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Recent advances in lignin-based polyurethanes

YUN-YAN WANG, CHARLES M. CAI, AND ARTHUR J. RAGAUSKAS

ABSTRACT: Given the rise in demand for sustainable renewable biofuels and promising developments in cellulosic ethanol, the valorization of lignin has become essential for biorefining operations, especially with today's low-cost energy production state of affairs. In the past 40 years, numerous efforts have been devoted to incorporate lignin and lignin derivatives into commercial polymeric materials. One of the promising strategies is to utilize multifunctional lignin macromolecules or oligomers as the replacement of polyols during polyurethane synthesis. In this review, recent advances in fabricating polyurethane foams, films, and adhesives with modified or unmodified lignins are examined. The mechanical and thermal properties of these lignin-based polyurethanes were correlated to their formulations, lignin molecular weight, and polydispersity, as well as the structural features of different lignin preparations. Recalcitrance and strong intermolecular interactions of lignin macromolecules are known to prevent them from effective incorporation into other polymeric materials, covalently or noncovalently. Therefore, this review intends to summarize the methods that improve the reactivity of lignin through chemical modification such as depolymerization, demethylation, and chain extension. Future developments and applications will be examined with a special emphasis on tailoring lignin structure to specific applications.

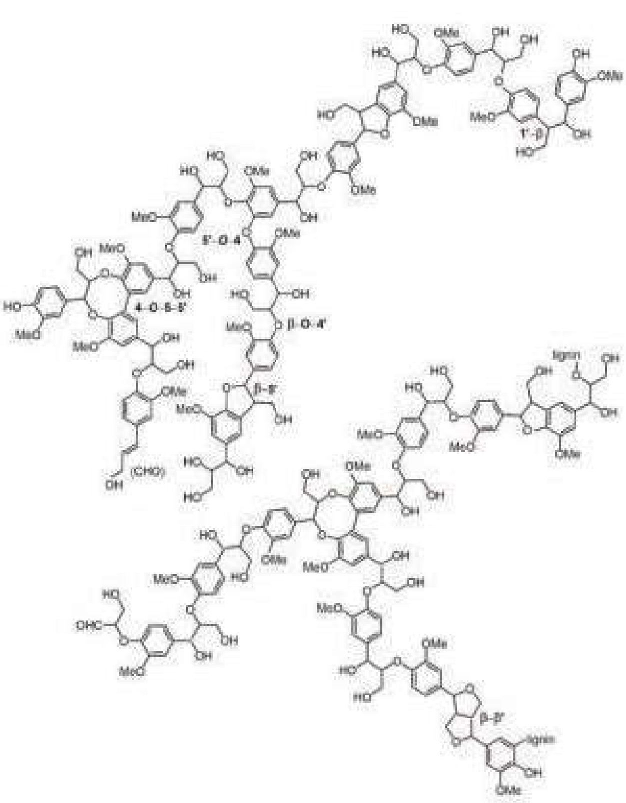
Application: Lignin can be used as polyols to produce polyurethane foams, films, and adhesives.

As the second most abundant renewable biopolymeric material in nature, lignin represents 15%–35% dry weight of plant lignocellulose. During lignin biosynthesis, lignin macromolecules are assembled to form hydroxyphenyl (H), guaiacyl (G), and syringyl (S) subunits through dehydrogenative coupling of three primary monolignols: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The contents of these subunits vary depending on the plant species (**Table I**) [1]. **Figure 1** depicts a model of macromolecular softwood lignin structure [2] with six predominant substructures, including *β*-*O*–4, *β*–5, *β*–1, 5–5, 4–*O*–5, and *β*-*β*.

