REVIEW PAPER

Polyurethane foams from vegetable oil-based polyols: a review

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Abstract

Polyurethane is a versatile material that can be converted into various forms according to applications. PU foams or PUFs are the most commonly used polyurethanes. These are materials of low density and low thermal conductivity that make them highly suitable for thermal insulating applications. Most of the synthesis of PUFs is still based on the petrochemical industry. There are issues associated with the oil industry, such as environmental pollution, sustainability, and market instability. More recently, we have experienced the COVID-19 pandemic which has destroyed the global supply chain of raw materials. Such sudden disruption of the supply chain affects the global economy. To eliminate the reliance on special ingredients, it is important to find and produce alternate and domestic raw materials. Vegetable oils are organic, cost-effective, and economically viable and present in abundant amounts. The oil consists of triglycerides. It can be functionalized to provide polyol for PU foam synthesis. Herein, we review the literature on factors influencing the properties of PUFs depending on polyols from vegetable oil as well as present a glimpse of the conversion of vegetable oils into polyols for PUF synthesis.

Keywords Polyurethane foams · Vegetable oil · Polyols · Flexible foams · Rigid foams

Introduction

Polyurethanes are a unique class of materials that can be used into different applications such as flexible foams, rigid foams, coatings, adhesives, elastomers, sealants, and films. Out of these types, foams based on polyurethane have a high demand. Polyurethane is also dependent on raw materials based on petroleum, just like other

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polymers [1]. The main ingredients required for the synthesis of polyurethane are isocyanate and polyols. Polyurethane foams are the most widely used substances in automotive industry where it is used to make suspension insulators, bumpers, car seats, headliners and other interior parts. These are also used in various industries such as furniture, insulation, medical, and household appliance. Newer applications are also cited such as the removal of oil from water [2–4]. In addition to the main reaction, the manufacture of polyurethane foam requires additional reactants such as a blowing agent and a surfactant. By extending the cells, blowing agents increase the volume and the surfactants initiate and stabilize the foam cells [5]. Due to environmental friendliness, water is the most common chemical blowing agent. Water reacts with isocyanate to create carbamic acid that is not stable and dissociates into amine and carbon dioxide immediately [6] (Fig. 1).

The versatility in the application is a manifestation of the amount and type of raw materials as well as some additives to achieve the final form. Since these raw materials are mainly focused on the petrochemical industry, problems such as price stability, insufficient feedstock and, more significantly, hazardous chemicals pollution and environmentally degrading greenhouse gas emissions are growing [7]. In comparison with the restricted and environmentally damaging products dependent on petroleum, agricultural products such as vegetable oils are not only sustainable because they are bio-derived, but also environment friendly [8]. Vegetable oils are plentiful and contain triglycerides as the key constituent which are nothing but esters of glycerol and fatty acid, making them a very valuable polyol resource. Figure 2 shows structure of triglyceride [9]. The additional advantage of using these vegetable oil products is biodegradability, solubility in most commercial solvents, fair cost and the prospect of producing industrially versatile and useful products.

The characteristics of polyurethane are closely related to the polyol from which it is derived. It is very essential that the polyol offers the performance needed as per application. The concern for health effects on the environment is a significant driving factor for replacing entire or part of the petroleum-based precursors for PU with those derived from agricultural precursors. Applying components from renewable
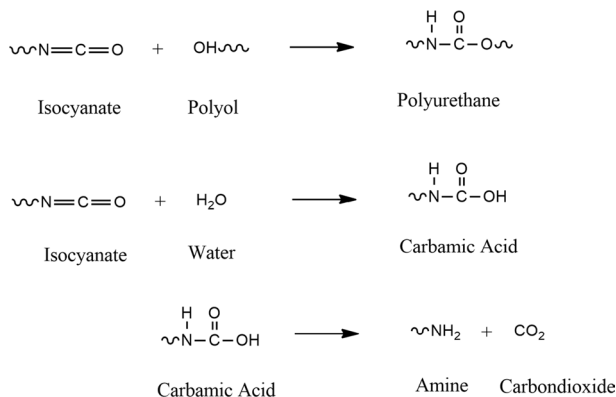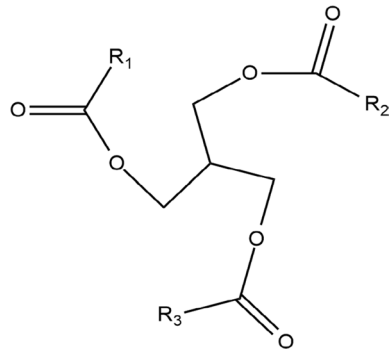

Fig. 1 Reactions of polyurethane synthesis, isocyanate with water

Fig. 2 Structure of triglyceride molecule

resources that fulfil all ideas of sustainable development is an innovative and environment-friendly strategy for polymer synthesis. Vegetable oils are those which are derived from seeds or other parts of plants such as fruits.

The major category of edible oils is used in cooking as well as medicinal (castor oil) purposes. Edible oils are a large group of oils that are used in polyol synthesis. It includes oil from soybean [10], linseed [11], olive [12], rice bran [12], corn [12], sunflower [13], rapeseed [14], canola [15], etc. Fatty acids are long carbon-containing chains of length from 4 to 28 but vegetable oil mostly have fatty acids of chain length 16 and 18. The fatty acid composition is the one that distinguishes one vegetable oil from another. Palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids are found in significant amounts in nearly all vegetable oils. In the given statement, the first number is for the number of carbon atoms and the second number is for the number of double bonds. Ricinoleic acid with a hydroxyl group at C12 is a major component of castor oil, a valuable vegetable oil used in industry [16]. The characteristics of common vegetable oils are reported in Table 1.

Vegetable oil-based polyols

Each oil contains various combinations and amounts of fatty acids in the triglycerides, allowing different raw materials to be designed for various applications. It is possible to change the unsaturation present in the vegetable oil into a hydroxyl-containing molecule. Epoxidation, hydroformylation, thiol–ene coupling, ozonolysis, transesterification or amidation are the routes to functionalize these oils (Fig. 3) [9, 18].

