Lignin as Renewable Building Block for Sustainable Polyurethanes

Subjects: Polymer Science

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Lignin, being a natural aromatic polymer rich in functional hydroxyl groups, has been drawing the interest of academia and industry for its valorization, especially for the development of polymeric materials. Among the different types of polymers that can be derived from lignin, polyurethanes (PUs) are amid the most important ones, especially due to their wide range of applications. Lignin, being a natural aromatic polymer rich in functional hydroxyl groups, has been drawing the interest of academia and industry for its valorization, especially for the development of polymeric materials. Among the different types of polymers that can be derived from lignin, polyurethanes (PUs) are amid the most important ones, especially due to their wide range of applications.

lignin polyols polyurethanes

1. Introduction

Polyurethanes (PUs) are among the most multifunctional polymeric materials. They are traditionally produced by the polyaddition reaction between a polyol (R–OH) and a diisocyanate (R–NCO), affording polymers that contain urethane linkages (–NH–CO–O–), also called carbamate esters, as schematically shown in **Figure 1**.

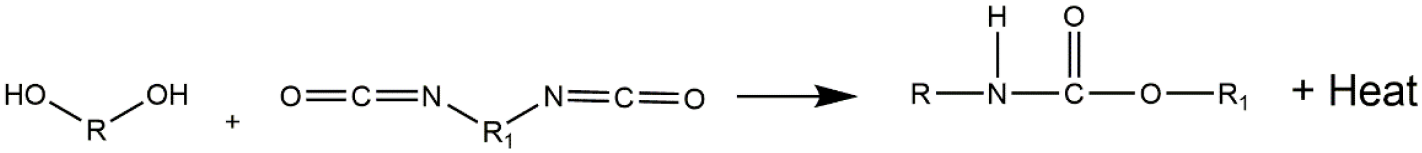

Figure 1. Schematic representation of the reaction between a polyol and a diisocyanate to form the urethane linkage.

The chemical structure of PUs contains soft segments and hard segments, the polyols being responsible for the soft part that contributes to the flexibility of PU chains, whereas isocyanates form hard segments and provide PU chains with rigidity. PUs have interesting properties such as low density, low thermal conductivity, mechanical strength, good chemical, and abrasion resistance [1][2]. These properties can be easily engineered by tuning their composition to suit various products such as foams (rigid and flexible), coatings, films, adhesives, elastomers, and other polymeric products that have versatile applications [3].

Industrially, almost all building blocks to produce PUs are derived from petroleum resources. In turn, isocyanates are produced by the reaction between amines and phosgene. Phosgene is a highly toxic gas produced from chlorine and carbon monoxide, which presents high risk to human health [4]. On the other hand, society's concern about the environment is one of the main issues of the 21st century. Recently, the Paris agreement signed by 196 countries aims for the world to be climate-neutral until 2050, which means reducing greenhouse gas emissions by 80% compared to the level of 1990 [5]. Concurrently, the PUs market size was valued at USD 72.82 billion in 2021 and is expected to expand at a compound annual growth rate (CAGR) of 4.3% from 2022 to 2030 [6]. In this context, both industry and academia have been developing strategies to replace or decrease the use of petrochemical resources and hazardous products with renewable and safer products that have at least the same characteristics as those of conventional products. One of the building blocks of polyurethanes, polyols, is already being produced using renewable resources, especially from vegetable oil. The main players in this kind of market are BASF SE, Bayer, Dow Chemical, Huntsman, Covestro, and Cargill [7]. Likewise, other industries are exploring new businesses involving market niches for their byproducts, for example, the pulp and paper industry.

Presently, the main purpose of the pulp and paper industry using the kraft pulping process is to remove enough lignin to separate cellulosic fibers from one another to produce suitable pulp and paper. In turn, up to now, the lignin present in the black liquor has been used essentially for heat and power production after the recovery of chemical reagents [8]. However, lignin contains some special characteristics, such as the abundance of hydroxyl groups (OH) that can contribute to the development of a novel generation of bio-based polyols and PUs, adding value to the byproduct of the pulp industry whilst reinforcing the circular economy and biorefinery approach [9][10]. **Figure 2** shows the main products involved in the transformation of lignin brown powder into a liquid polyol and finally into PUs foams and adhesives.

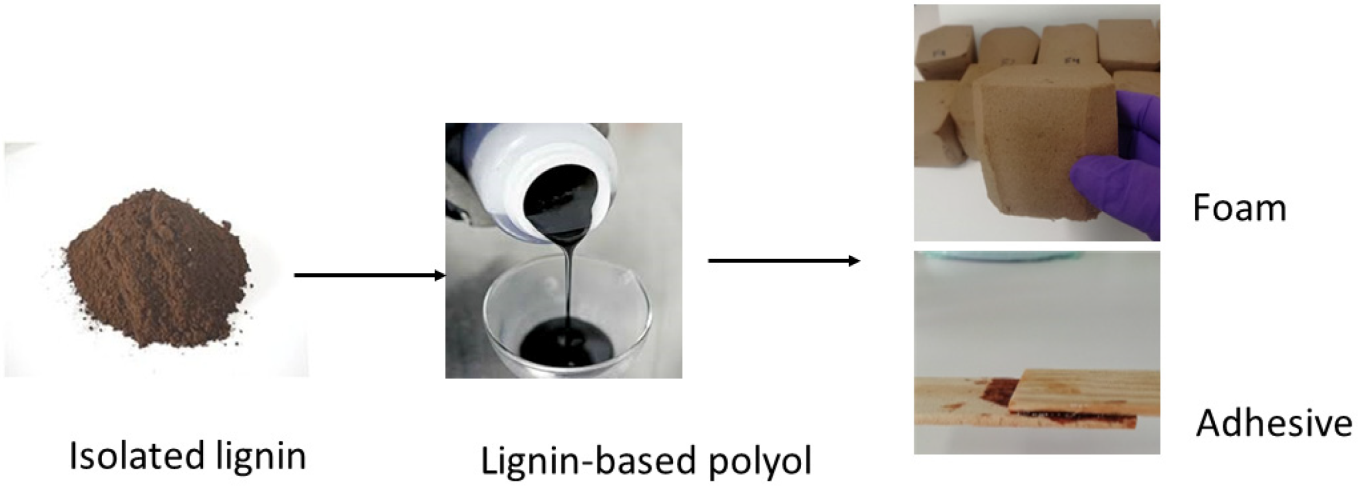

Figure 2. Polyurethane products from lignin-based polyol (LBP).

