Fabrication and Properties of Lignin Based Carbon Nanofiber

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Abstract

Lignin, the second most abundant biopolymer on earth, has the potential as a low cost and renewable precursor for carbon fibers. By creating lignin carbon nanofibers for lightweight structural composites for automobiles and functional applications as electromagnetic shields, the value of lignin will be enhanced. Under the Lignoworks Biomaterials and Chemicals Network program, we demonstrated the feasibility of producing carbon nanofibers from softwood Kraft lignin by electrospinning and heat treatment. The morphological, mechanical, and electromagnetic properties of the lignin carbon nanofiber were characterized. Results showed 10 times increase in strength for the lignin random nanofiber mats after carbonization. Alignment of fibers further improved the mechanical strength. By doping the lignin polymer with carbon nanotubes and functional nanoparticles such as magnetite, we demonstrated the feasibility of translating the strength and electromagnetic function respectively to the lignin nanofiber assemblies. The encouraging results demonstrated the potential of lignin as an engineering material thus establishing a pathway for adding values to the abundantly available lignin.

Keywords: Lignin; Carbon Nanofiber; Mechanical Properties; Multifunctional Nanofiber

1 Introduction

The increasing global energy demand and its consequential impact on the environment have prompted interest in renewable resources as feedstock for the manufacturing of value added products. Amongst the renewable materials lignin is relatively unexplored but holds great potential. Lignin is the second most abundant biopolymer on earth only after cellulose and is one of the three main constituents in trees [1-4]. Lignin varies with wood species as well as the process to isolate it. In softwood, lignin represents about 30% of the total mass, whereas lignin constitutes 20-25% in hardwood [3-6]. Native lignin is made up by peroxidase-mediated dehydrogenation of three types of phenyl propane monomer units (monolignols) and linked by carbon-carbon and aryl-ether linkages with random cross-linked polymerization from radical-coupling reactions between phenolic radicals [2-3]. The monomer units can be classified into three different types: guaiacyl, syringyl, and 4-hydroxyl-phenyl propane structures [2]. There are several different C-O

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and C-C inter-monomeric linkages between monolignols to form lignin structure [4]. Fig. 1 shows possible representative structures of the fundamental interunit linkages in lignin.

Fig. 1: Representative structure of softwood (a) and hardwood (b) lignin [2]

Lignin is unusual because it has heterogeneous structure and lack of a well-defined chemical structure. It is expected lignin is a high molecular weight aromatic polymer with three dimensional structure [5-6]. The chemical structure of lignin monomers and linkages that constitute these networks differ depending on morphological regions of the wood cell walls (middle lamella vs. secondary wall), different types of cells (vessels vs. fibers) and different types of wood (softwood vs. hardwood). For native lignin, no method could isolate it from plants so far. Chemical and physical modifications are necessarily for lignin isolation. The chemical processing of lignin isolation includes alkaline, acidic, or organic solvent processing, and lignin often undergoes fragmentation and degradation during chemical processing [1, 3]. The molecular weight, functional groups, degree of condensation, types of inter-monomeric linkages, and types and ratios of monomeric units vary depend on the type and length of chemical processing [1-5]. Therefore, the degree of polymerization of native lignin is quite difficult to measure.

Lignin is a byproduct of pulp and paper industry as well as cellulosic ethanol fuel production (Fig. 2 [7]). In the pulp and paper industry, Kraft pulping is the most dominant chemical pulping process in the world generating over 68 million tons of lignin yearly [3]. In Kraft pulping, a solution of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) is used to dissolve most of lignin in a temperature range of 155-175 °C for several hours. The resulting solution is called black liquid that can be separated from cellulose [3-4]. After Kraft pulping, the lignin solution can be concentrated and recovered to a dark brown powder. Kraft lignin is hydrophobic and its molecular mass is lower than the native lignin [3]. It is important to note that the large amount of lignin produced during pulping process, less than 2% of the lignin is applied for commercial products such as dispersants, adhesives, and surfactants [5]. Most of lignin is burned as fuel after recovery and the value of fuel is low (400 \$/tonne). Accordingly there are great interests in