

On Polyurethanes from Technical Lignin: Recent Advances and Challenges

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Abstract

The valorization of biomass lignin to renewable polyurethanes is a promising pathway for producing renewable plastics, provided that the process can be realized cost-effectively using environmentally sustainable methods. Due to its natural polymeric structure and diverse chemical functionality, lignin has been highly regarded as both an abundant and inexpensive bioresource that is capable of displacing conventional polyols for synthesis of polyurethane materials. Numerous efforts and resources have been invested in lignin-polyurethane research in the past decades. Like other lignin-containing/based polymeric materials, research efforts are progressing toward commercial applications. This review highlights the progress we made in the applications of technical/co-product lignin in polyurethane materials. We also outline recent strategies for synthesis of lignin-polyurethanes that have been developed based on the fundamental understanding of lignin physicochemical properties and molecular characteristics.

Key Words and Phrases

Lignin-Polyurethane, Correlation between Lignin Molecular Structure and PU Mechanical Properties, Rigid PU Foams, Valorization

1. A Brief History of Lignin-Polyurethanes

Since its invention in the early 20th century, polyurethane (PU), like other synthetic polymers, has evolved to now become an essential component for modern human society. A classical PU formulation involves three major components: (1) poly/diisocyanates, (2) polyols, and (3) chain extenders [1]. Chain extenders are usually aliphatic or aromatic diols and diamines employed to build up the polymer molecular weight and increase the block length of hard segments by reacting with the isocyanate compounds [2]. PUs can be synthesized by one-shot or prepolymer methods. For the one-shot method, polyols, isocyanates, and chain extenders are mixed and polymerize simultaneously. The prepolymer and segmented synthesis methods can produce PU macromolecules with more ordered structure and controlled properties by reacting a prepolymer with isocyanate end-groups with a chain extender. Depending on the chain flexibility, crystallinity, interchain interactions, and crosslinking density, PUs can be converted into rigid/flexible foams, adhesives, elastomers, synthetic fibers, thermoplastics, or coatings. Nowadays, the worldwide PU industry is responsible for millions of jobs and billions of dollars in economic output. PU products have been widely applied for household goods, building materials, aerospace, automotive manufacturing, and medical devices [3]. The global PU market is expected to grow at a 12% annual rate and reach \$150 billion in sales by 2023 [4].

The production of petroleum-based polyols requires massive energy inputs and creates environmental concerns. Searching for biomass-derived polyols has been an ongoing pursuit for both industrial and academic scientists. Lignin, a heterogeneous polymer found in terrestrial plant cell walls, is recognized as the second most abundant biopolymer, next to cellulose. The chemical composition of native lignin in plant cell wall varies depending on the plant species. Generally, the molecular backbone of lignin is built up from mostly guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) subunits that are connected by a variety of interunit linkages such as β -O-4' (β -aryl ether), β -5' (phenylcoumaran), β - β' (resinol), 5-5' (biphenyl), 4-O-5' (diaryl ether), and β -1 (spirodienone) (Figure 1) [5]-[7]. Technical lignin is a group of by-products obtained from pulp and paper industries with annual production of ~1.1 million tons, mainly from sulfite, Kraft, soda, and organosolv processes [8]. The molecular structure of technical lignin undergoes significant changes depending on the conditions and chemicals applied for pulping. However, as in its native form, most technical lignin has a high molecular weight and is composed largely of phenolic and aliphatic hydroxyl and carbonyl groups and other functional groups [2]. These characteristics can potentially position technical lignin for high-value applications in PU materials.