2. Lignin and Its Structural Features

Lignin is one of the most abundant natural polymers present in lignocellulosic biomass, representing 20–30% of the biomass; hence, it is a potential sustainable raw material for the development of novel PUs [11][12]. However, the development of lignin-derived polymeric materials and subsequent applications requires knowledge about the raw material, especially because lignin is a complex polymer, and its isolation processes can influence the final product.

Native lignin has an irregular and complex structure with high molecular weight, and it is highly branched and amorphous [11]. Its chemical structure consists of different types of phenylpropane units (PPUs or C_9), guaiacyl (G) and syringyl (S), and *p*-hydroxyphenyl (H) aromatic units, which differ in the number and position of the methoxyl groups on the aromatic ring, as presented in **Figure 3** as an example of hardwood lignin structure. These phenolic substructures are linked by C–O bonds (ether bonds such as β–O–4, α–O–4, and 4–O–5) and C–C bonds, as well as other bonds such as 5–5, β–5, β–1, and β–β. The amount and types of these phenylpropane units of lignin depend on the plant species and environmental conditions. For this reason, the molecular structure of lignin cannot be given exactly by a structural formula, but estimated from the elements (C, O, H) and methoxyl group [13].

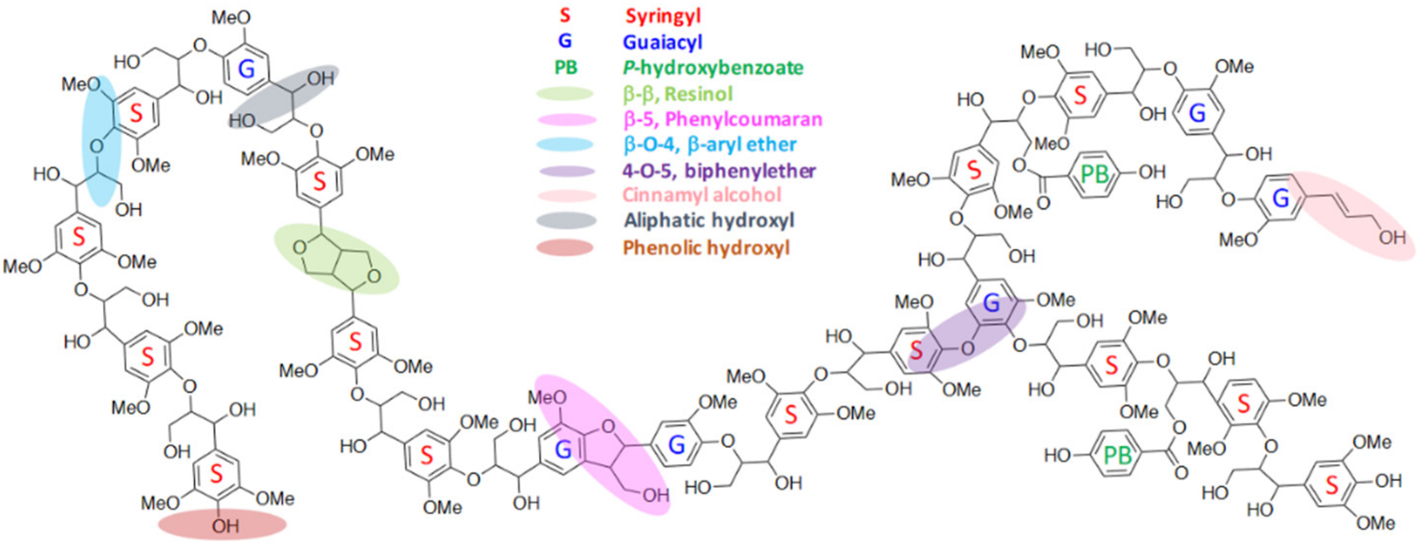

Figure 3. Example of hardwood lignin structure representation [13].

Hardwood trees (e.g., eucalyptus, beech) contain lignin with mainly S and G units. In turn, softwood trees (e.g., pine, spruce) contain lignins with mostly G units and low levels of H units. Grass lignin is made up of G, S, and H units in a wide range of proportions [14]. Furthermore, functional groups such as phenolic hydroxyl, aliphatic hydroxyl, carboxylic, and carbonyl groups attached to the basic phenylpropane skeleton of lignin have a great impact on their reactivity, optical properties, and dispersion characteristics. Methoxyl groups, though relatively less reactive, are also useful functional groups. From the amount of methoxyl group and elemental analysis (C, H, S, and O), the empirical formula of PPU (C_9) can be deduced [15].

