

Polyurethanes from Renewable Resources

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Abstract Factors such as the price and availability of petroleum, and societal concerns over global climate change continue to create increased market pressure on the industrial and domestic use of petrochemicals. Many industrial suppliers of basic chemicals are looking to alternative, sustainable sources of raw materials. In the polyurethanes industry, suppliers of polyols have been utilizing naturally sourced raw materials for many years in conjunction with petrochemical raw materials. Recently, the polyurethanes industry has moved toward greater replacement of petrochemical content with renewable resources. The principle sources of renewable feedstock are the triglyceride oils found in seeds such as soybean, canola, and sunflower. New, non-food sources of triglycerides such as *Lesquerella* and *Vernonia*, and even aquatic sources such as algae, are beginning to draw attention, even as old sources such as castor oil are getting a new look.

Keywords Algae · Castor · ESO · Foam · Polyurethane · Renewable · Triglyceride

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1 Introduction

Polyurethanes are highly versatile polymers that are used in a wide range of applications common to everyday life. The latitude of control over key design features, including features at the microscale (crosslink density and hard segment content), mesoscale (phase morphology), and macroscale (foam density and cell dimensions), enables polyurethanes to fulfill performance requirements for a wide range of products such as low temperature elastomers, high tensile adhesives, flexible, open-celled foams for bedding and furniture, and rigid, closed-cell foams for insulation.

Factors such as the price and availability of petroleum, and societal concerns over global climate change continue to create increased market pressure on the industrial and domestic use of petrochemicals. Many industrial suppliers of basic chemicals are looking to alternative, sustainable sources of raw materials. In the polyurethanes industry, suppliers of polyols have been utilizing naturally sourced raw materials for many years in conjunction with petrochemical raw materials. Recently, the polyurethanes industry has moved toward greater replacement of petrochemical content with renewable resources. The principle sources of renewable feedstock are the triglyceride oils found in seeds such as soybean, canola, and sunflower. New, non-food sources of triglycerides such as *Lesquerella* and *Vernonia*, and even aquatic sources such as algae, are beginning to draw attention, even as old sources such as castor oil are getting a new look.

2 Basics of Polyurethane Chemistry

2.1 Polyols and Isocyanates

Polyurethanes are composed of the reaction products of polyisocyanates and polyalcohols. The chemistry of polyurethanes has been under development for over

60 years, and the product chemistry is highly refined toward optimum performance in end-user applications. In order to guide the reader in understanding the challenges that are faced when introducing a completely new base of raw materials into polyurethane products, a focused introduction to polyurethane chemistry is in order.

Isocyanate chemistry is of itself a very complex field of chemistry, and even a brief description of the extent is outside the scope of this article. For a comprehensive description of isocyanate chemistry and its applications to polyurethane polymers, readers are directed to a handbook that is the standard in the industry [1]. A brief description follows for the purpose of introducing the role of isocyanates in polyurethane chemistry.

The two key isocyanates that are used in the greatest volumes for polyurethane polymers are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). Both isocyanates are produced first by nitration of aromatics (toluene and benzene, respectively), followed by hydrogenation of the nitro aromatics to provide aromatic amines. In the case of MDI, the aniline intermediate is then condensed with formaldehyde to produce methylene dianiline (MDA), which is a mixture of monomeric MDA and an oligomeric form that is typical of aniline/formaldehyde condensation products [2]. The subsequent reaction of phosgene with the aromatic amines provides the isocyanate products. Isocyanates can also be prepared by the reaction of aromatic amines with dimethylcarbonate [3, 4]. This technology has been tested at the industrial pilot scale, but is not believed to be practiced commercially at this time.

These two isocyanates are used individually in the monomeric form, or in blends (e.g., TM20, a TDI/MDI blend for automotive flexible foams), and are often pre-advanced into oligomeric forms with very low molecular weight diols to form isocyanate-capped prepolymers.

Isocyanates can also be advanced into a variety of intermediate products that contain different forms of condensation oligomers. These advanced products are typically used in applications where the reactivity or the viscosity of the isocyanate is modified for specific requirements in an end-use application.

Isocyanates that are produced from aliphatic amines are utilized in a limited range of polyurethane products, mainly in weatherable coatings and specialty applications where the yellowing and photodegradation of the aromatic polyurethanes are undesirable [5]. The aliphatic isocyanates are not used more widely in the industry due to the remarkably slow reaction kinetics of aliphatic isocyanates compared to their aromatic counterparts [6]. Due to the slow reactivity of aliphatic isocyanates, it is not practical to use them in the preparation of flexible or rigid foams, which are the main commercial applications for polyurethane chemistry.

Due to the necessity for aromatic structure in the commodity isocyanates, and the intensive chemical conversions required to derive the isocyanate reactant, no high-carbon frameworks derived principally from plant sources have been developed into isocyanates. The majority of the derivation of raw materials from high carbon conjugates has been focused on the development of polyols, for which the structural demands are a better fit for available renewable feedstocks. Although there are some notable exceptions [1], as a general rule modification of the

properties of polyurethanes are most commonly accomplished through structural modification of the polyol components.

Polyurethane chemistry began with the utilization of polyester polyols, principally prepared from diacids such as adipic acid and various diols. Later, polyester polyols were replaced by polyether polyols due to improvements in mechanical properties and moisture resistance. Polyether polyols now constitute the greater part of the volume in polyurethane polymers [1].

2.2 *Conventional Polyether Polyols*

Conventional polyether polyols are principally derived from polymers of propylene oxide (PO), optionally containing some ethylene oxide (EO). Usually, the copolymers contain a maximum of approximately 20% EO. The oxiranes EO and PO are derived from petroleum feedstocks. The process begins with the cracking of crude oil in a thermal catalytic cracker, which produces a mixture of ethylene and propylene, depending on the process configuration [7, 8]. The ethylene is then converted to EO in a direct oxidation process using air over a silver catalyst [9]. The analogous direct oxidation of propylene to PO has been the subject of substantial research, but no practical commercial process has been developed to date. Conventional technology converts propylene to propylene chlorohydrin via treatment with HOCl, followed by elimination of HCl to provide PO [10, 11]. More current technology can co-produce PO with styrene monomer, or more preferably, can produce PO via oxidation of propylene with hydrogen peroxide [12].

Polymerization of the oxiranes is typically propagated from a starter molecule that is chosen to define the functionality (f) of the final polyol. The functionality and the molecular weight of polyols are the main design features that define the polyurethane properties in the end-use applications. Additionally, the balance of EO and PO in the polyether polyols, mainly for flexible foam polyols, is tailored to enhance the compatibility of formulations and the processability of the foam products. The exact composition of the polyols defines the crucial performance features of the final polyurethane product. Even seemingly small differences in polyol composition can result in changes to polyol processability and polyurethane performance. This becomes a crucial issue when replacing conventional petrochemical polyols with polyols from different feedstocks. To demonstrate the sensitivity of commercial formulations to changes in feedstocks, a simple example is offered below.

Conventional polyether polyol technology involves alkoxylation of the starters with PO and EO using an alkali metal hydroxide catalyst such as potassium hydroxide. The catalyst can be neutralized and the neutral salt can be left in the final polyol, or optionally the catalyst can be extracted by washing with water or by deposition on an ion exchange medium. In recent years, a new catalyst technology has become widely adopted within the polyols industry, using zinc hexacyanocobaltate (double metal cyanide catalyst, or DMC), which runs at very high

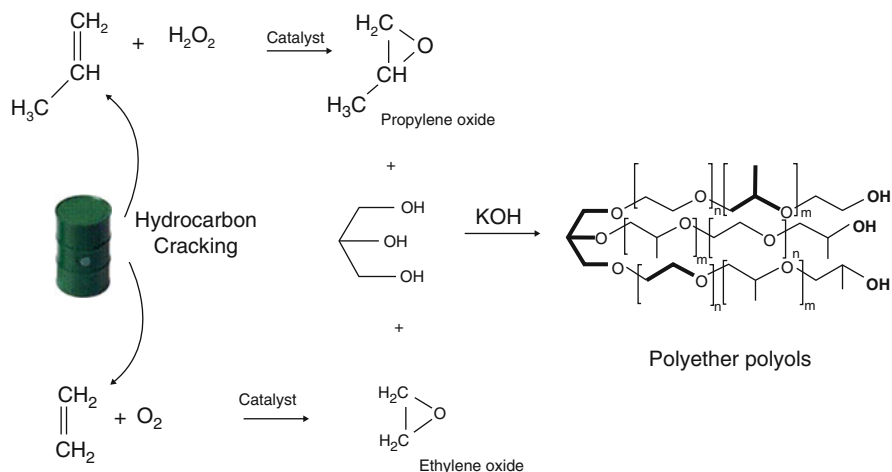


Fig. 1 Derivation of polyether polyols from petroleum oil

efficiency and does not currently require removal from the final polyol products [13–15]. Conventional KOH-produced polyols and DMC-produced polyols are not identical in composition, morphology or in reactivity, even when produced from the same combination of raw materials. Subtle differences such as the primary OH content, which is created by a slightly higher tail-to-tail addition defect when using the DMC catalyst, and major differences such as the average functionality of the final product create processing issues for the manufacturers of polyurethane products. When carefully designed, the polyols are similar enough that most polyurethane producers can make process adjustments to interchange products when similar KOH and DMC polyols are used. The production of polyols from petroleum feedstocks is outlined in Fig. 1.

Most polyurethane elastomers are prepared from high molecular weight (2,000–12,000) diols due to the high elongation required by many elastomer applications. Flexible foam formulations are comprised of polyols with lower molecular weight (3,000–5,000) and with a few exceptions are usually initiated from glycerin ($f = 3$). Rigid insulation foams are prepared from low molecular weight polyols (400–1,000) with high functionality ($f = 3$ –8). Rigid foam polyols in particular are often produced from blends of initiators such as glycerin, sucrose, sorbitol, or other natural carbohydrates to produce a polyol with a specified average functionality. The key design variables for polyether polyols are outlined in Fig. 2.

2.3 Making Polyurethane Polymers

As noted previously, polyurethanes are prepared by combining polyols and polyisocyanates. In reality, the term “polyurethane” is a misnomer because the

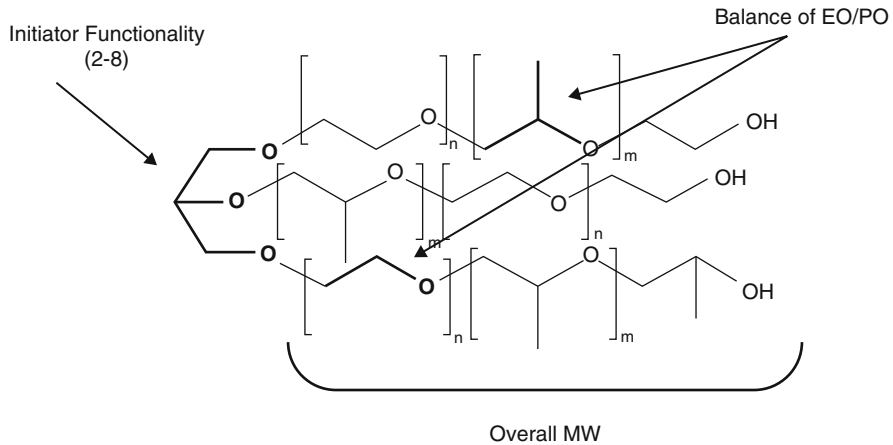


Fig. 2 Design features of polyether polyols

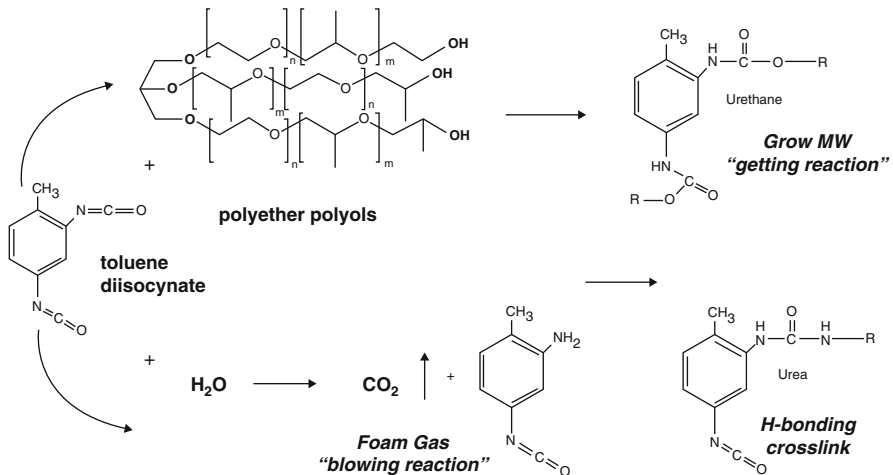


Fig. 3 The chemistry of polyurethane/polyurea polymers

urethane linkage in the polymer is a minor part of the polymer functionality. In many polyurethane formulations for foams, the reaction of isocyanate with water is the predominant chemical reaction, producing CO_2 as a "blowing" agent (water-blown foams) and re-generating the aniline precursor functionality. The aniline then reacts very quickly with another isocyanate to generate a urea functional group, creating the aromatic "hard segment" of the polyurethane and providing chain propagation through step-growth addition. The competing chemistries that produce polyurethane/polyurea polymers are outlined in Fig. 3.

