Open Journal of Polymer Chemistry, 2019, 9, 27-38
http://www.scirp.org/journal/ojpchem
ISSN Online: 2165-6711
ISSN Print: 2165-6681

Lignin: Renewable Raw Material for Adhesive

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How to cite this paper: Gadhave, R.V., Srivastava, S., Mahanwar, P.A. and Gadekar, P.T. (2019) Lignin: Renewable Raw Material for Adhesive. *Open Journal of Polymer Chemistry*, **9**, 27-38.
https://doi.org/10.4236/ojpchem.2019.92003

Received: January 30, 2019
Accepted: May 5, 2019
Published: May 8, 2019

Abstract

Biobased raw material like lignin used during manufacturing of wood and wood composite adhesive have been used extensively to replaced petro-chemical based adhesive because of their easy availability, low cost and biodegradability. Bio-based resources, such as lignin which is an abundant, constitute a rich source of hydroxyl functionality which is being considered as reactive raw material for the production of "adhesives". Lignin is mainly used for production of wood and wood composite adhesives by blending with soy protein, grafting with another polymer and reacting with isocynates. In this review, lignin as suitable alternative raw material to conventional petroleum sourced materials used as a raw material for adhesives is discussed.

Keywords

Polyol, Lignin, Wood, Adhesive, Biopolymer

1. Introduction

Most polymeric coatings and adhesives are generally based on fossil feedstocks. However, increasing oil prices and global warming demands a change from fossil feedstocks to renewable resources. Recently, researchers are increasingly devoting their efforts to the possible use of renewable feedstock as raw materials for the production of monomers and their polymeric coatings and adhesives. Renewable resources like vegetable oils based fatty acids, proteins and animal fats are readily available. There have been many studies of polymers based on vegetable oils, such as vinyl polymers, epoxy resins, alkyd resins, polyamides, and polyurethanes [1]. There has been a more research interest in the development of biobased wood adhesives from renewable resources. Various biomass resources such as lignin, starch, plant proteins, tannin, bark, and vegetable oils have been used as a renewable feedstock to synthesize bio-based adhesives [2]. Due to increasing economic and environmental issues, lingo-cellulosic biomass an abundant renewable resource becomes an ideal alternative to non-renewable petroleum resources. Lignins obtained in industry, however, are technical lignins, such consisting soda lignin, kraft lignin, lignin sulfonate, organosolv lignin, steam explosion lignin and enzymatic hydrolysis lignin. These are the byproducts of certain bio refinery processes [3]. Lignin is an amorphous natural polymeric material that is based on phenylpropane derivate and one of the most abundant materials and renewable resources on earth. It is well accepted that lignin is a phenolic polymer derived primarily from three hydroxycinnamyl alcohols or monolignols by free radical generation followed by chemical coupling process. The hydrocycinnamyls are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Lignin is never defined as a class of phenolic natural polymers with broad compositions and a variety of linkages between units [4]. Lignin has been attracting interest as a novel eco-friendly material because of its physical properties and favourable degradation characteristics. By transforming forest and agricultural feedstocks, new renewable, biodegradable, and biocompatible materials are being produced [5]. Lignin acts as a reactive component, and the active functional groups in lignin are further utilized for biocompatible materials [6].

2. Lignin: Use as an Adhesive

Most of the adhesive components were derived from petroleum, which are increasingly more expensive. Another problem is that the cured adhesives within panel products limit the reuse options of the discarded boards and production residuals. Both economical and health benefits could thus be obtained from synthetic resin-free production processes.

2.1. Blending of Lignin with Other Polymers

Soy protein has great potential as sustainable biobased wood adhesive but they have low moisture resistance. Lignin has more moisture resistance than soy protein. Bio based adhesive derived from blend of Soy protein and lignin could improve moisture resistance as well as economical. The wet strength of soy protein adhesive increased as lignin particle size decreased [7] [8] [9] [10] [11]. The lignin amine modified soy adhesive exhibited excellent water resistance and high dry and wet shear strengths for plywood. Because of the lignin used in this study largely retained its native highly branched structure, it is not soluble in water and most of organic solvents. However the preparation of partially de-polymerized lignin (PDL) increase solubility in solvents and hence increased accessibility of the hydroxyl groups for reactions. Comparing to PDL amine, the amine based on not de-polymerized lignin could more greatly enhance the adhesion strength and water resistance of soy protein based adhesives reaction is shown in **Figure 1** [12]-[18].

Starch based adhesives are susceptible to colonization by a variety of microbes including molds and fungi which can decrease the effective lifetime of the

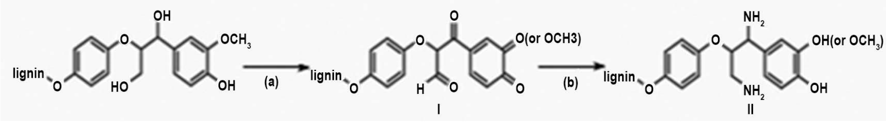

Figure 1. Synthesis route for preparation of lignin amine.

adhesive and the product into which lignin is incorporated [19]-[24]. The good compatibility and intermolecular interaction shown by PVA and lignin blend may contribute to sustainability and reduction in the environmental impact associated with disposal of oil-based polymers [25]-[33]. The nanokraft lignin particles when used with polyvinyl alcohol (PVA) increased the thermal stability of nano lignin/PVA blends more effectively compared to the original lignin/PVA blends [34]. In Urea formaldehyde resins, Decrease in formaldehyde release and increase in water resistance was observed by incorporation of lignin [35]-[44].

