

Lignocellulosic Biomass: The Future of Lignin-based Composites

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Introduction

Modern society requires feedstocks to ensure the effective function of the modern industrial society. The most promising, natural and renewable resource of feedstock is lignocellulosic materials. A considerable amount of such materials are being generated as by-product by various agro based industries. (Pérez et al., 2002). One of the common practice to disposed much of this lignocellulosic biomass is by burning process; this practice is so common and it not restricted to developing countries alone. However, due to its renewable nature, lignocellulose material has gained interest and special importance from research and economic point of view (Asgher et al., 2013; Ofori-Boateng and Lee, 2013). Therefore, instead of burned in the fields, huge amounts of lignocellulosic biomass can potentially be converted into different high value products including biofuels, value added fine chemicals, and cheap energy sources for microbial fermentation and enzyme production. (Iqbal et al., 2011a; Irshad et al., 2013; Isroi et al., 2011).

Structure and Chemistry of Lignin

Lignocellulosic materials including agricultural wastes, forestry residues, grasses and woody materials are mostly composed of three major units i.e., cellulose, hemicellulose and lignin. For most of the agricultural lignocellulosic biomass, the composition of lignin is about 10-25%, hemicellulose is 20-30%, and cellulose is 40-50% (Iqbal et al., 2011; Kumar et al., 2009; Malherbe and Cloete, 2002).

Figure 1 shows the the illustration of lignin, cellulose and hemicellulose in lignocellulosic biomass. Lignin contains three aromatic alcohols (coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol) produced through a biosynthetic process and forms a protective seal around cellulose and hemicelluloses. As a major structural component of plant cell walls, cellulose responsible for mechanical strength of the biomass. Hemicellulose macromolecules are often repeated polymers of

pentoses and hexoses within the plant cell wall (Calvo-Flores and Dobado, 2010; Jiang et al., 2010 ; Menon and Rao, 2012).

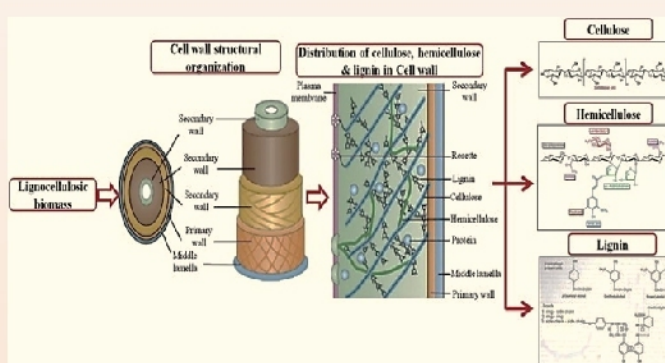


Fig. 1. Diagrammatic illustration of the framework of lignocellulose; cellulose; hemicellulose and lignin.
Source: Menon and Rao, 2012.



Fig. 2. Lignin

Although lignin only representing about 10-25% of the biomass by weight Figure 2. It is the most complex material with its long-chain and heterogeneous polymer that composed of phenyl-propane, methoxy groups and non-carbohydrate poly phenolic substance units most commonly linked by ether bonds. Lignin chains fills the gap between and around the cellulose and hemicellulose complexion and acts as a glue for all cell walls components (Hamelinck et al., 2005).

Processing of Lignin

Lignin is processed using different chemical processes, and each process has its own advantages and disadvantages (Pinkert et al., 2011). Three major processes for extraction of lignin are sulfite, kraft, and

soda. These processes follow either an acid- or base-catalyzed mechanism to break complex lignin structure into low molecular weight fractions and lignin physicochemical properties are affected by these processes (Lora and Glasser, 2002; Doherty et al., 2011).