Among vegetable oils, castor oil contains hydroxyl groups that occur naturally. Castor oil is a pale yellow and viscous oil produced in tropical and subtropical regions from castor beans (Ricinus Communis). Castor oil received a lot of attention at an early stage in bio-based PU elastomers [19, 20]. The presence of ricinoleic acid in large amount ~87% provides hydroxyl value approx. 160 mg KOH/g [2]. Following is the structure of the castor oil molecule [21] (Fig. 4).

Table 1 Typical fatty acid compositions, iodine values, double bonds of most common vegetable oils [9, 16, 17]

Vegetable oil	Lauric acid	Myristic acid	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid	Iodine value range (g I_2/100 g)	Double bonds[a]
Castor oil[b]	–	–	1.5	0.5	5.0	4.0	0.5	82–88	3
Coconut oil	47.1	18.5	9.1	2.8	6.8	1.9	0.1	90–119	–
Corn oil		0.1	10.9	2.0	25.4	59.6	1.2	102–130	4.5
Cottonseed oil	0.1	0.7	21.6	2.6	18.6	54.4	0.7	90–119	3.9
Linseed oil			6.0	4.0	22.0	16.0	52.0	168–204	6.6
Olive oil			13.7	2.5	71.1	10	0.7	75–94	2.8
Palm oil	0.1	1.0	44.4	4.1	39.3	10.0	0.4	50–55	1.7
Palm kernel oil	48.2	16.2	8.4	2.5	15.3	2.3		14–19	–
Peanut oil		0	11.4	2.4	48.3	31.9		84–100	3.4
Rapeseed oil		0.0	4.0	2.0	56.0	26.0	10.0	94–120	3.8
Safflower oil		0.1	6.8	2.3	12	77.7	0.4	140–150	–
Soybean oil		0.1	10.6	4.0	23.3	53.7	7.6	123–139	4.6
Sunflower oil		0.1	7.0	4.5	18.7	67.5	0.8	125–140	4.7

[a] Average number of C–C bond per triglyceride. [b] Contains 87% OH-bearing ricinoleic acid (C18:1)
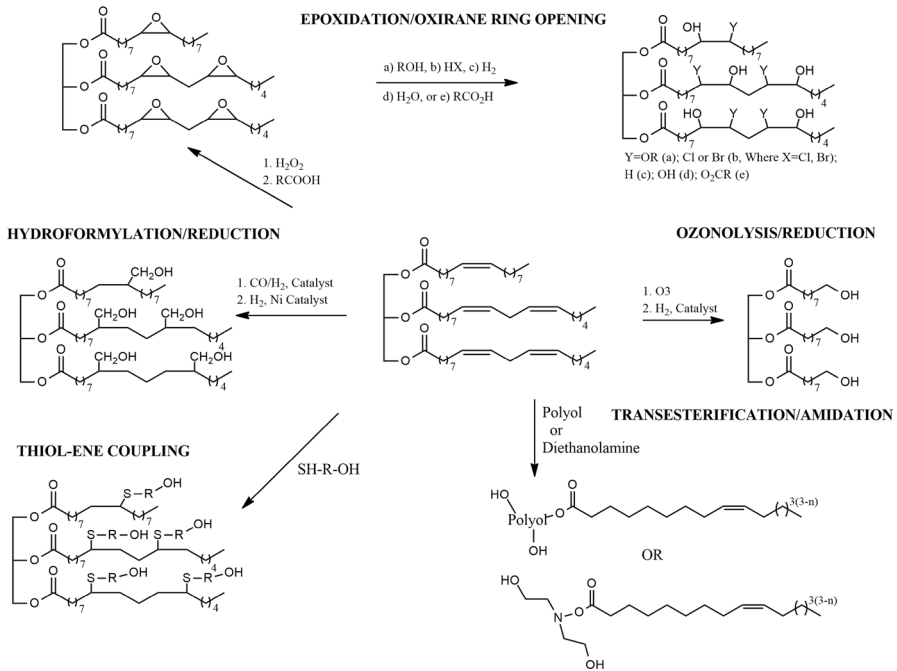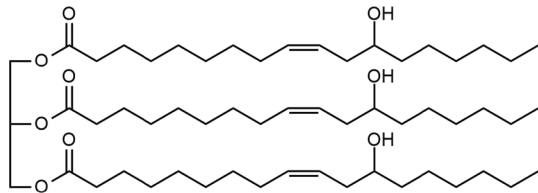
Fig. 3 Various routes to convert vegetable oil into polyol [9, 18]

Fig. 4 Castor oil triglyceride

This makes it suitable to directly be used in flexible PU foams. The hydroxyl value of 28–56 mg KOH/g and functionality of 3 is required for flexible PU foams and for rigid PU foam hydroxyl value of >200 mg KOH/g and functionality of 3–6 is required. The long pendant chain imparts flexibility and hydrolytic resistance. The low hydroxyl number gives material with low modulus [16]. In almost all vegetable oils, the reactive sites are esters and carbon–carbon double bonds, which can be modified to give a variety of monomers as per the following routes [9].

Epoxidation route

Peroxides, aldehydes, ketones, etc., are used to epoxidize the double bonds present in the triglycerides. Different proton donors, such as alcohols, water, organic or inorganic acids, open the epoxy ring. Epoxidation in the industrial process is carried out using peracetic acid, which is made from acetic acid and H_2O_2 [16, 21].

