

RECENT ADVANCES ON LIGNIN-DERIVED POLYURETHANE POLYMERS

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Abstract. The incentive for use of bio-based polyol instead of petroleum-based polyol is motivating extensive research on polyurethane (PU) materials derived from lignin as fillers or raw material. Lignin is an abundant, underutilized component of cellulosic biomass and it offers a prospect of becoming a crucial feedstock. Regards to PU polymers, lignin is mainly used for production of polyurethane foams, followed by elastomers and adhesives. The present review summarizes the substantial and novel progress on lignin-derived PU materials over last few decades, containing an introduction of the physical and chemical properties of lignin and PU materials. The work so far carried out indicates that lignin can be used as a bio-based polyol to fully or partly replace petroleum-based polyols, which is environmentally friendly and economical. The review also includes recommendations for further research on the compatibility between the lignin and the PU matrix and the mechanism of lignin in PU polymers.

1. INTRODUCTION

Polyurethanes (PUs) are firstly synthesized from a polyol and a diisocyanate by Otto Bayer in the 1940s from which PUs are paid great attention and well developed [1]. PUs are up to date the most versatile polymers due to the flexibility of structure design at the application site. They are mainly used in rigid and flexible foams, coatings, adhesives, sealants, elastomers and binders.

Increasing environmental awareness among producers and consumers has led to substantial interest and research in biomass resource instead of petrochemicals for PU synthesis [2-10]. Regarding to bio-based polyols, one of the most abundant naturally polymers in the nature is lignin, which together with hemicelluloses acts as a cementing matrix of celluloses within the structure of plants and trees and mainly protects the wood from decay [11]. Lignin exhibits much expectation as a renewable source and it has become the target of many processes designed to turn biomass into useful chemi-

cals. Lignin shows highly branched macromolecular network structure of aromatic nature, because its molecules is comprised of a series of functional groups, such as phenolic and aliphatic hydroxyl groups, methoxyl, carbonyl, and carboxyl groups in various amounts, depending on the origin and the isolation methods of this natural polymer [12]. In view of the phenolic and aliphatic hydroxyl groups, it is considered as a bio-based polyol for PU synthesis. Especially, numerous lignin derivatives are obtained via modification of lignin by certain monomer and/or various polymers [13].

In the last few years, the domain of lignin utilization is growing. In view of amorphous structure, it can be used as activated carbons for the environmental protection to remove the dye [14-17] or the hence metals [18-20] from aqueous solutions. And a review has been published which presented the summarization of lignin and lignin-based chars and activated carbons as adsorbents for the removal of substances from water. Furthermore, it can be used

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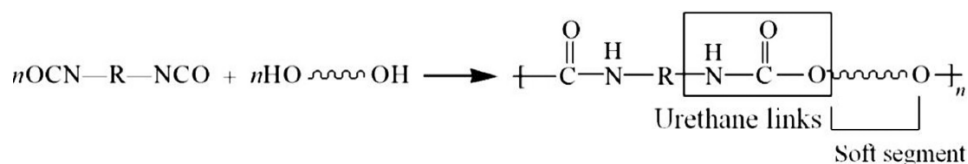


Fig. 1. The organic units of polyurethanes.

