

Chapter 2

Polyols and Polyurethanes from Vegetable Oils and Their Derivatives

Abstract Vegetable oils and their derivatives have been widely used for the production of various polymers including polyols and polyurethanes. Vegetable oil derivatives, such as fatty acids, fatty acid esters, and crude glycerol, can be obtained via hydrolysis or transesterification of vegetable oils. Polyols and polyurethanes with properties comparable to those of petroleum-based analogs have been prepared from vegetable oils and their derivatives for various applications such as foams, coatings, adhesives, etc. This chapter reviews the structures and compositions of vegetable oils and their derivatives, synthetic methods of producing polyols from vegetable oils and their derivatives, properties of these polyols, and performance and applications of the resulting polyurethanes.

Keywords Bio-based polyols • Polyurethanes • Vegetable oils • Fatty acids • Fatty acid esters • Crude glycerol

2.1 Introduction

Vegetable oils are triglycerides, also known as triacylglycerols, which are triesters of glycerol and different fatty acids (Fig. 2.1). Depending on the origin and type of fatty acids in vegetable oils, the fatty acid side chains contain carbon numbers ranging from 8 to 24 and carbon-carbon double bond numbers from 0 to 5 [1], leading to high variability of vegetable oil compositions. As shown in Fig. 2.2, most vegetable oils consist of five major fatty acids: palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic acid (C18:3), in which for the (Cm:n) designation, Cm indicates the number of carbon atoms and n indicates the number of double bonds [1, 2]. According to the USDA-FAS (United State Department of Agriculture, Foreign Agricultural Service) [3], the annual world production of vegetable oils has been steadily increasing from around 148.8 MMT (million metric tons) in 2010/2011 to 170.9 MMT in 2013/2014. Palm, soybean, rapeseed, and sunflower seed are four predominant types of vegetable oil feedstocks, accounting for approximately 86 % of the global production of vegetable oils [3]. Figure 2.3

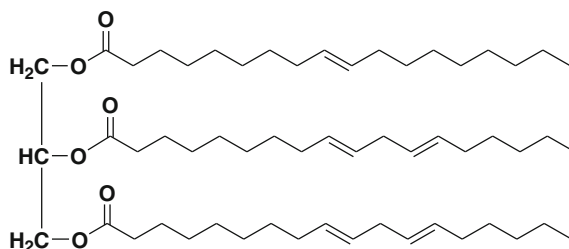


Fig. 2.1 Schematic representation of triglyceride structure of vegetable oils

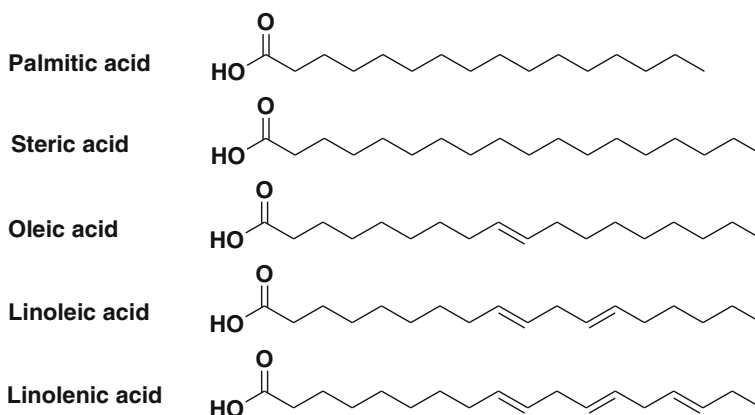


Fig. 2.2 Chemical structures of five major fatty acids found in vegetable oils

illustrates the 2013/2014 global annual production distributions of these major vegetable oils, and Table 2.1 shows the typical fatty acid profiles of vegetable oils.

Fatty acids, fatty acid esters, and glycerol are three different derivatives from vegetable oils. Fatty acids and fatty acid esters are usually produced by hydrolysis and transesterification of vegetable oils with water and alcohol, respectively. Scheme 2.1 shows schematic routes for the production of fatty acids and fatty acid esters from vegetable oils. Fatty acid methyl esters (i.e., biodiesel) are one type of important fatty acid ester and are obtained commercially by the transesterification of vegetable oils with methanol under the catalysis of sodium hydroxide or potassium hydroxide. Crude glycerol is a byproduct of the biodiesel production process. It is estimated that approximately 1 kg of crude glycerol is generated for every 10 kg biodiesel produced [5]. Compared to glycerol, crude glycerol has a significantly different composition and contains multiple impurities such as methanol, water, fatty acids, fatty acid methyl esters, soap, and glycerides [6]. The rapid growth in the production of biodiesel worldwide has generated large volumes of crude glycerol. Due to the high cost of refining it, especially for small- or medium-sized biodiesel producers [7], there has been extensive interest in the development of feasible biological or chemical approaches for converting low-value

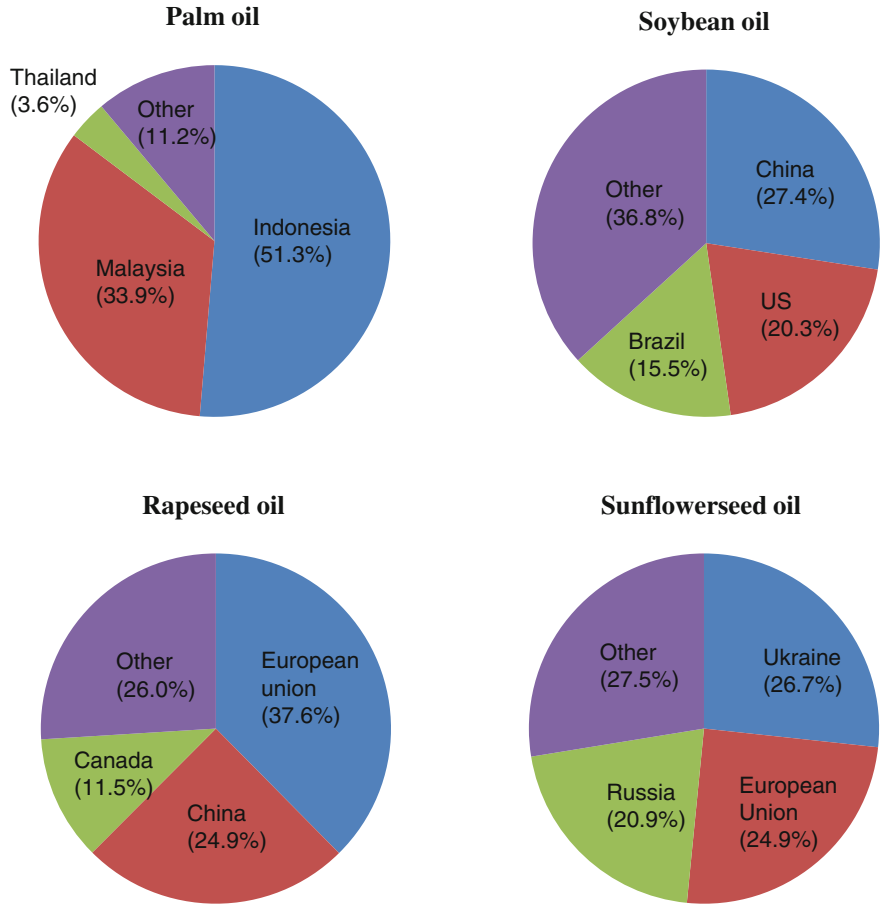


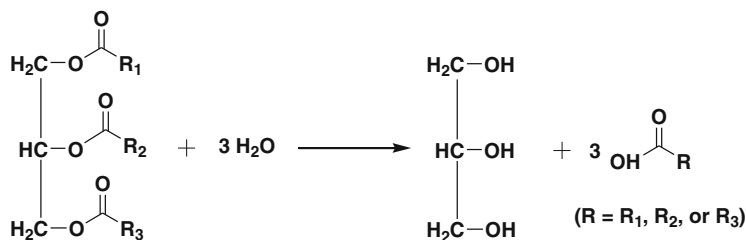
Fig. 2.3 Global annual production distributions (2013/2014) of palm oil, soybean oil, rapeseed oil, and sunflowerseed oil [3]

Table 2.1 Typical fatty acid profiles of major vegetable oils [1, 4]

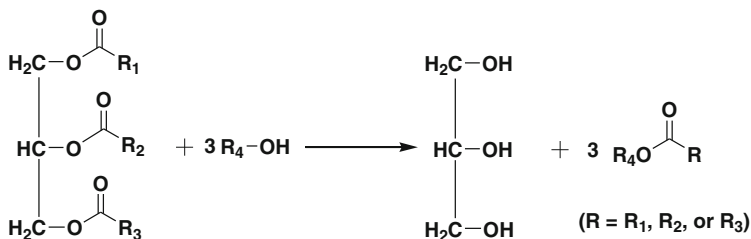
Vegetable oils	Fatty acid profiles (wt%)				
	C16:0	C18:0	C18:1	C18:2	C18:3
Palm oil	44.0	4.5	39.2	10.1	0.4
Soybean oil	11.3	3.4	23.1	55.8	6.4
Rapeseed oil	4.0	2.0	56.0	26.0	10.0
Sunflowerseed oil	5.9 (3.8) ^a	4.4 (4.1)	19 (78.4)	67.5 (11.3)	2.9 (trace)

^aValues in parenthesis are for high-oleic sunflowerseed oil

(a)



(b)



Scheme 2.1 Schematic routes for the production of fatty acids (a) and fatty acid esters (b) from vegetable oils (R_1 , R_2 , and R_3 are fatty acid chains and can be different or identical; R_4 is an alkyl group of an alcohol)

crude glycerol (approximately \$0.1/kg [5]) to value-added products, including polyols and polyurethanes (PUs) [8–12].