Several catalyst such aspolyoxometalates (POMs) which forms active intermediates, peroxopolyoxometalates (PPOMs) Q_3 (where $Q = [Bu4^nN]^+$, $[MeN(nC_8H_{17})_3]^+$, $[\pi-C_5H_5N(CH_2)_{15}CH_3]^+$; X = P, As, etc.; M = Mo, W, etc.) acidic ion exchange resins (AIERs) with a polystyrene matrix cross-linked with divinylbenzene (DVB) and metal catalysts such as Ti/SiO$_2$, sulfated SnO$_2$, Nb$_2$O$_5$–SiO$_2$ used in addition with H$_2$O$_2$ [22]. In the latest innovation manganese in combination with a racemic mixture of the *N,N′*-bis(2-picolyl)-2,2′-bispyrrolidine ligand (rac-BPBP) was proved to be highly efficient with yields more than 90% [23, 24]. Hydrogenation can also open the rings, resulting in solid products at room temperature. Solid products are also given by the ring opening by HCl, HBr. Methanol selection is favored as it results in liquid polyols. Epoxidation gives polyol with only secondary hydroxyl groups which are shielded by dangling chains. Ethoxylation improves reactivity by converting secondary groups into primary ones. The properties of polyols formed by epoxidation are influenced by various variables such as production factors, including feedstock characteristics and ring-opening agent forms [16, 25].

Ozonolysis

This reaction gives polyol with terminal hydroxyl groups. The C–C double bond is cleaved to give short-chain alcohols. Vegetable oil is first treated with ozone to form an ozonide, which is then reduced to an aldehyde by zinc and then further reduced to an alcohol by using Ni catalyst. The reduction in the molecular weight increases Tg and the mechanical properties of the final product. Both primary and secondary hydroxyl-containing polyols are given by the method with some modification. It is possible to ozonolyze and hydrogenate plant oils with low unsaturations such as canola oil, soybean oil to get polyol [9].

Transesterification/transamidation

To produce polyols, these reactions use the ester moieties of vegetable oils. Transesterification produces a product comprising hydroxyl groups, both primary and secondary. Castor oil, in presence of a base catalyst or enzymes, is transesterified with polyhydroxy alcohols, most commonly glycerol and pentaerythritol. It increases the hydroxyl value of the system thereby increasing the cross-linking and subsequently the hardness. The long chain of methylene contributed from the fatty acids imparts good flexibility thus resulting in the polyurethane with overall balanced properties. Unlike glycerol, which degrades to provide water due to *β*-hydrogen, pentaerythritol shows greater thermal stability in the reaction medium. Fatty acid amide is obtained through the reaction of amidation. Diethanolamine provides diethanolamides which contains primary hydroxyls [16].

Thiol–ene coupling

This involves addition of mercapto ethanol to the unsaturation present in vegetable oil. This is a simple one-step reaction with side reaction disadvantages such as

disulfide formation. Researchers have successfully developed polyols based on rapeseed oil by conducting thiol–ene reactions between oleic acid and 2-mercaptoethanol [26].

Hydroformylation/reduction

This is also one of the important reactions to get primary hydroxyl groups. This process involves reaction of syn-gas (carbon monoxide and hydrogen) with unsaturation to introduce aldehydes at 90–110 °C which is then converted into hydroxyl groups by hydrogenation. Rhodium carbonyl catalyst are the most efficient ones but due to cost limitations, cobalt carbonyls are used [27].

Metathesis route

Metathesis involves an exchange of alkylidene groups between the reactants in the presence of ruthenium catalysts. This reaction is categorized into self and cross-metathesis reaction. The self-metathesis has a complex mixture of linear oligomers macrocyclic structures, cross-linked polymers, as well as trans-/cis isomers that increase the reactivity of vegetable oil. The cross-metathesis with ethylene gives
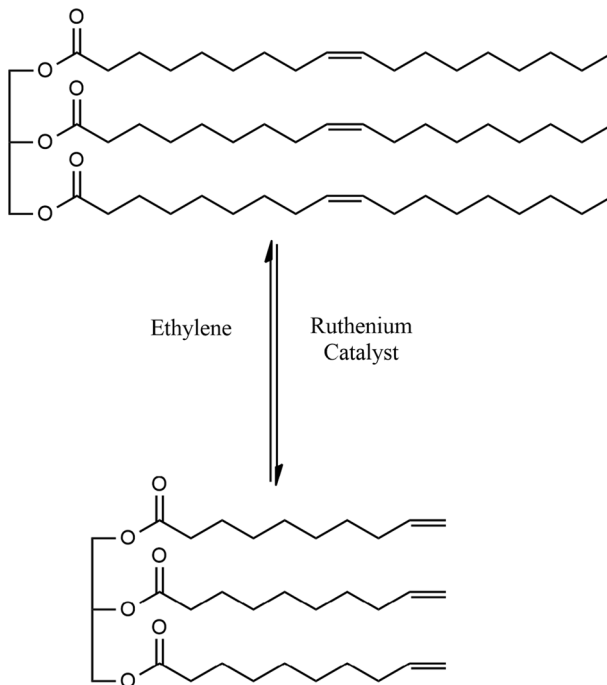

Fig. 5 Metathesis reaction of triolein with ethylene [30]

the triglycerides with terminal double bonds. The cross-metathesized product offers advantages like a less steric hindrance, absence of dangling chains etc (Fig. 5). The product obtained can be an epoxide which subsequently after ring opening can generate a polyol [28, 29].

Polyurethane foams from vegetable oil-based polyols

Polyurethane foams are expanded materials and the combination of polyols, isocyanate and blowing agents reflects their structure. Foams of polyurethane (PUF) account for 67% of global PU intake. In general, PUFs are classified mainly as flexible foams or rigid foams where other types such as flexible PU slabs, flexible molded foams, carpet backing or two-component formulations and reaction injection molding (RIM) are also being used [31]. The global polyurethane foams market is expected to grow at a compound annual growth rate (CAGR) of 7.5% between 2020 and 2025 to rise from USD 37.8 billion by 2020 to USD 54.3 billion by 2025. The key factors for the development of polyurethane foams include wider applications such as bedding and furniture, electrical, car, building and construction and the growing demand for these in emerging economies like India, Thailand and others [32]. PUFs are also used in medical applications such as regeneration of the cardiovascular system, peripheral nerve regeneration, cartilage and meniscus engineering, trabecular bone replacement and managed drug delivery systems [33]. Some other factors are driving the growth of the polyurethane foams industry, such as growing polyurethane foams in building insulations for power conservation and versatile and specific physical characteristics of polyurethane foams [32]. Global consumption of polyurethane is shown in Fig. 6.

