



Bio-Based Polyurethane Coatings: Pioneering Efficient and Eco-Friendly Solutions for Sustainable Applications

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Received:07 Aug 2024; Revised:25 Aug 2024; Accepted: 15 Sep 2024; Available online: 10 Oct 2024

Abstract: Bio-based polyurethane (PU) coatings are more sustainable compared with petroleum-based PU coatings because they can address the public concerns about the use of renewable resources and environmental impact. This review overviews the different categories of bio-based PU coatings: water-borne, solvent-less, powder, UV-curable, and hybrid coatings based on vegetable oils, lignocellulosic biomass, and carbohydrates. The development of these coatings is further characterized by good environmental performance in terms of volatile organic compound content (VOC) emissions and energy intensity and good performance in terms of durability, chemical resistance, and flexibility. However, there are some barriers involved in the commercial scale of bio-based PU coatings, such as cost and performance, but they remain very promising in the development of sustainable coating, therefore showing a way forward in the application of environmentally sustainable coatings from industrial applications.

Keywords: *Bio-based isocyanates; Bio-based polyols; Bio-based PU; Coatings; Polyurethane; Sustainable;*

1. INTRODUCTION

Polyurethanes are a class of polymers that have been used in a wide variety of applications, such as foams, coatings, adhesives, sealants, and elastomers [1], [2], [3]. Polyurethane (PU) coatings have long been a staple in various industries, known for their excellent mechanical properties, chemical resistance, and versatility [4]. PUs contain multiple urethane bonds ($-NHCOO-$). They are generally produced by polyaddition reactions between polyols and diisocyanate or polyisocyanate [5] (Fig. 01). Traditionally derived from petroleum-based polyols and isocyanates. These coatings have been widely used in automotive, construction, packaging, and many other applications [5]. However, the increasing awareness of environmental issues and the urgent need to reduce reliance on fossil fuels have driven the search for more sustainable alternatives [6].

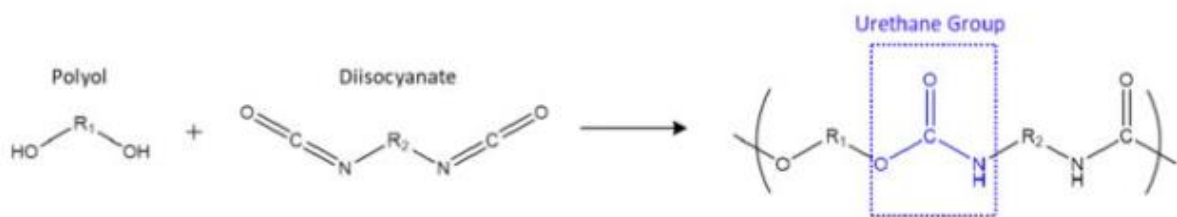


Fig. 01- Polyaddition reaction between polyol and isocyanate [7].

In response to these challenges, bio-based polyurethane coatings have emerged as a promising solution, which are formulated using polyols derived from renewable biological sources, such as plant oils, lignocellulosic biomass, and microbial fermentation [6], [8]. By replacing petroleum-based components with bio-based materials, these innovative coatings offer a way to reduce the carbon footprint and enhance the sustainability of industrial processes [6]. Bio-based polyurethane coatings not only help in reducing environmental impact but also often provide additional benefits, such as biodegradability, low toxicity, and lower volatile organic compound (VOC) emissions [9]. Despite these advantages, the transition to bio-based PU coatings is not without its challenges. Technical issues related to the performance and durability of these coatings, economic factors such as the cost of raw materials, and scalability concerns all play a significant role in their broader adoption. Previous reviews have already summarized the production of biodegradable polyurethane; however, this review primarily focuses on coatings made from bio-based polyurethane. By concentrating on bio-based PU coatings, this review highlights their unique properties, applications, and potential to contribute to the growing demand for sustainable and environmentally friendly materials.

This review article aims to explore bio-based polyurethane coatings by discussing their development, raw materials, synthesis methods, and performance characteristics. It also examines their diverse applications across various industries and highlights their environmental benefits.

2. RAW MATERIALS OF BIO-BASED POLYURETHANE COATINGS

Compared to conventional petroleum-based PUs, bio-based PUs are synthesized from renewable sources such as plant oils. Most of the principal raw materials employed in the manufacture of diisocyanates are derived from petroleum and its derivatives [10]. Thus, aliphatic diisocyanates from dimerized fatty acid which is originated from renewable resources are possible; and currently, there are already commercialized products available in the market. However, these polyurethanes can only be used as coatings and are not suitable for foam applications [11], [12]. On the other hand, the polyol component in some applications can be derived using renewable raw materials to make it bio-sourced [9].

2.1 Sources of bio-based polyols

Bio-based polyols are essential in the synthesis of bio-based PU coatings because they are one of the main raw materials required in the formation of Bio-PU. These polyols are obtained using renewable sources such as vegetable oils and biomass [8], [13], [14]. They have similar structures and properties. Therefore, the bio-polyols can be drop-in replacements for existing polyols. The renewable content of commercially available bio-polyols varies from 30% to 100%. It depends on the preferred building blocks and their origin. Consequently, the renewable content of polyurethane based on different formulations also varies substantially among various products and applications, with a range of 8–70% [15].

2.1.1 Vegetable oil-derived polyols

Vegetable oils are increasingly essential as renewable resources for producing polyols in the biopolyurethane industry. Castor oil is one of the first bio-polyols used for the synthesis of bio-based waterborne polyurethane (WPU) in wood coating applications [16]. Depending on the origin and type of fatty acids in plant oil such as soybean oil (Fig. 02–(a)), sunflower oil (Fig. 02–(b)), linseed oil (Fig. 02–(c)), canola oil (Fig. 02–(d)), and castor oil (Fig. 02–(e)), the fatty acid side chains contain carbon numbers ranging from 8 to 24, and carbon-carbon double bond numbers from 0 to 6 [17]. And also, certain fatty acid has specific functional groups. Vegetable oil-derived polyols show narrow molecular weight distributions with low Polydispersive index values <1.1 [18], [19]. The following table (Table 01) presents some primary sources of bio-based polyols used in synthesizing bio-based PU coatings and their characteristics.

