

Highly Functional Polyol Synthesis from Epoxidized Tall Oil Fatty Acids

Edgars Vanags*, Mikelis Kirpluks, Ugis Cabulis and Zuzana Walterova

Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006, Riga, Latvia

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ABSTRACT: In this work, free tall oil fatty acids were epoxidized with *in-situ* generated peroxyacetic acid. Reaction kinetics of epoxidation was investigated by oxirane content and iodine value titrimetric determination, as well as FTIR spectra analysis. A highly functional biobased polyol was synthesized by functionalizing epoxidized tall oil fatty acids with triethanolamine using *Montmorillonite K10* as a catalyst. The obtained polyol was analyzed by FTIR and MALDI-TOF MS. The most common chemical and physical characteristics of obtained polyol were determined.

KEYWORDS: Epoxidation, biobased polyol, ion-exchange resin catalyst, montmorillonite K10, tall oil fatty acids

1 INTRODUCTION

Plant oils have been one of the most important renewable feedstocks of the chemical industry in both the past and at the present time [1]. The demand to release the polymer industry from its close dependence on nonrenewable resources is an important environmental concern, pushing the search towards industrially applicable renewable alternatives. In that regard, plant oils offer many advantages and renewability. Their relatively low price makes them attractive and available for the industry. By modifying plant oils, it is possible to obtain a large variety of monomers and polymers [2].

One such valuable renewable source is tall oil fatty acids (TOFA), which are important renewable by-products of the kraft pulping process and are widely used for further processing into a variety of chemical products, such as adhesives, coatings, paints and varnishes, epoxy resins, lubricants, inks, *et cetera* [3–5], or rigid polyurethane foams [6, 7], not only as thermal insulation material, but also as a support for immobilization of lignin-degrading microorganisms [8]. TOFAs are a mixture of unsaturated free fatty acids which mainly consists of oleic (~50%) and linoleic (~45%) acids [3]. Relatively high unsaturation level makes TOFA an appropriate raw material for reactive

functional group introduction through C=C double bonds into the unsaturated hydrocarbon residues, thus making them a renewable feedstock for further polymer processing.

Plant oil double bond epoxidation has attracted a lot of attention and is considered to be an economical, environmentally friendly and non-noxious way to turn unsaturated plant oils into epoxides, which are easily convertible intermediates [9]. Epoxides have wide commercial use because of their varied chemical activity and have been used as raw materials for products such as alcohols, glycols, plasticizers, high-temperature lubricants, polyols and polymers like polyurethanes, polyesters and epoxy resins [10].

Various epoxidation methods of different kinds of plant oils, such as soybean [11], canola [12–14], mahua [15], castor [16], cottonseed [17], karanja [18], jatropha [19], wild safflower [20], grape seed [21] and others, have been reported. The most widely used method in these studies is triglyceride or methyl ester of fatty acids epoxidation with *in-situ* formed peroxy-carboxylic acid in the presence of an acidic catalyst, as shown in Figure 1. The method allows avoiding the use of pure peroxy-carboxylic acid in the epoxidation process. Combined with a strongly acidic ion exchange resin as a catalyst, which is considered to be a relatively mild acidic catalyst compared to mineral acids, could reduce the side reactions through oxirane rings during the epoxidation.

The main purpose of this study was to obtain a highly functional polyol from TOFA. The first step was to convert the C=C double bonds of the free TOFA into

*Corresponding author: edgarsvanags6@gmail.com

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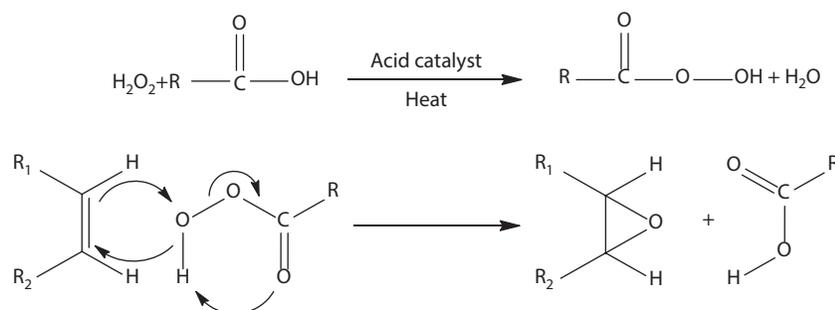


Figure 1 Reactions mechanism for epoxidation of C=C double bonds with *in-situ* formed peroxy-carboxylic acid.

