Conversion of biomass lignin to high-value polyurethane: A review

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A R T I C L E   I N F O

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A B S T R A C T

Lignin, as a major by-product of pulp and paper industry, has attracted extensive interest for the preparation of high-value-added products, due to the merits of abundant, sustainable, inexpensive, and unique functional groups. This review focuses on the strategies to develop high performance polyurethane (PU) materials from lignin on the basis of main reports, in which lignin was used not only as macromonomer to substitute petroleum-based polyols, but also as blending filler for PU industry. Pre-treatment approaches, especially lignin fractions extracted with various solvents and chemical modifications, e.g., depolymerization, hydroxalkylation, dealkylation, and esterification, were widely explored to enable lignin more reactive and available to synthesize PU products. In addition, lignin/PU blends were also prepared to fulfill industrial demand. With adjustment of lignin structure, the PU formulation, and synthesis procedures, various lignin-based PU products with advanced properties and a higher bio-substitution ratio have been developed, demonstrating the potential industrial application of lignin for high value-added sustainable materials.

1. Introduction

With the gradual depletion of fossil fuels and growing concerns on the environmental issues, natural resources have attracted extensive attention due to the merits of inexpensiveness, sustainability, high abundance, and biodegradability. Over the past decades, natural biomass has been widely studied to develop a variety range of products, which exhibited superior or comparable performance than petroleum-based materials (Gandini and Lacerda, 2015; Sun et al., 2015; Gandini et al., 2016). The attractive performance and environmental friendliness make them a promising candidate to replace petroleum derived feedstock and develop sustainable high-performance materials. Lignocellulosic biomass, which mainly includes cellulose, hemicellulose, and lignin, is the most abundant renewable and natural resource on the earth (Laurichesse and Avérous, 2014; Chen et al., 2017). Lignin, which comprises 15 wt%-30 wt% of biomass in the cell walls of plants, is considered as one of the most promising biomaterials due to the merits of high abundance, high functionality, and sustainability (Liu et al., 2015b; Yu et al., 2016). As a byproduct waste, approximately 50–60 million tons of lignin are produced per year in the pulp and paper industry (Brodin et al., 2017). The impressive polymer structure with various reactive groups enables lignin a promising feedstock to produce various advanced products via chemical reactions. However, most of them are burnt for heat, and only 2% of the lignin waste are utilized for commercial applications. Therefore, it is crucial to promote the utilization of lignin and develop efficient strategies of converting lignin to high value-added products for industrial applications.

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To date, extensive efforts have been made to develop high value-added materials from lignin and various products have been explored in a wide range of applications. Considering the macromolecular structure with a fair amount of aromatic rings and other functional groups, as shown in Fig. 1 (Upton and Kasko, 2016), lignin can be a potential source of aromatic compounds and chemicals via degradation, such as benzene, phenol, cresols, dimethyl sulfide, dimethyl sulfoxide, methanol, ether, and chemical mixture (Liu et al., 2015a; Mahmood et al., 2016b; Chio et al., 2019). In addition, lignin could also be converted to vanillin, vanillic acid, aromatic acid, quinones, and aromatic aldehydes by oxidation reaction (da Silva et al., 2009; Upton and Kasko, 2016). With the development of lignin depolymerization engineering, more chemicals and compounds could be efficiently obtained from natural lignin, which could be widely applied in industries as a substitute of petroleum-based feedstock. Moreover, lignin could be used as the cost-effective precursor for the production of carbon materials via carbonization, which exhibited potential application on energy storage devices, including supercapacitor and lithium ion battery (Wang et al., 2013a; Li et al., 2016; Azwar et al., 2018, 2020b). Furthermore, an extensive variety of high performance polymers, such as polyurethane (PU), epoxy resin, phenol formaldehyde, and polyester, have been synthesized with lignin as the macromonomer, which exhibited excellent thermal property and mechanical strength (Thakur et al., 2014; Liu et al., 2014b; Sun et al., 2016a, 2016b, 2017; Zhang et al., 2020). In addition, with high thermal stability, attractive intrinsic stiffness, antioxidant property, and biodegradability, lignin can also be incorporated into varied polymer matrix as reinforcing filler to improve the performance of the composites for special requirements (Liu et al., 2015b; Qian et al., 2015; Sun et al., 2015). During past decades, numerous researchers have been focused on converting lignin to high value-added polymer compounds, especially PU, which exhibited remarkable performance and has been widely applied in our daily life.

The PU is one of the most versatile polymers with superior mechanical performance, which have been widely applied in building construction, electronic products, biomedical applications, and other industrial products as items of paints, foams, coating films, elastomers, adhesives, integral skins, and rigid plastics (Akindoyo et al., 2016; Brodin et al., 2017). The PU is synthesized from the polymerization between hydroxyl groups (—OH) of polyol and isocyanate groups (—NCO) from diisocyanates. The reactive groups are cross-linked into urethane groups with three-dimensional network, thus forming PU polymers (Fig. 2). The physical and chemical properties of the PU depend on the incorporated types of polyol and diisocyanates, cross-linking density, and synthesis procedure. Generally, soft elastic polymers can be achieved from flexible long chains and low cross-linking, while short hard chains with high cross-link density lead to rigid and tough products (Akindoyo et al., 2016; Upton and Kasko, 2016). Owing to the versatility of monomers, formulations, and synthesize processing, a wide range of the PU products with tailored properties can be achieved to fulfill various specific requirements.

