



LIGNIN IN PHENOL-FORMALDEHYDE ADHESIVES

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Abstract- The major adhesive resin worldwide used in the manufacture of plywood is phenol formaldehyde resin. The raw material of this kind of adhesive is derived from petroleum oil. Because of rising prices of crude oil and scarcity of petroleum products, their replacement by natural resource based raw material has become a necessity. Lignin is a renewable, non-toxic, commercially available and low costing resource which has the potential of being utilized as a raw material for the polymer industry. The most promising application of lignin-polymer systems in recent years has been the development of thermosetting resins used as wood adhesives. Recent development of the macromolecular uses in lignin-polymer materials systems has shown an increased awareness on the potential of the structure of lignin. In this paper the present state of knowledge regarding current areas of lignin-phenol-formaldehyde systems in adhesives are reviewed.

Keywords- Lignin, phenol, formaldehyde, modified lignin, lignin-phenol-formaldehyde, adhesives, thermosetting polymer, copolymer.

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Introduction

Lignin is a natural polymer which contains phenyl propane units. It is an integral component of wood present in secondary walls of plants. It is one of the most abundant organic polymers after cellulose. Its most commonly noted function is the support through strengthening of xylem cells in wood. The wood is composed of 70-80% polymeric carbohydrates and 20-30% lignin. As lignin is hydrophobic in nature it helps in conduction of water in plant stems. The wood is widely used in paper industry for pulp production and lignin is the most unused part. Each year roughly 70 million tones of byproducts arise in a pulp mills during the production of pulp. More than 99% of the lignin from Kraft process is burned for the recovery of pulping chemicals and the provision of energy. Lignin is an amorphous; polyphenolic material arises from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, p-coumaryl (1), coniferyl (2) and synapyl (3) alcohols. The structure is well suited for its use as a raw material for the production of phenolic chemicals. This lignols are incorporated into lignin in the form of phenylpropanoids p-hydroxyphenyl, guaiacyl and syringyl respectively.

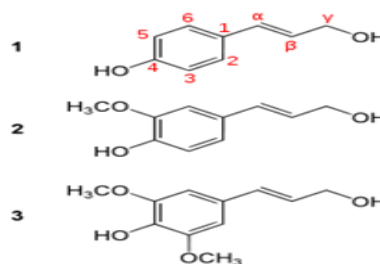


Fig.1- Structure of monomers

Lignin is highly crosslinked, three-dimensional aromatic polymer with phenyl propane units linked together by carbon-carbon or ether bonds and with phenolic and alcoholic hydroxyl groups. The waste lignin from paper industry is an attractive raw material for adhesives. Presently the adhesives used in wood applications are formaldehyde based such as urea-formaldehyde, phenol-formaldehyde, melamine-formaldehyde etc. Although lignin present in plants acts together with hemicelluloses as a perfect natural adhesive for cellulose fibers, isolated technical lignins generally

are poor binders for wood composites compared with conventional resin systems such as PF resins. Because of the phenolic nature of lignin polymer, there have been attempts to replace phenol with lignin derivatives in PF resins to formulate wood composites adhesives suitable for plywood, particle board and wafer board.

Nihat Sami et al. [1] developed a phenolic resin by partially replacing phenol with modified organosolv lignin in phenol-formaldehyde (PF) resin production. The method selected for manufacture of lignin resins deals with modification of lignin methylation route and organosolv lignin-based resins showed comparatively good strength and stiffness. Similarly, Marko Turunen et al. [2] have studied the lignin based chemicals, starch and urea as modifiers for phenol-formaldehyde resol resins. The effects of the addition stage of the modifiers used in the synthesis of the resins, the type of modification reagent on the structure of the resins, their molar masses and reactivities were investigated. Mohamad Nasir Mohamad Ibrahim et al. [3] extracted the lignin from oil palm empty fruit bunch after kraft and soda pulping process and studied the chemical and thermal properties of these lignins as well as determine their suitability for partial incorporation into phenol-formaldehyde resin. Lignin-phenol-formaldehyde adhesives for plywood were prepared using lignin obtained by acetosolv delignification of Eucalyptus globulus wood was studied by G. Vazquez et al. [4] A phenol-formaldehyde adhesives were used to prepare jute stick particle boards by A. K. Roy et al. [5]. It was observed that phenol in phenol-formaldehyde resin could be replaced up to a maximum of 50% by jute stick soda lignin. Xinglian Geng and Kaichang Li [6] prepared new formaldehyde free wood adhesive system consisting of kraft lignin and poly-ethylenimine (PEI) and the same was investigated for making two-ply plywood.