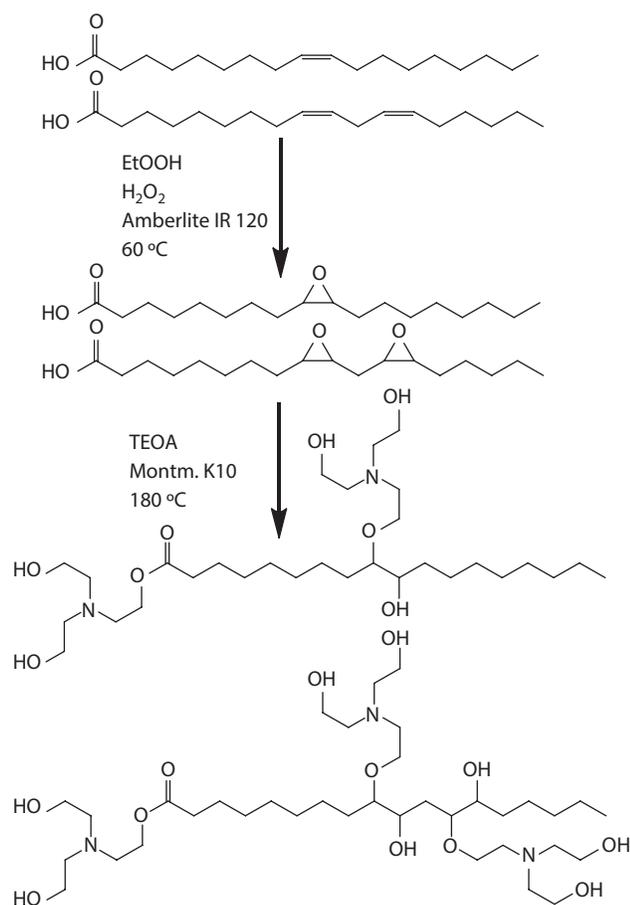


Figure 2 Idealized scheme of highly functional polyol synthesis from TOFA and TEOA.

oxirane rings without producing TOFA alkyl esters before epoxidation. The second step was to obtain a highly functional polyol from the epoxidized tall oil fatty acids (ETOFA) by opening the oxirane rings with triethanolamine (TEOA) in the presence of acidic clay *Montmorillonite K10*. The full scheme of the polyol synthesis is shown in Figure 2.

As potential benefits of the obtained polyol over conventional petrol-based polyols could be a relatively

high biocarbon content and high autocatalytic properties with isocyanates because of the tertiary amine groups included in the chemical structure of the polyol. The autocatalytic properties could help to significantly reduce the catalyst amount required in further steps of polyurethane processing.

2 EXPERIMENTAL

2.1 Materials

TOFA (trade name “for2”) with a high content of fatty acids (96%) and low content of rosin acids (1.9%) and unsaponifiables (1.8%) was ordered from Forchem Oyj, Finland. Hydrogen peroxide, purum p.a., $\geq 35\%$; glacial acetic acid (EtOOH), puriss, $\geq 99.8\%$; *Montmorillonite K10*, surface area 220–270 m² g; 4-(dimethylamino)pyridine (DMAP), reagent plus, $\geq 99\%$; acetylhydride, puriss, $\geq 99\%$; dichloromethane, puriss p.a., ACS reagent; ethyl acetate, puriss, 99.5%; *N,N*-dimethylformamide (DMF), ACS reagent, $\geq 99.8\%$; potassium hydroxide, puriss, $\geq 85\%$; potassium iodide, ACS reagent, $\geq 99\%$; tetraethylammonium bromide, reagent grade, 98%; perchloric acid, ACS reagent, 70%; and anhydrous sodium sulfate, puriss, $\geq 99.8\%$; were ordered from Sigma-Aldrich. TEOA, 99%, was ordered from BASF. *Amberlite IR-120*, strongly acidic, hydrogen form and sodium thiosulphate fixanal 0.1 M were ordered from Fluka.