3. Technical Lignins

Lignin can be isolated from different plants, but also from chemical pulping streams, which results in a technical lignin. The major production of industrial lignin comes from the pulp and paper industry, where most of the side streams are in the form of black liquor (annually, around 50–70 million tons are produced) which is mainly burned to supply internal energy and pulping reagents [16]. Commercially available technical lignins are often kraft, soda, and lignosulfonates associated with the corresponding industrial processes for wood delignification and cellulosic pulp production, e.g., kraft (using NaOH and Na_2S), soda (using NaOH), and sulfite (using aqueous sulfur dioxide), respectively. Another technical lignin is organosolv lignin, obtained by the delignification of wood using a mixture of water and organic solvents (mainly ethanol) with or without catalysts. The native lignin structure changes minimally during the organosolv process and the organosolv lignin is a good option for further functionalization/modification. Yet, this process is not in industrial use, because of technical concerns, extensive corrosion of the equipment, high energy consumption due to the solvents recovery process, and the lower quality of the pulp produced when compared to the kraft process [17][18]. Amid industrial processes, the kraft process is the most widely used (more than 90% of mills). After the kraft pulping, the black liquor is obtained (14–18% of solids), which contains mainly lignin as well as other chemical species, such as carboxylic acids and inorganics salts [19]. The black liquor is usually concentrated to 70–80% in a series of evaporation effects and burned in a recovery boiler to recover inorganic reagents and to produce steam and electricity. However, in most cases, the amount of black liquor exceeds the design limits of the recovery boiler, which represents the “bottleneck” of the process. A convenient way that can minimize this “bottleneck” is the acidification of black liquor. This leads to the precipitation of lignin from the black liquor which can subsequently be used for higher-value-added applications.

Regarding the technologies available to separate the kraft lignin from black liquor by acidification, the techniques are based on changing the solubility of lignin or fractioning [19][20][21]. The MeadWestvaco Corporation Company was one of the first to carry out the precipitation of kraft lignin using sulfuric acid at pH 2–3; this technical lignin is marketed as Indulin™. Kraft lignin obtained by acidification using mineral acids has noticeable amounts of ash, sulfur, and sugars, and the yield can be affected by high filtration resistance [19]. To avoid these constraints, Inventia company and Chalmers Technical University jointly developed a lignin extraction process based on the precipitation with CO_2 and acid, named the LignoBoost® process (process owned by Metso corporation). First, the black liquor is acidified with CO_2 at pH 9.0–10.5, precipitating the lignin. After flocculation, diluted sulfuric acid is added. In the last step, the lignin is isolated by filtration [21]. Presently, the kraft lignin isolated by the LignoBoost® process is commercialized by the Domtar company and marketed as BioChoice lignin. Recently, Stora Enso company is also producing LignoBoost lignin at 50,000 tons per year [22].

Although the LignoBoost® process provides lignin with high purity and solves the problem of filtration resistance that occurs with the acidification using strong acids, concerns about sulfur compounds (hydrogen sulfide, methyl mercaptan, dimethyl sulfide), that are malodorous and are hazardous to the health of humans, remain. FPInnovations group developed, in collaboration with NORAM Engineering company, the LignoForce™ process [23]. In this approach, before the acidification of black liquor with CO_2, the liquor is oxidized with O_2 until the sulfide concentration is reduced to a specific level and then follows the acidification and filtration steps, as illustrated in **Figure 4** [23].

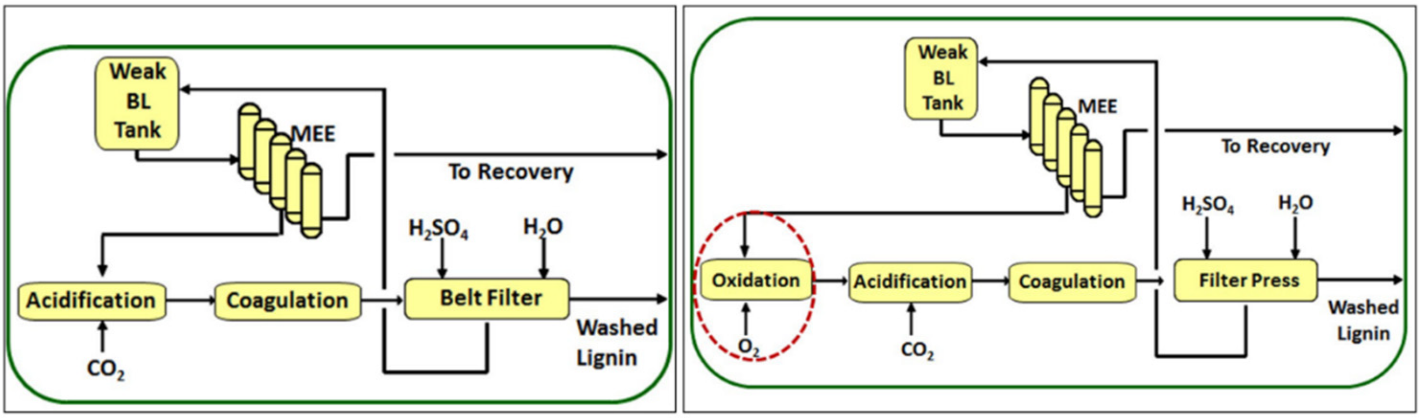

Figure 4. (**Left**) LignoBoost process; (**right**) LignoForce^{TM} [23].

When technical lignins are used for the preparation of polymeric materials, especially as a polyol in PUs synthesis, the quantification of hydroxyl groups and determination of molecular weight of lignin are the main chemical features but can be a constraint. In fact, both of these characteristics are related to the reactivity of lignin towards isocyanates, final properties, and applicability of PUs [24]. The reactivity of hydroxyl groups is highly dependent on steric hindrance factors, which explains why aliphatic OH groups are more reactive than phenolic OH groups [25].

4. Synthesis of Lignin-Based Polyether Polyols

4.1. Lignin-Based Polyol via Oxyalkylation Reaction

the oxyalkylation of lignin can be carried out using alkylene oxides, such as ethylene (EO) or propylene oxide (PO), by ring-opening polymerization yielding grafts of poly(propylene oxide or ethylene oxide) generally under basic conditions, high pressure, and high temperatures (usually 150–170 °C and 10–20 bar), as schematically illustrated in **Figure 5** [26]. Due to the safety risks involved in the manipulation of EO, the focus will be given to examples involving the use of PO, which is still a rather dangerous chemical to handle but does not require as strict safety operation conditions as EO. Acid catalysts can also be used, although the reaction is less efficient with phenolic OH groups [27]. In the oxyalkylation reactions, the hydroxyl groups of lignin, particularly the phenolic ones that are inside the molecule and difficult to access, are liberated from steric and/or electronic constraints, and, at the same time, the solid lignin becomes a liquid polyol, because of the introduction of multiple ether moieties.