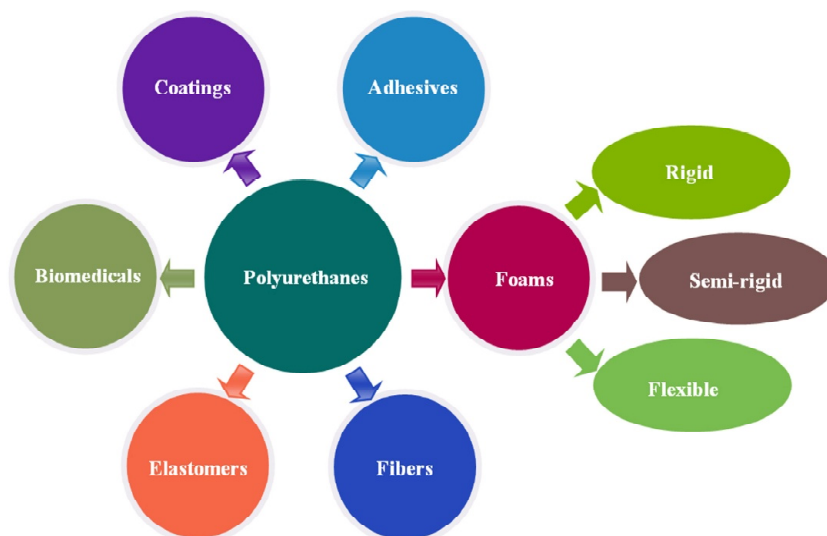


Fig. 2. Application domains of the polyurethane.

as a solid base catalyst, [22,23] as well as electrode [24-30]. Recently, a large number of lignin and its derivatives are used as fillers and raw components of PU materials which are the domain from coating to insulation materials.

Currently, the study on the lignin-derived PU polymer is half-baked. The reasons can be summarized as the following respects. Firstly, the lignin is a polymer with three-dimensional network structure, whose structure and physicochemical properties are dependent on the source and separation methods. Therefore, the control of properties for lignin-derived PU is substantially difficult. Secondly, the lignin is up to date mostly used as filler, and the filling content is limited, which is responsible for its availability. To solve the problem, the compatibility between the lignin and the PU matrix should be greatly enhanced. Liquefaction of lignin is an effective strategy to involve this problem and a new multiple-molecular network can be built. Liquefaction of lignin often follows two general approaches: (1) liquefied by polyols [31,32], (2) liquefied by non-polyols [33]. The advantage of the former one is no impurities in the PU matrix and no subsequent processing. However, the latter one needs a treatment of the solvent such as ionic liquid [34,35]. Furthermore, a variety of additives are blended in PU synthetic process which make it a complicated system. As lignin added in the system, the influence between the lignin and

additives requires further study. Therefore, complete participation of lignin in PU synthesis is critical important. And the exploration of the mechanism of lignin in PU polymers plays an important guiding role in the future PU study.

Here recent work on the substantial and novel progress on the lignin and its derivatives to make PU materials is reviewed. First, the short summaries of referred physics and chemistry of lignin and PU are presented. Consequently, recent work about lignin-derived PU materials with the lignin and its derivatives as fillers or reactants is summarized. Since the environmental protection is of much concern, finally, the degradation of lignin-derived PU materials is also discussed.

2. POLYURETHANES AND LIGNIN-PHYSICS AND CHEMISTRY

2.1. Polyurethanes

PUs are a broad class of polymers consisting of a chain of organic units joined by urethane links (Fig. 1). They meet multi-purpose design objectives for their versatility (Fig. 2). In the last nine years, a number of articles are published related to the main application (Fig. 3). Concern about environmental protection and efficient energy utilization, one of the problems related to the production of PU nowadays is their dependence on petroleum-derived products.

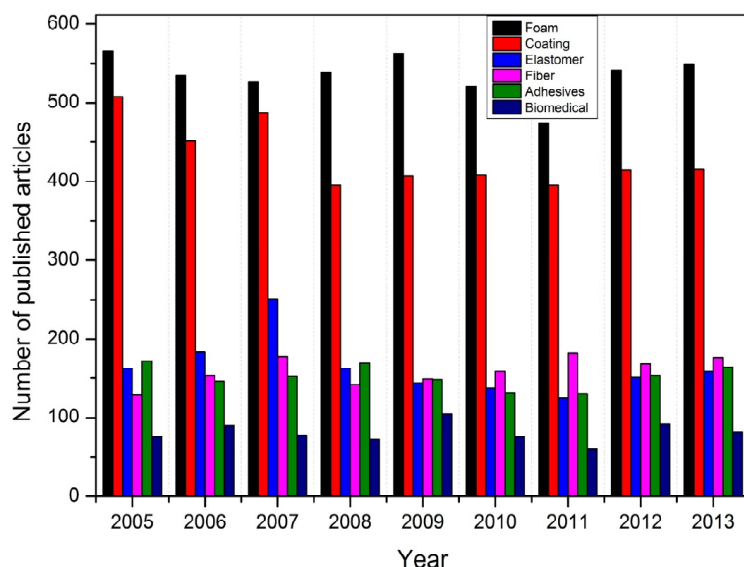


Fig. 3. Number of published articles on polyurethanes.