2.2 Epoxidation and Characterization of TOFA

A 500 mL four-necked round-bottom flask was filled with TOFA (140 g, 0.869 mol of C=C double bonds, iodine value 157 g I₂ 100g⁻¹). The flask was placed in a thermostatic water bath at 40 °C and stirred at 600 rounds per minute (rpm) using an anchor-type polytetrafluoroethylene (PTFE) stirrer. Reflux condenser and thermocouple were attached to the necks of the flask. After 15 min of stirring, glacial acetic acid (26.1 g,

0.435 mol) and ion exchange resin *Amberlite IR-120* (28.0 g, 20% of the mass of TOFA) were added to the flask. The mixture was stirred for 30 min. Then, an aqueous solution of hydrogen peroxide (128 g, 1.30 mol, 35%) was added dropwise to the flask over a period of 30 minutes by using a dropping funnel, while reaction temperature of the mixture was gradually increased to 60 ± 1 °C and kept unchanged until the end of the synthesis. The moment when the last droplet of hydrogen peroxide solution was added to the reaction medium was considered to be the start time of the reaction. After the addition of hydrogen peroxide was completed, the reaction was continued for 6 hours. After that, the reaction mixture was filtered from ion exchange resin and poured into a 1 L separating funnel followed by the addition of 600 mL of ethyl acetate. The organic phase was recovered and rinsed 4 times with 300 mL of deionized water, dried over anhydrous sodium sulfate and concentrated in a rotatory evaporator at 60 °C up to 10 mbar vacuum. Ruby red, viscous product (ETOFA) was obtained and stored at 4 °C.

The samples of homogeneous reaction medium for kinetics measurements (7.5 mL) were periodically taken at 0, 15, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360 and 420 minutes and poured into a 100 mL separating funnel. Ethyl acetate (25 mL) and deionized water (20 mL) were added. The organic phase was recovered and rinsed 4 times with 20 mL of deionized water, dried over anhydrous sodium sulfate and concentrated in a rotatory evaporator at 60 °C up to 10 mbar vacuum. The samples were stored at 4 °C. The kinetics of epoxidation was further investigated by a titration of oxirane rings and iodine value, as well as by FTIR (Fourier transform infrared) spectra.

2.3 Synthesis and Characterization of ETOFA/TEOA Polyol

Previously obtained ETOFA was preheated to 60 °C and 130 g was poured into a dropping funnel. A four-necked round-bottom flask was filled with TEOA (82.4 g, 0.784 mol) and acidic clay *Montmorillonite K10* (2 g). The flask was placed in a silicone oil bath, heated to 180 °C and stirred at 400 rpm using an anchor-type PTFE stirrer. Capillary tube with argon, Liebig condenser, thermocouple and dropping funnel were attached to the necks of the flask. Then, melted ETOFA was added dropwise to the flask over a period of one hour. The reaction mixture was stirred for 5 more hours until the acid value of the mixture decreased below 5 mg KOH/g. A dark brown, viscous product was obtained.

The acid value of polyol was determined by dissolving samples (1–2 g) in neutralized methanol (50 mL). Solutions were titrated with 0.25 M KOH

standard solution in methanol. Cresol red was used as an indicator.

The iodine value of polyol was determined by the Hanus method. Samples of polyol (approx. 0.15 g) were dissolved in chloroform (10 mL) and Hanus solution (0.5 M IBr, 25 mL) was added. Samples were left in a dark place for exactly one hour for C=C double bond iodation. Deionized water (100 mL) and potassium iodide solution (15 mL, 15%) were added and thereafter samples were titrated with 0.1 M sodium thiosulfate standard solution.

Samples of polyol (0.3–0.4 g) were dissolved in 15 mL of 1% DMAP solution in DMF. Acetic anhydride solution in DMF (5 mL, 10%) was added. After 15 minutes of stirring, 1.5 mL of deionized water was added and stirring of the samples was continued for 12 minutes. The samples were titrated with 0.5 M standard solution of potassium hydroxide in methanol. Cresol red was used as an indicator.

Epoxide content was determined according to ASTM D1652-04.

Polyol density was determined by using a set of hydrometers. A graduated cylinder filled with polyol was immersed in a thermostatic bath at 25 °C. Density was measured 20 minutes after hydrometer immersion.

The viscosity of polyol was determined according to DIN 53015.

