and reactivity would be more feasible for rigid PU foam production.

A combination of epoxy ring opening and transesterification of fatty acid triglycerides could lead to higher functionality, which would ensure high cross-link density of PU matrix that would convert to rigid PU foam with increased mechanical properties, good dimensional stability and high aging stability. A similar idea was explored by Acar *et al.* where water-soluble soya oil polyols were obtained with a molecular weight of 3800–5900 Da from oxidized soya oil polymer, but no PU materials were obtained [34].

In previous studies, Stirna *et al.* developed polyol synthesis by transesterification of rapeseed oil fatty acid triglycerides with TEA and transamidization with DEA [5]. The obtained polyols had high reactivity, only primary hydroxyl groups and high catalytic activity due to the presence of tertiary amine groups,

but their functionality was too low (~2.25) to obtain excellent quality rigid PU foams.

This study presents a modification of the established process for polyol synthesis from epoxidized vegetable oil by changing the epoxy ring-opening reagents. Different polyfunctional alcohols—diethylenglycol, TEA and DEA—were used to obtain polyols with high reactivity and high functionality. Novel polyols were designed to be used in spray applied rigid PU foam thermal insulation formulations to reduce or completely remove harmful catalysts. The following characteristics were determined for obtained polyols: hydroxyl value, acid value, viscosity, density and moisture. Chemical structure of obtained polyols was studied by Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC) and the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) technique. The average molecular weight (M_n), the weight average molecular weight (M_w), polydispersity index and average functionality of polyols were determined from GPC data. The obtained polyols were used to produce rigid PU foam thermal insulation material and their thermal conductivity, apparent density and compression strength were tested.

2 EXPERIMENTAL

2.1 Materials

Rapeseed oil (RO) (specifications: iodine value = 117 I₂ mg/100 g sample, acid value = 2.1 mg KOH/g, saponification value = 192 mg KOH/g sample) was obtained from Iecavnieks & Co, Latvia. The fatty acid composition was as follows: 62.4% oleic acid, 20.6% linoleic acid, 9.3% linolenic acid, 4.7% palmitic acid and 0.3% other fatty acids. DEA 99.2% and TEA 99.2% (Huntsman, The Netherlands) were used as purchased. Glacial acetic acid, hydrogen peroxide as 35 wt% aqueous solution, sulphuric acid (95 wt%) and diethylene glycol (DEG) were purchased from Sigma-Aldrich. Volumetric Hanus solution –0.1 M IBr and the acidic ion exchange resin (Amberlite® IR120 H) were obtained from Sigma-Aldrich.

For production of rigid PU foams, the following materials were used as purchased: tris(1-chloro-2-propyl phosphate 99% (TCPP) as flame retardant (Albermarle, UK), Solkane® 365 mfc, 1,1,1,3,3 pentafluorobutane 99.5% as physical blowing agent (Solvay Special Chemicals, Germany), distilled water as chemical blowing agent, Lupranol® 3422 – a higher functional polyether polyol based on sorbitol containing only secondary hydroxyl groups (BASF, Germany), tertiary amine (Polycat® 5) and 30% potassium acetate

in DEG as catalysts (Air Products Europe Chemicals B.V., The Netherlands) and Nix silicone L-6915 as surfactant (Momentive Performance Materials Inc., Germany).

Desmodur® 44V20L was used as isocyanate (NCO) component for all PUR materials. It is a solvent-free product based on 4,4'-diphenylmethane diisocyanate (MDI) and contains oligomers of high functionality (Bayer, MaterialScience AG, Germany). The average functionality is 2.8 to 2.9 and the content of NCO is 30.5–32.5% by wt.

2.2 Rapeseed Oil Epoxidation and Epoxidation Process Kinetics

Temperature influence on unsaturated fatty acid conversion into oxirane rings was evaluated at 55, 60 and 65 °C. The epoxidation reactions were carried out in a 1 L glass reactor equipped with a 5 cm diameter Teflon anchor-type stirrer and a reflux condenser. The reactor assembly was immersed in a thermostatic water bath, whose temperature was maintained within ± 1 °C. As catalyst, Amberlite IR120 H acidic ion exchange resin was used. Epoxidation was carried out using peracetic acid, which is the product of the reaction between a glacial acetic acid and hydrogen peroxide as 35 wt% aqueous solution, as seen from Figure 5. The following molar ratios of reagents were used between acetic acid, hydrogen peroxide and double bonds: 0.5/1.5/1.0. Before reaction, 300 g of RO was added into reaction (1.266 mol of double bonds), after which 37.97 g (0.635 mol) of glacial acetic acid and 60 g of Amberlite IR120 H acidic ion exchange resin catalyst was added. Amberlite IR120 H resin was taken as 20% of RO mass. Afterwards, the reaction mass was stirred using a mechanical stirrer (900 rpm) and heated up to 50–55 °C. When the reaction temperature was achieved, 184.34 g (1.905 mol) of 35% hydrogen peroxide was added during the next 25 min. The exothermic reaction process started immediately and the reaction mass heated up. The start of kinetic measurement was set when all hydrogen peroxide was added

and samples of oil were measured during the next 7 hours with 1-hour intervals.