So far, many types of polyols and diisocyanates have been explored to prepare the PU polymers. Aromatic isocyanates, such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), and aliphatic diisocyanates, including hexamethylene
diisocyanate (HDI) and isophorone diisocyanate (IPDI), are the most widely used diisocyanates in the PU systems (Ji et al., 2015; Sen et al., 2015; Zhang et al., 2015b). The intrinsic short chains and urethane groups via cross-linking give rise to stiffness and rigidity of the resultant PU products. Moreover, polyols with long flexible chain segments are the other crucial component to form the PU network. Poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), and poly(tetramethylene glycol) (PTMG) are widely applied in experimental and industrial PU products, which tune the elasticity, flexibility, and hardness of the PU for variety of applications (Reimann et al., 1990; Chiu and Schoen, 2002; Akindoyo et al., 2016). However, most of the polyols used to prepare the PU are obtained from petroleum sources, which increase the fossil consumption and aggravate environmental pollution. With the presence of hydroxyl groups as the reactive sites, lignin can be explored as a promising polyol for the synthesis of the PU products, and tremendous lignin-derived PU polymers have been developed to partially and fully replace petroleum-derived polyols (Hatakeyama, 2002; Brodin et al., 2017; Ponnusamy et al., 2019). Compared with the petroleum polyol-based materials, lignin-based PU are more biodegradable, low cost, and environmental friendly, exhibiting potential application for developing economic and sustainable materials.

2. Chemistry and structure of lignin

Lignin is a complex amorphous aromatic polymers with three-dimensional cross-linked structure, which is mainly composed of three phenylpropane units of p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) (Fig. 3) (Gadhave et al., 2018; Ponnusamy et al., 2019). As shown in Fig. 3, the phenylpropane units possess hydroxyl (—OH) and methoxy (—OCH3) groups and the difference between the phenylpropane monomers is the number of methoxy (—OCH3) groups. Lignin is formed by cross-linking of the three phenylpropane units via coupling of C—C bonds and C—O bonds (Naseem et al., 2016; Cao et al., 2018). The composition of the monomers depends on the plant species and isolate processes. The variety component of the monomers and cross-linkage between the units make lignin heterogeneous polymers with cross-linked network, high molecular weight, polydispersity, and widely varying structures (Constant et al., 2016; Wang et al., 2016). However, the complex structure and macromolecular architecture induce poor solubility of lignin in most of organic solvents, thus impeding the preparation process of lignin for various products. Therefore, it is crucial to develop effective strategies to optimize lignin structure for efficient utilization of lignin on various applications.

Despite the difference in structures, lignin possesses a variety of functional groups, including hydroxyl, methoxy, carbonyl, and carboxyl groups, which could be served as reactive sites to produce a large range of chemicals and polymers via varied chemical reactions (Kai et al., 2016; Mahmood et al., 2016b). Among them, hydroxyl groups which include both phenolic and aliphatic hydroxyl groups, are the most characteristic functions in lignin. They can react with isocyanate groups to form urethane bonds and generate lignin-based PU networks as macromonomer. Furthermore, lignin can be blended with PU matrix to optimize the performance of the composites through intramolecular interactions (Liu et al., 2013). Over the last decades, the utilization of lignin for the PU materials has been extensively investigated and great progress has been reported to promote lignin valorization and enhance the performance of resultant products (Xu and Ferdosian, 2017). The incorporation of lignin to the PU polymers follows mainly two approaches: as macromonomer to synthesize the PU polymers via cross-linking condensation, and blend with the PU matrix to form lignin/PU blend composites as filler. Owing to the presence of hydroxyl groups, lignin exhibits great potential to partially or fully replace petroleum-based polyols (Upton and Kasko, 2016). Most of the researchers have focused on the combination of lignin as macromonomer in the PU synthesis, and mainly three strategies are developed as follows (Fig. 4): 1) direct utilization of lignin as reaction agent without treatments, lignin can be directly cross-linked with isocyanates to produce the PU polymers with or without other polyols; 2) utilization of lignin after solvent fractionation which extracts more homogeneous and activated lignin via physical processing; and 3) utilization of lignin after chemical modification, such as fragmentation to increase solubility and content of hydroxyl groups, hydroxalkylation, and other functionalizations about dealkylation, esterification, and amination, to overcome steric constrains of hydroxyl groups and
3. Lignin as macromonomer

As lignin can directly react with isocyanates to achieve the PU in rather mild condition (Cheradame et al., 1989), an extensive attention has been paid on the incorporation of lignin as polyol precursor for the PU synthesis. Due to high content of aromatic rings and hydroxyl functionality, lignin acts as not only a cross-linking agent but also a hard segment to form the PU polymers with three-dimensional network. Tremendous PU polymers derived from lignin have been developed and various preparation strategies were investigated to promote the conversion of lignin into high value-added PU products.

3.1. Direct use of lignin as macromonomer

The presence of hydroxyl groups enables lignin a promising macromonomer to be directly used as-received for the PU synthesis without pre-treatments. In order to reduce the consumption of petroleum-derived polyols, great efforts have been made to produce the PU products with lignin as sole polyol. Duong et al. (2014) synthesized high molecular weight thermoplastic PU from lignin and MDI. The molecular weight of resultant PU was modulated via the reaction time and temperature, and the incorporated lignin could be as high as 42 wt%. Bonini et al. (2005) used steam-exploded lignin as the macromonomer to prepare the PU by reacting with 4,4’-methylenebis (phenylisocyanate), which exhibits potential application in wood adhesive. In addition, Yang et al. (2014b) reported a novel monolithic PU xerogel by polymerization between modified diisocyanate (MMDI) and lignin, which possessed high lignin content up to 71 wt%. As shown in scanning electron microscope (SEM) image (Fig. 5), the xerogel surface possessed a randomly rough structure with coralloid nanoparticle clusters and superhydrophobicity. Furthermore, it exhibited excellent selective oil absorption in the oil/water mixture with superior recycle ability, demonstrating the potential application on absorbents for spilled oil cleanup.