As polymer molecular weight grows, the polyurea hard segment reaches a percolation point, where the driving force for interchain hydrogen bonding exceeds

the free energy of randomization, and the hard segment components begin to organize into discreet domains. The precipitation of this second phase domain is expected to follow the classic surface area minimization thermodynamics observed in other amphiphilic polymer systems [16, 17]. If sufficient volume fraction of hard segment domain exists, the hard segment can attain a co-continuous morphology, which provides structural integrity to the growing polymer system, often well before the gel-point of the polymer matrix is reached. Such is the case in flexible foam systems where the actual covalent crosslink density is very low. The end-use applications for polyurethane flexible foams constitute the largest volume segment of the polyurethanes industry, and include bedding, furniture, automotive interiors, and other applications associated with human comfort.

There are a few key features of polyurethane components that maximize the opportunity for polyurethanes to achieve the mesoscale morphology that results in the desirable properties of these polymers. Uniformity of component raw materials is an important variable. Disruption of polyol hydroxy equivalent weight ($HEW = MW/f$) distribution outside the normal Poisson distribution achieved by conventional catalysis [18, 19] causes an accumulation of phase organizational defects, which increases as the breadth of polyol HEW increases. This disruption of phase organization (phase mixing) has a significant effect on the mechanical properties of the final flexible polymer products, the principle one being the elasticity or resiliency of the resulting flexible polymer. Polymer modulus is increased, and tensile and tear strength can be adversely affected. In some polyurethane flexible products, it is desirable to enhance phase mixing and this can be achieved by controlling hard segment content and by mixing polyether polyols of different HEWs [20]. Such products are prepared for viscoelastic bedding and furniture, and for sound dampening in some automotive interiors. In most conventional flexible foam applications, however, it is desirable to maximize phase segregation in order to achieve the best properties of the flexible products.

In high tensile and high elongation elastomers, it is also desirable to achieve a very high polymer molecular weight with high uniformity and little branching or crosslinking. The best performing elastomers are prepared from high molecular weight diol precursors with low polydispersity and low monol content, such as the polytetramethylene glycol (PTMG) polyols, prepared by cationic polymerization of THF [21]. Polyurethane/polyurea polymers prepared from these polyols are used in the preparation of Spandex fibers. The combination of high uniformity and low glass transition temperature (T_g) contribute to the ultrahigh performance of these elastomers.

3 Renewable Feedstocks in Polyols for Polyurethanes

The use of naturally derived complex carbon compounds as raw materials for polyurethane polymers is not new to the industry. Since the advent of polyether polyols, polyurethane polymers have utilized natural sources of renewable carbon.

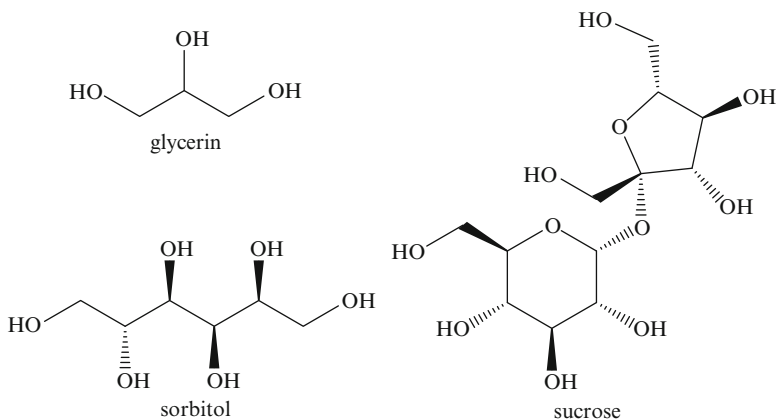


Fig. 4 Typical flexible and rigid polyol initiators

Glycerin, which is commonly used as the initiator for polyether triols, can be produced from petrochemical propylene [22, 23], but is most often derived from the triglycerides of animal fats or vegetable oils [24]. A recent increase in the global availability of glycerin as a feedstock has been driven by the development of biodiesel fuels, from which glycerin is a by-product of sizable volume. The resulting glycerin polyether triols are commonly used to produce flexible foam products such as mattresses, pillows, and cushions for bedding and furniture, or for automotive seating. Polyols with higher functionality are initiated from carbohydrates such as sucrose or sorbitol. These types of polyols are used in both flexible foams (high molecular weight polyols) and rigid foams for thermal insulation (low molecular weight polyols). Because of the low HEW values in rigid foam polyols, the renewable content of these components is often quite high, even when utilizing conventional petrochemical chain extenders. Figure 4 illustrates some of the most commonly used natural carbohydrates for initiators.

3.1 Seed Oil Triglycerides

Seed oil triglycerides are not new to the field of polyurethane polymers. The most common naturally hydroxylated seed oil, castor oil, has been used directly in the preparation of polyurethanes for many years. The formulations that contain castor oil benefit from improved weatherability, moisture resistance, and the low cost of castor oil, but the benefits are generally offset by some compromises in performance.

In recent years, industrial research has created new opportunities for the use of new types of plant-derived oils in polyurethane applications [25]. In addition to the use of natural glycerin or sugars as a starter for conventional petrochemical polyols,

these triglyceride oils have been chemically modified to produce a variety of polyols that are suitable for the preparation of polyurethane products.

Seed oil triglycerides consist of three fatty acids esterified to glycerin. Although most plants produce at least some C₁₆ fatty acids, the majority of the triglycerides are comprised of C₁₈ fatty acids. The balance of the fatty acids is quite specific to the plant from which the oil is derived, but the most prominent fatty acids among all plant species consist of a series of 18-carbon fatty acids containing zero, one, two, or three sites of unsaturation. These fatty acids are stearic, oleic, linoleic, and linolenic acids, respectively. These are the main fatty acids found in most seed oils and are illustrated in Fig. 5.

Oil-producing plants vary significantly in the exact composition of the fatty acids that make up the triglyceride. Triglyceride fatty acids contain from zero to as many as four olefins. Table 1 illustrates the fatty acid composition of several

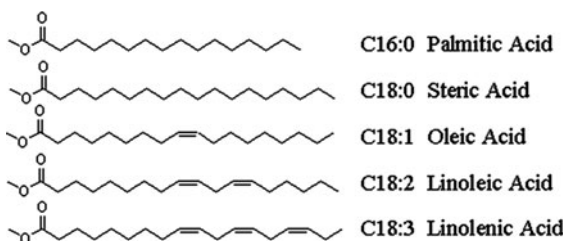


Fig. 5 The most common fatty acids found in seed oil triglycerides

Table 1 Fatty acid compositions of some common seed oil triglycerides

Seed oil	Fatty acid content (%)						
	C16:0 palmitic	C18:0 stearic	C16:1 palmitoleic	C18:1 oleic	C18:2 linoleic	C18:3 linolenic	C18:1 OH ricinoleic
Castor	1	0.7	–	3.1	4.4	0.9	89.6
Coconut	8.5	2.7	–	6.5	1.2	–	–
Corn	12.5	1.8	–	27.4	57.6	0.7	–
Cotton seed	25.8	1.9	0.5	16.7	54.2	Trace	–
Linseed	6.6	2.9	–	14.5	15.4	60.6	–
Olive	10.6	3.6	0.5	77.2	7.2	0.9	–
Palm	44	4.5	0.1	39.2	10.1	0.4	–
Peanut	9.9	2.3	Trace	49.3	34.1	1.4	–
Rapeseed (canola – low)	5	1.8	0.4	57.5	22.7	10.6	–
Safflower	6.8	2.5	–	12.6	77.4	0.1	–
Safflower (high oleic)	4.7	2.1	–	76.8	15.7	0.4	–
Sesame	10.1	5.7	Trace	39.7	44.4	Trace	–
Sunflower	5.9	4.4	0.2	19	67.5	2.9	–
Sunflower (high oleic)	3.8	4.1	–	78.4	11.3	Trace	–
Soyabean	11.3	3.4	–	23.1	55.8	6.4	–
Tung	–	1.8	Trace	5.8	6.5	Trace	–

common plant oils. The common nomenclature for the industry is utilized, where the number of carbons of the fatty acid is followed by the number of sites of unsaturation, e.g., C18:1 is the designation of oleic acid.

The olefins in the fatty acids serve several purposes. Unsaturation in a C₁₈ chain depresses the freezing point of the fatty acids. The olefins are all in the *cis* orientation, which creates more disorder in the carbon chain and reduces the freezing point further. The fully saturated C₁₈ fatty acid (stearic acid) has a melting point of 69–70°C, and the resulting triglycerides are solid at room temperature (e.g., hydrogenated vegetable oils). The monounsaturated fatty acid (oleic acid) has a melting point of 12–13°C and the resulting triglycerides are liquid at room temperature. Additional unsaturation introduced with linoleic (melting point, –5°C) and linolenic acid (melting point, –11°C) depress the melting points of the triglycerides even further. This structural feature ensures that the lipid/phospholipid bilayer membranes that make up the plant cell walls are able to maintain fluidity in cold weather climates [26]. This structural variation is not as prevalent in, for instance, palm oil, which is capable of sustaining high levels of saturated fatty acids (~49%) due to its tropical growing environment. The freezing behavior of different plant oils has been demonstrated to be related to the fatty acid composition of the triglycerides [27].

The unsaturation is not conjugated in the higher unsaturated fatty acids, but are each separated by a single carbon methylene group. This creates an allylic carbon at both ends of the unsaturation, and the methylene bridges between olefins are doubly allylic. These allylic carbons behave as built in antioxidants because they react readily with oxygen at ambient and elevated temperatures. The resulting allylic hydroperoxides undergo spontaneous scission to generate the low molar mass aldehydes that are responsible for the rancid odor of fats and oils. The degradation pathway of the fatty acids has been the subject of a great body of work due to the impact on food quality and shelf life of food oils.

Although a number of mechanistic pathways have been proposed for the formation of these oxidized fatty acid products, the generally accepted route is through the Hock cleavage [28–33]. The exact mechanics of the Hock cleavage have been proposed to proceed through more than one possible pathway, including intermediate dioxetanes or vinyl ethers. The competitive pathways each describe the formation of the observed final products. For a review of the oxidative degradation of olefins, readers are directed to an excellent review by Frimer [34]. Figure 6 illustrates the pathway, beginning from the rearranged initial hydroperoxide.

This oxidative degradation has significance to the application of triglycerides in commercial polymer applications. Many polymer products bear stringent quality requirements, including product odor. The natural odor of vegetable oils, which is often intensified by heat processing, has been found to persist through some of the different methods used to process the triglycerides into polyols for polyurethanes. This rancid oil odor has been a barrier to market adoption for some of the natural oil polyol technologies. As a product quality issue, odor is experienced to different degrees in different triglyceride polyol products, depending on the chosen triglyceride oils and the particular conditions of the manufacturing process [35–39].

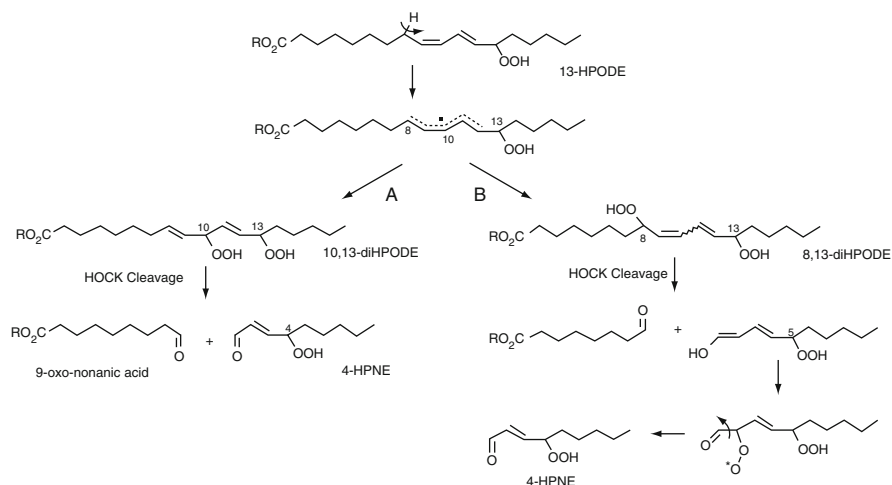


Fig. 6 Hock cleavage degradation of fatty acids. Reproduced from [33] by permission of Springer

Some producers of triglyceride-based polyols have reported the development of odor-remediation technologies for their products, but these developments are proprietary and details are not available at this time.

One key requirement for biochemical feedstock utilization of these oils in many different technologies such as biodiesel production, and production of polyurethane polyols outlined here, is a low relative content of the saturated fatty acids. The saturated fats cause problems in biodiesel fuels because of a relatively high freezing point. High saturated fat content in biodiesel fuels has been reported to cause gumming and fuel solidification problems in diesel automobiles, especially at high latitudes and altitudes with cooler weather [40]. Similarly, saturated fats cause issues in processing these oils into polyurethane polyols. The saturated fats are not amenable to the functionalization chemistries used to develop the desired polyol reactivity, and in most processes that use the triglyceride oils or the fatty acid methyl esters (FAMES) that are derived from them, the saturated fats simply go through the process as non-reactive diluents. Due to their inherently non-polar nature, they can also cause problems with formulation compatibility and can disrupt the phase segregation, which is necessary for the proper performance of flexible polyurethane polymers. In the final polymer products the saturated fats do not contribute to network connectivity. For these reasons, plant-derived oils that are lower in saturated fats are more desirable for the preparation of polyurethane polyols.