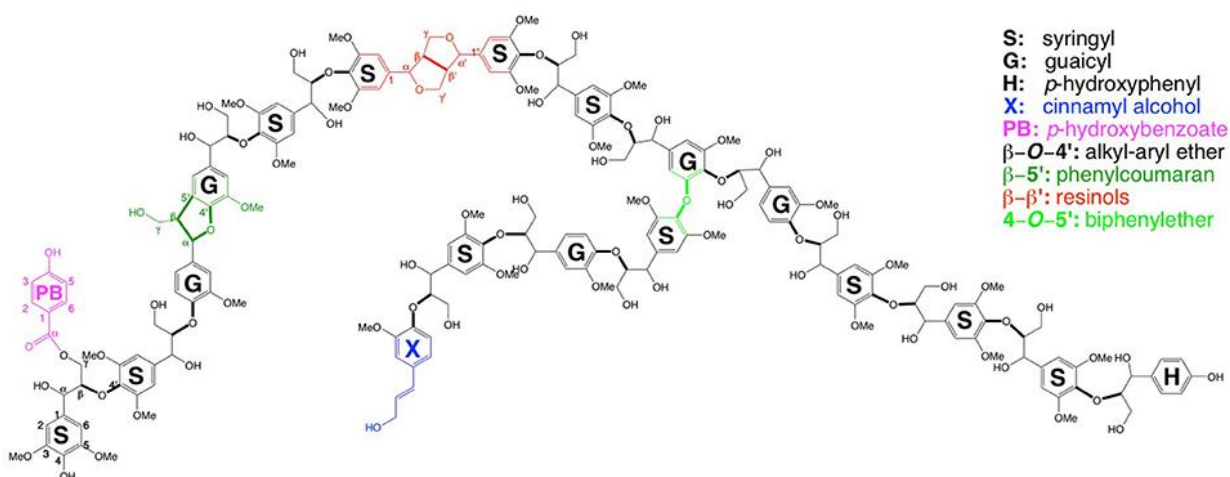


Fig. 1 A structural model of hardwood lignin [7]. Adapted with permission from [7].

As depicted in Figure 1, a native lignin macromolecule exhibits a hyper-branched structure with multiple functional groups that can allow lignin to crosslink with other polymers/monomers to form thermosetting networks. Given its unique chemical structure, association/aggregation behaviors have been observed when lignin macromolecules are dissolved in organic or aqueous media and blended with other polymers [9]. Such strong intermolecular interactions have been attributed to hydrogen bonding and π - π electron association of the aromatic rings [10], [11]. For blends or composites containing lignin, poor miscibility (weak interaction between lignin and other components) frequently results in rapid deterioration of mechanical properties if the lignin content is increased too much. [9] When lignin is crosslinked with other polymers in a solvent, a homogeneous network can be formed by delaying phase separation or demixing that occurs when the change in Gibbs free energy of mixing ($\Delta G_{\text{mixing}} = \Delta H_{\text{mixing}} - T\Delta S_{\text{mixing}}$), rises above 0 [12]. Therefore, the upper limit of lignin content in a crosslinked network could be increased by enhancing the lignin solubility through lowering its molecular weight and/or reducing its hydrogen-bonding capacity [13].

Disrupting the intra- and intermolecular hydrogen bonds can be achieved by chemical modification of lignin hydroxyl groups. For example, Kraft lignin had sufficient solubility in organic solvents after reacting with alkylene oxides that its hydroxypropyl derivatives crosslinked

with isocyanates to produce wood adhesives, engineered plastics, rigid foams, and films [14]-[17]. Lowering lignin molecular weight can be realized by chemical or biological degradation. However, reactions may bring in unanticipated structural modifications and impurities. Solvent-based fractionation has been a popular method to fractionate the parent technical lignins according to their molecular weight ranges. Kelley *et al.* demonstrated that fractionated hydroxypropyl Kraft lignin produced PU films with strength properties superior to those from unfractionated lignin [18]. The low-molecular-weight lignin cuts were usually enriched with hydroxyl groups and very soluble in the organic solvents, and thus they could be separated from the parent technical lignin by solvent-extraction. These low-molecular-weight technical lignin cuts are excellent polyol replacements that can be applied, without any chemical modification, for synthesis of PU coatings and adhesives [19], [20].