Natural vegetable oils, with the exception of castor and lesquerella oils, do not contain hydroxyl groups. When used as feedstocks for polyol production, vegetable oils are often chemically modified to introduce hydroxyl groups into their structures. Carbon-carbon double bonds and ester linkages are two major functional moieties present in structures of vegetable oils. Almost all synthetic routes for vegetable oil-based polyol production, including epoxidation followed by oxirane ring-opening, hydroformylation followed by hydrogenation, ozonolysis, thiol-ene coupling, transesterification, and amidation, start from one of these two functional moieties. Fatty acid esters and fatty acids have functional moieties similar to vegetable oils, such as carbon-carbon double bonds and ester linkages/carboxyl groups. The methods used for producing vegetable oil-based polyols can also be used to produce polyols from fatty acid esters or fatty acids. Besides these methods, other methods, such as dimerization of fatty acids and hydrosilylation of fatty acid esters, have been developed to functionalize fatty acids or fatty acid esters for polyol synthesis. The presence of multiple reactive components in crude glycerol allows for esterification and transesterification by which polyols can be produced for PU applications. This chapter mainly focuses on the methods commonly used for the preparation of polyols from vegetable oils and their derivatives such as fatty acids, fatty acid esters, and crude glycerol. The polyol properties and their derived PUs are also discussed.

2.2 Vegetable Oil-Based Polyols and Polyurethanes

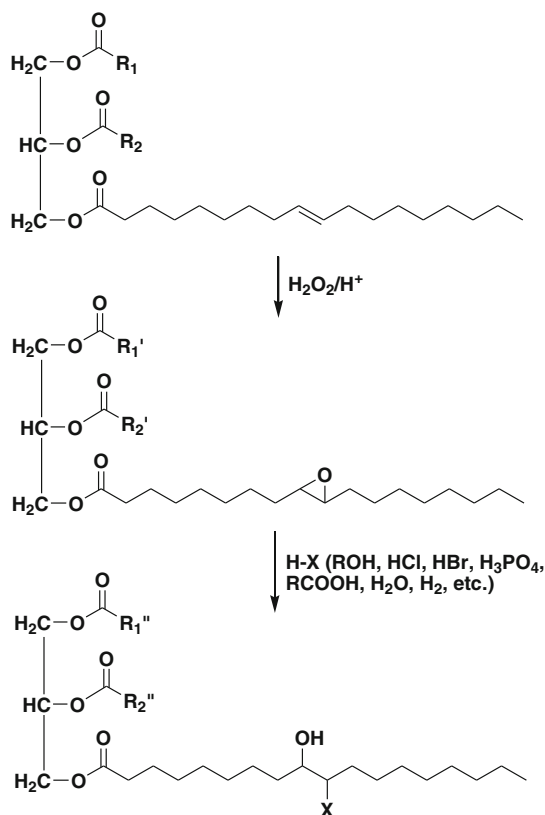
There are five different methods typically used to produce polyols from vegetable oils. These processes and the characteristics of the derived polyols and PUs are discussed in the following sections.

2.2.1 Epoxidation and Oxirane Ring-Opening Pathway

Epoxidation has been one of the most commonly used methods for the functionalization of carbon-carbon double bonds [13]. The epoxidation of vegetable oils can be conducted either in bulk or in solution with preformed or in situ prepared peracids, i.e. an active oxygen provider, under either homogenous or heterogeneous catalysis [14]. The epoxidation is usually conducted at a temperature between 30 and 80 °C for a reaction time of 10–20 h, depending on the types of feedstocks and ratios of reactants involved in the reaction. Under optimized conditions, conversion yields higher than 90 % can be achieved [15–17]. The undesirable side reactions of oxirane ring-opening during epoxidation can be largely minimized by conducting the reaction in a solution and at low temperature as well as under acidic ion exchange resin or lipase catalysis [14, 15, 18–21]. Polyols are produced from epoxidized vegetable oil by oxirane ring-opening reactions using a broad range of active hydrogen containing compounds such as alcohols, inorganic and organic acids, amines, water, and hydrogen [13, 19, 22–26]. A schematic representation of the production of polyols from vegetable oils by epoxidation followed by oxirane ring-opening is shown in Scheme 2.2. Usually, the epoxidation and ring-opening reactions are conducted in two separate steps, although a one-step process combining epoxidation and ring-opening reactions has been reported [27–29].

The properties of polyols produced by epoxidation and subsequent oxirane ring-opening depend on several production variables including feedstock characteristics and the types of ring-opening agents. Vegetable oils with a higher degree of unsaturation produce polyols with higher hydroxyl functionalities, resulting in PUs with higher crosslinking density and higher tensile strength [30]. Oxirane ring-opening agents are divided into three major categories: (a) **Alcohols**. When monoalcohols are used for ring-opening, each epoxy moiety only generates one secondary hydroxyl group, which are much less reactive than primary hydroxyl groups [31]. Methanol is the common choice of monoalcohols for ring-opening due to its low cost, low molecular weight, and low boiling point [1]. In order to produce polyols with higher functionalities and with primary hydroxyl groups, diols such as 1,2-propanediol and ethylene glycol have also been used for oxirane ring-opening reactions [22, 25]. However, the produced polyols tend to possess high viscosities due to their increased hydroxyl numbers. (b) **Acids**. Carboxylic acids such as formic and acetic acids have been used for ring-opening of epoxidized vegetable oils to produce polyester polyols, which have been shown to have potential for

Scheme 2.2 Production of vegetable oil-based polyols via epoxidation and oxirane ring-opening pathway (R_1 and R_2 are fatty acid side chains of vegetable oil; R_1' , R_2' , R_1'' , and R_2'' are modified fatty acid side chains of vegetable oil)



anti-wear applications [13, 26, 27]. Inorganic acids such as HCl , HBr , and H_3PO_4 have also been reported as ring-opening agents [23, 32]. Due to the incompatibility between inorganic acids and epoxidized vegetable oils, polar organic solvents such as acetone and *t*-butyl alcohol are typically added into the reactor to facilitate reactions. There are some drawbacks associated with the polyols from oxirane ring-opening reactions of epoxidized vegetable oils by inorganic acids. Polyols produced from oxirane ring-opening by HCl and HBr are waxes at room temperature [23], while those produced by H_3PO_4 contain significant fractions of oligomers because of the oligomerizations that occur between oxirane groups [32].

(c) **Hydrogen.** Polyols from ring-opening of epoxidized vegetable oils by hydrogen under Raney nickel catalysis are grease at room temperature, which has limited their applications in preparing PUs [23]. Table 2.2 lists properties of polyols produced from epoxidized soybean oil using different oxirane ring-opening agents.

Simultaneous oxirane ring-opening and transesterification [16] of epoxidized canola oil was achieved by using a strong acid catalyst (e.g., sulfuric acid) and excess amounts of diols (e.g., 1,2-propanediol or 1,3-propanediol). Because transesterification effectively removed the glycerol backbone from polyols, the

Table 2.2 Properties of polyols produced from epoxidized soybean oil using different oxirane ring-opening agents

