

## Review

# Advanced Methods for Hydroxylation of Vegetable Oils, Unsaturated Fatty Acids and Their Alkyl Esters

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**Abstract:** Vegetable oils and their derivatives have great potential as renewable and sustainable raw materials for the production of polyurethanes and bio-based polyols. For industry an important process is their modification. Chemical reactions that are carried out on vegetable oils and their derivatives are: transesterification, auto-oxidation, hydrogenation, epoxidation, hydroxylation, acrylation, isocyanation and others. One of the modifications are reactions performed on double bonds and/or carbonyl moieties of plants oils and their derivatives. These reactions result in products that are actively used as binders in coating materials due to their unique structural properties. In this manuscript, we describe important technological methods for the introduction of hydroxyl groups: opening of oxirane rings by nucleophilic reagents such as: water, alcohols, glycols, amino alcohols, carboxylic acids; direct hydroxylation of unsaturated bonds with carboxylic peracids in combination with hydrolysis of carboxyl groups and hydration; hydroformylation of unsaturated bonds with subsequent hydrogenation and alkoxylation; and ozonolysis of unsaturated bonds in combination with subsequent hydrogenation and alkoxylation.

**Keywords:** vegetable oils; hydroxylation; polyols



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## 1. Introduction

Triglycerides of vegetable oils, unsaturated fatty acids and their alkyl esters contain active sites which can be functionalized and used for polymerization using appropriate processes. The products indicated above can be modified: polymerization through autooxidation, chemical reactions and chemical reactions using their internal active sites. Built into double bonds enable the functionalization of these products through: epoxidation [1], hydroxylation [2], acrylation [3], maleinization [4], hydrogenation [5], halogenations [6], ozonolysis [7], dimerization [8] and metathesis [9]. Their derivatives have different physical properties depending on the aliphatic chain length and the distribution of unsaturated sites. Of the above methods, epoxidation and hydroxylation are the most common reactions involving double bonds in triglycerides of vegetable oils, unsaturated fatty acids and their alkyl esters.

Epoxidation of vegetable oils, unsaturated fatty acids and their alkyl esters have been carried out by many researchers in order to increase the epoxide yield and optimize the epoxidation reaction. Epoxidation can be carried out by several methods: the conventional method used in industry (Prileschajew) [10], catalytic epoxidation using acid ion exchange resin [11], chemoenzymatic epoxidation [12], epoxidation with phosphotungstate heteropolyacid catalysts and using the presence of phase-transfer catalysts [13], and metal-catalyzed epoxidation [14]. Epoxidized vegetable oils are increasingly available as raw materials for synthesis of polyols and can be substitutes for petrochemically derived raw materials in the production of polyurethane foams. Polyols are derived by oxirane ring opening reactions using a wide range of active hydrogen-containing compounds such as alcohols [15], inorganic and organic acids [16], water, hydrogen [17] and amines. The type

of reagent influences the content of  $-OH$  groups and the chemical nature of the polyol obtained, which may be a polyester or a polyether with hydroxyl groups. The epoxy ring opening is most often carried out with boiling methanol in the presence of tetrafluoroboric acid as a catalyst. The polyols resulting from epoxidation and subsequent epoxy ring opening contain predominantly secondary hydroxyl groups, which are much less reactive with isocyanates than primary hydroxyl groups. Additionally, the number of hydroxyl groups in polyols is considered as a parameter affecting the thermal and mechanical properties of polyurethanes [18]. Vegetable oils, with a high degree of unsaturation, subjected to hydroformylation and then hydrogenation, lead to polyols with a high content of  $OH$  groups. This results in an increase in crosslinking density of polyurethane (PU) chains, which may limit or prevent their use in flexible foams as in their use in flexible foams, which account for two thirds of all applications of polyurethanes.

## 2. Hydroxylation of Epoxide Vegetable Oils Using Glycols and Other Polyols

The method most often used for obtaining polyols is hydroxylation of epoxidized oils (soybean and rapeseed oils) by ethylene or diethylene glycol. This reaction permits formation of increased number of  $-OH$  groups, which is conducive to a higher rate of polyol reactions with diisocyanates in the process of polyurethane formation. The reaction is carried out in a simple reaction system. The reactor is charged with glycol in the equimolar amount with the number of epoxide groups in the oil and a catalyst. Very often a 95% sulfuric(VI) acid is used as a catalyst, in the amount of 1 g of the acid per 1 mol of epoxide groups. A high rate of the reaction is ensured by a temperature close to 110 °C. The reaction progress is controlled by determination of epoxy numbers in collected samples, previously neutralized by diethanolamine [19,20] and hydroxyl numbers [21].

The effect of the amount of the catalyst [20] on the rate of epoxide ring opening has been studied. Besides 95% sulfuric(VI) acid, also 85% phosphoric acid, *p*-toluenesulfonic acid and ice acetic acids were used as catalysts. In the presence of ice acetic acid, even at the molar ratio of 0.5 mol of ethylene glycol to 1 mol of epoxide groups in the oil, full conversion of the reactants was obtained. Apart from hydroxylation with glycol, subsequent reactions of earlier formed free hydroxyl groups from triacylglycerides with oxirane groups from neighboring chains took place in the system. The neighboring molecules of the products formed hydrogen bonds, which resulted in a significant increase in viscosity and molecular mass of the polyol.

The oxirane rings in epoxidized rapeseed oil were also subjected to hydroxylation of equimolar amount of diethylene glycol or resorcinol [22]. In order to shorten the time of syntheses, the reactions were carried out in the microwave radiation reactor. The obtained polyols of the hydroxyl number higher than 250 mg KOH/g were used for the production of rigid polyurethane foams. However, in the synthesis of polyurethane foams it is necessary to use polyols of lower hydroxyl numbers [23].

In a similar way, epoxidized soybean oil (85–90 wt.%) was hydroxylated with 1,2- and/or 1,3-propanediol (10–15 wt.%) in the presence of 0.2–0.5 wt.% of 84–86 wt.% phosphoric(V) acid as a catalyst [24]. The reaction was performed in a reactor with a reflux condenser at 105–135 °C, in the presence of neutral gas, for over 1 h, with continuous stirring. Hydroxylic derivatives of epoxidized oil obtained in the reaction with 1,2-propanediol were characterized by the hydroxyl number of 153 mg KOH/g and epoxy number of 0.379 mol/100 g. When the hydroxylation was performed in the presence of 1,3-propanediol, the hydroxyl number of the polyol was 199 mg KOH/g and the epoxide number was 0.366 mol/100 g. The hydroxylated soybean oil obtained was a high-quality reagent in the synthesis of polyurethane elastomers.

In view of its importance in production of polyurethanes, much attention has been paid to alcoholysis of epoxidized vegetable oils by other polyols than 1,3-propanediol [25]. At the first stage epoxidized vegetable oil was obtained. The epoxidation reaction was usually performed with the use of peracid formed in the reaction of a carboxylic acid (formic, acetic) with hydrogen peroxide. The epoxidized oil was washed with water in order to remove

carboxylic acid, residues of hydrogen peroxide and superacid, neutralized with a solution of sodium carbonate to pH of 6.5–7.5 and dried under vacuum. At the second stage of alcoholysis the epoxidized oil was reacted with polyol in the presence of a complex of  $\text{BF}_3$ -diethyl ether. The polyols obtained needed washing with water, neutralization to pH of 6.5–7.5 and drying.