3.2 Triglycerides from Algae

Concerns over the use of food stocks for fuel sources have heightened the awareness of the general public with regard to the socially responsible use of bioresources [41].

In response to this concern, many of the commercial parties involved in the development of alternative fuel and chemical feedstock resources are investigating non-food sources of triglyceride oils.

The research into non-food sources of triglycerides as a potential source of cheap and prolific high conjugate carbon compounds began several years ago [42, 43]. The US Department of Energy study concludes that low capital costs and high yield processes would be required to make microalgae fuel and chemical feedstock production competitive with today's petrochemical processes. Key technology hurdles are identified as (1) identification of microalgae species that meet several important criteria, including environmental adaptability, yield, productivity, and product compositions; (2) definition of cultivation and resource requirements, including temperature tolerance, nutrient demands, and water quality; and (3) development of processing technology, including harvesting and conversion of biomass to desired products.

The principle product from these algae-based production units is biodiesel fuel, which is produced by the transesterification of triglycerides with methanol followed by removal of glycerin in the conventional process. A key product requirement for biodiesel is a high level of unsaturated fatty acids in the source triglycerides, at least for the production of biodiesel that can be used year-round at higher latitudes [44]. The volumes of polyols used in polyurethanes are extremely small when compared to the potential volumes of biodiesel as fuel for transportation, so specifications for high unsaturation in oils from algae for chemical feedstocks are not likely to drive trends in the technology. Fortuitously, in this case, the key chemical feedstock requirements for low saturated fat coincide with the similar specification for biodiesel fuels, and this coincidence creates an opportunity for such oils in the chemistries described here for the preparation of polyols for polyurethanes.

Recent research into the use of algae as a fuel source has begun to make a stronger case for the qualities of algae as a raw material source [45]. Both public and proprietary sources of developmental algae triglycerides have successfully propagated algae with high oleic acid content in the oils, making these varieties of algae attractive for both fuel and chemical feedstock interests, at least with regard to product composition [46]. Figure 7 illustrates the gas chromatography analysis of triglyceride collected from one species of algae under development. Table 2 lists the identities and quantities of the identified fatty acids that were isolated from the algae source. Some work has already been published on the functionalization of algae triglycerides for industrial purposes [47].

Many different process approaches to growing algae for feedstock oils and biodiesel are being considered, including open pond techniques, growth in giant photoreactors (large transparent circulation loops in which triglyceride production is promoted via CO₂ sequestration and photosynthesis), and even in closed systems where the algae is fed carbohydrate nutrients [48] instead of the conventional photosynthetic technique. The number of commercial and federally subsidized programs pursuing this attractive area of research is too long to list here, and the

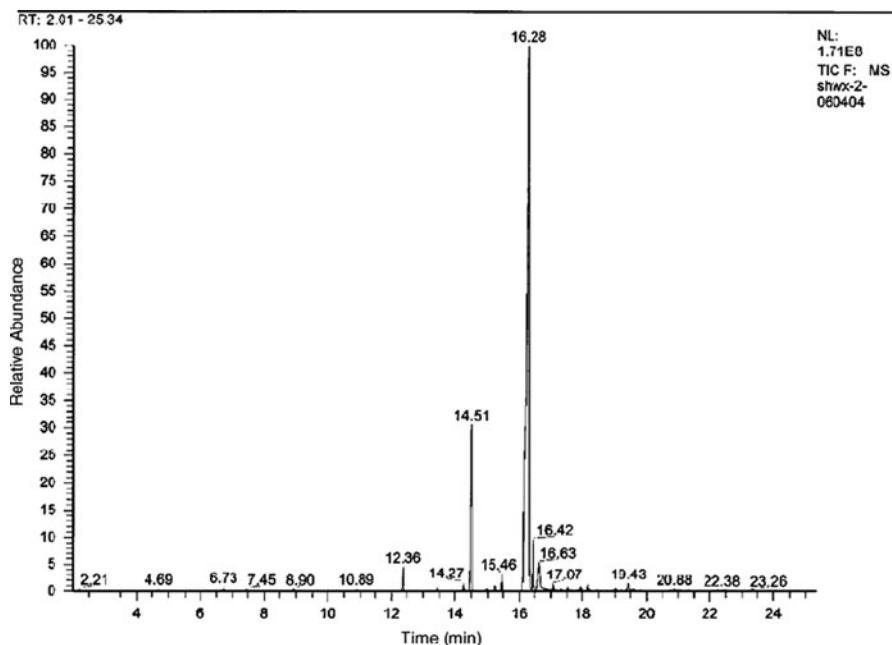


Fig. 7 Gas chromatography of the fatty acid methyl esters in biodiesel. Reproduced from [46] by permission of Elsevier Press

Table 2 Fatty acid methyl esters in biodiesel

Molecular formula	Relative molecular mass	Fatty acid methyl ester	Relative content (%)
$C_{15}H_{36}O_2$	242	Methyl tetradecanoate	1.31
$C_{17}H_{34}O_2$	270	Hexadecanoic acid methyl ester	12.94
$C_{18}H_{36}O_2$	284	Heptadecanoic acid methyl ester	0.89
$C_{19}H_{34}O_2$	294	9,12-Octadecadienoic acid methyl ester	17.28
$C_{19}H_{36}O_2$	296	9-Octadecenoic acid methyl ester	60.84
$C_{19}H_{38}O_2$	298	Octadecanoic acid methyl ester	2.76
$C_{20}H_{38}O_2$	310	10-Nonadecenoic acid methyl ester	0.36
$C_{21}H_{40}O_2$	324	11-Eicosenoic acid methyl ester	0.42
$C_{21}H_{42}O_2$	326	Eicosanoic acid methyl ester	0.35

technology options being investigated is outside the scope of this text. There are many skeptics on the topic of algae as a viable source of energy and chemical feedstock, and the debate over the thermodynamics and economics of the potential processes continues to this day [49]. Ultimately, the competitive hurdles that must be overcome to make any approach commercially viable will determine the survivability of these processes.

3.3 Naturally Hydroxylated Seed Oils

Some plants produce triglyceride oils with naturally appended hydroxyl groups, which are capable of reacting directly with isocyanates to produce polyurethanes. Of these oils, the two most common are castor oil and lesquerella oil, both of which are the subject of ongoing research and development for industrial applications.

3.3.1 Castor Oil

Castor oil is derived from the castor plant (*Ricinus communis*). The castor plant has a long and rich history of uses in human society. The oil from the plant is non-digestible, and is commonly known to be a medicinal purgative. The castor bean contains the protein ricin, a substance that is famously toxic in humans [50]. The lack of food value from the castor plant coupled with the issues of toxicity inherent in extraction of ricin has mostly limited the use of castor oil to the industrial sector.

The castor plant is widely considered to be a nuisance plant, because it proliferates rapidly in poor, depleted soils that cannot sustain other more important commercial crops. It spreads quickly as a weed, and in some places has been listed as an intrusive species to be eliminated [51, 52]. Nevertheless, in recent years the industrial volume of castor oil has increased dramatically, driven primarily by the global interest in renewable resources for fuel and feedstocks as an alternative to petrochemicals. The majority of the volume growth has come from the Asian continent, primarily from India, where the castor plant is harvested commercially [53]. In addition to its direct use in polyurethane products, the oil and its components have been the focus of innovative new derivatization strategies to improve their properties for use in plastics, while retaining high levels of renewable content in the final products. These developments will be described in Section 4.5.

Castor oil is a triglyceride that is well suited for use in polyurethane applications. Unlike most other oil-producing plants, the castor plant produces a triglyceride containing >90% of a single fatty acid, that being ricinoleic acid. Ricinoleic acid contains secondary hydroxyl groups appended to the C₁₈ fatty acid backbone (Fig. 8).

The high percentage of ricinoleic acid in the triglyceride, coupled with the presence of a single hydroxyl group on each ricinoleic acid makes the triglyceride very nearly 3.0 functional in OH groups directly as isolated from the plant. The component ricinoleic acid is an important component in lithium grease and other industrial lubricants [54–56].

Castor oil has been used in polyurethanes for decades. The natural abundance of castor, combined with the inherent proper functionality of the oil, has led to the

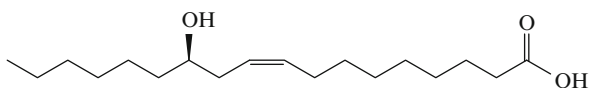


Fig. 8 Ricinoleic acid

widespread use of castor oil in the polyurethanes industry as a low-cost component to reduce the overall price of flexible foam formulations [57], and to impart improved moisture resistance and weatherability to coatings and elastomers [58–63].

Much work has been done on the incorporation of castor oil into polyurethane formulations, including flexible foams [64], rigid foams [65], and elastomers [66]. Castor oil derivatives have also been investigated, by the isolation of methyl ricinoleate from castor oil, in a fashion similar to that used for the preparation of biodiesel. The methyl ricinoleate is then transesterified to a synthetic triol, and the chain simultaneously extended by homo-polymerization to provide polyols of 1,000–4,000 molecular weight. Polyurethane elastomers were then prepared by reaction with MDI. It was determined that lower hardness and tensile/elongation properties could be related to the formation of cyclization products that are common to polyester polyols, or could be due to monomer dehydration, which is a known side reaction of ricinoleic acid [67]. Both side reactions limit the growth of polyol molecular weight.

One of the more advanced technical offerings from castor oil is a line of polyester diols, triols, and higher functional polyols derived from 100% castor oil as products for the preparation of polyurethane prepolymers and elastomers [68]. The Polycin line of polyols are prepared by transesterification of ricinoleic acid and derivatives. The producers (Vertellus) offer diol and triol products, as well as a recently developed series of diol and triol glyceryl ricinoleate esters that are stated to be prepared from 100% castor oil, making them fully renewable in content. The products are recommended for coatings, sealants, and adhesive applications.

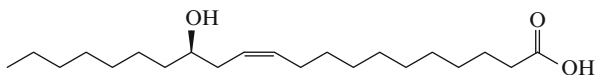
3.3.2 Lesquerella Oil

Lesquerella oil is a lesser known, naturally hydroxylated seed oil that is derived from the genus *Lesquerella*. Of many different wild species, *Lesquerella fendleri* is currently the only species being developed for commercial evaluation [69]. The plant is native to the southwestern USA, and is typical in mildly alkaline, arid soils. Some attempts to investigate the adaptation of *L. fendleri* [70–72] to a wider environment have indicated that the plant is not widely adaptable. Low adaptability, combined with difficult oil recovery and moderate acreage yield of the oil may be limiting factors in the broad commercial development of lesquerella oil.

The *Lesquerella* seed yields roughly 20–25 % oil by weight. The functional fatty acid from the profile is mainly the 20-carbon lesquerolic acid, or 14-hydroxy-11-eicosenoic acid (Fig. 9).

The parallels to castor oil and ricinoleic acid are clear. Some important differences exist. The hydroxylated fatty acids (hydroxyeicosenoic acid and

Fig. 9 Lesquerolic acid



hydroxyeicosadienoic acid) are ~57% by weight of the balance of fatty acids in the seed triglyceride. Increasing the percentage of lesquerolic acid content in the oil is a focus of agricultural development [69]. The yield of oil in tons per acre is lower than for castor, and at this point in time *Lesquerella* is not adaptable to a diverse range of global environments. However, the seeds of *Lesquerella* are not inherently poisonous, and the seed meal contains ~35% protein, making it a viable candidate for agricultural feed. *Lesquerella* is also not currently a food crop, making it a good candidate for the development of petrochemical feedstocks.

There are a few reports on the development of lesquerolic acid derivatives being used for the preparation of polyurethanes, with most of the success being in the development of high quality urethane coatings [73–79]. This is a typical sequence for the development of new natural feedstocks for polyurethane polymers, with coatings coming before the development of other products with more demanding processing requirements. Because of the similarity of *Lesquerella* to castor, further refinement of the genus could lead to more commercially interesting cultivars.

4 Strategies for Derivatization and Commercial Use of Triglycerides as Polyols

The direct use of naturally hydroxylated triglyceride oils in polyurethanes is limited by the performance compromises at higher loadings of oil in the formulations. Several chemical derivation strategies have been pursued in an attempt to increase the amount of renewable carbon in commercial polyurethanes while sustaining the high performance that is expected from polyurethane products. Some of these strategies proceed from naturally hydroxylated oils, and some begin from commodity food oils such as soybean oil, canola oil, or sunflower oil. Figure 10 illustrates the strategies that result in derivatization of triglycerides to polyols for polyurethanes.

4.1 Blown Oils (Air Oxidation)

The simplest of the chemically processed renewable oils for use in polyurethanes are the drying oils, the “bodied” or “blown” oils, so called because the process for producing them consists of blowing hot air through conventional seed oils, commonly linseed or soybean oil [80]. Blown oils are distinctly different from “stand” oils (primarily prepared from linseed oil), which are cured and thickened thermally in the absence of oxygen, thus precluding the formation of ethers, additional hydroxyl groups, and the other oxidation products that render the blown oils reactive in polyurethane formulations.