More attention has been paid on the production of PU from lignin with an environmentally-friendly pathway since 1970s [36]. The utilization of lignin in polyurethane synthesis often follows three global methods: (1) the direct utilization of lignin without any preliminary chemical modification, alone or in combination with other polyols, [37-41], (2) by making hydroxyl functions more readily available by chemical modification, such as esterification and etherification reaction [42,43] or (3) by making functions other than hydroxyl groups more available by chemical modification [44]. The first two approaches are widely used while there is rare utilization on the third one. The treatment of lignin with Lewis acids is a strategy of that, through demethylation of methoxy group on the ortho-position of phenolic hydroxyl group increasing the concentration of hydroxyl groups available to react with diisocyanate monomers. And it is proved that the PUs materials with lignin modified by Lewis acids showed substantial improvement in mechanical properties over both PUs containing unmodified lignin and pure PU that does not include lignin. On the other hand, the demethylation of lignin has no effect on the microstructure of PUs [44].

2.2. Lignin

Lignin plays a critical role as a renewable energy resource, because it can be converted into products to replace natural gas, petroleum and coal resources directly [45]. Lignin can be separated from trees and plants via physical, chemical or enzymatic treatments, with the composition depending on the tree and plant species. In the past few years, lignin

is mainly isolated from wood pulping and papermaking operations where it is used as fuel, and only a small amount of lignin (1–2%) is separated and employed in other kind of products [46]. Since it is a natural polymer, lignin is insoluble or slightly soluble in most of organic solvent so that it is difficult to be compatible with the synthetic compounds such as isocyanate from petroleum resources [47]. Modification of lignin by specific monomer such as acetic acid [48] and propylene oxide [49,50] is an effective strategy to make it more soluble in general organic solvent and easily to be made into polymer materials. On the other hand, an effective way is obtained through liquefaction instead of the direct use of lignin. More studies have conducted on the improvement of lignin-solubility [31,51-53]. Furthermore, due to complex molecular structure, fractionation of lignin is a better method to get compositions with narrow molecular weight distribution and this will promote the solubility of the compositions in organic solvents [54].

Lignin is a natural polymeric product mainly linked by arylglycerol ether bonds between the monomeric phenolic p-coumaryl (P), guaiacyl (G), and sinapyl (S) alcohol units as shown in Fig. 4 [55]. Lignin is divided into three basic types, that is soft, hard and grass wood lignin, due to their composition in structural units. A typical soft wood lignin, also called guaiacyl or coniferous lignin, is composed of guaiacyl alcohol units. Soft wood lignins separated by different methods and from different species are very similar in their structure. Hard wood or dicotyledonous angiosperm lignin is made up of guaiacyl and sinapyl alcohol units. Finally, grass, annual plant or monocotyledonous angiosperm lig-

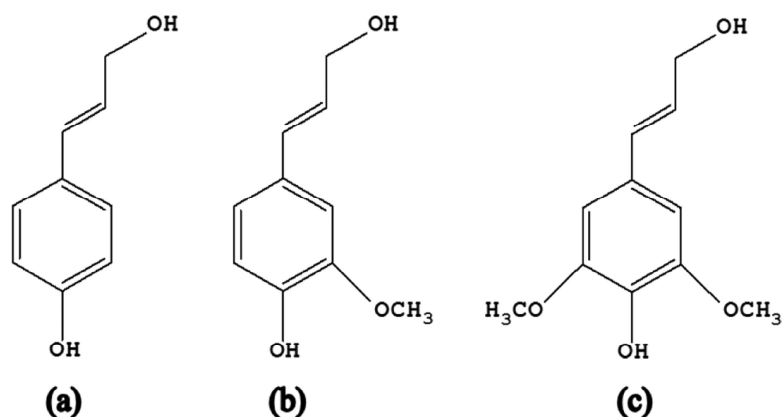


Fig. 4. Structure units of lignin: (a) p-coumaryl, (b) guaiacyl, and (c) sinapyl alcohol.