Ring-opening agents	Polyol properties						References
	Hydroxyl number (mg KOH/g)	Hydroxyl group type	Acid number (mg KOH/g)	f_n^c	Viscosity (Pa.s)	Molecular weight (g/mol)	
Methanol	199	Secondary	— ^b	3.7	12 (25 °C) ^d	1053	[23]
	180	Secondary	—	—	0.6 (45 °C)	—	[22]
	148–174	Secondary	—	2.6–3.2	—	1001–1025 ^a	[25]
1,2-Ethanediol	253	Primary, secondary	—	—	1 (45 °C)	—	[22]
	187–226	Primary, secondary	—	3.4–4.2	—	1005–1038 ^a	[25]
1,2-Propanediol	289	Primary, secondary	—	—	1 (45 °C)	—	[22]
	211–237	Primary, secondary	—	3.8–4.6	—	1010–1084 ^a	[25]
Lactic acid	210 ^a	Secondary	—	4.2	—	1120	[19]
	171 ^a	Secondary	3.6	5.3	47 ^e	1738 ^a	[26]
Glycolic acid	203 ^a	Primary, secondary	2.6	4.9	221 ^e	1352 ^a	[26]
Acetic acid	188 ^a	Secondary	1.8	4.3	55 ^e	1281 ^a	[26]
Formic acid	104–162	Secondary	1.8–2.5	1.9–3.2	3–10 (30 °C)	1027–1086	[27]
Linoleic acid	76–112	Secondary	4–25	—	1.4–2.8 (22 °C)	—	[24]
Ricinoleic acid	152–163	Secondary	5–16	—	7.7–9.4 (22 °C)	—	[24]
Hydrochloric acid	197	Secondary	—	3.8	Grease ^f	1071	[23]
Hydrobromic acid	182	Secondary	—	4.1	Grease ^f	1274	[23]
Phosphoric acid	153–253	Secondary	1.4–48	12.8–17.5 ^a	3.2–5.3	3870–4700	[32]
Hydrogen	212–225	Secondary	—	3.5–3.8	Grease ^f	938–947	[23, 34]

^aCalculated values^bNot reported^cFunctionality^dTesting temperature^eTesting temperature not reported^fAt room temperature

produced polyols had lower molecular weights (ca. 433 g/mol) and viscosities (about 3 Pa.s), and higher hydroxyl numbers (about 270 and 320 mg KOH/g) than polyols obtained by oxirane ring-opening alone [16]. In a more recent study, polyols with similar properties have also been produced from epoxidized soybean oil through simultaneous ring-opening and amidation reactions [33].

Epoxidized polyols (polyols derived from epoxidation and subsequent oxirane ring-opening) have been used for the preparation of many PU products such as resins, foams, and coatings. By controlling factors such as vegetable oil composition, ring-opening agent, and degree of epoxidation, polyols and PUs with varying properties have been produced. A close relationship between the properties of epoxidized polyols from vegetable oils and their derived PUs has been observed: the higher the hydroxyl number and functionality of the polyol, the higher the crosslinking density, the T_g , and the tensile strength of the PUs [25, 30, 35]. Halogenated (e.g., chlorinated and brominated) PUs possessed higher mechanical properties, higher T_g , and lower linear thermal expansion coefficients than non-halogenated ones (e.g., methoxylated and hydrogenated PUs), which could be attributed to their stronger intermolecular attractions, higher crosslinking densities, and lower free volumes resulted from large halogen atoms; however, compared to non-halogenated PUs, halogenated ones showed lower thermal stability and higher initial weight loss as a result of the dissociation of bromine or chlorine [36]. The effects of the structural heterogeneity of vegetable oils on the properties of epoxidized polyols and PUs were evaluated by preparing polyols from soybean oil with different hydroxyl numbers via partial hydrogenation of epoxy rings [34]. The negative effects of structural heterogeneity on PU properties were found to be more pronounced for PUs with lower crosslinking densities produced from polyols with lower hydroxyl numbers. In addition, the properties of PUs can be manipulated by the NCO/OH ratio. In one typical study, PU networks ranging from elastomeric to glassy plastics were obtained for NCO/OH ratios ranging from 0.4 to 1.05 [37].

Rigid and flexible PU foams have been prepared from epoxidized polyols derived from vegetable oils such as soybean oil and rapeseed oil. Compared to petroleum-derived polyols that contain mostly primary hydroxyl groups, epoxidized polyols from vegetable oils have lower reactivity and need longer curing time when they react with isocyanates for PU foam production.

Several strategies, such as addition of a crosslinker [38], post-modifications by alcoholysis [29], and mixing with commercial petroleum-derived polyols [39, 40], have been developed to produce rigid PU foams from epoxidized polyols. In view of its high hydroxyl number (1829 mg KOH/g) and compact backbone, glycerol has been proven to be an excellent crosslinker to increase the rigidity of epoxidized polyol-based PU foams [38]. Under preferred glycerol addition (10–25 wt% of soy polyol) and optimized foam formulation conditions, the produced rigid PU foams exhibited mechanical and thermal-insulating properties comparable to analogues prepared from commercial polyether polyols. Applying triethanolamine-based alcoholysis to post-modify hydroxylated rapeseed oil effectively increased polyol hydroxyl numbers from 100 to 367 mg KOH/g, and the resulting PU foams showed very similar mechanical and thermal-insulating properties to those prepared from a

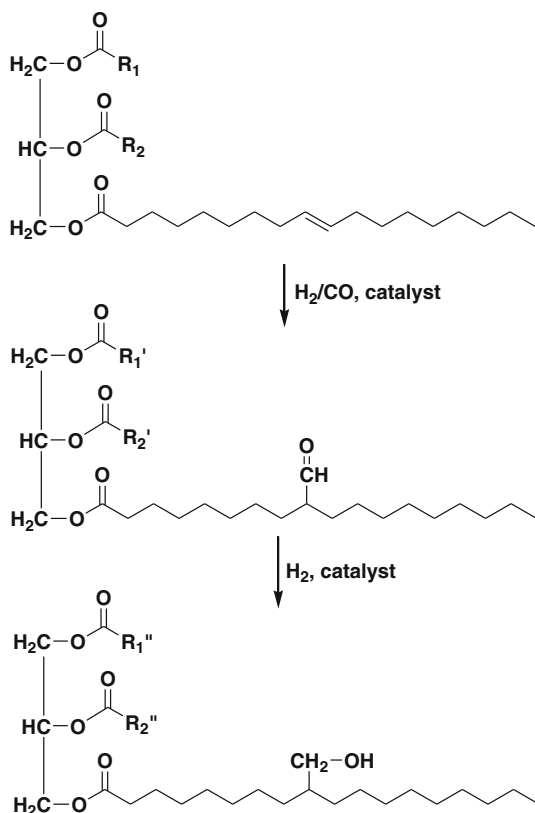
commercial petroleum-derived polyol [29]. Partial substitution of commercial petroleum-derived polyols by epoxidized polyols has been shown to be feasible for the production of high-quality rigid PU foams [39, 40]. Under optimal foaming conditions, PU foams produced with up to 50 % epoxidized polyol substitution possessed mechanical and thermal-insulating properties comparable with those based on 100 % petroleum-derived polyols [39, 40]. However, the epoxidized polyol-derived PU foams had the drawback of higher aging rates, i.e. an increase of thermal conductivity with time due to its higher N₂ permeation, than petroleum-derived foams, which may be alleviated by the addition of a crosslinker, such as glycerol [39]. Flexible PU foams from epoxidized polyols have also been prepared by this blending method. Mixing epoxidized polyols (up to 50 % by weight) with petroleum-derived polyols was found to increase the compressive strength and modulus of the resulting foams [41–45]. Several factors can contribute to this phenomenon including the existence of a high glass transition phase rich in vegetable oil-derived polyols, high hard segment concentration, and improved hard domain ordering in foam morphologies [43]. Flexible PU foams from epoxidized polyols also exhibited lower resilience values and higher hysteresis loss due to their decreased elasticity [45]. However, these issues may be alleviated through optimization of foaming formulations, which can be achieved by approaches such as controlling the amount and type of epoxidized polyols incorporated and the NCO/OH ratio [42, 44].

Waterborne PU dispersions, including anionic and cationic PU or hybrid dispersions, have been synthesized from methoxylated soybean oil polyols [46–51]. As the polyol functionality and/or hard segment increased, PU films exhibited increased crosslinking density, T_g , and tensile strength. By employing polyols with increasing functionalities ranging from 2.4 to 4.0, PU films ranged from elastomers to ductile plastics to rigid plastics [46, 49]. Urethane-acrylic and urethane-styrene-acrylic hybrid latexes have been prepared from soybean oil-based epoxidized polyols by emulsion polymerization [47, 50, 51]. Generally, these hybrid latex films showed improved tensile strength, Young's modulus, and thermal stability, compared to non-hybrid PU films [47, 50, 51].