Recently, COVID-19 pandemic has disrupted the global supply chain. To contain the spread of the COVID-19 virus internationally, various actions including a ban on international flights and import–export trade were taken. Such a ban on import–export of raw materials also affects the economy on a major level. The
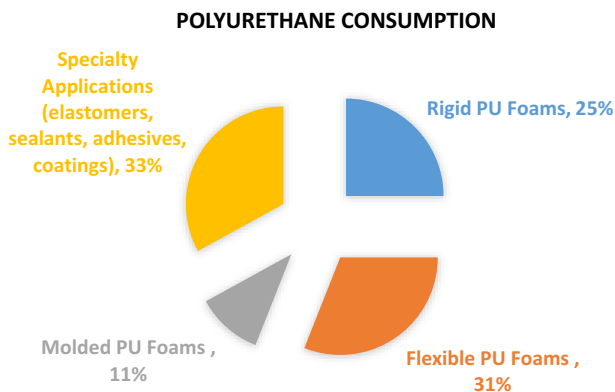

POLYURETHANE CONSUMPTION

Specialty Applications (elastomers, sealants, adhesives, coatings), 33%

Rigid PU Foams, 25%

Molded PU Foams , 11%

Flexible PU Foams , 31%

Fig. 6 Global consumption of polyurethane (PU) in 2016 [31]

pandemic has an immense effect on various factors from raw material manufacturers to end-use industries. The majority of polyol products are manufactured from crude oil, i.e, they are petroleum-based. The USA, China and Russia are the top three countries with the largest oil refinery capacity. Most of the polyols required for polyurethane production are exported from these countries to the world. Moreover, the depleting oil level in the earth's crust will eventually lead to a petrochemical crisis. Hence, it is a time to focus more on developing new materials which are sustainable and can be manufactured domestically. It is an opportunity for scientists and industries for the development of bio-based polyols and eliminate the dependency on fossil fuel-based polyols [32].

Rigid polyurethane foams

Rigid PU foams are used mainly as insulating material in the building industry and also as an insulating material in appliances such as refrigerators and freezers. The basic functions of these foams are to minimize the level of noise and to ensure that the temperature is constant. Properties such as thermal conductivity, thermal diffusivity and specific heat are becoming critical for such applications. One such study was carried out by placing the foam between the asbestos cement roof and ceramic slab. It was concluded that PU foam could be categorized into insulating material. The foam under study was made by castor oil-based polyol and MDI with a density of 40 Kg/m^3 and thermal conductivity of 0.045 W/mK. The foam was able to decrease approximately 6 °C temperature as compared to outdoor temperature [34].

The thermal conductivity of foams is determined mainly by the thermal conductivity of gas trapped in the foam cells. The nature of hydroxyl groups also plays an important role in thermal conductivity as the primary hydroxyl groups react more quickly in the blowing reaction as compared to the secondary groups. This creates a weak three-dimensional network that is weak in the retention of carbon dioxide gas produced during the blowing reaction [35]. The same was also concluded by Hu et al., who made rigid foams by using rapeseed oil and found that overall reactivity, rate of expansion and gelation was lower than that of the petroleum-based product. The physical properties were also inferior [36]. In addition to the lowering of compressive strengths, there was also a lowering in apparent foam density and closed cell structure. The heat-insulating properties also showed a negative impact with an increase in the quantity of polyol based on rapeseed oil. At a higher concentration of rapeseed oil-based polyol, the miscibility of it with petroleum-based polyol and slower reaction rate were the major issue [37, 38]. It was also found that the structure was weakened due to the poor miscibility of the polyol with petroleum-based polyol and its slower reaction rate [39]. In deciding the open and closed cell content, the role of blowing agents is very important, which also determines the mechanical properties of the foam. Water is commonly used as a blowing agent, but liquids such as cyclopentane, n-pentane, methyl chloride, acetone are often used because of their low boiling points [40, 41]. Acetone is not used as a sole blowing agent because, after some time, it induces foam shrinkage. However, acetone increases foam density and also serves as a coolant. Glycerin or polyols based on glycerin are

used primarily to avoid shrinkage. Glycerin often acts as a curing accelerator, but its addition usually decreases the foam's rigidity, thereby contributing to softening and flexibility [40].

Zieleniewska et al. studied rigid PU foam based on rapeseed oil polyol by replacing petroleum-based polyols with an increasing amount of 25, 50, 75 and 100%. The polyol was prepared by epoxidizing the oil and then opening the epoxy ring with diethylene glycol. To get PU foam, the polyol developed was reacted with MDI. FTIR spectroscopy has been used to measure the index of hydrogen bonding (*R*). The quantities of petroleum polyol were observed to increase the creation of hydrogen bonds linking the material's rigid segments. The thermal stability of such products is also important, which was shown by thermogravimetric data. $T_{2\%}$ and $T_{5\%}$ are the temperatures corresponding to a mass loss of 2 and 5%, respectively, which have been observed to increase with the increase in rapeseed oil polyol content, suggesting that the higher polyol content favors a decrease in volatile content as well as an increase in overall thermal stability [42] (Table 2).

In case of foam developed using soybean oil polyol (SBOP) with an OH value of 235 mg KOH/g, the density was increased only at 100% substitution and the average cell size with an increase in SBOP content was also lower. The smaller size of the cell is primarily associated with the higher SBOP viscosity. The type of surfactant also influences the aging efficiency of foams (hydrophilic or hydrophobic), i.e., the shift in thermal conductivity (*k* value) relative to time, which is also an important parameter for insulating appliances. After 150 days of aging, foams of 50% and 0% SBOP reported an steady rise from 23 to 24 mW/(m.K) to around 26.5–27 mW/(m.K). However, the foams aged much faster in the case of 100% SBOP and hydrophobic surfactant. The *k* value increased from about 24 mW/(m.K) to as high as 30.5 mW/(m.K). This variation in the *k* value is also due to a change in the composition of the gas over time. Owing to the partial pressure difference between the foam cell and its surroundings, ambient air normally diffuses into foam cells. The *k* value was higher for both N_2 and O_2 than CO_2 and other physical blowing agents such as *n*-pentane [43].