Although varied PU materials have been developed with lignin as sole polyol, the resultant polymers were usually brittle and hard, ascribing to the intrinsic stiffness of lignin and low molecular mobility of diisocyanates. Therefore, soft segments, such as PEG and PPG, are often incorporated as co-polyols to enhance the ductility of the resulting PU polymers (Hatakeyama, 2002; Wang et al., 2013b; Xue et al., 2014). H. Jeong et al. (2013) produced water blown flexible PU foams by condensation of softwood kraft lignin, PEG, and TDI. Ascribing to the filler effects and crosslinking effects, the prepared PU foams possessed impressive viscoelastic properties, demonstrating potential application on cushioning use. Similarly, lignin-based rigid polyurethane foams (LRPF) was also fabricated with high lignin amount of 37.19 wt%, which featured increased thermal conductivity (Xue et al., 2014). Carriço et al. (2016) synthesized semi-rigid polyurethane foams from bio-based polyols of castor oil, industrial residual glycerol, and kraft lignin without pre-treatment processes, which showed a great interest for industrial applications. Renewable lignin based PU bioplastic was also synthesized by the bridge of HDI with lignin, and biodegradable poly (ε-caprolactone) (PCL) as soft segment, which possessed long flexible aliphatic chains to improve the flexibility of the resulting PU polymers (Fig. 6) (Zhang et al., 2017, 2019b). The properties of varied PU films were thoroughly evaluated by adjustment of the content of lignin, molar ratios of NCO/OH, and the molecular weight of the PCL. The resultant PU films exhibited excellent mechanical properties. The tensile strength, breaking elongation, and tear strength could reach 19.35 MPa, 188.36%, and 38.94 kN/m, respectively, even when the lignin content reached as high as 37.3 wt%, which met the daily use in the bioplastic field.
3.2. Lignin fraction

Generally, lignin possesses a complex and heterogeneous structure with wide distribution of molecular weights, which sterically constrains the reactive sites and limits the processability of lignin to be directly used for the synthesis of high value-added products. To overcome this limitation, solvent fractionation has been widely investigated as an efficient pretreatment approach to separate homogeneous lignin fractions with relatively narrow polydispersity and improve solubility (Lovell and Hibbert, 1941; Thring et al., 1996; Evtuguin et al., 1998; Cui et al., 2014; Wang et al., 2018b). As the extracted solvent can be used for the further synthesis processing of the PU products, the excellent solubility of lignin greatly improves its processability in further applications. Furthermore, by using a sequential solvent with varied polarities and hydrogen-bonding capabilities, lignin fractions could be isolated with definite molecular weight and distinct group functionalities (Fig. 7) (Thring et al., 1996; Passoni et al., 2016; Jiang et al., 2017; Collins et al., 2019). The molecular weight of lignin fractions greatly correlates with its thermal and structure properties. Higher molecular weight fractions usually possess more content of aliphatic OH, less content of phenolic OH, and higher glass transition temperature than lower molecular weight fractions, while the structure of lower molecular weight lignin fractions were more homogeneous than fractions with higher molecular weight (Yoshida et al., 1987a; Sadeghifar et al., 2017). Therefore, lignin fractions with tunable chemical functionality and thermal properties could be achieved by proper solvent extraction, which improves the utilization of lignin for various applications (Saito et al., 2014).
Up to date, varied lignin fractions have been investigated from different solvents, which possess distinct structure and properties (Yoshida et al., 1987a; Park et al., 2018). For example, the ether-soluble fraction of lignin exhibited lower molecular weight and lower amount of hydroxyl groups than those from methanol (Thring et al., 1996; Vanderlaan and Thring, 1998), and the resulting PU polymers obtained from low molecular weight of lignin exhibited higher flexibility than those from the lignin with higher molecular weight (Yoshida et al., 1990; Vanderlaan et al., 1998). Furthermore, other solvents such as ethanol, 2-methyltetrahydrofuran (MeTHF), and 1,4-dioxane, have also been used to separate lignin fractions. The PU products ranged from soft to hard have been fabricated with varied lignin fractions, lignin contents, and NCO/OH ratios (Yoshida et al., 1987b; Reimann et al., 1990; Thring et al., 1997; Arshanitas et al., 2016), and the structure-property relationship has also been investigated. Low NCO/OH ratio and lignin content (lower than 20 wt%) usually resulted in the PU products rather soft and flexible, while hard and tough PU materials were often obtained at a rather high lignin content or high NCO/OH ratio (Yoshida et al., 1987b). With high lignin content of higher than 30 wt%, the corresponding PUs were usually hard and brittle regardless of the NCO/OH ratio and molecular weight of lignin used (Yoshida et al., 1990). Versatile PU films could be obtained with Young’s modulus up to 3.5 GPa, ultimate strength up to 50 MPa, and elongation up to 300% (Yoshida et al., 1987b; Reimann et al., 1990, 1999). Rigid PU foams have also been fabricated from ethanol organosolv lignin (12 wt%–36 wt%), PEG, and MDI (Pan and Saddler, 2013). Because of better miscibility with the poloy, organosolv lignin gave rise to better mechanical property and replaced more poloy in the resultant PU foams than the crude lignin. Recently, well-defined kraft lignin fractions with three molecular weight were refined by sequential precipitation from acetone-methanol-hexane cosolvent system (Wang et al., 2019b). After that, varied lignin based PUs were synthesized from lignin fractions and secondary polyls, such as PEG and PTMG. The mechanical and thermal properties of the lignin-based polyurethanes were influenced by the lignin macromolecular features and their intermolecular interactions with the secondary polyls.

