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Renewable building blocks for polyurethanes

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Abstract:

For the past 60+ years, polyurethane chemistry has been used to make a wide variety of everyday consumer products such as mattresses, automotive interior parts and foam insulation. Today, the vast majority of polyurethane products are made entirely from petroleum. Although polyols made from natural oils have made inroads during the past decade, cost and performance, as well as the presence of a large-scale established infrastructure around petroleum-based materials, remain as barriers to significant market penetration. Promising new developments such as sugar-derived raw materials have the potential to shift the balance of cost and performance, but they are at an early stage. While not a comprehensive review of the large volume of academic literature on renewable polyurethane chemistry, this article discusses several routes to renewable, commercially viable building blocks for polyurethanes, considering both established and emerging technology.

Keywords: Polyurethanes, polyols, isocyanates, sustainability, renewable raw materials, natural oil polyols, sugar, isosorbide, carbon dioxide, eco-efficiency analysis

DOI: 10.1515/psr-2017-0193

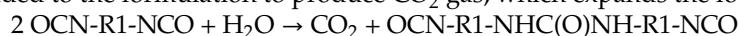
1 Polyurethane chemistry and applications

Ever since Otto Bayer filed the first polyurethane patent in 1937, polyurethanes have found use in a wide range of applications [1, 2]. Polyurethane foam is used for cushioning, insulation and automotive interior applications. Polyurethane elastomers are commonly used in footwear and sporting goods. The chemistry can also be used to formulate coatings, adhesives and sealants. Thermoplastic polyurethanes (TPU) can be processed with traditional extrusion equipment into tubing, wire coating, film or sheet. TPU can also be injection molded into parts such as shoe soles, automotive interior trim, caster wheels or mobile phone cases.

Polyurethanes are the product of diisocyanate and a polyol [1–3]:



The polyol typically has a molecular weight from 200 to 6000 and may have a functionality (number of hydroxyl groups) between 2 and 8 depending on the application. Flexible foam used in bedding, furniture upholstery and automotive seating, requires a polyol with functionality around 3, and equivalent weight (per hydroxyl group) typically between 1000 and 2000. The backbone of such polyols is typically polyether or aliphatic polyester. The backbone can be a polyether (mixture of propylene oxide and ethylene oxide) or aliphatic polyester. If the foam is molded, a higher reactivity polyol, endcapped with ethylene oxide (producing primary hydroxyl groups) is typically used. Either MDI or TDI is typically used as the isocyanate. Water is added to the formulation to produce CO₂ gas, which expands the foam (with an amine as the intermediate):



Formulations also contain a nonionic silicone surfactant to stabilize the foam bubbles, and one or more catalysts (most commonly tertiary amines and/or organotin compounds).

Rigid polyurethane foam is commonly used as insulation for appliance or construction applications [1, 2]. Polyols for rigid foam are typically polyether or aromatic polyester. The polyether polyols are typically lower equivalent weight and/or higher in functionality than those used in flexible foam. Sorbitol or sucrose-initiated polyethers are typically the main polyol component (leading to theoretical functionalities of 6 or 8), although low equivalent weight diols and triols can also be added to optimize processing. Polymeric MDI is most commonly used as the isocyanate. Water can be used as a chemical blowing agent as in flexible foam, but physical blowing agents such as hydrocarbons and hydrofluorocarbons are more commonly used, in order to achieve low thermal conductivity. Other components such as silicone surfactants and tertiary amine catalysts are typically added.

