

Review

Recent Developments in Lignin- and Tannin-Based Non-Isocyanate Polyurethane Resins for Wood Adhesives—A Review

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Abstract: This review article aims to summarize the potential of using renewable natural resources, such as lignin and tannin, in the preparation of NIPUs for wood adhesives. Polyurethanes (PUs) are extremely versatile polymeric materials, which have been widely used in numerous applications, e.g., packaging, footwear, construction, the automotive industry, the lighting industry, insulation panels, bedding, furniture, metallurgy, sealants, coatings, foams, and wood adhesives. The isocyanate-based PUs exhibit strong adhesion properties, excellent flexibility, and durability, but they lack renewability. Therefore, this study focused on the development of non-isocyanate polyurethane lignin and tannin resins for wood adhesives. PUs are commercially synthesized using polyols and polyisocyanates. Isocyanates are toxic, costly, and not renewable; thus, a search of suitable alternatives in the synthesis of polyurethane resins is needed. The reaction with diamine compounds could result in NIPUs based on lignin and tannin. The research on bio-based components for PU synthesis confirmed that they have good characteristics as an alternative for the petroleum-based adhesives. The advantages of improved strength, low curing temperatures, shorter pressing times, and isocyanate-free properties were demonstrated by lignin- and tannin-based NIPUs. The elimination of isocyanate, associated with environmental and human health hazards, NIPU synthesis, and its properties and applications, including wood adhesives, are reported comprehensively in this paper. The future perspectives of NIPUs' production and application were also outlined.

Keywords: lignin; non-isocyanate; polyurethane resins; tannin; wood adhesives

1. Introduction

Polyurethanes (PUs) have been extensively used in a wide range of applications, e.g., in packaging, footwear, construction, metallurgy, adhesives, automotive manufacturing, the light industry, insulation, bedding, vehicle parts, upholstery, fabrics, tissue engineering scaffolds, coatings, foams, biomedical applications, and many other sectors, due to their superior hardness, mechanical strength, biocompatibility, and elongation properties [1–3]. The versatile characteristics of PUs and their capacity of substituting other scarce materials led to their inclusion in many applications. PU coatings are explicitly used to impregnate

paper and manufacture garments that are corrosion-resistant. They are also used as chemical-resistant coatings for wood, masonry, and metal, as well as for high-gloss aircraft finishes. PUs may have a thermoplastic or thermosetting chemical structure, and may have a rigid solid physical form, a soft elastomer, or a foam. The chemical composition of PUs can also vary considerably, depending on the characteristic polyol and isocyanate types that react to polyurethane formation. Various chemical structures and physical forms make the PUs a commonly used polymer [4]. Currently, PUs are one of the world's most popular, flexible, and researched materials, widely used in elastomers, coatings, rigid foams, and adhesives since the mid-1950s [5,6]. These materials combine the endurance and hardness of metals with the elasticity of rubber, making it suitable to substitute some manufacturing goods, e.g., metals, plastics, and rubber [7]. The urethane group is the central repetitive unit in PUs formed from the reaction between alcohol (–OH) and isocyanate (–NCO), although PUs also include other groups, e.g., ethers, esters, urea, and certain aromatic compounds [2,8]. Since PUs are synthesizable from a wide variety of sources and based on their extensive range of specific applications, they can be divided into different groups based on their desired characteristics, e.g., rigidity, flexibility, thermoplastic nature, water-borne nature, binders, coating, adhesives, sealants, and elastomers [9].

PU foam is one of the most widely known polyurethane-based materials and is used in massive amounts worldwide. Customer needs consume approximately 50% of the total production of rigid PU foams, whereas the utilization of PUs in the composition of wood adhesives is still too scarce [9]. PU adhesives are characterized by excellent adhesion, flexibility, high cohesive strength, low-temperature efficiency, and efficient curing speed [9–11]. PU adhesives have strong bonding characteristics, while tight seals may be produced from polyurethane sealants.

Traditionally, PUs are successfully synthesized by the polycondensation reaction between a diisocyanate (or polyisocyanate) and a diol (or polyol) [11,12]. The discovery of the diisocyanate polyaddition technology led to the development of the PU industry in 1937 [13]. Two major PU synthesis pathways are known for industrial applications. PUs can be synthesized using one or two steps known as a prepolymer process [14]. Both methods are based on polyaddition, in the presence of low-molecule diols as a chain extender, catalyst, or another additive (e.g., coloring, fillers, moisture scavengers, cross-linking agents) of aliphatic or aromatic diisocyanates and oligomeric diols. Two steps of traditional PU synthesis are demonstrated in Figure 1. In the first stage, the reaction between diisocyanates and polyols leads to the formation of urethane prepolymers ended with isocyanate groups followed by the extension of prepolymer chains by low molecular weight chain extenders (e.g., diamines or diols) [14–16].

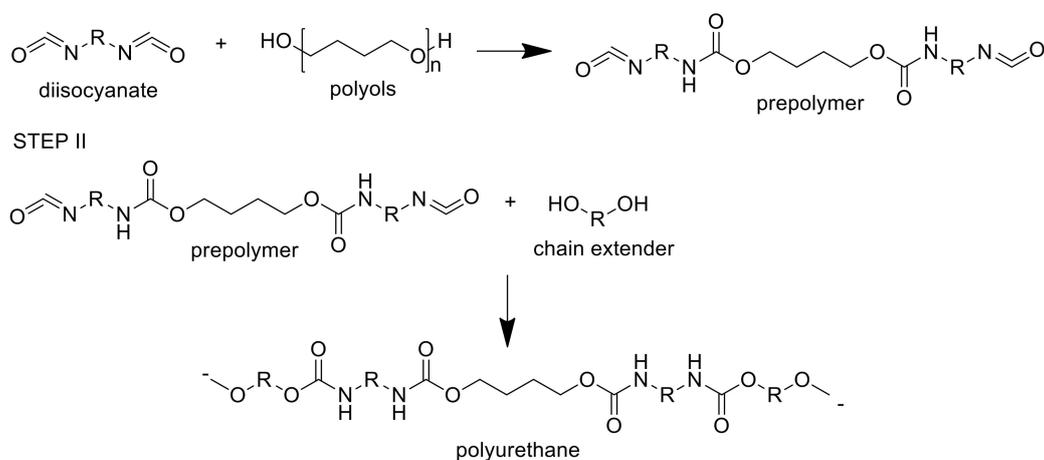


Figure 1. Traditional PU synthesis by a two-stage process using diisocyanate, polyol, and a low molecular weight chain extender [14–16].

In the beginning, most of the polyols used to prepare PUs were derived from petroleum, but the high demands of resources from the manufacturing process and environmental issues increased the need for more appropriate and environmentally sustainable alternatives. Recently, this attracted considerable commercial and academic attention to renewable resources, such as vegetable oils [3,17–19]. Furthermore, certain hazards and problems are associated with applying PU materials, especially concerning isocyanate monomers. PUs can be prepared from renewable polyols, such as lignin [20,21] and tannins [22–24]. Lignin and tannins have gained a significant scientific and industrial interest as potential sustainable raw materials for the development of wood adhesives, since they consist of natural plant-derived polymer compounds.

Wood adhesives are manufactured in large quantities and used for many large-scale applications, such as load-bearing structures, floors, furniture, doors, and windows [25]. Starting in the 1960s on a small scale, and increasing considerably starting from 2012 to 2013, some synthetic polymers derived from fossil materials due to their increasing costs were starting to be replaced by natural binders. The best case of this is the substitution of phenol-formaldehyde wood adhesives by vegetable tannin-based adhesives with and without formaldehyde [26]. The traditional petroleum-based thermosetting adhesives have numerous advantages, such as excellent adhesion properties and water resistance, ease of handling, low curing temperature, short press times, reasonable costs, etc. [6,26–29]. They, however, have a major drawback connected to the hazardous emission of free formaldehyde and other volatile organic compounds from the finished wood-based composites [30,31], associated with serious environmental problems and a number of significant human health-related hazards, such as such as eye, skin, and nervous system irritation, skin sensitization, nausea, and even cancer [32–34]. In 2004, the International Agency for Research on Cancer reclassified formaldehyde as “carcinogenic to humans” [35]. Formaldehyde is classified as a cancerous and toxic substance with a 100 mg/kg (rat) acute oral toxicity (LD₅₀) based on the scientific laboratory’s Material Safety Data Sheet (MSDS). However, polymeric diphenylmethane diisocyanate (pMDI) is considerably less toxic than formaldehyde with a total acute (LD₅₀) oral toxicity of >2000 mg/kg (rat), based on the Demilec (Dallas, TX, USA) LLC MSDS. For that reason, formaldehyde is forbidden in a variety of applications [36]. The stricter formaldehyde regulations and the increased consumer environmental awareness have shifted the industrial interest towards more sustainable materials, and less petroleum-based adhesive industry [37,38]. However, the bonding characteristics of bio-based adhesives should be very similar or incorporate other added values to substitute fossil adhesives with renewable equivalents effectively, and very crucially, costs must be equivalent to current unsustainable adhesives [25]. Traditional wood adhesive systems used in the production of wood-based composites are commonly made of four major synthetic thermosetting resins, namely phenol-formaldehyde (PF), urea-formaldehyde (UF), melamine-formaldehyde (MF) resins, and pMDI [39–41].