Furthermore, with homogeneous structure, the lignin fractions can cross-link the disocyanates more effectively to synthesize high performance PU products even without additional soft polyls. Griffini et al. (2015) produced the PU materials from 2-methyltetrahydrofuran (MeTHF) soluble lignin fraction (S-lignin) and TDI, in which lignin content was as high as 70 wt%–90 wt%. As shown in Fig. 8a, the S-lignin fraction exhibited lower molecular weight and a narrower molecular weight distribution compared with as-received lignin (A-lignin). With the cross-links of urethane groups and strong hydrogen bonds from residual hydroxyls in lignin, the resultant PU polymers exhibited improved thermal stability, high elastic modulus, and high adhesion on different substrates such as glass, metals, and wood, demonstrating their potential applications on high performance coatings and adhesives. However, the reactivity of hydroxyl functionalities was relatively low, in which high S-lignin content of 75 wt% (NCO/OH molar ratio of 0.12) was required to fully react with NCO groups (Fig. 8b). Moreover, Jia et al. (2015) prepared lignin-based PU films from fractionated lignin extracted through a high boiling solvent (HBS) of 1,4-dioxane. With large number of hydroxyl groups and high solubility in 1,4-dioxane, the HBS lignin exhibited excellent reactivity towards MDI as the only polyl. In addition, the resultant LPU films exhibited high solvent resistance, hydrophilicity, and high tensile strength with a maximum value of 41.6 MPa, which demonstrated potential application as coating and base (Figs. 8c and d). de Haro et al. (2019) successfully developed thermosetting PU coatings from cross-linking of lignin derived disocyanate based on vanillic acid and three technical lignin after solvent fraction, with high biomass content in the range of 92 wt%–96 wt%, improving the utilization of lignin in commercial industry. Furthermore, multiple approaches including fractionation and chemical modification have also been reported to optimize lignin. Lignin fractions isolated from hydroxypoyllignin were explored to modulate resultant PU networks, leading to better mechanical properties than those from nonfractionated lignin (Kelley et al., 1989b). Bio-based rigid PU foams (B-RPF) were developed from ethanol fractionated lignin with further oxypoylation (Li et al., 2020a). The lignin was extracted from different ethanol concentration (15 vol%–60 vol%, ethanol in
aqueous phase), and fractionated lignin with lower molecular weight and higher aliphatic-OH groups was precipitated in low ethanol concentrated, which encouraged corresponding B-PRF product with higher compressive strength, lower thermal conductivity, and better thermal stability.

Despite reported PU products were mainly synthesized from solvent soluble lignin fractions, methanol insoluble fraction of lignin with high molecular weight was also explored to fabricate thermoplastics PU, which possessed higher rigidity to be served as hard segment (Saito et al., 2012, 2013). In order to develop more available stiff macromonomer, methanol insoluble lignin fractions were pre-reacted with formaldehyde lignin (FC-lignin) to increase its molecular weight and create more interconnected structure. A series of PU thermoplastics were synthesized by cross-linking of FC-lignin and polybutadiene diisocyanates (OCN-PBD-NCO), with lignin content of 80 wt%–65 wt% (Fig. 9). Two characteristic values of $T_g$ around −32°C and 150°C for the lignin thermoplastic PU were observed, indicating the existence of two-phase morphology and formation of thermoplastic copolymers. The mechanical properties of the PU thermoplastics depended on the lignin content and cross-linking density. The PU with 75 wt% FC-lignin exhibited the highest Young’s modulus ((140 ± 28) MPa) due to its higher content of lignin, while with more urethane bridges, 65 wt% FC-lignin based PU exhibited higher Young’s modulus and lower elongation than the 70 wt% FC-lignin copolymer. With properly tuning the molecular weight and properties of both the lignin and rubber segments, robust lignin-based PU thermoplastics could be prepared with a wide range of desired properties. Although superior PU materials have been developed with the lignin fractions, long and repeated extraction steps are required to obtain considerable amounts of distinct lignin for further processing, which potentially increases the processing cost and constrains large scale applications.

