



An overview of raw materials to produce eco-friendly and biodegradable polyurethanes

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Abstract— This review highlights a critical concern in the manufacturing of polyurethane, which traditionally relies on substantial quantities of petroleum-derived materials. With the increasing awareness of environmental sustainability and the need for materials that minimize harm to the environment, researchers have been exploring bio-based raw materials as alternatives for synthesizing polyurethane. The focus on bio-based raw materials aligns with the growing demand for sustainable practices across various industries. This review delves into the potential applications of bio-based polyurethane in diverse industries, emphasizing the need for more environmentally friendly alternatives. Furthermore, the article examines recent advancements in the field of biodegradable polyurethane, reflecting a broader trend toward materials that break down naturally over time. This aspect is crucial in addressing concerns related to plastic pollution and waste management. Given the diverse range of vegetable oils and other biodegradable compounds available, the review places particular emphasis on the utilization of biodegradable materials for polyurethane. This approach not only provides a sustainable alternative to petroleum-derived materials but also capitalizes on the abundance and versatility of vegetable oils and other raw materials. The paper's concise overview of raw materials used in the production of biodegradable polyurethane and their applications provides valuable insights for researchers, industries, and policymakers. As the demand for sustainable materials continues to rise, the exploration and development of bio-based and biodegradable polyurethanes represent a promising avenue for addressing environmental concerns and creating more eco-friendly products.

Index Terms— biodegradability, eco-friendly polyurethane, polyisocyanate, polyols

1.0 INTRODUCTION

Among synthetic polymers, polyurethane (PU) is one of the most commonly utilized, with a rapidly growing global industry, which is called the 'fifth largest plastic' in the world with more than 80 years of history [1].

However, the worldwide consumption of polyurethane in daily life is multiplying more rapidly with time due to its highly durable nature via increased melting points and tensile strength [2]. PUs are made via exothermic reactions between polyfunctional alcohols (HO-R-OH) and poly-isocyanate (OCN-R-NCO) either in the presence of a catalyst or in the

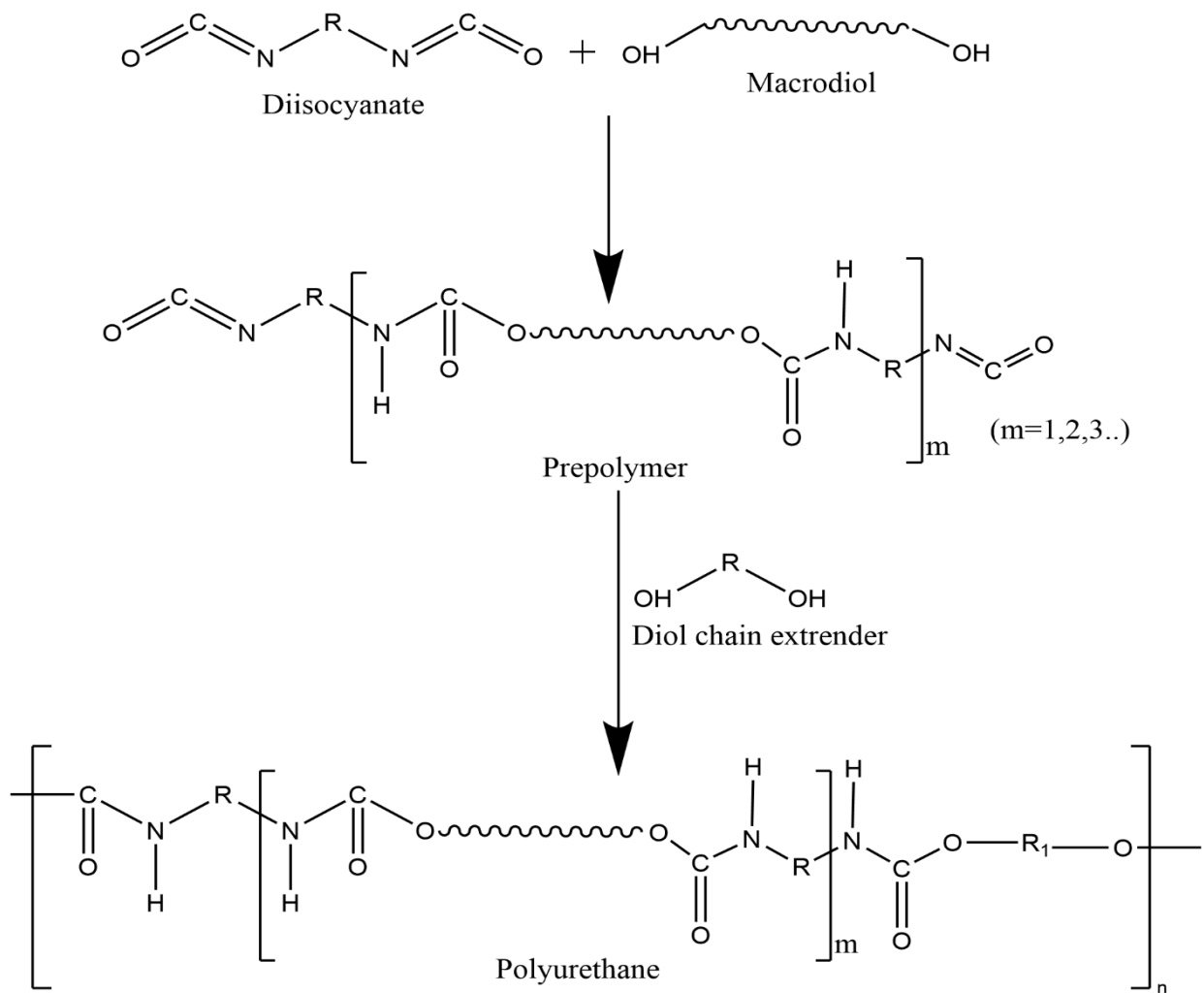


Fig. 1. Reaction for preparation of polyurethane

presence of UV activation through form urethane linkages (-NHCOO-) as repeating macromolecular compounds in the main chain, which as shown in Fig. 1.

Unfortunately, most PU materials are produced

from the petroleum-based PU raw materials that are ultimately derived from petroleum, which are led to serious environmental problems like growing land and water pollution problems due to their non-degradability nature in the natural environment and they are extremely microbially resistant [3]. PU raw ingredients derived from petroleum are also non-renewable and have short supply resources. Petro-based polyols have a significant energy consumption due to the drilling and extraction of oil from the earth, transportation to refineries, refinement, and production of the polyol. This method of polyol production is increased the number of steps which makes environmental pollution [4] Prices of petroleum-based feedstocks and crude oil have varied dramatically in recent years, as has the world crude oil stock, which is critical for producing a viable replacement for PU raw resources based on petroleum [5]. Today, the usage of natural renewable resources as the feedstocks for industrially important polymers is increased with an increment in the price of petroleum raw materials, tight environmental rules and regulations and the high shortage of petroleum products [6]. Nevertheless, the toxicity of diisocyanates that are gained from petro-based like phosgene is the major drawback of PU production caused the environmental hazards and health effects like asthma and skin irritation [7]. The considerable research and interest in biomass resources that instead of petrochemicals raw materials for PU synthesis is increasing due to the enhancement of environmental awareness among consumers and producers. Biodegradable PU (BPU) from renewable materials sustainably managed the carbon cycle while developing the impact of the material on the environment, which also reduces the potential of the global warming of material [8]. Nowadays, vegetable oils are highly used as a bio based raw materials in PU production due to their availability, biodegradability, low cost, renewability, sustainability, low toxicity and environmental friendliness [6]. These materials are also provided with a commercially viable and competitive alternative source to petro-based PU raw materials [5]. However, bio-based raw materials such as sugar, natural oil, starch and cellulose are the best suitor for the enlargement of innovative green PU materials [7]. Possible biodegradable raw materials in PU production are summarized in this paper.

The exploration of biodegradable polyurethanes derived from various biobased sources has indeed been a focus of extensive research globally. Researchers have been investigating the use of biodegradable starting materials, and one promising avenue is the utilization of fatty acids found in different vegetable oils for the production of biodegradable polyurethane. The versatility of these polyurethanes in formulating mechanical characteristics, ranging from soft elastomers to rigid materials, makes them suitable for a wide range of applications. The studies

conducted so far have confirmed the inherent biocompatibility of these materials, which is a significant advantage for their use in various biomedical, environmental and other applications.

Ongoing advancements in process techniques, sustainability, and the development of biodegradable polyurethanes are likely to have a significant impact in the near future. As the industry moves towards more sustainable practices, the polyurethane foam industry, in particular, should be prepared to embrace and capitalize on these potential new opportunities.

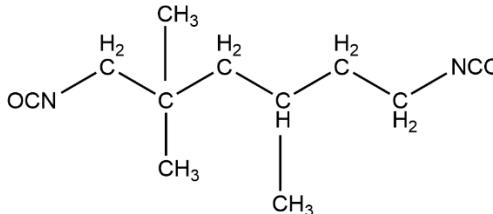
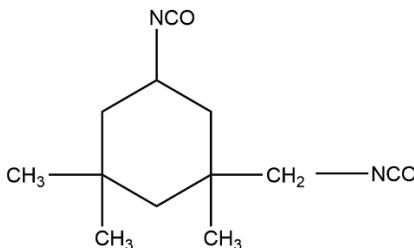

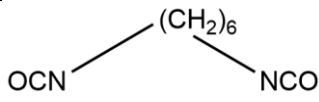
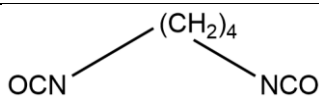
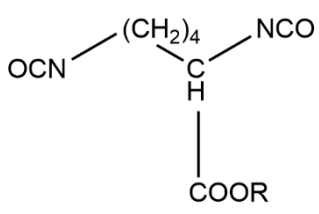
The adoption of biodegradable polyurethanes aligns with the global push towards environmentally friendly materials and sustainable practices. As technology continues to evolve, the polyurethane foam industry can play a crucial role in contributing to a more sustainable and eco-friendly future. It is essential for stakeholders in the industry to stay informed about these advancements and be ready to adapt to the changing landscape.