Moisture in polyol was determined by a Denver Instrument Model 275KF automatic titrator. A sample of polyol (~0.8 g) was taken with a syringe and weighted on analytical scales with an accuracy of 0.0001 g. The weight was entered in an automatic titrator. The polyol was injected into a titration cell. The syringe was weighted repeatedly and the weight was entered into an automatic titrator. The automatic titrator accomplished coulometric titration and the equivalence point was obtained. Results of measurements were calculated by an automatic titrator.

2.4 Polyol Analysis by FTIR and MALDI-TOF MS

Polyol structure was analyzed by Fourier transform infrared (FTIR) spectrometry data, which was obtained with a Thermo Scientific Nicolet iS50 spectrometer at a resolution of 4 cm⁻¹, 32 scans. The FTIR data were collected using attenuated total reflectance technique with ZnSe and diamond crystals.

The MALDI-TOF MS (matrix-assisted laser desorption/ionization time of flight mass spectrometry) was acquired with an Ultraflex instrument (Bruker Daltonics, Bremen, Germany) in positive ion reflection mode using delayed extraction. The spectra were

taken as the sum of 30000 shots with a DPSS Nd:YAG laser (355 nm, 1000 Hz). External calibration was used. The specimens were prepared by the dried drop-let method. The sample solution (10 mg/mL), DHB (2,5-Dihydroxybenzoic acid; 20 mg/mL) used as the matrix and sodium trifluoroacetate (NaCF_3COO ; 10 mg/mL) as a cationization agent in THF were mixed at a volume ratio of 4:20:1.1 μL . The mixture was deposited on the ground-steel target plate. The drop was dried under ambient atmosphere.

3 RESULTS AND DISCUSSION

3.1 Epoxidation of Unprotected TOFA

The first step of highly functional polyol synthesis was to find out how high oxirane content could be introduced into unprotected TOFA. The chosen method for epoxidation of unprotected TOFA has already been described in the literature as the epoxidation method of fatty acid esters and triglycerides [12].

Temperature, catalyst content and acetic acid content influence on C=C double bond conversion into oxirane rings were studied to find the most optimal synthesis conditions. The obtained data of the kinetics measurements from the oxirane content and iodine value analysis are collected in Figure 3. As can be seen, after 6 h of epoxidation the relative conversion to oxirane starts to decrease. The explanation could be that after 6 h the epoxidation process begins to become slower than the occurrence of side reactions through oxirane rings.

From the determined oxirane content, the percentage of relative conversion to oxirane was calculated by the following formula [20]:

$$\text{RCO} = \left[\frac{\text{OO}_{\text{ex}}}{\text{OO}_{\text{th}}} \right] \times 100 \quad (1)$$

where RCO is the relative conversion to oxirane, %; OO_{ex} is the experimentally determined content of oxirane oxygen, % and OO_{th} is the theoretical maximum oxirane % in 100 g of oil, which was calculated to be 9.02% using the following expression [20]:

$$\text{OO}_{\text{th}} = \left\{ \frac{(\text{IV}_0 / 2\text{Ai})}{100 + (\text{IV}_0 / 2\text{Ai}) \times \text{A}_o} \right\} \times \text{A}_o \times 100\% \quad (2)$$

where Ai (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 TOFA, $\text{g I}_2/100 \text{ g}$.

As depicted in Figure 3, the highest oxirane conversion (44%) was reached after 6 hours when C=C/EtOOH/ H_2O_2 ratio was 1/0.5/1.5 and the reaction temperature was maintained at $60 \pm 1 \text{ }^\circ\text{C}$. The result of this study of free TOFA kinetics research is similar to the results of those studies with triglyceride and methyl ester of fatty acid epoxidation [11–20]; the same circumstances and parameters give the highest oxirane conversion (Figure 5). The only difference is that the oxirane conversion is almost two times lower in the case of free fatty acids. It can be explained by the intensified occurrence of various side reactions