In the process of alcoholysis the polyol and oxirane oxygen were used in equimolar amounts. To a reactor charged with epoxidized oil, a catalyst dissolved in alcohol was added in doses, after the oil had reached a temperature of 60 °C. When using a mixture of epoxidized soybean oil and palm oil and ethylene glycol, the polyols of the following properties were obtained: hydroxyl number of 70–90 mg KOH/g, acid number 0.3–1.0 mg KOH/g, moisture content below 0.05%, and viscosity below 600–800 cP at 25 °C. The aforementioned method can be applied to obtain polyols from other vegetable oils and polyhydroxide alcohols (glycerol, pentaerythritol, sorbitol, xylitol, glucose and fructose).

#### *Hydroxylation of Epoxidized Oils by Methanol and Water*

Another method for polyols synthesis is the reaction of epoxidized oil with methanol in the presence of fluoroboric acid ( $\text{HBF}_4$ ) as a catalyst [26–29]. This process is discussed on the example of hydroxylation of epoxidized soybean oil. Methanol reacts with oxirane rings and forces introduction of  $-\text{OH}$  and  $-\text{OCH}_3$  groups to this oil.

In a typical procedure, the organic layer formed after soybean oil epoxidation with acetic superacid, is introduced to a solution of methanol and water solution of fluoroboric acid as a catalyst. The reaction is carried out at 50 °C for 1 h. The polyol obtained at room temperature [30] was characterized by the hydroxyl number 110–213 mg KOH/g and viscosity 1000–7000 cP. The properties of the polyol obtained depend also on the type of superacid used for epoxidation (acetic or formic). The polyols obtained contain secondary  $-\text{OH}$ , however, they show excellent thermal resistance because they do not contain easily polymerizing double bonds and they permit high quality elastic polyurethane foams to be obtained. Because of the presence of ether bonds, they are classified as methyl esters of hydroxylated vegetable oils. The hydroxyl number of these polyols varies in the range 184–215 mg KOH/g, while their viscosity in the range 7200–10,400 cP at 25 °C.

A wide range of polyols was obtained as a result of hydroxylation of epoxidized vegetable oils: euphorbia, rapeseed, sunflower, beet and soybean. At the second stage of hydroxylation, the oxirane rings were opened by such nucleophilic agents as water, monoalcohols, diols, alkanolamines and amines [31]. The oxirane ring opening in the aforementioned epoxidized oils has also been performed in boiling methanol in the presence of fluoroboric acid as a catalyst. The polyols obtained were characterized by the hydroxyl number from 173.6 to 247.8 mg KOH/g and viscosity of 1850–18,200 cP at 27 °C [32]. The polyols suitable for production of polyurethanes have been also obtained on the basis of the earlier obtained epoxidized unsaturated fatty acids or their alkyl esters [33,34]. Epoxidation was carried out using hydrogen peroxide in the presence of metal catalysts (Mo or W), while the ring opening was achieved as a result of heating with water. Table 1 summarizes properties of epoxidized vegetable oils and oil-based polyols.

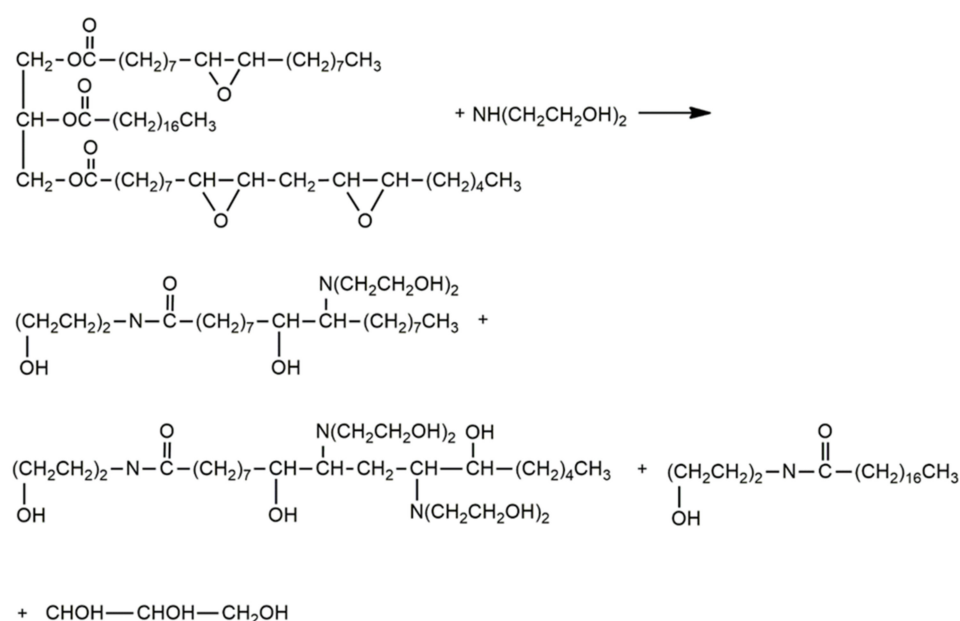
**Table 1.** Properties of epoxidized vegetable oils and oil-based polyols.

Oils	Epoxy Number [mol/100 g] or Epoxy Oxygen Content [%]	Used Catalyst	Epoxy Ring Opening Reagents	OH Values [mg KOH/g]	References
Soybean oil	0.353 <sup>a</sup>	H <sub>2</sub> SO <sub>4</sub>	Ethylene glycol	209.2	[19]
Soybean oil	0.379 <sup>a</sup>	H <sub>3</sub> PO <sub>4</sub>	1,2-propanediol	153	[23]
	0.366 <sup>a</sup>	H <sub>3</sub> PO <sub>4</sub>	1,3-propanediol	199	
Soybean and palm oil	2.02 <sup>b</sup>	Complex of BF <sub>3</sub> –diethyl ether	Ethylene glycol	70–90	[24]
Soybean oil	5.4 <sup>b</sup>	HBF <sub>4</sub>	Methanol	192	[25]
Soybean oil	-	HBF <sub>4</sub>	Methanol	184–215	[27]
Soybean oil	0.385 <sup>a</sup>	HBF <sub>4</sub>	Methanol	180.3	[28]
Soybean oil	7.0 <sup>b</sup>	HBF <sub>4</sub>	Methanol	110–213	[29]
Beet oil	5.95 <sup>b</sup>	H <sub>2</sub> SO <sub>4</sub>	Ethanol	144	[30]
Beet oil	5.95 <sup>b</sup>	H <sub>2</sub> SO <sub>4</sub>	n-Butanol	193	
Beet oil	5.95 <sup>b</sup>	H <sub>2</sub> SO <sub>4</sub>	Diethanolamine	462	
Canola oil	6.69 <sup>b</sup>	HBF <sub>4</sub>	Methanol	173.6	
Midoleic sunflower oil	6.32 <sup>b</sup>	HBF <sub>4</sub>	Methanol	163.5	[31]
Soybean oil	7.60 <sup>b</sup>	HBF <sub>4</sub>	Methanol	179.3	
Linseed oil	10.58 <sup>b</sup>	HBF <sub>4</sub>	Methanol	247.8	
Sunflower oil	7.82 <sup>b</sup>	HBF <sub>4</sub>	Methanol	177.8	
Corn oil	7.43 <sup>b</sup>	HBF <sub>4</sub>	Methanol	179.0	

Where: <sup>a</sup> means Epoxy Number [mol/100 g]; <sup>b</sup> means Epoxy Oxygen Content [%].