2.2.2 *Hydroformylation and Hydrogenation Pathway*

Hydroformylation followed by hydrogenation is another important pathway for the preparation of vegetable oil-derived polyols. During preparation, double bonds in vegetable oil structures are first converted to aldehydes via catalyzed hydroformylation by syngas (typically a 1:1 mixture of CO and H₂), and then to hydroxyl groups via the hydrogenation of aldehyde (Scheme 2.3) [52, 53]. Rhodium- or cobalt- based catalysts are the common ones used for the hydroformylation of vegetable oils. Excellent double bond to aldehyde conversion yield (95 %) has been obtained using rhodium catalysts as compared to that of cobalt catalysts (67 %) [52]. However, rhodium catalysts are expensive and, when used as hydroformylation catalysts, the hydrogenation process

Scheme 2.3 Production of vegetable oil-based polyols via hydroformylation and hydrogenation pathway (R_1 and R_2 are fatty acid side chains of vegetable oil; R_1' , R_2' , R_1'' , and R_2'' are modified fatty acid side chains of vegetable oil)



that follows requires an additional Raney nickel catalyst. In contrast, cobalt catalysts are less expensive and capable of catalyzing both hydroformylation and hydrogenation reactions, but they require harsher reaction conditions [1, 52]. A comparison between rhodium- and cobalt- based catalysts revealed that polyols obtained from the rhodium catalyzed process exhibited higher hydroxyl numbers and higher functionalities than those from the cobalt catalyzed process [52]. As a result, rigid plastic-like PUs were produced from rhodium-derived polyols, while hard rubber-like PUs from cobalt-derived polyols [52]. The major advantage of the hydroformylation-hydrogenation process is the formation of primary hydroxyl groups, which are preferred to the secondary hydroxyl groups usually obtained from the epoxidation and oxirane ring-opening pathway. Consequently, polyols produced by the hydroformylation and hydrogenation pathway are more reactive than epoxidized polyols and a smaller amount of catalyst is required for their reactions with isocyanates [68].

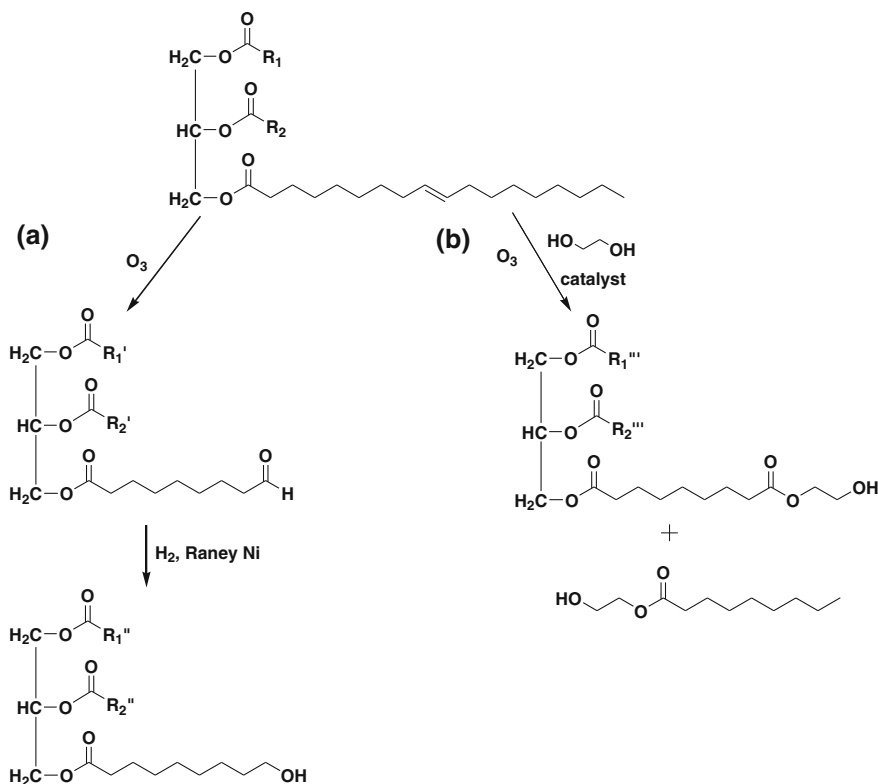
As only one hydroxyl group per carbon-carbon double bond is generated via hydroformylation and hydrogenation, the polyols have the same functionalities as the original vegetable oils. This makes the properties of polyols dependent on the compositions of the starting vegetable oils. In order to widen the structural and property versatility of polyols, other structural modifications have been introduced in

combination with hydroformylation and hydrogenation, such as methanolysis and polycondensation by which hyperbranched polyols with high molecular weights and functionalities [54] and triols with high molecular weights [55] were prepared.

When reacted with isocyanates for PUs, hydroformylated polyols (polyols derived via the hydroformylation and hydrogenation pathway) showed shorter gel time and better curing efficiency, compared to epoxidized polyols [56]. PU foams with enhanced rigidity can be produced from hydroformylated polyols when mixed with a crosslinker such as glycerol [56]. The effects of structural heterogeneity on the properties of hydroformylation-derived PUs have also been evaluated [53]. In one study, a commercial soybean oil-based hydroformylated polyol (hydroxyl number: 236 mg KOH/g) was partially esterified at different extents by formic acid to prepare a group of polyester polyols with hydroxyl numbers varying from 86 to 236 mg KOH/g [53]. PUs prepared from polyols with hydroxyl numbers larger than 200 mg KOH/g were glassy materials possessing high T_g and high crosslinking densities, and their properties were not negatively affected by the heterogeneity of polyol functionalities. In contrast, PUs obtained from polyols with hydroxyl numbers less than 200 mg KOH/g were rubbery materials with low T_g and crosslinking densities. The heterogeneity of polyol functionalities caused these rubbery PUs to have low strength and elongation, suggesting the necessity to consider polyol heterogeneity when developing flexible PUs [53]. In order to alleviate the negative effects of such heterogeneity on flexible PU applications, novel triols with high molecular weights and well-defined structure have been prepared from high-oleic sunflower oil via a series of modification and separation processes including methanolysis, fractionation, hydroformylation, hydrogenation, and polycondensation [55]. The resulting PU networks exhibited good elastomeric properties, indicating the suitability of triols for flexible PU foams applications [55]. The heterogeneity of hydroxyl functionality distribution of hydroformylated polyols has also been shown to negatively affect the performance of waterborne PU coatings [57]. Polyols with the narrowest functionality distribution resulted in coatings with the best balance of hardness, flexibility, and abrasion resistance, while polyols with the widest functionality distribution led to soft coatings with the lowest abrasion resistance.

2.2.3 Ozonolysis Pathway

Polyol production from vegetable oils by ozonolysis typically involves two steps (Scheme 2.4a): (1) formation of ozonide at the unsaturation sites of vegetable oils and simultaneous decomposition of ozonide into aldehyde and carboxylic acid; and (2) reduction of aldehyde into alcohols with a catalyst, such as Raney nickel. Because of the cleavage of all double bonds during ozonolysis, only one primary hydroxyl group is introduced at each unsaturated fatty acid chain no matter whether it is mono- or poly-unsaturated, thus polyols having a maximal functionality of three are obtained [58]. Depending on the composition of fatty acids of vegetable



Scheme 2.4 Production of vegetable oil-based polyols via ozonolysis and hydrogenation pathway (a) and via ozonolysis pathway with the addition of ethylene glycol (b) (R_1 and R_2 are fatty acid side chains of vegetable oil; R_1' , R_2' , R_1'' , R_2'' , R_1''' , and R_2''' are modified fatty acid side chains of vegetable oil)

oils, the ozonolysis-derived polyols are a mixture of different contents of mono-, di-, and tri-ols with triglyceride structures and saturated triglycerides. During the ozonolysis of vegetable oils, the cleavage of double bonds may also generate small alcohol molecules such as nonanol, 1, 3-propanediol, hexanol, and others [59], which could be valuable intermediates in chemical industries upon separation and purification. However, for the purpose of producing polyols for PU applications, small alcohol molecules are usually removed due to their detrimental effects on PU properties [58, 59]. Compared to polyols from epoxidization and ring-opening and from hydroformylation and hydrogenation, which have hydroxyl groups in the middle of fatty acids chains, ozonolysis-derived polyols only have terminal primary hydroxyl groups. As a result, ozonolysis-derived polyols have faster curing rates with isocyanates and effectively eliminate a majority of undesirable dangling chains. Ozonolysis-derived polyols typically have low molecular weights due to loss of part of the fatty acid chains that result from double bond cleavages [1]. Under different ozonolysis conditions, polyols prepared from canola oil have been

reported to have varied properties, such as hydroxyl numbers from 152 to 260 mg KOH/g and acid numbers from 2 to 52 mg KOH/g [58–60]. The high acid numbers are attributed to carboxylic acids, which form during ozonation processes and cannot be reduced to alcohols under subsequent hydrogenation conditions [58–60].

Ozonolysis-derived polyols have also been produced via a one-step reaction without hydrogenation. Typically, multi-hydroxyl alcohols, such as ethylene glycol or glycerol, were mixed with vegetable oil and a catalyst (e.g., sodium hydroxide, calcium carbonate, and sulfuric acid). With the bubbling of ozone, the alcohol reacts with ozonide intermediates generated from ozonolysis of vegetable oil to form ester linkages, producing polyester polyols with terminal hydroxyl groups [61, 62]. Scheme 2.4b shows a schematic route for the production of polyester polyols by ozonolysis with the addition of ethylene glycol. Besides its simplicity and potential low cost, this one-step ozonolysis pathway has the advantage of producing polyols with a broad range of properties by using different multi-hydroxyl alcohols.