Polyurethane elastomers are formulated primarily from polypropylene oxide diols ranging in molecular weight from 400 to 3000 [1, 2]. Polytetrahydrofuran, aliphatic polyesters (typically from adipic acid and butanediol or ethylene glycol), or polycaprolactone are also commonly used. Higher functionality polyols can be added in small amounts to achieve crosslinking. Low equivalent weight diols (e. g. ethylene glycol, propylene

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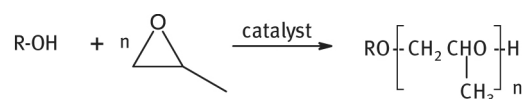
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glycol or 1,4-butanediol) are added as “chain extenders”, which react with the diisocyanate to form “hard segments.” During polymerization, the hard segments separate from the polyol “soft phase”, which becomes a physical crosslink in the material. Mechanical properties including hardness and tensile strength are adjusted with the polyol, crosslinker and chain extender. Polyurethane elastomers are most commonly made with 4,4'-MDI. However, aliphatic isocyanates (e. g. hexanediisocyanate, H₁₂-MDI or isophorone diisocyanate) can also be used, particularly if discoloration due to exposure to ultraviolet light is a concern.

TPU is typically formulated from diols, chain extenders and 4,4'-MDI [1, 2]. To produce a linear polymer, all components must have functionality close to 2.0. The diols are typically aliphatic polyesters and polytetrahydrofuran, with equivalent weight between 200 and 1500. Ethylene glycol, 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol are typically used as chain extenders. Aliphatic isocyanates (e. g. hexanediisocyanate, H₁₂-MDI or isophorone diisocyanate) can also be used. TPU is manufactured in a one-shot continuous process, using either a conveyor belt or reaction extruder [2].

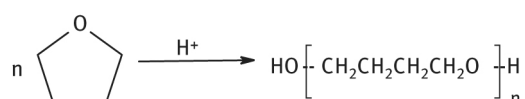
2 Traditional intermediates for polyurethanes

Over 90 % of polyols used for polyurethanes are polyethers [1]. Flexible and rigid polyurethane foam use polyethers incorporating propylene oxide (PO) and/or ethylene oxide (EO). These are produced using an alkoxylation process [2, 4]:

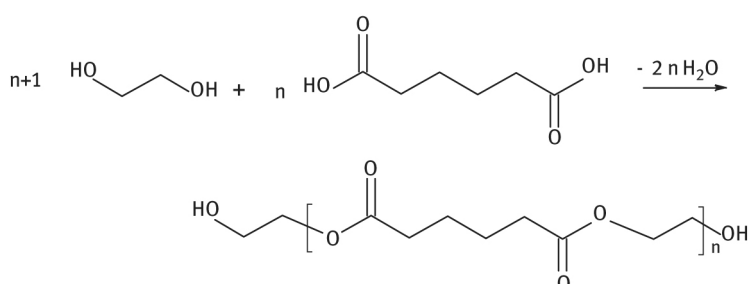


The polyol will have the same functionality as the initiator (i. e. 2 hydroxyl groups for propylene glycol, or 3 for glycerine). A mixed feed of PO and EO produces a statistical copolymer, while a sequential feed results in a block structure. Primary hydroxyl groups are formed if the end group is EO, and secondary hydroxyl groups result if the end group is PO. Primary hydroxyl groups provide faster reactivity and is desirable for molded articles (e. g. seat cushions and automotive trim parts), where cycle time is critical to manufacturing cost.

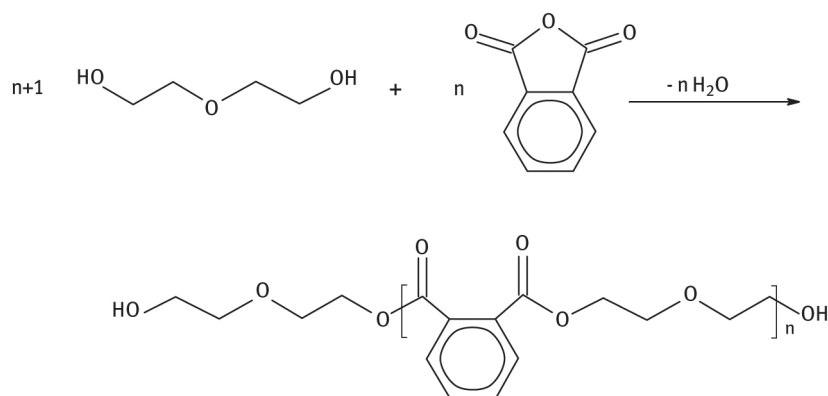
Polytetrahydrofuran (also known as Poly THF or PTMEG) is commonly used in cast elastomers and TPU. It is produced from the cationic polymerization of THF [5]:



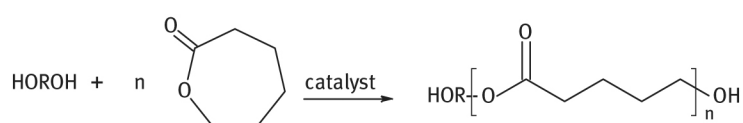
Aliphatic polyesters are produced from diacids such as adipic acid, and short diols such as ethylene glycol, 1,4-butanediol or 1,6-hexanediol [4].



Aromatic polyesters (for rigid foam) can be produced from copolymerization of a glycol with aromatic acid derivatives, such as phthalic anhydride or dimethyl terephthalate:

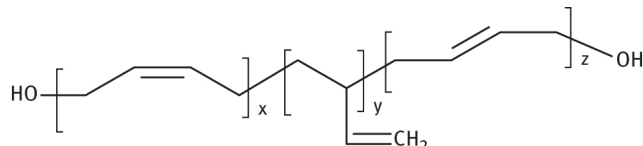


Polyester diols can also be produced from caprolactone, a cyclic ester.



A polyester polyol with a narrower molecular weight distribution is produced. Polycaprolactone polyols are used in cast elastomer or TPU applications.

Hydrophobic polyols can be produced from butadiene. Polyurethanes made from these polyols exhibit improved moisture resistance, increased electrical resistivity and lower solid density than conventional polyurethanes. The resulting polyol is a mixture of structures formed by either 1,4-cis, 1,4-trans, or 1,2-addition of polybutadiene [4]:

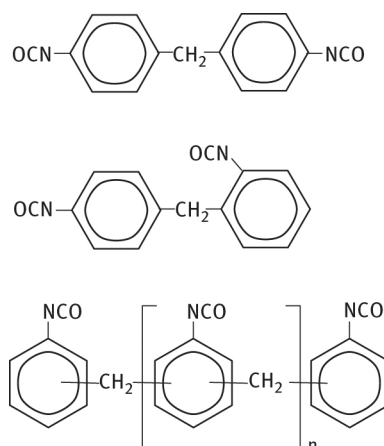


Free radical polymerization of butadiene, using a hydroxyl-containing initiator such as hydrogen peroxide, results in mostly 1,4-trans addition of butadiene, and 2.2–2.6 primary (mostly terminal) hydroxyl groups per chain. Commercial examples include Poly bd® from Total Cray Valley and Polyvest® HT from Evonik. Anionic polymerization of butadiene, followed by reaction with ethylene or propylene oxide, results in mostly 1,2-addition of butadiene, a more linear structure, narrow molecular weight distribution, and a functionality that is very close to the theoretical value of 2 hydroxyl groups per chain [4]. A commercial example is Krasol® from Total Cray Valley.

Since only one double bond reacts during the polymerization, polybutadiene polyols will contain double bonds in the backbone. The remaining double bonds are then available for crosslinking, either thermally, or by using sulfur or peroxide. Alternatively, the polyol can be hydrogenated in a subsequent step to saturate the double bonds.

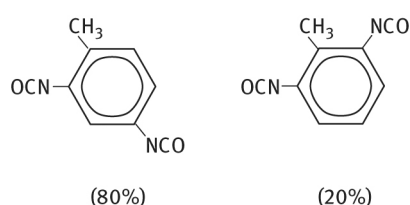
Common chain extenders such as ethylene glycol, propylene glycol, diethylene glycol and dipropylene glycol are produced from ethylene or propylene oxide. 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol are produced from other petroleum feedstocks.