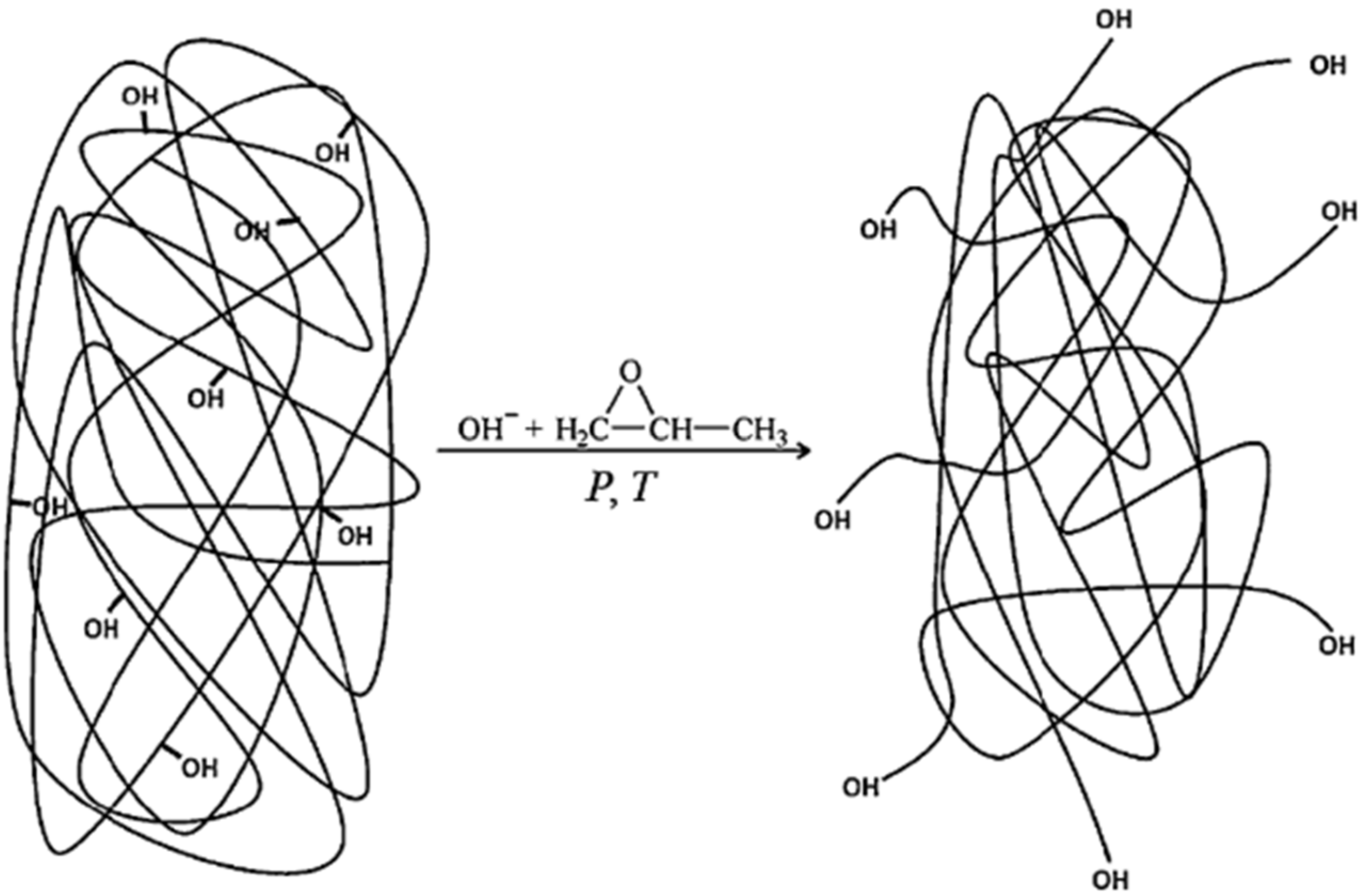

Figure 5. Scheme of oxypropylation reaction of biomass with PO [26].

Cyclic carbonates have been used over the years as reactive intermediates and inert solvents in several applications, such as carrier solvents applied in cosmetics and medications, as well as alkylating agents of phenolic resins. Cyclic carbonates can react with amines, alcohols, and carboxylic acids to initiate ring-opening polymerizations [28]. The first oxyalkylation of lignin using cyclic carbonates was reported in 1953 and patented by Monson and Dickson [29]. This patent described the oxyalkylation of a lignosulfonate using various types of cyclic organic carbonates, but this synthetic route has only recently been applied to other biomass residues. Oxyalkylation of lignins and tannins was recently performed using propylene carbonate (PC), yielding products that are structurally similar to those obtained by oxypropylation with PO [30][31]. Although PO is less expensive than cyclic carbonates, the latter present advantages compared to PO. Namely, the oxyalkylation with cyclic carbonates does not require high-pressure equipment nor the use of additional solvent because these compounds are high-boiling-point liquids and can act as reagent and solvent. In fact, their action as a solvent is an advantage in the alkylation of aromatic substances that have high melting points [28].

It is worth mentioning that the oxypropylation of biomass is also associated with the occurrence of side reactions, namely, the formation of significant amounts of homopolymer (e.g., poly(propylene) glycol), which has to be removed by solvent extraction with *n*-hexane [31][32]. Although the homopolymer is able to react with isocyanate to produce PUs, its proportion can affect the polyol quality and the yield of oxyalkylation reaction. The formation of homopolymer alongside oxyalkylation of biomass using cyclic carbonates has been mentioned in some works [33]

[34][35], and even crosslinking reactions have been reported involving chain coupling through transesterification reactions of biomass with cyclic carbonate [36], but this issue has not been discussed in depth. Usually, after the oxyalkylation, the product obtained is a mixture of oxyalkylated biomass, some unreacted cyclic carbonate, and perhaps homopolymer. Recently, Vieira et al. [34] performed the oxyalkylation of LignoBoost® kraft lignin with PC at 170 °C during 2.5 h using different catalysts and investigated the formation of homopolymer by high-performance liquid chromatography. It was concluded that only a minor proportion of PC (3–15%) was converted to propylene glycol/homoligomer.