Due to their low contents of fatty acid dangling chains, ozonolysis-derived polyols produce highly crosslinked PUs that feature strong hydrogen bonding and superior mechanical properties such as compressive strength and Young's modulus [63, 64]. The properties of PUs from ozonolysis-derived polyols can be manipulated by factors such as polyol structures and NCO/OH molar ratios. PU produced from trilinolein-based polyols had a high T_g and showed properties typical of rigid plastics, such as a high tensile strength of 51 MPa and a low elongation of 25 %, while PU from soybean oil-based polyols had a low T_g , tensile strength of 31 MPa and an elongation of 176 %, showing hard rubber-like properties [58]. This difference of PU properties is mainly attributed to different functionalities of trilinolein-based polyols ($f = 3$) and soybean oil-based polyols ($f = 2.5$) and the presence of fatty acid dangling chains in soybean oil-based polyols. Compared to PUs prepared from epoxidized and hydroformylated polyols, PUs from ozonolysis-derived polyols with the same functionality exhibited improved mechanical properties and higher T_g due to the absence or lower content of fatty acid dangling chains [58]. When the NCO/OH molar ratio increased from 1.0 to 1.2, T_g of PU plastic sheets produced from ozonolysis-derived canola oil polyols increased from 23 to 43 °C [60]. An NCO/OH ratio of 1.2 or higher could result in the formation of imperfect elastic networks due to the decreased concentration of elastically active network chains in PU networks [60].

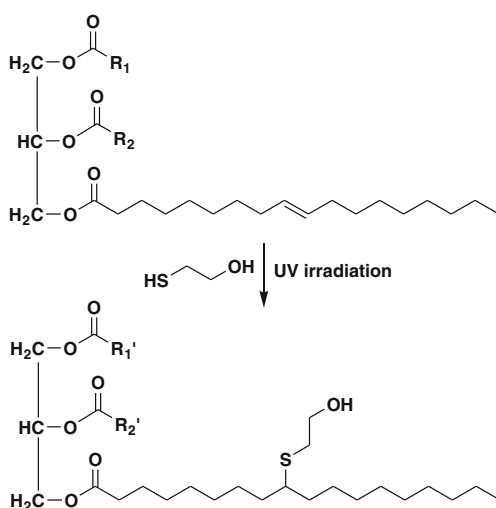
Zero or low volatile organic content (VOC) PU coatings from soybean oil glyceride polyols prepared by one-step ozonolysis with glycerol exhibited high hardness, gloss, and chemical resistance as well as excellent adhesion to metal surfaces [61]. They are suitable for industrial, automotive and architectural applications. Rigid PU foams prepared from a mixture of glycerol and the above soybean oil glyceride polyol at a 1:3 weight ratio also showed satisfactory mechanical and thermal properties, which were comparable to those of PU analogues from a commercial polyol [61]. The addition of glycerol not only increased the hydroxyl number of polyols but also acted as a crosslinker to improve the mechanical strength of the foams. Ozonolysis-derived polyols combined with poly(methyl methacrylate) (PMMA) have also been used to prepare sequential interpenetrating polymer networks (IPNs) with satisfactory

mechanical properties. IPNs showed varying performance for different applications depending on the PMMA content in the PU structure [65]. Additionally, 100 % bio-based PUs have been prepared from ozonolysis-derived polyols from canola oil and two oleic acid-based isocyanates (1,16-diisocyanatohexadec-8-ene and 1,7-heptamethylene diisocyanate, Chap. 1) [66, 67]. Lower Young's modulus and higher elongation were observed in PU from the former isocyanate than from the latter one due to more flexibility of the long chain of 1,16-diisocyanatohexadec-8-ene [66]. With the same ozonolysis-derived polyols, PU derived from 1,7-heptamethylene diisocyanate showed properties comparable to those of an analogue from petroleum-based 1,6-hexamethylene diisocyanate [67].

2.2.4 Thiol-ene Coupling Pathway

Thiol-ene coupling reactions involve a free radical chain mechanism by which thiols are grafted onto double bonds. They are not sensitive to oxygen and can be carried out in the absence of photoinitiators through a photoreaction [68]. Due to its high conversion yield and fast reaction rate, a UV-initiated thiol-ene coupling reaction is generally used for preparing polyols from vegetable oils and their derivatives with 2-mercaptoethanol as a common thiol monomer (Scheme 2.5). Soybean oil-based polyols have also been prepared via heat-initiated thiol-ene coupling which required longer reaction time than UV-initiated thiol-ene coupling [69]. During the thiol-ene coupling process of vegetable oils and their derivatives, side reactions occurred, including disulfide formation, double bond isomerization, and inter- and intra-molecular bond formation [70]. Despite these side reactions, most byproducts contained hydroxyl functional groups and could participate in PU formation. Similar to polyols from epoxidation followed by oxirane ring-opening

Scheme 2.5 Production of vegetable oil-based polyols via UV-initiated thiol-ene coupling pathway using 2-mercaptoethanol as a thiol monomer (R_1 and R_2 are fatty acid side chains of vegetable oil; R_1' and R_2' are modified fatty acid side chains of vegetable oil)

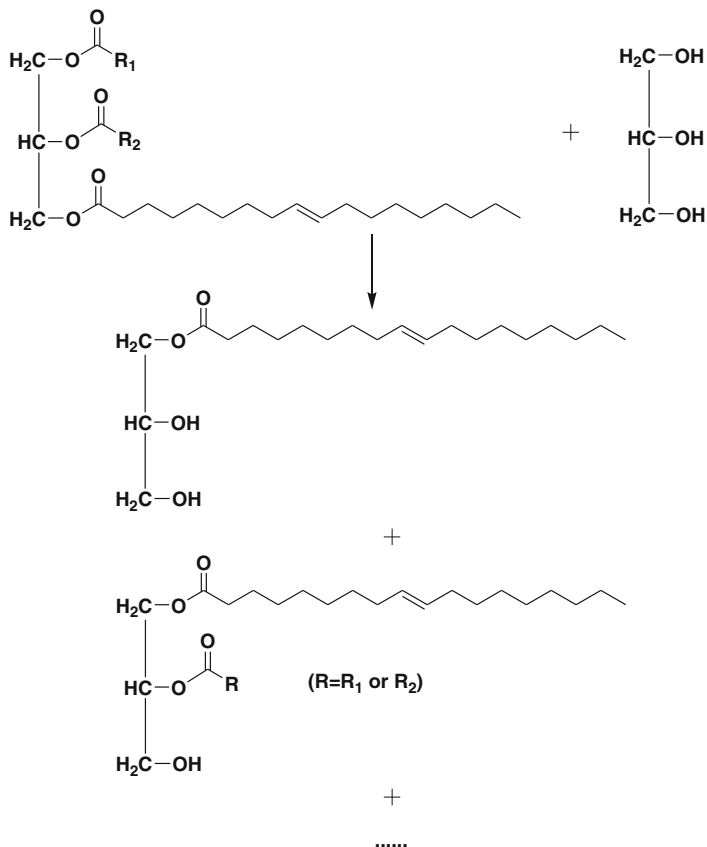


and from hydroformylation followed by hydrogenation, polyols from the thiol-ene coupling pathway also contain hydroxyl groups located in the middle of fatty acid chains, leaving part of the fatty acid chains as dangling components in PU structures. Currently, most thiol-ene coupling-derived polyols have been prepared from fatty acids or fatty acid esters. Reports on the preparation of vegetable oil-based polyols via thiol-ene coupling reactions are limited [69, 70]. Rapeseed oil-based polyols produced by UV-initiated thiol-ene coupling with 2-mercaptoethanol showed an acid number of 2.5 mg KOH/g, a hydroxyl number of 223 mg KOH/g, and an average functionality of 3.6. Soybean oil-based polyols produced by heat-initiated thiol-ene coupling with 2-mercaptoethanol showed an acid number of 2.5 mg KOH/g and a hydroxyl number of 200 mg KOH/g. PUs derived from these two polyols showed properties such as thermal and mechanical properties similar to those from a commercial polyol [69, 70].