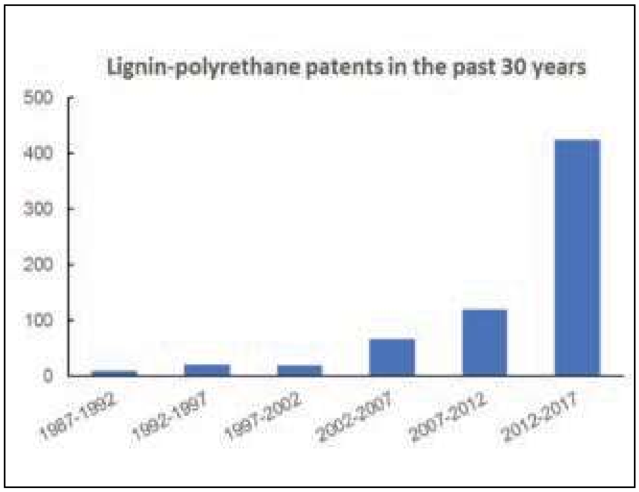
In the paper and pulping industry, the largest application of technical lignins that were considered a waste material is

Sample	S, %	G, %	H, %	S/G
Poplar	61.9	37.8	0.3	1.64
Pine	ND	98.3	1.7	ND
Corn	58.9	38.3	2.8	1.54
Arabidopsis	20.1	77.1	2.8	0.26
ND = none detected.				

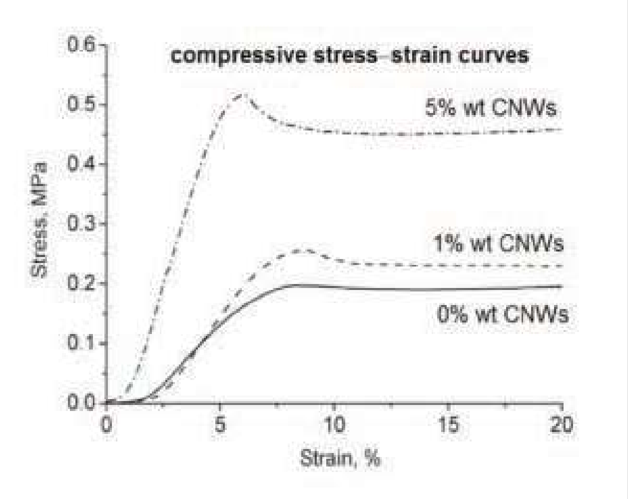
I. Molar % of syringyl (S), guaiacyl (G), and hydroxyphenyl (H) lignin subunits in the plant cell wall of different plant species as determined by two-dimensional nuclear magnetic resonance (2D NMR) spectroscopy [1].



1. An illustration of softwood lignin structure [2]. (Image adapted with permission of American Chemical Society, © 1998.)



2. Lignin-polyurethane patents published worldwide in the past 30 years.



3. Compressive stress-strain curves of lignin-based polyurethane foam reinforced by cellulose nanowhiskers (CNWs) [14]. (Image adapted with permission of Royal Society of Chemistry, © 2012.)

to combust them on site as a low-cost fuel and allow recovery of cooking chemicals; approximately 1%–2% of these technical lignins [3] are used as low-value additives for concrete admixtures, dust control, and oil well drilling muds [4].

These days, the growing demand for green energy has brought more attention to lignin utilization than ever before. The economic viability of converting lignocellulosic biomass to biofuel and commodity organic chemicals relies on the value-added coproduct lignins [5]. By 2022, about 62 million tons of lignin will be produced annually as a coproduct of second-generation biofuel generation in the United States [5], far exceeding the current lignin supply for the additives market worldwide. Therefore, robust commercial applications of lignin will be on the front burner for any lignocellulosic-related industries.

Petrochemical-based polyurethanes are polymerized with small blocks of polyesters or polyethers that are covalently connected through a urethane bridge (–NHCO–O–) [6]. The inherent versatility in polyurethane syntheses makes them a class of polymeric plastics that can be engineered to suit various industrial and residential applications such as rigid and flexible foams, adhesives, sealants, and elastomers. The total production of polyurethane in the United States was 2.4 billion tons with approximately $281 billion in revenues in 2014 [7]. Approximately 50% of the polyols in the North American market are used for the rigid polyurethane foams production annually [8].

The abundance of phenolic and aliphatic hydroxy (OH) groups allows macromolecular lignin to polymerize further in the presence of diisocyanate crosslinker to form the hard segments in polyurethane network [9]. As a heterogeneous polyol, one of key factors that governs the reactivity of lignin with isocyanate is the accessibility of OH groups. Higher conversion of isocyanate group (NCO) into urethane was found as content of aliphatic OH groups increased as a result of solvent fractionation [10].

