International Journal of Biological Macromolecules 89 (2016) 265–272

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

# Application of bioethanol derived lignin for improving physico-mechanical properties of thermoset biocomposites

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ARTICLE INFO

*Article history:*
Received 2 December 2015
Received in revised form 21 April 2016
Accepted 26 April 2016
Available online 27 April 2016

*Keywords:*
Biocomposites
Lignin
Physical and mechanical properties

ABSTRACT

Lignin is the most abundant of renewable polymers next to cellulose with a global annual production of 70 million tons, largely produced from pulping and second generation biofuel industries. Low value of industrial lignin makes it an attractive biomaterial for wide range of applications. The study investigated the application of wheat straw and corn stover based lignin derived from ethanol production for use in thermoset biocomposites. The biocomposite matrix constituted a two component low viscosity Araldite® LY 8601/Aradur® 8602 epoxy resin system and the lignin content varied from 0 to 25% by weight fraction. The analysis of the physical and mechanical properties of the biocomposites show bioethanol derived lignin can improve selective properties such as impact strength, and thermal stability without compromising the modulus and strength attributes.



## 1. Introduction

Lignin is the most abundant of renewable polymers next to cellulose with a global annual production of 50 million tons largely produced from pulping and second generation biofuel industries. It is found as a cell wall component in all vascular plants. The lignin content in woody stems varies between 15 and 40%, and it acts as a water sealant and plays an important part in controlling water transport through the cell wall. It also protects plants against biological attack by hampering enzyme penetration. Lignin acts as permanent glue, bonding cells together in the woody stems and thus giving the stems their well-known rigidity and impact resistance. Chemically lignin is a dendritic network of phenyl propene basic units as shown in Fig. 1. The two principal categories of lignin which have been commercialized are lignosulphonates (500,000 t/annum) and kraft lignins (100,000 t/annum) being generated during sulphite and sulphate pulping respectively [1].

Lignin has a complex chemical structure that is derived from phenypropanoid monomers joined to form a large amorphous network polymer. Fig. 1 shows a simplified structure of lignin and a tentative of schematic representation of wheat straw lignin. It specific structure is highly variable and depends on the specific plant source as well as the extraction method. Major differences occur between lignins derived from different pulping processes. The common sulfite process generates a water soluble polymeric derivative in admixture with degraded carbohydrates. An aliphatic sufonic acid function becomes part of lignin backbone making it water soluble in the presence of suitable counter ions like Na, Ca, Mg, and $NH_4$ etc. Kraft lignins are generally produced in alkaline medium. They contain a small number of aliphatic thiols groups that give the isolated product a characteristic odor from heat treatment. Kraft lignins are dark colored and dissolve in alkali due to presence of phenolic hydroxyl groups. Both kraft lignins and lignin sulfonates undergo a distinctive glass to rubber transition when heated. The $T_g$ of lignin is under 100 °C [2]. It is largely due to this variability it is restricted to a few commercial applications. With increased environmental concern and demand for biobased materials researchers have begun to look at lignin as a renewable, economical and multifunction filler for composites [3–6].

The use of kraft lignin as a copolymer or polymer additive has received a considerable amount of attention [6,7]. The most straightforward application is the use of lignin as a filler material in thermoplastic [3,4] and thermosetting [8,9] polymers and rubbers [10] with limited effects on the mechanical properties. Co-reaction of lignin with phenol-formaldehyde resins [11], epoxy-resins [12,13], polyurethane precursors, [14] and polyester precursors [15,16] has proven to be more successful. Mechanical property improvement or no deterioration has been related to a certain lignin loading level. Chemical modification of lignin can be used to introduce reactive sites for improving polymer lignin compatibility. The available hydroxyl groups on the lignin molecule are reactive, plentiful, and local centers of high-polarity capable

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http://dx.doi.org/10.1016/j.ijbiomac.2016.04.077
0141-8130/