About 7 ml of samples were taken, filtered to remove resin catalyst, rinsed with 5% NaHCO_3 solution and two times with distilled water to obtain epoxidized oil sample with a pH value of ~ 6.5 . Water was separated using a rotary evaporator and, finally, the sample was dried using dry Na_2SO_4 . The next day, epoxy value was determined using the titration method according to PN 87/C-89085/13 standard. From the oxirane content values, the relative oxirane conversion degree was calculated using the following equation [35, 36]:

$$R_{\text{EpC}} = \frac{\text{OR}_{\text{exp.}}}{\text{OR}_{\text{theor.}}} \cdot 100 \quad (1)$$

where R_{EpC} is relative oxirane group content, $\text{OR}_{\text{exp.}}$ (g/100 g sample) is the experimentally obtained oxirane oxygen, and $\text{OR}_{\text{theor.}}$ is the theoretically obtainable maximum oxirane oxygen, which was determined from the following equation:

$$\text{OR}_{\text{theor.}} = \left[\frac{(\text{IV}_0 / 2A_I)}{100 + (\text{IV}_0 / 2A_I) \cdot A_O} \right] \cdot A_O \cdot 100 \quad (2)$$

where A_I (126.9) and A_O (16.0) are the atomic weights of iodine and oxygen respectively and IV_0 is the initial iodine value of RO sample. Unmodified RO's iodine value was analyzed according to ASTM D5768-02 standard.

Additionally, to measure relative oxirane conversion degree, the double bond conversion into oxirane groups was monitored by FTIR spectra using a PerkinElmer Spectrum 100 spectrometer with attenuated total reflection (ATR) sampling at 4 cm^{-1} resolution. C-O-C oxirane ring stretching vibrations were identified at $830\text{--}820 \text{ cm}^{-1}$ [37].

2.3 Epoxidized Rapeseed Oil Oxirane Ring Opening with Polyfunctional Alcohols

High functionality polyols from epoxidized rapeseed oil (ROEP) were obtained using oxirane ring-opening reaction, with polyfunctional alcohols DEA, TEA and DEG used as a comparison. The molar ratios between oxirane rings and polyfunctional alcohols were set as 1.0/1.1. Using previously mentioned polyfunctional alcohols from ROEP, polyols with the following abbreviations were synthesized: RODEA, ROTEA and RODEG.

The example of polyol synthesis is as follows: 300 g of previously synthesized ROEP which contains

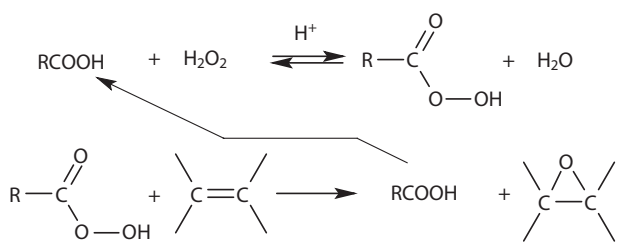


Figure 5 Double bond epoxidation in the presence of Amberlite IR120 H ion exchange resin as acidic catalyst.

1.05 M of epoxy groups was added into a 1 L glass reactor. Afterwards, 0.09 g of LiOH catalyst (0.3% wt of ROEP) was added and ROEP was heated up to 110 °C. In the next step, after preheating to 90 °C, 121.44 g of DEA was added during 20 min while stirring the reactor at 700 rpm. After all of the DEA was added, the reaction was carried out for 3 hours at 110–115 °C under inert gas atmosphere.

In the case of ROEP epoxy ring opening with TEA, a higher synthesis temperature was set at 140–145 °C. But in the case of ROEP epoxy ring opening with DEG, a different catalyst: 0.90 g of sulfuric acid (0.3% wt of ROEP) was used, as described by Zieleniewska *et al.* [38] and others [2, 6]. The LiOH catalyst was used for oxirane ring opening in the case of DEA and TEA because it should provide fewer of the reaction by-products which occurred in the case of ROEP oxirane ring opening with DEG.

All three polyols were dried using a rotary evaporator till moisture content reached below 0.3% wt. Afterwards, hydroxyl and acid values were determined using titrimetric methods according to DIN 53240-2 and DIN 53402 testing standards. The viscosity of polyols was analyzed using a Thermo Scientific HAAKE medium-high range rotational viscometer. The moisture was analyzed using Denver Instrument

Model 275KF automatic titration equipment, which is an alternative analysis method to the DIN 51777 standard.

Gel permeation chromatography was used to determine the values of the number-average molecular weight (M_n) and number-average functionality (f_n) of the obtained polyols. The number-average functionalities of polyols were calculated based on hydroxyl values, and number-average molecular weight was experimentally determined using Equation 3 [6]:

$$f_n = \frac{M_n \cdot OH_{val}}{56110} \quad (3)$$

where f_n is the number-average functionality, M_n is the number-average molecular weight, and OH_{val} is the hydroxyl value of polyol.