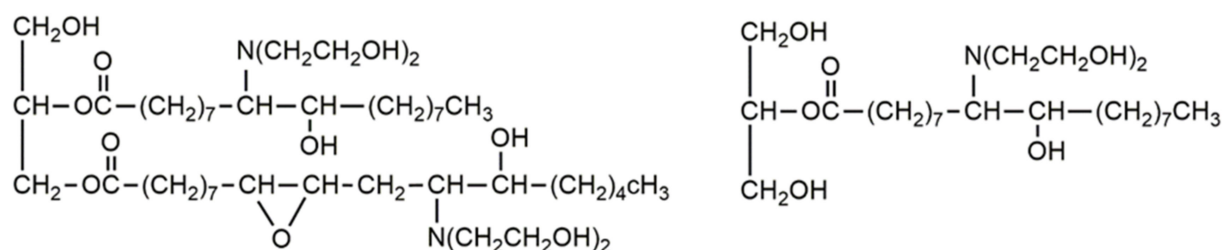
### 3. Hydroxylation of Epoxidized Oils with Alkanolamines

In this process the oxirane ring opening is realized by active hydrogen at the nitrogen atom in ethanolamine molecule and glyceride bonds undergo aminolysis. The polyols obtained by hydration of epoxidized vegetable oils with water, methanol or glycols, contain significant amounts of secondary hydroxyl groups, and their reactivity in the reactions with diisocyanates in the process of obtaining polyurethanes is much lower than that of the polyols of petrochemical origin. The reason is the fact that the latter contain a greater number of the more reactive primary hydroxyl groups [35]. An easy way to increase the number of primary hydroxyl groups in the polyols of vegetable origin was to react the epoxidized vegetable oil with diethanolamine. Thus the obtained polyols contain secondary and primary hydroxyl groups formed in the reaction of diethanolamine with oxirane rings and as a result of aminolysis of ester bonds (glyceride) in the epoxidized triglycerides. The main reactions of diethanolamine with oxirane rings and epoxidized glyceride groups in vegetable oils are presented in Figure 1.



**Figure 1.** Reactions of oxirane rings and epoxidized glyceride groups in vegetable oils with diethanolamine.

The reaction of secondary amine containing –OH groups (alkanolamine) with epoxidized oil makes it possible to obtain polyols more reactive than the conventional ones, by the way of opening of oxirane rings in the epoxidized glycerides using methanol, water or glycol. However, the product still contains secondary –OH, formed as a result of partial hydrolysis of glyceride groups (aminolysis) and a reaction of oxirane groups with diethanolamine. Selected products of partial aminolysis of glyceride groups and reaction of oxirane groups with diethanolamine are presented in Figure 2:

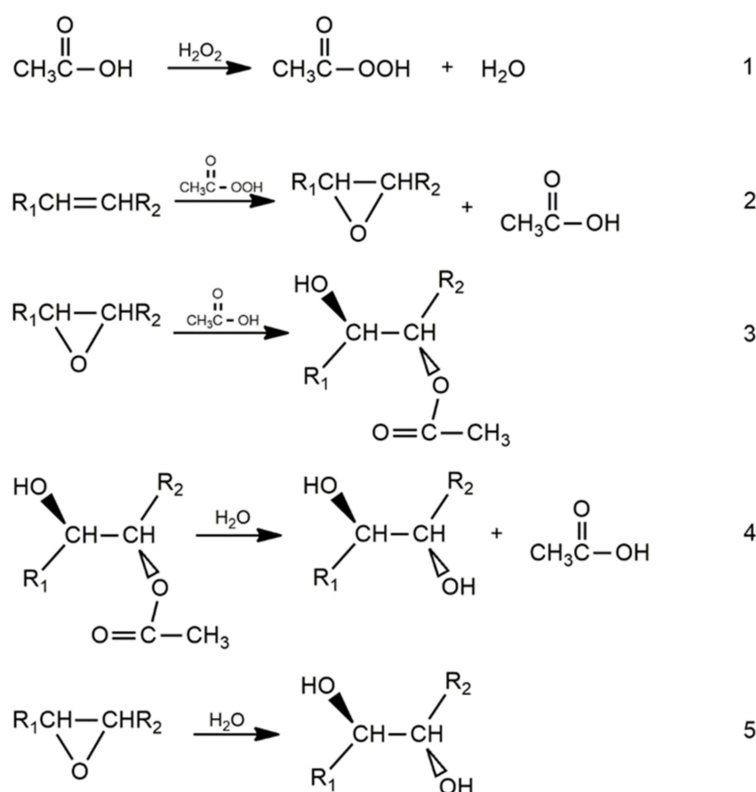


**Figure 2.** Selected products of partial aminolysis of glyceride groups (ester groups) and reaction of oxirane groups with diethanolamine.

#### *Aminolysis of Primary Polyols from Vegetable Oils with the Use of Hydroxyalkylamines*

The polyols obtained as a result of classical epoxidation and hydroxylation of oxirane rings (known as primary polyols) [19–38] are subjected to aminolysis by hydroxyalkylamines: (diethanolamine, 2-(ethylamino)ethanol)) in the presence of titanium (IV) 2-ethylhexoxide as a catalyst (0.1–0.2 wt.%) [38]. The ester bond in the primary polyols obtained undergoes aminolysis.

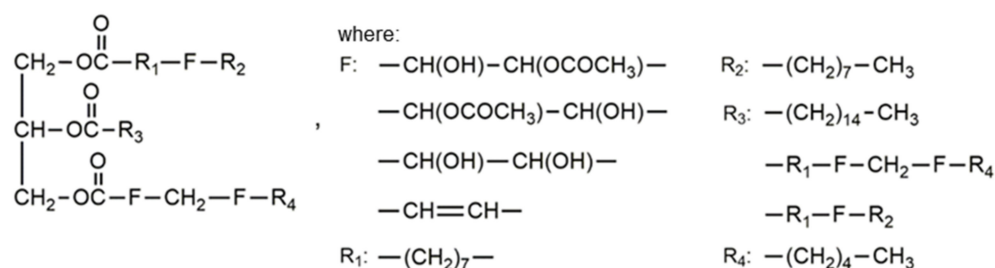
The reactions taking place in the process of obtaining primary polyols (epoxidation with carboxylic acid, water hydroxylation) are presented in Figure 3.



**Figure 3.** Reactions taking place in the process of synthesis of primary polyols (epoxidation with carboxylic acid, water hydroxylation).