### 3.3. Chemical modification of lignin

Despite crude lignin can be directly incorporated into the PU materials as macromonomers, only partial hydroxyl groups could cross-linked with isocyanates to form urethane groups, since the reactive sites are often sterically hindered by the complex structure of lignin and phenolic hydroxyl groups are less reactive towards isocyanate (Cheng et al., 2012). Moreover, the intrinsic brittleness property impedes its processability and the poor solubility enables only a small amount of lignin incorporating into polymers. To overcome this limitation, lignin modification is considered to be one of the most effective approaches to optimize its chemical structure with increased solubility, decreased brittleness, improved reactivity, and improved processability, thus generating more

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**Fig. 8.** (a) Gel permeation chromatography (GPC) chromatograms of fractionated lignin with MeTHF (S-lignin) and as-received lignin (A-lignin); (b) The FT-IR spectra of S-lignin based PU films at varying S-lignin/TDI weight ratios of 70/30, 75/25, 80/20, 85/15, and 90/10 (The S-lignin was included for comparison); (c) Swelling behavior of lignin-based polyurethane (LPU) films derived from 1,4-dioxane extracted lignin in dimethyl sulfoxide (DMSO) and water; (d) Tensile strength of LPU films at varied molar ratios of NCO:OH, 1, 2, and 3 represent pristine LPU films, LPU films after swelling in DMSO, and LPU films after swelling in distilled water, respectively. Reprinted with permission from Griffini et al. (2015). Copyright 2015 American Chemical Society. Reproduced from Jia et al. (2015) with permission from the Royal Society of Chemistry.
available starting materials for polymers synthesis (Laurichesse and Avérous, 2014; Sen et al., 2015; Kai et al., 2016; Upton and Kasko, 2016; Zhang et al., 2019c). To date, the chemical modification of lignin can be classified into two main strategies (Fig. 10): 1) fragmentation or depolymerization of lignin to cleave it into oligomeric feedstock; and 2) modification by producing new chemical active sites to increase the reactivity of functional groups or fulfill specific requirement in the synthesis processing. With various functional groups, lignin can be modified to produce more available feedstock for widespread application, such as hydroxyalkylation, dealkylation, esterification, nitration, and amination. This section will highlight the chemically modified lignin as macromonomer to be incorporated into the PU materials.

3.3.1. Fragmentation of lignin

Lignin possesses heterogeneous and complex structure, which is mainly composed of condensed linkages (e.g., 5–5 and β–1 linkages) and ether linkages (e.g., α-O-4 and β-O-4) (Chakar and Ragauskas, 2004). The depolymerization strategy is mainly to cleave the ether linkages to produce oligomeric lignin with low molecular weight (Azadi et al., 2013; Hu et al., 2014; Laurichesse and Avérous, 2014). In the last decades, lignin has been cleaved into varied small molecular weight fragments and other chemical compounds, which shows potential to replace fossil-derived feedstock (Liu et al., 2014; Xu et al., 2014). Various strategies have been investigated for lignin depolymerization, such as thermochemical treatment, mechanical treatment, chemical catalysis, and biological treatment (Pandey and Kim, 2011; Xue et al., 2017; Zou et al., 2018; Chio et al., 2019). Through depolymerization of lignin, resultant lignin with reduced molecular weight and high functionality was produced, enabling them higher reactivity and processability for further utilisations as reagent (Mahmood et al., 2013, 2016b; Chio et al., 2019). Furthermore, the distinct structure and superior properties make depolymerized lignin more suitable to incorporate in the PU systems, thus replacing a higher amount of petroleum-based polyols.

Mahmood et al. successfully prepared rigid PU foams using hydrolytically depolymerized kraft lignin as bio-polyols which replaced 50 wt% of PPG400 or sucrose polyols (Mahmood et al., 2015), and liquefied hydrolysis lignin (LHL) based polyol (Mahmood et al., 2016a), respectively. The resultant PU foams showed superior compression modulus and thermal conductivity than those with fully PPG400 or sucrose polyols. With modulating the lignin content and formulation of the PU network, varied bio-based PU foams ranging
from soft to rigid can be achieved and applied for extensive applications, such as oil absorbent (Mohammadpour and Mir Mohamad Sadeghi, 2020). Cinelli et al. produced flexible PU foams with the combination of liquefied lignin and soft chain extender, such as polypropilenglycol triol and castor oil (Cinelli et al., 2013; Bernardini et al., 2015). With the addition of soft chain extenders, chains mobility was efficiently improved in the macromolecular structure, thus reducing $T_g$ of the materials and enabling PU foams flexible.

Furthermore, Li et al. (2017) successfully prepared lignin-based PU elastomers (LPUe) by direct cross-linking of depolymerized lignin as hard segments and poly-(propylene glycol) tolylene 2,4-diisocyanate terminated (PPGTDI) as soft domains (Fig. 11). With low molecular weight ($M_n = 600$) and high amount of hydroxyl group hydroxyl group (9.2 mmol/g), depolymerized lignin was well reacted with PPGTDI to form a continuous network. Moreover, strong hydrogen bonding was formed between carbonyl group/C—O—C group and N—H groups from adjacent urethane chains/excess O—H groups from depolymerized lignin, which gave rise to homogeneous morphology of LPUe with well dispersion of lignin in the PU matrix. Consequently, the LPUe exhibited excellent strength and ductility with high toughness of 264.7 MJ/m$^3$ with 40 wt% of depolymerized lignin, which improved the development of biomass lignin in the preparation of high-performance renewable PU elastomers. However, due to the poor solubility and steric hindrance effect of as-received lignin ($M_n = 3600$), microaggregates were dispersed among the LPUe samples, which resulted in rather poor mechanical performance. High performance LPUe was also successfully synthesized from depolymerized enzymatic hydrolysis lignin (DEL), polytetramethylene ether glycol (PTMEG), and HDI by Liu et al. (2019) (Figs. 11d and e). They found that the cross-linking network structure and the interfacial hydrogen bonds between lignin and the PU matrix facilitated the orientation of chain segments and led to strain induced crystallization, contributing to enhanced tensile strength up to 60.7 MPa and the maximum toughness up to 263.6 MJ/m$^3$, much better than control samples without lignin and with un-depolymerized lignin. It also exhibited excellent elastic recovery higher than 95% and thermal reprocessing ability for cycle processing.