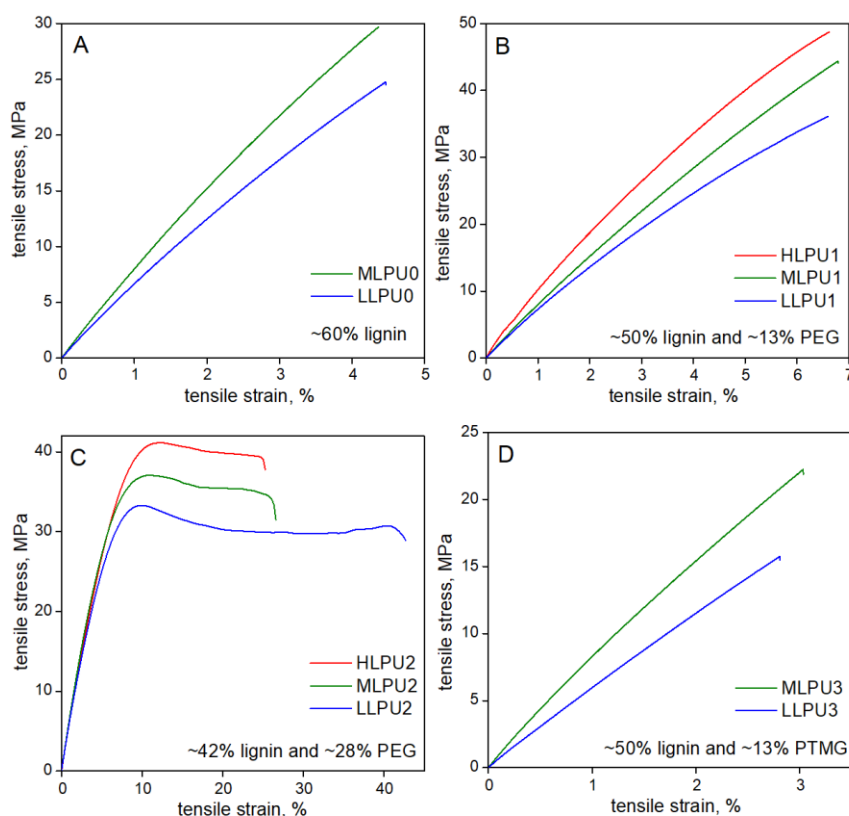


Fig. 2 The tensile properties of (A) medium-molecular-weight lignin PU (MLPU) and low-molecular-weight lignin PU (LLPU) using Kraft lignin as the sole hydroxyl provider; (B) high-molecular-weight lignin PU (HLPU), MLPU, and LLPU containing ~50 wt% lignin and ~13 wt% poly(ethylene glycol) (PEG), (C) HLPU, MLPU and LLPU containing ~42 wt% lignin and ~28 wt% PEG, and (D) MLPU and LLPU containing ~50 wt% lignin and ~13wt% poly(trimethylene glutarate) (PTMG) [21]. Reprinted with permission from [21]. Copyright 2019 American Chemical Society.

2. Recent Advances in Lignin-PU materials

This section summarizes our progress over the past decade in fabricating high-performance lignin-PU materials with high lignin content. It covers two aspects: 1) increasing the upper limit of lignin content incorporated into PU networks and 2) incorporating of lignin into PU materials. As discussed in the previous section, reducing the lignin molecular weight can enhance its miscibility and dispersion in the PU matrix and consequently improve the final PU mechanical properties. Our group developed a simple and fast fractionation method to isolate technical lignin cuts according to targeted molecular weights and simultaneously remove impurities such as ash, salt, and carbohydrates [22]. In brief, a binary solvent mixture was prepared based on the Hansen solubility

parameters to optimize the solubility of the target technical lignin in the mixture. Then the resulting material was fractionated by sequential precipitation by the gradual addition of a nonpolar solvent such as hexane. As the solvent environment changed with the increasing polarity of the solvent mixture, the precipitated fractions showed a strong correlation with lignin molecular weight rather than concentration of hydroxyl and other polar functional groups.