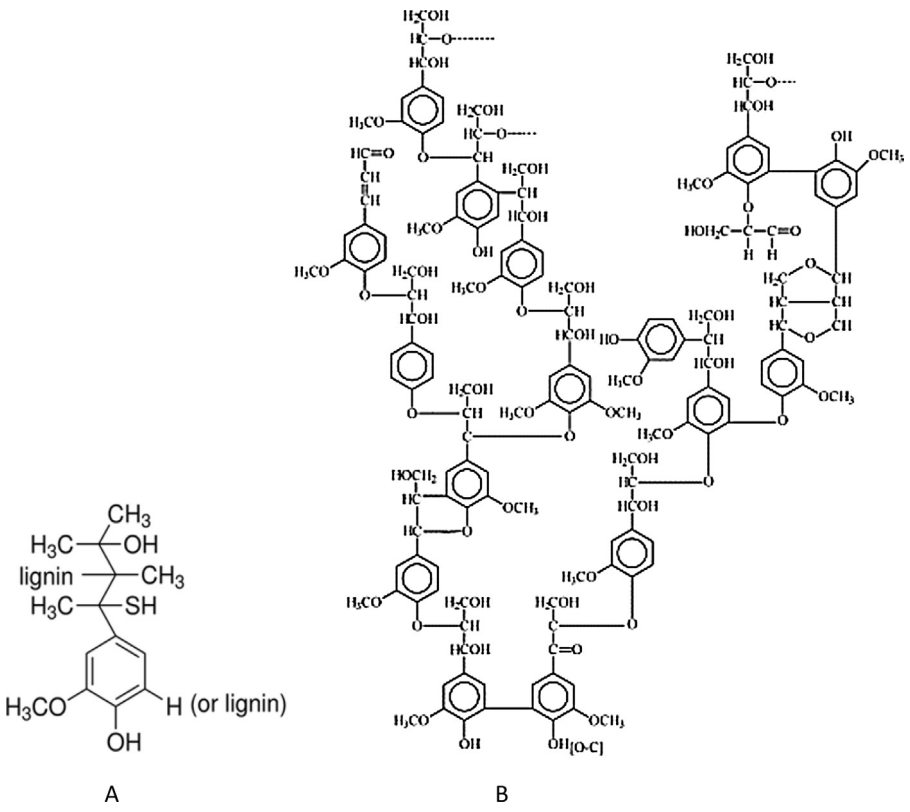


**Fig. 1.** Schematic representation of lignin. (A) A simplified structure of lignin, (B) Chemical structure of wheat straw lignin [4].

of hydrogen bonding [4]. Options to valorize lignin ($0.13/kg) into adhesives and plastics are being developed in the laboratory but, have not yet resulted in commercial products [5,17]. However, the challenge in commercialization of lignin residues as a raw material is in its lack of uniformity (depending on source) and its brittleness [18].

More recently sulphur free lignin from biomass conversion technologies (mainly from alcohol production), and soda and solvent pulping is emerging in the market [19]. Having no sulphur and being a moderate macromolecule size these lignins are more closely related to native lignin and they show distinct properties as compared to kraft or sulfite lignins. The biomass conversion technologies used typically involve a hydrolytic pretreatment. The pretreatment is either catalyzed by added mineral acids or autocatalyzed by biomass derived organic acids generally found in steam explosion or autohydrolysis [20]. These treatments make the carbohydrate component susceptible to saccharificaion and or fermentation therefore resulting in sulphur free lignin. The lignin is extracted from pretreated biomass by treating it with an organic solvent or aqueous alkali followed by precipitation. The lignin obtained through this process is largely insoluble in water under neutral or acidic conditions, however it is soluble in organic solvents. Table 1 shows some of the typical properties of lignins recovered from several biomass conversion technologies [21].

In 2013 approximately 1 million metric tons of lignin was thrown away in landfills. Low value of industrial lignin makes it an attractive biomaterial for wide range of applications. The major drawback of adding lignin in thermoplastic polymer matrices is its poor compatibility resulting in a weak interface. However lignin can be used in thermoset resins to make lightweight and sturdy composite materials. These eco-friendly materials can be used for various applications such as electronic components, non-food packaging, automotive and building products. Previous studies have shown positive impact of lignin on the mechanical properties and shelf lives of packaging materials [2]. Lignin helps to make composite matrices stronger, more durable, and economical and more UV and water resistant. Addition of lignin as filler/reinforcement helps to reduce the cost of matrix.

The goal of this study was to investigate the application of agricultural crop based lignin derived from ethanol production process using diluted sulfuric acid technique for manufacturing thermoset biocomposite materials. The main objectives of this research were:

1. To determine the utility of biobased-lignin generated by ethanol plants in thermoset biocomposites.
2. Characterize the physical and mechanical properties of biocomposites developed from using bioethanol lignin as a filler in thermoset matrix.

Biocomposite properties evaluated in this study include lignin properties, particle size analysis, density, moisture absorption, tensile and strength properties, impact, hardness and thermal stability.

## 2. Materials and methods

### 2.1. Lignin

Wheat straw and corn stover based low sulphur and low ash content (0.5%) bioethanol lignin was kindly donated by Tenessesse Valley Authority, Muscle Shoals, AL USA. This lignin was a byproduct of ethanol production using wheat Straw (WS) and corn stover (CS) and as feedstocks. It was produced through hydrolysis of cellulosic sugars (xylose) followed by dilute acid conversion using sulfuric acid and second stage hydrolysis. The two stage hydrolysis used 1–3% $H_2SO_4$ at steam pressures of 1.2 and 1.9 MPa respectively. After all the cellulose was converted into glucose the remaining solids were washed using solvent and allowed to dry to obtain the lignin material [22]. The particle size of the