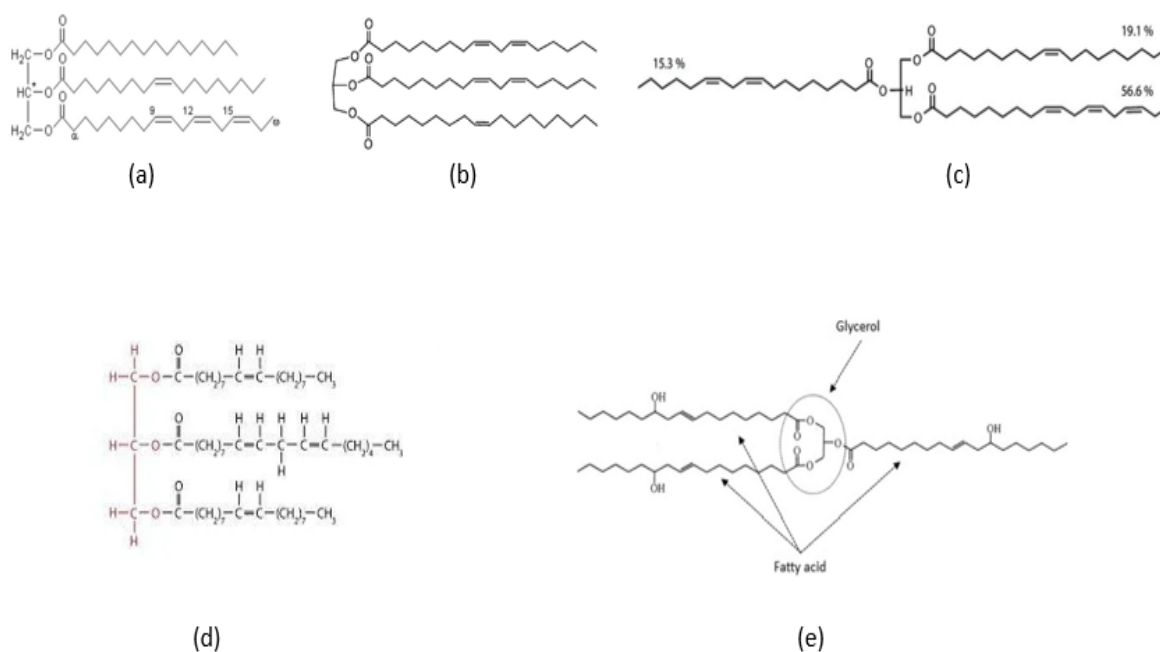


Fig. 02. Chemical structure of (a) soybean oil [17], (b) sunflower oil [20], (c) linseed oil [21], (d) canola oil [22], (e) castor oil [23].

Table 01 – Source, Characteristics, and Applications of Vegetable oil derived polyol

| Vegetable oil | Source | Characteristics | Applications | Ref. |
|----------------------|---|--|--|------------|
| Soybean oil | Soybeans (<i>Glycine max</i>) | Renewable, abundant, and cost-effective. Modified to enhance hydroxyl content for PU ^a production. | Flexible coatings, foams, and adhesives | [24], [25] |
| Linseed oil | Seeds of the flax plant (<i>Linum usitatissimum</i>) | Lacking hydroxyl (OH) groups, it is unable to react with diisocyanate. Therefore, transesterification of LO ^b with glyceride (GL) was required to obtain OH-containing LOG ^c . Good drying properties. Provides excellent adhesion and mechanical strength. Main fatty acid component is linolenic acid 53.2%. | Protective coatings (wood coatings), varnishes, and paints. | [26] |
| Canola oil | Seeds of the canola plant (<i>Brassica napus</i>) | High degree of monounsaturated fatty acids and very low in saturated fatty acids. Consists of approximately 60% oleic acid. | High solid PU coatings, adhesives, and elastomers. | [27], [28] |
| Castor oil | Bean of the castor plant (<i>Ricinus communis</i>) | Non-toxic, biodegradable, renewable resource. High hydroxyl content, making it highly reactive in PU formulations. Ricinoleic acid comprises approximately 92–95% of the fatty acid composition, which provides flexibility and good mechanical properties to the resulting Pus. | Coatings for automotive (anticorrosive), self-healing coating, construction, and industrial applications where flexibility, water resistance, and durability are required. | [29], [30] |
| Sunflower oil | Seeds of the sunflower plant (<i>Helianthus annus L.</i>) | Contains around 85% unsaturated and 15% saturated fatty acid, with 44–75% linoleic acids and 14–43% oleic acid content. It provides good flexibility and compatibility in PU formulations. | Coatings, adhesives, and foams where a balance of flexibility and mechanical properties is desired. | [31], [32] |

^a- Polyurethane (PU)

^b-Linseed oil (LO)

^c-linseed oil glyceride (LOG)

2.1.2 Polyols from liquefied lignocellulosic biomass

Wood derived from plants is the most significant source of the lignocellulosic biomass. This biomass is containing three main components, 30–35% of cellulose, 15–35% hemicellulose, and 20–35% lignin. Lignin, in particular, is rich in aromatic structures, making it an excellent candidate for producing aromatic polyols [33], [34], [35]. This biomass, through the liquefaction process, can be transformed to valuable aromatic polyols which has several desirable characteristics in the formation of PU. In liquefaction of lignocellulosic biomass, the complex molecular structure is broken down into smaller, reactive components. It takes place under rather severe conditions of temperature 130 °C and 180 °C, and pressure and reagents employed include solvents (phenol, polyhydric alcohols), and catalysts [35], [36], [37].

2.2 Bio-Based di/poly(isocyanate)

Bio-based di/poly isocyanates are an important component of forming bio-polyurethane coatings. These isocyanates are derived from renewable biological sources such as amino acids, furan derivatives, carbohydrates, lignin-based aromatics, cashew nutshell liquid, and vegetable oils.

2.2.1 Amino acid-based isocyanate

L-lysine is an amino acid derived from biomass. These amino acids have been used as a starting material to synthesize methyl or ethyl esters of L-lysine diisocyanate (MELDI or EELDI), respectively [38], [39]. The chemical structure of L-lysine Diisocyanate (LDI) is shown in Fig. 03. LDI leads to the formation of polyurethanes with an amorphous nature because it has an asymmetric aliphatic structure [40]. Therefore, LDI also produces low glass transition temperatures (T_g) hard segments compared with T_g of other aromatic diisocyanate-based hard segments [41].

LDI especially presents the advantage of low vapor pressure relative to aromatic polyisocyanates. Considering the inhalation toxicity of many isocyanates (petroleum-based), the low vapor pressure of LDI presents significant handling and processing advantages [42].