By employing this method, softwood Kraft lignin was refined with an acetone-methanol-hexane solvent system to obtain well-defined molecular weight cuts with high, medium, and low molecular weights ($M_w \sim 54000$ g/mol, ~ 15000 g/mol and, ~ 4000 g/mol). These fractions were combined with a small portion of polyester or polyether to prepare lignin-based PUs by solvent casting from THF [21]. As shown in Figure 2, the mechanical strength of Kraft lignin-based PU was enhanced by lignin molecular weights provided the medium and low-molecular-weight Kraft lignin cuts complete dissolved in THF. A polyether, polyethylene glycol (PEG), and polytrimethylene glutarate (PTMG) polyester were added as secondary polyols to improve the solubility of Kraft lignin cuts in THF by disrupting hydrogen bonding between lignin macromolecules. It was found that PEG was more efficient in reducing brittleness and enhancing the ductility of Kraft lignin-based PUs.

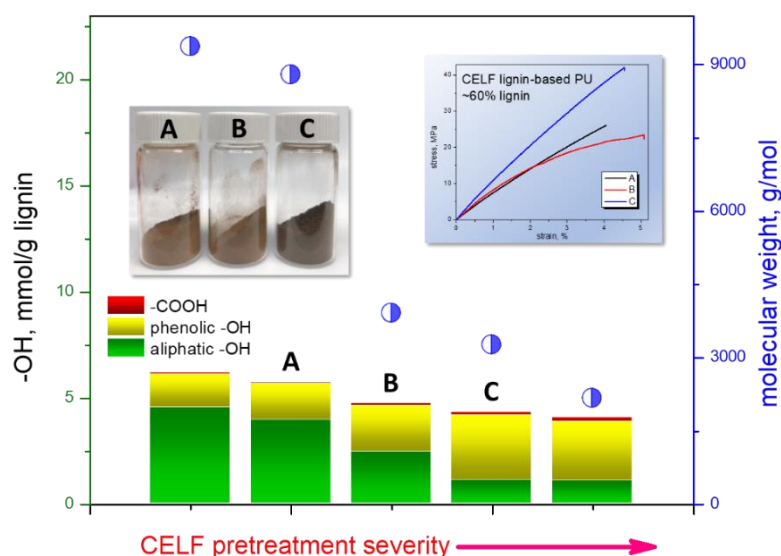


Fig. 3 Correlation between CELF lignin molecular structure and the tensile properties of CELF lignin-based PUs [23]. Sample A, B, and C represent CELF lignin extracted at 150 °C, 160 °C, and 180 °C, respectively. Reprinted with permission from [23].

A new type of clean lignin streams can be produced by Co-solvent Enhanced Lignocellulosic Fractionation (CELf), a solvolysis-type co-solvent pretreatment that employs aqueous THFs mixtures with dilute acid to enhance deconstruction of plant cell walls and separate lignin as a highly pure co-product known as CELf lignin [24]. In a study on the impacts of the severity of the CELf reaction on CELf lignin, it was found that the lignin macromolecules underwent further cleavage and additional condensation reactions at high reaction temperatures. Therefore, simply by raising the reaction temperature from 150 °C to 180 °C, the molecular weight of lignin was effectively reduced by 3.5 fold (Figure 3) [23]. Although it contained more condensed structures due to action of the dilute acid, the CELf lignin extracted at 180 °C was readily soluble in polar organic solvents like THF up to high concentrations at room temperature, and PU was produced with desirable mechanical properties for such applications as adhesives, coatings, and foams. In the most recent study, we prepared three CELf lignin samples with similar molecular weights ($M_w \sim 1000$ g/mol) but rather different chemical structures to investigate the correlation of lignin

molecular structure and PU mechanical properties [25]. Again, understanding the solvation behavior of lignin was critical for formulating lignin-based PU materials. In addition to polyethers, monomeric diols with different chemical structures were strategically applied to increase the solvent hydrogen bonding capacity. At the same time, they were copolymerized with lignin as chain extenders to reduce the brittleness of lignin-based PUs.