PF resins, with an approximate annual consumption of up to three million tons [5], are the second most widely used adhesives for wood composites, preceded only by the UF resins. PF resins are typically synthesized under alkaline conditions from the phenol-formaldehyde reaction. They provide high adhesion and mechanical strength [42], temperature stability [43], low starting viscosity, and high water resistance of the cured resins [44,45]. In exterior-grade products such as the oriented strand board (OSB), softwood plywood, and sidings, which require external exposure durability, these resins are extensively used [23,40,46–48]. UF resins, obtained by the reaction of urea and formaldehyde, are the most predominant synthetic adhesives, used for production of interior-grade wood composites, such as particleboards and medium-density fiberboard (MDF) for furniture and a number of other applications, in which dimensional stability and surface uniformity are critical requirements [49]. UF resins require a shorter pressing time and lower pressing temperature than PF resins, resulting in accelerated performance and relatively low energy use; they are ideal for producing light-colored decorating products [40]. MF resins are usually used for sundry applications, such as paper processing, laminate

decoration, and paper coating. Due to the relatively high price of melamine, MF resins are typically mixed with UF resins for particular applications, produced and traded as melamine-urea-formaldehyde (MUF) resins [26]. pMDI adhesives are characterized by quick curing, formaldehyde-free emission characteristics, low loading amounts, and excellent weather resistance; they are mainly used in the production of OSB and other similar particulate wood-based panels [40,50]. The relatively greater price of pMDI compared to the other common wood adhesives is the main limiting factor for their wider industrial application. Manufacturing of these resins has relied on non-renewable petroleum-based resources [51].

There is also an increased interest towards the development of sustainable, bio-based, “green” adhesives from different renewable biomass feedstocks, such as proteins [52–56], starch [57,58], tannins [37,58–61], and lignin [62–72]. In addition, other biomaterials were utilized in the development of bio-based adhesives, e.g., cashew nutshell liquid (cardanol) [73], vegetable oils [74], fungal mycelium [75], etc. However, most of these raw materials were reported only as conceptual bioadhesives, and no industrial trials have been performed.

The production of bio-based adhesives raises additional challenges; adhesives made from renewable natural materials often have low water resistance or are too costly to compete effectively with fossil-derived polymers. The often broad variations in properties due to different growing conditions, source form, growth time, access to nutrients, climate, and other factors, are another challenge when using bio-based polymers. The extraction and fractionation processes that are important for the bio-based polymer isolation would also affect the adhesives’ final properties and costs. Therefore, the complete replacement of robust synthetic polymers, having well-known and reproducible characteristics, with fully bio-based polymers as wood adhesives at an industrial scale is challenging [25]. The aim of the present review is to summarize the current state of research and recent developments in the field of lignin- and tannin-based NIPUs for wood adhesives.

2. Types of Polyurethane

For functional and practical purposes, PUs can be classified into two major categories: elastic PUs, e.g., flexible foams, elastomers, coatings, adhesives, fabrics, etc., and rigid PUs, e.g., rigid foams, structural foams, wood replacements, solid PUs, etc. The classification of PUs into elastic and rigid ones is based primarily on the structure of oligo-polyol [76]. Owing to the wide variety of sources from which PUs can be synthesized and given their wide range of particular applications, PUs can also be divided into many different groups based on the desired properties [4]. Table 1 summarizes the essential types of PUs and their typical applications.

2.1. Thermoplastics PUs

Thermoplastic polyurethanes (TPUs) show large combinations of physical properties and applications for processing. They are typically flexible and elastic, and have a substantial effect, abrasion, and weather resistance. With TPUs, a wide variety of techniques is available for coloring as well as manufacturing. Thus, the incorporation of TPUs could increase the overall durability of several products [77,78]. TPUs are melt processable, similar to other thermoplastic elastomers. They can be produced by extrusion, blowing, compression, and injection in molding equipment [79]. They can also be solution-coated or vacuum-formed, making them ideal for a wide variety of manufacturing techniques. Several combinations of properties of TPUs make them suitable for several applications, e.g., automobiles, footwear, and construction [77,80].

Table 1. Essential types of PUs and their typical applications [4].

Type of Polyurethane (PU)					
Thermoplastic PU	Flexible PU	Rigid PU	PU Ionomer	Water-Borne PU	Thermosetting PUs
Keyboard protector, external cases of mobile equipment, car instrument panels, casters, power equipment, sporting goods, medical equipment, drive belts, boots, inflatable rafts, and a wide range of extruded film, sheets of paper, and profile applications.	Cushion materials, carpet underlays, furniture bedding, automotive interior parts, packaging, biomedicine, and nanocomposites.	Thermal and sound insulators.	Artificial hearts, connector tubing for heart pacemakers, and haemodialysis tubes.	Coatings, adhesives, sealant, binders.	Beds, quilts, packaging materials, isolation materials, footbed, fender, door panel, vehicle exterior tire, seal, car bumper or synthetic leather.

The TPU's synthesis consists of novel fatty-acid-based diisocyanates in which the synthesized content has already shown considerable thermal stability at temperatures below 235 °C without substantial weight loss [77]. Productive synthesis of rigid spiroacetal-moieties-based sustainable thermoplastic was also published, with related materials produced at a very high yield [81]. Product analysis with Dynamic Mechanical Thermal Analysis (DMTA) and Differential Scanning Calorimetry (DSC) showed a glass transition temperature (T_g) of about 85 °C. Additionally, no significant acid-mediated degradation of the synthesized PU was observed during the hydrolytic stability testing. An utterly bio-based thermoplastic PU was produced from dimer-fatty-acid-based diisocyanate and sustainable diols, such as 1,4 butanediol and Dianhydro-D-glucitol. A one-step batch processing method was used to prepare a PU material that was found to be suitable for coating materials, automobile industries, construction, adhesives, and textile applications [82]. Moreover, according to the water-insoluble, non-ionic, and inert properties of TPUs, they were already effectively used in applications such as polymer control systems for drug release [83] and healthcare tubes because their high mechanical strength could allow thin-wall tubes without obviously integrating a plasticizer [79]. In another experiment, macrodiols were used to produce TPUs which are already traditionally ether- and ester-types [84,85]. Carbonate-type macrodiols can be an alternative to enhance flexibility, hydrolytic stability, and abrasion resistance [86–98]. Significant attention has been given to understanding the chemical structure-property interaction among carbonate-type macrodiols and subsequent TPUs [87,91–97]. Significant characteristics of carbonate-type macrodiols and subsequent TPUs, e.g., biocompatibility [88,98], clarity [89], and self-healing [90,99], were also added. However, the majority of researchers used commercially produced macrodiols [88–90,94–98].

2.2. Flexible PUs

Foams are microcellular structures made from gas bubbles formed during the mixture of PU polymerization. The method of forming a bubble in PU foams is called blowing. The blowing process is one of many reactions in the final PU formulation when it is foaming.

The chemical component in the gas-supply mixture is called the blowing agent. Low-boiling liquids added to aid with the foaming process are considered auxiliary blowing agents. Usually, the term urethane or PU is associated with flexible foams. Flexible PU foams are developed in various shapes by clipping or molding. They are widely used in upholstered beds, mattresses, automotive seats, etc. Furniture and bedding (e.g., mattress core and bags, even furniture covers), transport (e.g., soft seat and trim panel), door panels, armrests, head restraints and power absorption (semiflexible), and carpeting (e.g., virgin and linked underlay) are the most relevant markets of flexible PU foams [4].

Flexible PU (FPU) foams contain some block copolymers based on the separation of the process between soft and hard segments [100]. The compositional ratios of these segments can be changed intentionally by manipulating the PU foams. In terms of density and toughness, for example, strength, tearing resistiveness, combustibility, and surface elastics, they can be graded as FPU depending on specific physical characteristics, and

every combination of these characteristics will guarantee a strong PU compound versatility. For many consumer and industrial items, including carpet underlays, chairs, bedding, car interior parts, packaging, biomedicine, and nanocomposites [101–104], FPU foams are used as coil materials. Two key stages often include the synthesis of FPU foams: blowing and gelling. The blowing reaction produces carbon dioxide and urea, expands, and gets entangled by the reaction mix, whereas urethane connections are formed by isocyanate and polyol hydroxyl reactions. The morphology and the microstructure of the FPU foams are determined by several parameters including the degree of interlinking following the reaction from polyol to diisocyanate, the urea group's segmental motion, the nature of the interaction between polyol and urea, etc. In their study, Chen et al. [105] reported preparation of FPU foam from lignin and oxypropylated lignin. Some technological aspects were identified that could increase the versatility of the materials; for example, the cross-linking density can be kept low by reducing the NCO/OH ratio, and the introduction of a flexible chain to the primary PU backbone via a chain extender can potentially reduce the glass transition temperature in order to achieve highly flexible PU foams. Due to their high degree of linkage and ample crystallinity, these FPUs are chemical resistant, but their tensile and tear properties are low. Hybrid laminated high FPU foam was prepared and analyzed to resolve these deficiencies [106]. It was then proposed that textiles such as aramid, carbon, basalt, and glass could strengthen the FPU foam. Additionally, significant amounts of poisonous gases such as CO, NO_x, and HCN can be emitted to the atmosphere during combustion due to the high fuel properties of FPU. Anti-flammable properties must also be integrated into their formulation during processing [106].

2.3. Rigid PUs

Rigid PU foams are one of the most popular ones, widely used in thermal insulation applications. Reports from the U.S. Energy Department revealed that heating and cooling are one of the primary uses of energy in most homes [9] and responsible for about 48% of the overall energy usage in a typical U.S. home [107]. PU foams and polyisocyanurate are widely used to create a constant temperature and a decreased noise level for both home and commercial areas. These foams have been efficient as insulators and used in windows, walls, roof insulation applications, and barrier sealants.