3.3.2. New chemical reactive sites

(1) Hydroxyalkylation. So far, various new chemical reactive sites have been introduced in lignin structure to synthesize more reactive and available macromolecular (Sen et al., 2015; Kai et al., 2016; Cao et al., 2018). Among them, lignin hydroxyalkylation serves as a useful chemical modification processing, and has been widely studied to improve the reactivity and enable modified lignin more available to produce homogeneous PU networks. Lignin hydroxyalkylation is usually conducted with formaldehyde or alkylene oxide, such as ethylene oxide (EO), propylene oxide (PO), and butylene oxide (BO), and performed in aqueous alkali solutions (Glasser et al., 1984; Nadji et al., 2005; Yang et al., 2014a; Wang et al., 2016). It focuses on the preferred etherification of the phenolic hydroxyl groups to aliphatic hydroxyl groups, which are more reactive to the isocyanate groups (Kelley et al., 1989a). Moreover, this
strategy can also convert lignin with extended polyether chains with hydroxyl groups at the end, which reduces the steric constrains of hydroxyl groups and improves the miscibility of hydroxypropyl lignin in further applications (Glasser et al., 1982; Ahvazi et al., 2011). Hydroxypropyl lignin derivatives possess lignin content of 50%–70%, in which the flexible aliphatic ether phase is covalent bonded with high modulus lignin chains (Glasser et al., 1984). The incorporated soft ether chains effectively promote the segmental mobility of lignin based copolymers and improve the viscoelastic property of the resultant products, enabling higher content of lignin incorporated in the PU systems (Wu and Glasser, 1984; Wang et al., 2019a). This strategy provides a better control on the formulation and performance of the resulting PU products, compared with the directly reaction of unmodified lignin with isocyanates.

Numerous hydroxypropyl lignin has been used as prepolymer for engineering plastics (Glasser et al., 1982; Glasser and Leitheiser, 1984; Li and Ragauskas, 2012a). A series of the PU films were synthesized with hydroxypropyl lignin as the only polyl component and the structure-property relationship was investigated (Saraf and Glasser, 1984). With high lignin amount more than 43 wt%, the PU products all exhibited high Young’s modulus and low ultimate strain less than 16%, corresponding to the characteristic of rigid materials. Recently, Zhang et al. (2019a) developed oxalkylated lignin with ethylene carbonate and polyethylene glycol, which effectively produced more accessible and reactive aliphatic hydroxyl groups for the subsequent formation of rigid PU foams. The oxalkylation conditions, such as reaction temperature, PEG400 ratio, and lignin mass loading, were investigated to tune the viscosity and OH number of lignin. Under optimal conditions, oxalkylated lignin-based PU foams with densities from 51 kg/m³ to 60 kg/m³ and compressive strengths from 139 kPa to 204 kPa could be achieved. Li et al. prepared rigid PU foams from oxypropylated lignin and commercial polyols (sucrose polyol and glycerol polyol), respectively (Li and Ragauskas, 2012b). Due to the rigidity of aromatic structure and the high functionality of lignin, oxypropylated lignin derived rigid PU foams without other polyols exhibited better mechanical property than products derived from commercial polyols, demonstrating potential application of lignin in the PU industry. In order to improve the toughness of the lignin-based PU products for wide variety of practical use, additional PO was
involved to covalently bond to the hydroxypropyl lignin, producing a star like copolymer with a rigid aromatic lignin center and flexible polyether arms with hydroxyl groups on the end. The PU networks from the chain-extended hydroxypropyl lignin exhibited high elongation of 100%, demonstrating the feasibility of this strategy to effectively modulate the mechanical property of lignin-based PU products (Kelley et al., 1988, 1989a).

Moreover, additional polyether polyols were also involved to modulate the chain flexibility and mechanical property of the PU networks. A series of lignin-PEG based thermoset PU were prepared by using hydroxypropyl lignin and PEG with molecular weight of 400–4000 u (Saraf et al., 1985). The glycol content had a significant effect on the mechanical properties, in which both Young’s modulus and tensile strength were decreased with increasing PEG content, and ultimate strain was significantly increased. Finally, the PU products with a wide range of $T_g$ (38–158 °C), Young’s modulus (380–1670 MPa), and ultimate strain (6%–43%) were achieved by varying the glycol content, glycol molecular weight, and the type of diisocyanates. Furthermore, Bernardini et al. (2015) developed novel flexible PU foams from oxypropylated soda lignin, with polypropylene glycol triol (PPG triol) or castor oil as a chain extender. Compression strength of the PU foams ranging from 0.007 MPa to 0.07 MPa was achieved with lignin amount in the range of 6 wt%–13 wt%. Comparative PU foams from bio-based polyols (lignin and rapeseed) and petrochemical polyol were synthesized and investigated (Kurańska et al., 2020). The substitute of the petrochemical polyol with oxypropylated lignin lead to the PU foams with an acceptable performance for insulating materials, even with high content up to 30 wt%, promoting the application of lignin on the PU industry. Recently, Wang et al. (2019a) synthesized PEG-2000 grafted alkali lignin (AL-PEG2000), which was subsequently employed as a partial substitute of petroleum derived polyols to prepare highly resilient PU foams (Fig. 12). The grafted PEG chains provided flexibility to the resulting PU network. Moreover, the reaction activity and the compatibility between lignin and PU matrix were improved to generate homogeneous structure, in contrast to the obvious aggregates appeared in unmodified lignin-based PU.
foams, which contributed to the greatly enhanced mechanical strength. All the lignin-based PU foams exhibited large elastic recovery higher than 93% and improved energy absorption.

