



## UTILIZATION OF INDUSTRIAL WASTE LIGNIN IN POLYMER SYSTEMS

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**Abstract-** The use of biologically derived polymer is emerging as an important component for economic development. By transforming forest and agricultural feedstock a new class of renewable / biodegradable and biocompatible material can be introduced. Biodegradability of biopolymer is the base for their application, however their processibility, performance and in particular price as compared to synthetic, petrochemical base polymer are of extreme importance. To this end materials such as agricultural residues, bioprocessing byproducts are obvious source of low cost, biomacromolecule material. Lignin a naturally occurring material in plant is a promising compound to be used in polymer because of its phenolic base structure which could lead to the improvement of mechanical and thermal properties when incorporated in polymers. This paper opens onto a general discussion on the development of new polymeric material obtained from lignin polymer systems.

**Keywords-** Lignin, Modified lignin, Thermosetting and thermoplastic polymer, lignin grafting, copolymer, filler, lignin polymer composite.

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### Introduction

Lignin is one of the most abundant organic polymer in the plant world whose contents mainly depends upon the plant species. Lignin is found as a cell wall component in all vascular plants and in the range 15-30% by weight. Lignin is a permanent glue, bonding cells together in the woody stems and thus giving the stems their rigidity and impact resistance. Lignin is generally defined as a polymeric natural product arising from an enzyme initiated dehydrogenative polymerization of three primary precursors, trans-coniferyl alcohol, trans-sinapyl alcohol and trans p- coumaryl alcohol. The enzyme initiated polymerization results in bonds of exceptional stability: biphenyl carbon-carbon linkages between aromatic carbons, alkyl-aryl carbon-carbon linkages between aliphatic and aromatic carbon, and hydrolysis-resistant ether linkages (see figure-1). The only linkage relatively weak and hydrolyzable is the  $\alpha$ -aryl ether bond. These stable linkages make lignin very resistant against degradation. The most characteristic functional groups [1] present in lignin are methoxyl, hydroxyl, carboxyl, car-

bonyl and presence of other double bonds conjugated with aromatic system.

Enormous quantity of wood material is utilized by pulp and paper industries. Several pulping processes such as soda process, sulphite process and sulphate process are used for delignification. The lignin thus removed from the wood is a major waste product of pulp and paper industries. It is in the form of black liquor.

The global production of lignin is approximately 70 million tons per annum. Increasing and recurring production and very less utilization of lignin creates a disposal problem and has become a matter of environmental concern. Lignin is considered as a source of different functional groups for the polymer products. The lignin is a promising compound to be used in polymers because of its phenolic base structure which could lead to the improvement in the mechanical properties when incorporated in plastics. The application of lignin in polymers includes filler in thermoplastics, coreactant for thermoplastics, and coreactant in thermosetting phenolic, epoxy and polyurethane resins. The use of kraft lignin (KL) as a

polymer additive is of great importance [2-4].

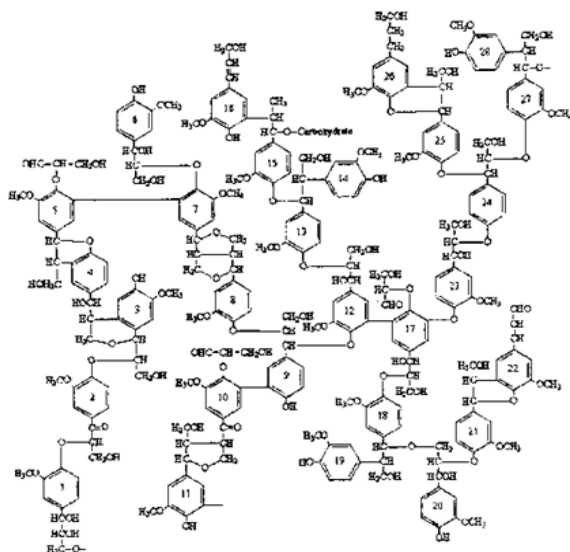


Fig. 1- Structure of lignin

### Lignin polymer blends

Kraft lignin has a glass-transition temperature of about 142°C, which can be increased by chain extension reactions [5]. Thus the addition of lignin to existing resin has the potential to increase the glass-transition temperature of unsaturated polyester resins. Lignin also increases the electrical resistance in polyolefins, making them more attractive in electrical shielding applications. Basically in wood, lignin helps to protect the cellulose fibers against biological attack, in addition to adhesion of the cellulose fibers. However, lignin is found to be degradable by certain wood-rotting fungi making it possible to break down lignin based materials in some environments.

Lignin was found to increase the polymer modulus while decreases the melt temperature of various crystallizing thermoplastics. Maldure A. V. et. al. [6] reported the thermal and structural studies of polypropylene blended with esterified industrial waste lignin. All the blend showed higher crystallization temperatures and continuously reducing the percentage of crystallinity with increasing modified lignin proportion in the blends. SEM analysis showed good dispersion / miscibility in polypropylene matrix indicating modification in lignin is useful. The important application of lignin-polymer blend is their potential as a precursor for carbon fibers. Carbon fibers were obtained by carbonization of dry spum fibers of lignin dissolved in an alkaline solution and plasticized with poly (vinyl alcohol). Kadla et al, [7] obtained general grade carbon fibers from kraft lignin without any chemical modification by blending lignin with less than 5% poly (ethylene oxide).