The preparation of rigid PU foams can be achieved with both oil-driven polyols and bio-driven polyols from vegetable oils or lignin from plants. The properties of the formulated PUs are determined by the hydroxyl group category in the polyols. Glycerin is a petroleum-based polyol, containing three hydroxyl groups. The secondary hydroxyl groups are found in vegetable oil-based polyols (e.g., beaver oil). Thus, there are numerous physical and mechanical features of PUs synthesized using both of these polyol groups [108]. Moreover, the reaction between a secondary polyol containing a range of hydroxyls and isocyanates is slower than between the primary polyol containing a range of hydroxyls and isocyanates. A mixture of primary and secondary polyols that contain hydroxyl groups are commonly used to minimize the petroleum-based polyol intakes [108]. For example, a mixture of glycerine and castor oils was used to manufacture rigid PU foams with high physical and mechanical properties [3]. Additionally, it can influence the physical properties of PUs by the presence of different polyols. For example, having a secondary hydroxyl group, a trans-esterified palm-olive-based polyol can reduce the reactivity of the rigid PU foaming profile [109]. It is stated that the formulation of PU foam increased the gel time, cream time, and track-free time compared with the petroleum polyol-processed PU foams.

Many structural modifications or changes are often needed for obtaining features comparable to petroleum-based polyols from vegetable counterparts. For example, soy oil's hydroxylation with formic acid and peroxide was performed by Vinícius et al. 2011 [110]. To improve the –OH functionality, the transesterification was carried out by adding some multifunctional alcohol [110]. High flame retardant rigid PU foams were synthesized from phosphorylated polyol obtained from epoxidized soybean oil in another report. The product properties were identical to commercial polyol-based foams and were demon-

strated to have a high flame-retardant capacity [108]. Similarly, in further analysis, some nitrogen-phosphorus-based inflammatory residues such as dihydrooxa phosphophenanthrene oxide benzylenaniline (DOPOBA) strengthened the flame-retardant properties of rigid PU foams. In addition to the flame-retardant properties, the resulting foam's physical and thermal characteristics were greatly enhanced. When 20% of wt DOPOBA was used in rigid formula PU [111], the limiting oxygen index (LOI) of the synthesized rigid PU increased from 20.01% to 28.1%. Rigid PU foams from cardanol and melamine-derived polyols were also developed. In contrast to other traditional PU foams, the material was extremely flame-retardant with greatly improved compressive strength and thermal stability [112]. Flame retardants obtained from castor oil were also used in other research studies to synthesize rigid PU foams. Many different applications of the developed PU foams, based on the observation of improved properties, were found [113].

2.4. PUs Ionomer

In PU backbone chains, ionic groups' presence has various advantages, such as enhanced dispersion in polar solvents due to increased hydrophobicity and improved thermal and mechanical properties [114]. The materials to be used in biomedical devices should have shape memory and biocompatible features [114–128]. Shape memory PUs (SMPUs) have a shape memory effect (SME) that is thermo-responsive and therefore have different mechanical properties than the other PUs [116,117,125–128]. The PUs can “memorize” permanent form through the presence of hard and soft segments (responsible for the frozen and reversible phase) [114,118]. If the materials are heated past switch temperature, the permanent form can be retrieved from the temporary form [114]. The glass segment's soft and transition temperature is correlated with the switching temperature and provisional deformations, and the hard segment gives permanent shape memory. The content and molecular structure of hard and soft segments within PU molecules influence the PUs' SME. The change in the glass transition temperature in the soft segment and the hard segment crystallization affects the SME.

Owing to the presence of ionomers in PUs, these properties can be modified. Ionic group integration can be accomplished by either ionic diols or ionic diisocyanate-containing groups during PU preparation [114,115]. Ionomer can be made by post-functionalizing the PU. Cationomers based on PU can be created through the ternization of a sulfur atom or a nitrogen quaternization. Diol has to contain nitrogen or sulfur to be used in the PU preparation. MDI and poly-(butylene adipate) diol were synthesized in a form memory PU. The diol was expanded using MDI and poly-(butylene adipate) diol, while 40°C acetic acids were used for quaternization at chain extension [123,124]. The biocompatibility is also essential for the polyurethane ionomers (PUIs). The PUIs have been studied for blood compatibilities in the sulfonate and phosphatidylcholine groups [119]. Li et al. observed better haemo compatibility of segmented PU and polyureas, where the better performance of the former was demonstrated compared with medical PU [129]. These materials can be successfully used for various medical applications for artificial hearts, pacemakers, and hemodialysis tubes [114].

2.5. Water-Borne PUs

Adhesives and coatings that mostly use the water solvent are waterborne polyurethanes (WPUs) [130,131]. The new stricter environmental legislation has limited the number of organic solvents and other harmful air contaminants that can be released into the atmosphere. Therefore, most commercial and industrial use is based on PU dispersions (PUDs) or waterborne PU dispersions (WPUDs) [132,133]. PUDs have the particular benefit of not relying on the polymer's molecular weight for the dispersion viscosity. Therefore, high solid content WPUs (HSCWPUs) can be produced only through a drying phase. The dispersion is a colloidal two-phase model that involves polyurethane and water media particles. Some pendant acid or tertiary groups of nitrogen in the PU chain are neutralized to form salts that produce water dispersibility centers. This dispersion's different properties depend

on forms and amounts of polyol, isocyanate, ionomers, and chain extender used. A new method for the synthesis of HSCWPU [134], in which the bimodal particle size distribution was strictly controlled, was recently developed (a two-phase emulsification procedure). The parameters for the viscosity determinations and the solid content interrelation were fundamental in terms of the distribution of particle sizes [135]. This form of materials with a high solid content also improved the reactors' space and time, and decreased the time required to produce the film [136]. The synthesis of new WPU medium-length fluorinated diols was part of a recent research study. In this analysis, dodeca-fluoroheptyl acrylate (DEFA) fluorinated diol 3-(bis-(N,N-dihydroxy ethyl)) was first developed by using the Michael addition method from dodeca-fluoroheptyl acrylate and diethanolamine. There were substantial improvements in organic solvent/water resistance and in mechanical and thermal characteristics. For example, the tungsten strength increased from 9 MPa to 15 MPa, while the extensibility decreased from 520% to 280% [137]. Other remarkable WPUs that were investigated involve a WPU with polycarbonate diol based on silica. In the case of a high abrasion resistance, it was stated that the material produced had a suitable coating usage on flexible materials, such as fabrics, paper, and leather [138]. For fully bio-based WPUs, a new synthesis route was also given. The method was approved to guarantee compliance with protection criteria, and the high hydrophobic and thermal properties of the synthesized product were determined. It was also suggested as a suitable alternative of the traditional oil-based materials [139].

2.6. Thermosetting PUs

Thermosetting polymers have immense potential to advance modern industries. Thermoset PUs (TSPUs), such as soft foam and hard foam, are available in different varieties. Soft foams are used to manufacture furniture, quilts, and fabrics for packaging, while hard foams are used as thermal insulation materials. The TSPUs are made from linear and preferably crystalline molecules. They can be used for manufacturing wear-resistant materials, such as footbeds, fenders, door panels, car tires, seals, bumper cars, synthetic leather, etc. [140]. Thermosetting PUs are commonly used as manufactured products because of their physical characteristics and ease of processing. Nevertheless, they tend to become permanent and are negatively affected by certain solvents, so their use at high temperatures is often restricted. The stable elastomeric PU composition, which can be vulcanized during or after processing with free radical curing agents, would be advantageous since the shortcomings mentioned above would be partially compensated [4]. The properties of macromolecular compounds are usually closely related to temperature variations. At sufficiently low temperatures, amorphous polymers are hard and glassy, whereas they take on a weaker and softer form at critical temperatures, the T_g . The polymer chains display an increase in the flexibility of temperatures above the T_g value, which allows the bulk material to flow. Flexibility is minimal, and the polymer behaves correctly as a glassy, elastic solid in temperatures below the T_g value. The temperature of a glass transformation of the polymer depends on chemical structure, chemical or physical binding, and molecular weight. The value of T_g is the crucial indicator for classifying a plastic compound either as a thermoplastic compound or as a thermosetting polymer [141].

Thermoplastic PU is a linear segmented block copolymer, composed of hard and soft segments that can be deformed plastically under the influence of heat and return to solid when cooled. On the other hand, TSPU is a highly cross-linked polymer and behaves differently as it cannot be melted after the curing process [142]. TSPUs have usually consumed petroleum as their raw material in products, such as coated fabrics, wire coatings, shoe soles, and sporting goods for thermoplastic, while the TSPUs that are tough and durable at high temperatures are found in some polymeric coatings, electronic chips, and composites. The increased global trends for petroleum substitution with natural renewable sources are due to the fluctuating petroleum prices and stringent environmental rules. Vegetable oils may also be an essential raw material because they are mainly composed of triglycerides. It is an ester from glycerol and fatty acids, which are mostly saturated and

unsaturated compounds. As shown in Figure 2, TSPUs are synthesized with a single-pot polymerization [142].