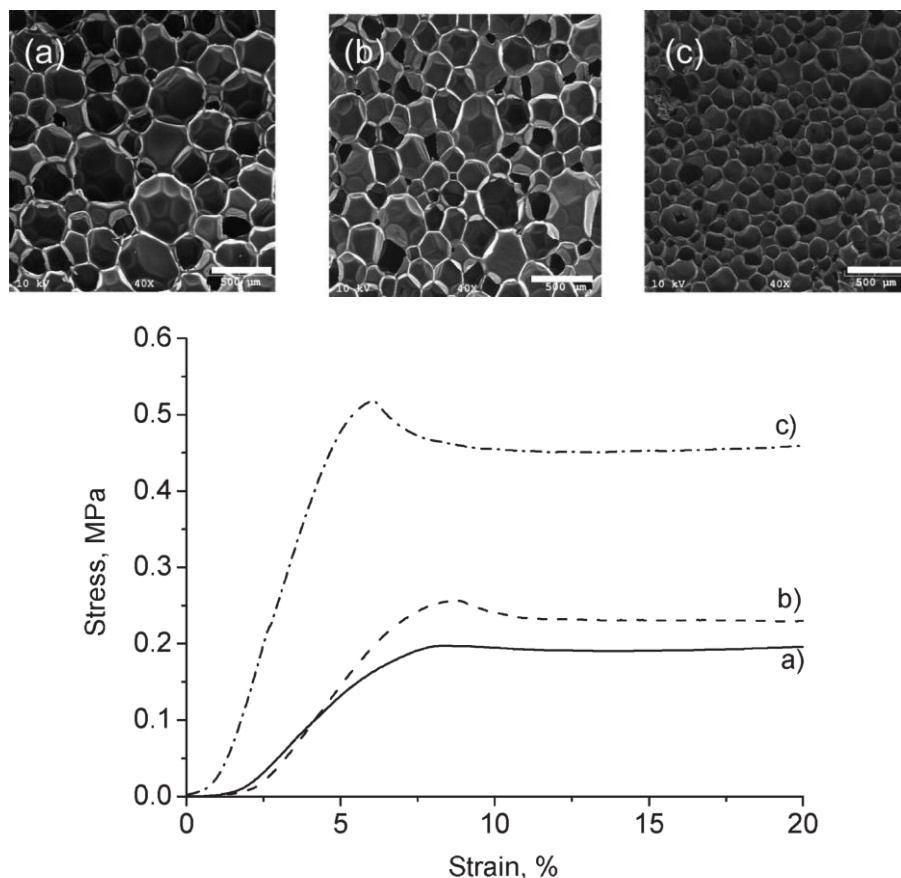


Fig. 4 SEM images of rigid oxypropylated ethanol lignin-PU foams reinforced with (a) 0 wt%, (b) 1 wt%, and (c) 5 wt% of cellulose nanowhiskers (scale bar = 500 μm) and their corresponding compressive stress-strain curves [26]. Adapted with permission from [26]. Copyright 2012 the Royal Society of Chemistry.

On the application front, rigid PU foams were produced from derivatized Kraft lignin and ethanol organosolv lignin, respectively. A commercial softwood Kraft lignin solid power was transferred into a liquid polyol by reacting with propyl oxide. Rigid PU foams synthesized from polyols composed of up to 100 wt% of oxypropylated Kraft lignin showed a closed-cell structure with a ~650 μm cell diameter and ~30 Kg/m³ foam density. Our previous studies revealed that cellulose nanowhiskers (CNWs) could reinforce rigid PU foams at a low concentration (≤1 wt%) [27]-[29] and reinforcement by CNWs was effective on organosolv lignin-based PU foams [26]. Before reacting with polymeric methylene diphenyl diisocyanate, the oxypropylated ethanol organosolv lignin was mixed with CNWs suspended in water, and water was then removed under high vacuum to prevent agglomeration of CNWs. CNWs proved to increase the crosslinking density by covalently attachment to the PU network [30]. Therefore, as the CNWs concentration increased from 0 to 5 wt%, vast improvements were observed in the density (+85%) and compressive properties (stress + 160% and modulus + 210%) of the oxypropylated ethanol organosolv lignin-based rigid PU foam (Figure 4) [26].