### Lignin as copolymer

The presence of different functional groups and the chemical structure with its phenolic base structure in lignin suggests its potential as a comonomer in phenolic thermosetting polymers[8]. As it contains large number of aliphatic and aromatic hydroxyl groups in its structure, attempts were made to prepare lignin modified phenolic resin by partially replacing phenol with lignin[9], preparation of epoxy polymer[10] and also some polyurethanes. The

incorporation of lignin in various polyurethanes through alcohol-isocyanate reaction improved the mechanical properties and higher glass-transition temperature compared to polyurethanes without lignin. The addition of lignin also resulted in improved thermal stability, loss of flexibility and an increased strength. Incorporation of lignin with acid chloride in polyesters resulted in a rigid polyester materials.

Lignin can act as a coreactant in phenol formaldehyde resin. Most of the plywood and particle board industries use phenol formaldehyde adhesives. These resins possesses high strength and moisture resistance but they are very costly because of the reagent used i.e. phenol. As lignin is phenolic in nature, it can be used in place of phenol but it is not structurally equivalent to phenol. Phenol has five free sites on aromatic ring and no ortho and para substituents around the hydroxyl group. In all lignin phenolic hydroxyl groups, the aromatic ring is para substituted by propyl chain of the 1-propylphen-4-ol (coumaryl) structural unit. Thus lignin reacts more slowly with formaldehyde than that of phenol.

### Lignin as filler

Among the important applications of lignin in polymers most important is the use of lignin as a filler material in thermoplastics, thermosetting and rubbers to improve their mechanical properties. Thielmans and coworkers[11] have used lignin as filler in thermosetting unsaturated polyesters and vinyl esters. They also tried modifications of lignin to improve its effect on matrix properties by adding double bond functionality. Kharade and kale[12] have used dry lignin powder as a filler in low-density polyethylene (LDPE) and high-density polyethylene (HDPE) and polypropylene (PP). The lignin filled polyolefins showed considerably higher electrical resistance.

Some studies have been made on the application of lignin as a filler in rubber vulcanizates. Setua and coworkers[13] used lignin and modified lignin as filler in nitrile rubber. Kumaran and De[14] used lignin as a replacement of carbon black in styrene-butadiene rubber and natural rubber.

### Lignin grafting

The studies on grafting of lignin are very much concentrated, this is largely due to the free radical inhibiting capability of the phenolic hydroxyl group in lignin[15], capable of forming quinonic structures stabilized by resonance over the whole lignin molecule. Lignin was grafted with methyl methacrylate and vinyl acetate, styrene, acrylonitrile, acrylic acid, and acrylamide, maleic anhydride. As well as the use of polar solvents such as alcohols has a beneficial effect on the grafting efficiency by swelling the lignin molecules, improving lignin accessibility. High concentration of methanol resulted in improved grafting efficiency and rate of grafting of lignin with styrene. Chemically initiated grafting, with a decomposing initiator molecule to generate active sites, was found to be more effective than photo induced grafting for hydrochloric lignin. Whereas all polymerization reactions could be used to graft lignin molecules. Feldman et al. [16] reported the effect of double esterification and radical polymerization of the double bonds. Meister et al. [17] followed the similar approach of generating active sites on the lignin molecule using calcium chloride and a hydroperoxide. This initiation system attacks lignin repeat units, effectively creating active polymer chain growth sites.

### Modified lignin in polymers

The properties of lignin based blends and composites can be improved by appropriate chemical modifications. The modification of lignin is more significant as chemically modified lignin can be used to improve the polymer-lignin compatibility and to introduce reactive sites. It initiates the interaction between or among the compounds of these materials, essentially by reducing the corresponding interfacial energy and thus enhancing their compatibility. The hydroxyl groups on lignin molecule are reactive and plentiful. These groups can act as local centers of high polarity capable of hydrogen bonding. Few publications [18] on the use of modified lignins are claimed a major breakthrough in developing thermoplastic material with very high lignin contents. Lin Y, Sarkanen S. reported some properties of "100% KL-based polymeric material" which give in fact methylated and/ or ethylated lignin. Another interesting family of materials involving modified lignin was described by Gasser's group who prepared blends of biodegradable thermoplastics including cellulose ester, polyhydroxybutyrate and a starch-caprolactone copolymer with different lignin esters.

A recent discovery of an accidentally prepared lignin sulphate [19] has opened potentially valuable avenues of medicinal applications.

Esterification of the hydroxyl groups and acetylation are the commonly used methods. Acetylation renders lignin soluble in a variety of organic solvents such as acetone, tetrahydrofuran and chloroform. Other modification reactions for kraft lignin include sulfonation, sulfomethylation, amination, halogenation and nitration. Copolymerization of etherified lignin with methyl methacrylate resulted thermoplastic and cross linked polymers, depending on the functionality of lignin.

### Conclusion

Although a large amount of lignin is unutilized, it has a greater potential to be a major source of polymer base products for different industries which includes fillers, adhesives, binders and coatings. Lignin is a non toxic, renewable, commercially available source to replace expensive petrochemical products. This study emphasized on the future development and utilization of lignin for a diverse variety of potential applications. The use of lignin as a macromolecular compound in different polymeric systems is of increasing importance. Progress has already been made in few fields such as lignin graft copolymers, lignin thermosetting polymers and lignin-elastomer- blends and continued research in this areas will no doubt yield an increased demand for lignin and lignin products in the future.

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