2.0 RAW MATERIALS IN BIODEGRADABLE POLYURETHANE PRODUCTION

2.1 ISOCYANATES

Isocyanates work as chemically reactive material to produce PU, which is also used as a hardener and curing agent. Bio-based isocyanates are gained from renewable resources. Biodegradable polyurethanes are mostly produced by aliphatic diisocyanates types which examples are shown below in Table 1. Commonly, aliphatic diisocyanates are selected to prevent toxicity issues in biomedical applications. Among these, Ethyl 2,6-diisocyanatohexanoate (ELDI) and Methyl 2,6-diisocyanatohexanoate (MLDI) are specially used for biodegradable PU due to, the release of non-toxic lysine when degradation of urethane or urea linkages. 1,6-Hexamethylene diisocyanate (HDI) is widely used to produce biodegradable polyurethanes due to its non-toxic nature of byproduct (diamine 1,6- hexane diamine) during PU degradation.

Table 1. Chemical structures of aliphatic di-isocyanates to produce biodegradable PU

Chemical name	Isocyanate structure
2,2,4-Trimethyl hexamethylene diisocyanate(TMDI)	
Isophorone diisocyanate (IPDI)	
1,4-Cyclohexane diisocyanate (CHDI)	
1,6-Hexamethylene diisocyanate (HDI)	
1,4-Butanediisocyanate (BDI)	
Ethyl 2,6 diisocyanatohexanoate (R= Ethyl, ELDI) and Methyl 2,6 diisocyanatohexanoate (R= methyl, MLDI)	

Both BDI and HDI diisocyanates are produced the hard segment better ordering via intermolecular hydrogen bonding due to their symmetrical molecular structures, which makes the high strength elastomers. For instance, elastomers with up to 95% elongation and up to 60 MPa ultimate tensile strength are produced, when using the HDI-based polyurethanes formulation.

Diisocyanates with non-linear structures like IPDI and CHDI are also used to produce biodegradable polyurethanes to a much lesser extent. They also produce stiffer materials than their linear analogues due to their less flexibility of backbone structure that gains from

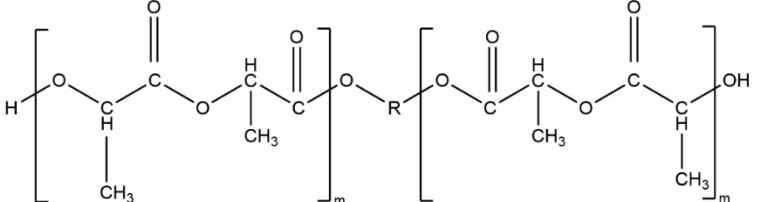
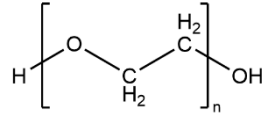
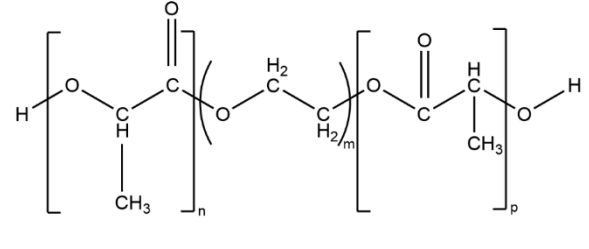
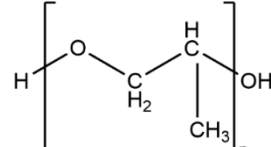
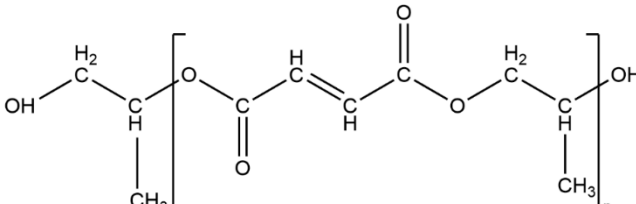
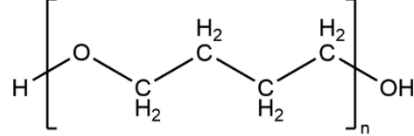
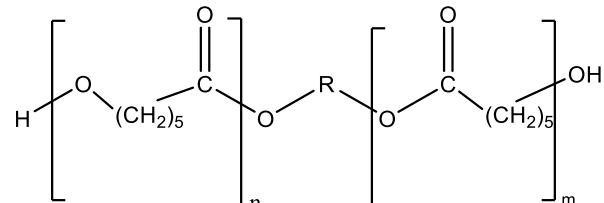
cyclohexane rings [9]. The non-isocyanate PUs or polyhydroxy urethanes are produced from the isocyanate-free technique to obtain the carbamate group produces non-isocyanate PUs or polyhydroxy urethanes, which is a reliable technique that is neither hazardous to humans nor destructive to the environment. To gain the carbamate group, which is a reliable technique with no hazardous nature for humans and is not harmful nature to the environment [7].

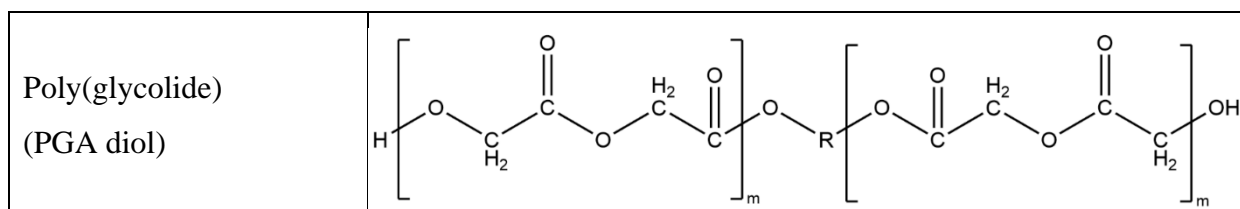
2.2 POLYOLS

Isocyanates chemically react with polyols with two or more –OH groups to produce PU, which works as a soft segment and influences its flexibility. Initially, most of the polyols are produced from petroleum sources then the demand for renewable polyols is increased to fulfil the environmental concerns [10]. The oligomers with hydroxyl end functional groups which have two or higher functionality are used to make biodegradable polyurethanes [9]. However, bio-based polyols, such as vegetable oils and their derivatives, are being used to make PUs, which are made up of triglyceride molecules of different reactive groups such as carbon-carbon double bonds, ester and hydroxyl groups, and are made by transesterification or epoxidation of oils followed by a ring-opening reaction with glycerol, alcohol, or ethanol [11].

Bio-based polyols generated from vegetable oils have the potential to partially replace petroleum-derived polyols, particularly when they are cross-linked with isocyanates [10]. Furthermore, the reaction that produces oleic and 10-undecenoic acids from alkyne-derivatized fatty acids and thiol-yne produces renewable polyols and diols for biocompatible PU products that use in tissue engineering purposes [12]. The degradation of polyurethanes and hydrophobic and hydrolytic characteristics are dependent on the polyol's chemical structure. The main degradation is hydrolytic degradation, where certain enzymes will initiate the degradation of the soft segment. The PU to a lesser extent only produced, when using the oligomers with amine end-functional groups in the formulations. Table 2 lists the various formulations of commonly used polyols in biodegradable polyurethanes.

Table 2. Chemical structures of polyols to produce biodegradable polyurethanes

Chemical name	Polyol structure
Poly (D, Lactide) (PLA-diol)	
Poly (ethylene oxide) (PEO-diol) or PEG- diol	
Poly (lactic acid ethylene glycol-co lactic acid) diol (PCL- co-PEG-co PCL)	
Poly (propylene oxide) (PPO-diol)	
Poly (propylene fumarate diol (PPFdiol)	
Poly(tetramethylene oxide) (PTMO diol)	
Poly (ε caprolactone) (ε PCL-diol)	



The ring-opening polymerization of the cyclic ether monomers are used to produce the most biodegradable polyether polyols. For instance, propylene oxide is used to produce the poly(propylene glycol) by ring-opening polymerization with a catalyst and an initiator like amines or alcohols, where usually three groups of catalysts are used as coordination catalysts, base catalysts and acid catalysts. The acid-catalyzed condensation polymerization or ring-opening polymerization of the corresponding hydroxy acids is used to produce the biodegradable polyester polyols based on lactides, caprolactone and glycolide. Poly(caprolactone) diol is widely used to produce biodegradable PU with good elastomeric properties because of its low glass transition.

The consumption of petroleum-based polyol will reduce by using a combination of primary and secondary polyols with hydroxyl groups. For instance, high mechanical and physical qualities stiff PU foams are reported when using a mixture of castor oils and glycerin. The physical properties of the PU also can change by using different polyols. For an example, the reactivity of the rigid PU foaming materials can reduce by using trans esterified palm olein-based polyol that has the secondary hydroxyl group. Bio-based polyol formulated PU has reported an increment in the time to apply the cream, time to remove the tack, time to rise, and time to gel than petroleum-based polyol [10].

2.3 CHAIN EXTENDERS

Chain extenders are diols or diamines with a low molecular weight in PU production to lead the reaction between isocyanate-terminated prepolymer and active hydrogen-containing compounds to enhance the block length of the hard segment and resin curing into the desired shape [11].