The blown oils have been used in the coatings industry for decades, and are principally used in the preparation of drying oils for protective coatings. The process of

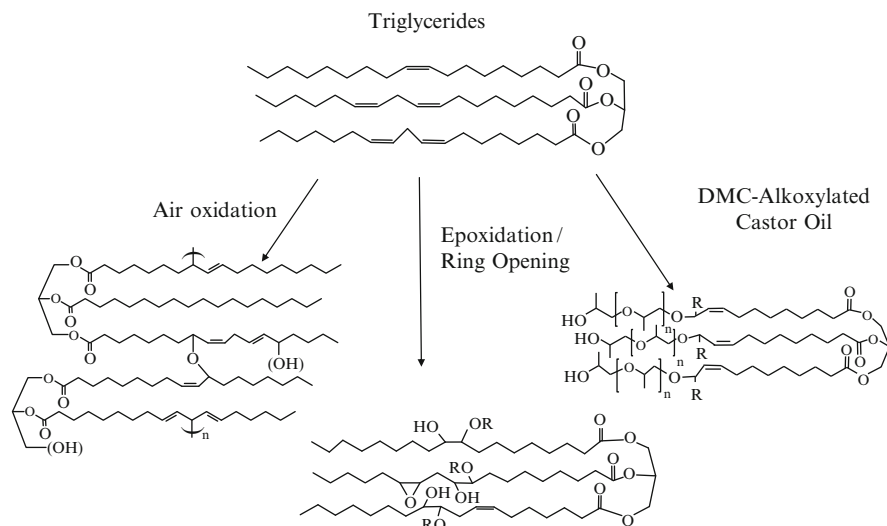


Fig. 10 Strategies for the preparation of triglyceride-based polyols

treating oils with hot air in order to advance the polymer curing and increase viscosity is a standard process. Linseed oil (from flax) is highly utilized for coatings because the high content of polyunsaturated fatty acids (see Table 1) leads to a more rapid curing via the oxidative coupling chemistry.

The blowing process results in a cascade of chain coupling and chain scission chemistries that are initiated by hydroperoxide formation. The ensuing oxidation results in an overall increase in the viscosity of the oil mixture, while simultaneously generating some hydroxyl functionality in the oil, enhancing the reactivity in polymer applications. The fatty acid hydroperoxides thermally decompose to form conjugated radicals that combine or add to other sites of unsaturation to form fatty acid oligomers linked by ether groups or by carbon–carbon bonds from radical coupling. The high concentration of allylic hydrogens ensures that the rate of chain transfer greatly exceeds chain propagation, so that the growth of molecular weight resembles the step-growth polymerization of a high functionality monomer. The resulting polyol product grows in molecular weight and functionality, with a large and diverging polydispersity, while simultaneously containing mostly unreacted triglyceride. The gel permeation chromatography (GPC) analysis in Fig. 11 demonstrates the difference between refined soybean oil triglyceride and the sol fraction of the product of a soybean oil air-oxidation process [81].

In recent years, blown oils have found their way into the polyurethane industry. The additional hydroxyl content introduced through the oxidation process makes the oils more reactive toward isocyanates [82]. The oils can usually be incorporated at low levels into conventional formulations with little compromise to the mechanical properties of the finished polyurethanes. Blown oils have since found utility in carpet backing, insulation foams, and other polyurethane products [83]. At least a

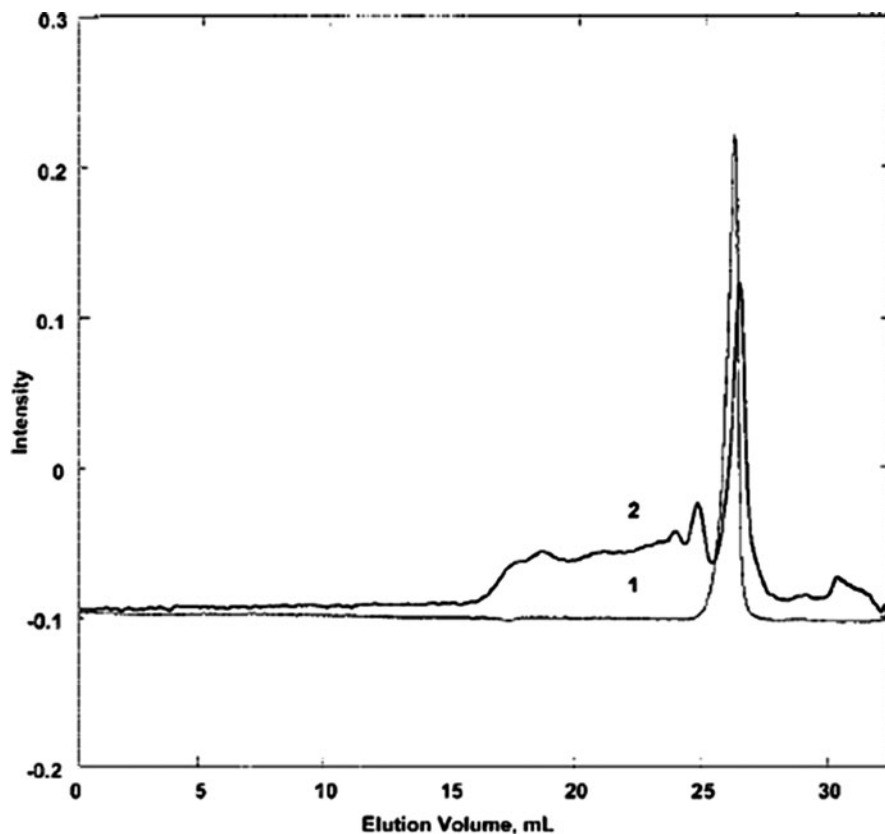


Fig. 11 GPC chromatogram of (1) soy oil and (2) soy polyol. Reproduced from [81] by permission of John Wiley and Sons

few patents are to be found that relate the use of blown oils in polyurethane polymer applications [84–88]. One interesting extension of the blown oil chemistry is found in a patent filed by Bayer Materials Science, disclosing the alkoxylation of blown oils (provided by Urethane Soy Systems) by reaction with PO using the DMC catalyst [89]. Generally, foams were somewhat softer (lower indentation force) and had slightly lower tear strength when compared to control foams prepared from a polyether triol of 3,000 molecular weight.

4.2 Ozonolysis

The ozonolysis of olefins has been studied for over 60 years, and is still the subject of current research. The principle interest lies in the complex mechanism of dipolar additions, chain scissions, and recombinations that are the source of the complexity

of ozonolysis products. Following many years of product characterizations and mechanistic hypotheses, the currently accepted mechanism is that proposed by Criegee in 1975 [90–92]. The original Criegee reference provides details of the complexity of the ozonolysis process and products, and readers are directed to the original reference [90] and following references [91, 92] for a more thorough development of this interesting organic synthesis.

The ozonolysis mechanism was recently studied again via the use of ^{17}O isotope labeling, following the suggestion from previous research [93], and also by spectroscopic and chromatographic methods [94]. Authors of the recent study obtained results that are consistent with the previously published oxidation mechanisms. Figure 12 outlines the oxidative degradation and cleavage pathway that is outlined in reference [94].

Ozonolysis has been applied to the oxidative functionalization of triglycerides. Papers and reviews, and a few patents, have been issued on the ozonolysis of seed oils for the production of plastics [95, 96]. Theoretically, the oxidation products that are accessible via ozonolysis of fatty acid esters are the same as those that are isolated from the photo-induced singlet oxygen cleavage of the same substrates, via Hock cleavage [28–33]. The mixture of products that come from the ozonolysis of

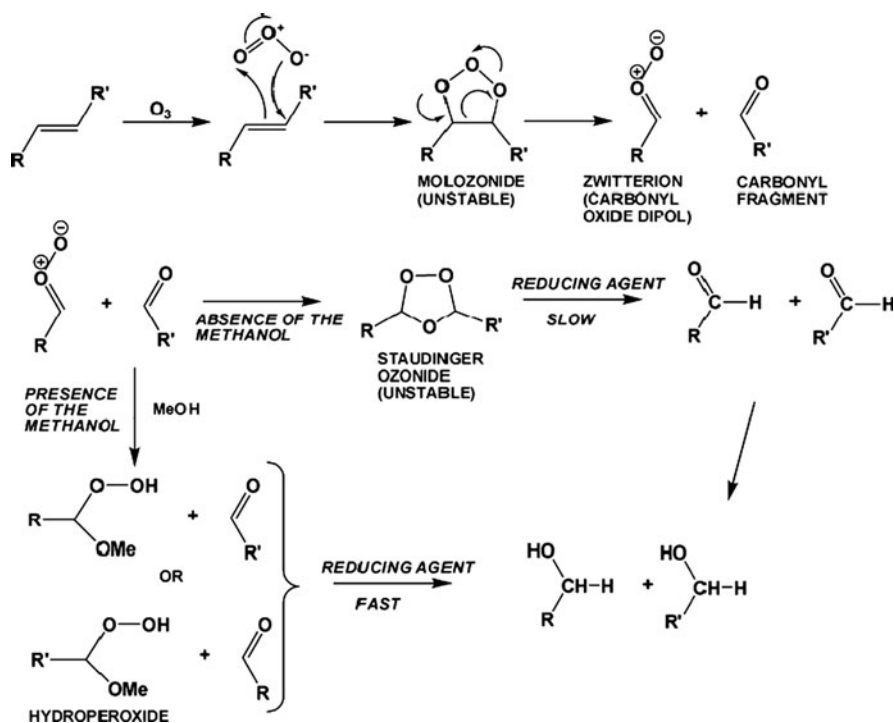


Fig. 12 The process of olefin oxidation and chain cleavage. Reproduced from [94] by permission of Association of Chemical Engineers of Serbia

fatty acids is dependent on the specific conditions of the process, including temperature, reaction solvent (if any), and the degree of completion of the ozonolysis. The principle products are always chain cleavage products, directed at scission through the olefins within the target molecule. The saturated fatty acids that occur naturally in the seed oils are inert to ozone. The ozonolysis of seed oil triglycerides creates a mixture of many compounds.

The mixture of the reaction products can be shifted from oxidation to reduction products depending on the method chosen to work up the reaction mixture, and can include chain scission products such as alcohols, aldehydes, ketones, carboxylic acids, and diacids.

The collection of products from the ozonolysis of seed oils can be challenging to use in plastic products directly as prepared by ozonolysis and work-up, but may be more amenable to the isolation of individual components (diols, diacids) from which a predictable stoichiometry then can be derived [97–99].

One recently successful development in ozonolysis has been obtained by Petrovic et al., using the mild ozonolysis of trilinolein, canola, and soybean oil [100]. The ozonolysis was carried out under cryogenic conditions (-34 to -40°C) as a 10% solution in methylene chloride, followed by reductive work-up with sodium borohydride to provide primary alcohol-terminated triglycerides. The resulting low molecular weight polyols were waxy solids at room temperature, which is typical of polyester polyols. The authors report high conversion and high yields of the corresponding alcohols, and the thermal and mechanical analyses of the resulting MDI-based polyurethane elastomers were consistent with high molecular weight polymers. Figure 13 illustrates the compounds prepared in these studies [100].

4.3 Epoxidized Oils

The epoxidation of vegetable oil triglycerides is a well-known technology. Epoxidized vegetable oils found use in other industrial applications before their

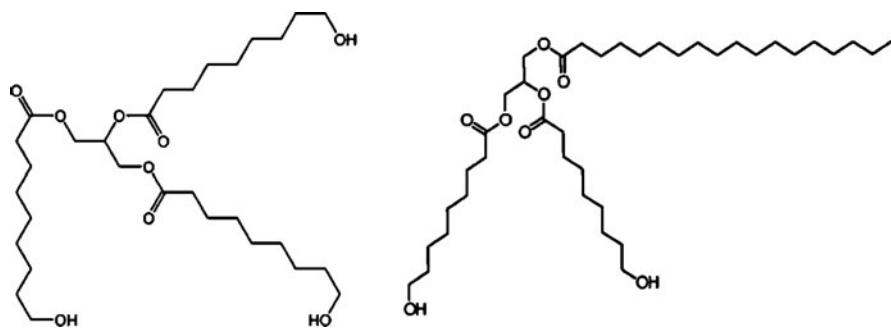


Fig. 13 Alcohols from the cryogenic ozonolysis of seed oils followed by reductive isolation. Reproduced from [100] by permission of *Biomacromolecules*

enlistment as a source of polyols for polyurethanes. Epoxidized soybean oil (ESO) and the acrylated form of ESO have been used as photocurable inks and coatings [101], and as base stock resin for sheet molding compounds [102]. ESO and epoxidized linseed oil have been used as reactive plasticizers in epoxy resins and in compounded PVC [103], as well as in latex coatings, [104], as base stock for industrial lubricants [105–108], and recently as a precursor to soaps [109].

Many companies, such as Cognis, ICC Chemical, Arkema, Sartomer, Ferro Corp. and Varteco Quimica offer commercial grades of ESO, which are ready for use or for further chemical derivation.