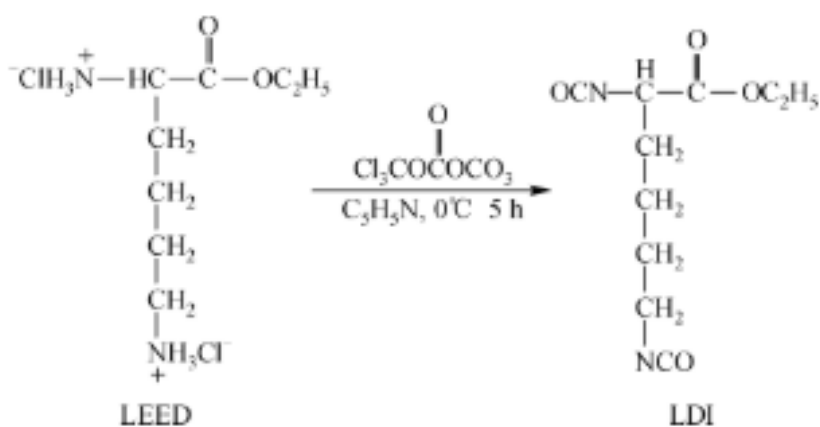


Fig. 03. Synthesis of LDI. Adapted from [43]

2.2.2 Sugar-based diisocyanates

Penta methylene diisocyanate (PDI) is obtained from fermentative lysine (sugar), and it is also an aliphatic diisocyanate [44]. PDI is the first bio-based diisocyanate [45]. The synthesis of PDI is shown in Fig. 04. PDI-based PU coatings present a low drying time [44]. PID-based PU coatings indicate good mechanical properties and better weather properties [44].

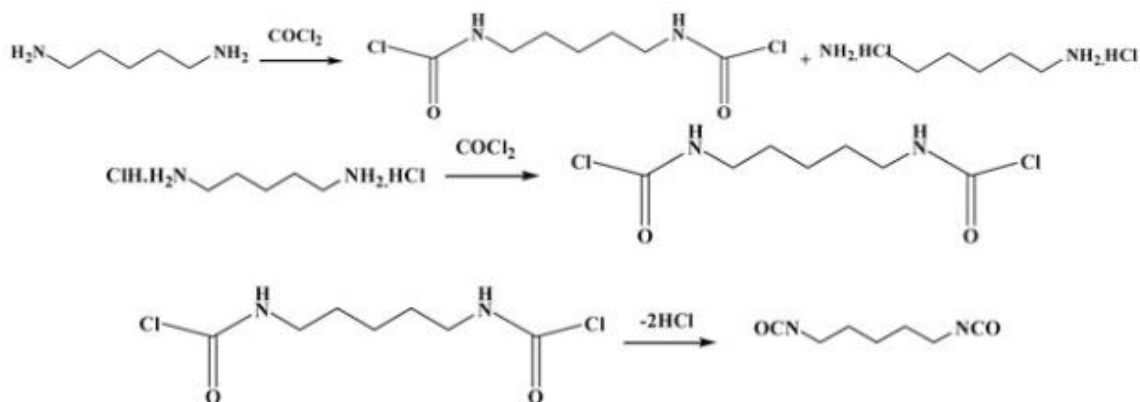


Fig. 04. Synthesis of pentamethylene diisocyanate groups by bio-based pentanediamine [46].

2.2.3 Furan-based diisocyanates

Oats and corn husks are rich in cellulose and hemicellulose, which makes them good sources for producing furan and its derivative [47]. Significantly, all furan-based diisocyanates are liquids that are relatively stable in the pure state at around 0°C [48]. Furan-based diisocyanates are produced by the conversion of furfural by chemical reactions in which isocyanate groups are incorporated [47]. Furfural is first transformed into furfuryl alcohol, and the latter can be further functionalized to form the required diisocyanate moiety [48]. This process enables the generation of diisocyanates with furan rings, which is advantageous in that furan rings have an aromatic character and impart mechanical properties and stability to the polymer in its final application [47].

2.2.4 Vegetable oil-based diisocyanates

Recently, bio-derived diisocyanates based on vegetable oil have emerged as potential substitutes for the conventional petrochemical-derived diisocyanates used in polyurethanes. Vegetable oils and their derived fatty acids are important raw materials for the synthesis of bio-based isocyanate [13]. Some of these diisocyanates are produced by modification from bio-renewable feedstocks, including soybean, castor, and linseed oils, which, after undergoing chemical transformations which, involve the conversion of the double bonds in fatty acids to isocyanate groups [40]. This approach provides the extra advantage of making the process friendly to the natural environment by using the renewable triglycerides that are naturally found in vegetable oils, hence being less dependent on nonrenewable fossil resources [45]. The obtained polyurethanes are also more biodegradable than conventional ones, while the final product properties can be controlled based on the type of vegetable oil used. This makes them suitable for a number of uses,

particularly in areas where environmental impacts have been of paramount importance, including in applications such as coatings, adhesives, and foams [44]. Nonetheless, the problems of improving production costs and increasing performance continue to exist, so future research in this sphere is actively being developed to expose the potential of vegetable oil-based diisocyanates in industries.

3. SYNTHESIS OF BIO-BASED POLYURETHANE COATINGS

The synthesis of bio-based PU coating involves the incorporation of renewable materials, especially bio-based polyols and isocyanates. These components combine and produce PU coatings, that are environment-friendly and highly efficient. The process generally proceeds as a step as in the traditional PU synthesis, but the inputs used are bio-based to improve sustainability.

3.1 Chemical pathways for producing bio-based polyols

The preparation of bio-based polyols involves various pathways. Such as epoxidation/oxirane ring-opening, transesterification/transamidation, polycondensation, hydroformylation, ozonolysis, and metathesis [49].

3.1.1 Epoxidation/oxirane ring-opening

Epoxidation is the process of introduction of an oxygen atom in the double bonds in the unsaturated fatty acid to form an oxirane ring [50], [51], [52]. This reaction is usually done in the presence of peracids or hydrogen peroxide, which are strong oxidizers. Other examples of oxidizing agents are peracids like peracetic or performic acids and hydrogen peroxide [53], [54], together with formic acid to form peracids. The peracid or hydrogen peroxide thereafter attacks the carbon-carbon double bond to form a new epoxide ring. This process can also be catalyzed to enhance selectivity and efficiency [55], [56], [57]. For example, the epoxidation of vegetable oil can be represented by the Fig. 05 (a).