Degradable hard segments can be made by incorporating degradable chain extenders that can be either diesters or amino acids. The diol and diamine chain extenders composed of amino acids are employed to improve mechanical properties with the presence of degradable ester linkages than more conventional chain extenders. Low-molecular-weight polyamines are used

in reactive injection molding due to their high and fast reactivity towards the isocyanate group, which requires short cycles. Usually, ethylene glycol and water are incorporated as chain extenders into biodegradable PU formulation. Fig. 2 and Fig. 3 are shown as ethylene glycol-based synthetic approaches for bio-based PU and water respectively.

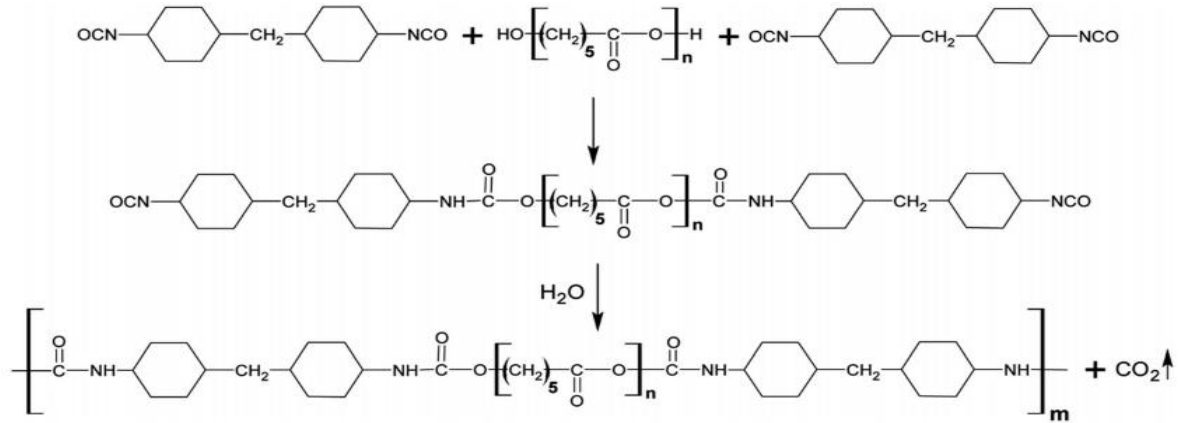


Fig. 2. Biodegradable PU developed with an ethylene glycol chain extender

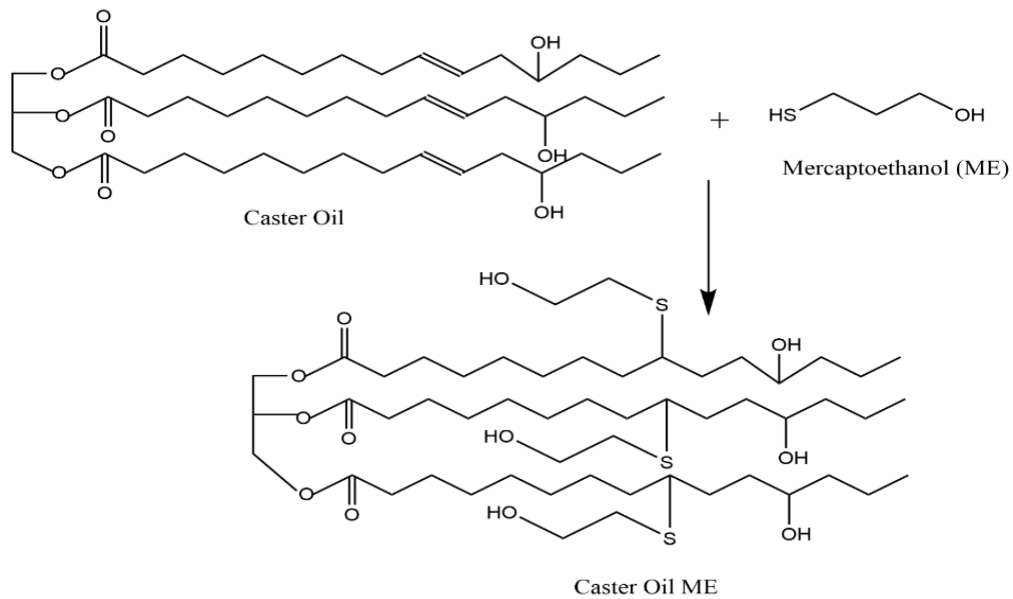


Fig. 3. Water as a chain extender in the production of biodegradable PU

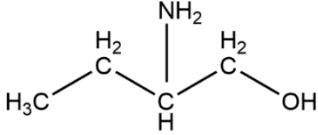
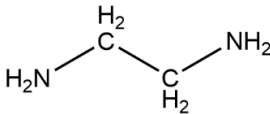
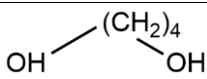
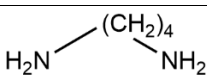

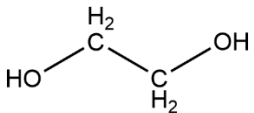
The innovative chain extenders are employed to speed up the hard segment's deterioration. The commonly used chain extenders and novel chain extenders in BPU formulations are listed in Table 3 and chain extenders with degradable linkages is shown in Table 4.

Table 3. Chemical structures of chain extenders to produce biodegradable polyurethanes

Chemical Name	Chain extender structure
Bis(2-hydroxyethyl) phosphate (BGP) Bis (2-hydroxyhexyl) phosphate (BHP)	
1,1-(Hexane-1,6-diyl) bis(3-2hydroxyethylurea)	
2-Hydroxyethyl-2-hydroxypropanoate	$\text{HOCH}_2\text{CH}_2\text{OCOCH}(\text{CH}_3)\text{OH}$
Ethane-1,2-diyl bis (3-(4 hydroxyphenyl) propanoate	
4-((1-(1-Amino-2 phenyl ethoxy) ethoxy) methyl cyclohexyl) methyl-2-amino-3-phenylpropanoate	

Most biodegradable polyurethane is produced using conventional chain extenders like 1,2-ethylenediamine, 1,2-ethanediol, and BDO in PU formulations. The naturally occurring compound like putrescine (1,4-butanediamine) is also used as a chain extender to produce biodegradable PU due to its low toxicity. The amino acids based on chain extenders are used to increase the enzyme-mediated degradation of PU [9].

Table 4. Examples of chain extenders with degradable linkages to produce biodegradable polyurethanes

Chemical name	Chain extender structure
2-Amino-1-butanol (ABDO)	
1,2-Ethanediamine (ED)	
1,4-Butanediol (BDO)	
1,4-Butanediamine (BDA)	
1,4-cyclohexanedimethanol (CHDM)	
Ethylene glycol (EG)	

3.0 ENVIRONMENT DEGRADABILITY OF POLYURETHANES

The environmental degradability patterns of PU are differed due to their variety of properties like chemical composition and topology. According to the Kanavel et al. research, the sulfur-cured polyester and polyether PUs are exhibited some fungal inertness, nevertheless, fungal growth on the polyester PUs also observed due to the adverse effects of most fungicides on the formulations [13]. The environmental degradability also depends on the hard segment size, which was investigated by Santerre and Labow. Where the result showed the environmental degradability decreased with the increment of hard segment size restricted their polymer chain mobility and the environmental degradability [14]. In some important fields like medical fields are used PU elastomers as a substitution for other elastomers due to their resistant nature to humidity oxidation and tear, and higher toughness and elasticity. In those cases, those medical field PUs are more resistant to environmental degradability because of their resistance nature to hydrolysis, calcification and macromolecular oxidation. Those degradability problems have led the researchers to find that PU degradability by either biodegradable or chemically

degradable [2]. According to the Huang et al. research, the polyester PUs biodegradability is increasing via enhancing the chain length of the polyesters, where the polyester PUs are made using polycaprolactone diols to produce the biodegradable PUs in the medical field [15].

4.0 RECENT DEVELOPMENTS IN BIODEGRADABLE POLYURETHANE

Sneha et.al, synthesized novel bio-based polyol with excellent purity from corn oil and 2-mercaptoethanol by a single-step thiol-any reaction, that is being utilized as a polyol substitute for petroleum-based polyol in PU foams production [16]. Fig. 4 shows the synthesis of polyol from corn oil. The influence of varying amounts of dimethyl methyl phosphonate (DMMP) in the resulted foam formulation demonstrated that the incorporation of DMMP into the foams improved the overall char stability, where the closed-cell content is over 95% and a well-defined cellular structure is obtained in all the foams. Further, the results of the combustion test exhibited a significant decrease in the overall rate of heat release. However, this research discovered a method for producing industrially manufacturable stiff polyurethane foams using sustainable corn-oil polyol [16].