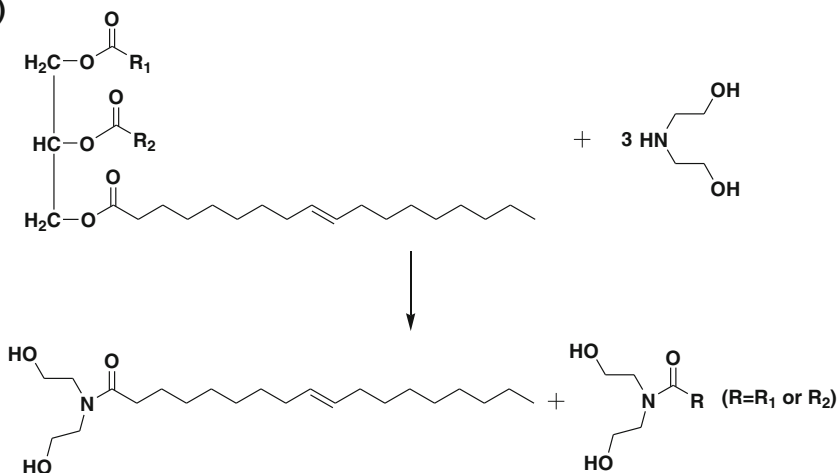
2.2.5 *Transesterification/Amidation Pathway*

All of the above discussed pathways for the production of vegetable oil-based polyols take place at the double bond moieties of vegetable oils. Transesterification and amidation use a different approach that makes use of the ester moieties in the structures of vegetable oils to produce polyols (Scheme 2.6) [1]. Glycerol is the most predominantly used alcohol for the transesterification of vegetable oils, but the use of other alcohols, such as pentaerythritol [71] and triethanolamine [72], has also been reported. During transesterification, the addition of a small amount of soap acts as an emulsifier that can improve the compatibility between glycerol and triglycerides and thus increase the production efficiency of monoglycerides [73, 74]. Transesterification reactions are mostly catalyzed by organic and inorganic bases such as methoxides of sodium, calcium, and potassium [71, 75–77]; sodium hydroxide; and calcium hydroxide [73], and by metal oxides such as lead [78, 79] and calcium oxides [80]. Enzyme-catalyzed transesterification has also been reported [81]. Polyols produced from vegetable oils by transesterification with glycerol (i.e., glycerolysis) are a mixture of mono-, di-, and tri-glycerides and residual glycerol. Among these components, monoglycerides, which contain two hydroxyl groups per molecule, play an important role for PU production. Depending on reaction conditions and feedstocks used, polyols with monoglyceride contents ranging from 48.3 to 90.1 % and hydroxyl numbers ranging from 90 to 183 mg KOH/g have been obtained [73, 80, 82]. Since all hydroxyl groups in polyols derived from transesterification of vegetable oils, except for castor oil, are located on the glycerol backbone, all of the acid side chains would act as dangling components when polyols are crosslinked with isocyanates. In applications where flexibility is preferred, these dangling chains are beneficial due to their plasticizing effects, while in applications that require high rigidity, these plasticizing effects are detrimental and undesirable.

(a)



(b)



Scheme 2.6 Production of vegetable oil-based polyols via transesterification with glycerol (a) and amidation with diethanolamine (b) (R_1 and R_2 are fatty acid side chains of vegetable oil) [1]

Polyols produced by the transesterification of vegetable oils can be partially or completely substituted for petroleum-derived polyols for the preparation of PU foams and coatings. Compared to epoxidized and hydroxylated soy polyols, a mixture of glycerolysis-based soy polyols (90.1 % of monoglyceride, 1.3 % of diglyceride, and 8.6 % of glycerol) and glycerol propoxylate (Mw: 400 g/mol) exhibited higher reactivity with isocyanates and resulted in flexible PU foams with more uniform cell structure [73]. Increasing the portion of glycerolysis-based polyols from palm oil in blends with diethylene glycol (DEG)/polyethylene glycol (PEG, Mw: 200 g/mol) produced semi-rigid PU foams with higher flexibility. This was mainly caused by the increased content of monoglycerides, which served as soft segments in the foam structures [82]. A mixture of glycerolysis-based polyols from Nahar oil and PEG (Mw: 200 g/mol) has also been used to produce PU coatings [79]. As the molar ratio of NCO/OH increased, PU coatings showed improved properties including impact resistance, hardness, gloss, and adhesive strength, which can be attributed to the increased crosslinking densities in PU networks. By reacting with trimers of isophorone diisocyanate, PU coatings based on 100 % glycerolysis-based polyols were prepared from linseed, soybean, and sesame oils. The produced coatings generally showed satisfactory flexibility and adhesion properties as well as good chemical resistance [83].

Similar to the above transesterification processes, amidation with amines, usually diethanolamine, can also convert vegetable oils into diethanol fatty acid amides for producing PU foams and coatings. Compared to commonly used transesterification with glycerol at 230–250 °C [73, 78, 80], the amidation of vegetable oils with diethanolamine are carried out at a lower temperature, usually at 110 °C [72, 84–87]. Amidation-derived polyols from vegetable oils, such as linseed, soybean, rapeseed, sunflower, coconut, Nahar, and cottonseed oils, have been used for the development of PU foams and coatings with satisfactory physical and mechanical properties [72, 84, 88–90]. PU resins from amidation-based polyols from Nahar and linseed oils showed superior coating performance, such as adhesion, gloss, hardness, and chemical resistance, compared to polyester resins from the same oils [84, 89].

2.3 Castor Oil-Based Polyols and Polyurethanes

As an exception to common vegetable oils, castor oil contains naturally occurring hydroxyl groups. Approximately 90 % of fatty acids in castor oil consist of ricinoleic acid, which is a mono-unsaturated 18-carbon fatty acid with a hydroxyl group on its 12th carbon [2] (Fig. 2.4). An in-depth structural analysis of castor oil showed that castor oil had an average hydroxyl functionality of 2.7, which resulted from the contributions of 70 % triols (triricinoleate of glycerol) and 30 % diols (triacylglycerols having only two ricinoleyl groups), and the absence of monoalcohols (triacylglycerols having one ricinoleyl group) [91]. Due to its naturally occurring hydroxyl groups and wide availability, castor oil has long been a versatile and valuable feedstock for direct use in the PU industry.

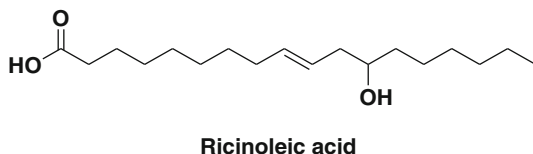
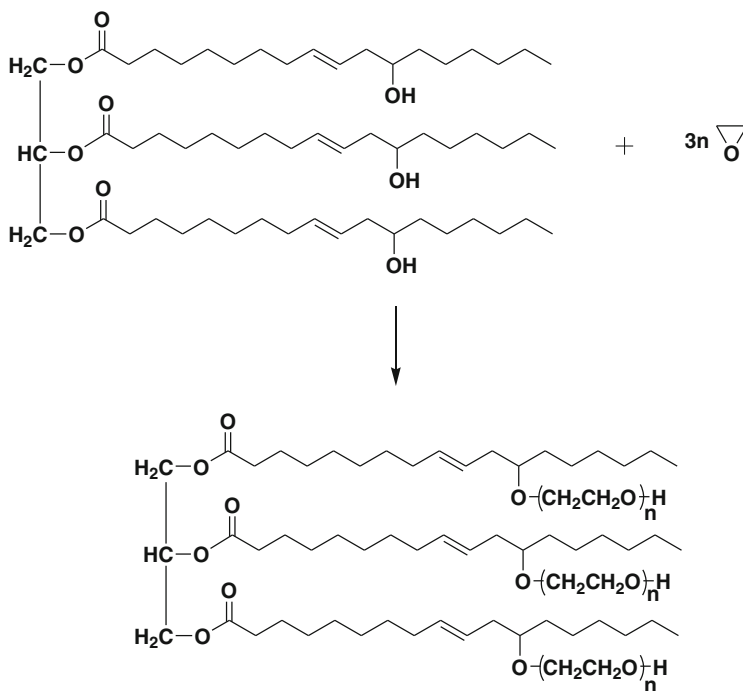


Fig. 2.4 Chemical structure of major fatty acid in castor oil

Castor oil has low functionality and possesses low reactivity due to the secondary hydroxyl groups in the ricinoleic acid chains, resulting in castor oil-based PUs with semi-flexible or semi-rigid properties [92]. Two major modification pathways have been widely used to improve the properties and applicability of castor oil-based polyols for producing PUs with improved properties and wider applications. One is the transesterification/amidation of castor oil using its ester moieties, and the other is the alkoxylation of castor oil using its hydroxyl groups. The functionality and hydroxyl number of castor oil-based polyols can be increased by transesterification with glycerol, pentaerythritol, and other polyols [1], or amidation with diethanolamine [93]. As a result, PUs with more rigid properties have been obtained. For example, castor oil-based polyols prepared by transesterification with triethanolamine and amidation with diethanolamine, showed hydroxyl numbers ranging from approximately 291 to 512 mg KOH/g. Their derived PU coatings exhibited higher tensile strengths (19.8–57.4 MPa) and glass transition temperatures (T_g , 44.5–84.5 °C) than those from an unmodified castor oil-based analogue (tensile strength: 14.1 MPa; T_g : 18.6 °C) [93]. Alkoxylation is a polymerization process by which epoxide monomers (e.g., ethylene oxide and propylene oxide) are incorporated into an alcohol for the formation of polyols. Castor oil can be converted to polyols with higher molecular weights and lower hydroxyl numbers by ethoxylation (alkoxylation with ethylene oxide) or propoxylation (alkoxylation with propylene oxide) [94]. Due to the incorporation of long polyether chains from castor oil, high quality flexible PUs such as foam mattresses can be produced. Scheme 2.7 shows a schematic synthetic route for castor oil-based polyols via ethoxylation.