MDI and TDI are the most commonly used isocyanates. MDI is produced from phosgenation of MDA, which is produced from aniline and formaldehyde [1, 2]. The process produces a distribution of oligomers and isomers:



4,4'-MDI, 2,4'-MDI, and oligomers of functionality 3 and higher are the primary products, which are refined by distillation. Polymeric MDI is a mixture of monomeric MDI, and the higher oligomers. Different grades with various oligomer distributions are available.

TDI is produced from phosgenation of TDA, which is produced from toluene with dinitrotoluene as an intermediate. The process produces a mixture of 2 isomers, 2,4-TDI (80 %) and 2,6-TDI (20 %) [1, 2]:

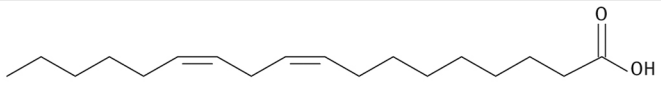
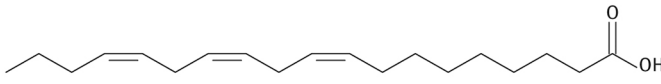
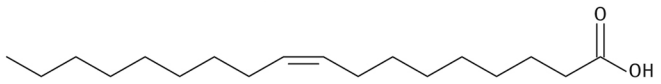
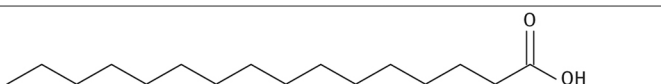
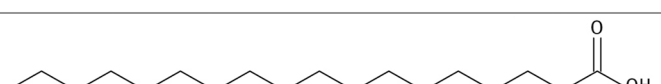


3 Polyols and isocyanates from natural oils

Natural oils, such as vegetable, castor and palm oils, are good sources of building blocks for renewable polymers. These oils are typically triglycerides (esters of fatty acids and glycerine). Reactive sites in the oils are mainly carbon-carbon double bonds and ester groups, which are then converted to the desired functional groups (e. g. hydroxyl groups to produce polyols). This can be achieved through double bond reactions such as epoxidation, hydroformylation, metathesis, or through ester bond reactions (e. g. transesterification or transamidation) [6]. Since most oils contain multiple reactive sites, the resulting polymer will be crosslinked, leading to a thermoset. Therefore, the most common applications of vegetable oil based polyurethanes are rigid and flexible polyurethane foams.

When functional groups are introduced at the position of double bonds, the distribution of functional groups and structures is preserved. Therefore, hydroxyl groups introduced in the vegetable polyols are not terminal as in petroleum-based polyols. This leads to a network with dangling chains, which act as internal plasticizers and lower the T_g of the polymer [6]. Although the resulting network structure has a shorter distance between crosslinks, the presence of the dangling chains is likely beneficial in viscoelastic foam.

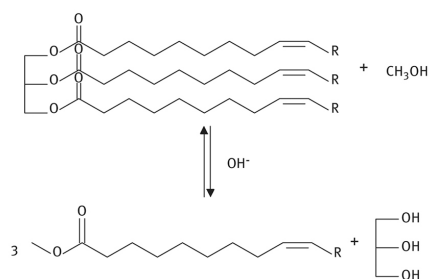
Soybean oil is most commonly used in North and South America, palm oil is used in Asia and rapeseed oil is used in Europe. Soybean oil is a triglyceride which contains 4.6 double bonds per molecule on average. The structure of soybean oil may vary from molecule to molecule, since it combines five different fatty acids: linoleic, linolenic, oleic, palmitic and stearic acids.