Sulfite process is an acid catalyzed process that involves the cleavage of the α -ether linkages and β -ether linkages of lignin. Traditionally, sulfite process has been used in pulping industries and lignin is a byproduct pulping process (Doherty et al., 2011). Three main reactions have been found to take place in the pulping process; (1) reaction between free sulphurous acid and lignin leading to the formation of lignosulfonic acid, (2) soluble lignosulfonates formation with cations (e.g., Mg, Na, or NH_4^+), and (3) lignosulfonates fragmentation. In addition to the formation of lignosulfonates in the sulfite process, degraded carbohydrates are also produced in this reaction (Doherty et al., 2011; Botros et al., 2006).

Kraft process which is frequently used for the preparation of lignin. Unlike lignosulfonates from sulfite process, kraft lignin produced using craft pulping has been found to exhibit a dark color as most of the time lignin degraded and dissolved into black liquor (Huang et al., 2004). It is insoluble in water and solvent but dissolved in alkali solutions owing to the high concentration of phenolic hydroxyl groups present in kraft lignin. Compared to other types of lignins, kraft lignin contains the highest quantity of the phenolic hydroxyl groups.

Lignin possesses significant potential for being a component of value-added products; however, there has been little success in creating lignin-derived high performance materials. Various researchers have synthesized and characterized lignin containing polymers. Rigid lignin molecules were blended with flexible polymers (Feldman and Lacasse, 1994) and subsequently crosslinked (Kelley et al., 1990; Rials and Glasser, 1984; Hofmann and Glasser, 1994) or copolymerized to form polyurethane, (Reimann et al., 1990; Bonini et al., 2005) polyesters (Bonini et al., 2005) and other copolymers (de Oliveira and Glasser, 1994; Thielemans and Wool, 2005) of different morphologies including interpenetrating polymer networks. However, most of these reported lignin-derived polymers were thermosets and brittle materials, i.e. barely recyclable.

The brittleness of these materials is related to the high crosslink density due to the low molecular weight of the

lignin segments. The highly polydisperse molecular weight of lignin molecules was likely the primary hindrance to synthesizing recyclable high-performance lignin copolymers. Lignin-containing recyclable thermoplastics have not been developed, while such products will have a significant impact on lignin usage as new advanced bio-derived polymers.

The other challenge in using lignin in composites is the poor dispersion of lignin attributed to its propensity to self-aggregate. Lignin is an irregular polymer made up of substituted phenyl rings and phenolic and aliphatic hydroxyl groups, and aggregation is likely due to intermolecular association from hydrogen bonding between the carboxylic acid groups and various ether oxygens and hydroxyl groups, van der Waals attraction of polymer chains, and π - π stacking of aromatic groups (Lindstrom, 1979; Deng et al., 2012). Modification of lignin by esterification (Thielemans and Wool, 2005) etherification (Lora and Glasser, 2002) has been used to improve its dispersion in thermoplastics and thermosetting materials and leads to improved performance in composite materials. Graft polymerization is an attractive approach to covalently modify the surface of lignin, resulting in a lignin based copolymer that can be used in a broader range of applications, and allows for the design of novel materials with tailored properties (Kim and Kadla, 2010; Nemoto et al., 2012).

Applications of Lignin-Based Polymer Composites

Depending upon the applications, the nature of the matrix varies from a synthetic to a natural polymer (Kadla et al., 2002). For most of the applications, the matrix is obtained from synthetic polymers, and very recently, biopolymers are being used as the matrix material (Yue et al., 2012). In general, the reinforcing materials are fibers, either synthetic or natural. Both the polymer matrix and the reinforcement have been found to play an important role in determining the overall physicochemical properties of the composites (Chaochanchaikul et al., 2012; Marklund et al., 2008).

Lignin-based polymer composites have received the interest of the research community all over the world (Megiatto et al., 2008; Park et al., 2008; Nenkova, 2007). Intense efforts are being made to use lignin as a low cost eco-friendly reinforcement to prepare high performance composites (Morandim et al., 2012; Pupure et al., 2013; Stiubianu et al., 2009). However, for some applications, it

is often difficult to blend lignin with other systems such as biopolymers. Some researchers have made efforts to modify lignin with different techniques in order to make it compatible with the polymer matrices (Adcock et al., 2003; Batog et al., 2008).