Technical lignins purified by ultrafiltration process were better materials for making lignin-based PF adhesive. Adhesives made from ultrafiltration-fractionated ammonium-based SSL were examined with wafer board by Shen and Clave [7]. The best board properties were obtained with low-MW (<5000) lignosulfonates whereas fractions with high MW (>5000) gave boards with poor mechanical properties.

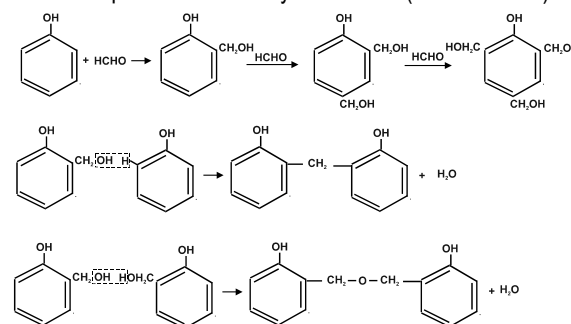
This paper presents review of research work of lignin-phenol-formaldehyde systems and various new methods of modification of lignin which will increase the compatibility of lignin in lignin-phenol-formaldehyde system.

Lignin-phenol-formaldehyde resin

Phenol-formaldehyde (PF) adhesives are currently used in about one tenth of all plywood and particle board industries. The binding technology represented by these "Bakelite" resins would be more widely applied if the reagents, particularly the phenol, were cheaper using lignin in place of phenol will sharply reduce the cost of binder. An alternative cheaper source of phenols would be of great interest to all users of PF resin. There has been a great deal of research performed concerning lignin.

Unfortunately, lignin is not structurally equivalent to phenol. Phenol has five free sites on the aromatic ring and no ortho and para substituents around the hydroxyl group. Lignin has only 35 phenolic hydroxyl groups per 100 C9 repeat units, 5 benzylic hydroxyl groups per 100 C9 repeat units. For virtually all lignin phenolic hydroxyl groups, the aromatic ring is para-substituted by the propyl chain of the 1-propylphen-4-ol (coumaryl) structural unit. The impli-

cation of this structure on the lignin reactivity in lignin phenol formaldehyde crosslinking polymerization can be seen from the mechanism of phenol formaldehyde reaction (see scheme 1).



Scheme 1

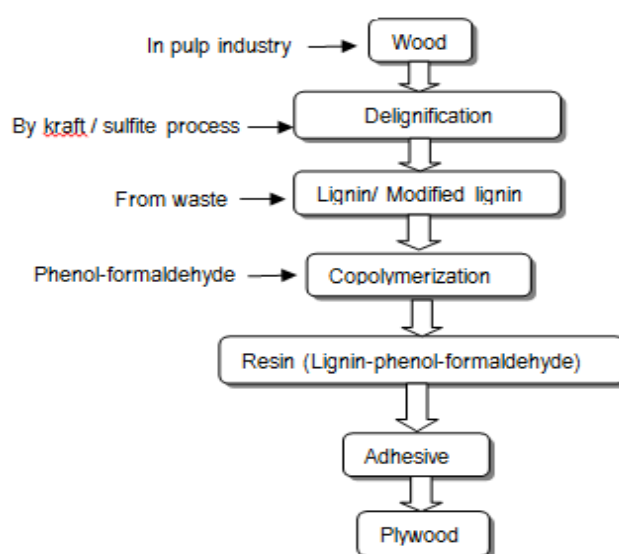


Fig.2- Diagram of the process

In cross linking with formaldehyde, an aromatic hydroxyl group ionizes to form ortho (2,6) and para (4) anionic sites through which to react with a positively charged methylene group. Lignin has most sites ortho and para to its aromatic hydroxyl group blocked by organic, functional groups. This is why lignin reacts more slowly with methanal (formaldehyde) than does phenol and can only be used to replace between 40 and 70 wt% of the phenol in an adhesive formulation.