Linoleic Acid	
Linolenic Acid	
Oleic Acid	
Palmitic Acid	
Stearic Acid	

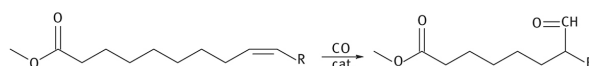
Although direct oxidation of double bonds introduces hydroxyl groups to the vegetable oil, controlling the process is challenging due to the many byproducts formed (i. e. peroxides, aldehydes or ketones). These byproducts often give rise to odor, lower functionality or higher acid value requiring additional post processing and increasing cost. Epoxidation of the double bonds is one alternative route. This can be achieved by catalytic hydrogenation, reaction with hydrochloric or hydrobromic acid and by acid catalyzed ring opening [6]. However, a range of polyol structures is produced that may impart different properties to the final polyurethane.

Commercial soybean oil polyols include RenuvaTM polyols sold by Dow, and BiOHTM polyols sold by Cargill. A commercial scale process to produce soybean oil polyols has been reported by Dow [7]. In the first step, soybeans are extracted with methanol to produce fatty acid methyl esters. Hydroformylation of double bonds in the soybean oil and subsequent reduction produces aldehydes and alcohols. A catalyst (most commonly rhodium or cobalt carbonyl) is required for hydroformylation reactions. Total recovery of the catalyst is required to keep the process cost-effective. The monomers are then polymerized with an initiator to prepare the final polyol through a transesterification reaction. The resulting polyol includes an extra carbon at every double bond, resulting in longer chains, and ultimately softer and more elastic materials [6].

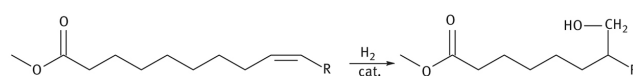
Methanolysis:



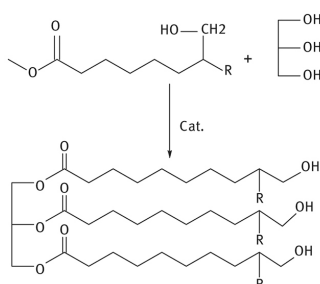
Hydroformylation:



Hydrogenation:

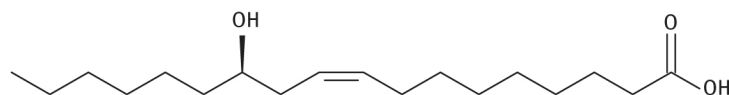


Polymerization:



Castor oil is a triglyceride containing 90 % ricinoleic acid, which has one hydroxyl group on the 12th carbon, and a double bond between the 9th and 10th carbon.

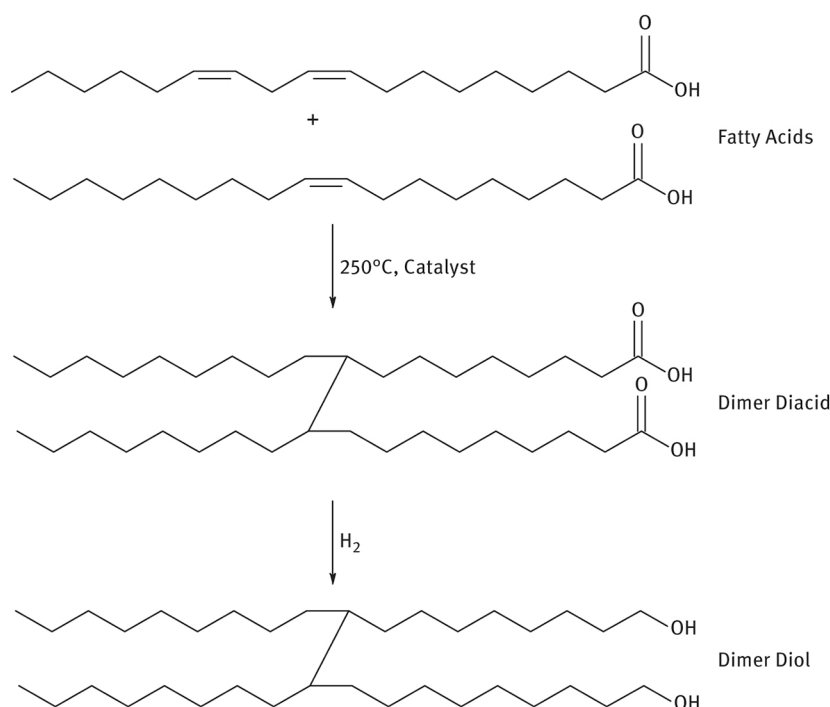
Ricinoleic Acid:



Unmodified castor oil can be used as a urethane polyol [6, 8]. Although it has a hydroxyl functionality of 2.7, its hydrophobicity and molecular weight of approximately 1000 restrict its use in flexible foam. A limited amount can be added to flexible or rigid foam formulations, but will have a negative effect on properties and processing. Smiecinski et al [8] describe a propoxylated castor oil polyol (marketed by BASF as Pluracol® Balance™50), which addresses these issues. Castor oil accounts for 31 % of the polyol, and foams made from the polyol contain up to 20 % renewable content. The propylene oxide in the polyol backbone provides sufficient molecular weight and compatibility with the other formulation components, in contrast to castor oil and most other natural oil polyols. Therefore, the polyol can be used as the sole polyol in flexible slabstock foam with minimal changes in formulation, processing or physical properties, compared with foam made using a standard petroleum-based polyol.

Bradlee et al. conducted a life cycle analysis of castor oil/propylene oxide polyols for flexible slabstock foam using an internal eco-efficiency analysis [9]. Comparisons were made to the standard petroleum-based polyol. Overall costs, primary energy consumption, ozone depletion potential, acidification potential, photochemical ozone creation (smog), water emissions, solid waste generation, raw material consumption, toxicity potential, risk potential and land use were considered. In general, the environmental impact of the castor oil/PO polyol depended on its molecular weight. The lower molecular product was more viscous and required heat in order to pump the product, and this affected the analysis. Overall, the high MW castor oil/PO product was the most eco-efficient.

Dimerized fatty acids, also known as “dimer diacids”, are produced from natural oils such as soybean oil or tall oil. They are obtained by processing a mixture of fatty acids at elevated temperature and pressure using a catalyst, followed by distillation and hydrogenation [10, 11].



The resulting 36-carbon, di-functional acid can be converted into the corresponding diol, or can be chain extended with a short chain diol (e. g. ethylene glycol), and optionally another diacid (e. g. adipic acid) to produce a polyester diol [10]. Dimer-based polyols are sold under brand names such as Sovermol® (BASF), Priplast™ and Pripol™ (Croda). The dimer-based polyols were shown to produce polyurethane elastomers, which have comparable hydrolysis resistance to PTMEG, and are significantly more hydrolysis resistant than for typical polyester diols (e. g. hexanediol-adipate) [10]. Moreover, the polyurethanes from the dimer-based diols exhibit less moisture uptake than those from PTMEG, or from any other typical polyether or polyester polyol. The dimer-diol polyesters are also more resistant to heat, oxidation and UV attack since they do not contain ether linkages. In addition to elastomers, dimer-based polyols can be used for coatings, adhesives and flexible foams.

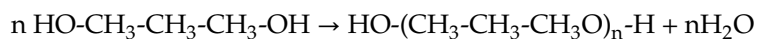
A diisocyanate based on a dimer diacid, DDI 1410, is sold by BASF [6, 12]. The product is used mainly in coatings to achieve increased flexibility and moisture resistance. It is also less toxic than typical aliphatic diisocyanates.

4 Sugar as a source for polyols and chain extenders

DuPont Tate&Lyle produces Susterra® propanediol from corn sugar using a proprietary process [13]. The material can be used as a chain extender in TPU or polyurethane elastomers, replacing 1,4-butanediol, or petroleum-based 1,3-propanediol. DeSalvo et al. [13] compared the performance of Susterra® Propanediol to 1,4-butanediol in MDI and TDI polyurethane elastomers made by the prepolymer method. Physical property performance was comparable, with improvements in abrasion and increased pot-life in some cases.