Until a study was conducted by Hsieh et al., the effect of the viscosity of SBOP polyol on PU rigid foam was little understood. The viscosity of soy polyol is about 1.4–3.5 times higher at 22 °C than that of petroleum-based polyol. The petroleum-based polyol OH number was 1.85 times greater than that of soy polyol. The

Table 2 The results of thermogravimetric analysis [42].

Sample	$T2\%$ [°C]	$T5\%$ [°C]
100PP	219 ± 2	247 ± 1
75PP/25RP	232 ± 2	259 ± 2
50PP/50RP	235 ± 3	262 ± 1
25PP/75RP	234 ± 2	261 ± 2
100RP	234 ± 1	261 ± 2

Adopted from [42] T2%–the temperature corresponding to a mass loss of 2%; T5%–the temperature corresponding to a mass loss of 5%

PP Petroleum-based polyol, *RP* Rapeseed oil-based polyol

cross-linking density and foam density decreased as the percentage of soy polyol increased. For mechanical properties, such as compressive strength, the viscosity relationship was quite different. The compressive strength of SBO PU foams made from polyol of low viscosity (21514 cP) showed a decrease in value for up to 30% replacement of polyol but then compressive strength increased with an increase in % replacement. The compressive strength of foams made of a polyol of high viscosity (31,351 cP) remained approximately at the same level for up to 30% replacement and then progressively increased for up to 50% [44]. Bodied SBO has also been used for the manufacture of rigid PU foams. The soybean oil and glycerol were heated together to get glycerol functional bodied SBO. The mechanical properties found were inferior to those of petroleum-based PU [45].

A low viscosity polyol from canola oil was prepared by epoxidation followed by ring opening and transesterification with 1,2-propandiol and 1,3-propandiol, respectively, as shown in Fig. 7.

The polyol obtained was of low molecular weight with a viscosity of approx. 3 PaS. The polyol produced using 1,2-propanediol had only secondary hydroxyl groups, but the polyol produced using 1,3-propanediol had both primary and secondary hydroxyl groups so that the gel time for these PU foams was between 100 and 20 min [15]. The position of the OH group on the polyol chain also affects the structure of the cell, as seen by comparing the foams produced by polyols based on castor oil and soybean oil. The position of OH is fixed in polyol based on castor oil as it is around 90% ricinoleic acid and therefore shows a more uniform structure, but the foam structure is less uniform and composed of larger elongated strip-like pores in the case of soy-based polyols. In the transverse direction, mechanical properties such as Young's module and yield stress are smaller compared to the rising direction. The difference in mechanical properties is due to anisotropy in the internal cellular structure. When measured, Young's modulus and yield stress of petroleum polyol were higher than that for soy and castor oil-based polyols in both directions even though the OH values were 330, 447, 393–441 mg KOH/g, respectively. The overall structures of polyol and isocyanate contribute to the assessment of the mechanical properties. The lower mechanical properties were due to dangling soy polyol chains that had OH groups in different positions. The type of bond also affects the thermal
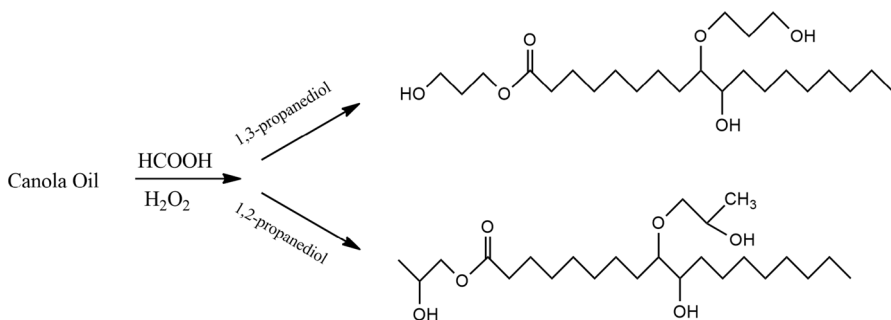

Fig. 7 Synthesis of poly (ether ester) polyols from canola oil [15]

properties, the polyol based on petroleum and vegetable oil had polyether and poly-ester bonds, respectively [46].

Dielectric polarization is also influenced by these primary hydroxyls. It was analyzed by comparing rapeseed oil polyols, which were formed by epoxidation/ring opening using diethylene glycol (EPO), transesterification with triethanolamine (TRE) and transamidation with diethanolamine (TRA) with hydroxyl numbers 230, 307, 387 mg KOH/g, respectively. Of these, the formulation of PU-TRA demonstrated the fastest decrease in dielectric polarization. The effects of primary hydroxyl and the presence of a free electron pair in nitrogen were mixed in the case of TRE and TRA polyol. The structure of EPO-based PU foam was isotropic, which had a positive impact on mechanical properties, particularly the compressive strength [47]. Crude glycerol was also polymerized to produce polyglycerols that were then transesterified with castor oil to produce polyol with a hydroxyl value of 460 mg KOH/g. These bio-polyol foams showed a decrease in cell size to a certain limit, which certainly helped to improve the compressive strength of foams. The conductivity of gas contained in the foam influenced overall thermal conductivity of foam. Foams with a high fraction of biopolyols were able to dissipate more energy by internal friction and molecular motion, so these materials were able to cope with high stresses [48].