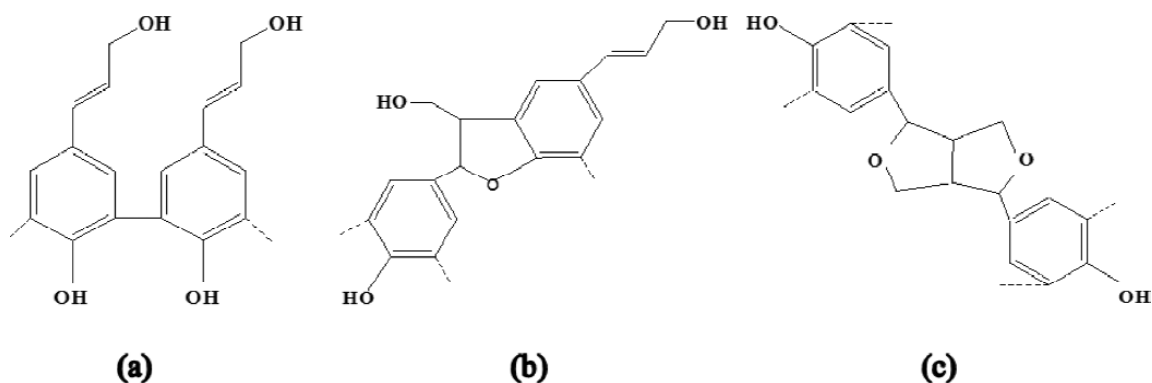


Fig. 5. The possible branching lignin subunits between random two units of p-coumaryl, guaiacyl and sinapyl alcohol units. OCH₃ group is possible in the dotted line position.

nin is made up of guaiacyl, sinapyl, and p-coumaryl units [56]. The possible branching lignin subunits between random two units are shown in Fig. 5, where the bonding sites mainly arise from double bond, hydroxyl and ortho-position of carbon atom linked with the hydroxyl on benzene ring. Based on those subunits, further combination is formed.

Differently with the inner structure, the reaction point between the lignin and related organic monomer is primarily attributed to hydroxyl, such as the reaction with carboxyl [57]. A typical reaction is the phenolic hydroxyl and $-N=C=O$ group of isocyanate to form a useful material of polyurethane (PU).

3. APPLICATIONS

Lignin is primarily employed in polyurethane foams, followed by elastomers and adhesives, rarely in other polyurethane fields.

3.1. Foams

Foams represent one of the most important commercial products of PU. These foams are commonly classified as rigid, semi-rigid, or flexible, depending on their mechanical performance and core densi-

ties. The main field of PUs application is in the furniture industry that makes use of rigid PUs followed by automotive applications (seat cushioning, bumpers, sound insulation, etc.) where flexible and semi-flexible PUs are mainly put to use.

3.1.1. Rigid polyurethane foams

Rigid polyurethane (RPU) foam is a highly cross-linked polymer with a closed-cell structure. Due to the excellent insulation and mechanical properties, they are widely used in construction, automotive industry, freeze sectors, equipment manufacturing, nautical applications, etc. [58].