2.4 Rigid PU Foam Sample Preparation Using Developed Polyols

The polyol component was obtained by weighing all necessary components (novel polyols, the catalyst, blowing agent, surfactant and flame retardant) presented in Table 1 and stirring them for 1 min with a

Table 1 Polyol formulation, renewable material content in PU foams, technological parameters, free rise density and closed cell content of PU foams.

Polyol formulation	RO DEG	RO DEA	RO TEA
Green Polyol, pbw	100.0	100.0	100.0
Cross-linkage reagent (Lupranol 3422)	39.5	36.8	36.2
Flame retardant (TCPP)	25.2	23.5	23.2
Blowing reagent (water)	3.5	3.3	3.2
Blowing agent (Solkan 365/277)	20.6	19.1	17.7
Tertiary amine catalyst (Polycat 5)	1.5	0.9	-
Potassium acetate 30%	2.2	0.9	-
Surfactant	2.4	2.2	2.3
Polyisocyanate (pMDI)	224.7	281.2	233.9
Isocyanate index	130	130	130
Characteristics of system			
Renewable materials in PU, %	19.2	16.4	16.2
Technological parameters			
Start time, s	17	15	20
Stirring time, s	40	37	43
Tack-free time, s	47	47	60
End time, s	44	42	55
Temperature of polyol system before foaming, °C	21	21	14
Apparent density of molded PU foams, kg/m ³	36.3	38.2	35.1

mechanical stirrer at 2000 rpm. PU foams were prepared after conditioning the polyol system at room temperature for at least 2 h in a sealed container to remove the mixed-in air.

To prepare PU foam, isocyanate (pMDI) and the polyol component were weighed and mixed by a mechanical stirrer at 2000 rpm for 15 s. For the isocyanate index, 130 was chosen for all three PU foams, which was the ratio of the equivalent amount of isocyanate used relative to the theoretical equivalent amount times 100. Then, the reacting mixture was poured into an open top mold that was preheated to 50 °C and placed on a balance. An appropriate amount of the reacting PU mass was poured into the mold and the PU foam was cured at 50 °C in an electric oven for 2 h. The renewable material content was calculated based on the mass of renewable materials used in PU foam formulation. Stoichiometric ratios of the RO as well as the sorbitol content in Lupranol 3422 were taken into account.

As seen in Table 1, the polyol system containing ROTEA polyol did not have any catalysts and was still too reactive to be foamed at room temperature, thus it had to be cooled to 14 °C. This might be a positive thing for formulations designed for spray-foam application.

The physical and mechanical properties of the foams were measured in accordance with the following standards: foam density – ISO 845; compression strength – ISO 844; closed cell content – ISO 4590, and thermal conductivity – ISO 8301. The compression strength of PUR was tested parallel and perpendicular to foam rise with one offset from ISO 844 standard – sample size; cylinders with a diameter of 20 mm and a height of 22 mm were tested. Mechanical testing of PU was done on Zwick Roell 1000N testing machines.

3 RESULTS AND DISCUSSION

3.1 Temperature Influence on Rapeseed Oil Epoxidation

The CH_3COOH was chosen as an oxygen carrier in epoxidation reaction instead of HCOOH because it has been shown by Dinda *et al.* that this acid, despite the slower formation of oxirane, has higher ultimate conversion degree. Also, using HCOOH resulted in a higher amount of side products [35]. In the first step of this study, temperature influence on the epoxidation rate of RO was investigated for three different temperatures: 55, 60 and 65 °C. Goud *et al.* showed that ion exchange resin is a suitable replacement for H_2SO_4 epoxidation reaction catalyst and the process can be carried out without the use of a solvent [36]. The most

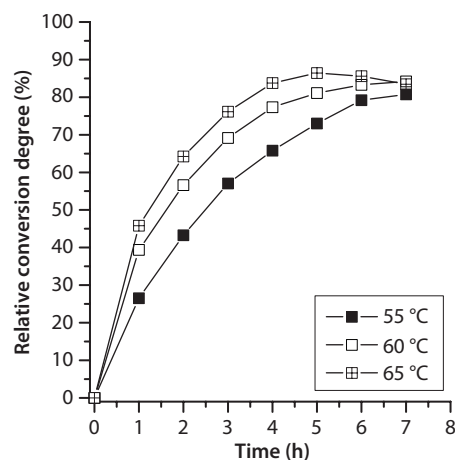


Figure 6 Temperature influence on double bond conversion degree into oxirane rings.