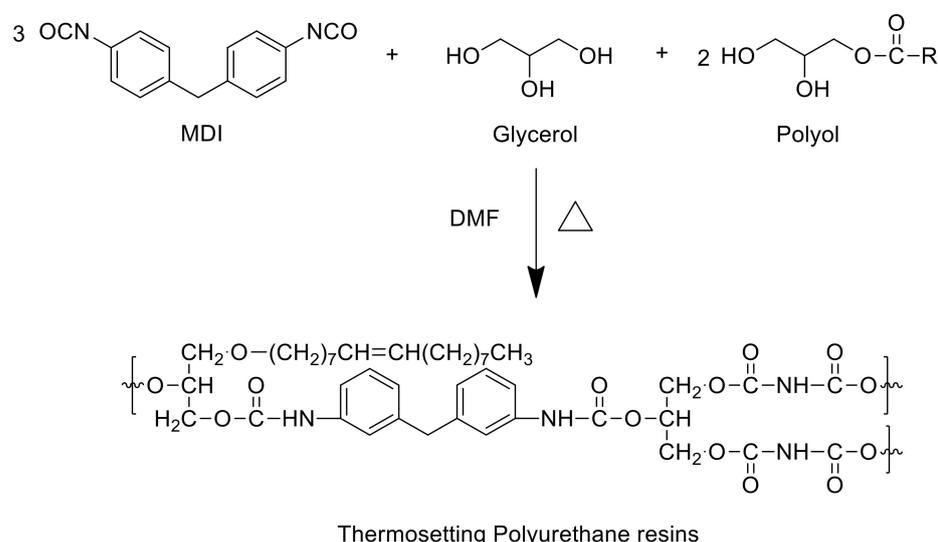


Figure 2. Thermosetting polyurethanes synthetic pathway (TSPUs) using pMDI, polyol, and glycerol [142].

3. Route for Non-Isocyanate PUs (NIPUs)

PUs can be manufactured by various methods [143]. A reaction between the polyol (an alcohol with two or more hydroxyl groups in one molecule) and the diisocyanate is the most important and common process [76,144]. For PU preparation, isocyanates are highly required components. They can be classified as difunctional or heterofunctional, and aromatic or aliphatic by nature. Methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), and aliphatic diisocyanates are among the most frequently used options available. Environmental concerns led researchers to look at better ways in which environmental problems and other toxicity issues related to diisocyanates can be minimized or possibly eliminated. For example, sustainable PU from carbonated soy oil, 3-aminopropyltriethoxysilicane, and lignin was studied. A reaction between cyclic carbonate and amines [145] was followed on the non-isocyanate path, and polyol was prepared from lignin using the oxypropylation method [146]. An additional analysis used lignin-based PU with oligomeric polybutadiene diisocyanate [147]. A related study responded to the preparation of PUs by lignin-aminated polyol and diphenyl diisocyanates. The properties of formulated non-isocyanate-based PUs are mainly dependent on lignin content in most reporting. The quality of the lignin defines the relationship between the materials and the modulus.

Efficient alternative methods for PU synthesis must be established with due regard to environmental protection and health safety. The replacement of fossil-fuel feedstock with renewable bio-based resources associated with reducing petrochemical procedures and using fossil fuels is one of the potential green alternative routes for PU synthesis [16,148]. DuPont (Wilmington, DE, USA), BASF (Ludwigshafen, Rhineland-Palatinate, Germany), BioAmber (Princeton, NJ, USA), Myriant Technologies LLC (Quincy, MA, USA), General Mills Co. (Minneapolis, MN, USA), Covestro (Leverkusen, Rhine-Westphalia, Germany), Henkel Company (Düsseldorf, Rhine-Westphalia, Germany) and Allessa GmbH (Frankfurt, Hesse, Germany) are the most renowned companies supplying organic raw materials to synthesize PU. Furthermore, a phosgene-free and isocyanate-free synthetic strategy was developed [16]. The use of toxic and moisture-sensitive diisocyanates provided by toxic phosgene eliminated from the non-isocyanate synthesis routes to PUs. Four different methods for NIPUs synthesis, i.e., step-growth polyaddition, polycondensation, ring-opening polymerization (ROP), and rearrangement reactions, were reported in the literature [14,149–155], as shown schematically in Figure 3.

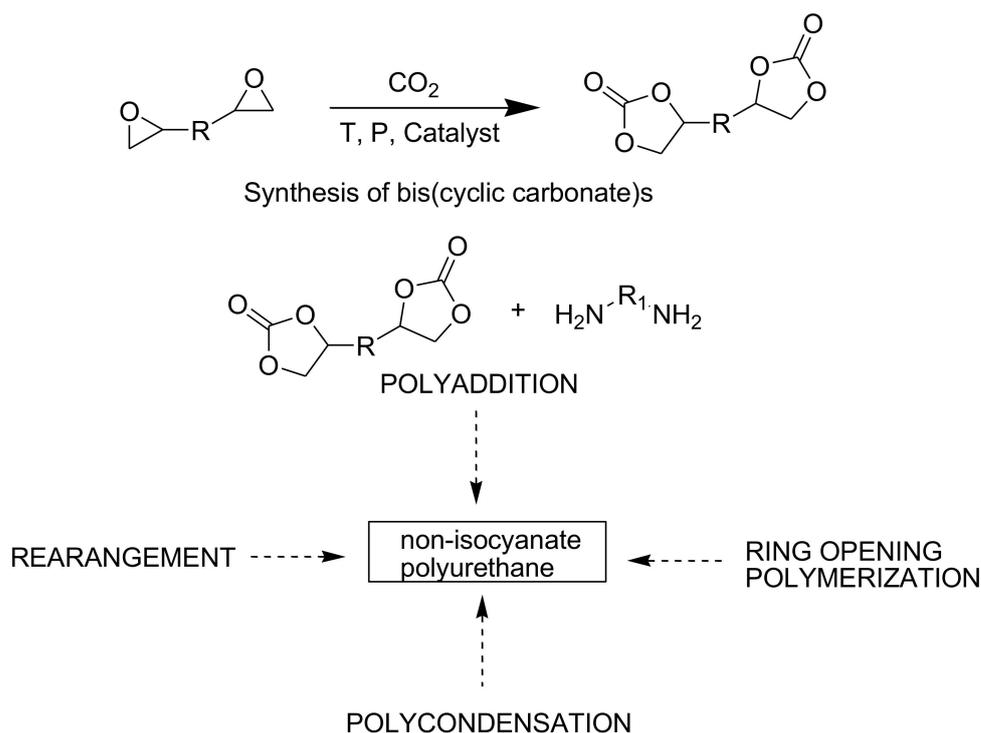


Figure 3. Possible pathways for synthesis of NIPUs [15].

Published research papers showed the feasibility of using Hoffman rearrangement, Curtius rearrangement, and Lossen rearrangement. Unfortunately, substrates' toxicity such as carboxamide, acyl-acid, and hydroxamic acids limits their use in non-isocyanate PU synthesis. This issue also concerns the reagents used in ring-opening polymerization. Aliphatic cyclic carbamates are typically derived from highly dangerous phosgenes and aziridines [150]. Dyer and Scott carried out the first polycondensation synthesis of NIPUs [156]. The polycondensation pathway synthesis of NIPUs is linked to the reaction between di- or polycarbonates and diols [80], di- or polycarbonates and amino alcohols [145] or diamines [157], polychloroformate and polyamines, as well as polycarbamoyl chloride and polyol [150]. This approach to industrial application is constrained by the development of side-products (e.g., H₂O, HCl, alcohols). Furthermore, the synthesis is typically carried out in solvents, using catalysts and under particular reaction conditions, such as long reaction times or high temperatures (150–220 °C), which are economically unfavourable from an industrial point of view [14].

A polyaddition of bifunctional cyclic carbonates with primary di- or polyamines containing poly(hydroxy urethane)s (PHUs) with other primary or secondary hydroxyl groups in the side chain, shown in Figure 4, is the most examined and the best possible synthesis path for preparing NIPUs. Drechsel and Groszos first researched this route in 1957 [158]. The group's hydroxyl can form inter- and intra-molecular hydrogen connections with the groups of urethane carbonyl [14,150,154,157]. The use of ecologically benign bio-based materials and carbon dioxide fixation is also a benefit of the polyaddition process. Furthermore, without catalysts and solvents, synthesis could be achieved [14]. This generates enhanced chemical resistance to organic solvents in obtained PHUs. Additionally, PHUs have increased thermal stability due to a lack of labile biurets and allophanate thermally unstable groups [159]. PHUs also benefit from the ability to react with various chemical functional groups of constituted hydroxyl groups [160]. In contrast with standard polyurethanes, literature studies show inconsistent evidence of PHU water intake during exposure to water [150,152,154]. The chemical structures of both traditional isocyanate-based and hydroxy-functional isocyanate-free polyurethanes are presented in Figure 5.

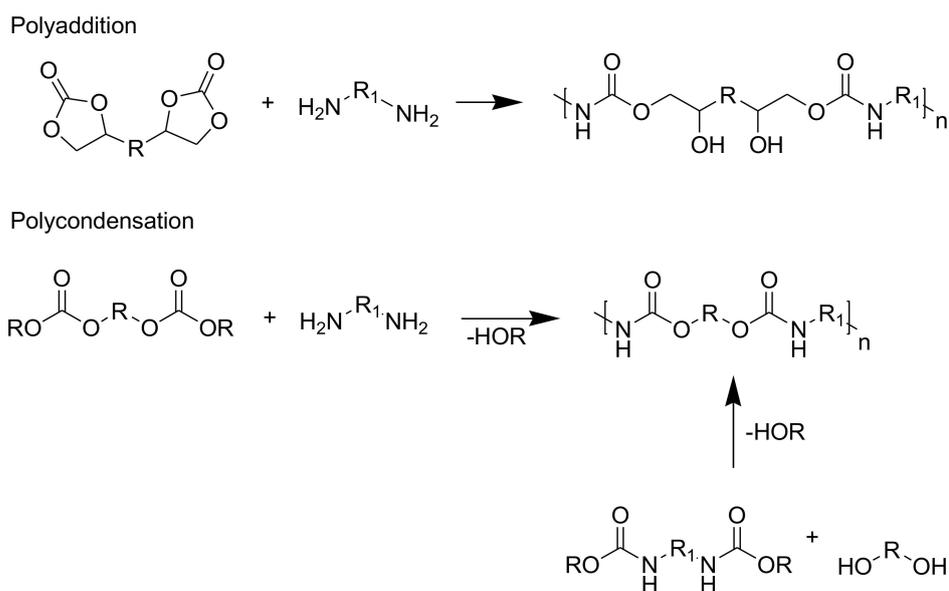


Figure 4. Comparison of NIPU structure produced by polyaddition of bifunctional cyclic carbonate and diamine as well as polycondensation [80,149].