4.2. Lignin-Based Polyol via Liquefaction with a Polyhydric Alcohol

An alternative to oxyalkylation with PO or cyclic carbonates is the liquefaction of lignin using polyhydric alcohols such as polyethylene glycol (PEG), polypropylene glycol (PPG), ethylene glycol (EG), glycerol, or a combination of them in the presence of acid or basic catalysts. The most frequently used conditions include the use of sulfuric acid (H_2SO_4) and moderate–high temperatures (110–180 °C) under atmospheric pressure [37][38][39][40][41]. When the reaction is carried out using base catalysts, higher temperatures are required; in general, 250 °C [42].

During the acid liquefaction of lignin, degradation and repolymerization are the main processes that occur. The hydroxyl groups of lignin are linked to the PEG and or glycerol via ether bonds in the liquefied product, but the mechanisms involved in this process are quite complex, and recondensation reactions have also been proposed [43]. The occurrence of these recondensation reactions between lignin and solvents takes place at the same time and competes against the liquefaction reaction. If these reactions are dominant, the percentage of residue increases, leading to lower efficiency of the liquefaction [44]. Many possible reaction paths have been proposed to explain the occurrence of side reactions and depolymerization of lignin. Jasiukaityté et al. [43] studied the structural changes of lignin during the liquefaction with glycerol and ethylene glycol. They confirmed the grafting of glycerol and diethylene glycol onto lignin at the Cα and Cγ positions associated with the increase in primary and secondary hydroxyl group content using ^{31}P NMR spectroscopy. The liquefaction of lignin was predominantly due to the condensation reactions between the aromatic lignin sub-units, as indicated by the decrease in total phenolic hydroxyl group content, followed by the incorporation of glycerol and diethylene glycol moieties [43][45].

Typically, the product obtained from the liquefaction process is a mixture of liquefied lignin and solid residue, the latter being a limiting factor of the liquefaction yield. To overcome or avoid the formation of residue and recondensation reactions, reaction parameters such as temperature, time, catalyst loading, and lignin/solvent ratio can be optimized. Furthermore, the choice of solvent type also has an important role in the production and characteristics of the polyol since the polyhydric alcohol works as solvent and polyol [38]. For instance, a mixture of polyethylene glycol (PEG 400, Mw: 400 g/mol) and glycerol is the most commonly used as liquefaction solvent to produce polyols for PUs foam production [37][39][41][46]. In addition, the use of glycerol has been reported to prevent recondensation reactions [47]. Regarding the solvent: lignin ratio (*w*/*w*), significant amounts of solvent are necessary to liquefy the lignin, which ranges between 3:1 and 9:1, to obtain high efficiency and minimize recondensation reactions. In fact, most of the studies found that the optimal solvent/lignin ratio is 5:1.

4.3. Quality of Lignin-Based Polyol and Its Characterization

For petroleum-derived polyols used in the preparation of polyurethanes, the main characteristics that are normally quantified are the content of hydroxyl groups (hydroxyl number, I_{OH}), the acid number of polyol, water content, viscosity, and molecular weight as they have a direct impact on the formulations. The required values depend on the type of PU to be produced, i.e., foams, films, or adhesives [3]. **Figure 6** schematically illustrates these main characteristics.

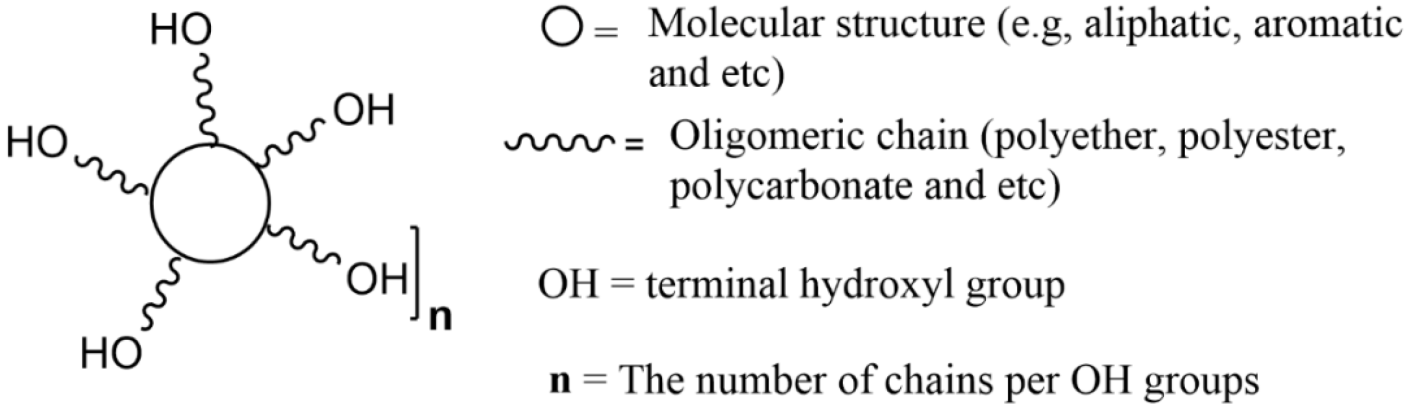

Figure 6. Scheme of the general formula of polyol, adapted from [2].