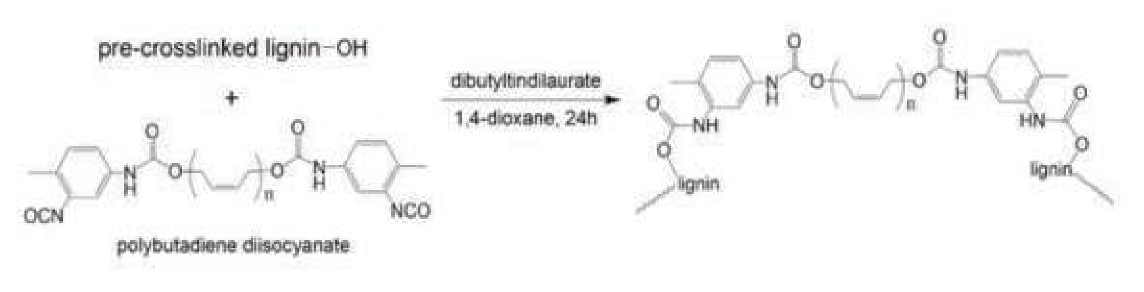
Over 600 patents related to polyurethane containing lignin have been published worldwide in the past 30 years; more than 60% of them were documented since 2012 (**Fig. 2**). It is well recognized that, as a green replacement for petrochemical polyols, the commercialized utilization of low-cost coproduct lignin will reduce the manufacturing cost of polyurethane products, including thermoplastics, foams, and coatings [11-13], and in return will support lignocellulosic biorefinery industries that eventually lead to affordable biofuels and bioproducts for end-use customers.

LIGNIN-BASED POLYURETHANE PRODUCTS

Rigid foams

Li et al. reported the reinforcing effect of cellulose nanowhiskers on a lignin-based rigid polyurethane foam [14]. The reaction between the oxylpropylated ethanol organosolv lignin (weight-average molecular weight, M_w = 3700 g/mol, PDI = 2.2) and polymeric methylene diphenyl diisocyanate (MDI) was catalyzed by dimethylcyclohexaneamine and a Mannich base catalyst. In the presence of 5% cellulose nanowhiskers, the density and compressive strain of the corresponding polyurethane foam increased significantly by 185% and 260%, respectively (**Fig. 3**). The lignin content in the foam is estimated to be less than 33%. Similarly, in the study of rigid polyurethane foam reinforced with pulp fiber, the compressive strength dropped dramatically as the content of alkaline lignin increased gradually to 37.2%, yet reinforcement of the additional 1%–5% pulp fiber was quite limited compared to the impact of lignin content [15].

Instead of using filler, monomeric 1,4-butanediol was examined as a bifunctional chain extender in a hardwood organosolv lignin-base (12%–36% w/w) rigid polyurethane foam [16]. It was found that when the ratio of NCO/OH was kept constant, additional 3.5% butanediol could improve foam compressive strength by 30%.

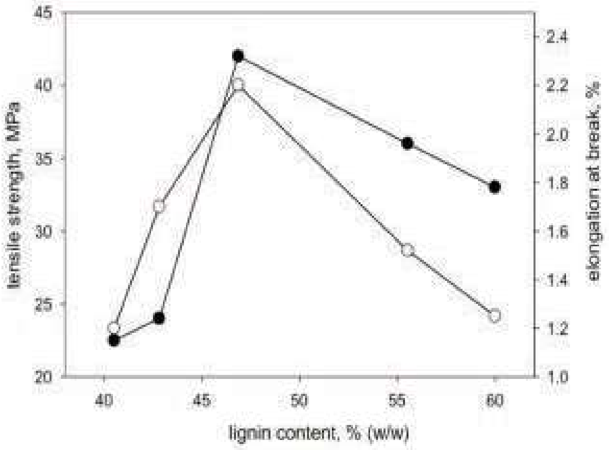


4. Lignin-based polyurethane film synthesized from the pre-crosslinked solvent-extracted lignin and oligomeric polybutadiene diisocyanante [18]. (Image reproduced with permission of Royal Society of Chemistry, © 2013.)