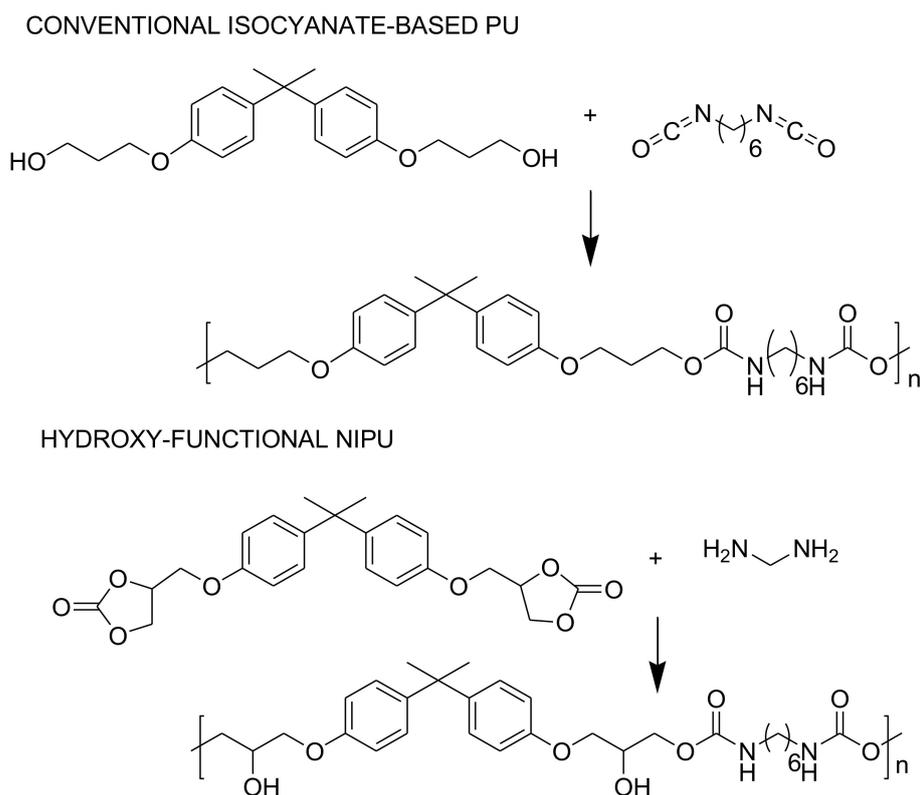


Figure 5. The conventional method of polyurethane synthesis in comparison with a route to hydroxyl-functional NIPUs [149].

The first successful application of NIPUs in the industry was achieved by Nanotech Industries, Inc (Daly City, CA, USA). Under the trade name Green Polyurethane, the company patented phosgene and isocyanate-free commercially available materials obtained using bio-based resources by the cyclic carbonate, epoxy oligomer, and aliphatic or cycloaliphatic polyamines reaction. These materials are characterized by increased adhesion

properties and hydrolytic stability, as well as improved corrosion and wear resistance compared with the traditional, commercially available PUs [152].

Gradually reducing the number of fossil resources could lead to a predicted scarcity of polymer synthesis substrates. Recent years demonstrated the use of bio-based and renewable monomers and their derivatives, e.g., vegetable oils, fatty acids, sugar, terpenes, and even carbon dioxide [161]. The preparation of PU-based adhesives comprising biosourced, sustainable raw materials involves the synthesis of non-isocyanate PUs. This approach, excluding the use of harmful isocyanates, has gained a significant research interest in the recent years.

4. Lignin-Based NIPUs Adhesive

Lignin is a polyaromatic macromolecule, and the second most abundant polymer in nature, preceded only by cellulose. The structure of lignin is composed of different units and repeated structures, depending on the plant species, and growing conditions, constituting approximately 24–33% of the wood substance in softwood and 16–24% in hardwood species, respectively. At present, lignin is regarded as a waste or by-product of the pulp and paper industry with an approximate annual 80–100 million tons worldwide [162]. Currently, less than 2% of the total lignin is used for value-added applications, such as dispersants, surfactants, adhesives, polymer reinforcement materials, dispersants, etc., while the rest is burnt for heat and energy purposes [162,163].

The different technological processes, used in the pulp and paper industry to obtain lignin include mechanical, chemical, and enzymatic processes, which consequently produce different types of technical lignins, e.g., organosolv lignin by an organosolv treatment; hydrolytic lignin obtained by an enzymatic hydrolysis process; alkali lignin, derived by the Kraft process; and lignosulfonates, obtained by the sulfite pulping method.

Native lignin is a complex polymer and must be partially degraded to allow its separation from the cellulose and hemicelluloses. Reactivity of different lignins depends on their chemical structure; therefore, different lignin samples contain different types and numbers of these functional groups, which can be used to manufacture industrial biomaterials and biocomposites [164–166]. The high solids content and availability of black liquor as the main by-product of the pulp and paper industry make great use of black liquor as a strategic and promising raw material for lignin. This isolated lignin from black liquor is referred to as technical lignin. Technical lignin can be converted to the industrial one by fractionation. Technical lignin has a broad molecular weight distribution, between 1000 g/mole and 100,000 g/mole, making it difficult to utilize lignin commercially. Fractionation of lignin produces lignin fractions that have useful properties for various applications. The fractions of lignin are more suitable to be used as building blocks for bio-based polymers such as bio-based PU resins [167].

Urea, melamine, and phenol-formaldehyde resins, commonly used in wood adhesives, are highly susceptible to hydrolysis and cause environmental and health problems as a result of formaldehyde volatilization over the lifetime the finished products [168]. Thus, it requires an adhesive that is environmentally friendly and with no indicated formaldehyde emission, with the characteristics of short heat curing temperatures, with short pressing time, and with high power, instead of widely used adhesives [169]. As binders in the production of engineered wood products, e.g., cross-laminated timber, NIPU adhesives can have advantageous adhesion characteristics of all adhesives [170]. They can be colorless and flexible with wood, metal, glass, plastic, rubber, ceramic, sand, and textile fiber bonds (Table 2). Some of the disadvantages of PU adhesives include high adhesive penetration in wood, low tear resistance, and unsatisfactory gap filling properties. Though rigid fillers such as calcium carbonate can be added to overcome these problems by raising viscosity, the issue is not resolved. To overcome these problems, lignin is an alternative solution. Lignin was reported to increase delamination resistance, cohesion failures, and the absence of filling properties in the NIPU adhesive formulations [171].

Table 2. Advantages of NIPUs compared to other adhesives.

Parameter	Lignin- and Tannin-Based NIPUs Adhesives	Other Wood Adhesives	References
Bonding properties	High delamination resistance, adhesion, and cohesion strength. Tensile strength and deformation are comparable to traditional isocyanate PUs.	UF, MF, MUF give over penetration in wood, lower tear resistance, and lower adhesion compared to NIPUs	[150,152,154,171]
Physical properties	Comparable water resistance and dimensional stability to isocyanate PUs	Lower water resistance of formaldehyde-based adhesives compared to NIPUs	[147–153]
Mechanical properties	High value of hard to soft ratio resulting in satisfactory mechanical properties	Mechanical properties are lower than NIPUs adhesives	[14–16]
Chemical properties	Having greater chemical resistance for about 30–50% than other adhesives	Lower chemical resistance and permeability than NIPUs adhesives, except for isocyanates	[150,152,154,171]
Thermal properties	Thermal stability enhancement owing to the presence of aromatic lignin and tannin	Lower thermal stability than NIPUs, except for isocyanates	[14–16,149–155]
Renewability	Derived from renewable biomass of lignin and tannin	Derived from petroleum that is not renewable	[150,152,154,171]
Toxicity	Less toxicity due to being isocyanate free	Release formaldehyde and contain isocyanate that are carcinogenic	[150,152,154,171]
Price	Cheaper than isocyanate PUs, but still more expensive than those of formaldehyde-based resins	Isocyanates are expensive, but formaldehyde-based resins are cheaper	[14–16,150,152,154,171]

Lignin incorporation as a polyol substitution into the NIPU matrix is expected to improve the final polymer's aromatic content. Lignin is moderately stable at high temperatures and is an aromatic and has a cross-linked substance [172,173]. The addition of lignin is therefore required to increase the temperature of glass transition and thermal stability of adhesives [174,175]. The structure, chain length, and several hard and soft segments are parameters that significantly affect the temperature of the glass transition, thermal decomposition, and the mechanical strength of the NIPU lignin-based compound [175]. Chahar et al. indicated that the shear strength decreases as polyethylene glycol (PEG) chain length is increased, and the NIPUs that contain 50% W/V of polyol have optimum characteristics (PEG with a molecular weight of 200). Additionally, the initial decomposition temperature increased to 50% W/V of polyol from 270 to 285 °C as lignin content increased [174]. The mechanical characteristics of polyurethanes are largely determined by the interconnecting density, which depends on their stoichiometry and functionality. Even though lignin substitutes polyol in the soft segment NIPU (NIPU structure), its aromatic structure normally makes it the tough segment, thus increasing the mechanical strength of lignin-based NIPU [175]. Lignin, because of its aromatic composition, typically enhances the mechanical resistance and thermal properties of blends, copolymers, and composites. Lignin affects the quantity and chemical composition of the final adhesive. It contains different functional groups, i.e., methoxyl, hydroxyl, and carbonyl groups, which allow its chemical modification, intended to increase its reactivity. The main reason for its application in the formulation of wood adhesives is due to its polyphenolic structure, mostly as a partial substitution of phenol (C₆H₆O) in PF resins. Lignin was reported to increase the thermal stability and cause phase separation, resulting in a poor stress transfer and eventually weakening the mechanical properties of end products. One of the key barriers to broader usage of condensing adhesives is the poor reactivity of lignin and lignin-derived compounds towards condensation reactions [174], delamination [171], and abrasion resis-

tance [176] by significantly adding it to the polyurethane matrix. However, with lignin volumes greater than 60% in total, the breakability is increased [175] and causes phase separation [177], resulting in a poor stress transfer and eventually deteriorated mechanical properties of end products [174,177,178].