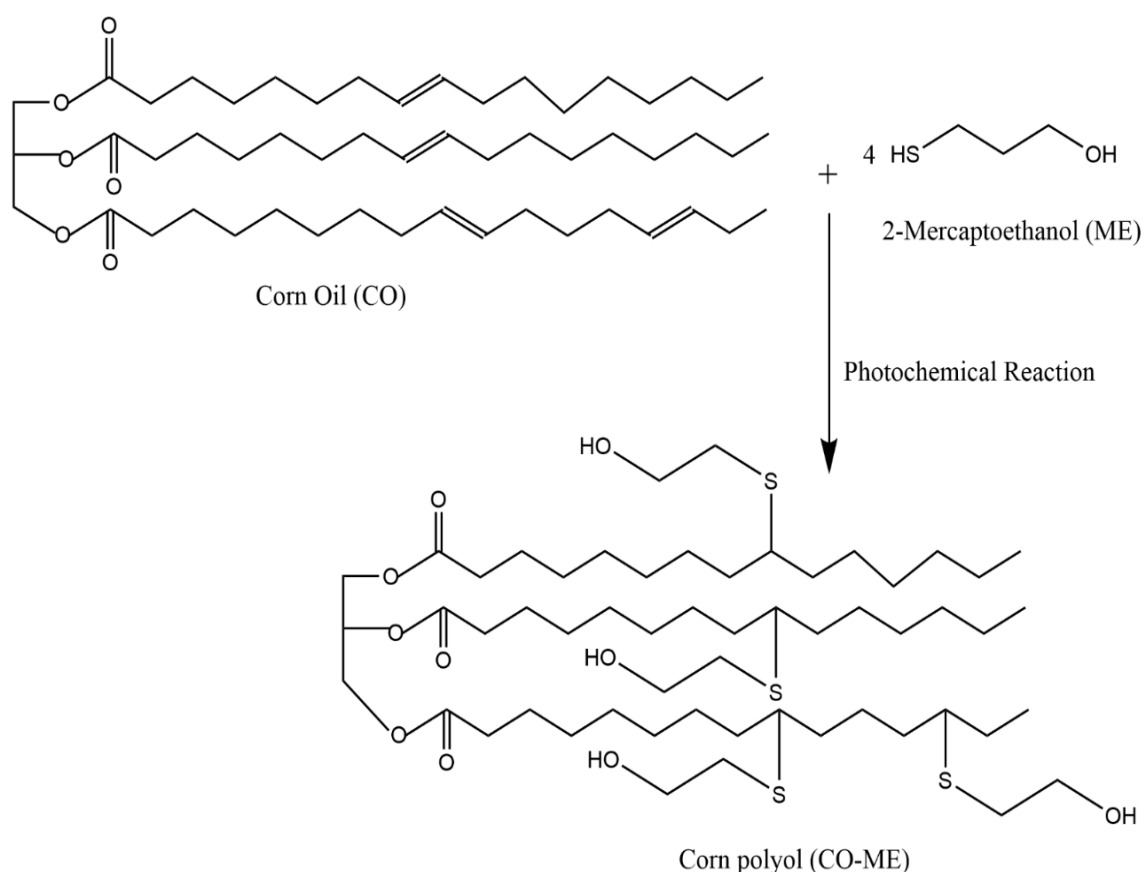


Fig. 4. Production of a polyol derived from corn oil

Camila et.al, created a sustainable stiff polyurethane foam with excellent thermal insulation using a renewable polyol derived from simple physical mixing of crude glycerol and purified castor oil, which could be used directly in polyurethane synthesized [17]. Fig. 5 shows the castor oil structure and glycerol molecules. The castor oil and crude glycerol binary mix with variable proportions were utilized to enhance the functionality of this bio polyol while obtained by physically combining raw ingredients and eliminating the extra costs of chemical modifications and pre-treatment. Where the mixtures were easily synthesized because three hydroxyl groups and a short chain characterize crude glycerol and better miscibility in the castor oil. When a chemical blowing agent (water) was used instead of physical blowing agents (cyclopentane and n-pentane), the foam produced had bigger cells. Also, thermal conductivity, density, young's modulus, and compressive strength all reduced as the water content in the material increased while producing the higher CO₂ for the development of bigger cells. The foam formulations with higher amounts of catalyst slightly enhanced the thermal conductivity, young's modulus, compressive strength, and decreased density values. This bio foams

development is simple, sustainable, inexpensive, and environmentally friendly products with commercial applications that are simple to produce while reducing the fuel prices and this can help the biodiesel sector make a profit [17].

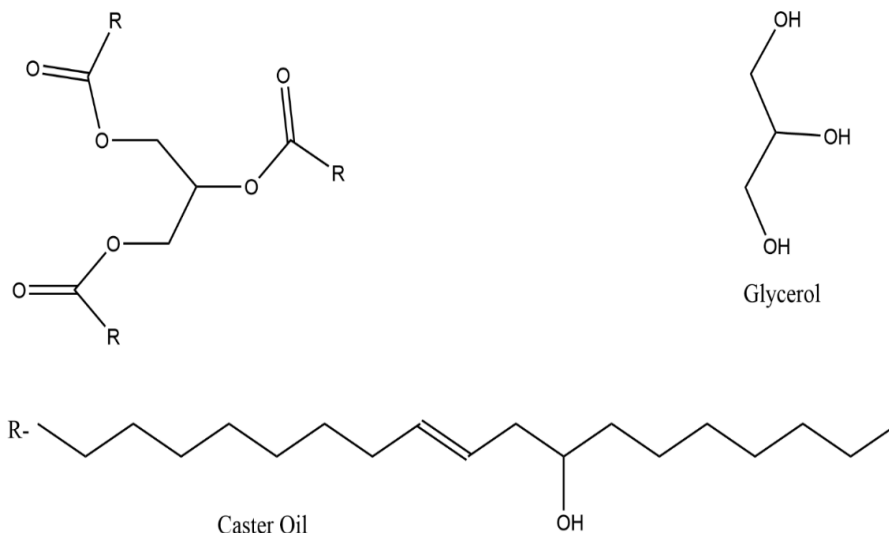


Fig. 5. Structure of the castor oil (ricin oleic acid is the main component) and glycerol molecules.

Ravindra et.al, demonstrated the possibility to produce bio-renewable adhesive from bio-renewable sources that can replace the PU adhesive and relies on petrochemicals to minimize environmental impact and cost while enhancing the availability and biodegradability [8]. Fig. 6 demonstrates the vegetable-oil-based polyol manufacturing technique. Bio-renewable and eco-friendly adhesive production from vegetable oils like jatropha, castor, soybean, and palm, starch derived from potatoes, lactic acid, and alternative green energy resources, which are known as manufacturing "greener" PU adhesives. Ravindra et.al also demonstrated the properties and possibilities of Lignin-polyurethane-based biodegradable foam. Lignin is a renewable biomaterial, cost-effective, easily available, and widespread in plants, which is available in the paper industry and the pulping industry's black liquor. Lignin was utilized mainly in the production of high fungal degradable PU foams, PU elastomers, and wood adhesives. Due to its low toxicity and biodegradability, lignin could improve the qualities of PU, such as compression performance, heat resistance, superior mechanical, and ageing resistance. Where the PU materials could be easily produced at a lignin concentration is low, whereas the PU materials could be difficult to produce at a high concentration of lignin concentration [8].

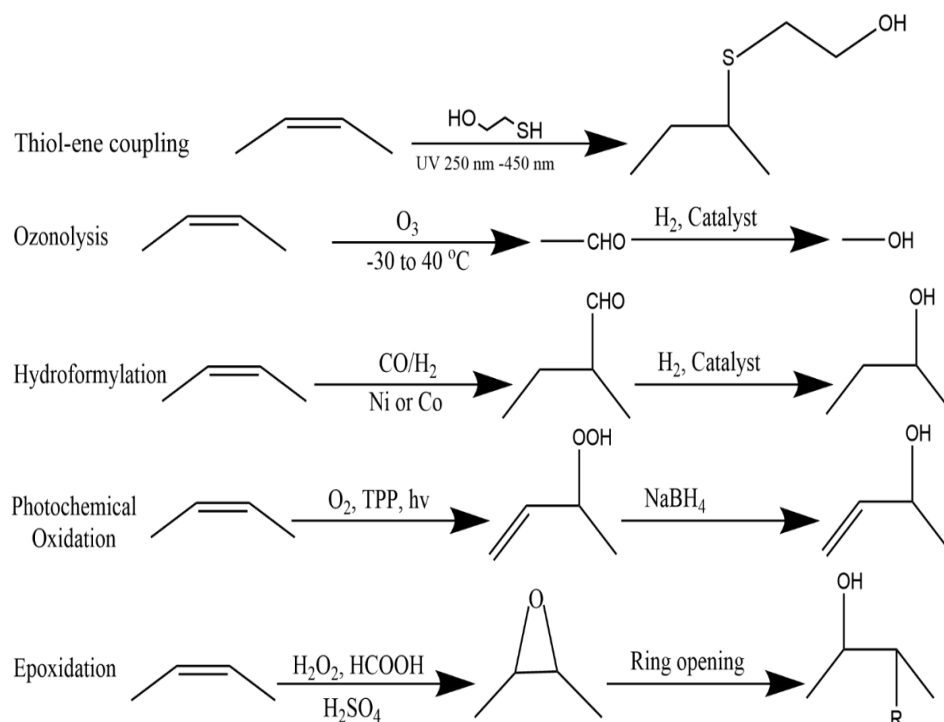


Fig. 6. Vegetable-oil-based polyol production

Mikelis Kirpluks et.al, demonstrated the creation of PU foam using various bio-based raw ingredients such as tall oil (TO) and rapeseed oil (RO) as renewable polyols or hydroxyl derivatives from vegetable oil and other natural oils [5]. Fig. 7 is shown the basic structure of TO components, where, transesterification with polyfunctional alcohols and epoxidation, followed by oxirane ring-opening, create polyols and rigid PU foams from TO and RO. TO consists of a combination of fatty and rosin acids which can be customized as available and cheap raw materials rather than competing with food production. That is obtained as a result of the processing of forest biomass and a by-product of cellulose production, which is not an agricultural product. Two or more hydroxyl groups should be introduced into TO and RO by chemical modification to utilize as a source of PU raw materials. RO has been utilized as the second renewable material feedstock [5].