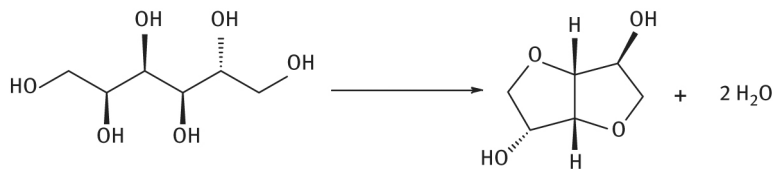
Susterra® propanediol can also be reacted with adipic acid, or another suitable diacid to produce an aliphatic polyester polyol. Use of such a polyol in combination with the renewably sourced diol as a chain extender increases the renewable content even further. DeSalvo et al. [13] evaluated adipates made with Susterra® propanediol of molecular weight between 500–2000 Da in MDI elastomers using the prepolymer method. Use of Susterra® propanediol as the chain extender has resulted in elastomers with up to 55 % renewable content. Overall properties of the studied elastomers were comparable with industry standards, with some improvements reported in resilience and abrasion.

By polymerizing the bio-sourced propanediol in the presence of a catalyst, a 100 %-biosourced polyether polyol is produced:



The polyol, also referred as polytrimethylene ether polyol, PTMEPOL or “PO3G”, has been produced in molecular weights between 500 and 3000, and has been marketed under DuPont’s brand name Cerenol™[14]. TPU or polyurethane elastomers with similar properties to those based on polytetrahydrofuran can be produced using this polyol.

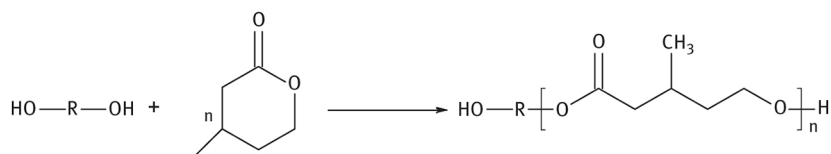
Isosorbide (1,4:3,6 diandrosorbitol or dianhydro-D-glucitol) is a diol which is formed from the double dehydration of sorbitol (sorbitol can be obtained from hydrogenation of glucose) [15]:



Due to the rigidity of the molecule, it is a potential alternative to Bisphenol A. Unfortunately, the two hydroxyl groups do not have equivalent reactivity, since the molecule forms an asymmetric planar structure, resulting in one of the hydroxyl groups hydrogen-bonding with the neighboring ether oxygen [15]. This creates difficulty in using the molecule as a chain extender for elastomers, or into polyester polyols, since the different reactivity will inhibit molecular weight build. However, use of isosorbide in polyurethanes is still possible though appropriate use of catalysts and elevated reaction temperature. Additionally, isosorbide is not soluble in typical flexible polyether polyols. Capping isosorbide with ethylene oxide or propylene oxide could result in a material suitable for use in elastomers or TPU.

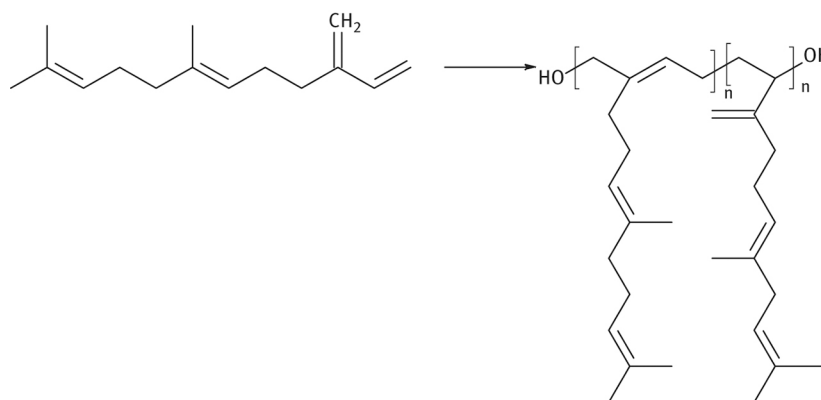
Ionescu et al. [15] demonstrated the use of isosorbide in rigid polyurethane foam. Isosorbide was successfully added directly to the foam formulation by dissolving it in a sucrose-initiated polyether polyol, and the foam had properties comparable with typical rigid foam.