2.2. Lignin with Different Cross-Linkers

Corn stalk lignin was used to react with non-volatile and non-toxic glyoxal under the catalysis of a sodium hydroxide solution, and a wood adhesive based on glyoxal modified corn stalk lignin was prepared. Lignin-based environmental wood adhesives were prepared by mixing modified lignin and epichlorohydrin (ECH), and the dry strength of plywood reached 1.58 MPa. The mechanical strength and water resistance of plywood was improved significantly by mixing some aqueous emulsion into lignin-based adhesives [45]-[50]. The hydrogen in phenolic group of lignin interacts with functional group of protein forming a cross-linked structure thereby increasing the tensile strength, thermal stability and young's modulus while decreasing water absorption of protein [51] [52] [53].

2.3. Lignin as Reactive Raw Material

Grafting vinyl acetate onto lignin, the mechanical and thermal properties of lignin were enhanced and also made better material with more desirable properties. The hydrophobic character of lignin improved by grafting reducing moisture absorption [54] [55] [56] [57] [58] (**Figure 2**).

The hydroxyl group of lignin reacts with isocyanate group to form polyurethane adhesive A series of waterborne polyurethane (WBPU)/modified lignin amine (MLA) adhesives was prepared using MLA as a chain extender by a prepolymer mixing process [59] [60] [61]. The addition of lignin into the formulated PF resin improved the thermal properties and varied the flow behavior of PF resin from Newtonian to Pseudo plastic type. The phenolic nature of lignin makes it prone to replace phenol with lignin derivatives in PF resins to formulate wood composite adhesives suitable for plywood, particle board and other similar kind of composites, replacing current synthetic PF resins which are based on petrochemical, non-renewable sources [62]-[72]. There is a growing demand to develop renewable aromatic compounds to replace the petroleum based Bis-phenol A. Here lignin can be used to develop Renewable epoxy networks economically with low ecological harm as shown in **Figure 3** [73]-[78].

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^{\bullet-} \quad \text{—— (1)}$$

$$SO_4^{\bullet} + H_2O \longrightarrow HSO_4^{-} + HO^{\bullet} \quad \text{—— (2)}$$

$$Fe^{2-} + S_2O_8^{2-} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \quad \text{—— (3)}$$

$$Fe^{2+} + SO_4^{\bullet-} \longrightarrow SO_4^{2-} + Fe^{3+} \quad \text{—— (4)}$$

$$\text{Lignin-OH} + SO_4^{\bullet-} \longrightarrow \text{Lignin-O}^{\bullet} + HSO_4^{-} \quad \text{—— (5)}$$

$$\text{Lignin-OH} + HO^{\bullet} \longrightarrow \text{Lignin-O}^{\bullet} + H_2O \quad \text{—— (6)}$$

$$\text{Lignin-O}^{\bullet} + nM \longrightarrow \text{Lignin-O-Mn} \xrightarrow{\text{Propagation}} \text{Grafted lignin} \quad \text{—— (7)}$$

$$HO^{\bullet} \text{ or } SO_4^{\bullet-} + nM \longrightarrow \text{Homopolymer} \quad \text{—— (8)}$$

$SO_4^{\bullet-}$ - sulfate radical anion

Figure 2. Grafting of monomer onto lignin.

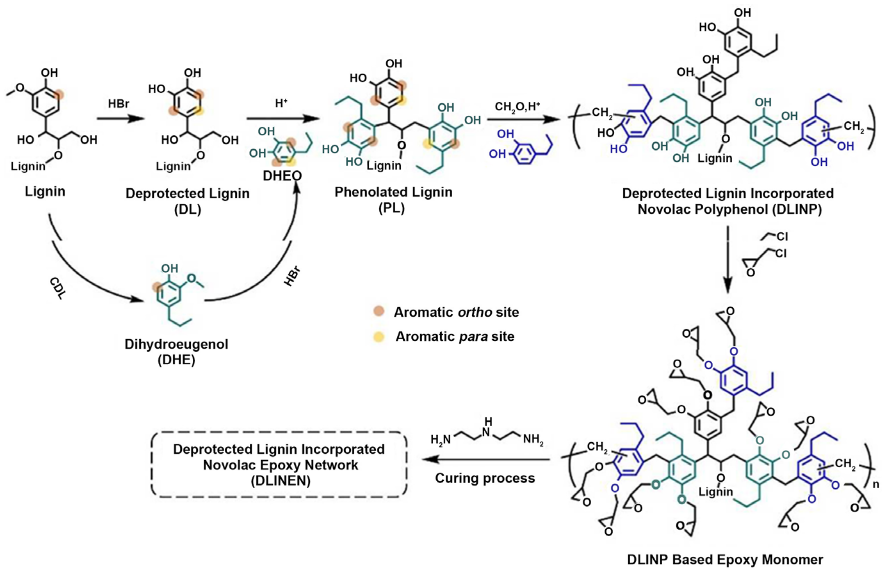

Figure 3. Lignin incorporated Epoxy network.