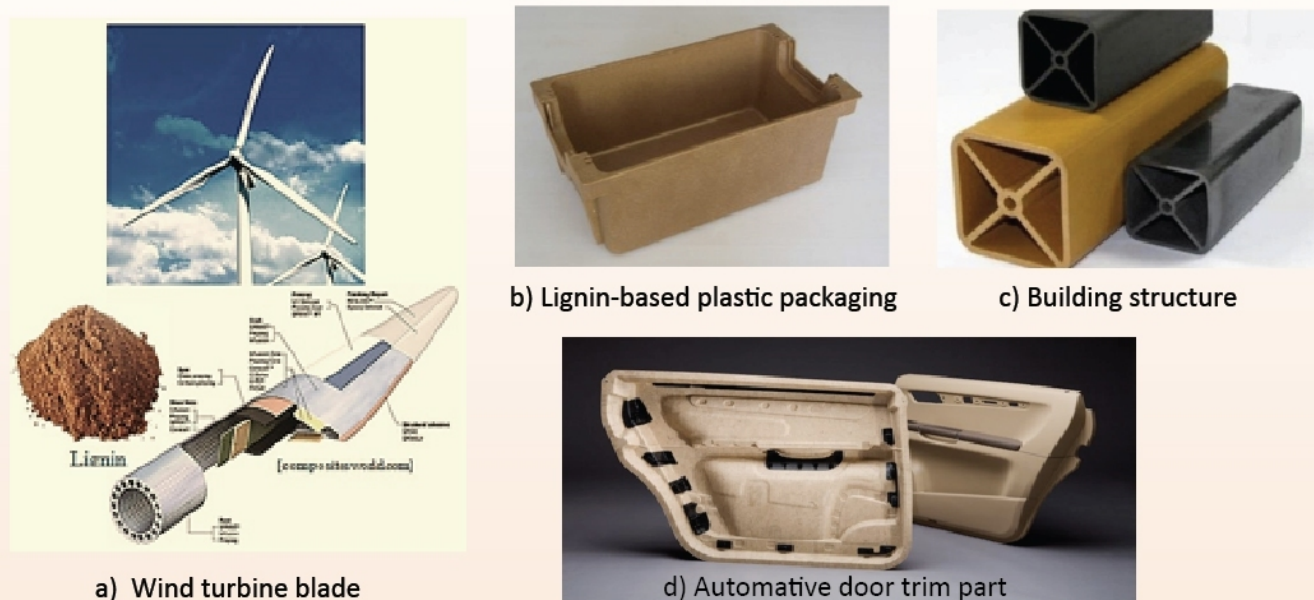


Fig.3. Applications of Lignin-Based Polymer Composites

Conclusion

Biorenewable materials have been frequently used as low cost reinforcement for polymer composite applications. Most of the environmental friendly polymer composites designed for different applications are based on natural cellulosic fibers. Along with these cellulosic fibers, lignin is a promising alternative for traditional petrochemical-based reinforcement material.

Lignin, cellulose and hemicellulose are the major components of natural polymers that provide strength and rigidity to plant stems. Lignin is the most abundant byproduct of the paper industry because it was produced during the processes aimed at retrieving the polysaccharide component of plants.

Recently, researchers have started exploring the use of lignin as potential reinforcement in polymer composites. The inherent properties of lignin being biodegradable, CO₂ neutral, available abundantly in industrial waste, low in cost, and environmentally friendly, and having antioxidant, antimicrobial, and stabilizer properties make lignin a promising low cost reinforcement. Due to the above-stated advantages, lignin-based polymer composites are promising as a new class of environmentally friendly, low cost, composite materials.

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