Films

A solvent-extracted hardwood lignin sample (equivalent to that of trademarked Alcell lignin) was pre-crosslinked through reaction with formaldehyde [17]. The pre-crosslinked lignin possessed a quite broad molecular weight distribution pattern with polydispersity index (PDI) of 61; meanwhile, its number-average molecular weight (M_n) increased from 1840 to 12500 g/mol [18]. A series of polyurethane films were synthesized by reacting the pre-crosslinked lignin (65%-80% w/w) with polybutadiene (PBD) (M_n ~2500 g/mol) ended with an isocyanate group on each side (OCN-PBD-NCO) as depicted in **Fig. 4**. It was expected that the rubbery polybutadiene segments would toughen lignin-based polyurethane thermoplastics. Phase separation was confirmed through differential scanning calorimetry (DSC) analyses as two distinct glass transition temperatures (T_g) representing PBD (-30°C) and lignin (150°C) were observed. The Young's modulus of lignin itself was reported to be 2.3~4.7 GPa [19]; however, the modulus of the rubbery plateau and tensile behaviors of the lignin-based polyurethane thermoplastics showed strong dependence on the crosslinking density rather than the amount of lignin present in the thermoplastics. When the lignin content reaches 80%, the resultant polyurethane became very brittle [18].

In another study that lignin was employed as the only source of hydroxyl groups, Jia et al. extracted a dilute hydrochloric acid pretreated spruce wood meal with 80% (w/w) 1,4-butanediol aqueous solution at 220°C for 1 h [20]. The obtained lignin preparation exhibited a low molecular weight (M_n = 2483 g/mol) with narrow polydispersity pattern (PDI = 1.52). The monolithic polyurethane film was cast from dioxane at 85°C; MDI and triethylamine were used as crosslinker and catalyst, respectively. Such a simple formulation produced polyurethane films containing more than 40% lignin, and the best tensile properties (**Fig. 5**) were achieved when the NCO/OH ratio reached 1.7 and the corresponding lignin content was 47%.



5. Effects of lignin content on the tensile strength (dark dot) and elongation of break (open dot) of 1,4-butanediol aqueous extracted lignin-based polyurethane films [20]. (Image reproduced with permission of Royal Society of Chemistry, © 2015.)

Adhesives and coatings

Griffini et al. conducted direct reactions of unmodified softwood kraft lignin with toluene diisocyanate (TDI) in 2-methyl tetrahydrofuran (MeTHF) [21]. In this work, the kraft lignin applied in polyurethane was MeTHF-soluble fraction (M_n = 1310 g/mol, PDI = 1.8, T_g = 92°C) that accounted for approximately 50% of the crude kraft lignin sample. The highest T_g was observed as 143°C when NCO/OH ratio reached 0.16, equivalent to 70% (w/w) lignin incorporated in the polyurethane. The adhesion strength of 80% (w/w) lignin-polyurethane adhesive was investigated by performing pull-off adhesive tests on different substrates such as glass, metal, and wood. It was found that the best application of this lignin-polyurethane adhesive would be on the woody surface due to the high nature affinity of lignin with wood. Moreover, another potential application of this adhesive would be on a glass surface, as the corresponding adhesive strength achieved 7.6 MPa. In addition, Nacas et al. converted a technical grade kraft lignin and MDI into polyurethane adhesive in tetrahydrofuran [22]. It was claimed that the presence of a greater amount of free isocyanate groups would contribute to the lap shear strength on wood, and the highest lap shear strength (6.3 MPa) was observed when NCO/OH was 1.2.

MODIFIED LIGNIN IN POLYURETHANE

Demethylation

The crosslinking density in lignin-based polyurethane is governed by the frequency of hydroxyl group in lignin components. Some studies [23-26] demonstrate that the aromatic methoxy groups can be substituted by hydroxyl group through demethylation. Wu et al. reported that sulfur dioxide-mediated demethylation could increase the contents of the phenolic hydroxyl group and carboxyl group by 54% and 55%, respectively [25]. The hydrobromic acid (HBr)-treated alkaline lignin exhibits a 28% increase in hydroxyl group compared to unmodified lignin sample [26], and subsequently, 6.5-fold increase in modulus was achieved due to higher crosslinking density of the resultant polyurethane network. However, the HBr-treated lignin-based polyurethane was too brittle, and an additional 40% polyethylene glycol (M_n = 200 g/mol) was needed during the polyurethane syntheses, which eventually lowered the lignin content to 17% (w/w).