Controlled modification of lignin is done to form maleimide lignin derivative and were reacted through an extremely fast thiolene "click" polymerization with thiol containing linkers. Increasing the thiol linker functionality from 2 to 4 results in more crosslinked material [79]. Lignocellulosic ethanol residue(ER), as the by-product of lignocelluloses ethanol production, is rich in activated lignin and usually treated as waste. The ER was used as a renewable and valuable resource to partially replace phenol in the range of 10% - 70% to prepare lignin–phenol formaldehyde adhesive [80] [81]. Lignin-phenol-formaldehyde resin adhesives with 10% - 60% substitution rates and low residual toxicity were successfully synthesized. These results indicate that the lignin-phenol-formaldehyde resin adhesives synthesized using the designed formulation could effectively control formaldehyde emissions without any significant drop in the bonding strength of the bonded plywood [82].

Polyurethanes are a heterogeneous family of polymers that include in its backbone the urethane group (-NH-CO-O), also known as carbamate group. The urethane linkages generally result from the reaction between an isocyanate group and a hydroxyl function. For polyurethane synthesis purposes, lignin can act as a source of reactive hydroxyl site; it contains within its structure, both aliphatic and aromatic hydroxyl groups can potentially act as reactive sites for isocyanate groups to form urethane linkages as shown in Figure 4.

3. Conclusion

To conclude, lignin has shown to be a potential raw material for adhesive manufacturing, looks promising both as inert filler and as a reactive component. The depletion of natural sources, increasing environmental problems and tightening regulations have not only directed but also pushed adhesive manufacturers to look for more sustainable and renewable solutions. Incorporation of lignin, one of the most widely available natural polymers, into our adhesives is definitely a step in this direction. The feasibility studies and preliminary results discussed in this review show a positive sign for adhesive manufacturers looking for low cost, eco-friendly alternatives for traditional materials. Even though as a limited replacement to petroleum based materials, the discussion of various studies and research articles show a path to reduce our dependency on naturally expensive and depleting sources.

4. Futuristic Approach

Lignin is one of the most common naturally occurring renewable materials. Millions of tones of lignin is incinerated as waste each year. The current trends

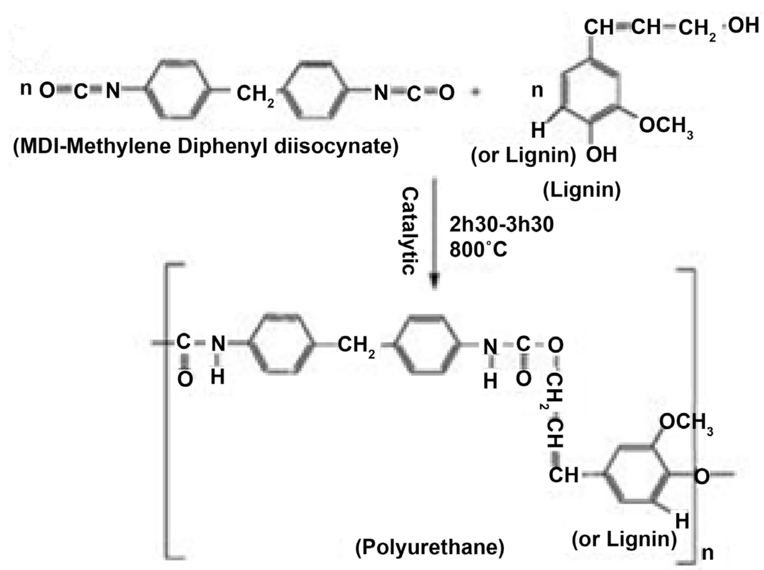

Figure 4. Reaction between lignin and isocyanate.

related to use of lignin, as discussed in this review, show that lignin has various advantages when incorporated in adhesives. The high phenolic content in lignin adds fire retardancy while the components derived from de-polymerized lignin can replace synthetic phenols in phenol-formaldehyde adhesives. From epoxies, phenol-formaldehyde, polyurethanes to poly vinyl acetate based glues; lignin can be incorporated in various systems across chemistries either as filler or as a reactive starting material.

The future developments with regards to lignin's role in adhesives seem to be in replacing and also improving performance of traditional adhesives. It can be used to fulfill many roles depending on the desired properties and can be suitably modified to optimize performance. The low cost, sustainable sourcing and biodegradability of lignin will help adhesive manufacturers looking for eco-friendly and greener alternatives to traditional raw-material sources. Further exploration on characterization, modifications and incorporation of lignin in various adhesive systems is required to get more benefits from incorporating lignin in the system and get further acceptance by chemical manufacturers.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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