The final step of the process involves the ring-opening of the epoxide rings with the purpose of adding hydroxyl groups to the epoxidized oil in order to obtain polyols. This step can be achieved with many kinds of nucleophiles like alcohols, acids, or water, depending on the properties of the future polyol. Some well-known nucleophiles are alcohols like methanol, ethanol, formic and acetic acids, and water with catalysts. The nucleophile also attacks the less hindered carbon of the epoxide ring, leading to the formation of the (–OH) group [58], [59], [60]. These reactions can be accelerated by other reactions, such as acids or bases, to increase the rates of reaction and determine the kinds of products produced [61], [62], [63]. For instance, the ring opening of epoxidized vegetable oil with methanol can be described in the following Fig. 05 (b) Hussain et al. [64]. Synthesized polyurethane coatings from epoxidized soybean oil (ESBO). The Soy-polyol was synthesized by the alcoholysis of ESBO with glycerol, and the PU coatings containing different molar ratios of isocyanate were prepared. From the PU coatings prepared, an increase in the molar ratio of the hardener was observed, which depicted an increase in the gel content and hardness of the PU coatings.

3.1.2 Transesterification/ Transamidation

It is considerable, however, that both transesterification and transamidation reactions make use of the ester groups contained in the molecules of vegetable oils to form polyols. The polyols that are obtained from vegetable oils through transesterification with glycerol are a blend of monoglycerides, diglycerides, and

triglycerides of unsaturated fatty acids [65]. Among these parts, monoglycerides that have two hydroxyl radicals per molecule are widely used in the production of polyurethanes. Pre-polymer is synthesized from diols such as monoglycerides and diisocyanates to make polyurethane. The obtained unsaturated pre-polymers are cross-linked by radical polymerization of the double bonds in a cross-linked network. It is applied in the production of urethane alkyd coatings. Because fatty acid portions dominate the formation of the triglycerides, in the ratio of about 9:1, it follows that most of the physical-chemical properties stem from the various fatty acids that are esterified with glycerol [66], [67]. The reaction of transesterification is shown in Fig.05 (c).

Similar to the transesterification process, transamidation with amines, especially with diethanolamine can transfer vegetable oils, such as linseed, soybean, rapeseed, and sunflower oils to ethanol fatty-acid amid for use in polyurethane products. Ethanolamines are basically bifunctional compounds and enhance the mutual solubility of many polyols with the required physical-mechanical properties of polyurethane. The reaction of transamidation is shown in Fig. 05 (d).

You will also see different reactions of double bonds applied for the conversion of an unsaturated triglyceride of vegetable oils for preparing polyols. The four widely applied reactions are (i) epoxidation, (ii) ozonolysis, (iii) hydroformylation, and (iv) metathesis [17].

3.1.3. Hydroformylation/reduction

Another important pathway to produce vegetable oil-based polyols involves hydroformylation followed by hydrogenation. The hydro- formylation of vegetable oils (Fig. 05 (e)) where refers to the change of carbon-carbon double bonds in the fatty acid chains to aldehydes within the range of 70 to 130 °C utilizing rhodium or cobalt catalyst and syngas (a combination of H₂ and CO) and afterward the hydrogenation of aldehyde for primary hydroxyl groups [68]. Regarding the hydroformylation, the hydroxyl functionality of the vegetable oil-based polyol depends on the number of unsaturation that are available in the vegetable oil. Out of all the mentioned oils, linseed and soybean oils are said to be mainly used as the first feed material, but other common oils include sunflower oils [69]. The hydroformylation path-way provides a polyol with primary hydroxyl functions copious to the functions in the isocyanate and was ranked distinctly superior to the epoxide ring-opening/methanolysis path-way in this respect [70]. Thus, the cross-linking density, the glass transition temperature, and the mechanical properties of the obtained polyurethanes depend mainly on the hydroxyl functionality of polyol and the nature of isocyanates. Hence, hydroformylated polyols have higher curing ability and, thus, lower gel time during reaction with isocyanates for polyurethanes than epoxidized polyols [71]. For the enhancement of the property of polyols, other structural changes that were studied included methanolysis and polycondensation to derive hyperbranched polyols with high functionalities, molecular weights, and triols with high molecular weights as well [72]. In this context, it has been elucidated that the hydroxyl functionality distribution of hydroformylated polyester polyols is responsible for the negative effect on the properties of waterborne PU coatings. Although all the polyols gave good films, polyols of intermediate functionality distribution gave the best combination of flexibility, abrasion resistance, and hardness without the decrease in smoothness that was observed when the broad functionality polyols were used [73]. Dow Chemical Co bio-based RENUVATM polyols derived from soybean oil are also in use as monomers in coating, adhesive, sealing, flexible foam, and elastomer.

3.1.4 Thiol-ene coupling

Thiol-ene chemistry is applied widely for many types of coatings due to its versatility and comparatively low temperatures for curing. There are several advantages of using thiols to break up carbon-carbon double bonds instead of the more commonly used acrylate system, such as reduced oxygen sensitivity, slower gelation, and lower levels of shrinkage stress [74]. Thiol-ene coupling is a one-step reaction with the chain mechanism in which the double bonds of unsaturated fatty acids react with thiols such as (2-mercapto ethanol), (3-mercapto propionate), and glyceryl di mercapto acetate and produces primary hydroxyl groups (Fig. 05 (f)). Among the various polymerizations, thiol-ene is preferred because it has a photoreaction and a high reaction rate with high conversion. Thermally initiated thiol-ene coupling was slower than the UV-initiated thiol-ene coupling [75]. Caillol et al. synthesized soybean oil-based polyols [76]. A few UV-curable, thiol-ene coatings systems with castor oil as the base have been synthesized. Black and Rawlins synthesize thiol-ene UV-curable coatings from the vinyl ether derivatives of castor oil and allyl, acrylate, and combinations of multifunctional thiols. The factors such as auto-oxidation of the double bond residue of triglycerides were useful in enhancing the cross-link density of the PU coating which in turn enhanced chemical resistance, hardness, and solvent resistance [77]. Based on the cardanol, Wang et al. synthesized a cardanol-based polyol with higher numbers of hydroxyl groups by thiol-ene coupling and then prepared polyurethane materials with higher tensile strength, elastic modulus, and hardness [74]. Also, cardanol-based polyurethane has higher thermal stability than commercial polyols due to the absence of phenolic hydroxyl converted to aliphatic hydroxyl. Another useful strategy was developed by Fu et al. [78]. Castor oil-based undecylenic acid was transformed into a diisocyanate by Curtius rearrangement of thiol-ene coupling 3-mercaptopropionic acid. The prepared diisocyanate was used in the preparation of waterborne polyurethane dispersions. The polyurethane coatings derived from the thiol-ene coupling reaction xerographic had high gloss and good adhesion on the metal surface. Also, the fatty acid chains from vegetable oils were effective in the enhancement of coating flexibility, and the values of tensile strength, tensile modulus, and chemical resistance were low.