Schneiderman et al. [16] reported another route to polyurethanes using sugar as a starting material, producing foams and elastomers with similar properties to petroleum-based polyurethanes. A polyol was synthesized in the bulk from β -methyl- δ -valerolactone (MVL).



MVL can be produced from sugar, at potentially low cost. The backbone of the polyol (pMVL) resembles polycaprolactone, which is currently used as a building block for polyurethane elastomers. Furthermore, the polymer degrades back to monomer upon heating between 200 and 250 °C. The MVL monomer can be recovered through distillation, resulting in the added benefit of closed loop recyclability for this material. Chemical recycling of typical polyurethanes (through hydrolysis or glycolysis) is not straightforward and yields a mixture of recycled polyols with limited utility.

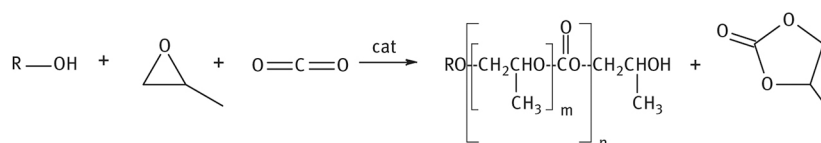
Yoo et al [17] reported a route to unique sugar based polyurethanes using poly(trans- β -farnesene) diols, developed by Amyris and Total SA. The monomer, β -farnesene (BioFene™), is produced by yeast fermentation of sugar syrups. Hydrophobic diols (with characteristics comparable with polybutadiene diols) are produced by anionic polymerization and can be used for cast elastomers or thermoplastic polyurethanes. The resulting polymer diols have a narrow molecular weight distribution and a dense “bottlebrush” structure:



The dense side-chain structure inhibits chain entanglement, even at high molecular weight. The viscosity of the polymer is lower than a comparable polybutadiene. Hydrogenation of the structure leads to tighter chain packing, reduced free volume and higher T_g . Properties of polyurethane elastomers based on poly(trans- β -farnesene) diols were not reported.

5 Carbon dioxide as a building block (polyether carbonates)

Carbon dioxide can be incorporated into polyols through copolymerization with propylene oxide using a double-metal cyanide catalyst to form an alternating polyethercarbonate with propylene carbonate as a by-product [18, 19]:



While not bio-sourced, CO_2 is a renewable material, available from the atmosphere, or from a fossil fuel power plant with carbon capture. A lifecycle analysis [18] indicated that incorporating 20 wt% CO_2 reduces greenhouse gas emissions by 11–19 % and reduces fossil resources by 13–16 % compared to production of conventional polyether polyols. However, the process does emit a net positive amount of CO_2 , and thus is not a sink for greenhouse gas.

Since the polyol has relatively low viscosity and produces polyurethanes with low glass transition temperature, it is suitable for use in flexible polyurethane foam. Physical properties of flexible polyurethane foams produced using a polyethercarbonate polyol are comparable to those produced using conventional polyether polyols [19].

6 Future outlook

Starting with products derived from vegetable oils, renewable materials have made inroads as building blocks for polyurethanes. However, most polyurethane will continue to be made from petroleum for the near future. Issues to overcome are primarily the cost of the renewable materials compared with their performance, as manufacturers and consumers are generally not willing to pay simply for renewable content. Many of the most recent innovations are from sugar-derived materials. New innovations will continue to drive the use of renewable materials in polyurethanes, especially where unique properties are obtained, and when economies of scale can be reached in order to lower costs.

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