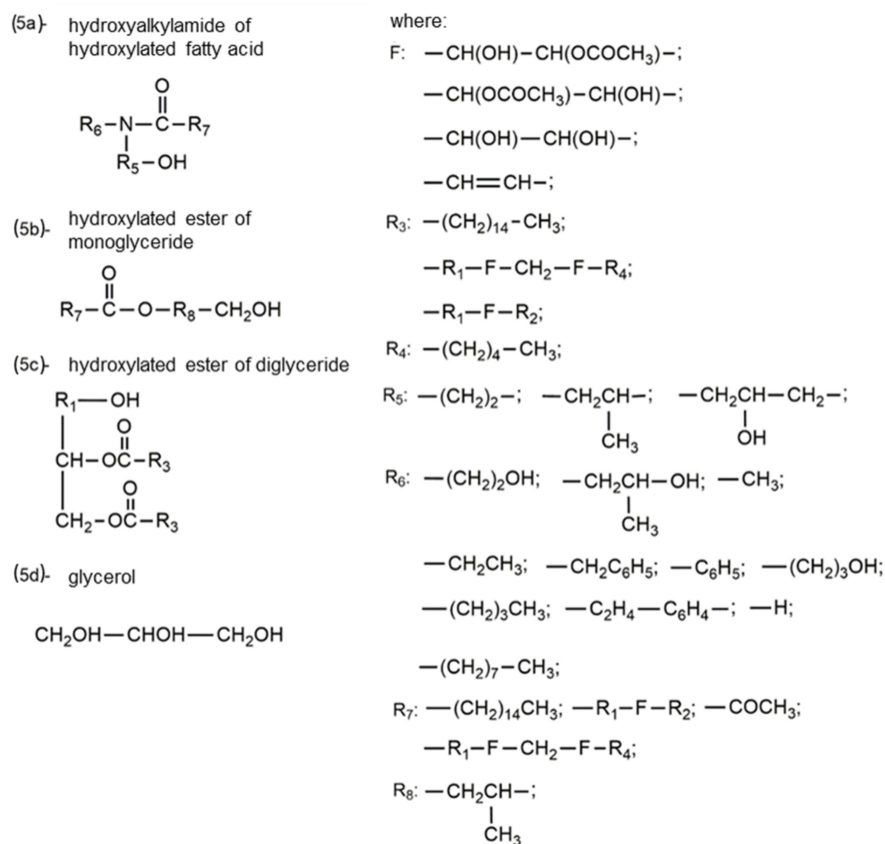
General structures of primary polyols obtained from vegetable oils are shown in Figure 4.





**Figure 4.** General structures of primary polyols obtained from vegetable oils.

The primary polyols from vegetable oils contain mainly secondary hydroxyl groups, localized near the center of the fatty acid chain [39]. These groups remain unchanged upon aminolysis with hydroxyalkylamines. The hydroxylalkylamides formed introduce additional hydroxyl groups, localized near the originally present ones. The secondary polyols obtained as a result of aminolysis are mixtures of four types of chemical compounds shown in Figure 5. The hydroxyl numbers and structures of hydroxyl groups in the secondary polyols depend on the ratio of the hydroxyl groups in the hydroxyalkylamines to those in the primary polyols and on the structures of the primary polyols and hydroxyalkylamine. A general chemical structure of hydroxylalkylamide of hydroxylated fatty acid is shown in Figure 5a, while a general structure of ester of hydroxylated monoglyceride is shown in Figure 5b, a general structure of ester of hydroxylated diglyceride is shown in Figure 5c and the structure of glycerol is shown in Figure 5d.



**Figure 5.** General chemical structures of secondary polyols, formed as a result of aminolysis of primary polyols with hydroxyalkylamines: hydroxylalkylamide of hydroxylated fatty acid (5a), ester of hydroxylated monoglyceride (5b), ester of hydroxylated diglyceride (5c) and glycerol (5d). R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> as in Figure 4.

The composition of secondary polyols beneficial for polyurethanes production [in wt.%] is the following: 51–84 hydroxyalkylamide of fatty acid, 13–31 hydroxylated ester of monoglyceride, 0–21 hydroxylated ester of diglyceride, 0–3 glycerol. The hydroxyl number of such a mixture is 240–450 mg KOH/g, and its viscosity is 260–6000 cP at 25 °C. The secondary polyols of such or similar properties are formed when using in aminolysis 9–36 wt.% of hydroxyalkylamines with respect to primary polyols. The primary polyols obtained from vegetable oils (epoxidation with acetic superacid, hydroxylation) were characterized by the hydroxyl number of 69–195 mg KOH/g, viscosity from the range 119–35,000 cP at 25 °C, acidic number below 10 mg KOH/g, iodine number of 5–115 g/100 g, average molecular mass of 1600–2200 g/mol and water solubility below 0.004 wt.%.

Aminolysis of primary polyols by diethanolamine was performed in a reactor equipped with a stirrer, at 140–150 °C, for 12–24 h [40]. The secondary polyols obtained were characterized by the hydroxyl number 240–539 mg KOH/g and viscosity 260–5530 cP at 25 °C. Very important for the character of the products is the type of hydroxyalkylamine used in the process of aminolysis. Many times the polyols obtained showed viscosity even below 260 cP at 25 °C. The primary, secondary, tertiary and cyclic hydroxyalkylamines have been used. The molecule of hydroxyalkylamine should contain at least one hydroxylic group and at least one secondary amine group. The molecular mass of hydroxyalkylamines used varied from 74 to 166 g/mol. The secondary polyols obtained showed greater reactivity in the reaction with diisocyanates and greater solubility in the reaction environment than the primary polyols. The polyurethanes obtained from secondary polyols were characterized by higher mechanical strength than those obtained from primary ones. The reactions were carried out in the presence of the following hydroxyalkylamines: methylaminoethanol, diethanolamine, 2-(ethylamine)ethanol, N-benzylethanolamine, 3-methylamine-1,2-propanediol, diisopropanolamine, 2-(butylamine)ethanol, 2-(tert-butylamine)ethanol, 2-(3-aminepropylamine)ethanol. The catalysts used in aminolysis of primary polyols included: ethanolate, isopropanolate, n-propanolate, and titanium(IV) n-butanolate. They were used in the amount from 0.05 to 0.20 wt.% with respect to the ester of hydroxylated vegetable oil. No waste products are formed in the process of aminolysis, while the side alcohols obtained (e.g., glycerol) remain in the product and react with diisocyanates in the process of polyurethane formation.

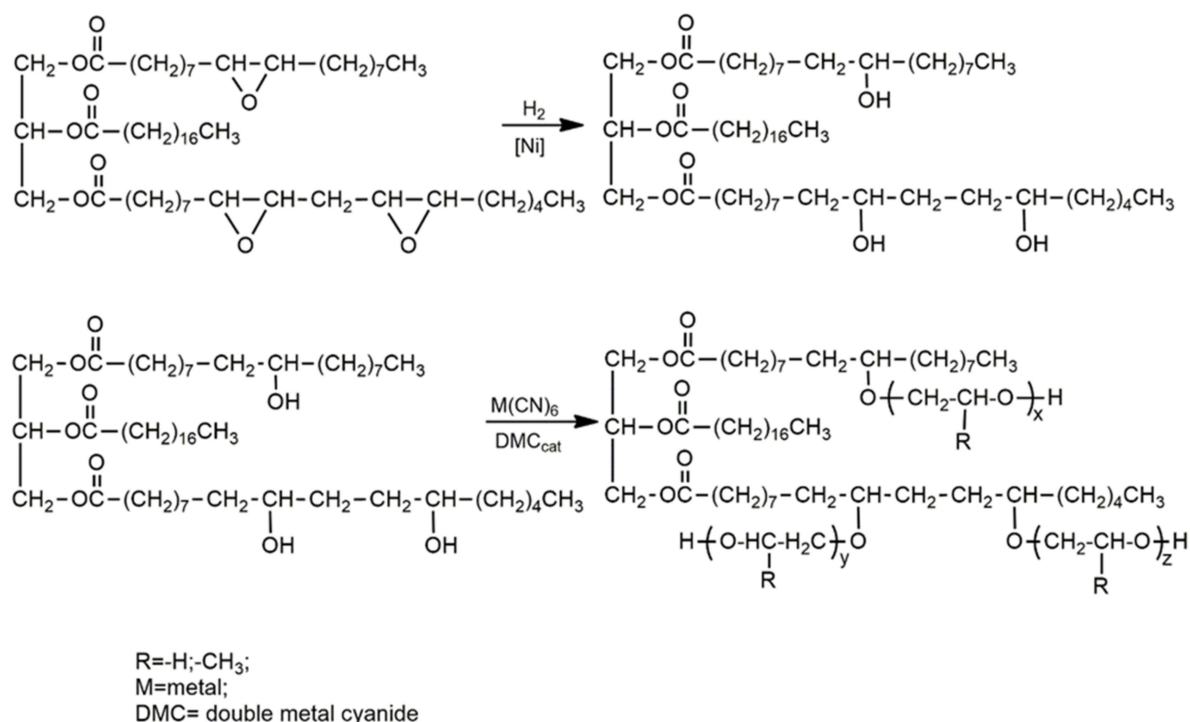
Results of a two-stage synthesis of polyols from rapeseed oil with the use of triethanolamine at the stage of aminolysis of primary polyols are reported in [41]. At the first stage rapeseed oil was epoxidized with performic acid obtained in situ in the reaction of hydrogen peroxide and formic acid. After over 10 h a full hydration of transient oxirane rings took place. Then, the organic layer containing the primary polyol and hydroxylated rapeseed oil of the hydroxyl number 100 mg KOH/g, acid number 5 mg KOH/g and viscosity of 400 cP at 25 °C, was separated. After washing and purification, hydroxylated rapeseed oil was subjected to aminolysis with triethanolamine in the presence of lithium hydroxide as a catalyst. The reaction was performed at 150 °C. As a result of aminolysis the hydroxyl number of polyols obtained increased to 367 mg KOH/g, the acid number was 0.14 mg KOH/g and viscosity was 1600 cP at 25 °C.