Various methods of lignin modification, such as demethylation [179–182], hydroxy-methylation [183,184], phenolation [185–187], oxidation [188], etc. were reported to improve lignin reactivity. Among them, demethylation seems to be an efficient and forward-looking process [181,182], as certain aromatic methoxyl groups are converted into phenolic hydroxyl groups under mild reaction conditions. The proportion of reactive sites would therefore be increased [179,180], providing the presence of more catechol moieties in lignin and their reactivity enhanced by the use of HI [189], HCl [190], and various other hydrolysis reactions, fungi (white or brown-red fungi) [191], and bacteria (*Pseudomonas* or *Sphingomonas*) [192]. However, some disadvantages were determined, including environmental concerns such as acid state, high processing temperature (up to 225 °C) [179], longer processing time, and high processing pressure [182]. More effective approaches should therefore be preferred to replace these intense reaction conditions. In the demethylation phase, where a nucleophilic substitution reaction occurs between hydroxyl and sulphite ions, lignin is converted to sulphite pulp [179]. Then, aryl methyl ethers of aromatic compounds are broken down by nucleophilic substitution reactions with sulphite ions, resulting in a decrease in the methoxy group's content and an increase in the reactivity of modified lignin. Figure 6 shows the potential route of conversion of lignin to NIPUs. Demethylation of lignin could be performed using 1-dodekanetriol (DSH) and dimethylformamide (DMF). Because demethylated lignin has more phenolic hydroxyl groups, lignin has been regarded as building blocks for NIPUs. Carbonation with dimethyl carbonate may create carbonyl groups that can be used as precursors for NIPUs. The NIPUs are cured with the aid of hexamethylene diamine.

Polyester polyols synthesized from potato starch and vegetable oils by transesterification were used in the development of PU wood adhesives by reaction with toluene diisocyanate [193], with adhesive performance being similar or superior than the commercial synthetic PU adhesives.

Oxidation is a standard process used in the production of starch wood adhesives [194]. Recently, some researchers drew attention to the selective oxidation of plant meals in terms of their efficacy in the application of adhesives [195,196]. Periodate is a particular oxidant that cleaves carbon to carbon bonds, presenting vicinal aliphatic hydroxyl groups to form aldehydes and dialdehydes [195–197]. In certain instances, the lignin structural units present on their aliphatic portion both hydroxyl groups vicinal to the β -O-4 bonds to another lignin unit. The β -O-4 linkage is easily oxidized so that aldehydes and possibly dialdehydes are formed. Moreover, the more significant proportion of aromatic hydroxyl groups also increased aromatic ring reactivity due to demethylation. Thus, aldehydes formed by periodate oxidation are likely to respond to create a more robust hardened network at hydroxyl-activated reactive phenolic areas. This adhesive can be known as a bio-based product. In their study, Chen et al. aimed at improving and testing its bonding efficiency as a sustainable, lignin-derived wood adhesive that has a high biomass level without any external-added aldehydes by two steps: demethylation and oxidation. The sodium sulfite was synthesized under a moderate condition as a catalyst for directly mixed sodium periodate (NaIO_4) at atmospheric pressure [70]. Because certain methoxy groups have become phenolic hydroxyl groups through a nucleophilic substitution reaction, the process of demethylization will increase lignin reactivity so that more reactive areas can be formed in the lignin. A particular oxidant (NaIO_4) was added into the reaction system to enhance adhesive efficiency of demethylated lignin wood adhesives, due to its specific demethylated lignin precisely. Specific oxidation of carbohydrates and any other substance with carbons carrying vicinal hydroxyl groups by NaIO_4 is a well-known reaction in carbohydrate chemistry producing aldehyde groups. It was applied to demethylated lignin where it was able to cleave the aliphatic chains in lignin with a generation of aldehydes

that then contributed to the cross-linking of lignin. In lignin where the carbohydrates were not completely eliminated, the carbohydrates were also cleaved, producing a variety of aldehydes contributing fully to lignin cross-linking and hardening. This results in a more interconnected hardened network which produces a better bond strength and some water resistance. When the sum of NaIO_4 is 20%, bonded wood specimens' adhesion strengths reach a maximum value. Thus, it is shown that the adhesive form is a lignin adhesive without external aldehydes but with lignin-generated aldehydes by periodate treatment. It presents a high bio-mass material, has very convenient preparation, is low-cost and, can be applied to wood fastening [70].

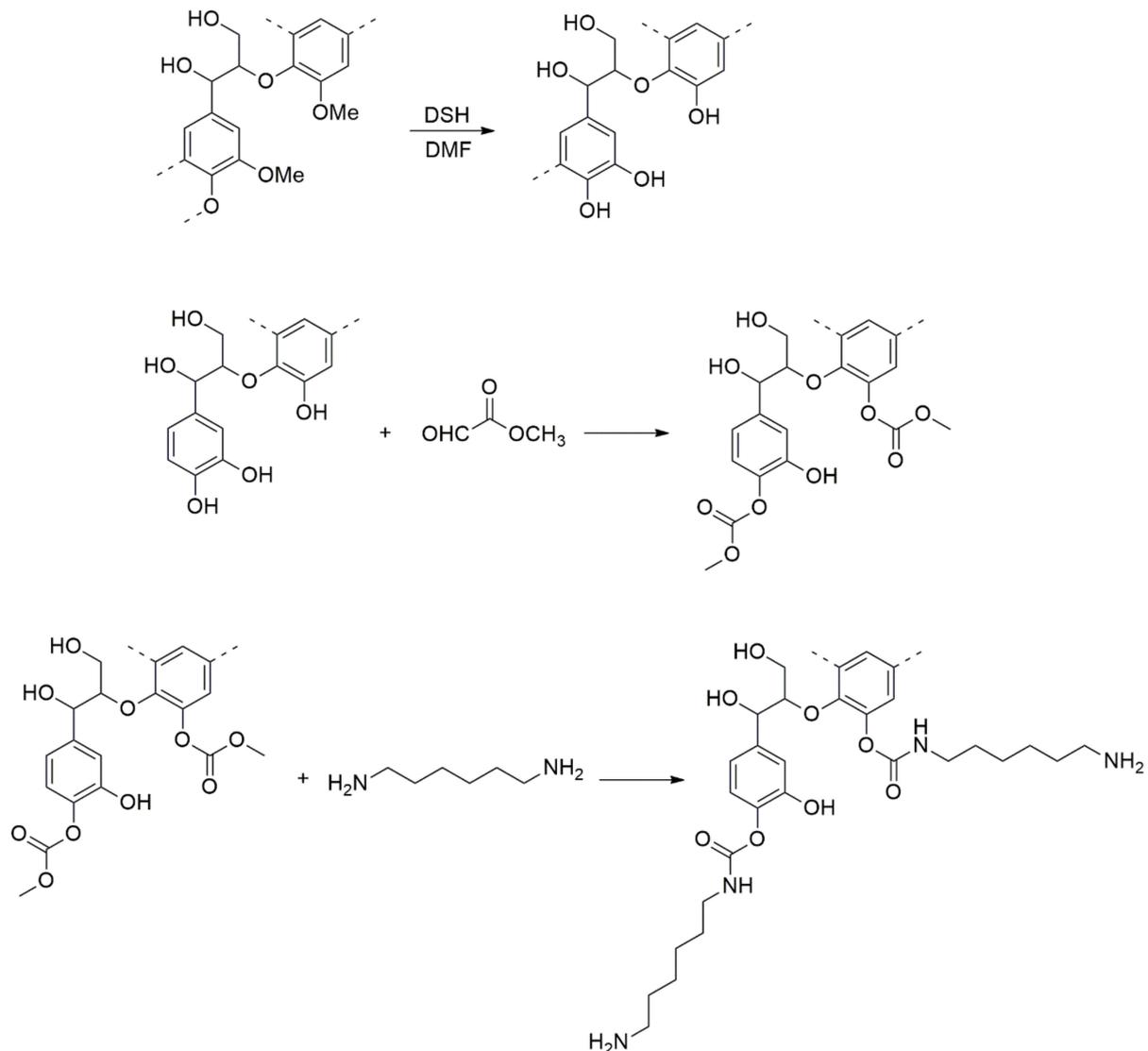


Figure 6. Possible pathway for reaction of lignin-based NIPUs by demethylation and carbonation [70].