There are two sources of epoxidized triglycerides, the first is the isolation of naturally epoxidized oils, and the other is the preparation of epoxidized triglycerides via oxidation of the more readily available unsaturated seed oils.

4.3.1 Naturally Epoxidized Triglycerides

The obvious advantage of allowing nature to perform the derivation of commercially interesting raw materials is the motivation behind the cultivation of naturally occurring epoxidized oils. Similar to castor oil, these plant oils are not digestible and cannot be used as cooking oils and, discounting their questionable medicinal value, their only interest to humans is for industrial purposes. The broad commercial application of epoxidized vegetable oils, which are produced industrially by oxidation of vegetable oils after conventional refining, creates an incentive to avoid the costly oxidation process by isolating the epoxidized oils directly from the agricultural source. Although there is currently no large volume source of naturally derived epoxidized oils, there are technically sound sources of oils that are under development for their potential as viable additions to our commercial agriculture. Naturally epoxidized seed oils are common to the two genera *Vernonia* and *Euphorbia*; the principle fatty acid component of interest is known as vernolic acid and is illustrated in Fig. 14. The two species are both the subject of agricultural development programs in their respective geographies.

Vernonia Oil

Vernonia oil is most commonly derived from the plant species *Vernonia galamensis* (ironweed), which is a weed native to eastern Ethiopia. It was originally identified only in 1964 [110]. The seed contains roughly 40% oil by weight, and the oil contains as much as 80% vernolic acid. The oil is very low in saturated palmitic and stearic acids, making it a high yield source of the epoxy acid of interest [111]. The principle triglyceride from *Vernonia* is trivernolin, which contains three vernolic

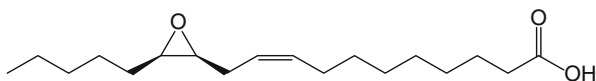


Fig. 14 Vernolic acid

acid groups esterified to glycerin. The triglyceride has been demonstrated to be versatile and amenable to extensive chemical derivation [112]. The high content of epoxy functionality in the oil has enabled its use as a feedstock for direct conversion to the acrylate and methacrylate derivatives for copolymerization in epoxy resin formulations [113].

The saponification of vernonia oil followed by recombination with glycerin has been demonstrated to provide a mixed oligomeric polyol that is useful for the preparation of rigid polyurethane foams [114]. The inventors disclose that polyols prepared in this manner have the advantage of a lower formulation viscosity compared to conventional polyethers with comparable hydroxyl content. The lower viscosity is advantageous in promoting uniform foam flow during rigid foam formation. Preparation of the vernonia oil polyol is outlined in Fig. 15 [114].

The ring opening can be carried out using alcohols, carboxylic acids, or other nucleophiles in the presence of a Lewis acid catalyst, or optionally with hydrogen or water at elevated temperatures and pressures (150–250°C, 1–100 bar) to provide a highly functionalized polyol, which has been demonstrated in rigid polyurethane foams [115].

At least one study has compared vernonia oil to partially epoxidized soybean and linseed oils, to investigate claims that vernonia oil is advantaged due to inherently lower viscosity. Authors conclude that partially epoxidized soybean and linseed oils have viscosity and reactivity that are similar to vernonia oil in formulated coating systems, and provide improvements to viscosity, content of volatile organic compounds (VOCs), and curing time in alkyd coatings when compared to conventional formulations and formulations containing fully epoxidized soybean oil [116].

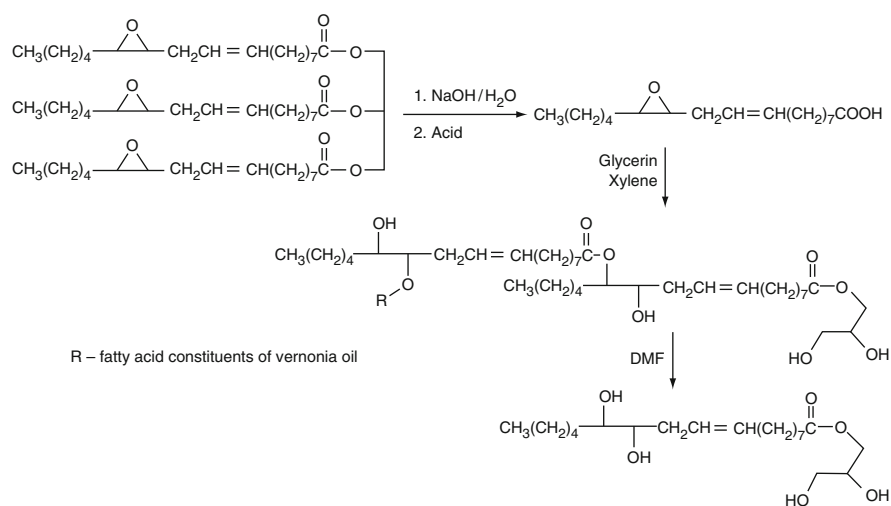


Fig. 15 Ring-opening oligomerization of vernonia oil. Reproduced from [114] by permission of The University of Southern Mississippi

Euphorbia Oil

Euphorbia lagascae has recently raised interest as a potential new plant for industrial development [117]. Euphorbia has a high abundance of vernolic acid in the triglyceride (58–78%) and a high percentage of oil in the seed crop (~50% by weight). Euphorbia has some traits that create challenges for cultivation and harvesting, including indeterminate growth (growth that is not terminated) and a long maturity season, which will ultimately limit the range where the plants can be grown to the lower latitudes. It also has the unpleasant disadvantage of producing latex, which makes automated harvesting difficult and potentially impacts the yield [118]. The plant has at least one registered commercial cultivar (Vernola), developed cooperatively by Centro de Investigación y Desarrollo Agroalimentario (Murcia, Spain) and Institut für Pflanzenbau und Pflanzenzüchtung (Göttingen, Germany). Vernola has the advantage that the seed pods do not split open upon maturity (indehiscence), as is normal for the native varieties [119]. Efforts are now underway to define environmental adaptability and trait expression as a function of growing conditions.

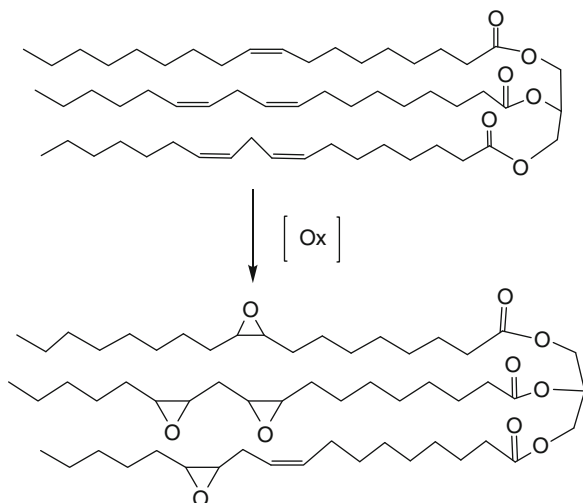
One species of *Euphorbia* in Brazil (*Bernardia pulchella*) has been determined to contain more than 90% vernolic acid in the triglyceride [120]. This level of single-component purity is equivalent to the level of ricinoleic acid typically found in castor oil. These different varieties of epoxidized oil plants will probably continue to be the subject of agricultural development in the coming years.

4.3.2 Synthetic Epoxidized Triglycerides

The formation of oxirane functionality from the unsaturation in seed oil triglycerides is a more chemically specific process than several of the processes previously discussed. The epoxidation is carried out directly from the triglyceride oils, by combination with an oxidizing agent, typically peroxyacetic acid or hydrogen peroxide in a carrier such as methanol, formic acid, or acetic acid [121–123]. The oxidation is relatively specific, and is run under mild enough conditions to prevent the over-oxidation of the fatty acids. Figure 16 shows the epoxidation of triglyceride oils with any of a variety of oxidizing agents.

The epoxidation is followed by opening of the oxirane with acid hydrolysis (such as phosphoric acid or acetic acid) or a nucleophile (such as methoxide or acetate) to form a secondary alcohol [124]. Oxirane ring opening results from attack of a nucleophile on one of the carbons of the three-membered ring. The reaction is referred to in some publications and several patents as the “hydroxylation” step of the polyol synthesis. The opening of the oxirane generates a secondary alcohol. This alcohol is also a nucleophile, and can attack another oxirane to generate an ether linkage between two fatty acid moieties, along with a new alcohol. This side reaction results in oligomerization of the fatty acids [125], and thus a broadening of the polydispersity index (weight-average molecular weight/number-average molecular weight, M_w/M_n) of the triglyceride polyol [126].

Fig. 16 Epoxidation of triglyceride oils



The resulting polyol resembles the product that is hypothesized for the oligomerization of triglycerides via air oxidation, with the exception that there is a large increase in the hydroxyl content of the polyol product, and there is very little, if any, of the starting epoxide left unreacted. In addition, the epoxidation process does not produce low molecular weight chain scission products, which are a by-product of the blown oil process. The hydroxylation of epoxidized triglycerides is illustrated in Fig. 17.

A structural analysis of the product that results from this approach to the preparation of triglyceride polyols has been described in at least one elegant investigation [125]. Authors found evidence for polyethers in the backbone of the ring-opened epoxy oil, consistent with the attack of the triglyceride alcohol on an epoxy ring. Figure 18 illustrates the ^1H NMR analysis of the polyol oligomer.

When the epoxidation/hydroxylation process is performed on oils with multiple unsaturation sites, the resulting oligomerization produces polyol chains with hyperbranching and high average functionality per polyol chain [127]. Figure 19 illustrates the MALDI-TOF (matrix-assisted laser desorption/ionization–time-of-flight mass spectrometry) analysis of the oligomeric product described in reference [125].

The desire to minimize this competitive oligomerization has motivated research into alternative means to decrease the polydispersity and simultaneously increase the molecular weight of the seed-oil derived polyols. Recent patents [128, 129] investigate an approach previously demonstrated for the hydroformylated polyols [130–132], i.e., hydroxylation of the fatty acid alkyl ester followed by polymerization from a petrochemically derived initiator molecule. Inventors state that this approach provides an improvement over previous epoxidized/hydroxylated polyols by allowing better control of the molecular weight and the functionality of the polyol products.

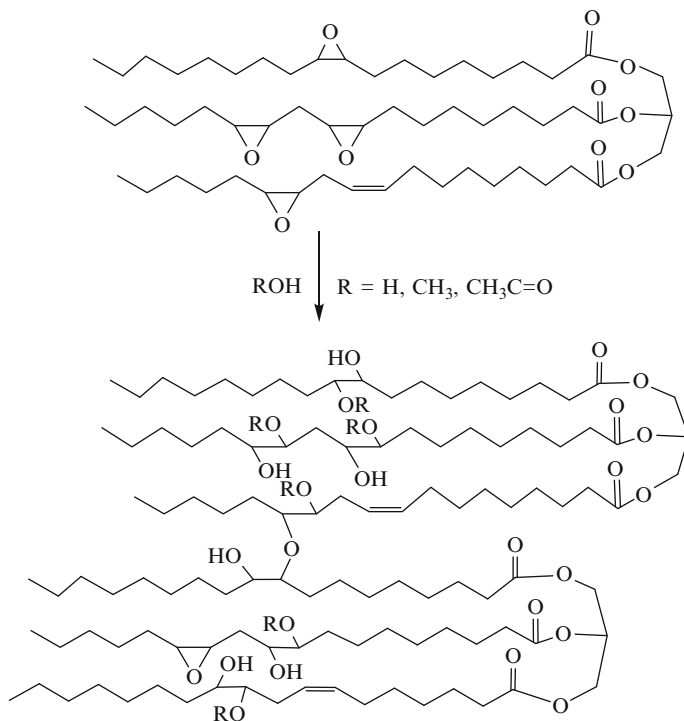


Fig. 17 Oligomerization of epoxidized triglycerides by ring opening

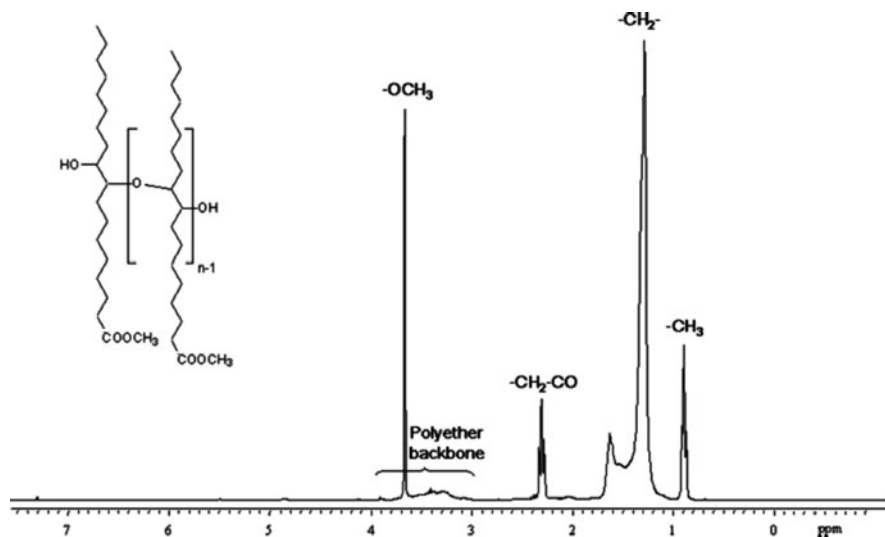


Fig. 18 *Left:* Ether linkage in the backbone of oligomerized ESO polyols. *Right:* ^1H NMR spectrum (CDCl_3 , 300 MHz) of oligomer A. Reproduced from [125] with permission from Wiley Interscience