Similar multi-stage processes of obtaining secondary polyols with the use of amines and ethanolamines [38,42] of molecular mass below 175 g/mol and primary polyols coming from vegetable oils. According to one solution, the first stage was alcoholysis of rapeseed oil by a polyhydric alcohol in the presence of alkali metal hydroxides as catalysts. At the second stage, the monoesters of unsaturated fatty acids and polyhydric alcohols that were obtained were epoxidized by organic peracids. At the third stage the epoxide rings were opened in parallel with aminolysis with ethanolamines and amines. After each stage the organic layer was washed with water in order to purify the intermediate product. The final product was also purified to remove the residues of alcohols, carboxylic acid and hydrogen peroxide (left after epoxidation). The best products, i.e., those characterized by the high hydroxyl numbers, were obtained using the following tertiary amines: triisopropanolamine, triethanolamine, methyldiethanolamine, methyldiisopropanolamine.



#### 4. Alkoxylation of Secondary Hydroxyl Groups

One of the methods for increasing the number of hydroxyl groups, including primary ones, is the alkoxylation of secondary  $-OH$  groups in the primary polyols by ethylene or propylene oxide [39]. According to this method, the first stage is the hydrogenation of oxirane groups, while at the second stage the hydroxyl groups were ethoxylated or propoxylated with ethylene or propylene oxide in the presence of a metal cyanide as a catalyst. The best results were obtained in the presence of a complex catalyst made of zinc and cobalt cyanides, containing tert-butyl alcohol and propylene glycol, a DMC (double metal cyanide) catalyst. The course of the reaction is presented in Figure 6.



**Figure 6.** Introduction of primary  $-OH$  groups by alkoxylation of the originally  $-OH$  substituted secondary groups.

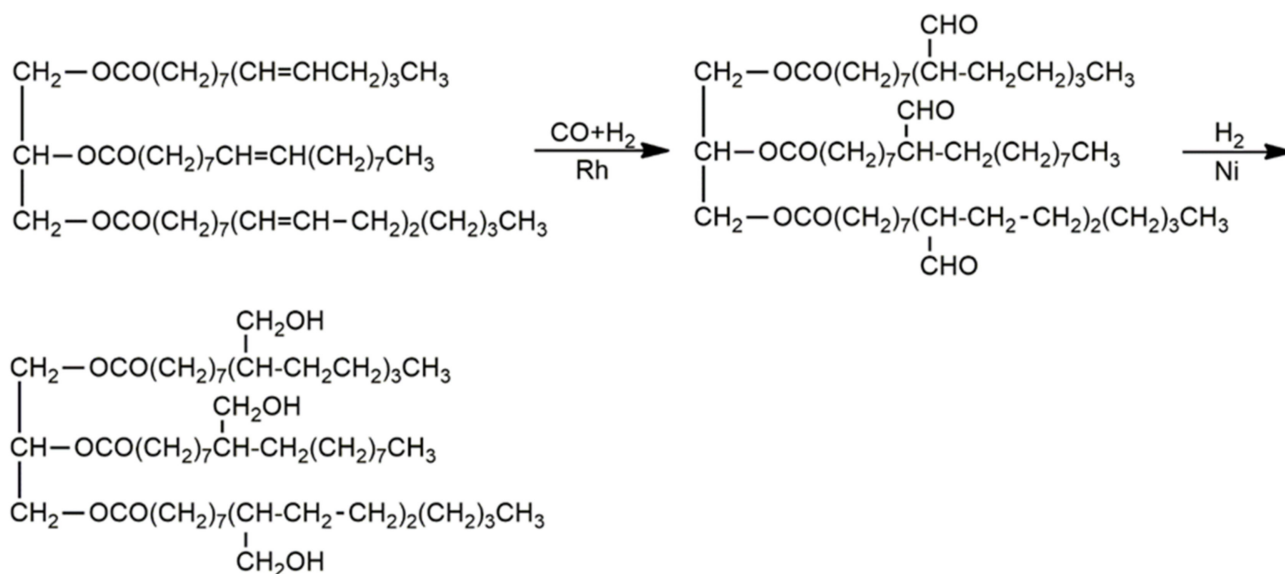
The polyols obtained were used in the production of rigid and flexible polyurethane foams. The content of bio-based carbon in these foams was close to 20%.

A general method for alkoxylation of hydroxylated vegetable oils has been presented in [40]. The polyols of triglycerides of soybean oil were obtained in the reaction of glycerides with carboxylic superacid in the presence of phosphoric acid as a catalyst. The addition of alkylene oxide was carried out in the presence of the complex catalyst composed of zinc and cobalt cyanides, tert-butyl alcohol and polypropylene glycol, a DMC (double metal cyanide) catalyst. In a typical solution [41] soybean oil hydroxylated with a superacid was dried by heating at 120 °C, then at least 2 moles of ethylene or propylene oxide per each hydroxyl group were introduced. The process of alkoxylation was run at 140–170 °C, at no more than about 75 psig pressure for at least 1 h. The average molecular mass of the polyol prior to alkoxylation was 1000–4000 g/mol and after alkoxylation it increased to 2500–8000 g/mol. The polyols obtained were used for production of rigid polyurethane foams.

##### 4.1. Polyol Synthesis by Hydroformylation of Vegetable Oils

In the process of hydroformylation of a vegetable oil, the double bonds  $-C=C-$  are replaced by the hydroxymethyl groups  $(-CH_2OH)$ , Figure 7. Initially the formyl groups  $(-CHO)$  are at these sites with a small contribution of hydroxymethyl ones. At the next stage the formyl groups are catalytically hydrogenated. The hydroformylation is performed

with the use of the synthesis gas  $-(\text{CO} + \text{H}_2)$  in the presence of rhodium catalyst. The hydrogenation needs the presence of a classical nickel catalyst.