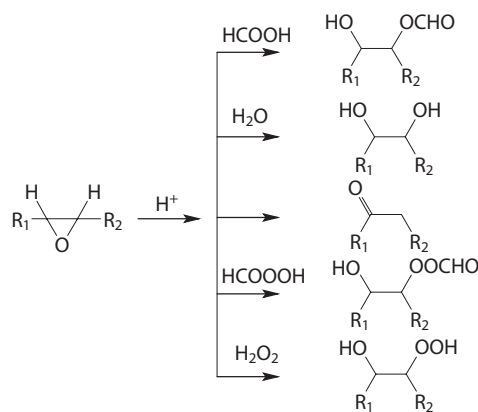


Figure 7 Possible side reactions of epoxide group [35, 39–41].

common solvent for such reaction is toluene, but it has to be separated from oil before the next polyol synthesis step. Also, several hazards can be related to toluene, carcinogenicity being one of them. Thus a solvent-free polyol synthesis method will result in cheaper final product and it will agree with green chemistry principles. The use of Amberlite IR120 H ion exchange resin acidic catalyst also simplified RO epoxidation because the catalyst was removed by simple filtration. The change of the relative oxirane conversion degree calculated using Equation 1 over synthesis time is shown in Figure 6.

The highest epoxy group yield of 86.4% was achieved at 65 °C after 5 h of synthesis but afterwards epoxy group content started to decrease. The decrease of epoxy groups is explained by different side reactions suggested by Gamage *et al.*, Meshram *et al.* and others [35, 39–41], which are shown in Figure 7.

The epoxidation process was also monitored by FTIR spectroscopy, where C-O-C oxirane ring stretching

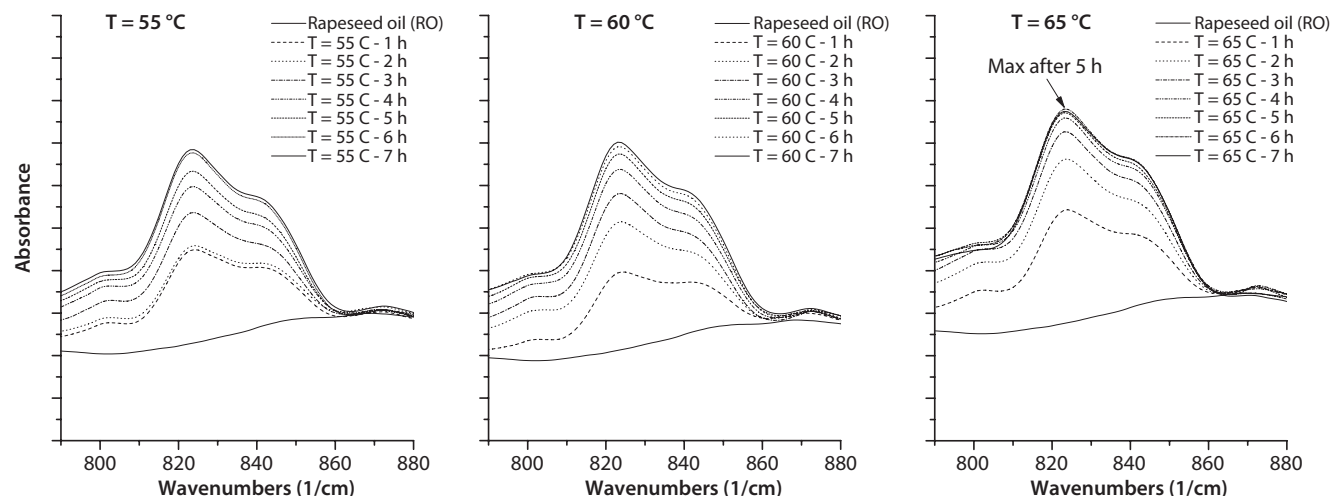


Figure 8 FTIR spectra of the epoxy group absorption peak increase over RO epoxidation at 55, 60 and 65 °C.

vibrations were identified at $830\text{--}820\text{ cm}^{-1}$ [37]. The epoxy group absorption peak increased during the synthesis process, as seen in Figure 8. A slight decrease of its intensity was observed in the case of epoxidation at 65 °C after the 5 h synthesis mark. This correlates with conversion degree results and confirms side reaction occurrence. Although the highest conversion of double bonds into epoxy groups was achieved at 65 °C, the synthesis at 60 °C is preferable due to a more controllable reaction process. After 5 h of RO epoxidation at 60 °C the conversion degree was 81.1% and after 7 h it was 84.2%, which is still comparable to 65 °C synthesis.

The obtained results are similar to those presented by Goud *et al.* [36] of jatropha oil epoxidation. Jatropha oil's chemical structure is similar to RO, thus no significant difference between results was expected. The yield of oxirane rings was noticeably higher than for cotton oil and RO epoxidation in the presence of H_2SO_4 catalyst [35, 41], showing an additional advantage of solid phase ion exchange resin catalyst. Also, Meshram *et al.* presented a design of a pilot-scale chemical reactor for such catalyst use in the up-scaled process [39]. However, the stability of the repeated use of this type of catalyst must be studied before this technology can be further up-scaled. Because this catalyst is intended for biobased product use, different impurities of natural oils could react with sulphonic groups, thus reducing its activity. Also, mechanical damage of resin beads could be a potential problem.