Various ring-opening agents, such as HCl, HBr, were used to produce halogenated soy polyols. In contrast to methoxylated (1.116 g/cm^3) and hydrogenated (1.09 g/cm^3) polyol, the PU made from halogenated polyol displayed a high density (1.26 g/cm^3 for brominated and 1.15 g/cm^3), but the reactivity of halogenated polyol was found to be lower. Among other properties, the glass transition temperature of chlorinated PU was the highest. The situation was thought to be related to PVC and PVBr, but PVBr has Tg higher than that of PVC by 20 °C. The opposite situation in case of PU could be due to some loss of bromine during the reaction [25]. Phenol and cyclohexanol also allow the ring opening of epoxidized soybean oil, where it was clear that density increases with the increase in substitution. Phenol-based polyurethane has the highest density and thermal conductivity. In phenol-based PU, compression strength also increased as phenol's rigidity is incorporated into it. Due to the plasticization effect of the aliphatic six-membered ring and its non-uniform cell structure, the compression strength of cyclohexanol-based PU was lower, but the excessive introduction of phenol groups led to an increase in steric hindrance, which decreases the reactivity of hydroxyl groups with isocyanate and urea formation [49].

To explore the effects of reduced isocyanate usage, Hsieh et al. prepared several rigid foams with isocyanate indices ranging from 50 to 110. Foams with epoxidized soybean oil were also produced as a 20 and 50% replacement of petroleum polyol with an OH number of 490. They found a decrease in foam density when the isocyanate index decreased from 110 to 60, but there was sufficient catalyst to accelerate the reaction of isocyanate in foams containing epoxidized soybean oil (ESBO) with isocyanate index 100 or higher, and the observed density was also higher. Due to lower cross-linking density, the compressive strength declined with a decrease in isocyanate content [50]. Factors such as the compatibility of polyol based on vegetable oil with petroleum polyol are also important, as the blends may be stored for a long time before use. Pratheep et al. did one

such study. They produced polyol based on palm kernel oil and stored the blends for up to 6 months to check compatibility. Palm kernel polyol, due to the majority of the saturated fatty acid content in it, has a lower hydroxyl value. Due to the dangling chains, these oil-based polyols primarily showed plasticizing effects in foams. All blends with up to 70% polyol of vegetable oil were found to be stable for up to 6 months. Long-term thermal conductivity was also measured and it was noted that the smaller cell size and thickness of the cell wall were significant factors in reducing the gas diffusion rate. Just 10 and 20% of palm-based polyol also achieved higher mechanical and thermal properties. It was due to efficient segregation of the hard segments into domains for these samples. The reactivity was decreased with higher replacement (more than 50%), which reduced cross-linking density [51]. When unmodified linseed oil was used in the foam formulation, the plasticizing effect of vegetable oil was noted. When used more than 5% by weight, the oil reduced mechanical and thermal properties by creating a porous structure. The OH functionality for forming urethane bonds is reduced due to an increase in oil content. The higher oil content reduced the thickness and density of the cell wall, thus reducing foam compressive power [52]. 100% substitution of soypolyol for petroleum polyol is also feasible. Kai Guo and the team have rectified the problems such as lower glass transition temperature and lower rigidity associated with dangling chains. The use of new microreactor technologies has also nullified other concerns, such as different side reactions that consume newly produced hydroxyl groups. A novel hydroxyl compound formed by reacting styrene oxide and glycerine provided the ring opening of epoxidized soy oil. Higher compression strength and thermal stability, lower k value, better dimensional stability and slightly higher Tg were found in the prepared foams [53].

In a study, thermal properties were improved and attempts were made to make flame retardant PU rigid foam by using castor oil. First, the castor oil was alcoholized with glycerol and epoxidizedusing formic acid and hydrogen peroxide and then the ring-opening reaction was carried out with diethyl phosphate. It was observed that at only 3% content of phosphorous, the limiting oxygen index was reached up to 24.3% without any other flame retardant [21]. In another analysis, the monoglycerides of castor oil were developed by using glycerol and pentaerythritol termed MCO1 and MCO2, respectively, and then, both monoglycerides were modified with phthalic anhydride and termed as MCO3 and MCO4. Polyurethane foams were developed to explore flame retardancy by applying ammonium polyphosphate (APP) to both monoglycerides and reference foams. The combustion time of the reference foam was 125 sec and for foam formed by MCO2 was 210 sec rather than 155 sec for foams formed by MCO4. It was concluded that APP creates char layer on foams effectively, giving synergistic effects [54]. To open the rings of epoxidized soybean oil, phosphoric acid was also used. The amount of phosphoric acid was managed in such a way that polyol of high and low molecular weights was produced. The difference in molecular weight is primarily due to differences in the amount of phosphate esters (mono, di and tri esters). The oxygen index also increased with the rise in phosphorous content in this case [55]. The effect of increasing the isocyanate index on the properties of foam has been investigated. The properties are also influenced by the type of

Table 3 Properties of rigid polyurethane foams

Vegetable oil	Reaction mechanism	Hydroxyl value (mgKOH/g)	Replacement	Isocyanate	Properties					References
					Density (Kg/m³)	Compressive strength (KPa)	Thermal conductivity (mW/m.K)	% Closed cell	%OI	
Rapeseed	HO and TRE with triethanolamine	367	NA	pMDI	40.8	178 (at 10%)	25	NF	NF	[28]
Rapeseed	EPO and RO with diethylene glycol	264	30%	pMDI	41.9	280–290	22.9	86.6	NF	[29]
Rapeseed		230.0	70	pMDI	38.6	320 (at 10%)	23.5	94	NF	[38]
Rapeseed	TRE with triethanolamine	307	70	pMDI	37	180 (at 10%)	23.5	87.2	NF	[38]
Rapeseed	TRA with diethanolamine	387	70	pMDI	36.5	170 (at 10%)	24.5	93	NF	[38]
Palm	EPO and RO with water	102	30	pMDI	32.1	154 (at 10%)	30.6	49.4	NF	[30]
Soybean polyol	NA	235.0	50.0	pMDI	39.8	138.0	24	88.7	NF	[34]
Soybean	EPO and TRE with EG	265.0	30.0	pMDI	46.2	400.0	27.8	85-86	NF	[35]
Soybean	RO with methanol	175.0	25.0	pMDI	38.2	188.0	21.8	NF	NF	[41]
Soybean	RO with cyclohexanol	150	25.0	pMDI	40.2	174	23.3	NF	NF	[41]
Soybean	RO with phenol	164	25.0	pMDI	45.2	229	24.4	NF	NF	[41]
Soybean	RO with phosphoric acid	186	75	pMDI	39.1	NF	NF	NF	20.1	[46]

NA Not applicable, *NF* Required information could not be found or not reported in paper, *HO* Hydroxylation, *EPO* Epoxidation, *RO* ring Opening, *TRE* Transesterification, *TRA* Transamidation, *EG* Ethylene glycol, *OI* Oxygen index, *pMDI* Polymeric methylene diphenyl diisocyanate

functionalization and the direction of foam rise. The high index of isocyanate led to the creation of isocyanurate rings that improved thermal stability. The foams developed by the isocyanate index 250 showed very good flame retardancy with the lowest rate of heat and fumes emitted [56]. Properties of Polyurethane rigid foams are shown in table 3.