The RPU foam is easier to be obtained, because of the closed-cell structure, than the flexible foam which is a three-dimensional polymer with an open-cell structure. Many researches on the partial addition of lignin to the RPU foams are based on the premise that the products should be useful in PU industry. Generally, at low lignin contents of 0-25%, the resulting RPUs exhibit considerable density, compressive strength and cellular structure [59]. As for higher lignin contents, favorable foams can be obtained through oxypropylation of Kraft lignin [46]. Yang Li et al. studied on the oxypropylated lignin

derived RPU foams and the optimal compressive property of foams was achieved using lignin polyol without the addition of any other commercial polyols primarily attributed to the rigidity of lignin aromatic structure and the high functionality of lignin hydroxyl groups [50]. Unfavorably, the addition of lignin to rigid PU foams have little effect on the natural aging or heat aging resistance [60,61]. The thermal treatment with higher temperature such as above 200 °C is necessary under a nitrogen atmosphere to prevent the PU materials from oxidation [62].

RPU foams with specific function are in demand. For example, to obtain foams with flame-retardant performance, lignin is chemically modified with flame retardant elements and then partly used instead of petroleum polyol as raw material to synthesize rigid foams [63].

In a word, the successful implement is achieved for the lignin-derived RPUs and the related research on these materials is relatively sufficient so that it is basking in large industrial stage.

3.1.2. Semi-rigid polyurethane foams

Semi-rigid polyurethane (SPU) foams are widely investigated in the last few decades [64-66]. They are widely used in specialty applications including transportation for automotive seating, carpet foam backing and furniture for sofas, mattresses, pillows, and office furniture foam padding. It has an advantage of load bearing compared to rigid closed-cell materials.

A study about a fire retardant prepared by a complex of a SPU foam and expandable graphite (EG) with various particle sizes is reported, from which it is suggested that the composites exhibited substantial enhancement in flame retardant properties via forming a surface isolation layer with the graphite size of 150 μm to 960 μm compared to the neat foam, and no contribution was found as the graphite size is smaller than 150 μm. However, EG particles show slight effect on the thermal stability of the composite [67].

3.1.3. Flexible polyurethane foams

So far, there are few reports on flexible polyurethane (FPU) foams synthesized from lignin polyols [31,68], which remains on research stage and have a prospective development. If the lignin is directly added to the raw materials during the preparation of FPU foam, it will greatly affect the mechanical properties of the foam which has a specific open pore structure containing numerous edges, where the thick-

ness and homogeneity have critical contribution to the mechanical properties. Thus, lignin used as a raw polyol is more favorable and makes it a steady partial soft segment of FPU foams. However, a key problem is the solubility of lignin to an appropriate solvent and the solvent has a promise of no negative effect on the properties of FPU foams. Lignin is soluble in few alcohol components, which is beneficial for synthetic reaction of PU, since the alcohol components associated with lignin can be used as reagent for making FPU without further separation or purification [47]. Content of lignin can be up to 45% by weight of total liquefied products with the Polyethylene glycol (PEG) 400 and glycerol as liquefying agent [31].

The reticulated polyurethane foams are partially or fully reticulated FPU foams with higher open pores rate and a skeletal structure. It is suited for a variety of applications such as for filtering, absorbing, wiping, and padding and medicals/healthcare [69]. However, there are few reports up to date on the lignin-derived reticulated polyurethane foams and therefore there is plenty of room for growth.

3.2. Elastomers

Elastomer polymers exhibit excellent elasticity, high mechanical strength and abrasion resistance due to specific micro-phase structure between the hard and soft segments. Hard segments (isocyanate) are contributed to high temperature properties, while soft segments (polyol) participate in elastomeric properties of polymer at low temperatures [70,71]. The addition of lignin in PU elastomer is a blends process but not a reaction process. Generally, the PU elastomer and lignin need predissolve by dimethyl formamide solutions, and the products are lignin-polyurethane films obtained after solvent removing by thermal curing in an oven at 105 °C for 12 h [45]. On the other hand, the soft segment has a substantial effect on the elasticity of PU elastomer [72]. Meanwhile, PU elastomers produced with higher lignin content however are too brittle to test [73], so that the lignin content by weight of the elastomer need be low to 10% [48].