3.2 Epoxy Ring Opening for High Functionality Polyol Synthesis

Previously synthesized ROEP was used in high functionality polyol synthesis. Epoxy ring opening with DEG was used as comparison material because it is

one of the most common reagents for sustainable polyol synthesis from epoxidized vegetable oils and such polyols have been used to obtain good quality PU materials [12, 42]. For this study TEA and DEA amine-based polyfunctional alcohols were used to introduce tertiary amine groups into polyol structure to obtain polyols that would have high functionality and high catalytic activity. The two proposed reactions are shown in Figure 9.

The main characteristics of synthesized polyols are shown in Table 2. The hydroxyl value of all polyols was in the range of typical commercial polyols used in rigid PU foam formulations as well as moisture and density. The acid value of RODEG polyol was slightly higher than that of the standard $< 5.0\text{ mgKOH/g}$ due to H_2SO_4 catalyst used in the epoxy ring-opening reaction. LiOH epoxy ring-opening catalyst was chosen for RODEA and ROTE A polyol synthesis because it propagates epoxy ring-opening reaction at lower temperatures than H_2SO_4 catalyst and reduces by-products [7]. Also, the H_2SO_4 catalyst was not chosen because it should be removed from polyol mixture because it could increase the acid value of polyol, as seen from Table 2. This is not desirable mostly because of the potential decrease of PU material formulation shelf life. The H_2SO_4 could react with added PU material curing catalysts, which usually are amine-based compounds. The highest viscosity of synthesized polyols was for RODEA but it was still in the range of standard polyols used in the PU industry, especially for polyols with high functionality and branched structure. The GPC analysis showed that the obtained polyols have typical M_n and polydispersity and calculated average functionality showed that they have high functionality. Polyols with the functionality of 3–8 are typical for rigid PU foam production [1].

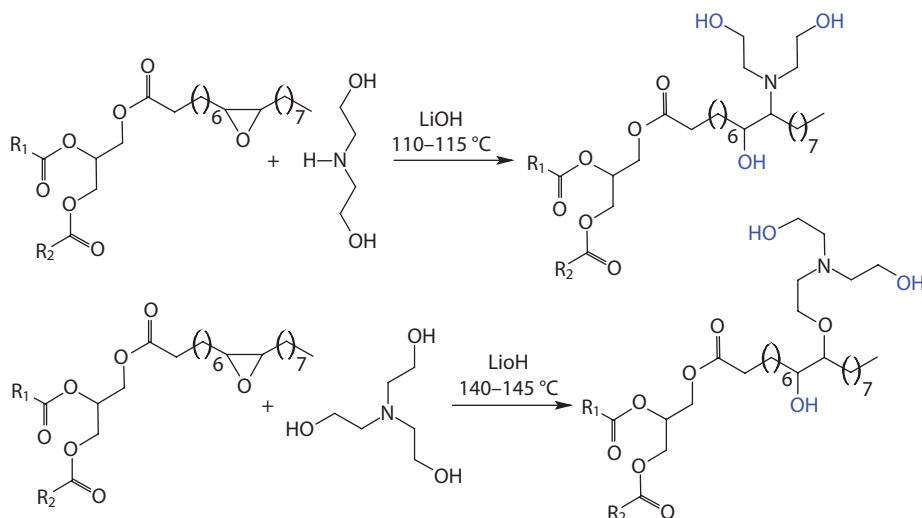


Figure 9 The opening of epoxy rings of ROEP using DEA and TEA in the presence of LiOH catalyst.

Table 2 Hydroxyl value, viscosity, acid value, moisture content, average functionality, number average molecular mass, polydispersity and RO content of synthesized polyols.

Polyol	OH val., mgKOH/g	Viscosity (20 °C), mPa·s	Acid val., mg KOH/g	Moisture, %	Density at 20 °C, g/cm ³	f_n	M_n , g/mol	M_w/M_n	RO content in polyol, %
RODEG	242	6500	8.6	0.322	1.025	3.3	768	1.23	70.8
RODEA	471	22000	< 2.0	0.046	1.022	4.6	553	1.06	71.0
ROTEA	430	1800	< 2.0	0.026	1.031	4.3	567	1.09	63.4

f_n , M_n and M_w/M_n were obtained from GPC analysis of polyols; RO content in polyol was calculated taking into account stoichiometric ratios of RO and epoxy ring-opening reagents.