The hydroxyl number (I_{OH}) represents the amount of hydroxyl groups available for the reaction with isocyanates. The number can be determined by the reaction of the terminal hydroxyl groups using organic anhydrides (acetic anhydride or phthalic anhydride) [3]. The range of I_{OH} values of polyols required for the production of PUs is quite wide, e.g., polyether polyols used to produce rigid foams have I_{OH} values between 300–800 mg KOH/g, while for PU adhesives production the range of I_{OH} values is usually lower [3][48].

The acid number is related to the amount (in mg) of potassium hydroxide needed to neutralize one gram of sample [49]. The importance of the acid number is due to the fact that the presence of residual acidity decreases the catalytic activity of the tertiary amines used in the reaction of polyols with isocyanates to produce PUs. For polyurethane formulations, the acid number should be around 0.05–0.1 mg KOH/g for polyether polyols, and 2 mg KOH/g for polyester polyols [26].

Water content is also an important issue since isocyanate groups are highly reactive towards water; thus, it competes with the hydroxyl groups of polyols during the synthesis of PUs. The determination of this characteristic is carried out by the classical Karl Fischer method, and the required values for producing PUs are between 0.05–0.1% [3].

Viscosity indicates the processability of a polyol, which can be determined using a Brookfield viscosimeter or a rheometer. Furthermore, it can provide an indication of the reactivity of a polyol with an isocyanate to afford the final PU. It was observed that polyols with low reactivity (0% primary hydroxyl, i.e., having only secondary hydroxyl groups) have the lowest viscosity increase over time. In turn, highly reactive polyols, having 85–100% primary hydroxyl content, have the highest viscosity increase over time [3]. For the production of PUs, the range of viscosities can be wide, depending of the type of PU, but must be below 300 Pa.s [26].

The molecular weight (MW) and polydispersity of polyols can be rigorously determined by size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC). The molar mass sensitive detection is based on both viscometry and universal calibration [50]. The MW is an important parameter because this feature will impact the network structure and crosslinking density, which influences the physical properties of PUs. Generally, for use in the production of polyurethane foam (PUF), polyols that have large MW will lead to amorphous regions that impart flexibility to Pus, whilst polyols with low MW will lead to rigid PUs [3]. Regarding the required values for PU production, in general, polyols have MW in the range of 400–5000 Da, depending on the type of PU product [51].

Since lignin has a very complex structure and variable characteristics, LBPs must be well characterized in order to better predict the behavior of the ensuing PUs and understand the relationship between the structure of the polyol and the properties of PUs. The difficulty in characterizing these structures has led many researchers to characterize only the most essential features of LBPs such as the I_{OH}, viscosity, and MW, as is normally performed for petroleum-based polyols, as mentioned earlier. Nevertheless, the characterization of LBPs can be quite complex and can present some challenges. Hence, it must be performed carefully, and sometimes different methods need to be used when compared to their petroleum-based counterparts. For example, the determination of the number of terminal hydroxyl groups of petroleum-based polyols involves the esterification of the alcohols with acetic anhydride or phthalic anhydride using solvents/catalyst such as pyridine or N-methylimidazole [52]. However, the dark color of LBPs can induce significant errors during the conventional titration using phenolphthalein as an indicator. Potentiometric titration circumvents the problem, but sterically hindered alcohols and phenolic alcohols present in LBPs can result in some inaccuracies. The alternative is to use ^{1}H NMR and ^{13}C NMR spectroscopies to quantify the number of hydroxyl groups [53].

GPC is one of the most commonly used techniques to determine the average molecular weight of polyols. The eluents used can be organic solvents (THF, DMF, or DMSO) [54]. Polystyrene standards are frequently used to obtain the calibration curve, though in the case of lignosulfonates, polystyrene sulfonates standards have also been used. With regard to the detectors and characteristics of the columns, the ultraviolet (UV) or refractive index (RI) detectors are the most common, whilst the type of column depends on the molar mass range of the polymer and eluent compatibility. Yet, care should be taken for lignin-derived polyols because the UV detector is not always accurate, due to the different extinction coefficient of lignin fractions. Typically, mixed pore columns are preferred due to the larger range of linear calibration. However, LBPs can present some issues due to their complex structure.

5. Lignin as a Building Block to Synthesize Polyurethanes

The use of lignin in the production of PUs can be carried out in different ways: unmodified, being directly incorporated into polyol formulations, after fractionation, or after chemical modification (in order to make it more reactive), alone, or in combination with other polyols [24][25][55][56][57][58][59][60]. Depending on its interaction with the isocyanate, lignin can act as filler or as reagent, i.e., as polyol, also referred to as cross-linker. Although the use of lignin without any treatment is widely reported, if its OH groups do not react with the isocyanate and become chemically bonded to the PU network, it should not be described as a building block. The direct exploitation of lignin, as a polyol on its own or blended with industrial polyols, is energetically and environmentally advantageous [61], and the ensuing biomass-based PUs are more biodegradable than those derived from petroleum-based polyols. Even though the direct use of lignin as the only polyol can be very appealing, generally, lignin macromonomers have low reactivity towards isocyanate groups yielding products without the desirable performance, and end up acting essentially as fillers [24][62][63].

Recent advances to circumvent the drawbacks of direct incorporation of lignin as polyol in the production of PUs include (1) the use of diols and glycerol as compatibilizer and cross-linker, and (2) lowering the lignin molecular weight using solvent fractionation. Since kraft lignin is the most commonly produced technical lignin, most of the studies are focused on this type of lignin. For example, Haridevan et al. [64] recently evaluated the dispersion and solubility of kraft lignin in different types of polyols at room temperature for the production of polyurethanes based on microscopic, gravimetric, and rheological analyses. The study demonstrated that kraft lignin has different degrees of dispersion in various polyols, depending on the structural characteristics such as solubility parameter, molecular weight, and monomeric unit type. In fact, it was observed that a higher degree of dispersion of kraft lignin was achieved in the lower-molecular-weight diethylene glycol (106.1 g/mol) than in polyethylene glycol (400 g/mol). Although the low dispersibility of lignin in polyols has not yet been solved, systematic studies such as this one are important contributions to increase lignin dispersion. In addition, the performance of PUs can be improved by heating the polyol/lignin dispersions at 120 °C prior to the reaction, which enhances the disaggregation of lignin microparticles, yielding a better lignin dispersion within the polyol system [65][66]. On the other hand, reducing the kraft lignin molecular weight by solvent fractionation can enhance its miscibility and dispersion in the PU matrix, and consequently can improve some properties of the resulting PU such as the mechanical properties [67]. The use of binary organic solvent mixtures such as acetone–methanol [68], aqueous two-phase systems (ATPSs) composed of $(NH_4)_2SO_4$ and ethanol [69], and the use of ionic liquids [70] are examples of strategies used to reduce the molecular weight of lignin as well as its heterogeneity. However, it is important to take into account that commercializing low-molecular-weight lignin has been economically unfeasible until now.