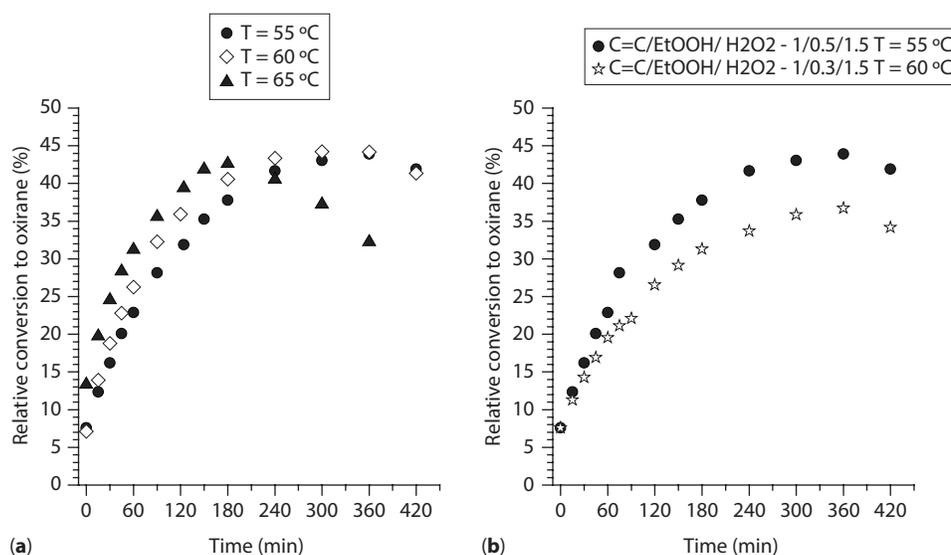


Figure 3 (a) Relative conversion to oxirane depending on temperature, where C=C/EtOOH/ H_2O_2 : 1/0.5/1.5. (b) Relative conversion to oxirane depending on EtOOH amount, where C=C/EtOOH/ H_2O_2 : ☆ – 1/0.5/1.5, 55 $^\circ\text{C}$; • – 1/0.3/1.5, 60 $^\circ\text{C}$.

through oxirane rings, especially the dimerization of epoxidized fatty acids with nucleophilic carboxylic groups of TOFA. Possible unwanted side reactions with epoxy rings are shown in Figure 4 [20].

From the iodine value kinetics investigation, it was determined that 81% of all C=C double bonds

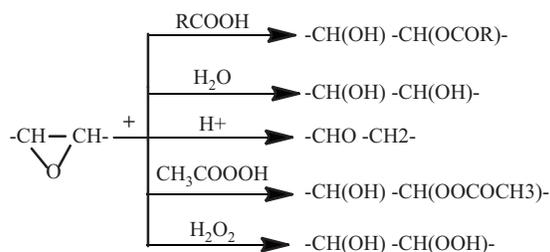


Figure 4 Possible side reactions of epoxide rings.

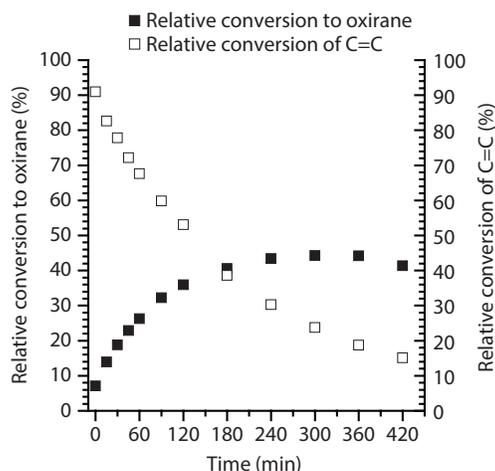


Figure 5 Oxirane (■) and C=C double bond (□) conversion during synthesis: C=C/EtOOH/ H₂O₂ = 1:0.5:1.5, 60 °C.