In addition to these two modification methods, mixing castor oil with petrochemical-derived polyols is also an effective way to obtain fast reaction rates with isocyanates and to fine-tune product properties in the PU production process. By adding triisopropanolamine to the PU formulation, castor oil-based rigid PU foams showed increased compressive strength [95]. Millable PU elastomers prepared from castor oil and poly(propylene glycol) showed a wide range of physical and mechanical properties via varying PU formulations, such as the content of polyols and chain extenders [96]. They varied from soft elastomers to hard plastics. In comparison to a petroleum-based sample (e.g., Urepan 600), castor oil-based PU elastomers exhibited comparable tensile strength, compression set, and resilience and slightly inferior abrasion resistance and elongation at break [96]. Castor oil, in combination with recycled polyethylene terephthalate (PET), adipic acid, and polyethylene glycol (PEG), has been used to prepare PU coatings for insulation applications [97, 98]. Higher tensile strength and better electrical insulation

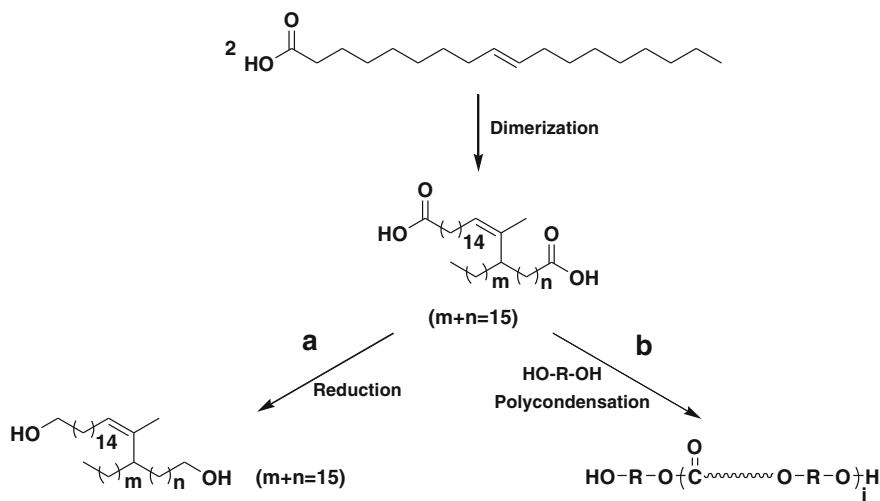


Scheme 2.7 Production of castor oil-based polyols via ethoxylation [94]

performance (comparable or superior to regular PU insulation) were generally obtained with increasing crosslinking density in PU networks. These coatings also exhibited excellent resistance to acid (1 or 10 % sulfuric acid) and alkaline (1 % sodium hydroxide) solutions, and a certain degree of swelling in toluene and DMF [97, 98]. Additionally, castor oil has been extensively used in the preparation of PU-based interpenetrating polymer networks (IPNs) [99–102]. PUs with 100 % bio-based materials have also been prepared from castor oil and soybean oil-based isocyanates, showing low Young's modulus and tensile strength due to the absence of hard segments [103].

2.4 Fatty Acid- and Fatty Acid Ester-Based Polyols and Polyurethanes

Fatty acids and fatty acid esters have carbon-carbon double bonds and carboxyl groups/ester linkages, which can be converted to hydroxyl groups with the above mentioned methods for vegetable oil-based polyols. Besides these methods [54, 67, 104–108], other methods have been reported for the synthesis of polyols from fatty



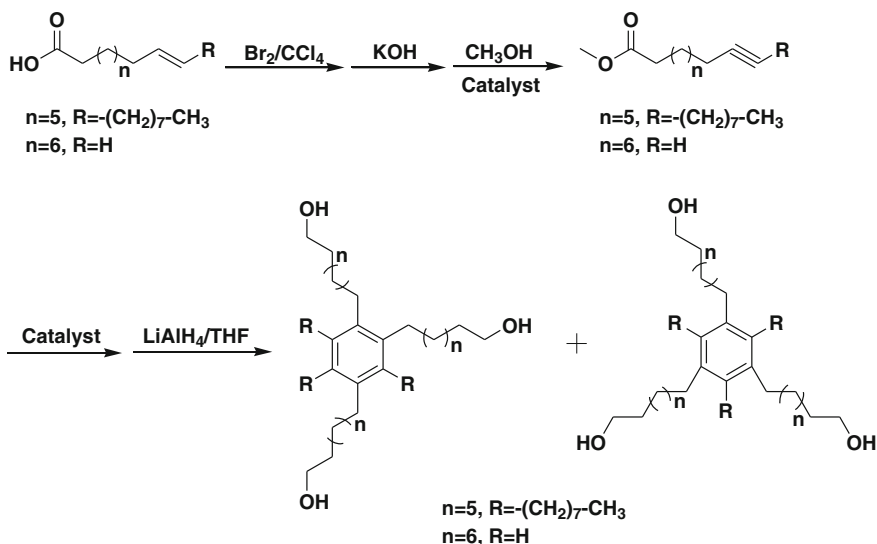
Scheme 2.8 Production of bio-based polyols via dimerization of oleic acid followed by reduction (a) or by polycondensation with glycols (b) [68, 110]

acids and fatty acid esters, including dimerization of fatty acids, cyclotrimerization of alkyne fatty acid esters, self-metathesis of fatty acids, cationic polymerization of epoxidized fatty acid esters, and hydrosilylation of fatty acid esters, all of which were followed by a reduction reaction.

Dimerization of fatty acids is a complex reaction that can proceed under various catalysts, such as alkaline metal salts, Lewis acids, and clays [109]. Through further reduction (Scheme 2.8a) or polycondensation with glycols (Scheme 2.8b), dimeric fatty acid diols/polyester polyols are obtained [68, 110]. Waterborne PU coatings synthesized from dimer fatty acid-based polyester polyols exhibited high water resistance and thermal stability but low toluene resistance and mechanical properties [110]. The introduction of adipic acid to dimer fatty acid-based polyester polyols could improve the toluene resistance and mechanical properties of dimer fatty acid-derived PU coatings.

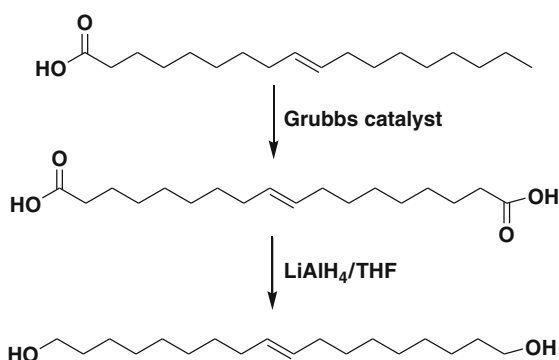
Fatty acid-based cyclotrimerization (Scheme 2.9) has also been reported for producing polyols. Through a series of modifications, including bromation, dehydrobromination, and esterification, oleic acid and 10-undecenoic acid (derived from ricinoleic acid) were first converted to methyl 9-octadecynoate and methyl 10-undecynoate, which then underwent cyclotrimerization using heterogeneous Pd/C as a catalyst and subsequent reduction of ester groups with LiAlH_4 to yield primary hydroxyl groups [111]. Because of the plasticizing effect of the long aliphatic chains in oleic acid-derived aromatic triols, oleic acid-based PUs showed a lower T_g value than 10-undecenoic acid-based analogues.

Unsaturated linear diol with terminal primary hydroxyl groups was synthesized via the self-metathesis of oleic acid with a Grubbs catalyst followed by reduction with LiAlH_4 (Scheme 2.10) [105]. By reacting with an oleic acid-derived



Scheme 2.9 Production of fatty acid-based polyols via cyclotrimerization pathway [111]

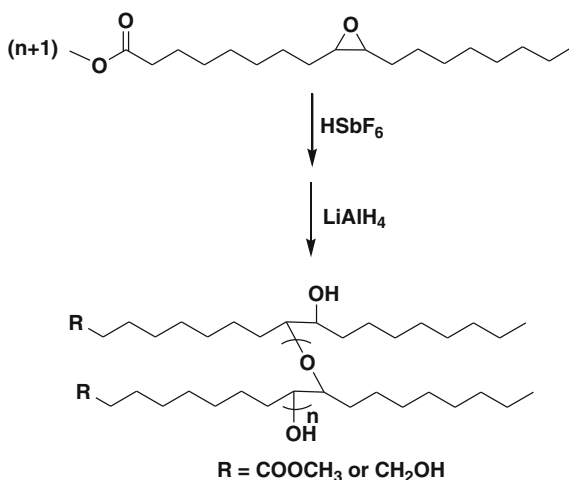
Scheme 2.10 Production of fatty acid-based linear diol via self-metathesis followed by reduction [105]



diisocyanate (1,7-heptamethylene diisocyanate, Chap. 1) in the presence of a bio-based chain extender (1,9-nonanediol, derived from ozonolyzed oleic acid) [67], 100 % bio-based thermoplastic PU (TPU) has been prepared from the unsaturated linear diol. The TPU showed similar phase behavior but lower tensile strength and elongation at break, compared to an analogue prepared from the diols with a petroleum-based diisocyanate (i.e., 1,6-hexamethylene diisocyanate). The difference of properties between these two TPUs was due to the effects of odd- and even-numbered methylene groups in 1,7-heptamethylene diisocyanate and 1,6-hexamethylene diisocyanate [105].