3.3 FTIR Analysis of Synthesized RO Polyols

The chemical structure of the polyols used was studied by FTIR spectroscopy. Figure 10 presents the FTIR spectra of unmodified RO, ROEP and three spectra of biobased high functionality polyols. Peaks at 3416–3370 cm^{-1} indicated the presence of OH groups in the polyols which were not present in unmodified RO. Also, as expected, the double bond stretching at 3008 cm^{-1} of unmodified RO disappeared after the epoxidation process. The C–O–C oxirane ring stretching vibrations were identified at 823 cm^{-1} for ROEP and this peak disappeared after the oxirane ring was opened with selected polyfunctional alcohols. All three polyols showed ether bond –C–O–C– symmetric stretching at 1103 cm^{-1} , which is present due to epoxy ring opening with alcohols. The tertiary amine groups' vibrations were seen at 1048–1037 cm^{-1} for RODEA and ROTEA. The most significant difference between RODEA and ROTEA was the presence of amide peak at 1619 cm^{-1} for RODEA, which resulted from the transamidization reaction of fatty acid triglycerides. A similar process was described by Stirna *et al.* [5], where polyols from

RO were synthesized using only transamidization reaction. Peaks at ~ 2930 and ~ 2860 cm^{-1} are identified as coming from C–H symmetric and asymmetric stretching. All polyols, as well as neat RO and ROEP, showed a C=O bond stretching peak at 1742–1736 cm^{-1} [6, 43].

3.4 MALDI-TOF Analysis of Synthesized RO Polyols

MALDI-TOF analysis and corresponding mass spectra were used to identify molecular ions of synthesized polyols. Parent ions were primarily MH^+ and $\text{M}\cdot\text{Na}^+$ cations. The $\text{M}\cdot\text{Na}^+$ cations were formed from alkyl salts in the matrix sample as well as from impurities of synthesized polyols due to reagents used for drying polyols [44, 45]. Several groups of parent ions were identified for all polyols corresponding to the different chemical structures of obtained substances. The RO is a triglyceride structure containing unsaturated fatty acids of oleic (62.4%), linoleic (20.6%), and linolenic acids (9.3%), and other unsaturated fatty acids, as well as saturated fatty acids of palmitic (4.7%) and other fatty acids (0.3%). Epoxy ring-opening reaction

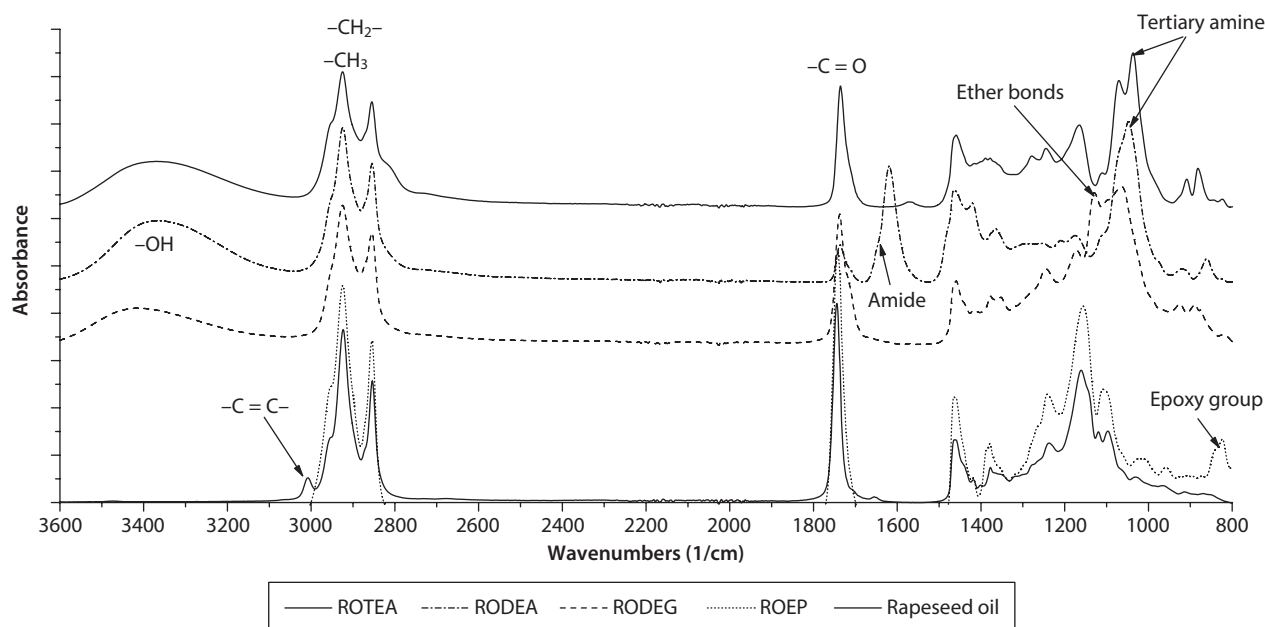


Figure 10 FTIR spectra of RO, ROEP and synthesized RODEA, ROTEA and RODEG polyols.

in combination with several side reactions as well as transesterification reactions is attributed to a broad range of different mass peaks seen in Figure 11. Also, it is likely that the presence of different families of peaks is due to the association of the polymer molecules with Na^+ ions.