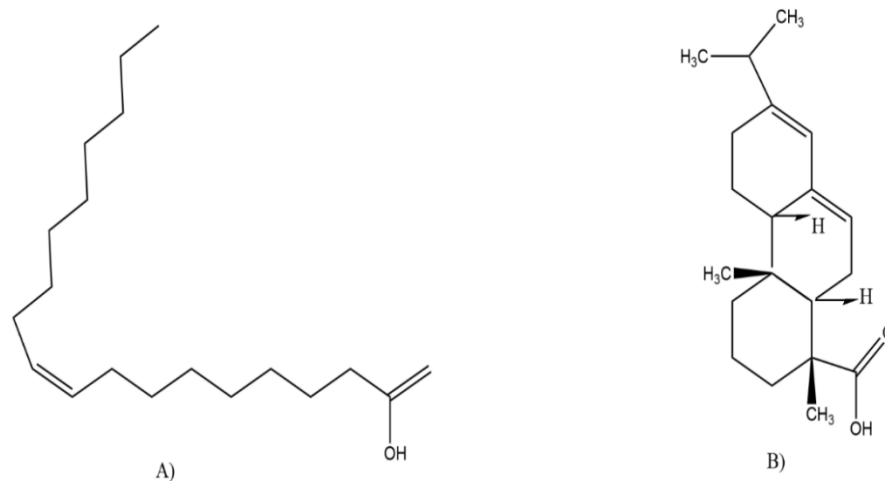


Fig. 7. TO components' basic structure: (A) fatty acid (oleic acid) and (B) rosin acid (abietic acid)

Yanhong Hu et.al, investigated a novel polyol type from rapeseed oil for the production of rigid PU foam [18]. Fig. 8 describes the chemistry of hydroxylation of the double bond in rapeseed oil. The hydroxylation of the double bonds and alcoholysis of the hydroxylated rapeseed oil was used to make the polyol. Where the double bonds found in the long chains of rapeseed oil's unsaturated aliphatic hydrocarbon were hydroxylated with peroxy acid and the alcoholysis of the hydroxylated rapeseed oil with triethanolamine enhanced the product's hydroxyl value. The production of fine chemicals was done due to the free availability of rapeseed oil, and the potential for functionalization. It was found that after hydroxylation of the double bonds and alcoholysis of the hydroxylated rapeseed oil, the polyol based on rapeseed oil might be used as one of the raw materials in the production of stiff PU foams [18].

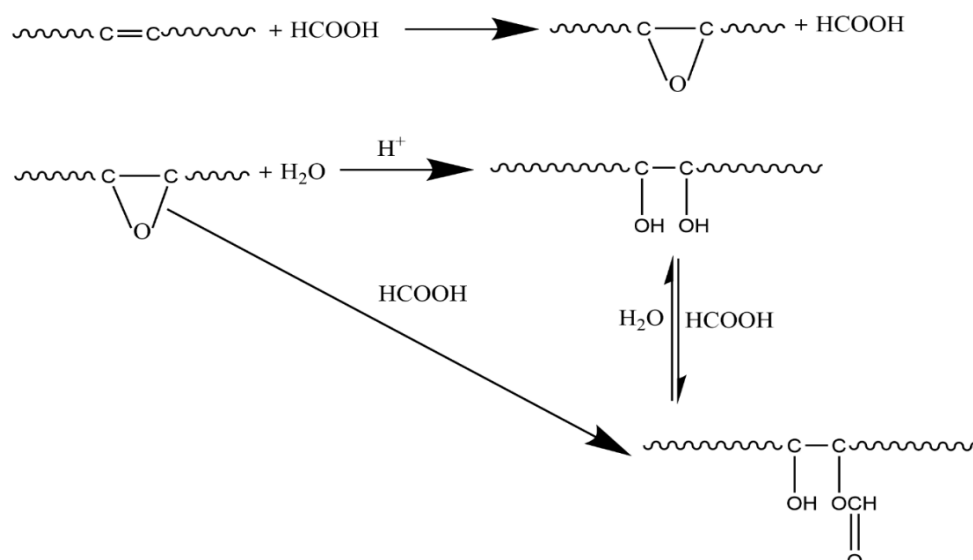


Fig. 8. Hydroxylation of the double bond in rape seed oil

Novel bio-based polyurethanes were developed using cyclocarbonated broccoli seed oil and various di- or triamines by Patrick Loulergue et.al. [7]. Fig. 9 shows the PU synthesis from broccoli oil. The long-chain fatty acids are abundant in broccoli seed oil, particularly erucic acid, and also have four unsaturations available in its chemical structure to further chemical modification. This isocyanate-free strategy to create the carbamate group in polyhydroxy urethane is an efficient method to synthesize non-isocyanate PUs, which are not harmful to the environment and are not hazardous to humans. Different amines and/or carbonate to amine ratios provide different effects showing the possibilities for PU manufacturing with mechanical qualities that can be adjusted. The tensile strength was between 0.46 and 0.71 MPa as a result, young's modulus was in the range of 0.50 to 1.15 MPa, elongation at break was observed and between 85 percent and 272 percent. Further, the glass transition temperatures (T_g) of various PU samples ranged from 15 to 23 degrees Celsius, that were depending on the type of amine and the amine to carbonate ratios [7].

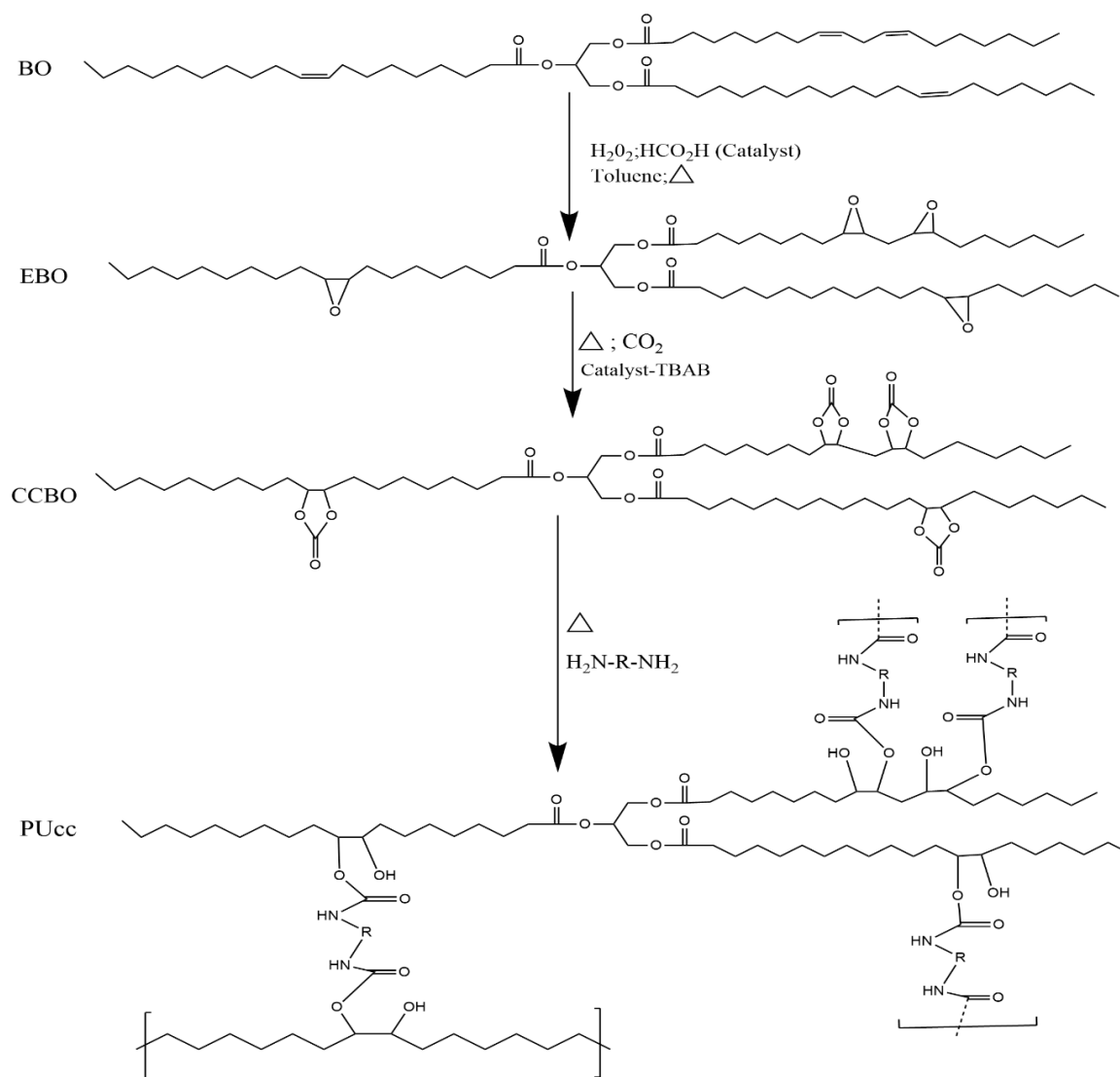


Fig. 9. PUcc synthesis from broccoli oil

Zoran S Petrovi et.al studied the soy-based polyols' structural heterogeneity and its impact on polyol and PU properties [19]. Soybean oil structure is shown in the Fig. 10. It was found that polyols with various hydroxyl numbers were created via formic acid, hydroxyls are hydroformylation and partially esterified. The polyols and diphenylmethane diisocyanate were permitted to react to produce various crosslinking densities of PUs. The weight average functionality of most polyols was between 5 and 2.5, resulting in gel points ranging from 53 to 83 percent conversion. The mechanical properties of rubbery polyurethanes were negatively affected by the heterogeneity of polyols and this must be careful during the polyol design for flexible applications [19].