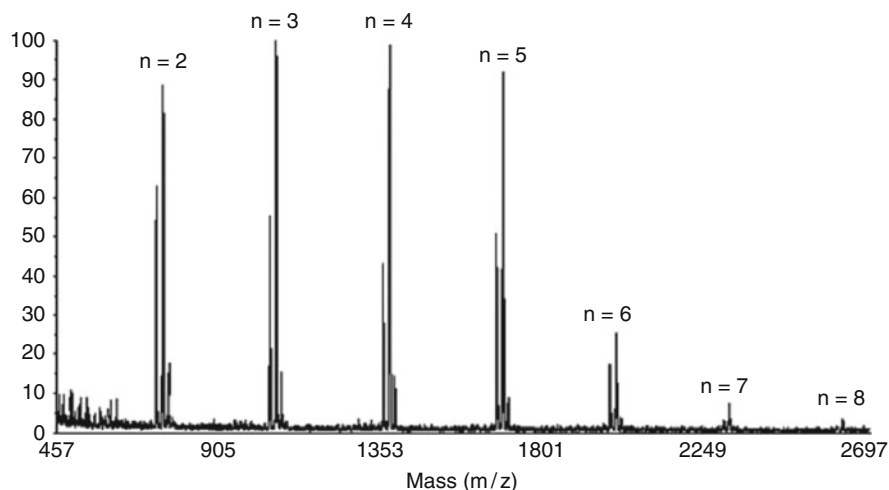


Fig. 19 Chain propagation and oligomerization in the ring opening of epoxidized seed oils. MALDI-TOF MS spectrum of oligomers doped with silver trifluoroacetate, showing the ion series $\text{H}[\text{O}-\text{C}_{19}\text{H}_{36}\text{O}_2]_n\text{-OH-Ag}^+$ (mass = $312n + 18 + \text{Ag}^+$), $[\text{O}-\text{C}_{19}\text{H}_{36}\text{O}_2]_n\text{Ag}^+$ (mass = $312n + \text{Ag}^+$), and $\text{CH}_3[\text{O}-\text{C}_{19}\text{H}_{36}\text{O}_2]_n\text{-OH-Ag}^+$ (mass = $312n + 32 + \text{Ag}^+$). Reproduced from [125] with permission from Wiley Interscience

One interesting study determined the reaction kinetics of the oxirane opening in glacial acetic acid, in an attempt to minimize degradation products during oxirane formation, and provide a lower distribution of product molecular weights [133]. It was demonstrated that the degree of oligomerization of ESO can be controlled with the selection of nucleophilic oxirane-opening agent, and that the resulting functionality of the ESO polyol can be controlled in this manner. The relationship between the functionality of the polyols and the tensile strength of the resulting polyurethane elastomers was directly proportional [134].

ESO derivatives, with the secondary alcohol functionality situated midway down the 18-carbon backbone of the fatty acid, typically display reaction rates with polyisocyanates that are considerably slower than the reaction rate of a similar fatty acid substituted with a primary hydroxyl in the same position [135], or even more slowly than polyols prepared with secondary OH groups derived from PO [136]. The exact reason for this has not been proven, but steric accessibility is high on the list of probable influences. The slower reactivity of epoxidized/hydroxylated triglycerides creates challenges in the processing of foams in commercial production equipment in some higher volume, more demanding polyurethane product applications. Enhancement to reactivity of these ESO-based polyols has motivated research into increasing the primary hydroxyl content by derivation of the ESO polyols with primary alcohols [135].

The ready availability of ESO has contributed strongly to the commercial development of polyurethane polyols derived from this chemistry. Of all the approaches to developing renewable polyols for polyurethane applications, the

derivations of epoxidized seed oils constitute the most commonly available products. A growing body of patents is emerging, assigned to companies such as Hobum (Merginol polyols), Cargill (BiOH polyols) [137, 138], BioBased Technologies (Agrol polyols) [122, 123] as well as non-commercial entities such as Pittsburg State University [139, 140]. Formulation experience and product development will no doubt bring continued product introductions to this field of polyol offerings.

4.4 Hydroformylated Oils

Hydroformylation is the process of coupling carbon monoxide to an olefin with a reductive catalyst and hydrogen to produce an aldehyde-functionalized substrate. This coupling is typically followed by hydrogenation to produce a primary hydroxyl group. Several academic and commercial programs have participated in the development of hydroformylated triglycerides and fatty acid derivatives for use in polyurethanes. Two main processes for the hydroformylation of seed oils have been utilized.

When triglycerides are used as the substrate, the final product is a triglyceride functionalized with hydroxymethyl groups. One hydroformylation process uses the less expensive cobalt catalyst, requires more harsh process conditions, and generally results in lower yields of the aldehyde products. This approach was investigated by Petrovic et al. at the Pittsburg State University [141]. The typical reaction scheme is outlined in Fig. 20.

Another approach begins with the isolation of methyl esters of fatty acids from triglycerides with concurrent liberation of glycerin. This is the commercial process

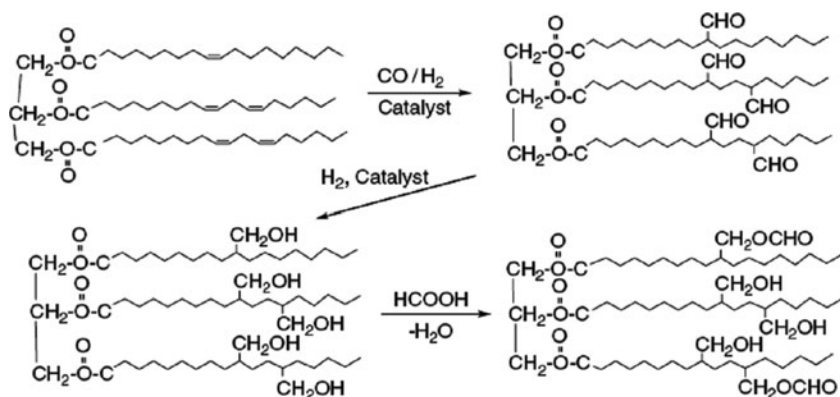


Fig. 20 Hydroxymethyl-functionalized triglycerides, ultimately formate esterified. Reproduced from [141] by permission of John Wiley and Sons

for the preparation of biodiesel [142]. The biodiesel fatty acid methyl esters (FAMES) are then treated with carbon monoxide and hydrogen in the presence of rhodium catalyst to form the intermediate aldehyde. Hydrogenation of the aldehyde provides quantitative conversion to the mixture of hydroxymethyl fatty acid methyl esters, which serve as A-B_n monomers for further polymerization, where A is the methyl ester group, B is the hydroxymethyl group, and B_n designates the average number *n* of hydroxymethyl groups per fatty acid, which is controlled by the hydroformylation process. The hydroxymethyl monomer is then combined with a selected initiator, which is chosen to fit the intended final application for the polyol product. Methanol from the polyol polymerization is then recycled back again to make biodiesel. The strategy is outlined in Fig. 21.

The hydrogenation step following hydroformylation serves two important purposes. It reduces the aldehyde intermediate product to the desired primary alcohol functional group, which is the primary site of reactivity of the polyol with isocyanates. It also reduces the residual olefins in the FAMES to saturated hydrocarbons, thus eliminating the pathway to Hock degradation and odor development, which is inherent to other processes that leave fatty acid unsaturation in the polyols. This step eliminates the typical vegetable oil odor from the final natural oil polyols of this process.

The hydroxymethyl-substituted methyl esters can then be transesterified with any number of different initiator types to tailor the structure of the polyol to the end-use application, and all from a single raw material source. The stoichiometry of the polyol is adjustable, to produce polyols of any molecular weight. This synthetic strategy was developed by The Dow Chemical Company as the Renuva polyols.

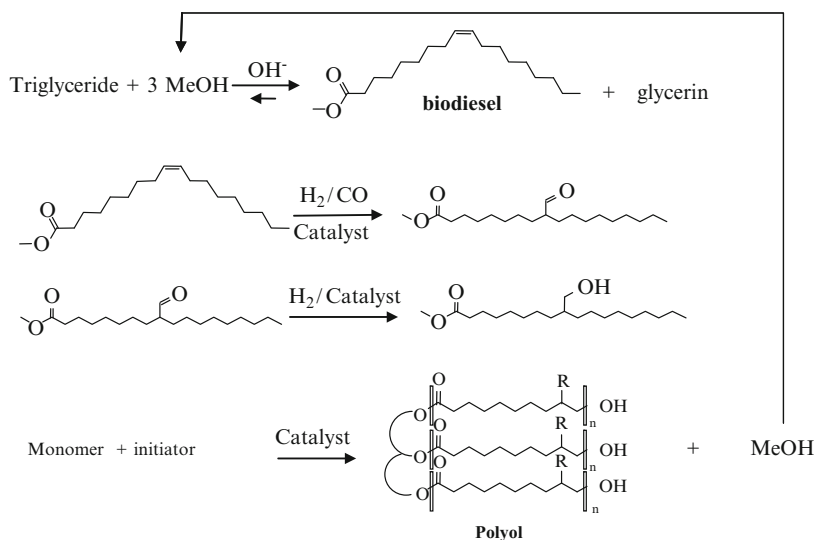


Fig. 21 Strategy for the preparation of polyols from biodiesel

The resulting slate of polyols has been demonstrated in conventional flexible slabstock foam [143], viscoelastic foam [144], and high resiliency slabstock and molded foams [145].

In 2006, Dow performed a detailed Life Cycle Analysis study of the process for producing Renuva polyols [146]. The study determined that the process of refining soybean oil through to the polyols of this process was a net-sum zero generator of CO₂. The boundaries of the analysis included growth, harvesting, and transportation of the soybeans; refining of the vegetable oil; and processing to final polyol. In addition, the process to final polyol only uses 42% of the fossil fuel resources typical of a petrochemical polyol process.

4.5 Alkoxyated Triglyceride Oils

As mentioned previously, castor oil has been used directly in polyurethane formulations for decades. The triglyceride plant oil has a molecular weight of approximately 1,000, which is an atypical molecular weight for triols in polyurethane applications. A more typical molecular weight range of polyether polyols for applications in flexible foams such as bedding and furniture is 3,000–4,500. Although acceptable foam performance has been demonstrated by incorporating low levels of castor oil directly into formulations, one innovative way to make castor more useful for quality performance applications is to alkoxyate the castor triglyceride with PO, just as conventional polyethers are alkoxyated from glycerin, up to a higher and more useful molecular weight. This optionally can be done with pure PO or a mixture of oxides such as EO and PO.

This type of alkoxylation chemistry cannot be performed with conventional alkali metal hydroxide catalysts because the hydroxide will saponify the triglyceride ester groups under typical alkoxylation reaction conditions. Similar competitive hydrolysis occurs with alternative catalysts such as triflic acid or other Brønsted acid/base catalysis. Efficient alkoxylation in the absence of significant side reactions requires a coordination catalyst such as the DMC catalyst zinc hexacyanocobaltate. DMC catalysts have been under development for years [147–150], but have recently begun to gain more commercial implementation. The use of the DMC catalyst in combination with castor oil as an initiator has led to at least two lines of commercial products for the flexible foam market. Lupranol Balance 50 (BASF) and Multranol R-3524 and R-3525 (Bayer) are used for flexible slabstock foams and are produced by the direct alkoxylation of castor oil.

BASF has published the results of a Life-Cycle Analysis environmental study of the commercial manufacturing process for Lupranol Balance 50 polyol [151]. The study indicates a positive trend on the environmental impact of manufacturing the polyols by the new process. The actual impact of the current offering is difficult to gauge from this study, since in some cases the theoretical improvements

of the process are calculated on the basis of 100% replacement of all flexible foam demand from NAFTA (North American Free Trade Agreement) participating countries, based on 2007 market data.

5 Biodegradability

Only one prominent study has been performed on the biodegradation of polyurethanes based on triglyceride polyols [152]. The study indicates that the biodegradability of polymers such as oxidatively polymerized seed oils is rapid under normal conditions in the soil, but that conversion of these same triglycerides to polymers containing amine and urethane linkages essentially eliminates short-term biodegradation. Polymer degradation was studied by respirometry in soil samples, and was compared to soybean oil as a control. Figure 22 illustrates the result of the study, and indicates that the synthetic polymers all have substantially lower decomposition rates as compared to the native soybean oil.