In addition to PUF, different types of lignins and LBPs have also been used to prepare other forms of Pus, such as adhesives [71][72][73], elastomers [74][75][76], coatings [77][78], and films [79]. Elastomeric PUs are a class of PU materials that have the characteristics of rubber, and their application has increased in recent years due to the high demand for advanced applications such as in biomedicine, shape memory materials, self-healing materials, and gel materials. Mechanical properties such as toughness, tensile strength, and high elongation at break are highly desirable for the production of PU elastomers, and the use of modified or unmodified lignin in the synthesis of PU elastomers has shown that it plays an important role in improving these properties, where a percentage of lignin up to 40 wt.% (based on mass of polyol) did not jeopardize their mechanical properties [80][81][82].

In conclusion, the properties of lignin have a profound impact on the resulting PU product performance, e.g., foams, elastomers, coatings, and films, regardless of the lignin source and isolation process [77][78][80]. Nevertheless, with the exception of a few examples, the exact role of the structural features of lignin during the reaction with isocyanates is hardly discussed. Instead, the mixture of unmodified lignin with other polyols or of LBPs is treated globally as the polyol component of the PU. Yet, with the advancement of fractionation methodologies, a better understanding of the role of structural features of this renewable OH-rich aromatic material will certainly become clearer and bring further insights.

6. Lignin as a Building Block to Synthesize Non-Isocyanate Polyurethane (NIPU)

The industrial synthesis of isocyanates involves the reaction between primary amines and phosgene at high temperatures (100–200 °C). The latter is a highly toxic gas, produced by the reaction between carbon monoxide and chlorine gas. In turn, diisocyanates cause acute adverse health effects, such as irritation of the respiratory tract, eyes, and skin, being a major cause of occupational asthma in workers employed by the polyurethane industry [83][84][85][86][87]. Moreover, the two most widely used isocyanates in the PU industry, MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate), are highly reactive chemicals that bind to DNA and are probably genotoxic [88]. Furthermore, various household PU products, such as mattresses, pillows, cushion packaging, and insulating materials in building construction, among others, exhibit detrimental environmental impact on aquatic life, soil health, plants, and humans due to the presence of toxic components such as isocyanates, flame retardants, and amine-based catalysts [89]. Additionally, some compounds, such as carbon dioxide, carbon monoxide, hydrogen cyanide, acetaldehyde, and methanol, are released when PU products are burned and/or landfilled at their end-life, contributing to the greenhouse effect and having toxic effects on human health [90][91]. All these reported issues led the European Union to adopt the regulation where it was proposed to reduce the content of isocyanate, with the main goal being to ban its use in the future [92].

There are a few routes described in the literature to synthetize NIPU, but the main ones are the rearrangement of acyl azide, the ring-opening polymerization of cyclic carbamates, the polycondensation (or transurethanization) between polycarbamate and polyol, and the polyaddition between bis-cyclic carbonate and diamines. Recently, some works [90][93][94][95] dedicated to exploring the synthesis of NIPU were published, which identified that the most promising routes to produce NIPU are polycondensation and polyaddition (**Figure 7**).