Composite rigid foams

Castor oil-phosphate-based rigid PU foams containing expanded graphite (EG) were made by Zhou et al. Glycerolysis of castor oil was performed with subsequent epoxidation and ring opening with diethyl phosphite (COFPL). The foam formulation also contained triethyl phosphite as a flame retardant, but due to the plasticizing effect, its quantity was restricted. The foam structure of COFPL and EG was compact and durable, suggesting the compatibility of EG and COFPL due to the adhesion-promoting surfactant effect of diethyl phosphite on the castor oil chain. This promotion of the adhesion of EG in foams based on COFPL lead to an increase in compressive strength. The limiting oxygen index (LOI) increased linearly and reached a maximum for COFPL foams containing triethyl phosphate (TEP) due to the rise in the weight fraction of EG in glyceroid CO foams [57]. The role of EG is to provide a fire barrier to the polymeric matrix by generating voluminous insulating layers. EG was also applied by Kurańska et al. to rigid foams made from rapeseed oil and polyisocyanurate. During the foaming process, the addition of EG decreased the maximum temperature. In contrast to the unmodified foam, EG also increased the apparent foam density and decreased the brittleness of the foam. The smaller cell size percentage also increased with the addition of EG [58].

Reactive reinforcing filler such as lignin creates small cell size structures. After a certain degree of dosing, this reactive filler influences the ordered bonding of urethane-urethane and urethane-ester linkages. Compared with reference soypolyol PU foams, the foam with a lignin content of 10% showed the highest density and other mechanical properties [59]. Most of the fillers such as wood fibers and nanoclays also decreased the average cell size in PU foams [60, 61]. Cellulose micro/nanocrystals gave higher Tg and rigidity to polyol foams of rapeseed oil [62], and these nanocrystals often change DMA curves to higher temperatures due to the reaction between crystal hydroxyl groups and isocyanate. The impact on the tensile modulus was exceptionally strong. The modulus of 1-wt% of filled nanocrystal foams was 42% higher than that of the unfilled one [63]. Such crystalline nanocellulose serves as a nucleating agent (reduction in cell dimensions) and as a particulate surfactant (coarser nature of struts), depending on the amount of added NCO [64]. Likewise, nanoclay also performed effectively in soy polyol-based PU at a maximum load of 0.5 wt%. At this loading, the compression and flexural strength were maximum, which is why excessive dispersion of nanoclay at a higher dosage in the polyol increases as polyol viscosity increases with an increase in nanoclay loading [65]. Carrot nanofiber (CNF), which mainly consists of cellulose, was separated from bleached raw juice residue. PU foams containing these CNF also had optimal

mechanical properties in castor oil polyol at a dosage rate of max 0.5 wt% [66]. Chicken feathers (CF) have been also used as reinforcing fillers in foam. Before adding to the polyol system, chicken feathers were dried at 80 °C, cut into 10 mm fibers and then mechanically grinded. Keratin contains an amine group that binds chemically with isocyanate to form urea. The 0.1% addition of CF showed a strong improvement in mechanical and thermal insulation properties. CF content up to 5% has no comparable performance as unfilled foam, but the results deteriorated above 0.5% of CF filling [67]. Properties of polyurethane rigid composite foams are shown in table 4.

Flexible foams

Flexible polyurethane foams are used in furniture, cushioning, packaging, automotive seating, mattresses, transportation, textiles, packaging, medical supplies, sporting goods, biomedical materials and smart materials as cell absorbers. This provides a very high level of comfort and protection that is not available with any other cushioning materials. Low-density PU flexible foam is usually in more demand due to its lower costs [14, 68]. Catalyst and surfactant concentrations play a very important role in the foaming process and the resulting cellular structure in PU flexible foams. Increased catalyst quantity typically accelerates the gelling reaction, which is usually quicker than the foaming reaction, resulting in increased rigidity and the number of closed cells. As the blowing agent, such as water, shifts the formation of polyurethane into polyurea, higher concentrations of water and more hard segments are formed. The density is also found to decrease due to gas release [69].

Eceiza et al. found that, in the reaction phase, the molecular weight of the polyol is directly related to the relative movement of chains. The isocyanate index was maintained constant, the quantity of NCO groups increased by increasing the equivalent OH groups with the incorporation of corn based polyol. They observed that the density first reached minimum at 10% replacement with corn-based polyol and then increased with increase in corn polyol content. At the minimum value, the increase in viscosity is due to the formation of allophanate and biuret cross-links, which hinders the reaction. An increase in density leads to an improvement in mechanical properties, such as tensile strength and decrease in cell size. At 10% substitution, the tensile strength was 125KPa and foam density was 38.55 Kg/m^3, which was the lowest value and at 15% substitution, it increased to 200 KPa and with foam density 39.2 Kg/m^3 [70]. By nature, flexible foams are elastic, which is accomplished by keeping the density of cross-links low. The low hydroxyl value of polyol helps to preserve adequate cross-linking density and elasticity. As compared to other vegetable oils, palm oil has less unsaturation. Palm oil is the cheapest vegetable oil in the market, and polyol prepared from it also has a low hydroxyl value, so it is ideally suited for polyol synthesis needed for flexible polyurethane foams. Palm oil-based polyols had a good impact on mechanical properties such as tensile strength as per the results obtained in the work carried out by Prociak et al. While the functionality of petrochemical polyol was higher (3.0) than the average number of hydroxyl groups of palm oil polyol (2.5), foams made of palm oil polyol had higher tensile