From the MALDI-TOF spectra in Figure 11a it can be seen that epoxy ring reaction occurred together with transesterification of ester bonds of triglyceride structure with DEG, as seen from the peak group at 409–515 m/z. The peaks in this group are attributed to monoglyceride and trans-ester fatty acid structures. The calculated mass of Na^+ associated ion of DEG ester of epoxidized oleic acid opened with DEG is 515.67 Da, which closely correlates with a peak of highest intensity of 515 m/z. Diglyceride products can be seen at 796–902 m/z and hypothesized polyol is seen at 1182–1288 m/z. Also, mass peaks attributed to different oligomerization products can be seen at 1568–1674 m/z.

Similar to RODEG, the RODEA polyol had transamidization products as well as epoxy ring-opening reaction products. Noteworthy is the peak at 491 m/z, which is attributed to MH^+ ion of polyol seen in Figure 11b. A similar structure of polyols obtained from vegetable oils has been reported by Acar *et al.* [34] but in the case of this study significantly smaller molecular mass polyols have been obtained with calculated mass of 490.72 Da and theoretical functionality of 5. The diglycerides of DEA opened fatty acids are seen between 742–877 m/z and traces of the RODEA triglycerides are seen between 1157–1282 m/z.

The MALDI-TOF analysis showed that the higher temperature of ROTEA synthesis contributed to the formation of different side reactions of epoxy groups. The idealized structure of ROTEA polyol was attributed to the mass peak of 548 m/z but the mass peak of 430 m/z was attributed to oleic acid TEA ester where the epoxy group has been converted into ketone group. Also, sets of diglyceride and triglyceride products were seen at 711–902 m/z and 1142–1252 m/z respectively.

The calculated average functionality of synthesized bio-polyols seen in Table 2 was comparable to the proposed chemical structures in Figure 11. Despite the formation of by-products in the case of ROTEA, this polyol can still be considered as high functionality and suitable for rigid PU foam development. Nevertheless, further studies of obtained compound structure and composition have to be done and synthesis parameters should be optimized to reduce by-product formation.

3.5 Rigid PU Foams Developed from Synthesized High Functionality Polyols

Three synthesized polyols were used to prepare rigid PU foams according to the formulation seen in Table 1 and the common characteristics of rigid PU foams were tested. This was done to see the suitability of these polyols for further material development. The literature describing polyol synthesis usually covers PU material production in later articles.