3.3. Adhesives

Lignin and lignin derivatives can be used to prepare formaldehyde free wood adhesives [74]. Meanwhile, PU materials have been used for adhesives for few years. For example, PU-based flexible electrically conductive adhesives exhibit excellent electrical conductivity (resistivity $\approx 1.0 \times 10^{-5} \Omega \text{ cm}$) and the

resistivity does not change when bending at a 2.64% flexural strain, rolling at a radius of 8 mm or pressing under 250 kPa [75].

Regarding for lignin-derived PU adhesives, related studies still could be found. S. Chahar et al. studied on several polyurethane samples prepared from laboratory black liquor (LBL) by reacting varying amounts of lignin ranging from 5 to 70% (w/v) in poly(ethylene glycol) (PEG) (having molecular weights of 200, 600, 1000, 1500, and 4000) with tolylene 2,4-diisocyanate (TDI). It is found that mechanical properties is deteriorated and T_g increases with increasing lignin content so that an optimum combination of thermal and mechanical properties can be prepared using poly(ethylene glycol) of molecular weight 200 and a lignin concentration of 50%. Unfortunately, increase in lignin concentration results in a decrease in coating qualities with poor adhesion strength [76]. Therefore, the lignin or modified lignin as filler to produce PU adhesive is more unfavorable relative to direct utilization of pure lignin or PU material as adhesives, because the latter strategy is more economical, simple and easier to obtain preferable properties.

3.4. Coatings

The addition of lignin helps improve the biodegradability and enhance the strength of polyurethane-based coatings [77]. Since 1976, Hsu et al. had studied on the PU coatings from modified lignin; then Mozheiko et al. investigated PUs derived from oxypropylated lignin which was suitable for use in coatings in 1981 [78,79].

In the next few decades, researchers still pay close attention to lignin-derived PU coatings. For example, the coated films with PU/nitrolignin coating exhibited superior water resistivity and dimensional stability, and can shade the ultraviolet light in the range of 300~400 nm relative to pure PU coating [80] A study on lignin-based polyurethane hydrogels by Peng, et al revealed that the hydrogels presents enhanced thermal stability via the introduction of lignin and it can be used as coating materials to prepare a slow-release fertilizer [77].

4. BIODEGRADATION

Although lignin degradation has been studied for decades, especially by decay fungi species [81], there is a substantially necessary to focus on degradation of lignin-derived materials. In the past few years, the biodegradation of PU in the environment is of much concern. The combination of biobased

lignin into the PU foams is a remarkable strategy to improve polyurethane degradation, which is more acceptable and feasible and represents a popular alternative environmental-friendly and economically justified process compared to the chemical and physical degradation.

Related research can be found from Amaral group on the lignin-based foams degradation by placing them in liquid media or soil conditions, for 90 days at 30 °C. After 90 days treatment, morphological changes were clearly visible at the surface (cell wall) of the two lignin-based foams indicating a stronger effect of the microorganisms' activity in these samples. And it is concluded that the lignin-based foams presented a pronounced degradation behavior compared to the commercial foams [58]. Obviously, above strategy presents a condition close to the real environmental condition, and gives a guidance to the future study on the degradation of biomass-derived materials.

5. CONCLUSION

Lignin is easy-obtained from the abundant and cheaper crop residues (wheat and corn straw, et al., use of it for raw materials of PU materials is reliable and more attempts have made to that. The solubility of lignin is a limit to the number of application, fortunately, it is soluble in few alcohol components and they can be used as combined polyol without purification of alcohol components. Another utilization limit is its complex molecular structure and wide molecular weight distribution and the solution is fractionating by organic solvents and performing more chemical analysis on it. More researches are carried out on lignin-derived PU foams, followed by elastomers and adhesives, rarely in other polyurethane fields. At low lignin content, the PU materials can be easily obtained, whereas it is difficult to get lignin-derived PU materials with high lignin content. Thus, complete replacement of lignin to polyol is a motivate goal. Remarkable, from the practical point of view, further research on the compatibility between the lignin and the PU matrix should be enhanced. From the academic point of view, it is very necessary to probe functional mechanism of lignin with other additives in PU polymers.

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