3.1.5 Ozonolysis/reduction

The preparation of polyol from vegetable oils through ozonolysis usually has two steps, as illustrated in Fig. 05 (g). The process includes the formation of ozonide at the carbon-carbon double bonds of vegetable oils and, in the subsequent steps, the reduction of an aldehyde into polyols with the help of the Raney nickel catalyst [79]. The sodium borohydride reduction of ozonide in solvents like dichloromethane methanol directly gives the primary alcohol. Narine et al. described the catalytic synthesis of polyols from unsaturated canola oil through the process of ozonolysis and hydro-generation reactions [80]. As a result, the fatty acid composition of vegetable oils brought about the ozonolysis of polyols and accumulated constitution of mono, diol, and triols with triglyceride structures and saturated triglycerides [79]. The dismantling by the ozonolysis process was able to halve every fatty acid chain. It prevented the formation of dangling chains from being incorporated into the polyurethane, as it tends to act as a plasticizer to the material. Having thus described the ozonolysis-based polyols, it would be seen that polyols based on ozonolysis cure much faster than isocyanates. The polyols formed from the ozonolysis process have 30-40% lower molecular weight compared to the earlier processes involving the carbon-carbon double bonds (hydroformylation/reduction and epoxidation/oxirane ring-opening), and the material has a low viscosity

which melts. Polyols via ozonolysis-based have also been synthesized through hydrogenation-free one-pot synthesis. In general, polyols like glycerol and ethylene glycol react with vegetable oil in the presence of a catalyst (e.g., calcium carbonate and sodium hydroxide) to form a mixture of primary and secondary alcohols, respectively [81]. The ozonides obtained from the ozonolysis of vegetable oil and reaction with ethylene glycol's hydroxyl moieties, resulting in ester linkages and terminal hydroxyl, are shown in Fig 06. For the low VOC polyurethane coatings from soybean oil glyceride polyols, Benecke et al. used one-step ozonolysis with glycerol that proved to have excellent gloss, hardness as well as adhesion properties to a metal substrate [82].

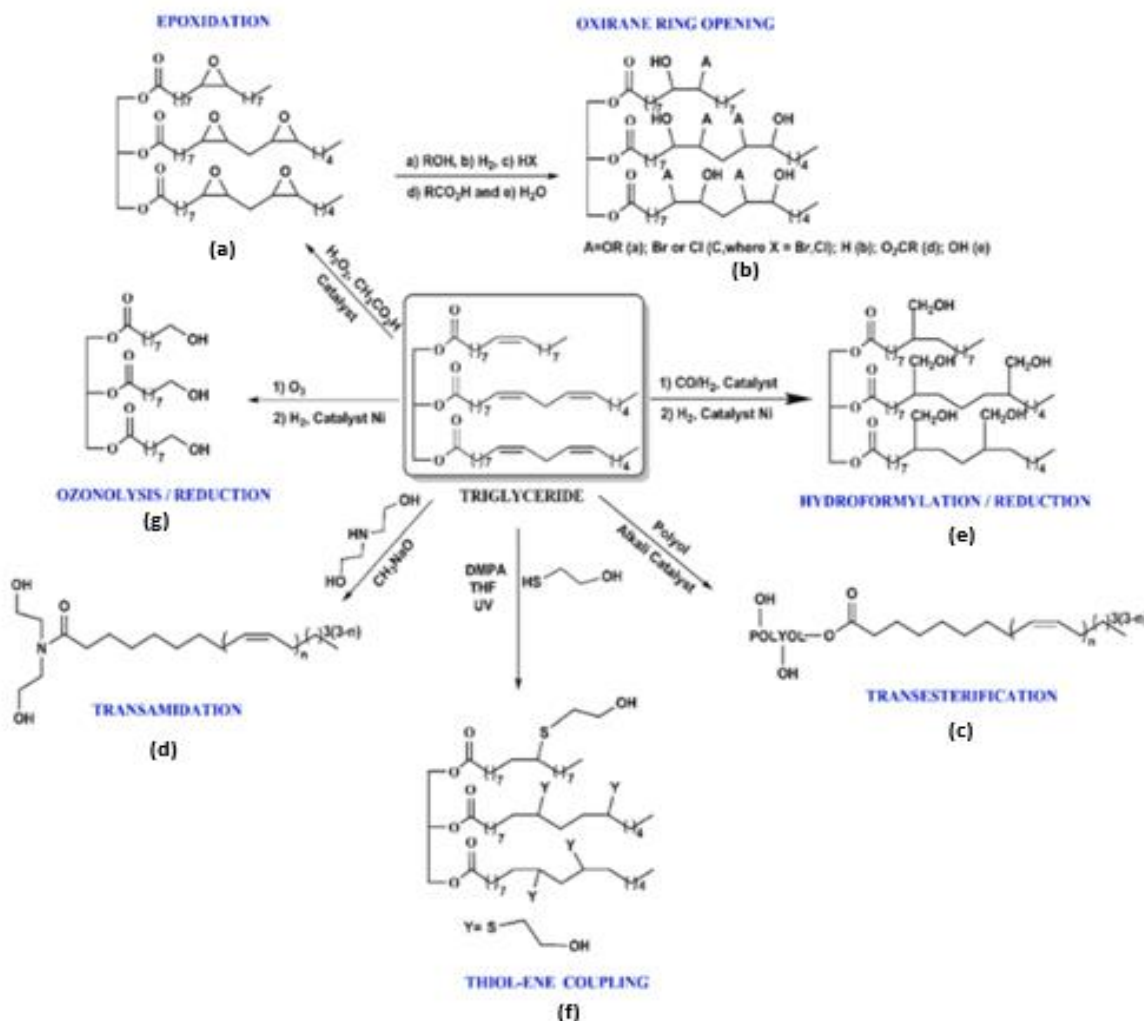


Fig. 05 (a) Epoxidation reaction of Jatropha oil, (b) Ring-opening reaction, (c) Reaction of Transesterification, (d) Reaction of Transamidation, (e) Hydroformylation/reduction, (f) Thiol-ene coupling (g) Ozonolysis/reduction[13].