**Figure 7.** Introduction of primary  $-\text{CH}_2\text{OH}$  groups by hydroformylation and hydrogenation.

A suitable raw product for obtaining hydroxyl derivatives to be used in production of polyurethanes are the mixtures of aldehydes and alcohols forming in the process of hydroformylation, transesterified vegetable oils (methyl esters of unsaturated fatty acids) [43–47]. A typical composition of the mixture after hydroformylation of these oils is (in wt.%): 10–95 monoformyl substituted fatty acid or alkyl ester of fatty acid or alkyl ester of fatty acid, 1–65 diformyl, 0.1–10 triformyl. The mass ratio of diformyl to triformyl structures should be 3:1. A mixture of alcohols obtained after hydrogenation of formyl substituents is composed of hydroxymethylated ( $-\text{CH}_2\text{OH}$ ) fatty acids containing [in wt.%] 10–95 mono(hydroxymethyl) acids, 1–65 di(hydroxymethyl) acids, 0.1–10 tri(hydroxymethyl) acids or alkyl esters of fatty acids of which less than 10 wt.% are unsaturated fatty acids. In some syntheses of elastic polyurethane foams, the oligomers of these polyols were used. The polyols of this structure do not contain the ether or ester bond, that is formed upon opening of oxirane ring with the use of alcohol or carboxylic acid. The above results have been obtained using the soybean, sunflower, rapeseed and flax oils.

#### 4.2. Obtaining of Polyols by Ozonolysis of Oils

Ozonolysis of the double bonds in triglycerides leads to formation of formyl groups  $-\text{CHO}$  in glyceride chains and aldehydes of smaller molecules. The molecular mass of so modified triacylglycerides is smaller than that of the initial glycerides. After hydrogenation of the  $-\text{CHO}$  groups, the hydroxymethyl groups  $-\text{CH}_2\text{OH}$  are the terminal ones of the carbon chains, so they are more reactive in the reaction with diisocyanates. One of the possible solutions is presented in Figure 8.

After distilling off the low-molecular aldehydes, the formyl groups are hydrogenated to the primary hydroxyl groups [48,49]. If the low-molecular aldehydes are left in the product subjected to hydrogenation, they will form low-molecular alcohols such as propanol, 1,3-propanediol, hexanol, nonanol and others. These compounds can also react with isocyanates, but they reduce the crosslinking of the final polyurethanes, slow-down the foam formation and speed-up polyurethane degradation. Prior to the distillation, the polyols are characterized by a too high acid number, above 10 mg/g. Besides the type of diisocyanate, the properties of the obtained polyurethanes depend on the number and position of hydroxyl group in polyols, the number of double bonds in them and the content of free fatty acids (acid number). The properties of polyurethanes obtained depend on the position of

–OH groups in the glyceride part of the polyol and the number of unreacted double bonds. The polyols obtained by ozonolysis have been applied in production of paints, lacquers and filling compounds. The hydroxyl groups in the polyols obtained by this method are less ordered than in the polyols of petrochemical origin, which disturbs the reproducibility of the polyurethanes produced with their use.

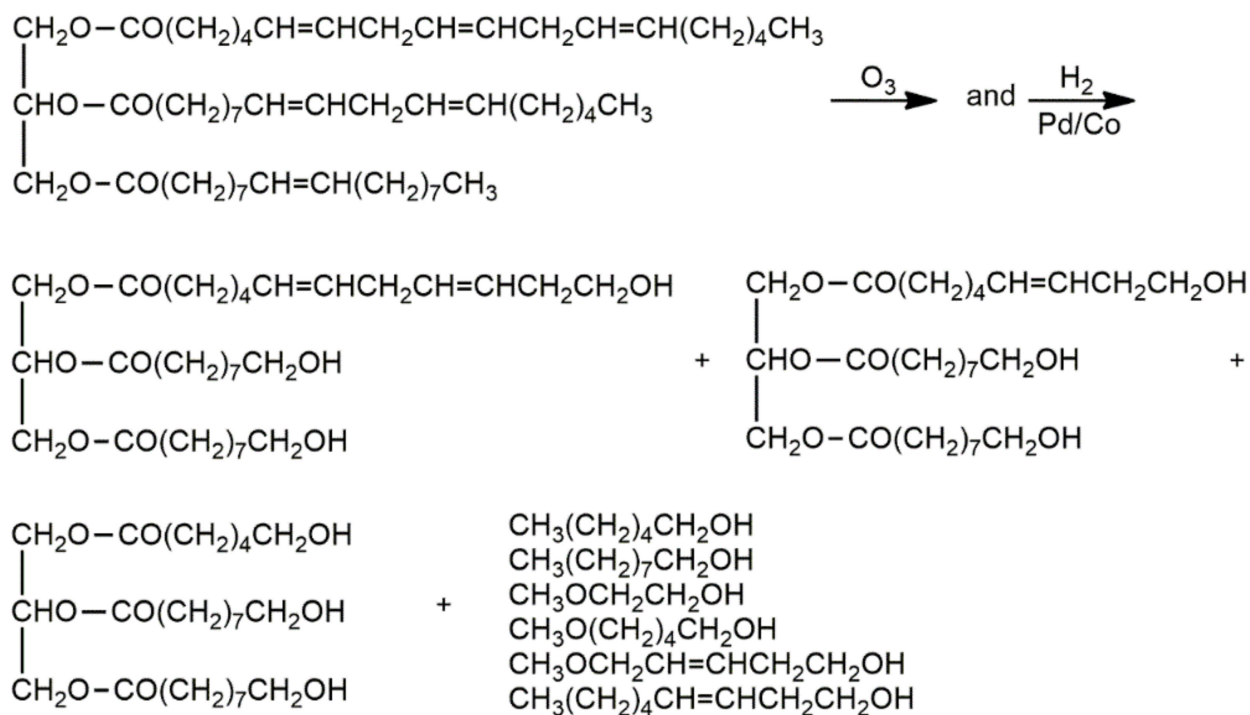
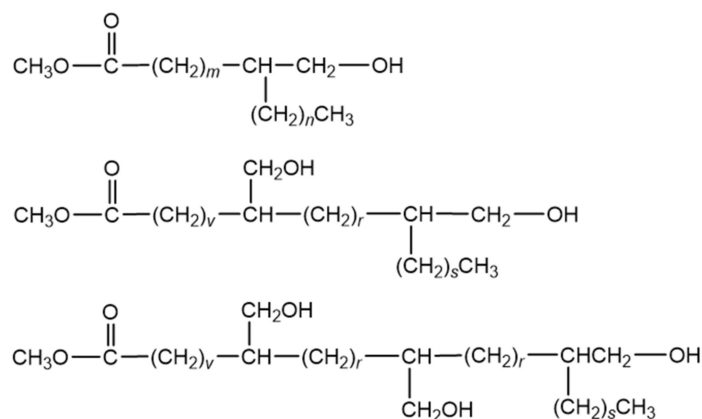


Figure 8. Preparation of polyols from vegetable oils by ozonolysis.

### 5. Polyols Attractive for Production of Polyurethane Resins

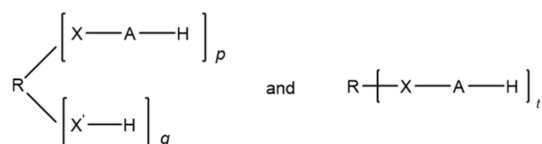
The polyols showing properties desirable for production of polyurethane resins are obtained in the reaction of an initiator with methyl esters of hydroxymethylated fatty acids, the vegetable oil-based monomers VOB) [50,51]. The initiator of the general formula  $\text{R}(\text{XH})_p$  has to contain at least one active hydrogen atom, capable of reacting with methyl esters of hydroxymethylated fatty acids. In this formula R stands for a linear or cyclic alkyl chain that may contain ethyl or ether bonds C–O–C, X stands for O, N or NH,  $p$  varies from 1 to 8. Exemplary initiators are polyols, polyamines, amino alcohols such as: ethylene glycol, 1,2-propylene glycol, neopentyl glycol, trimethylolpropane, 1,4-butanediol. The most important are: glycerol, pentaerythritol, sorbitol, saccharose, ethoxylated or propoxylated glycerol, ethoxylated or propoxylated pentaerythritol, diethanolamine. At least one hydroxyl or amine group should react with ethylene or propylene oxide with formation of ether polyols, e.g.,  $\text{R}(\text{OCH}_2\text{CH}_2\text{OH})_p$ ,  $p = 1-5$ . The structures of methyl esters of fatty acids (VOB) are presented in Figure 9a.