Chain extension

Converting phenolic OH groups into long chain aliphatic ones has been considered an effective approach to improve the reactivity with NCO by reducing the steric and/or electronic constraints. A flexible linear chain polymer such as propylene oxide has been introduced to the lignin-based polyurethane system as the soft segments through oxyalkylation [27]. The chain-extended hydroxpropyl lignin exhibited better solubility in organic solvents and lower glass transition temperature compared to underivatized lignin. The toughness and elongation at break of a lignin-based polyurethane network can be further improved by incorporation of soft segments through blending [28].

Esterification is another effective method to incorporate soft segments into the lignin-based polyurethanes. Organosolv hardwood lignin produced from the Alcell process (M_n = 1000 g/mol, PDI = 2.28) was esterified with oleic acid by using a solvent-free and catalyst-free method [29]. A new hydroxyl group was added to the double bond of oleic acid via epoxidation followed by oxirane ring-opening reaction. The resultant lignin-fatty acid based macropolyol mixture was then reacted with an isocyanate prepolymer prepared with poly(propylene)glycol with different molecular weights to form the final biobased polyurethane with lignin content up to approximately 37% (w/w). Such lignin-fatty acid based polyurethanes are rubbery materials with elongation at break ranging from 170% to 360% and highest value of ultimate tensile strength reaching 9.6 MPa. Thermal analyses by DSC and dynamic mechanical analysis (DMA) indicated that the elastomeric properties arose from microphase separation [30].

The lignin-based polyurethanes containing soft segments in general exhibit multi-step thermal decomposition patterns, depending on the components in the network [31]. A typical example can be found in the study of the polyurethanes containing both xylaric acid-lignin ester and polyethylene glycol [32]. Four decomposition temperature ranges were observed when the samples were heated up to 700°C. The decompositions occurring at 190°C and 550°C were correlated to the degradation of urethane bonds and aromatic moieties in lignin, respectively.

Depolymerization

Cinelli et al. [33] studied the syntheses flexible polyurethane foams with depolymerized Indulin AT lignin (MeadWestvaco Corp.; Richmond, VA, USA). The lignin was depolymerized in the presence of glycerol and polyethylene glycol (M_n = 400 g/mol) in a microwave oven at 180°C for 3 min to form a liquefied mixture. However, such a mixture was not suitable for preparing flexible polyurethane foam due to its excessive viscosity and a very high OH value; therefore, additional polyols were added to reduce the viscosity and T_g of the final polyurethane foam as well. The lignin contents by weight in the resultant flexible polyurethane foams were always below 14%.

CONCLUSION

As the quest for high lignin content polyurethane systems continues, more attention will be placed on producing polyurethane using lignin as the main or sole hydroxyl group provider. The NCO/OH ratio, solubility of coproduct lignin in organic solvents, the interactions between lignin and non-lignin components, and between lignin macromolecules [2] will all affect the incorporation level of lignin in polyurethane in a synergistic way. Considering the production cost and environmental impact of lignin-based polyurethanes, minimal chemical modification on coproduct lignin will be preferred in the competition with conventional petrochemical polyols [34]. **TJ**

ACKNOWLEDGMENTS

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ABOUT THE AUTHORS

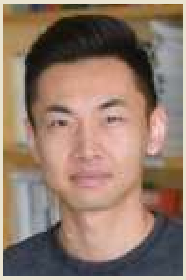
We created this review because valorization of co-product lignin is currently a frequently mentioned research topic, and converting lignin into polyurethane is widely studied.

One of the most difficult aspects of research in this area is how to increase the lignin content in the polyurethane, while maintaining its mechanical properties. Consequently, various modification approaches have been reviewed in the paper.

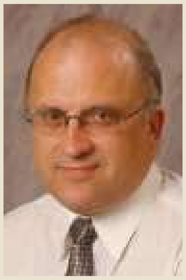
One finding in the review is that lignin-based polyurethanes can be synthesized by using lignin as the sole resource for phenolic and aliphatic hydroxy (OH) groups.

If lignin-based polyurethane can be commercialized, mills can make profit from co-product lignin instead of burning it as low-cost fuel. The next step is to explore the feasibility of producing polyurethane containing very high amounts of lignin, as well as studying lignin's solubility in organic solvents so that its reactivity is improved.

Wang



Cai



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