(2) **Other functionalization strategies** Except hydroxyalkylation, lignin is often reacted with other chemicals to generate new reactive sites and improve processability. Dealkylation is an efficient strategy to increase the content of hydroxyl group and improve the reactivity of lignin towards the PU formation. **Chung and Washburn (2012)** proposed the Lewis-acid-catalyzed reaction with the presence of hydrobromic acid and hexadecyltributylphosphonium bromide (TBHDPB) to synthesize HBr-modified lignin, in which the ether cleavage and demethylation were carried out in lignin ([Fig. 13](#fig13)). Upon modification, hydroxyl group content increased 28% compared with pristine samples, resulting in improved hydrophilicity, reactivity, and processability. The HBr-modified lignin was effectively cross-linked with TDI and integrated into the urethane networks, leading to improved performance of the PU materials which exhibited 6.5-fold higher in modulus and 15.5-fold higher stress at 10% strain than unmodified lignin-based PU. **Chen et al. (2020)** investigated the demethylation conditions of lignin under varied heating temperature from 105°C to 125°C, in which the content of methoxyl groups decreased compared with the increase of hydroxyl groups, and a 36.5% increase in hydroxyl content of lignin was achieved under optimal condition. Compared with unmodified lignin, demethylated lignin was better integrated into the PU interconnected network due to the improved reactivity and covalent linkage density, leading to higher thermal stability and mechanical properties of the PU adhesives, in which the tensile strength could be up to 91.21 MPa.

Lignin can be esterified to improve its solubility in common solvents. Lignin esterification is often performed by using organic acids such as acid anhydrides or acyl chlorides in the presence of suitable acids or basic catalysts. **Laurichesse et al. (2014)** prepared lignin-oleic acid based polyol (LOAP) by esterification of lignin, epoxidation of oleic acid double bond, and oxirane ring-opening synthesis. As shown in [Fig. 14](#fig14), the LOAP was highly branched with secondary hydroxyl groups, and its chain mobility was greatly improved with the incorporating of soft segment as arms. Subsequently, this polyol was employed as building block to synthesize the PU macromolecular architectures with varied NCO/OH molar ratios (from 0.2 to 1.0) and PPG chain length. All the PU products exhibited a rubbery plateau at high NCO/OH molar ratio, while a decrease of storage modulus was observed at low NCO/OH molar ratios, ascribing to low cross-linking density. Furthermore, all these materials demonstrated rubbery behavior with high elongation within the range of 170%–360% and corresponding rather lower modulus about 0.2–2.8 MPa. The high biomass content of 89 wt% in the systems and advanced properties improved the valorization of lignin in industrial applications. In contrast to improve the reactivity of lignin, **H. Jeong et al. (2013)** synthesized partially acetylated lignin, which was non-reactive to isocyanate groups, to produce thermoplastic PU. Ascribing to the decreased reactive hydroxyl groups and crosslinks in resultant PU, thermoplasticity of the resultant PU was improved. With lignin contents lower than 40 wt%, the resultant PU exhibited dominant viscoelasticity, whereas viscoelasticity was observed for the resulting PU with lignin content of higher than 40 wt%.

Lignin can also be nitrated with nitrating agents (such as nitric acid) to produce nitrolignin. **Zhang and Huang (2001a; 2001b)** synthesized nitrolignin based PU (PUNL) from castor oil and diisocyanate, forming star-like PU interconnected networks with lignin as core. Thermal stability of the PUNL films was improved compared with pure PU without nitrolignin. With nitrolignin content of 2.8 wt%, tensile strength and breaking elongation were 2 times higher than that of pure PU film (Zhang and Huang, 2001b). Furthermore, nitrolignin was incorporated into waterborne PU (WPU) systems as chain extender or additives after emulsification (Huang and Zhang, 2002). Similarly, the nitrolignin was also reacted with isocyanate groups by hydroxyl group in nitrolignin,
producing great star-like cross-linked network in the WPU. With the addition of 3.0 wt% nitrolignin, strength of the WPU reached 71.3 MPa, and strength and elongation were 1.8-fold over those of unmodified WPU.

Amination of lignin has also been investigated through Mannich research, which is often carried out with diethylamine and formaldehyde. The lignin amination can be incorporated into the PU synthesis as reactive precursor or a filler to enhance the properties of the composites (Zhou et al., 2017). The PU foams were also prepared from lignin-aminated polyol, PEG, and MDI in the presence of water as blowing agent (Huo et al., 2012).

Moreover, isocyanate functionalized lignin (k-IPDI) was also synthesized to replace approximately half of the hydroxyl groups, which was subsequently cross-linked with isocyanates to form flexible PU foams as an additive (Gómez-Fernández et al., 2017). Ascribing to higher chemical attachment of k-IPDI to the PU matrix, the PU foams with k-IPDI were softer and more flexible, while more rigid PU foams with higher elastic modulus and higher energy absorption were obtained with the addition of kraft lignin which served as reinforcement in the PU matrix. Over all, through different functionalize strategies, various new chemical reactive sites could be introduced in lignin structure, which enabled lignin more available to produce various PU materials with different properties for satisfying a wide variety of applications.