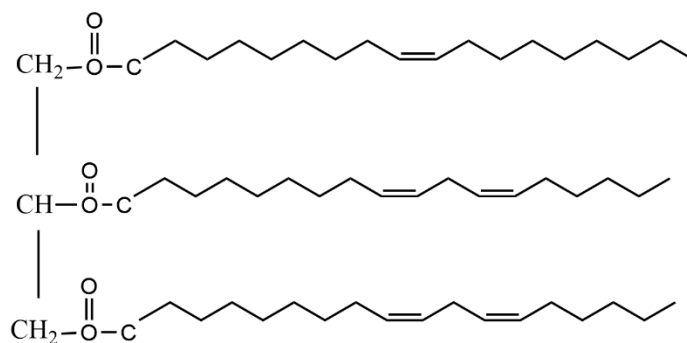


Fig. 14. soybean oil structure

Paweena Ekkaphan et.al has investigated the preparation of water-blown rigid polyurethane (PUR) foams by utilizing sesame seed oil and pumpkin seed oil-derived polyols via hydroxylation and alcoholysis reaction [20]. The bio polyols react with manufactured polymeric methylene diphenyl diisocyanate (PMDI) was used to produce PUR foams blown with water N, and N-dimethyl cyclohexylamine (DMCHA) was used as silicone surfactant and catalysts. This investigation showed that the OH number of the resultant polyols is in the range of 340–351 mg KOH/g. These PUR foams have a compressive strength of 237.7–240.2 kPa and a density of 40–45 kg/m³ and exhibited satisfactory mechanical and thermal performance. However, the result was exhibited that, these bio-based polyols could be utilized as a substitute for PUR. From the detailed experimental data, obtained RPUR foams showed behaviors similar to commercial foams in terms of potential and economics as a renewable resource [20].

L. B. Tavares et.al researched the production of polyols made from recycled industrial waste like lignin as a substitute renewable natural source for petroleum-based polymers [21]. Fig. 11 shows the castor oil modification reaction. Numerous PU-type compounds have been created by combining technical Kraft lignin (TKL) with castor oil (CO) or modified castor oil (MCO1 and MCO2) to increase reactivity towards diphenylmethane diisocyanate (MDI). The findings demonstrate that lignin increases crosslinking density, glass transition temperature, and ultimate stress, especially in MCO₂ and 30 percent lignin content samples, which increased from 8.2 MPa to 23.5 MPa. According to the results of this research, different technical grade Kraft lignin content could be exhibiting the ability to create PU type products with a vast variety of mechanical properties, from big elastic or low Young modulus PU to brittle or high Young modulus PUs, by combining an industrially low-cost, commonly available waste with

a non-edible renewable source oil, which properties can make it suitable for the replacement of petroleum-based PU on several applications [21].

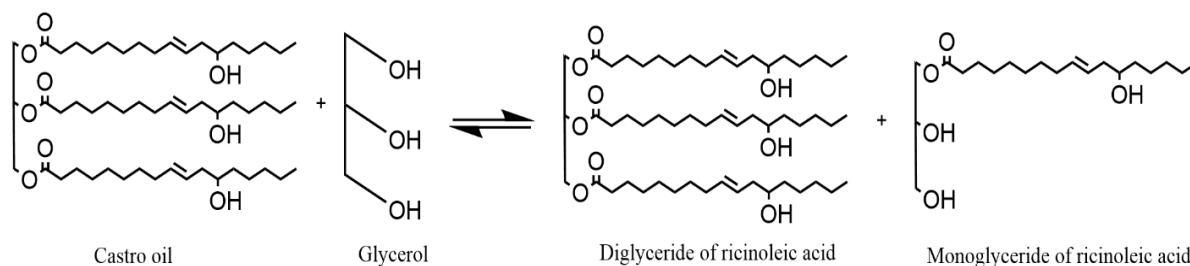


Fig. 15. castor oil modification reaction

Castor oil, poly(ethylene glycol) (PEG) or macro glycol poly(ϵ -caprolactone)diol, and diphenylmethane diisocyanate, with or without a chain extender, were explored in a variety of castor oil modified hyperbranched PUs by Niranjana Karak et al. The degree of branching of the polymers varied from 0.7 to 0.8 measured by their respective using model chemicals to create H-NMR spectra. The thermal degradation and crystallization of the hyperbranched polymers could have been influenced by the content of the hard segment, the composition of the polymers, and the nature of the macro glycol. The results of DB values exhibited that they are dendritic polyurethanes with a lot of branches. Further, the materials developed can also be used in shape-memory techniques. due to the good crystallization behavior of the macro glycols [22].

For the production of bio-based PUs, a novel polyol mixture containing epoxidized soybean oil (ESO) and isopropanolamine was developed by Shida Miao et al. [23]. The chemical method for generating PU networks from epoxidized soybean oil (ESO) and isopropanolamine is shown in Fig. 12. The hydroxyl number of the produced polyol mixture was 317.0 mg KOH/g. Synthesized polyol containing 1,6-diisocyanatohexane was combined with a varied amount of 1,3-propanediol (PDO) as a chain extender and allowed to cure to produce a series of PUs. The results of tensile tests showed the range from 2.74 to 27.76 MPa in the PUs' yield strengths, which depend on the content of PDO. All of the PU samples had a glass transition temperature between 24.4 and 28.7 degrees Celsius. The results of the thermogravimetric analysis exhibited; that the polyurethanes began to degrade thermally at 240–255 degrees Celsius. However, because of its simple preparation technique and renewable feature, bio-based polyurethane could have a wide range of uses [23].

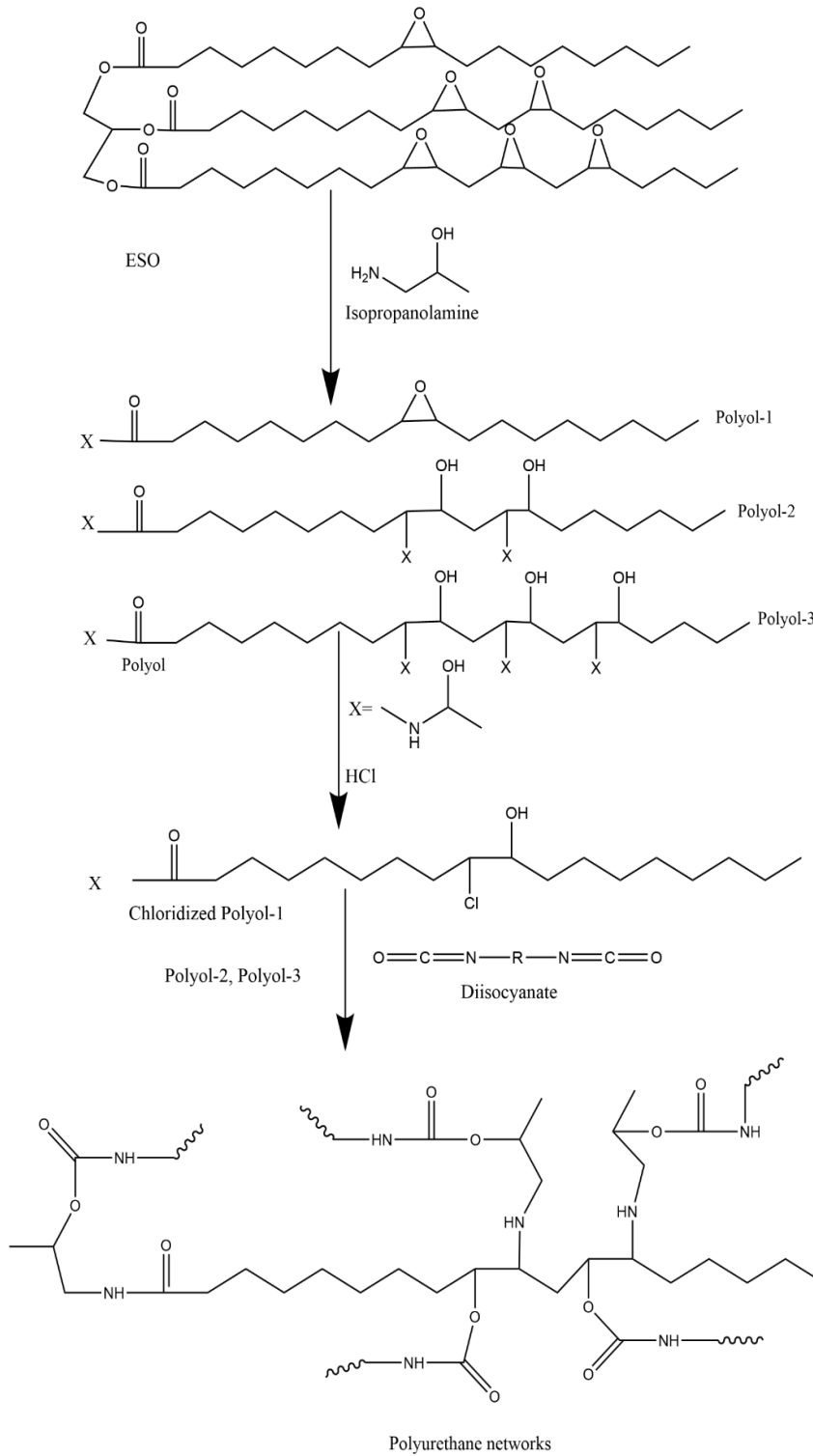


Fig. 17. Reaction pathway for polyurethane networks made from epoxidized soybean oil (ESO) and isopropanol-amine

Maria Oliviero et.al, demonstrated that a novel succinic acid-based bio polyol was used as a substitute for a conventional synthetic polyol in several polyurethane foam's compositions [24]. Where, the foam properties, on bio-succinic polyol replacement PU the effects of water

content and carbon black addition were examined. The findings revealed that increments in the interconnectivity and the addition of bio-succinic polyol modified the mechanical properties of foam shape substantially. Carbon black (CB) changed the shape of the cells and increased the foam density. The addition of CB and water also created bio-based PU foams with superior morphology and physical qualities using this technology. The partial replacement of synthetic polyol with natural polyol improved the compressive performance of the foams. The polymer chains were stiffened by the ester linkages of the "green" polyol more than polyurethane with conventional polyol due to the more rigid chemical structure. The addition of bio-succinic polyol improved the sound absorption capacity of the foams in the high-frequency band (1000–6000 Hz) by increasing airflow resistivity via the existence of tiny cavities with a higher number of interconnecting pores. These produced bio-foams could be used as potential substitutes for conventional flexible polyurethane foams to reduce noise pollution, and vibrations while enhancing the comfort of automobile and aircraft industries because of the unique combination of mechanical and acoustic qualities. However, it was found that ideal combination of BP, CB, and water might produce long-lasting PU foams with desirable qualities [24].