Lignins are generally divided into two major classes: guaiacyl and guaiacyl-syringyl lignins. The guaiacyl lignins include the majority of Hardwood lignins, while softwood lignins belongs to the guaiacyl-syringyl lignin class. The rate of the hardwood lignin/formaldehyde reaction is, as would be expected from the demethoxy substitution on the ring, only 46% as fast as phenol at 30 °C and only 12% as fast as at 60 °C. Softwood lignin has, under the same reaction conditions, a rate that is 68% as fast as phenol at 30 °C and 14% as fast at 60 °C. The open ortho position on softwood lignin obviously allow the softwood lignin to react more readily with formaldehyde and should lead to more extensive crosslinking of softwood lignin as compared to the hardwood lignin [8]. G. Vazquez et al.[3] used the formaldehyde/ phenol mole ratio (F/P) was varied be-

tween 1.5 and 2.5, the soda/ phenol mole ratio (S/P) between 0.4 and 0.6 and the percentage of substitution of phenol by lignin between 20 and 40%.

Modification of lignin

Another approach to improving the strength properties of lignin-based adhesives is to increase the reactivity of technical lignins toward formaldehyde. Modifications including demethylation, hydroxyalkylation and phenolation will be used to improve the reactivity of lignins. Gupta and Sehgal [9] showed that demethylation imparts better reactivity to kraft lignin and better glue adhesion properties are obtained with esin made from the demethylated lignins. Hydroxymethylation reaction was used to increase cross-linking sites for reaction with PF resin. There were few studies on the utilization of grass lignins for making lignin-based adhesives. However, industrial soda bagasse lignin was shown to have much higher reactivity toward formaldehyde because it has a lower degree of condensation and more phenylpropanoid units [10].

Mozaffar Alam Khan et al. [11] prepared wood adhesive lignin-phenol-formaldehyde (LPF) by using bagasse lignin. The parameters for the preparation of a LPF adhesive (lignin concentration, formaldehyde to phenol molar ratio, catalyst concentration, reaction time and reaction temperature) have been optimized. It was found that up to 50% of phenol can be substituted by bagasse lignin to give LPF. G. Vazquez et al. [12] obtained lignin from Eucalyptus wood by acetic acid pulping was methylolated or phenolated and used to prepare lignin-phenol-formaldehyde resins. The amount of formaldehyde consumed in methylation reaction and supporting comparison of pre- and post-methylation H^1 and C^{13} NMR spectra showed the reactivity of the crude acetosolve lignin with formaldehyde reactively high.

Among the various lignin modifications, which increase the chemical reactivity or number of reactive sites in lignin, the most promising are phenolation and methylation [13].

A. R. Chaudhari [14] was modified the kraft lignin by Rieman-Tieman reaction of lignin (grafting of aldehyde group on phenyl ring) and the possible interactions between phenol, formaldehyde and lignin were assessed through Infrared studies. Similarly, the use of polar solvents such as alcohols also has a beneficial effect on the grafting efficiency by swelling the lignin molecules, improving lignin accessibility. The double effect of esterification and radical polymerization of double bonds also reported by Feldman et al. [15]

Dolenko and Clarke [16] prepared a similar adhesive compound for plywood and wafer board production using methylolated kraft lignin and phenol-formaldehyde resol.

Conclusion

With adjustments in compositions to compensate for the chemical features of each aromatic hydroxyl source, a wood binder formulated with any of the materials discussed above will be deemed highly effective if it can be (1) formulated at lower cost, (2) applied with conventional equipment, (3) reacted under the same process conditions, and (4) so strong an adhesive that wood parts formed with it fail in the wood phase most of the time and not in the adhesive phase

The market that not only has the highest rate of growth but also promises the largest increases in utilization of lignin is that which

makes use of lignin as an adhesive in wood composites. Lignin constitutes 17% of the solids in most exterior grade plywood and will become progressively larger fraction of the binder in laminates and fiber, strand and wafer boards.

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