Ravindra et al. have successfully synthesized lignin-based NIPUs for wood adhesives using lignins as part of polyol [198]. Adhesive lignin-based NIPUs were achieved by replacing 1%, 3%, and 5% of polypropylene glycol (PPG) with kraft lignin, and reacted further by monomeric diphenylmethane diisocyanate (MDI). In the stoichiometry, the aliphatic lignin hydroxyl level was not considered to determine how the end product would affect the 100% free NCO. Fourier-transform infrared spectroscopy (FTIR) was applied to test the chemical structures of the synthesized lignin-based NIPU adhesive. The lap shear strength of the adhesive was also tested. The results showed that by increasing

the weight % of lignin in such lignin-based NIPU adhesives, the free isocyanate content decreased (NCO). Toxicity was also decreased due to lower free NCO in the final wood adhesive. A slower setting time and better adherence to the wood substrate were observed compared with the standard PU, leading to a slower setting time, but higher shear strength values were observed. The existence of aromatic rings in lignin improved the hardness of the film. The thermal properties of the adhesive lignin-based NIPU showed that the system molecular weight and glass transition temperature increased with the increased lignin content. These findings support lignin-based NIPU adhesive production as a natural and renewable polyol, enabling this industrial waste to be reused into valued added applications [198]. Lignin-based NIPUs could be used to produce plywood and particle board that meet minimum requirement of the products. The addition of Na_2SO_3 , KH560 (Silane coupling agent), and NaIO_4 could enhance the adhesion strength of lignin-based NIPUs adhesives.

Table 3 Lignin-based PU adhesives and their application for wood the latest literature data on lignin-based PU adhesives and their application in the fabrication of wood-based composites. Lignin-based NIPUs could be used to produce plywood and particle board that meet minimum requirement of the products. The addition of Na_2SO_3 , KH560 (Silane coupling agent), and NaIO_4 could enhance the adhesion strength of lignin-based NIPUs adhesives.

Table 3. Lignin-based PU adhesives and their application for wood bonding.

Cross-Linker	Type of Wood Composite	Bonding Strength (MPa)	References
Na_2SO_3	Plywood	1.10	[199]
KH560 (Silane coupling agent)	Particleboard	1.06	[200]
NaIO_4	Plywood	1.72	[70]
Hexamine	Particleboard	0.77	[71]

5. Tannin-Derived NIPUs Adhesive

Tannins are natural phenolic compounds (polyhydroxy polyphenolics) available in many plants, including fruit, wood, leaves, and bark [38,201–203], but only a few species have adequate concentration to be isolated. Tannins can be easily extracted from a wide range of plants. The largest concentration of these chemical compounds is contained in the bark of tree species [204]. In modern polymer industries, they become increasingly useful because tannins have unique features such as anti-cancer, antimicrobial, antioxidant, or anti-inflammatory properties [205]. Extensive studies on the application of tannins in the development of tannin-based wood adhesives were carried out. Tannins were used because they are more reactive than phenol, but they are also costlier than phenol. Bark tannins were industrially used around 1850 in Lyon for the black coloring of silk for women's blouses and further used in leather production since the 1970s, but they have become more important for several other industrial uses in the last decades. Besides leather, tannins were utilized in the development of wood adhesives at an industrial scale [5,206,207], but extensive study into their use has led to a range of other potential uses, such as metal primers, pharmaceuticals, and many other applications. Extraction of plant material and subsequent purification of isolates, accompanied by spray drying, yield powdered tannins [59].

Tannins are usually graded as hydrolyzed and as condensed compounds in two major classes (polyflavonoid tannins). Hydrolyzable tannins are derivatives of gallic acid and are categorized according to products derived from their hydrolysis. They are also classified into gallotannins (comprised of gallic acid and glucose) and ellagitannins (comprised mainly of digallic and ellagic acids and penta-galloyl-glucose). They consist of various combinations, the main components of which are n-galloyl-glucose oligomers and their re-arrangement derivatives, such as vescaline and vescalagin. Pentagalloyl glucose and polyesters made of gallic acid and hexahydroxydiphenic acid are the central repeating unit

in the hydrolyzed tannin structure. Simple phenol structures of tannin are shown in Figure 7. The flavonoid units that have undergone different condensation degrees are composed of condensed tannin extracts (polyflavonoid). Their precursors (flavan-3-ols, flavan-3,4-diols), other flavonoid analogs, carbohydrates, and traces of amino- and imino-acids were always correlated with them [204,208]. Monoflavonoids and acids containing nitrogen are present in amounts that are much too small to affect the whole extract's chemical and physical characteristics. Nevertheless, simple carbohydrates (hexoses, pentoses, disaccharides) and complex glucuronates (hydrocolloid gums), also oligomers obtained from hydrolyzed hemicelluloses, are commonly present in sufficient amounts. Likewise, carbohydrate chains of varying lengths are also often connected to flavonoid units in tannins. It is also well known that tannins are vulnerable to modifications by hydrolysis, polymerization, copolymerization, or acetylation to produce new materials [209]. Esmaili et al. reported the preparation of carbonated glycidyl ethers of gallic acid and tannic acid by catalytic fixation of CO₂. Cyclic carbonates obtained were cured with amines in the next step to obtain new bio-resourced NIPUs using natural polyphenolic waste [205].

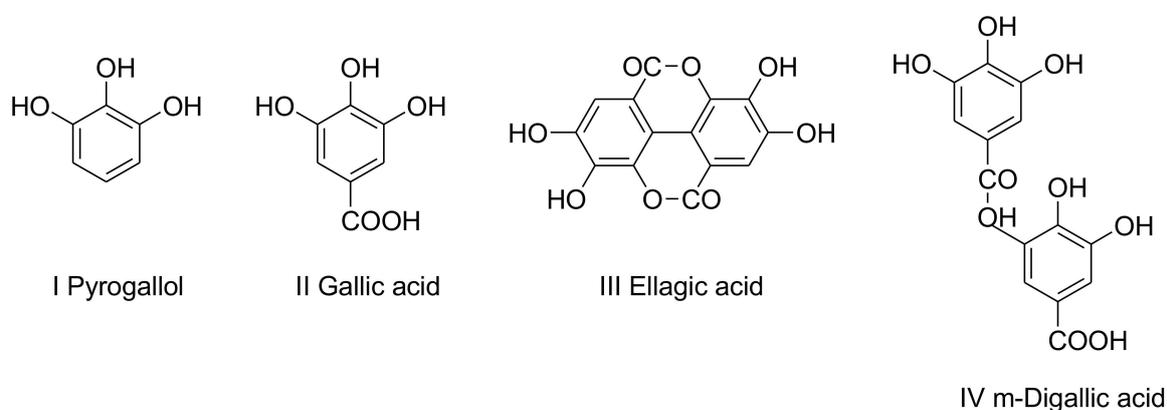


Figure 7. Simple phenol structures in tannin [210].

There are two main approaches for the development of PU adhesives from hydrolysable or condensed tannins. The first one involves modification of the flavonoid tannin to facilitate the reaction with isocyanates. The second method includes the use of a fully non-isocyanate approach to ensure the eco-friendly character or the formulated adhesives.

NIPU resins were recently designed to remove toxic isocyanates from their preparation by cyclically or bicyclically produced synthetic polyols followed by diamine reactions, some of which constitute the seminal approach to pioneer in working with this effective technique. Through this path, NIPUs were prepared with synthetic materials and several very different bio-based materials. Recently, tannins were used to manufacture NIPUs, particularly for surface coating, as well as other several applications. The preparation of tannin-based polyhydroxyurethanes is based on the carbonation of tannin with dimethyl carbonate and further reaction with hexamethylene diamine (Figure 8). As hexamethylene diamine is biosourced, it can be derived from furfural, so the prepared PUR is composed well in excess of 85% of biomaterials. In the course of these works, it was observed that tannins and carbohydrates in tannin extracts reacted to form NIPUs, especially in the case of the hydrolysable tannins, the backbone of which is rich in carbohydrates. This discovery then led to the attempt to acquire NIPUs from glucose and sucrose and apply them for various applications. Thus, mostly biosourced NIPUs were prepared from glucose and sucrose, by reaction with dimethyl carbonate and hexamethylene diamine, and the NIPUs oligomers obtained were determined. The glucose NIPUs resins were also tested as thermosetting wood joint adhesives and the sucrose NIPUs for particleboard adhesives with most encouraging results [211].

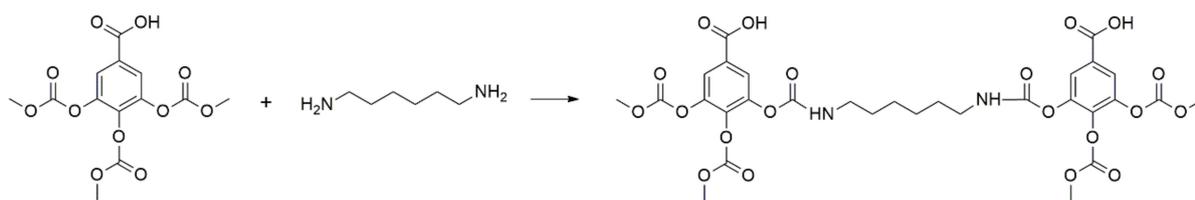


Figure 8. Scheme representation of the tannin-based non-isocyanate polyurethanes (NIPUs) preparation reaction obtained by reaction of hydroxyl groups of tannins with dimethyl carbonate and by hexamethylene diamine [211].