4. Lignin as filler for lignin/PU blends

Except using lignin as chemical reactant for constructing the PU polymers, physical blending lignin with the PU matrix is another way to develop lignin-based high value-added PU materials. However, due to poor compatibility between lignin and PU matrix, various attempts have been made to fabricate lignin/PU (LPU) blend composites (Feldman and Lacasse, 1989, 1994; Zhang et al., 2015a). Ciobanu et al. (2004) prepared a series of lignin/PU blends from the PU elastomer and various proportions of lignin (from 4.2 wt% to 23.2 wt%) by solvent casting technique. The presence of lignin accelerated the decomposition of the LPU blends at lower temperature, and the thermal property greatly depended on the lignin content and PU soft segment properties. Lignin could improve the strength of the LPU blends in detriment of elasticity with contents up to about 10 wt%, while more lignin induced highly depressed mechanical properties probably due to the agglomerate of lignin within the matrix. It showed a promising strategy to achieve the PU elastomer with superior strength and biodegradability, together with lower elasticity and decomposition temperature by blending lignin with no more than 10 wt%, and preferably up to 5 wt%. In order to improve the utilization of lignin as filler in lignin/PU composites, modified lignin with enhanced compatibility was also explored to incorporate in the PU matrix. For example, lignin amines were introduced in the PPG-TDI prepolymer during emulsification by Liu et al. (2013) to generate a homogeneous waterborne PU (WPU) emulsion. The modified lignin exhibited high solubility in water and good compatibility between the lignin and PU, contributing to the enhanced hydrogen bonding and superior mechanical property of the resultant WPU. The tensile strength and elongation at break increased after incorporation of lignin amine within content of 0.5 wt%–7.5 wt%. With inherent radical scavenging properties of lignin, the WPU materials exhibited excellent antiaging performance. Recently, Garcia Gonzalez et al. (2017) prepared lignin nanoparticles (nanolignin, NL) by ultrasonication which were incorporated into thermoplastic WPU matrix as bioderived filler to obtain advanced polymer nanocomposites. With the ultrasonication process, lignin particles were greatly decreased around 10–50 nm along with excellent colloidal stability in lignin-water dispersions, contributing to the excellent dispersion and distribution of nanolignin particles into the WPU matrix, as opposed to untreated lignin (IND) (Fig. 15). Finally, the mechanical properties of the nanolignin-based nanocomposites were significantly improved compared with untreated lignin-based composites.
Furthermore, lignin-based nanocomposites such as lignin/TiO$_2$, lignin/ZnO, and lignin/graphene were also developed as fillers to enhance the properties of PU matrix. Yang et al. (2019) synthesized well-dispersed lignin quaternary ammonium salt (LQAS)/TiO$_2$ nanocomposites to blend with the WPU. Ascribing to the excellent ultraviolet (UV) absorption ability and good compatibility with the WPU matrix, the LQAS/TiO$_2$ nanocomposites could obviously increase the UV absorbance and mechanical properties of the resulting blended WPU composites. Moreover, the WPU hybrid film exhibited good visible light transmittance and excellent ultraviolet aging properties. In addition, lignin/ZnO (Wang et al., 2017, 2018a) and lignin/silica hybrids (Xiong et al., 2017) were also synthesized and investigated to reinforce the UV-absorption ability and mechanical properties of the resulting blended PU films. Besides, lignin-modified graphene (LMG) aqueous dispersion was prepared and directly mixed with the WPU for casting film (Seyed Shahabadi et al., 2017). The WPU/LMG nanocomposite coatings exhibited increased storage modulus, impressive UV stability, fast self-healing, and decent conductance, demonstrating potential application as anticorrosive or antistatic coatings. These researches not only improve the high value-added utilization of lignin, but also extend the application of lignin for varied requirements.

5. Conclusions and future perspectives

With abundant in nature and outstanding properties, lignin has received growing attention as renewable feedstock for the preparation of high-value PU materials. As hydroxyl groups from lignin can be directly reacted with isocyanate to form urethane groups, various strategies have been devised to incorporate lignin into the PU products not only as a blend component, but also as a macromonomer with or without chemical modification to replace petroleum-derived polyols. A series of the PU products with varied thermal and mechanical properties were produced as the items of coatings, elastomers, adhesives, and foams. The performance of the resulting PU products greatly depended on the amount of lignin, formulation, and cross-linking density, and varied lignin-based PU polymers ranged from soft to hard were developed for a variety application of particle use. Considering the merits of excellent biodegradation, low cost, and environmental friendliness, lignin-based materials exhibit potential application for sustainable materials. Although tremendous lignin-based high value products have been investigated, the complex structure of lignin and complicated procedure for lignin pre-treatment impede its scale-up utilization from laboratory to industry. Moreover, most of the lignin-based polyol production strategies require some organic solvents, high temperature, or expensive catalysts, which increase the cost of the final products. Therefore, newly facile and economic synthetic techniques are expected to develop more available lignin for preparing useful products for commercial applications.

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References


Fig. 15. The SEM images of (a) PU/untreated lignin (IND) composites and (b) PU/nanolignin (NL) nanocomposites with lignin content of 10 wt%; (c) Strain-stress curves of PU, PU/IND-20, and PU/NL-20 composites. Reprinted with permission from Garcia Gonzalez et al. (2017). Copyright 2017 Wiley Periodicals, Inc.