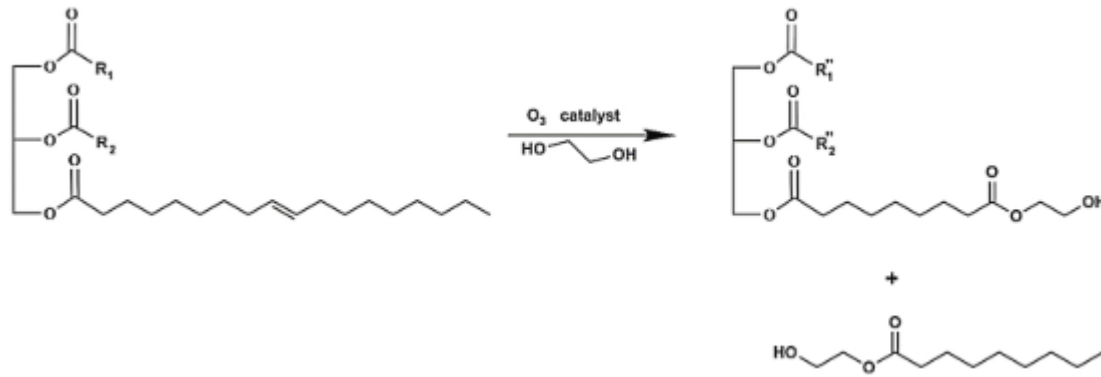


Fig. 06. Ozonolysis route with the reaction of ethylene glycol (R₁ and R₂ are fatty acid chains of vegetable oil, R₁, and R₂ are modified fatty acid chains of vegetable oil [13].

4. TYPES OF BIO-BASED POLYURETHANE COATINGS

Bio-based polyurethane (PU) coatings are divided according to the type of bio-based polyols and isocyanates that are being used for the preparation of the coatings and the field of their application. These coatings are environmentally friendly in comparison with traditional PU coatings while maintaining high-performance parameters. The major categories of the bio-based PU coatings are:

4.1 Hyperbranched PU coatings

Dendritic polymers are classified into three major categories: dendrimers, hyperbranched polymers, and dendrigrafts. Consequently, hyperbranched polymers and dendrimers, due to their structural features like the high surface functionalities and no entanglement, are among the important classes of polymeric materials in the last few years. Besides, they have high reactivity, high solubility, low viscosity, and optimized degree of cross-linking. Nonetheless, these hyperbranched polymers are preferred dendrimers because of their one-step synthesis and the reduction in the number of steps of purification during the synthesis [83]. It is also observed that the hyper-branched structures exhibit better properties compared to the linear structures [84]. Raju et al. discussed the properties and features of hyperbranched polyols, polyesters, and polyurethanes [85].

Furthermore, Deka et al. have described vegetable oil-based hyperbranched PU coatings [86]. They first prepared vegetable oil-based monoglycerides and used a glycerol chain extender with poly (ϵ -caprolactone) diol to synthesize hyperbranched polyol which in turn they converted to hyperbranched polyurethanes with different segmental ratios. These segmental ratios significantly affected the coating performance, meaning thermal-mechanical and physical properties.

Vegetable oil also helped reduce the resin's viscosity and increase the hardness of the coatings; these coatings were well adhered to the substrate, flexible, and had good gloss [87]. Wei and co-workers have prepared waterborne hyperbranched polyurethane UV curable coating from hyperbranched polyester polyol which is synthesized from castor oil and 2,2-bis (hydroxymethyl) propionic acid [88]. Then, hyperbranched polyurethane acrylate emulsion using water as the dispersed phase was synthesized through the reaction of a hyperbranched polyester polyol with maleic anhydride and isocyanate-bearing semi-adduct (IPDI- HEA)

that taken at different molar ratio without the use of any emulsifying agent. The prepared coatings possessed high transparency, and the adhesion characteristics were also found to be very good. Further, high-performance surface coating material has also been synthesized using hyperbranched poly (ester amide) derived from castor oil, and the respective coating possessed improved thermal stability about the degree of branching. Also, there is the property of biodegradability as one of the green advantages in the advanced surface coating technology of types of hyperbranched poly (ester amide) [89]. Hyperbranched PU based on soy oil derived from thiol-ene reactions revealed significant transparency and strong tensile strength which brings the bio-based material to application in coating. Applying hyperbranched polyurethane and polystyrene bio-based polymers, Silica/Reduced Graphene Oxide (RGO) nanohybrid loading at level 0.01–0.1 wt% results in the formation of efficient anti-corrosive coating nanocomposites [90]. The set nanocomposite coating possessed a good degree of thermal stability, surface energy, and mechanical strength, even with a much lesser amount of nanohybrid loading overall.

4.2 Waterborne PU coatings

Conventional solvent-borne PUs possess some serious limitations, such as high VOC, toxicity, flammability, etc. [91]. These limitations can be effectively addressed by Waterborne PUs (WPU), which are binary colloidal systems where stabilizing groups containing PU particles are dispersed in a water medium. WPUs are generally synthesized from less toxic diisocyanate, polyol, and ion-generating dihydroxy acid like 2, 2-bis(hydroxymethyl) propionic acid [92]. The application of WPU varies from Wood coat, pigment, primer, paint, additive, sealant, thickener, dye for the textile, metal, fiber, eco-friendly adhesive for wooden and other substrates, etc. [93]. The natural vegetable oil triglyceride chains provide some challenges for the synthesis of WPUs, such as the hydrophobic nature of vegetable oil. Furthermore, this hydrophobic nature of vegetable oil improves the physical and chemical properties of WPUs with hydrolytic stability [94], [95].

For example, Fu et al. [96]. synthesized fully bio-based WPU dispersions from castor oil, and the optimization of the amphiphilic behavior was realized by the addition of a carboxylated castor oil-based chain extender. Other WPU dispersions in wood coatings were also studied by using rape-seed fatty acid methyl esters as raw material with special references to particle size and dispersion stability [97]. Furthermore, the rapeseed oil based WPU was prepared and investigated by Bullermann et al. [98] with emphasis given to the hydrophilic charges' degree of neutralization, which determines the polymer dispersibility. It was also possible to use Jatropha oil-based polyols in the synthesis of WPU intended for coating [99]. particle-size distribution and several mechanical and surface characteristics are connected with the degree of polyols –OH functionalization, with hard segment content and internal emulsifier content. Methoxylated epoxidized soybean oils can lead to stable water-dispersible cationic polyurethanes, according to it [100].

4.3 High solid PU coatings

The coating industry has recently shifted towards high-solids coatings because of concerns about environmental regulations. In general, high solids coatings contain higher amounts of solid paints (70-80 %) in paints and are low in VOC content as compared to conventional solvent-based coatings. At present, polyol-derived coatings are the highest solid coatings in the protective and marine coatings industry [101]. However, researchers are also working on 100% solids polyurethanes. High solids coatings have low

solvent outputs, narrow molecular weight range and other features similar to the traditional systems with improved properties and durability. Therefore, can be used in the coating industry. A better high-solids coating material should be capable of having satisfactory spray viscosity without having to affect the performance characteristics in one way or the other. Nonetheless, the main disadvantage of high solids coatings' viscosity and lower molecular weight is the coatings' drying behavior and low stability [102]. Compared to the polyols derived from other sources, the polyols derived from vegetable oil have relatively high (contents deleted).