Several experimental improvements were studied concerning wood adhesives, which rely on the new environment in which wood adhesives should be used. The relative shortage of tannins produced worldwide resulted in numerous studies on the expansion of tannin resources in order to obtain greater amounts. Millions of tons of tannins can be extracted annually, and the extraction facilities have increased worldwide. This trend is still relatively small, but it is developing. The second approach is related to the expansion of the tannin with other abundant and natural raw materials, which led to the production and use of tannin furfuryl alcohol adhesive formulations and furfuryl alcohol as a bio-based material, as well as to the development of adhesives based on copolymers of tannins and lignin or copolymers of tannin and protein or soy flour [212–214]. Nevertheless, the main drawback of the second approach is related to the removal of formaldehyde emission from tannin-based adhesives. The first solution is to remove formaldehyde completely and replacing it with aldehydes that are less or non-toxic and non-volatile, e.g., glutaraldehyde, glyoxal, or vanillin, the latter to produce truly bio-based tannin adhesives with even aldehydes formed by a sodium periodate action on glucose, sucrose, or even oligomeric carbohydrates. The second solution is to apply nonaldehyde hardeners, such as tris(hydroxymethyl)nitromethane and tris(hydroxymethyl) aminomethane furfuryl alcohol, which also act as a hardener and contribute to a copolymer tannin/furan. Applying hexamine with $-\text{CH}_2-\text{NH}-\text{CH}_2-$ formation bridges between tannin molecules where the secondary amine can absorb formaldehyde emission from wood heating itself, as well as all other formaldehyde emissions, resulting in fully formaldehyde-free wood-based panels. Finally, the hardening of the tannins occurs by auto-condensation without the addition of a hardener, and auto-condensation is catalyzed by the wood substrate itself in the case of fast-acting procyanidin tannins, such as pine bark tannins, and for slower tannins by addition of silica or silicate or other accelerators [215–218], allowing the fabrication of particleboards for indoor applications [219].

Condensed tannins were used to develop tannin-based NIPUs, which reacted with dimethyl carbonate [22]. Then, hexamethylenediamine was applied to these mixtures to form urethane bonds. The resulting materials were analyzed by FTIR spectroscopy, Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrometry, and thermogravimetric analysis (TGA), and the resulting analysis suggested that the products obtained from tannins were polyurethanes. Tannin-based NIPUs adhesives cannot be dissolved, which means that part of their mass has been cured, and three-dimensional polymeric cross-linkages formed. However, some of the mass containing polyurethane oligomers could be dissolved for analysis with spectrometry from MALDI-ToF, which could provide interpretations supporting the existence of carbonated and urethane moieties; TGA analysis showed that such polyurethane begins to degrade at 180 to 200 °C, which is good enough for wood adhesive applications [22]. Table 4 reveals the latest literatures on tannin-based NIPUs adhesives and their application in wood-based panels. Tannin-based NIPUs could be used to produce particleboard and medium-density fiberboard. Incorporation of 2% cellulose nanofibers remarkably improved the adhesion performance of tannin-based NIPUs compared with only using hexamine [172].

Table 4. Tannin-based NIPUs adhesives and their application in wood-based panels [172].

Cross-Linker	Products	Bonding Strength (MPa)
1% Cellulose Nanofibers	Particleboard	0.96
2% Cellulose Nanofibers	Particleboard	0.98
3% Cellulose Nanofibers	Particleboard	0.86
Hexamine	Medium Density Fibreboard	0.15
Hexamine pH 9	Medium Density Fibreboard	0.45
Hexamine pH 10	Medium Density Fibreboard	0.65
Furfuryl Alcohol	Particleboard	0.40

6. Future Perspectives

Many scientists concentrated on a non-isocyanate process for PU production at the beginning of the 20th century [220]. The most significant drawbacks that led to an increase in interest in non-isocyanate methods for synthesizing green PUs are toxicity, susceptibility to moisture, and diisocyanate synthesis based on phosgenes [14]. To manufacture NIPU foams, Cornille et al. have been working on the isocyanate-free synthesis of PUs based on the reaction between diamines and cyclic carbonates [221–223]. The scientists reported that the most prospective alternative to Isocyanate PUs is polyhydroxyurethane (PHU). The cyclic carbonate aminolysis reaction can generate these materials. PHU is distinguished by its unique characteristics as higher tolerance to chemical degradation and higher adhesion and resistance to wear than standard PU materials because of the presence of hydroxyl groups in the principal macromolecular chain [150,224]. The results demonstrated that the future outlook of the NIPUs in the plastics industry is positive. All the above examples demonstrate that bio-renewable products are among the most popular products developing in the chemical industry sector. The research on bio-based components for PU synthesis confirmed that they have good characteristics as an alternative to the petroleum-derived components used.

Though NIPU research has been thoroughly developed over the recent years, NIPU synthesis still has an important issue, namely the cyclic carbonate amine reaction's low reactivity. Consequently, it is crucial to synthesize NIPU with a high response temperature and long reaction time, which means that the object NIPU curing takes a long time. The epoxy group can be used as a "bridge" to prepare solvent-based ambient curable NIPUs to improve the curing process. A modern hybrid NIPU epoxy resin, which has demonstrated well-balanced flexibility of traditional polyurethane resins and physical-chemical properties with conventional epoxy-amine [225]. The synthesis consists of two steps: creating an amine-finished NIPU and a small molecular epoxy resin chain extension. The response time for preparing NIPU has significantly decreased because epoxy-amine reactivity is much higher than that of cyclic carbonate-amine reactivity, and NIPU-epoxy hybrid resins are also very strong. However, these hybrid resins were still organic solvent-borne, and there are currently no waterborne NIPU-epoxy hybrid resins.

Due to the urgency of developing high-efficiency NIPU resins, other bio-based resources, such as adipic acid and 1,6-hexanediol, for the development of polyols will soon be made accessible [226–228]. The above chemicals are substrates for the manufacture of aliphatic polyester polyols. Aromatic monomers for PU synthesis gained more attention in recent years. The most important examples of chemicals that demonstrated a significant application in the development of polyester polyols and PU are 2,5-furandicarboxylic acid and vanillic acid [229]. Polyesters, e.g., furandicarboxylic acid, developed using the bio-based aromatic monomer, were investigated as an alternative to bio-based terephthalates. Polymers such as poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT), are all petroleum-based thermoplastic polymers. 2,5-furandicarboxylic acid and 1,4-butanediol are used to synthesize poly(butylene 2,5-furandicarboxylate) (PBF) [230,231]. The thermal properties of poly(butylene terephthalate) and poly(ethylene terephthalate) of petrochemical origin compare with the achieved thermal properties of PBF. Other bio-based aromatic monomers, which are essential ingredients

in the manufacturing of polyester, polyamides, or PUs, consist of 2,5-bis-(hydroxymethyl) furan and 2,5-diformylfuran. The above two monomers are derived from C6 sugar dehydration 5-hydrated hydroxymethylfurfural. Mou et al. investigated the synthesis of three monomers, 5,50-dihydroxymethyl furoin (DHMF), 5,50-bihydroxymethyl furil (BHMF), and 5,5-bihydroxymethyl hydrofuroin (BHMH), which could become precious components of PU materials [232,233]. PU materials were prepared and tested based on the new polyols obtained. A detailed description of all forms of organic polyester polyols (aliphatic and aromatic), along with the ever-growing range of new research in the field, provides realistic prospects to use entirely bio-based polyols at an industrial level.

Different chemical approaches were explored to synthesize new polyols and multi-isocyanates with triglycerides or fatty acids as starting materials. Cayli and Kusefoglu synthesized iodo isocyanate soybean oil by processing iodine isocyanate with double bond triglyceride in soybean oil [234]. Hojabri and others used oleic acid to manufacture 1,7-heptamethylene diisocyanate and 1,16-diisocyanatohexadec-8-ene. The processing first involves conversion of oleic acid into diacids then into diisocyanates. The investigators then prepared bio-based PUs for the material properties in a comparative analysis. The physical properties of PUs based on 1,7-heptamethylene diisocyanate are similar to those of petroleum-derived 1,6-hexamethylene diisocyanate, while Pus based on 1,16-diisocyanatohexadec-8-ene exhibited an even higher tensile strength than those typically derived from petroleum-based 1,7-heptamethylene diisocyanate [220].

7. Conclusions

Different approaches on synthesizing non-isocyanate polyurethanes (NIPUs) from lignin and tannin were comprehensively presented. Lignin and tannin have the potential to be used as an alternative material for polyols in the manufacture of polyurethane as wood adhesives. The polycondensation pathway synthesis of NIPUs is linked to the reaction between di- or polycarbamates and diols, di- or polycarbonates and amino alcohols or diamines, polychloroformate and polyamines, as well as polycarbamoyl chloride and polyol. Carbonation of lignin and tannin with dimethyl carbonate and a further reaction with hexamethylene diamine was reported, resulting in NIPUs based on lignin and tannin. Several studies confirmed that they have good characteristics as an alternative to the petroleum components concerned. The addition of Na₂SO₃, KH560 (Silane coupling agent), and NaIO₄ could enhance the adhesion strength of lignin-based NIPUs adhesives, while the incorporation of cellulose nanofibers and furfuryl alcohol remarkably improved the adhesion performance of tannin-based NIPUs.

The development of a non-isocyanate method for the production of NIPUs and their application in wood-based composites and plastic industry industries were also outlined. Different chemical approaches have been explored to synthesize new polyols and multi-isocyanates with triglycerides or fatty acids as starting materials. 5,5-dihydroxymethyl furoin, 5,5-bihydroxymethyl furil, and 5,5-bihydroxymethyl hydrofuroin could be converted into NIPUs. Oleic acid could also be used to manufacture 1,7-heptamethylene diisocyanate and 1,16-diisocyanatohexadec-8-ene. The properties of NIPUs based on 1,7-heptamethylene diisocyanate-derived oleic acid are similar to those of petroleum-derived 1,6-hexamethylene diisocyanate. Further, the NIPUs-based on 1,16-diisocyanatohexadec-8-ene exhibited an even higher tensile strength than those typically derived from petroleum-based 1,7-heptamethylene diisocyanate. All the above examples demonstrate that bio-renewable products can be used to produce NIPUs as an alternative to the petroleum-derived polyol and polyisocyanate.

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