3. Synthesis of Lignin-based Non-Isocyanate PU (NIPU)

As mentioned above, toxic isocyanates are frequently used for production of conventional PUs. To address resulting health hazard concerns, significant progress has been made in recent years to develop alternative PU synthesis technologies that does not require the use of isocyanates. The PUs obtained in this way are generally termed as non-isocyanate PU (NIPU). NIPU could be synthesized via various routes, including rearrangement reactions between carboxamide and polyol, polycondensation reactions between carbamate and polyol, ring-opening-polymerizations of cyclic carbamate, and polyadditions between carbonate and polyamine [31]. Among these routes, the last synthesis pathways leading to the NIPU using amines and carbonate gained a great deal of attention in the polymer community because carbonates are typically not toxic or moisture sensitive. In addition, cyclic carbonates could be easily derived from the corresponding epoxide via simple carbonation. The polymers obtained are usually referring as polyhydroxy urethane (PHU) due to the presence of extra hydroxyl groups hanging off the main polymer chain (Figure 5). Although the opportunity to synthesize biobased NIPU (e.g., cellulose, terpene, and vegetable oil) following this route has not been ignored in the literature [32]-[34], to date, however, reports of lignin-based NIPU are still rare due to the complex characteristics of lignin structures. Generally speaking, there are two ways to synthesize lignin based NIPU: (i) polyaddition between cyclic carbonate functionalized lignin and pure amines and (ii) aminated lignin and pure cyclic carbonate. The synthetic routes put forward in the literature have been largely focused on the former methodology, possibly due to the very limited reactivity of aromatic amines toward cyclic carbonates, especially the five-member ring. It has been reported that aromatic primary amines and secondary amines have low reactivity due to their relatively low nucleophilicity and large size [31]. In addition, the structure of carbonate, solvent, catalysts, and other reaction parameters all significantly influence the properties of NIPUs. On the other hand, carbonate functional groups could be incorporated into the lignin macromolecular via glycidylation of lignin-based bisphenol followed by appropriate cycloaddition with CO₂ [35]. Several studies then showed that polyaddition reactions between this kind of lignin-based carbonate and pure diamines could lead to formation of lignin based NIPU, however, these NIPUs usually suffer from relatively poor mechanical properties [36], [37].

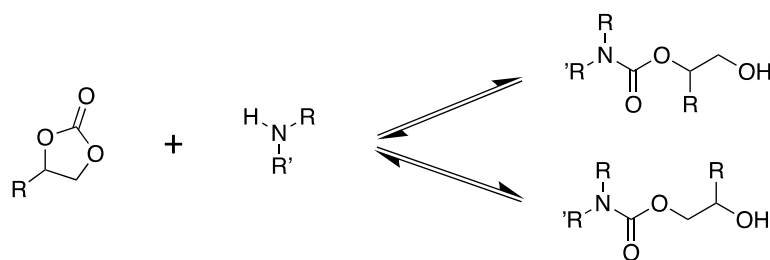


Fig. 5 Synthesis of NIPU linkage via addition between cyclic carbonate and amines.

4. Conclusions

Besides ~1 million tons of technical lignin from the pulp and paper industry, a substantial annual supply of co-product lignin will be generated by emerging lignocellulosic biorefineries. However, converting these lignin streams into profitable PU materials remains a challenge. Regardless of the isolation method, thermal degradation of lignin macromolecules (~150 °C to 400 °C) usually occurs within the glass transit region, thereby creating a technical barrier for manufacturing lignin-containing/based polymeric materials by thermal processing such as extrusion or compounding. Therefore, for the integration of lignin into polyurethane materials, solvent casting was often used to overcome lignin's poor processibility. In recent years, novel organosolv lignin streams have been generated by various advanced biorefinery pretreatments using green organic solvents. The excellent solubility of lignin in various organic solvents makes these organosolv lignin streams suitable bio-based polyols for incorporation into PU by liquid

injection molding. The integration of biorefinery pretreatment and PU synthesis can effectively reduce the production cost and valorize lignin while avoiding use of hazardous isocyanate compounds and environmental concerns from degradation of PU materials. Thus, research interests are growing on non-isocyanate PU materials derived from lignin, given that they inherit biodegradability from lignin and can be synthesized via nontoxic chemical synthesis approaches.

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