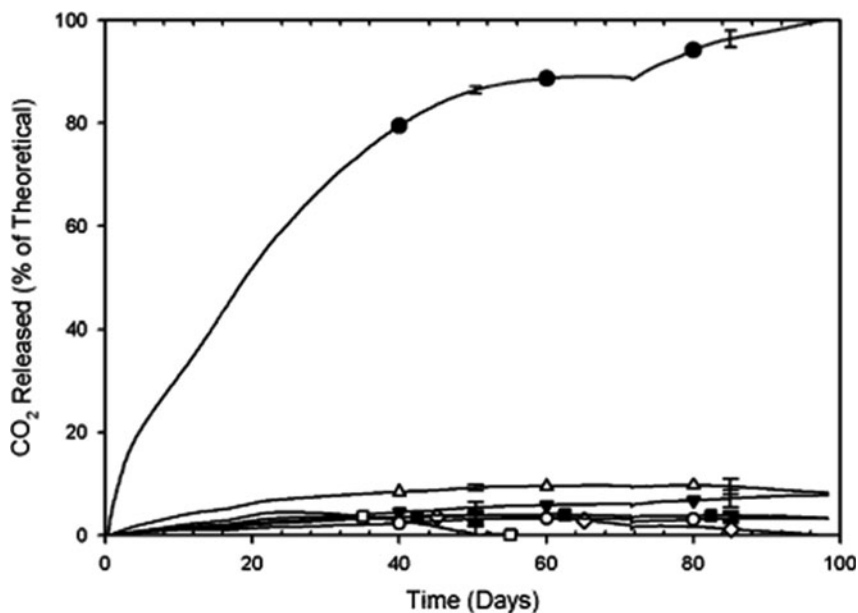


Fig. 22 Respirometry of vegetable oil-based polyurethanes made from the following polyols: triolein-met (arrowhead), soy-HF (filled square), soy-met 180 (open diamond), soy-met 206 (open circle), and linseed met (open square). Also shown is ESO/BF3 polymer (open triangle) and soybean oil control (filled circle). Temperature was increased from 30°C to 55°C on day 71. Note that hydroxyl number of 180 has the functionality of 3.3 and that of hydroxyl 206 is 4.0. Met refers to polyol made from ESO and methanol; HF refers to polyol from hydroformylation and reduced ESO. Reproduced from [152] by permission of *Journal of Polymers and the Environment*

6 Characterization of Renewable Content in Polyurethanes

As renewable raw materials began to enter the marketplace, it was inevitable that claims to the level of renewable content in commercial offerings would become an issue of public debate. As previously pointed out in this article, some renewable raw materials have been common to the polyol chemistry for many decades, so claims to at least some renewable content are justified. Because the commercialization of different renewable polyol chemistries has created a highly competitive environment, some scientists in the field have promoted a method for the independent verification of the renewable sourced carbon in the final product [153]. ASTM International has published a concise and informative briefing paper on the method development for the determination of renewable carbon content in carbon-containing substances [154]. The method involves the analysis of ^{14}C content in the finished polyurethane products via radiocarbon dating [155]. The technique is fast and accurate, and has become commonly available by contract analysis through independent analytical laboratories [156].

The method builds on the fundamentals of radiocarbon dating via ^{14}C analysis, an analytical method that relies on the nuclear decay of radioactive carbon that is incorporated from the atmosphere into all living, respiring plants. The ^{14}C is present in the atmosphere as $^{14}\text{CO}_2$. The level of ^{14}C is extremely low, only one part per trillion of the natural abundance of carbon in the atmosphere. When plant respiration ceases, the uptake of $^{14}\text{CO}_2$ stops, but the slow radioactive decay of ^{14}C continues. Accurate detection of the amount of ^{14}C in a natural organic substance allows calculation of the age of the sample. This radioactive isotope of carbon undergoes beta decay with a relatively short half-life of approximately 5,730 years. The sensitivity of detection makes the quantification of ^{14}C applicable to specimens dating back as far as approximately 50,000 years.

The radiocarbon method works because even though ^{14}C is lost through nuclear decay, it is constantly replenished at a rate that offsets the rate of loss. The two lighter isotopes of carbon (^{12}C and ^{13}C) are formed in the normal process of nuclear fusion in stars, through which most elements are formed [157, 158]. This is not the case for ^{14}C , which is formed primarily through bombardment of nitrogen with cosmic rays in the upper atmosphere [159]. The accuracy of radiocarbon dating rests on the assumption that the flux of cosmic rays into the upper atmosphere has been relatively stable on a geological time scale, thus maintaining a relatively constant concentration of ^{14}C . One recent investigation has determined that atmospheric ^{14}C concentrations have been more variable than previously considered. The study provides a detailed map of ^{14}C concentrations across the full range of the useful timescale accessible through the dating technique (~50,000 years), and should contribute to the continuing refinement of the accuracy of the method [160]. It should be stressed that the refinement of accuracy of the radioisotope dating method is only peripherally related to the determination of renewable content, since freshly harvested plant carbon has a complete complement of ^{14}C , and petroleum-based carbon has essentially none. By simply ratioing the amount of ^{14}C in a

synthetic article to the natural ^{14}C abundance, the ratio of renewable carbon is calculated.

7 Applications for Polyurethanes with Renewable Content

7.1 Flexible Foams

Flexible foams are the largest segment of the polyurethane global market. They fall into several different categories based on end-use markets and performance requirements. Most people are aware of the applications of polyurethane foam in bedding (mattresses, pillows) and furniture (cushions, bolsters), and in automotive seating. In addition, flexible foam is used in other applications such as carpet backing [161], many applications in automotive interiors [162], clothing, noise abatement, protective packaging, and even filtration. Each of these application areas has specific performance criteria that separate them from the other classes of flexible foams. The goal to produce polyols to meet the variety of application demands for flexible foams alone is a significant challenge for polyol producers.

7.1.1 Flexible Slabstock Foams

Three main competitive technologies have entered the commercial arena in the area of conventional flexible slabstock foams. Alkoxyated castor oil polyols (such as the BASF product Lupranol Balance 50) [151], epoxidized/hydroxylated triglycerides (such as the Cargill BiOH polyols) [163], and the polyols based on hydroformylated/hydrogenated biodiesel (such as The Dow Chemical Company Renuva polyols) [130–132]. Large-scale foam producers such as Foamex, Recticel, Carpenter, and Sanko Espuma are adopting the manufacture of foams based on renewable polyols as OEMs (original equipment manufacturers) for mattresses and furniture are launching product lines containing polyurethane foam with renewable content. For further information visit the commercial literature of these and other polyurethane foam producers.

Flexible slabstock foam is one of the largest application areas of polyurethane polyols, encompassing applications in bedding, furniture, clothing, packaging, and a long list of smaller volume specialized applications. Conventional flexible slabstock foam is therefore an attractive market segment for large-scale polyol producers who seek to gain economically competitive cost structure through the improved economics of large scale manufacturing (economy of scale). Commercial flexible slabstock polyols are often required to meet very demanding performance specifications for the processing and production of the foam (experienced by the foam manufacturer) and for the performance of the foam in the final application. These performance criteria are so specific that virtually any change to the chemistry

of the components of the formulation has a measurable impact on either foam processing or performance, or both. A thorough understanding of the changes to polyol performance that result from the inclusion of biorenewable polyols is a crucial step on the path to commercial offering and market adoption of these new materials.

A well-controlled foaming study of epoxidized/hydroxylated triglyceride polyols in low-density slabstock grade foams was performed by Zhang et al. [164] and was based on polyols prepared by the Kansas Polymer Research Center [165]. The preparative method used for the polyol allowed a reduction in the competitive oligomerization of the polyol, resulting in a relatively lower amount of oligomeric polyol, seen when the GPC analysis is compared to that of the blown oil polyol (Fig. 10). An idealized structure of the polyol, along with a GPC analysis is represented in Fig. 23.

Authors carefully investigated the potential causes of an increase in compressive modulus, which had been previously reported for flexible slabstock foams prepared from the polyols of the study [166]. Flexible foams prepared from a standard formulation containing two different levels of the epoxidized/hydroxylated soybean

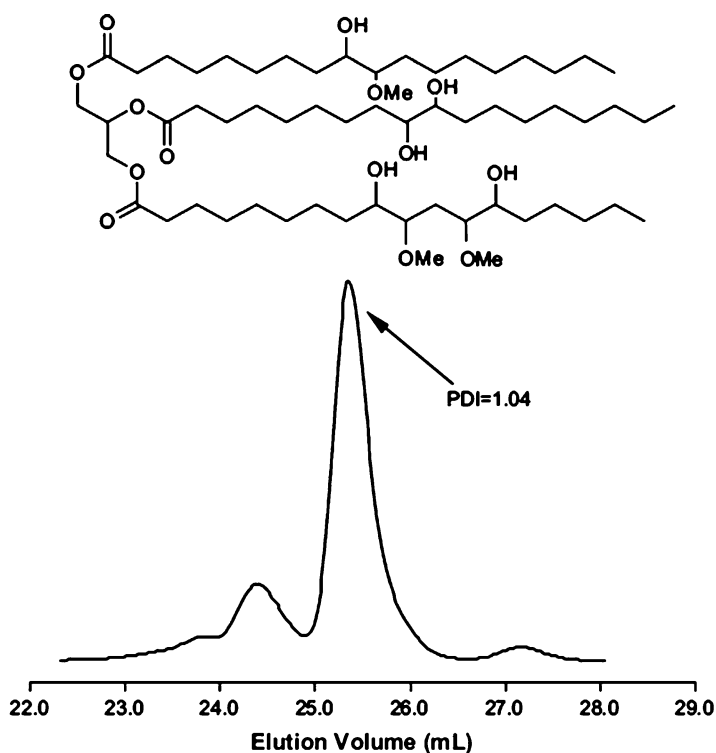


Fig. 23 Idealized structure of the soybean oil polyol (*top*) and GPC trace of soybean oil polyol used in the study (*bottom*). Reproduced from [164] by permission of Elsevier Press

oil polyol were compared to foam from a control polyether polyol foam containing a commercial styrene/acrylonitrile copolymer polyether polyol (a polyol-dispersed reinforcing polymer), and foam from a formulation containing a low molecular weight crosslinker. By a combination of thermal and mechanical analyses, small-angle X-ray scattering (SAXS) data, infrared analysis, and atom force microscopy (AFM) surface analysis of hard and soft domain size and disposition, it was demonstrated that hard domain size is smaller in the foams prepared from the natural oil polyol, and that there is a lower contrast between hard and soft domains (suggesting more phase mixing). Contributions to higher modulus are proposed to be the higher inherent T_g of the natural oil polyol (-35°C versus -68°C for the polyether) and the increased interfacial boundary between the hard and soft domains that constrains a higher percentage of the soft domain at the interface.

Foams prepared from the soybean oil polyol exhibited low temperature soft segment thermal transition (using dynamic mechanical analysis, DMA) at the same temperature as the control polyether foam. Scanning to a higher temperature did not reveal clean, well-defined second transitions corresponding to a second soft segment phase, but instead indicated a broad transition to lower storage modulus, which became broader and less well defined as the soy polyol content was increased. This appears to indicate a degree of phase compatibility between the soybean oil polyol and the conventional polyether that is somewhat short of complete miscibility. Figure 24 illustrates the DMA analyses for these foams.

Foam hardness is an important property of flexible foams because foam producers typically segregate grades of foam on the basis of the combination of foam hardness and density [163]. Foam formulations that can increase foam hardness without increasing density, or without the addition of hardening additives

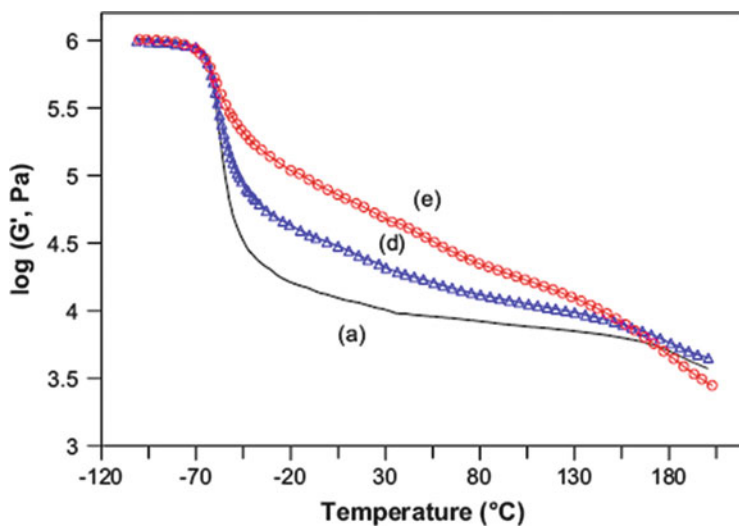


Fig. 24 DMA results for (a) control foam, (d) 10% soybean oil polyol, and (e) 30% soybean oil polyol. Reproduced from [164] by permission of Elsevier Press

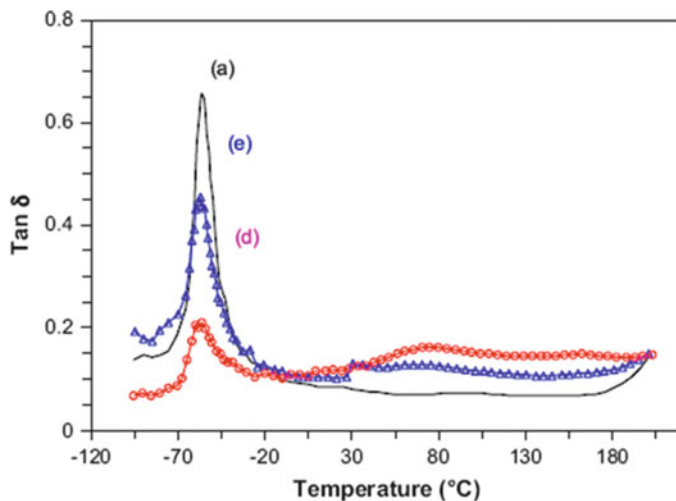


Fig. 25 Tan δ versus temperature plots for (a) control foam, (d) 10% soybean oil polyol, and (e) 30% soybean oil polyol. Reproduced from [164] by permission of Elsevier Press

such as copolymer polyol, potentially bring value to the foam producer. However, these improvements cannot be adopted at the expense of other important performance features. Although properties specifically related to foam resiliency were not discussed in the foam study by Zhang et al., the tan δ (G''/G') values of the natural oil foams were demonstrated to be higher than those of the control polyether foam in the region of room temperature, and an increase in this property typically accompanied some loss of foam resiliency. Figure 25 shows the tan δ versus temperature plots from this study [164].