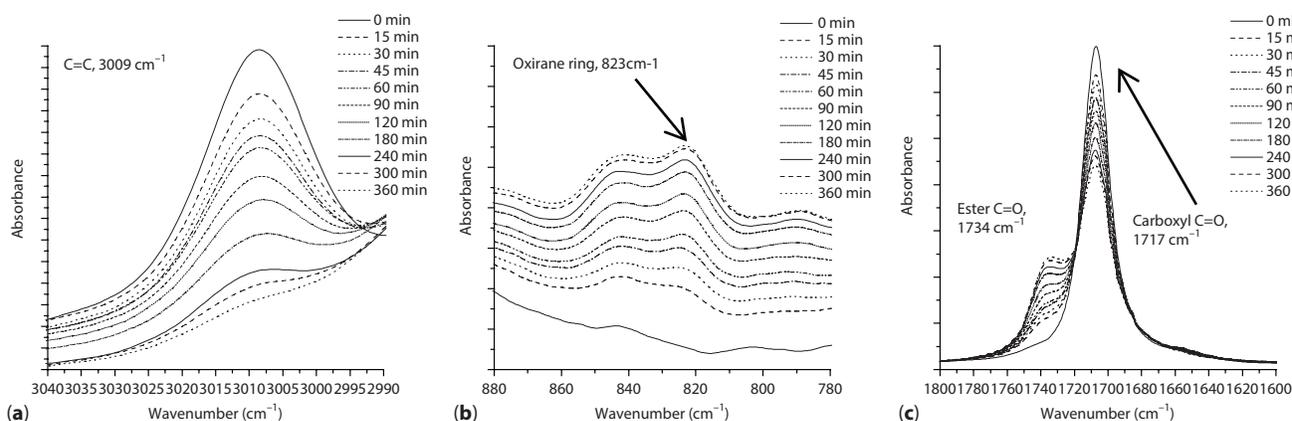


Figure 6 Stacked FTIR spectra plots showing change of: (a) C=C double bonds, (b) oxirane rings and (c) carboxyl group conversion to esters over epoxidation time, at 60 °C and a 0.5 molar ratio of acetic acid against C=C double bonds.

during the synthesis has been reacted after 6 hours (Figure 4).

Double bond epoxidation selectivity was calculated to be 54% after 6 h according to the following equation, where epoxidation selectivity is defined as the relative C=C double bond conversion to oxirane to the unsaturated bond conversion:

$$S = \frac{RCO}{UB_C} 100\% \quad (3)$$

where S is the selectivity, %; RCO is the relative conversion to oxirane, % and UB_C is unsaturated bond conversion, %.

The kinetics of TOFA epoxidation was investigated using FTIR spectra as well. The obtained data from the FTIR spectra of reaction kinetics are summarized in Figure 6. From the spectra, it is clearly visible that during the epoxidation process, the characteristic alkene C-H stretching vibration at 3009 cm⁻¹ is reduced with the time of synthesis, while characteristic oxirane ring vibration at 823 cm⁻¹ is increased. Also, the occurrence of side reactions is observable in the FTIR spectra. The absorbance, which is characteristic of carboxyl C=O stretching vibration of carboxylic acids at 1717 cm⁻¹ is decreased, while the absorbance characteristic of C=O stretching vibration of esters at 1734 cm⁻¹ is increased. FTIR results confirm that oxirane ring cleavage is occurring with the carboxyl groups of TOFA.

After optimal reaction conditions of TOFA epoxidation were determined, TOFA was epoxidized in larger amounts in a 2 L round-bottom flask. Iodine value, acid value and oxirane oxygen content of ETOFA were 28 g/100 g; 142 mg KOH/g and 3.98% respectively. Relative conversion to oxirane of the obtained ETOFA was 44%.

3.2 Results of Polyol Synthesis from ETOFA

The next step of highly functional polyol synthesis was ETOFA functionalization with TEOA. As a result, highly functional polyol ETOFA/TEOA was obtained. The idealized scheme of polyol synthesis is shown in Figure 2.

According to the literature source [22], the heterogeneous catalyst *Montmorillonite K10* is one of the most efficient heterogenic acidic catalysts for the oxirane ring cleavage due to its high oxirane ring opening catalyzing potential with hydroxyl and amine groups (up to 96%) under solvent-free conditions. The catalyst is environmentally friendly and is considered not to remarkably acidify the final product of the synthesis.

Montmorillonite K10 has also been used for the alcoholysis of epoxidized palm oil olein where the yield of final products (palm-based polyols) was more than 90% [23].

Montmorillonite K10 was chosen for this research as an acid catalyst for epoxide alcoholysis and aminolysis over conventional acid catalysts because of the superior advantages mentioned above.

3.3 Physical and Chemical Properties of Polyol

The most significant physical and chemical properties of ETOFA/TEOA polyol are summarized in Table 1.

As can be seen in Table 1, the polyol possesses high functionality and hydroxyl value, as well as relatively low viscosity compared to conventional crosslinking polyols. These parameters make the polyol suitable for rigid polyurethane processing.