VOB monomers (methyl esters of hydroxymethylated fatty acids) are obtained by hydroformylation [38,52–55] of unsaturated fatty acids. Prior to polyaddition with diisocyanates they are subjected to hydrogenation and esterification with methanol. These semi-products are obtained upon alkaline hydrolysis of soybean, rapeseed, sunflower, castor and other oils with a water solution of NaOH. Then, the semi-product contains 70–90 wt.% of unsaturated fatty acids.

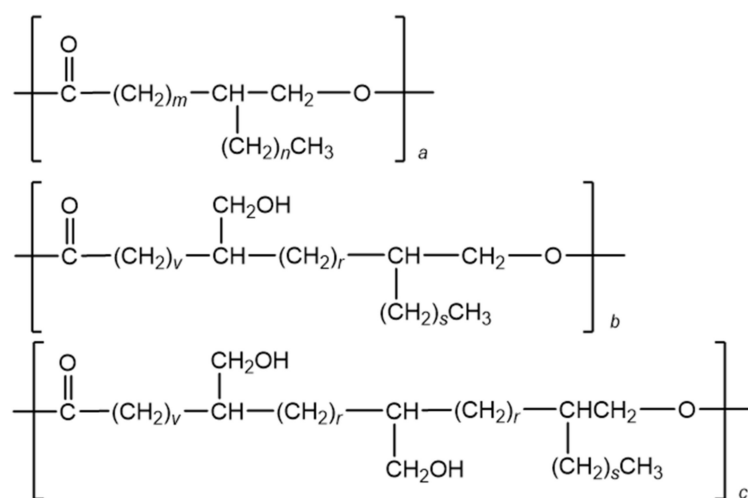


$m, n, v, r, s$  are integers,  $m > 3$ ,  $n = 0$  or greater,  $r = 0$  or greater,  $s = 0$  or greater,  $m + n = 11 - 19$ ,  $v$  is greater than 3,  $v + r + s = 10 - 18$

(a)



(b)



$a, b, c$  - are integers,  $a, b, c = 0 - 35$

(c)

**Figure 9.** (a). The methyl esters of hydroxymethylated fatty acid (VOB monomers) used in the preparation of new polyols, where:  $m, n, v, r, s$  are integers,  $m > 3$ ,  $n = 0$  or greater,  $r = 0$  or greater,  $s = 0$  or greater,  $m + n = 11-19$ ,  $v$  is greater than 3,  $v + r + s = 10-18$ . (b). Structure of vegetable oil based monomer (VOB), where R is the residue of a polyol, polyamine or amino alcohol, X and X' can be the same or different and stand for O, N or NH,  $p, q = 1-5$  is an integer,  $p + q + t = 3-8$ . A and A' can be the same or different and is selected from the groups shown in the (c). (c). Structure of vegetable oil based monomer (VOB), where:  $a, b, c = 0-35$  are integers;  $m, n, v, r, s$ , are integers;  $m$  is greater than 3;  $n, r$  and  $s$  is 0 or greater;  $m + n = 11-19$ ;  $v$  is greater than 3;  $v + r + s$  is from 10 to 18.

In a typical procedure for obtaining new polyols, the initiator and VOB monomers were mixed, volatile components were removed and the mixture was heated to the reaction temperature. After reaching it, a catalyst was introduced and the temperature was increased to about 210 °C, at the same time pressure was decreased to 6.8–27.2 at. The reactor contents were degassed upon heating at 50 °C under pressure of 27.2 and upon removal of methanol. The reaction was carried out for the time from 1 h to maximum 12 h. The following compounds were used as catalysts: tin octanoate (caprylate), dibutyltin(IV) dilaurate, tetraisopropoxy titanium(IV) and an enzyme (lipase). Tin or titanium catalysts were used in the amount 1000–1500 ppm relative to the total amount of the reaction mixture. The molar ratio of VOB monomers to the reactive groups of the initiator was 20, however, it can be lower. Moreover, an initiator can be a polyol that contains at least one reactive and unreacted group. Thus, the general structure of VOB polyol can be described by the formula presented in Figure 9b.

The polyols obtained in this way contain hydroxyl groups in a number required for the synthesis of elastic polyurethane foams and are characterized by appropriate molecular mass and viscosity.

## 6. Properties of Polyols and Their Application

The polyols of vegetable oil origin have been used for production of polyurethanes either alone or in mixtures with the polyols of petrochemical origin [45]. The polyols used for the production of polyurethanes to be used as elastomers, e.g., flexible foams, coatings, glues, are characterized by the hydroxyl number 60–200 mg KOH/g, maximum acid number of 2 mg KOH/g and maximum moisture content of 0.1% mass. Other compounds used in the process of production of such polyurethanes are catalysts, curing agents, adhesives, flame retardant, plasticizers, surfactants, pigments, dyes, water removing agents, cross-linking agents or acidity reducing agents. The properties of the polyurethanes produced on the basis of hydroxylated vegetable oils can be modified by introduction of acrylonitrile and methyl methacrylate with the polyols. The coatings obtained from such polyurethanes showed high resistance to scratching or impact and high flexibility [56]. Moreover, the polyurethane coatings obtained from polyols produced from castor, rapeseed and flax oils were transparent and showed luster [46,57].

The polyols of rapeseed oil origin showed properties needed to produce rigid polyurethane foams [58]. The physicochemical properties of such polyurethanes were the same as those of the reference foams obtained from polyols of petrochemical origin. The production of polyurethanes involved hydroxylation of rapeseed oil with formic superacid followed by aminolysis with triethanolamine. The polyol obtained showed the hydroxyl number of 367 mg KOH/g and viscosity of 1600 mPa·s. Introduction of boron ( $H_3BO_3$ ) into the polyols used for the synthesis of polyurethanes has significantly improved the physicochemical properties, thermal stability and structure of the coatings made from the polyurethanes [46,56,57]. These polyurethanes are characterized by very high resistance to alkaline media and provide excellent protection against corrosion. Boron in the process of their production acts as a modifier and a cross-linking agent. Another type of polyurethane coating, showing excellent properties such as high mechanical strength, high rigidity and low emission of organic volatiles [59], has been obtained on the basis of phosphate esters of polyols of flax oil origin [60].

The use of polyols obtained from vegetable oils in the production of polyurethanes increases their biodegradability [46,61–66]. The polyurethanes made on the basis of polyols of this origin are used for production of rigid and flexible polyurethane foams, coatings, glues, fillers, elastomers. The properties of polyurethanes depend on the number and positions of hydroxyl groups in the polyols, on the polyol stereochemistry, degree of unsaturation and conditions of syntheses. In the majority of polyols hydroxyl groups occur in the central part of the triester chain. That is why, upon curing of polyurethane, the long aliphatic chains make serious steric hindrances. For production of flexible polyurethane foams, usually the polyols of lower molecular masses and smaller viscosity are used.