Chaoqun Zhang et.al, worked on bio-based polyols preparation using canola, linseed, castor oil, olive, and grape seed via solvent/catalyst-free, a novel synthetic method [25]. Fig. 13 exhibits the preparation of vegetable oil-based polyol. Where the biobased triglyceride oils were first oxidized into epoxidized vegetable oils with hydrogen peroxide and formic acid, then ring-opened with castor oil fatty acid. It was shown that the polyols from castor oil had the highest minimum OH values, whereas the polyols from olive oil had the lowest. Cross-linking densities, young's modulus, tensile strength, and Tg values of PUs all increased as OH numbers of polyols increased. Because of the difference in cross-linking densities, Rr reduced from olive castor polyol-based PUs (98.19%) to canola castor polyol-based PUs (78.97%) [25].

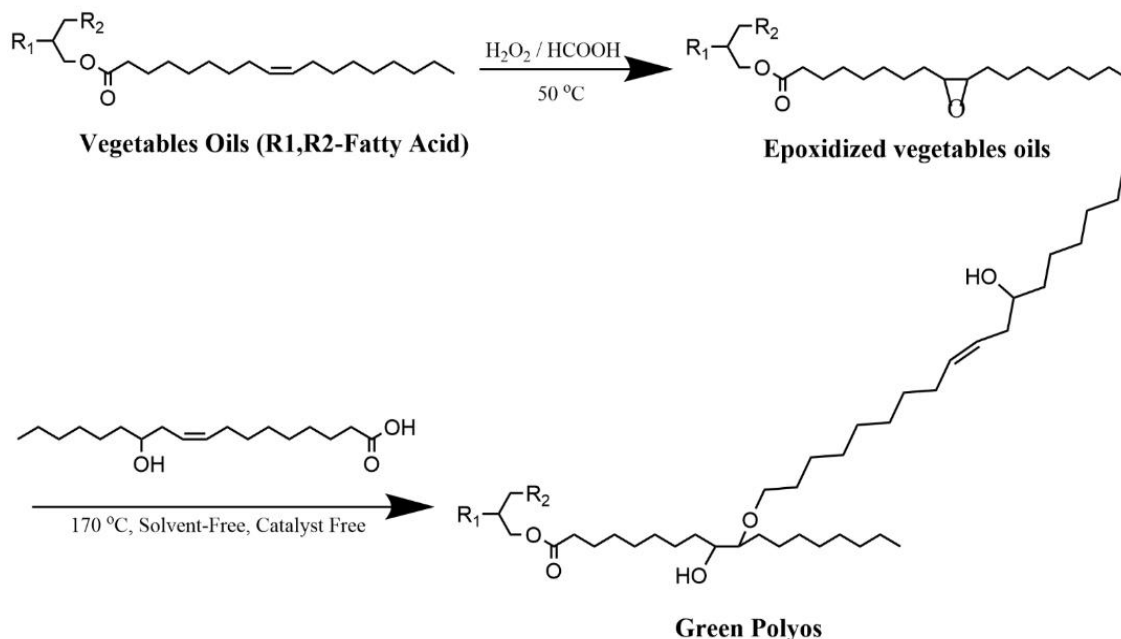


Fig. 19. Preparation of vegetable oil-based polyol

The characteristics of polyurethane foams (PUF), made with crude glycerol (CG) and polyethene glycol (PEG)-based sawdust liquefaction were investigated by Nahid Rastegarfar et.al. The liquefaction solvent was polyols with varied weight loadings of PEG to CG, which were used to test the various forms of foam. PU foams with compressive strengths ranging from 200 to 311 kPa, thermal conductivity of 0.031 to 0.040 W/m K, and densities ranging from 0.042 to 0.08 g/cm³ were produced. It was discovered that foams with a more homogeneous and regular cell structure exist in CG/PEG-based liquefaction than in CG liquefaction. When PEG to CG was increased in liquefaction, the closed-cell concentration of foams increased and cell size decreased. However, all tested foams exhibited similar thermal degradation curves and the weight ratio of PEG to CG is greater in liquefaction, showed the maximum thermal decomposition temperature. PU foams made with a PEG/CG based liquefaction technique have better qualities than foams made using CG liquefaction of sawdust. Hence, foams made from bio polyols were proved to have the same behavior as petrochemical polyols and could be used as a replacement in similar usages [26].

Li HongWei et.al, researched the extraction of bio-oil as a bio-polyol with a hydroxyl number of 77.8 mgKOH/g was used to make bio-based flexible PU foams, with the crude bio-oil coming from quick pyrolysis of wheat straw extracted with ethyl acetate [27]. The extracted bio-polyol has a higher number of molecules having numerous hydroxyl groups than the crude

bio-oil. The resulting foam from 30 wt.% bio-polyol, 22.1 wt.% PMDI, 17.9wt.% PM200 and 0.5 wt.% crosslinking agent exhibited 37.0% of resilience that was thermally stable up to 200 °C under the optimized conditions. Also, in the optimal condition, the BPU foam exhibited 80.0 kPa of tensile strength, which is somewhat lower than the 85.0 kPa reference foam strength. Although, the tensile strength and resilience values of the bio-based PU foams with a 30–50% bio-polyol tear strength ratings and the substitution ratio were both lower than those of the reference PU foam exhibited greater value than the reference foam. However, the prepared BPU foams could be utilized as flexible foams in various applications such as cushioning material in automobile industry [27].

Kattimuttathu et.al, researched on a new biobased polyols production by using cardanol, which is a renewable resource, and it is a byproduct in cashew processing industry [28]. It contains phenolic molecule with a 15-carbon side chain at meta position and various levels of unsaturation. Fig. 15 is described the processing diagram and Fig. 16 is shown the structure of cardanol. PU foams were obtained by oxidizing sidechain unsaturation with hydrogen peroxide, an environmentally friendly reagent. The foaming characteristics exhibited that these polyols were effectively used in the production of rigid PU foam with excellent mechanical and physical properties. The viscoelastic characteristics, density, compressive strength, and morphology of the prepared foams exhibited better properties than standard petroleum-based polyols. The SEM showed the uniform cell structure morphology in prepared modified cardanol polyol [28].

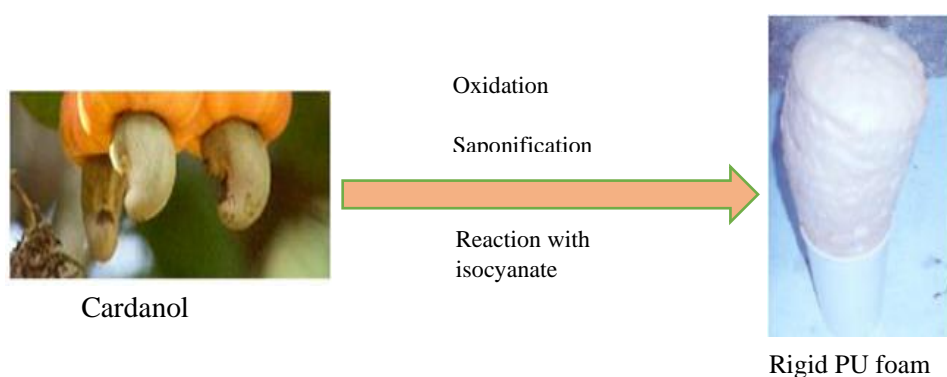


Fig. 21. Processing diagram of cardanol to rigid PU foam

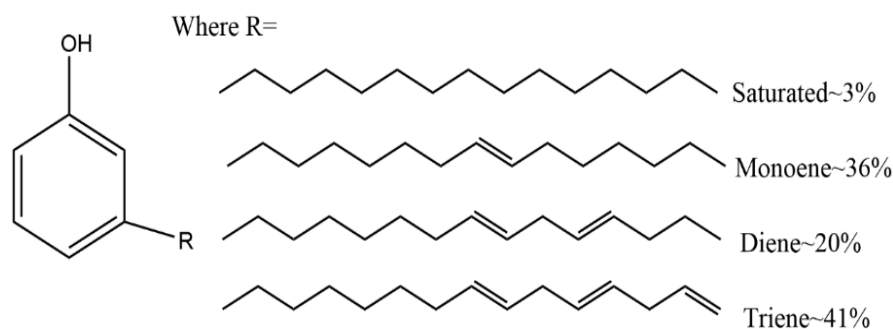


Fig. 23. Structure of cardanol

Polyol from soybean oil by using a continuous micro-flow system was carried out by Dong Ji et.al [29]. The commercially available epoxidized soybean oil was used for comparison purposes. The prepared polyol showed a higher hydroxyl number, narrow molecular weight distribution, and lower viscosity than commercially available epoxidized soybean oil due to their more substantial oligomers by oligomerization. Although, the polyurethane rigid foams from prepared polyols had a fine, homogeneous, and closed-cell morphology and had higher crosslinking because of their decreased viscosity and higher hydroxyl number, which properties also benefit thermal insulation, higher Tg, compression strength, thermostability, and dimensional stability. The micro-flow technology offers numerous benefits in the production of high-quality polyol [29].