3.4 Polyol Analysis by FTIR

The synthesized highly functional polyol ETOFA/TEOA was analyzed using FTIR absorption spectroscopy. The spectra of TOFA, ETOFA, and obtained polyol ETOFA/TEOA are shown in Figure 7.

Table 1 The properties of ETOFA/TEOA polyol.

Analyzed parameter	Value
Acid value, mg KOH/g	2.33 ± 0.13
Hydroxyl value, mg KOH/g	527 ± 2
Moisture, %	0.041 ± 0.004
Viscosity, Pa s	5.64 ± 0.04
Density, g cm ⁻³	1.047
Functionality	6.2
Average molecular weight, Da	649

By analyzing obtained FTIR spectra it is seen that various reactions have taken place. A broad and pronounced absorbance in the region between 3050–3600 cm⁻¹ with an absorption maximum at 3362 cm⁻¹ is characteristic of intermolecular hydrogen bond vibration and confirms the high content of hydroxyl groups in obtained ETOFA/TEOA polyol.

The disappearance of the characteristic intensive absorption peak of carboxyl group C=O stretching vibration at 1707 cm⁻¹ and appearance of the characteristic intensive absorption peak of ester group C=O stretching vibration at 1733 cm⁻¹ prove that during the synthesis of polyol, carboxylic groups are completely converted to ester groups.

Also, the disappearance of the characteristic absorption peak of oxirane ring vibration at 823 cm⁻¹ proves that oxirane rings are completely opened during the synthesis.

3.5 Polyol Analysis by MALDI-TOF MS

The MALDI-TOF MS technique was used for the average molecular weight and functionality determination of the synthesized polyol. Figure 8 shows the MALDI-TOF MS spectra of the obtained polyol. The given data provides information about the composition of the obtained polyol—it shows that the synthesized polyol is a mixture of various hydroxyl derivatives of fatty acids and its esters with triethanolamine with a wide scatter of molecular weight. Also, dimerization

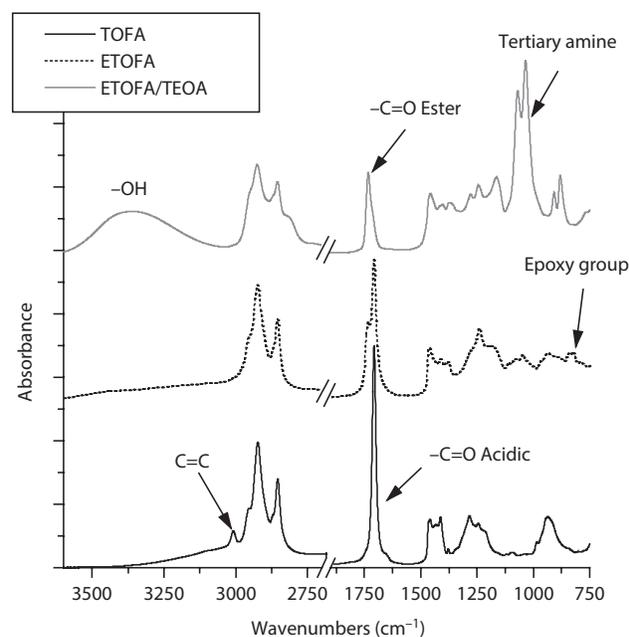


Figure 7 FTIR spectra of TOFA, ETOFA, and ETOFA/TEOA polyol.