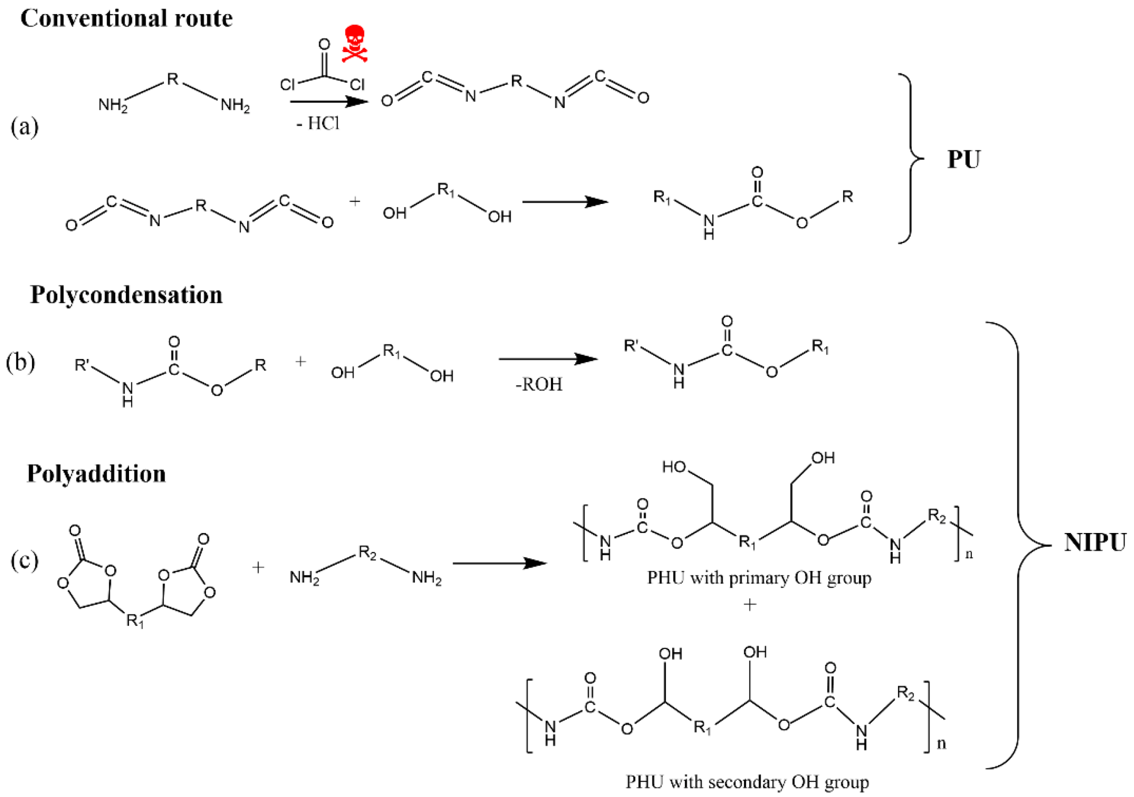

Figure 7. Chemical routes to produce PU by (**a**) conventional route, NIPU by (**b**) polycondensation, and (**c**) polyaddition.

The polycondensation reaction between carbamate monomers (bis-alkylcarbamates or bis-hydroxyalkylcarbamate) and a polyol affording urethane linkages have similar features compared to conventional PU. However, the polycondensation between bis-alkyl carbamates and polyol requires longer reaction times (over 24 h), higher temperatures (100–200 °C), and involves the formation of low-molecular-weight byproducts (i.e., methanol). Altogether, this has limited the extension of polycondensation on a commercial scale [96].

Another approach to obtaining NIPU involves the polyaddition of di- or polyamines to bis-cyclic carbonate, yielding poly(hydroxy urethane)s (PHUs). The most common cyclic carbonates used to synthetize PHUs are five-membered cyclic carbonates, such as EC, PC, GC, and VEC (mentioned in Section 4.1), and are already commercially available. Nowadays, the main route used to produce these cyclic carbonates is the carboxylation of epoxides, which is a less environmentally aggressive approach when compared to the previous synthetic route involving phosgene.

Beyond the strategies using phosgene-free routes to replace isocyanates, renewable resources have been extensively investigated to produce NIPU to obtain safe and green products. Recently, interesting papers were published, mainly focused on the synthesis of intermediate cyclic carbonates derived from renewable resources and their reaction with polyamines to produce bio-based NIPU [97][98][99].

An alternative to the isolation of specific aromatic compounds from lignin is its use as a macromonomer in the synthesis of NIPU.

Kraft lignin powder was also reacted directly with DMC and then with a diamine (e.g., HDMA) to yield NIPU. The products obtained were tested as coatings on the surface of beech wood [100]. In the same line of research, Arias et al. [101] prepared NIPU bio-adhesives for wood panels, reacting kraft lignin, organosolv lignin, tannin, and soy protein with DMC, and the intermediate products were reacted with hexamethylenediamine (HDMA). The research group evaluated the environmental profiles of these novel adhesives using the life cycle assessment (LCA) methodology and compared them with formaldehyde-based resins. The results showed that these bio-adhesives have the potential to replace synthetic resins, as they have a lower damage score than phenol-formaldehyde resin.

Although it is clear that lignin has high potential to be used as a macromonomer in the synthesis of cyclic carbonates or even in the direct production of NIPU, its application still requires much research to further tailor the process and properties of these novel cyclic carbonates and NIPU.

7. Concludsion

On the one hand, technical lignin is a byproduct of the pulp and paper industry that consists of natural aromatic polymers with high carbon content and is a valuable energy source. For example, in the kraft pulp industry, lignin is used entirely for energy recovery. On the other hand, technical lignin has great potential to replace, at least partially, petroleum-based polyols used in the formulation of PU products. Yet, at the moment, to obtain an LBP that is competitive with petroleum-based polyols in terms of characteristics and price is still a challenge. Indeed, there is an old saying among the lignin experts: “you can make anything out of lignin, except money”. This is due to the difficulties involved in obtaining technical lignin with homogenous reproducible characteristics, the cost to convert the solid lignin in a liquid polyol or other chemicals, and the poor compatibility of lignin with many synthetic polymers. However, the pulp and paper industry, in cooperation with the chemical industry, have shown that it is possible to earn money from lignin, otherwise companies would not be investing in it. Although LBPs are not yet on the market, polyurethane foams with added lignin (20–25 wt.%) in the formulations are already a reality in the market. Furthermore, developments regarding the depolymerization and fractionation of lignin into well-defined oligomonomers are required to avoid the need for chemical modification. Indeed, these developments will also contribute to a better understanding of the relevance of the structural features of lignin during the reaction with isocyanates and/or other chemicals, as well as their exact impact on the properties of the ensuing PUs. Likewise, in-depth studies regarding the dissolution of lignin into polyols, especially those obtained from renewable resources, show that this is also a challenge, and an opportunity exists to make the use of this rich and versatile material economically and environmentally viable. As final recommendations on the development of lignin-based polyurethanes, researchers and industry should pay attention to LCA studies and technical–economic assessments. These studies are of paramount importance to find solutions regarding current challenges, such as technology scaling up for lignins and LBPs, high process and product cost, and different environmental and social impacts, as well as regulatory and policy implications.

Beyond the development of bio-based polyols to produce polyurethanes, significant efforts have also been made to replace the toxic isocyanate, developing non-isocyanate polyurethane. The main chemical route employed is the reaction between cyclic carbonates and diamines. Moreover, in recent years, lignin has been studied as a building block in the synthesis of cyclic carbonates for the development of new isocyanate-free polyurethanes. It is evident that there are still many challenges to be overcome, but what is expected is that in the future, technical lignin will be used as a raw material for the production of polymeric products such as polyurethanes, and not just burnt for energy, thus contributing to a more sustainable society.

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