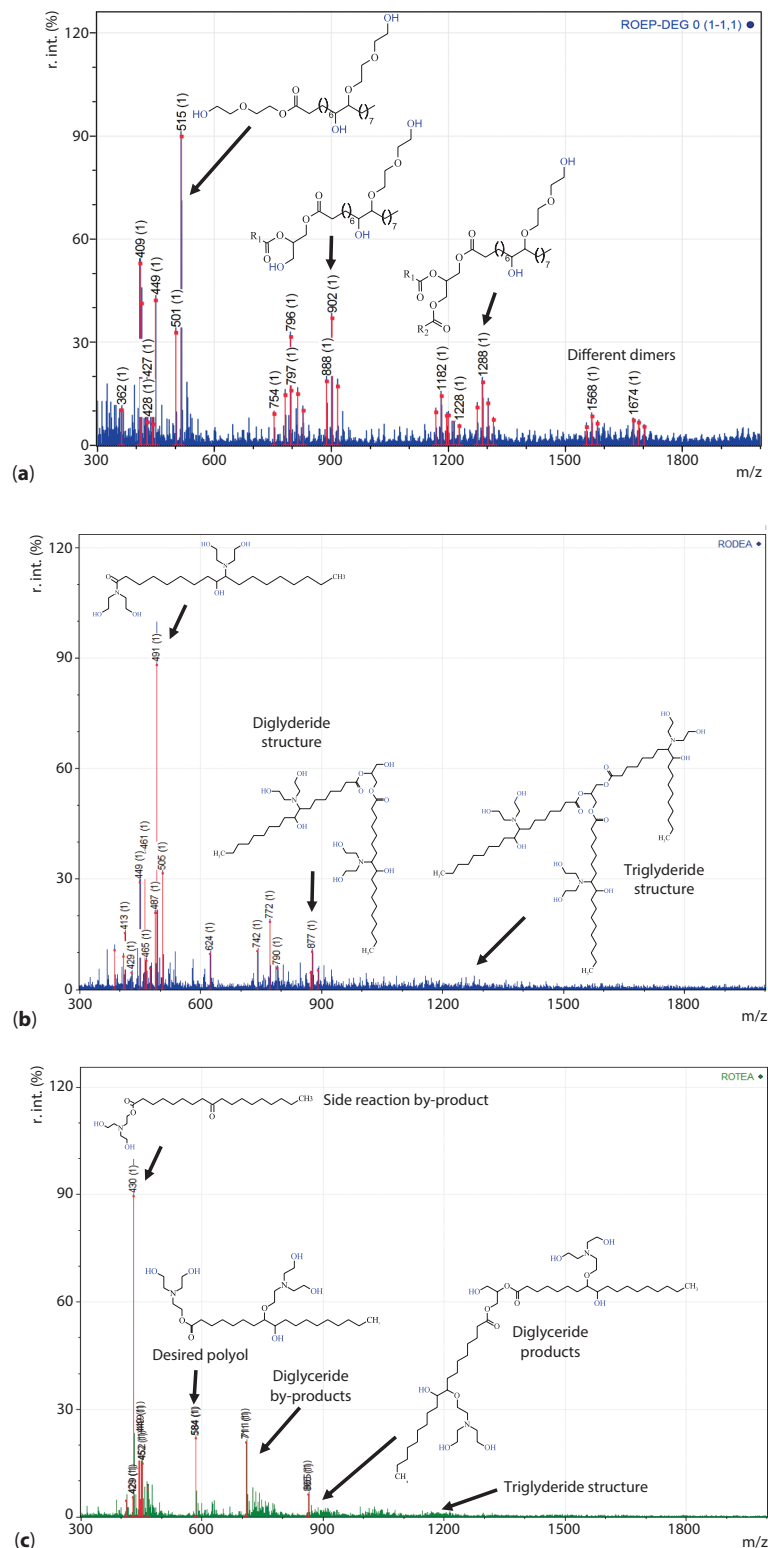


Figure 11 MALDI-TOF spectra of the (a) RODEG; (b) RODEA and (c) ROTEa polyols.

The PU samples were obtained at laboratory scale and only the most common characteristics of the thermal insulation material were tested and they are displayed in Table 3. Rigid PU foam samples

from all three polyols had very similar mechanical strength. The RODEA PU foam sample had the highest compression strength and modulus at 0.30 and 8.7 MPa respectively. The mechanical characteristics

Table 3 Mechanical and thermal insulation properties of developed rigid PU foams based on synthesized RO polyols.

Compression properties								
Polyol type	Compression modulus				Compression strength			
	Perpendicular to foaming direction (MPa)		Parallel to foaming direction (MPa)		Perpendicular to foaming direction (MPa)		Parallel to foaming direction (MPa)	
RODEG	2.2	±0.2	5.4	±0.2	0.11	±0.01	0.23	±0.01
RODEA	2.2	±0.1	8.7	±0.3	0.13	±0.01	0.30	±0.01
ROTEA	2.3	±0.2	4.3	±0.4	0.15	±0.01	0.24	±0.01
Thermal insulation properties								
Polyol type	Apparent density (kg/m ³)		Thermal conductivity, mW/m·K		Closed cell content %			
RODEG	36.3	±1.0	21.58		98			
RODEA	38.2	±2.2	23.47		95			
ROTEA	35.1	±1.3	23.29		93			

were normalized to an average PU foam density of 36.5 kg/m³ between all three samples according to Hawkins *et al.* [46] to be able to compare their properties. There was a slight difference between sample apparent densities as the PU foam formulation was not fully optimized for each new polyol. Nevertheless, 0.23 MPa compression strength is considered above industry requirements, especially if the rigid PU foam density is below 40 kg/m³. There was a difference between the properties of materials tested parallel and perpendicular to PU foaming direction because samples were prepared in an open-type mold.

All three samples had optimal thermal conductivity close to 22 mW/m·K, which is typical for this type of insulation material. Also, PU foams had fully closed cell structure with closed cell content above 90%. The high mechanical properties of RODEA are related to the chemical structure of this polyol and its high functionality of 4.6. The PU polymer matrix is most likely crosslinked and it contains a high amount of hard segments. However, the hard segment content and this polyol's influence on PU polymer matrix should be further studied.

4 CONCLUSIONS

This study showed that it is possible to obtain good quality polyols and rigid PU foams that are comparable to petrochemical materials and conventional biobased polyols. The temperature influence on the RO epoxidation process in the presence of solid phase ion exchange catalyst was studied and obtained results were comparable to the literature data of other natural oil epoxidations. Epoxidized RO was used to synthesize high functionality biobased polyols. All polyols showed average functionality up to PU

industry standards; RODEA and ROTEA had slightly higher functionality ($f_n = 4.6$ and 4.3) than RODEG ($f_n = 3.3$) polyol. The functionality of synthesized polyols correlated with MALDI-TOF analysis of synthesized bio-polyols. The obtained RODEA and ROTEA polyols had much higher reactivity than RODEG polyol due to tertiary amine groups confirmed by FTIR. Whereas in the case of RODEA polyol PU foam formulation, the catalyst content was decreased by half and in the case of ROTEA no PU foaming and curing catalyst was used compared to the formulation based on RODEG. This could be beneficial for PU foam producers as the catalysts are one of the more expensive components in PU foam formulations and are also usually hazardous and toxic compounds. RODEA and ROTEA polyols show promise for use as highly active crosslinking reagent and catalyst replacement. Upon studying the mechanical properties, an increase of compression strength was seen in the case of RODEA polyol over RODEG polyol. Further studies of developed PU polymer matrix should be carried out to analyze this polyol's influence on hard segment formation.

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