Oligomeric polyether polyols were synthesized via fluoroantimonic acid-catalyzed cationic polymerization of epoxidized methyl oleate and subsequent controlled reduction of ester groups (Scheme 2.11) [112]. Depending on the degree

Scheme 2.11 Production of methyl oleate-based polyether polyols [112]

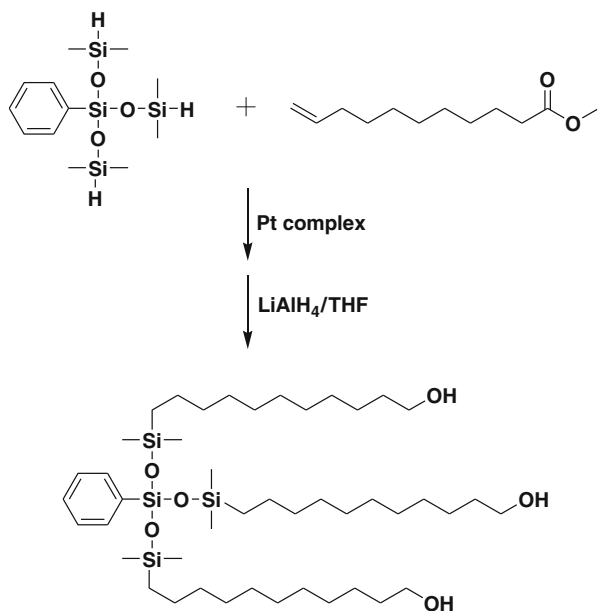


of reduction reaction with lithium aluminum hydride, polyols had hydroxyl numbers ranging from 94 to 260 mg KOH/g and molecular weights from 1220 to 1149 g/mol, and varied from clear liquids to white, waxy solids at room temperature. Thermal and mechanical analyses indicated that the produced PUs could be used as hard rubber or rigid plastics [112].

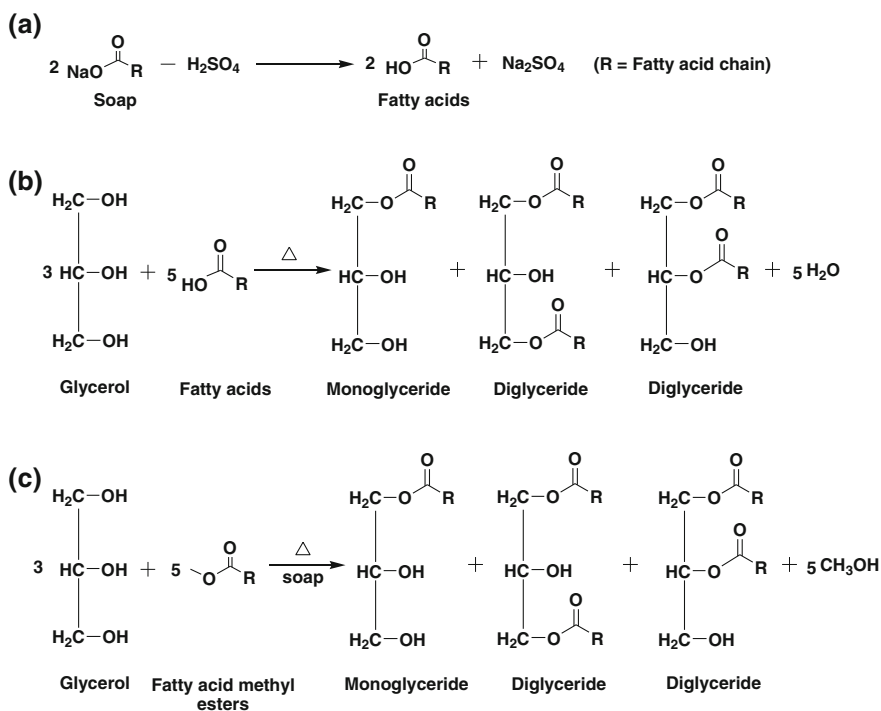
Through platinum-catalyzed hydrosilylation with phenyltris(dimethylsiloxy)silane followed by reduction with LiAlH_4 , methyl 10-undecenoate was converted to a silicon-containing polyol with terminal primary hydroxyl groups (Scheme 2.12), which had a hydroxyl number of 194 mg KOH/g [113]. The incorporation of silicone endowed the resulting PUs with enhanced thermal stability under atmospheric conditions, suggesting their potential applications as fire-retardant materials [113].

2.5 Crude Glycerol-Based Polyols and Polyurethanes

Recently, the feasibility of utilizing crude glycerol as a renewable feedstock for the production of polyols and PU foams and coatings has been investigated [9, 11, 12]. Through a one-pot thermochemical process, crude glycerol, in the presence of sulfuric acid, was successfully converted to polyols with suitable properties for applications of PU foams and coatings. The reactions involved in the thermochemical process mainly included the acidification of soap, esterification of glycerol and fatty acids, and transesterification of glycerol and fatty acid methyl esters, as shown in Scheme 2.13. Crude glycerol-based polyols were a mixture primarily consisting of monoglycerides, glycerol, and diglycerides. Under preferred reaction conditions of 200 °C, 90 min, and 3 % sulfuric acid loading, the crude glycerol-based polyols produced showed a hydroxyl number of approximately 481 mg KOH/g and an acid number of approximately 5 mg KOH/g. PU foams produced from this crude



Scheme 2.12 Production of a silicone-containing polyol from fatty acid ester [113]



Scheme 2.13 Reactions mainly involved in the one-pot thermochemical conversion of crude glycerol for the production of polyols

glycerol-based polyol and polymeric methylene-4,4'-diphenyl diisocyanate (pMDI) presented a compressive strength of approximately 184.5 kPa and a density of approximately 43.0 kg/m³, which were comparable to those of some petroleum-based analogs [9]. Crude glycerol has also been used for producing polyols and PU foams in combination with PET and diethylene glycol [10]. With an increase of the weight ratio of crude glycerol to PET and DEG, polyols showed increased hydroxyl numbers, which resulted in PU foams with increased density and compressive strength but decreased thermal stability. A decreased content of aromatic segments was responsible for the decreased thermal stability of PU foams. Under vacuum conditions, a crude glycerol-based polyol with a lower hydroxyl number (e.g., 378 mg KOH/g) was also prepared by a one-pot thermochemical process and had components similar to polyols obtained under atmospheric conditions [11]. Waterborne PU coatings from this polyol and isophorone diisocyanate (IPDI) showed excellent adhesion to steel surfaces, good pencil hardness, but relatively low flexibility. The incorporation of petroleum-based polyether polyols can improve the flexibility of crude glycerol-based waterborne PU coatings [11].

2.6 Summary and Future Prospects

Vegetable oils and their derivatives including fatty acids, fatty acid esters, and crude glycerol have good potential as renewable and sustainable feedstocks in producing bio-based polyols and PUs. Modifications made on the double bond and/or carbonyl moieties (i.e., ester linkages or carboxyl group) of vegetable oils and their derivatives allow the synthesis of polyols with different reactivities, functionalities, molecular weights, and other properties. Because of their high versatility, polyols from vegetable oils and their derivatives have been used to produce various PU materials such as foams, elastomers, rigid plastics, and coatings, which have shown properties mostly comparable to those of their petroleum-based analogs.

In spite of their promise, vegetable oils and their derivatives still face challenges such as technical and/or cost barriers to production of high resilient flexible foams. Future efforts in this field will be of high interest. Crude glycerol, a byproduct of the biodiesel industry, is a promising renewable feedstock for producing polyols and PUs. However, its varied composition makes it difficult to obtain polyols with consistent quality and properties. This problem will be effectively solved by adjusting the composition of crude glycerol with the addition of crude fatty acids or fatty acid methyl esters. The inherent structural heterogeneities of vegetable oils also challenge the production of polyols and PUs with consistent properties. The use of single components or derivatives, such as one type of fatty acid, and advances in genetic engineering should lead to polyols and PUs with more homogeneous structures and consistent qualities. Currently, bio-based polyols and PUs may still have higher costs than petroleum-based analogues. However, with the continuing advances in technologies and the inevitable depletion of the world's petroleum resources, the future of bio-based polyols and PUs looks very promising and bright.

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