Polyols are intermediate products in production of plasticizers of vinyl polychloride [67]. In this process also unsaturated fatty acids, their methyl esters or triglycerides of fatty acids (flax, castor, saffron oils) are used. These raw-products are subjected to hydroformylation, hydrogenation to polyols ( $\text{H}_2/\text{CuCrO}_3$ ) and acetylation with acetic anhydride. Thus the plasticizer obtained is introduced into the polymer in the amount of 32% mass. It shows good compatibility with the polymer and the final product was thermally stable at low and high temperatures, and characterized by low content of volatile products.

The polyols of natural origin are produced from widely available vegetable oils: soybean, rapeseed, flax, castor or oils of no nutrition value (jojoba, mahua) of the degree of unsaturation described by the iodine number 40–240  $\text{gI}_2/100 \text{ g}$ . The polyols of good thermal and mechanical properties are obtained from soybean oils in a single-stage process of epoxidation with formic superacid [68] followed by hydroxylation with the formed formic acid and water. The highest efficiency has been obtained at the molar ratio of soybean oil/double bonds/formic acid/ $\text{H}_2\text{O}_2$  of 1:3:1:5. Upon vigorous stirring, at room temperature, hydrogen peroxide was introduced to a mixture of soybean oil and formic acid. After completion of hydrogen peroxide addition, the temperature was increased to 65 °C and full hydroxylation took place. The progress of hydroxylation was regulated by changing the reaction time. After the preset time and cooling the post-reaction mixture to room temperature, the excess of hydrogen peroxide was removed with a 10% solution of sodium sulfate (IV). After addition of ethyl ether, the organic layer was neutralized with a 10% solution of sodium carbonate, dried ( $\text{Na}_2\text{SO}_4$ ) and ether was removed. The polyols obtained were characterized by the hydroxyl number of 53–162 mg KOH/g.

Of great importance in polyurethanes production are the polyols obtained in the autocatalytic reaction of epoxidized vegetable oil with diethanolamine or N-methylethanolamine. In a literature procedure, to a reactor containing epoxidized vegetable oil, at 110–130 °C alkanolamine was gradually introduced. The reaction was carried out for 2–6 h after completion of introduction of alkanolamine in the amount of 55–65 wt.% relative to the reaction mixture. From the post-reaction solution, the unreacted alkanolamine, glycerol and side products were distilled off at 160 °C and under pressure lower than 1 mmHg. The product was characterized by the hydroxyl number of 200–300 mg KOH/g and amine number of 1.5–3.5 mval/g [69,70].

Of similar importance in production of polyurethanes are the polyols obtained from vegetable oils (hydroxyl number 240–530 mg KOH/g, viscosity 200–5300 cP at 25 °C), in the reaction of primary polyols (epoxidation with carboxylic superacid, hydroxylation) with hydroxyalkylamines (usually with diethanolamine) of molecular mass lower than 200 g/mol [38,71]. In the solutions reported in literature, the primary polyols reacted with hydroxyalkylamine at 140–150 °C, for 3–24 h in the presence of titanium (IV) 2-ethylhexanolane as a catalyst. In the recently proposed processes, secondary polyols are produced by aminolysis of the primary polyols with hydroxyalkylamines. The product contains variable amounts (in wt.%) of hydroxyalkylamide of hydroxylated fatty acid 0–94, hydroxylated ester of monoglyceride 0–34, hydroxylated ester of diglyceride 0–60, glycerol 0–16, Figure 5. The polyglycols to be used for production of polyurethanes should contain the lowest possible number of unsaturated bonds and the highest possible number of the primary hydroxyl groups. The polyurethanes obtained on the basis of such polyglycols show better properties such as higher resistance to oxidation, exposure to elevated temperatures, the elements, higher resistance to scratching and good flexibility.

Bio-polyols obtained from epoxidized soybean and linseed oils and caprylic and 3-phenylbutyric acids by a solvent-free method using triethylamine (TEA) as an alkaline Lewis catalyst were characterized by narrow polydispersity (1.1–1.4) and relatively low molecular weights of 1600–2400 g/mol. They were used to prepare flexible polyurethane foams with open cell structure, which were characterized by slightly lower compressive deflection values than the reference foam [72].

Open-cell polyurethane foams were also obtained from polyols based on palm oil epoxides: refined, unrefined and reprocessed used frying oil. It was shown that the



addition of bio-polyols from unrefined oil and used frying oil had a favorable effect on the mechanical strength of the resulting foams [73].

In order to improve the mechanical properties, water resistance and thermal stability of PU based on epoxidized vegetable oils, nanofillers can be introduced into the system. For example, PU films prepared from epoxidized jatropha oil reacted with 4,4'-diphenylmethane diisocyanate, with the addition of cellulose fibres showed significantly enhanced mechanical properties [74].

Polyurethane based on rapeseed oil polyol with reduced graphene oxide functionalized with long-chain amines, exhibited significantly higher thermal stability and tensile strength, reduced moisture absorption and water vapor permeability, compared to unfilled PU [75].

One of the directions for the development of polyurethanes, aimed at reducing the use of volatile organic compounds in the synthesis of these polymers, are waterborne polyurethane dispersions for coating applications. An important raw material in such dispersions is castor oil, due to the presence of a hydroxyl group in the fatty chain. However, the low number of hydroxyl groups in this raw material resulted in the fact that, in order to obtain adequate mechanical and thermal properties of the final materials, coatings obtained on the basis of aqueous polyurethane dispersions were modified by adding a filler to the dispersion, which were, among others, microfibrils of modified cellulose [76] and sodium alginate [77].

Castor oil and polyols derived from ESO have been used to produce aqueous polyurethane dispersions, mainly for coating the surfaces of flammable materials such as wood, leather and fabrics to increase their flame retardancy. Flame retardancy was due to the incorporation into the structure of the polyurethane of [bis(2-hydroxyethyl)amino]-methylphosphonic acid dimethyl ester [78].

## 7. Conclusions

This review discussed a few ways for hydroxylation of vegetable oils, unsaturated fatty acids and their alkyl esters for the development of sustainable products. Vegetable oils, unsaturated fatty acids and their alkyl esters have great potential as renewable and sustainable raw materials for the production of polyurethanes and bio-based polyols. An important process for industry is their modification. One of the modifications are reactions performed on double bonds and/or carbonyl moieties of plants oils and their derivatives. Such modifications allow the synthesis of polyols with different properties, e.g.,: reactivity, functionally and molecular weight. Polyols are used to produce various polyurethane materials: elastomers, foams, coatings and rigid plastics. Vegetable oils and their derivatives with environmentally and industrially promising properties still face challenges such as technical and economic barriers to the production of flexible high resilience foams. A renewable raw material for polyols and polyurethanes is crude glycerol which is obtained as a by-product of the biodiesel industry. The disadvantage is the varied composition, which makes it difficult to obtain polyols with consistent quality and properties. This problem can be resolved by adjusting the composition of raw glycerol by adding either raw fatty acids or fatty acid methyl esters. Another challenge to obtain polyols and PUs with consistent properties is the diversity in the structure of vegetable oils and their derivatives. The competitiveness of such materials is not only due to the use of renewable raw materials, but many times comparable properties to or more beneficial than petrochemical polymer products that meet the requirements of various industries. Using bio-based raw materials to obtain various functional materials is an excellent approach to green chemistry. With such solutions, we are able to keep our environment clean and solve the problem of decreasing petroleum-based raw materials.

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