Table 4 Properties of rigid polyurethane composite foams

Vegetable oil	Type of mechanism	Hydroxyl value	% Replacement	Isocyanate	Type of filler	Filler %	Properties					References
							Density (Kg/m³)	Compressive strength (Kpa)	Thermal conductivity (mW/m.K)	% Closed cell	Flexural strength (KPa)	
Soybean polyol	NA	272	50	pMDI	Lignin	10%	76	460	NF	NF	870	[49]
						15%	86	320	NF	NF	670	
Rapeseed	EPO and RO with diethylene glycol	264	NA	pMDI	Cellulose nanocrystals	2%	39.1	NF	23.5	80.5	NF	[52]
						3%	40.7	NF	23.1	82.5	NF	
Castor polyol	NA	350	NA	pMDI	Carrot nanofiber	0.5%	46.0	300.0	NF	79	NF	[56]
						1%	49.0	240.0	NF	88	NF	
Soybean	NA	156	10	pMDI	Keratin feathers	0.1%	42.0	210	27	94	1200	[57]
						0.5%	40	170	28	87.2	750	

NA Not applicable to the system, *NF* Required information could not be found or not reported in paper, *EPO* Epoxidation, *RO* Ring opening, *pMDI* Polymeric methylene diisocyanate

strength. It was found that this effect was based on the composition and positioning of the main chain hydroxyl groups. The development of short segments that ultimately result in increased tensile strength was observed when groups are placed in the middle of the chain. The position of hydroxyl groups also had a better effect than the cross-linking density induced by the higher petrochemical polyol functionality. Resilience is another important property for flexible foams/viscoelastic foams. It depends on the proportion of soft and hard segments. As palm-based polyol is increased, increased resilience can be associated with an increase in the content of closed cells. It is because of the quick response in closed cells due to the compressed air [71]. Palm oil has more saturated alkyl chains than unsaturated chains. In general, due to the existence of long alkyl chains, this palm oil-based polyol provides soft segments [8]. Structural regularity provides the foams with uniform properties. Vegetable oil monoglyceride offers regular positioning of primary hydroxyl groups, thus giving the foams a more uniform and regular structure [72].

The existence of open cells in large quantities is necessary for flexible foams to perform well [10]. Prociak et al. noted that there was a decrease in foam density due to the creation of urea and biuret connections by keeping the NCO/OH ratio higher for polyol based on rapeseed oil. Mechanical properties such as compression and tensile strength simply depend on the density of the cross-link, which depends on the value of hydroxyl and the isocyanate index. With an improvement in plasticizing effect in foams provided by lower polyol functionality, durability increases. The variety of chains between hydroxyl groups causes lower resilience [14]. More hard segments are created by increasing the water content, which reduces resilience but the reduction in water level provided a more uniform cell wall structure. As the amount of rapeseed oil polyol increased, its resilience decreased. It was also observed that this oil-based polyol acts as an additional surfactant which leads to the generation of the lower number of cells but with a bigger size. Another significant characteristic is foam hardness or comfort factor, especially applicable to bed mattresses. The temperature of the foaming reaction is also influenced by the presence of secondary hydroxyl groups in polyol-based rapeseed oil. Because of the existence of secondary hydroxyl, the foaming temperature for bio-based polyol is low compared to petrochemical polyol [73]. Compared to vegetable oil polyol, the petrochemical polyol usually gives a more open cell structure. This is also the effect of primary hydroxyl groups [74].

The cross-metathesis reactions are used to convert vegetable oil into short-chain oil with a terminal double bond, hence, the product will have primary hydroxyl groups and fewer dangling chains will be there. The self-metathesis reactions of vegetable oil increase mass and produce oligomeric structures. The results obtained for these oligomers were good [75]. Adduct of PEI was also used as a blowing agent. At first, glycidyl ether of alcohol was prepared and was grafted on the PEI, and finally, CO_2 was reacted to get CO_2 adducts of PEI. In reaction, these adducts released CO_2. The foam density was dependent on CO_2 content and efficiency to release it. The mechanical properties of foam were dependent on the dispersion of the blowing agent in the polyol system [76]. The foams made from vegetable oil are generally much more susceptible to biodegradation. Estenoz et al. produced foams from castor oil and maleic anhydride

modified castor oil. The foams were studied after 60 days of incubation in a liquid culture medium of *Pseudomonas sp.* strain.

The amount of maleic anhydride modified castor oil contributed to influencing biodegradation. With the increase in hydrophilicity in the foams, the degradation also increased. The ester bonds got converted into hydroxyl groups due to bacterial enzymatic attack during the hydrolysis reaction and the tensile strength increased and elongation at break decreased after the incubation period [77].

Conclusion

This review states the importance of vegetable oil-based polyol in polyurethane foams. Vegetable oils (VO) contain triglycerides which is the key ingredient in developing polyols. The use of these VO-based polyols as a replacement for traditional polyols will play a tremendous impact. This will not only increase the green carbon footprint but also decrease the dependency on fossil fuel-based products. This review also briefs us about various methods used in developing polyols from VO. Because of the range of available nucleophiles, the generation of polyol through epoxidation followed by ring opening is the most commonly used method. Polyurethane foams have a special market due to their marked properties such as low density, lightweight, low thermal conductivity and high comfort factor. This makes them suitable for use in different industries, such as heat insulators, house roofing, cushioning. The biodegradable PUFs may improve environmental impacts caused by petroleum-based PUFs. A significant majority of investigations in the previous decade have been carried out on the use of vegetable oils as alternatives to PU foams. However, there are some shortcomings like 100% replacement of petroleum polyols with VO polyols is not possible with current modifications as it shows some deterioration of properties mainly in rigid foams. While the prospect of using PUF based on VO seems bright, further research and innovations are required for the complete replacement of conventional polyol.

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