As soft segments, hydroxyl telechelic oligomers from natural rubber (HTNR), polycaprolactone diol (PCL), and waste tire crumbs (HTWT) were used to make a bio-based PU foam (PUF) by Suwat Rattanapan [4]. The foam production rate was higher when the PCL diol content was increased due to the faster reaction nature of PCL diol. Although the density of foam varied somewhat depending on the molar ratio, all samples had similar specific tensile strengths. The growing contents of the PCL diol level enhanced the average diameter of the cell. Elongation at break and compressive strength are also reduced when the PCL diol was added. The HTNR-based foams exhibited almost polyhedral closed cells. PUF samples exhibited ~ a 7-11% of biodegradation percentage and 33 days of the induction time. The molar ratio of HTWT/PCL had a significant impact on the kinetic rate of foam production and the morphology of the foam. The thermal degradation temperature of the PUF was increased by the addition of the PCL diol. However, the thermal degradation temperature and biodegradation parameters of HTNR-based PUF were lower than those of HTWT-based foams [4].

Then, biodegradable PU foam from liquefied wastepaper (WP), in the presence of poly-hydric alcohols was studied. The liquefied-WP-based polyol was suited to prepare the biodegradable polyurethane foam because of its apparent molecular weight, viscosity, and hydroxyl value, it can be used to make hard PU foam with the right foaming agents such as liquid wood and starch-based polyols. Produced foams obtained suitable densities and mechanical characteristics. At initial weight loss, the created foams demonstrated the same thermal stability that was exhibited the leaf mold can biodegrade to some extent, with no carcinogens or mutagens in the water extracts of the foams [30].

Using different levels of lignin (8.33-37.19 percent w/w) in the production of lignin-based rigid polyurethane foam (LRPF) was investigated as a replacement for petroleum-based polyol (ref). Different weight ratios (1, 2, and 5 wt percent) of pulp fiber were used to strengthen the LRPF with 37.19 percent lignin where the pulp fiber-reinforced bio foams exhibited the larger regular cells and the foam density is lower due to the pulp fibers in the bio-foam. which are a benefit to the thermal conductivity and higher heat transferability of PU foam than smaller cells in PU foam. The compressive strength of the LRPF was reduced as the lignin content increased, but the addition of pulp fiber didn't affect the compressive strength. However, the combination of lignin and pulp fiber in bio-foam production is an economical and green way to use the most abundant natural biopolymers [1].

Fabrication of viscoelastic bio-based polyurethane foams (PUFs) with polyols derived from acid liquefaction of coffee grounds wastes as the polyol component was done. The influence of four isocyanate concentrations on hydroxyl numbers (0.6, 0.7, and 0.8), as well as three different catalyst percentages (3, 5, and 7%) on the polymerization reaction, was examined. Prepared foams exhibited very interesting mechanical properties due to their viscoelastic behavior. Due to its thermal stability nature, the prepared foam exhibited suitability in heat insulation applications where the damping properties could be enhancing the value of this prepared foam [31].

Mechanical and thermal properties of novel bio-based polyurethane (PU) nanocomposites films made from PU based on PCL, which was designed as a soft segment, and isophorone diisocyanate (IPDI)-butane diol 1.4 (BDO1.4), which was designed as a hard segment, as well as cellulose nanofiller derived from the rachis of the date palm tree where the cellulose nanofibrils (CNFs) and cellulose nanocrystals are utilized as nanofibers (CNCs). In comparison to tidy PU, bio nanocomposites showed tremendous mechanical characteristics. When

comparing both nanofillers, the nanocomposites based on CNF showed a greater improvement in mechanical and thermal properties, which might be explained by CNF's higher aspect ratio as well as greater dispersion in the PU matrix [3].

The PU industry and other sectors within the polymer industry have witnessed a surge in the development of biodegradable, eco-friendly, and non-toxic polymers in recent years. This growth is fueled by the notable advantages these materials possess over synthetic polymers, notably their capacity to decompose in the environment into harmless substances [32, 33].

5.0 APPLICATIONS OF BIODEGRADABLE POLYURETHANES

Biodegradable polyurethane finds application in various industries due to its environmentally friendly nature. Some notable applications are biodegradable polyurethane can be used in the production of eco-friendly packaging materials, reducing the environmental impact of disposable packaging. The textile and fashion industries can benefit from biodegradable polyurethane in creating sustainable and biodegradable fabrics, coatings, and accessories. Biodegradable polyurethane films are employed in agriculture for mulching and as protective covers for crops. These films break down naturally, minimizing environmental pollution. The production of sustainable and biodegradable footwear components, such as soles and insoles, is another application area for biodegradable polyurethane in the fashion and footwear industries. Biodegradable polyurethane can be incorporated into automotive interiors, such as seat cushions and interior components, providing an environmentally friendly alternative in the automotive sector. It can be also used in construction for manufacturing sustainable and biodegradable insulation materials, coatings, and sealants. The electronics industry can utilize biodegradable polyurethane for certain components, reducing the environmental impact of electronic waste. Also, it can be employed in the production of eco-friendly toys and sporting goods, ensuring that these products have a reduced environmental footprint. Some personal care items, such as biodegradable sponges and applicators, can incorporate biodegradable polyurethane as an environmentally conscious alternative.

The biodegradable polyurethanes are used in the therapies and tissue-engineered products due to their controlled biodegradation in in-vivo environments and improved biocompatibility nature, whereas PU is used to fabricate scaffolds into tissue engineering applications because of their ability to tailor physiochemical, mechanical and biological properties of PU. Scaffolds

are made from biodegradable PU with good tensile strength, elasticity, and biocompatibility for cardiovascular tissue engineering. The biodegradable polyurethanes are also used in musculoskeletal applications, where utilized in the fabrication of scaffolds to help the regeneration of bone and cartilage. Nowadays, the knee-joint meniscus also uses biodegradable scaffolds, which are fabricated with biodegradable polyurethanes. The biodegradable PU is being used in the fabrication of nerve regeneration scaffolds to transfer either growth factors generating cells or growth factors for peripheral nerve healing. The liquid two-part urethane system is used to react and mix under mild conditions, which system is particularly useful for applications to deliver growth factors or other promoters to enhance cell growth, such as bone void fillers bone cement, and orthopedic fracture fixation. PUR scaffolds also provide cell-friendly nature for the proliferation and growth of various cell types like fibroblasts, smooth muscle cells, osteoblasts, stem cells, chondrocytes, and endothelial cells [9]. The applications of biodegradable polyurethane are diverse and continually expanding as industries seek more sustainable and eco-friendly materials for their products.

6.0 CONCLUSION

Understanding the raw materials of biodegradable polyurethane is crucial for several reasons, as it plays a significant role in the development, production, and environmental impact of this material. Knowledge of raw materials helps assess the overall environmental impact of biodegradable polyurethane. Understanding the source, extraction process, and biodegradability of raw materials contributes to determining the ecological footprint of the entire production process. Also, identifying sustainable and renewable raw materials is essential for the development of environmentally friendly biodegradable polyurethane. Utilizing bio-based feedstocks reduces dependence on fossil fuels and supports the transition towards more sustainable materials.

Different raw materials can influence the biodegradability and decomposition rates of biodegradable polyurethane. Understanding these aspects helps in predicting how the material will behave in various environmental conditions and ensures it aligns with the goal of reducing environmental impact. The properties of biodegradable polyurethane, such as mechanical strength, flexibility, and thermal stability, are influenced by the choice of raw materials. Understanding these relationships is crucial for tailoring the material to specific applications and ensuring it meets performance requirements.

Understanding the raw materials is essential for compliance with regulations and standards related to environmental protection and product safety. This knowledge helps in ensuring that the production and use of biodegradable polyurethane meet legal requirements.

Conducting a comprehensive life cycle assessment (LCA) involves evaluating the environmental impact of a product from raw material extraction to end-of-life. Knowledge of raw materials is critical for accurate LCA studies, enabling a thorough understanding of the overall sustainability of biodegradable polyurethane. Again, understanding raw materials fosters innovation in the development of new biodegradable polyurethane formulations. Researchers and manufacturers can explore alternative raw materials to improve performance, reduce costs, and enhance the environmental profile of the material.

A thorough understanding of raw materials contributes to building a resilient and sustainable supply chain. Awareness of potential shortages, price fluctuations, or environmental risks associated with raw materials allows for proactive planning and risk mitigation.

In summary, understanding the raw materials of biodegradable polyurethane is essential for achieving a balance between performance, environmental sustainability, and regulatory compliance. This knowledge supports the development of materials that contribute positively to the circular economy and reduce the environmental impact of traditional polyurethane products. This overview of raw materials used in the production of biodegradable polyurethane provides valuable insights for researchers, industries, and policymakers. As the demand for sustainable materials continues to rise, the exploration and development of bio-based and biodegradable polyurethanes represent a promising avenue for addressing environmental concerns and creating more eco-friendly products.

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