Molecular mobility and carry pendant dangling chains for low modulus and low T_g . Kong et al. synthesized polyols by epoxidation/hydroxylation of vegetable oils (sunflower, camelina, linola flax, nulin flax, and canola) then esterification reactions with diols (1,3 propanediol and 1,2 propanediol). A polyol that is used to produce polyurethane coatings with high solids was obtained through the reaction of such polyols and isocyanate [103]. It was observed that all the polyurethane coatings had bio-based content of about 60%, and due to chemical interaction, the adhesion was good. Thus, low molecular weight, few pendant chains, and higher functionality also have a significant function in enhancing these coatings' characteristics. Likewise, the solvent-free strategy also enhanced the coating's hydrophobicity through the enhancement of the cross-linking density of the coating. Somani et al. synthesized the low-viscosity castor oil derivatives and formed high-solid PU coatings with the help of different aromatic and aliphatic isocyanates regarding flexibility and impact strength [49]. In the case of high-solids coating, one of the efficient and attractive techniques when implementing the coating system is the use of reactive diluents. Mehul M et al. have successfully synthesized soya-based novel polyester polyol by blending SOPEP with monoglyceride and enhanced the cross-linked density network structure of PU-coating to further improve the mechanical properties like hardness, impact, and adhesion for all PU-coating and satisfactory results for chemical properties and thermal analysis of all PU-coating have good thermal stability [104]. This PU-coating can cure at room temperature and during curing does not release any volatile compound; hence environmentally friendly. Therefore, it was employed in high-solid PU coatings. Moreover, Mannari et al. synthesized soy polyols for the two-part high-solids polyurethane coatings [105]. This research demonstrates that soybean oil-based phosphate ester polyols are capable of functioning as hydroxyl components and a reactive diluent for polyurethane coating systems.

4.4 UV curable PU coatings

Generally, conventional PU coatings are through thermal curing and polymerization with the use of catalysts and even solvents. Compared to thermal curing, UV curing technology is noted as 5E, which means Economical, Environmentally friendly, Efficient, Energy-saving, and Enabling; thus, the process is recognized as "clean and green" [106], [107]. Generally, UV-curing systems comprise three building blocks: It consists of i) Oligomer (mono or multifunctional acrylate terminated prepolymer), ii) Monomers (reactive diluents), and iii) Photoinitiators. To date, various kinds of additives are continually used in such systems [108], [109], [110]. The polyurethane acrylate (PUA) molecular chemical structure mainly includes the polyols chain, urethane segments, and the acrylate hydroxyalkyl ester segments. The acrylate functionality helps to bring about even more improved characteristics to the PU coating as compared to the conventional PU. Features like superb flexibility, and great tack on various surfaces (metal, wood, and plastic), which are exhibited by the PUA have placed this polymer at the forefront as a coating in the UV curable coatings industry [111]. Further, PUA-based UV curable coatings displayed properties like impact

resistance, abrasion resistance, transmittance and scratch resistance, and etc. [112]. Vegetable oil, in this case, is used as a feedstock together with oligomer and reactive diluents since vegetable oil contains functionalities like hydroxyl, unsaturation carboxyl, and epoxy functionality, thus making it suitable for numerous transformations [113], [114]. On types of polyols used, prior work had studies on vegetable oil-based PUA, which has been used in UV curing of coatings and coatings that showed good adherence to substrates, low volume shrinkage, high gloss, and hardness [115], [116], [117]. In addition, hydroxyl groups can be incorporated into vegetable oil via the proposed paths, and the synthesized polyol will react with diisocyanate and acrylate functionality mono, di, and tri towards the preparation of the PUA oligomer.

The reaction mechanism of Itaconic-based PUA is presented as follows in Fig 07. In the work of Bastürk et al. soybean oil-based methacrylate urethane acrylate oligomer was synthesized with a two-stage mechanism [118]. Firstly, maleinized soybean oil (MSO) monomer was synthesized through the reaction between methacrylates and soybean oil, and then the obtained MSO monomer reacted with isophorone diisocyanate to form an isocyanate-terminated oligomer. The second stage involved the preparation of isocyanate-terminated oligomer, which was then reacted with 2-hydroxy ethyl methacrylate (HEMA) to get methacrylated urethane acrylate. Thus, Liu et al. synthesized polyfunctional polyurethane acrylate from cardanol with polyfunctional acrylate precursor and prepared the coating obtained from the reaction of isophorone diisocyanate with pentaerythritol triacrylate, enhanced thermal and mechanical performance, good adhesion, and flexibility are observed [119]. Also, the unsaturation notification on vegetable oil contributes significantly to UV-curable cross-linking. Moreover, Su et al. also synthesized vegetable oil (grapeseed oil, canola oil, corn oil, rapeseed oil, peanut oil, olive oil, and palm oil) based on acrylate prepolymer by a one-step acrylation method [113]. They studied how variation in the contents of unsaturation influenced the grafting rate and the product's characteristics. It is emphasized that the investigation showed that the unsaturation in vegetable oil increased because of the increase in the extent of the reaction rate and the grafting number of products to improve the functionality and cross-linking density of UV-curable coating.