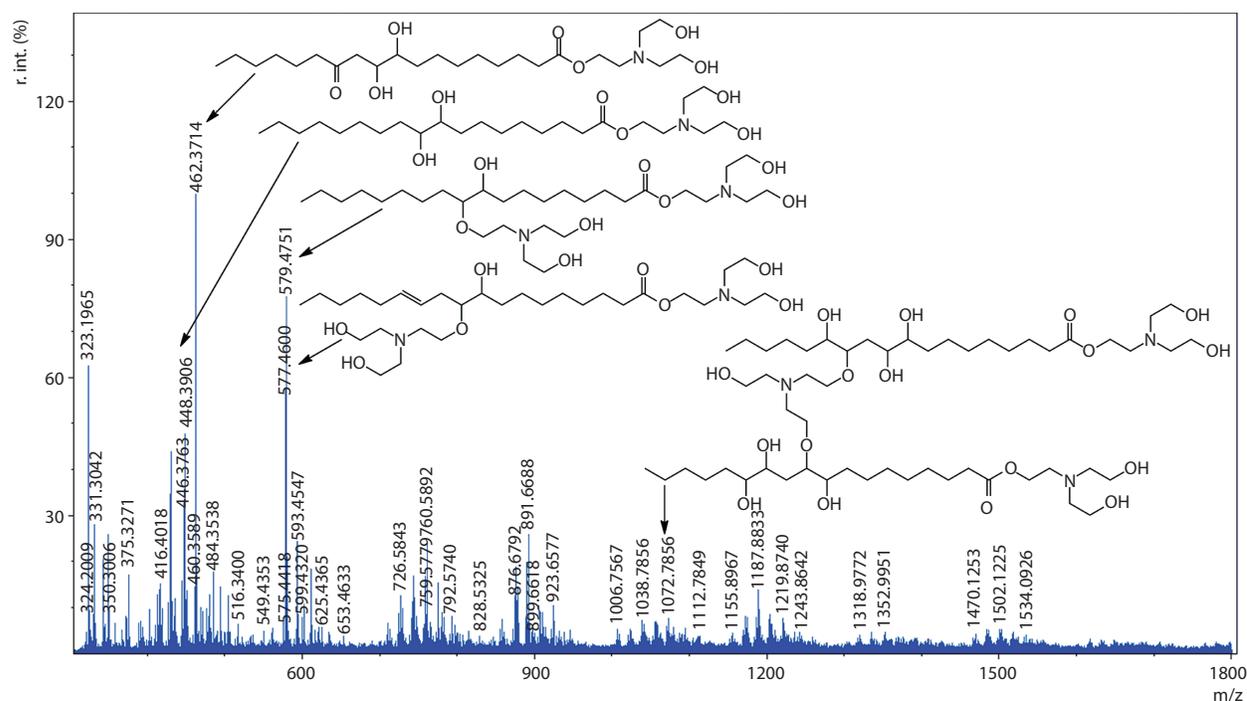


Figure 8 Positive ion MALDI-TOF MS spectra of ETOFA/TEOA polyol.

seems to occur. Wide scatter of molecular weight can be explained by various mutual reaction combinations of different types of fatty acids and their derivatives during the epoxidation and functionalization stages.

From the given MALDI-TOF MS spectra 80 different compounds were identified by the relevance of theoretical and determined molecular ion mass. Individual functionalities of these compounds vary from 2 up to 14 OH groups per molecule. Average functionality of ETOFA/TEOA polyol was estimated according to the following equation:

$$f = \sum \left(\frac{I_n}{\sum I_n} f_n \right); \quad (4)$$

where f is average functionality of polyol; I_n is signal intensity of identified compound; $\sum I_n$ is sum of all identified compound signal intensities; and f_n is functionality of an identified compound.

The average molecular weight of polyol was estimated according to the following equation:

$$M = \sum \left(\frac{I_n}{\sum I_n} M_n \right) \quad (5)$$

where M is average molecular weight of ETOFA/TEOA polyol, Da; and M_n is molecular weight of identified compound, Da.

Average molecular weight and functionality of ETOFA/TEOA polyol are summarized in Table 1.

4 CONCLUSIONS

The results of this work show that free tall oil fatty acids can be epoxidized with a relative conversion to oxirane of 44% and epoxidation selectivity of 56% using *in-situ* formed peracetic acid. The highest degree of epoxidation with 3.98% oxirane oxygen content was noted when the temperature of the reaction medium was 60 °C, the molar ratio of C=C/EtOOH/H₂O₂ was 1/0.5/1.5 and a catalyst (*Amberlite IR-120*) amount of 20% of TOFA.

The ETOFA was subsequently functionalized under solvent-free conditions with TEOA; acidic clay (*Montmorillonite K10*) was used as an oxirane ring opening catalyst. As a result, highly functional biobased polyol ETOFA/TEOA was obtained with an average functionality of 6.2, OH value of 527 ± 2 mg KOH/g, the viscosity of 5.64 ± 0.04 Pa s and average molecular weight of 649 Da. The synthesized polyol is an attractive intermediate for the polyurethane processing.

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