A similar foaming study was performed on epoxidized/hydroxylated soybean oil polyols supplied from a different source [167]. A study sponsored by the United Soybean Board investigated the performance of ESO that had been hydroxylated by the opening of the epoxide with acetic acid. The authors concluded that the intensity of the peak tan δ in flexible slabstock grade foams is diminished and that the T_g of the resulting polymers is systematically increased as the content of soy-based polyol is increased. The broadening of the tan δ peak to higher temperatures was thought to reflect a greater degree of phase mixing (hard and soft domains) as the amount of soy polyol is increased, a proposal that was consistent with SAXS results of that study. The effect was seen to be more pronounced in the ESO polyols with higher hydroxyl content. The test results were also affected by the cellular morphology of the foams, which changed slightly to more anisotropic cell dimensions as the amount of renewable content was increased. These changes are to be expected as the hydroxyl content of the polyol is changed. Some of the macroscale cellular morphology differences may be addressed by adjusting the catalyst and surfactants in the foam formulation, but this approach does not address fundamental differences in mesoscale morphology and properties such as T_g and tan δ .

One area of building and construction materials into which flexible foam with renewable content has been introduced through polyurethane chemistry is in carpet for flooring. The US federal government is the single largest purchaser of commercial-grade indoor carpet. Federal regulations established by the Department of Agriculture require that certain federal procurements be subject to a mandated requirement to meet a specification for biorenewable content [168]. Round 3 of the procurement rules designated carpet as a construction material to be subject to requirement for a minimum renewable content, which was specified at 7% minimum. This federal procurement requirement for biorenewable content has created a mandate for materials, which can be addressed with polyurethanes based on biorenewable polyols.

Two different technologies already exist for the inclusion of renewable polyurethane foam into carpet. The most common part of the carpet installation that is prepared from polyurethane is the foam padding underneath the carpet, between the carpet and the floor of the building. This foam is either prepared as a coating bonded to the carpet backing (common for commercial grade carpet), or the carpet underlay is prepared separately as “rebond” foam pad. Rebond foam for carpet padding is typically used in residential carpet installation, and is prepared from scrap and recovered or recycled waste foam. Since the full measure of recycled foam is currently conventional petrochemical-based polyurethane, a significant market entry for biorenewable foam will be required before the levels in scrap foam reach the threshold of 7% renewable content. However, the demand for carpet pad from rebond foam exceeds the supply of scrap and recycle, even when recycled foam is imported, so virgin production foam is sometimes produced for the purpose of converting to rebond foam for carpet padding. This is one option for the introduction of biorenewable foam into construction materials.

When added to the opportunities that are now being created through tax incentives for environmentally responsible commercial and residential construction, flexible foams in housing and construction applications appear to be headed for future growth.

7.1.2 High Resiliency Foams

Of all the applications for polyols from renewable resources, the use of high concentrations of renewable polyols based on triglycerides in flexible molded and high resilience slabstock foams is perhaps the most challenging. These types of foams, which are used in automotive seating and premium bedding products, are distinguished by high resiliency as defined by the ball rebound resiliency test [169]. The product performance requirements for high resiliency foam are very stringent, and the polymer morphology required to deliver that performance is relatively more difficult to obtain through polymer processing. The polymer morphology requires a high weight fraction of polyol with a high HEW. The resulting low hard segment content (urethane/urea) means that the phase segregation of the hard domain is late in the cure profile of the polymer, and the molecular weight and viscosity of the

polymer foam is much higher at the phase transition than it is in conventional flexible foams. As a result, the foam cell opening, which is triggered by phase segregation of the hard domain [170–173], is difficult to achieve in high resiliency foams. The rigidity of the phase segregated, co-continuous hard segment is minimally present in these foams to stabilize the cell structure after cell opening, so phase segregation and cell opening are delayed until very late in the polymer cure. The close proximity of this phase segregation to the gel point of the polymer means that the processing latitude (the robustness of the foam processing conditions to slight variations) is small. Small changes in processing conditions can lead to foam collapse due to incomplete gellation, or foam shrinkage due to a high percentage of closed cells from over-gellation. Preparation of high resiliency foams requires relatively uniform polyols with high molecular weight, and low T_g polyol segments between hard segment linkages. Polyol structures such as low molecular weight polyols, or short side-chain polyol branches that participate in the network connectivity, are generally not well tolerated in high resiliency foams.

Inherent to the property of high foam resiliency is a low $\tan \delta$ at the test temperature [174, 175]. The low T_g of polyethers is therefore preferred over the higher T_g of polyester polyols [176]. High content of seed oil polyols tends to mimic the addition of polyester polyol to formulations, increasing T_g and dampening resiliency and elasticity with increasing weight fraction of triglyceride polyols.

An attractive solution to this technology gap currently is just out of reach. The use of castor or *Lesquerella* oils [177] as an initiator for high molecular weight polyols has previously proven an effective strategy for the preparation of flexible foams. As previously mentioned, alkoxylation of these starters is not possible with conventional acid or base catalysts, but instead requires a coordination catalyst such as the zinc hexacyanocobaltate catalyst. Unfortunately, at this time, the DMC catalyst has not been demonstrated to directly produce the high primary –OH functionality required in polyols for high resiliency foams [178] through the efficient end-capping of the high molecular weight polyols with ethylene oxide [179]. In addition, under typical reactor conditions, the DMC catalyst produces a trace of a very high molecular weight polypropylene oxide (4×10^5 – 1×10^6 Da), which is a very efficient de-foamer and causes foam collapse, particularly for high resiliency foams. For these reasons, the DMC catalyst is not a straightforward solution to the preparation of polyols for high resiliency flexible foam applications. The extension of triglyceride-initiated polyols for high resiliency slabstock and molded foams awaits further enabling catalyst development.

In 2008, Dow Chemical reported an advance in the preparation of molded foams using the flexibility of the Renuva technology [145]. Polyurethane molded foams prepared from the Generation 1 conventional foam polyols were compared to a Generation 2 foam more specifically designed for high resiliency foam applications. For a compromise of only 4% in renewable carbon content, improvements in almost all categories of performance were demonstrated in both TDI high resiliency and MDI high resiliency foams. Substantial improvements to resiliency and foam compression set were achieved with no compromise in important mechanical properties. Foams were produced of 10–14% renewable content with fully acceptable

Table 3 Comparison of TDI foam made with Dow's Generation 1 and Generation 2 natural oil polyols [145]

Property	Generation 1 (18% renewable carbon)	Generation 2 (14% renewable carbon)	Units
Core density	28	30	kg/m ³
Indentation (IFD) 25%	84	107	N
Indentation (IFD) 65%	260	299	N
Sag factor	3.1	2.8	–
Resiliency	51	56	%
Tensile strength	110	98	kPa
Elongation	110	78	%
Tear strength	190	188	N/m
50% CS	17	8.9	% Ct
75% CS	27	8.6	% Ct
50% Humid aged CS	17	5.6	% Ct

IFD indentation force deflection, *CS* compression set, *% Ct* compression set expressed as a percentage of original thickness

Table 4 Comparison of MDI foams (95 index): a standard formulation, and Generations 1 and 2 natural oil polyols [145]

Property	Standard	Generation 1	Generation 2	Generation 2	Units
Renewable carbon	–	10.1	10.2	13.3	%
Core density	50.3	50.2	51	50	kg/m ³
CFD 25%	4.5	4.7	3.8	3.7	kPa
CFD 40%	5.9	6.4	5.0	4.9	kPa
CFD 65%	13.3	14.6	11.3	11.5	kPa
Sag factor	3.0	3.1	3.0	3.1	
50% CS	9.6	11.1	9.7	8.7	% Ct
50% Wet set	10.6	12.9	11.0	9.9	kPa
Resiliency	58	45	52	51	%
Tear	159	144	153	130	N/m
Tensile	140	140	130	120	kPa
Elongation	81	66	76	72	%

CFD compression force deflection, *CS* compression set, *% Ct* compression set expressed as a percentage of original thickness

performance features as compared to conventional molded high resiliency foam products. Tables 3 and 4 present the foam testing data from the Generation 1 and Generation 2 products of these high resiliency foam polyols.

One of the more advertized advances in commercial offering of polyurethanes from renewable resources was the introduction of soy-based polyol in the 2008 Ford Mustang [180, 181]. Ford partnered with Lear Corp. to produce automotive seats containing up to 40% soy-based polyol. This was hailed as a throw-back to the early days of Ford Motor Company, when Henry Ford incorporated as much as 60 pounds of soybeans into paint components and molded body parts for the Model T.

7.2 *Rigid Foam*

Rigid foams are distinguished from flexible foams in several aspects. The first and most noticeable difference is that rigid foams are hard and inflexible. On the macroscale they are characterized by a very high content of closed foam cells (cell windows are intact). The best quality rigid foams have very small average cell size. The principle application for rigid polyurethane foam is for thermal insulation. This property makes rigid polyurethane foams useful in refrigerators, water heaters, and other domestic appliances, and as pre-fabricated insulation board for interior walls and roofing in building construction. Rapid-cure rigid polyurethane foams have been developed for spray-foam applications, where the foam is sprayed from a commercial dispensing unit onto a surface such as commercial or residential roofing. Most rigid foams are applied as a reactive mixture to the substrate or into the container in which they will permanently reside, although a small percentage of rigid foam is prepared in free-rise blocks and is then cut to shape. Most uses for rigid foam are in the manufacturing of appliances or in the thermal insulation of residential housing and commercial building construction.

The use of renewable resources in the construction industry is promoted in many countries by legislation that encourages or requires the use of renewable content in construction materials in some sectors of the construction industry. Polyurethane spray foams that are prepared with renewable resources are gaining popularity with the early adopters of legislative promotions in the commercial and residential construction industries. Recent work has demonstrated the relative viability of some grades of closed-cell rigid foams for insulation, based on ESO chemistry [182]. These foams are beginning to make inroads into commercial and domestic thermal spray-in insulation [183, 184]. These polyurethane rigid insulation foams have gained increasing attention in the building and construction industry due to their contribution to the accumulation of LEEDS (Leadership in Energy and Environmental Design) points [185] or improvements to the Home Energy Rating System Index [186], which enable qualification for property tax credits through US federal, state and local governments [187–189]. Builders who incorporate high levels of renewable resources in building materials often benefit directly through property tax incentives provided by these green building certification processes.

Some claims appear in the patent literature relating to the thermal and flammability performance of polyurethanes created from ESO polyols [190], but such claims should be carefully evaluated under the conditions of local, state or federal flammability testing methods, or of regional construction regulations.

8 **Conclusions**

Polyurethanes prepared via the use of renewable carbon sources are a relatively recent introduction to the commercial market. The opportunity is driven primarily by the high and volatile cost of petroleum, and by societal concerns over the

consumption of non-renewable resources. The nature of polyurethane chemistry has dictated that the best fit for the incorporation of renewable resources is in the polyol component of the polymers. The only sources of renewable carbon that are produced in the volumes that can readily address commercial demands for raw materials are triglyceride oils from commodity annual plant sources. Different chemical technologies for the production of these polyols are evolving along independent lines of development, with the objective of attaining established positions based on meeting the cost and performance requirements of the marketplace. Technologies range from simple thermal oxidation processes to integrated chemical manufacturing schemes. Products that address potential applications in flexible slabstock and molded foams for bedding, furniture, and automotive interiors; flexible foams and elastomers for carpet backing; and rigid foams for housing and construction are beginning to establish regular appearances in commercial forums.

The quality demands for product performance constitute a significant hurdle to market adoption of these new raw materials. The market has so far demonstrated that interest in adoption of cost-effective products with renewable content is sustainable as long as product performance is not compromised. The different chemistries that have been harnessed to pursue this opportunity are still in an evolutionary stage, as polyol producers respond to market pressures for the high quality and low price that has previously fuelled the success of the petrochemical progenitors. Time will tell which, if any, of the approaches to replacement of petroleum with renewable hydrocarbons will sustain a market presence, and will succeed at impacting the consumption of global petrochemical stocks.

For current information on the commercial uses of triglyceride oils, readers are directed to follow the periodic communications from the New Uses Committee of the United Soybean Board [191], which is staffed with informative professionals who remain current in the alternative applications of soybean oil, and who support the efforts of industry to develop alternative sources of feedstocks to reduce dependence on petroleum.

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