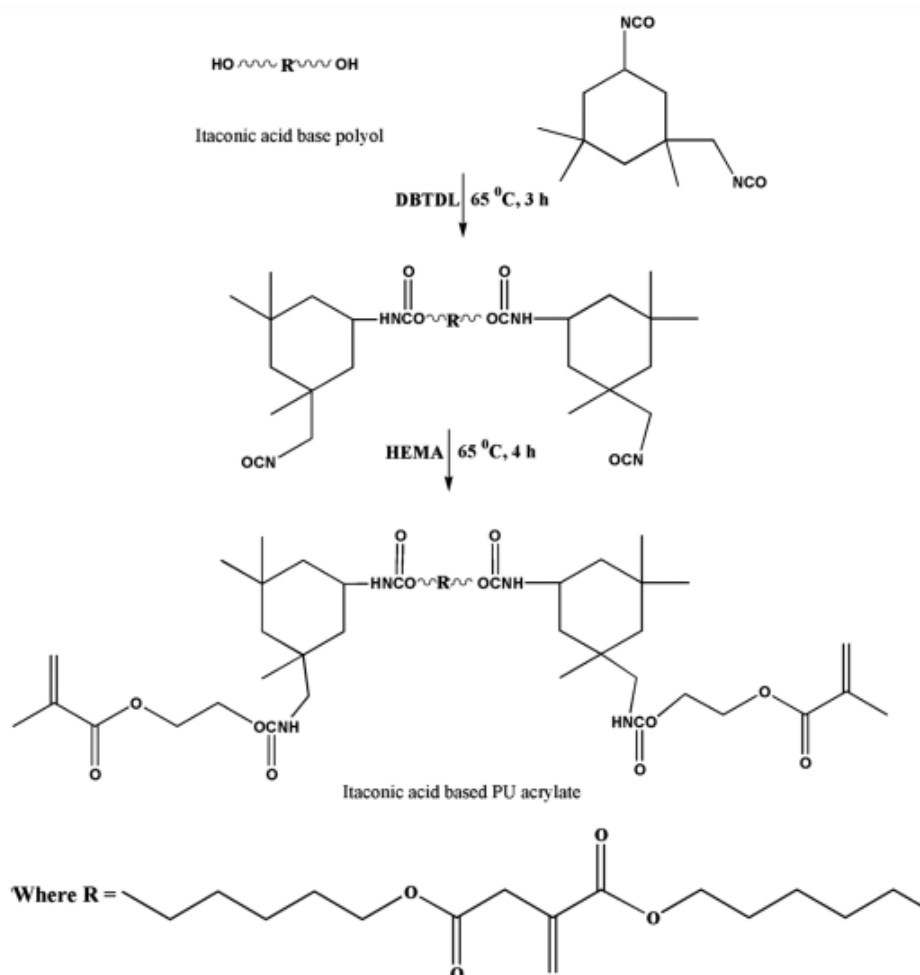


Fig. 07. Synthesis route for UV curable PUA resin [120].

4.5 Non-isocyanate polyurethane (NIPU) coatings

Both environmental and health concerns can be addressed through the creation of water-borne bio-based non-isocyanate polyurethane (NIPU) dispersions [121]. Among the two methods used for synthesizing NIPUs, cyclic carbonate aminolysis and trans carbamoylation are the most common [122]. Production of NIPUs through the polyaddition of cyclic carbonates and amines differs from conventional polyurethanes is not involving toxic phosgene and isocyanate during its synthesis. Concerning the sustainability aspects of such NIPUs, the wave of bioderived diamines or bis (cyclic carbonate) monomers can help to decrease the reliance on fossil resources. There is a high overall interest both in the academic and industrial communities to employ NIPUs for all the applications in which conventional PUs are used today, and for novel potential applications. NIPUs are already said to be utilized as adhesives and coating materials in the present commercial market. Nevertheless, the significant problems associated with employing NIPUs as coating materials are lower T_g and mechanical properties because of their lower molecular weight and the presence of H in their structure compared to PUs. It is stated that after cross-linking with NIPU, there are enhancements in mechanical and chemical aspects as coating materials [123], [124]. Fig. 08 shows the synthetic pathway of NIPU production from vegetable oil-based materials.

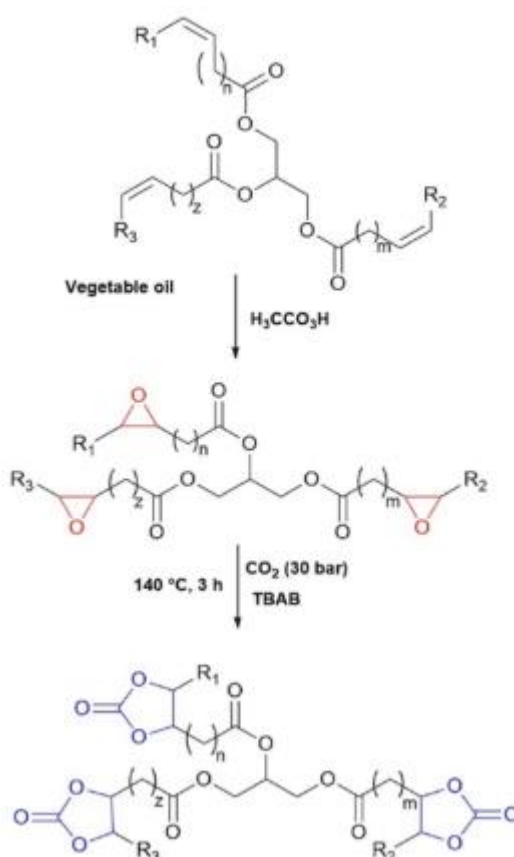


Fig. 08. Vegetable oil-based NIPU production [125].

Table 02. Type of PU coatings and potential applications of bio-based PU coatings

| Type of PU Coating | Potential applications | Ref. |
|--|---|------------------------|
| Sunflower oil-based biodegradable hyperbranched polyurethane | Advanced coating materials Thin film materials | [84] |
| Castor oil/pentaerythritol triacrylate-based UV curable WPU acrylate | Advanced surface coating materials | [119] |
| Polyurethane dispersions (PuD) | Automotive base coats Vinyl upholstery topcoats Wood floor coatings | [9] |
| Isocyanate-free polyurethanes from bis-cyclic carbonate | NIPU self-healing coatings Corrosion resistance coatings | [122], [123], [126] |
| UV-curable acrylate epoxidized soybean-based | Flame retardant hybrid coating | [118] |
| Soybean oil-polyester polyols based | Surface coatings High solid PU-coating | [104] |

CONCLUSION

Bio-PU coatings are considered environmentally friendly and, to some extent, superior to petroleum-based coatings without the much needed performance degradation. Embedded in these coatings, the use of renewable resources like vegetable oil, lignocellulosic biomass, and carbohydrates meets new social trends and demands where the general public becomes increasingly concerned about the proper utilization of resources. The performance of water-borne, solventless, powder, UV-curable, and hybrid bio-based PU coatings outweigh the conventional solvent-borne PU coatings in terms of durability, chemical resistance, flexibility, low or negligible VOC emission, and reduced energy inputs.

However, there are significant challenges to the commercialization of bio-based PU coatings, especially in the areas of cost and performance. These are significant barriers, but the possibility of using bio-based PU coatings is enormous and will change the coatings industry. More work needs to be done to eliminate current drawbacks and make the most of the application of these green coatings in an effort to save the environment and costs. With industries expanding their concentrations on environment-friendly products, using bio-based PU coatings is expected to be the solution for the foreseeable advance in coating applications. The future of bio-based polyurethane is promising, with growing demand for sustainable materials and advancements in renewable technologies driving its development.

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