LIGNIN – AN ADHESIVE RAW MATERIAL OF THE FUTURE OR WASTE OF RESEARCH ENERGY?

Hemmilä, V[1]., Trischler, J[2]., Sandberg, D[3].

ABSTRACT

Lignin has been studied as an adhesive for more than 100 years, but there are only a few industrial applications. The reason for the current interest is the high availability and low price of lignin. Lignin is the main by-product of paper pulping processes and is typically burned as fuel. Being the natural glue in plants and having a phenolic nature makes lignins an attractive replacement for wood adhesives.

An adhesive system for wood composites consisting mainly of lignin has yet to be developed. Lignin has less reactive sites in the aromatic ring than phenols, and the steric effects caused by the macromolecular structure further hinder its reactivity. The low reactivity leads to slow curing and causes problems in applications where the curing speed is a critical parameter. Modifications such as phenolation, methylolation, and demethylation have been shown to have a positive impact on the reactivity of lignin.

This paper presents properties of particle boards produced using unmodified and oxidized Kraft lignin adhesives. The paper also describes recent research relating to lignin as a base for wood adhesive and discusses the possibilities for future research.

The boards produced with unmodified and modified lignin adhesives under equivalent pressing conditions performed poorly compared to the reference board made with standard UMF adhesive. Oxidation at the correct pH level improved the adhesion of the boards compared with those based on unmodified lignin. Efforts to produce an industrially viable lignin-based adhesive system will continue, and promising combinations of modifications and alternative hardeners are being studied.

Key words: particle board, modification, oxidation

[1] PhD student, Department of Forestry and Wood Technology, Linnaeus University, SE-351 95 VÄXJÖ, Sweden, E-mail: venla.hemmila@lnu.se

[2] PhD student, Department of Forestry and Wood Technology, Linnaeus University, SE-351 95 VÄXJÖ, Sweden, E-mail: johann.trischler@lnu.se

[3] Professor of Forest Products, Linnaeus University, SE-351 95 VÄXJÖ, Sweden, Professor of Wood Technology, Luleå University of Technology, SE-931 87 SKELLEFTEÅ, Sweden,
E-mail: dick.sandberg@lnu.se

INTRODUCTION

Together with cellulose and hemicellulose, lignin is the principle component of plants. Lignin is a hydrophobic polymer and its purpose is to give mechanical support, act as a decay retarder, form a barrier for evaporation, and help to channel water to critical areas of the plant as a part of its cellular structure. The structure of lignin varies depending on the growth environment, age, and species of the plant. Lignin is composed of highly cross-linked phenolic C_6C_3 units. These phenylpropane units are connected by series of carbon-oxygen (ether) and carbon-carbon linkages (Heitner 2012). The crowded macromolecule structure of lignin inevitably leads to less reactive systems in adhesive formulations (Tejado et al. 2008).

Lignin is available in large quantities, being the unwanted by-product of pulping process for papermaking. The process produces a pulp rich in cellulose and a liquor rich in degraded lignin that is typically burned for energy. The most important chemical pulping process is the Kraft-process using sodium sulfide and sodium hydroxide. Other pulping processes are the soda, anthraquinone, polysulfide, sulfite and organosolv processes. (Heitner 2012). There is a large difference in the water-solubility of lignin from different pulping processes, e.g. lignosulfonates from sulfite pulping are water-soluble in the presence of suitable counter-ions, wheras Kraft lignin is water-soluble only in a highly alkaline environment (Lora and Glasser 2002, Widsten and Kandelbauer 2008)

Lignin as an adhesive
Lignin as an adhesive has been the subject of several reviews (Rowell 2005, Pizzi 2006, Hu et al. 2011, Imam et al. 2012, Mankar et al. 2012). The simplest way to use lignin as an adhesive is to use it as a partial replacement for phenol in PF resins. A lot of work has been done on this for different lignin types and in various percentages and P/F ratios, and it can be concluded that for applications that require fast curing, the use of unmodified lignin is not cost-effective (Danielson and Simonson 1998, Sarkas 2000, Zhang 2013).

Modification of lignin adhesives
The chemical structure of lignin limits its reactivity and several modifications have been proposed in the literature. The most popular methods of modifying lignin are methylolation (hydroxymethylation), phenolation, demethylation, and reduction reactions. Methylolation and phenolation are industrially the most interesting due to their low cost. The use of the premethylolated form of lignin in the presence of synthetic PF and pMDI has been said to be one of the biggest steps forward in the field of lignin adhesives. In this case, part of the reaction with formaldehyde is carried out before it is added to the PF resin. In the main reaction, hydroxymethyl groups are incorporated into the lignin aromatic rings to increase the reactivity of the molecule (Pizzi 2006). The reactivity of lignin in methylolation also depends on the pulping conditions, i.e. pH, temperature, and pressure (Benar et al. 1999).

In phenolation, the amount of phenolic hydroxyl groups in the lignin is increased by allowing it to react with phenol before the phenolated lignin is combined with formaldehyde. The advantage of phenolated-lignin-formaldehyde resins compared to unmodified lignin has been studied and it is a popular modification especially for

lignosulphonates. Reports on the replacement of different percentages of PF by phenolated lignin can be found in the literature (Cetin 2002, Khan 2004).

As methyl groups block potentially reactive aromatic hydroxyl groups, the reactivity of lignin and its ability to form crosslinks can also be improved by demethylating the lignin aromatic rings. Demethylation can be done enzymatically or chemically using oxidative methods e.g. laccase or peroxidase. The benefits of oxidation should be great enough to outweight the extra cost of the oxidation step. For example, Goncalves et al. (2001) studied oxidized organosolv lignins, but the fractionation did not significantly increase the reactivity of lignin with formaldehyde. Enzymes such as laccase act on phenolics via non-specific oxidation. Different fungi can also be used to decompose wood and modify lignin, e.g. brown-rot fungi can demethylate lignin and partially oxidize its side chains. The process of modifying lignin with certain fungi and producing thermosetting lignin-phenol-formaldehyde (LPF) resins for OSB and plywood has been patented (Zhang et al. 2012).

Lignin with different crosslinking agents
Some authors report a total replacement of synthetic resin by using lignin in combination with glyoxal and pMDI or tannins. Tannin is a natural and often more reactive substitute for phenol, but it is less available and more expensive. Glyoxal is a non-toxic aldehyde, but less reactive than formaldehyde. Its reactions with lignin have been studied by MALDI-TOF and CP-MAS 13C-NMR by Navarrete et al. (2012). El Mansouri et al. (2007) used lignosulphonate in combination with glyoxal and pMDI and produced high quality boards when the pMDI content was greater than 40 %. An adhesive with a natural origin content of 94 % was produced by Mansouri et al. (2011) from wheat-straw-derived organosolv lignin, glyoxal, tannin and hexamine. Board with an amount of tannin less than 45 % had too low an internal bond (IB) strength to be considered for industrial applications (Mansouri et al. 2011).

The total replacement of synthetic resin with lignin and glutaraldehyde, which is a dialdehyde that can be obtained from natural sources, had also been studied. Da Silva et al. (2013) used industrial organosolv sugarcane bagasse lignin for the preparation of lignin-formaldehyde and lignin-glutaraldehyde resins. The impact strength and flexural strength of the resin made from organosolv lignin and glutaraldehyde were higher than those of the PF resin.

OBJECTIVES

The purpose of this study has been to evaluate the usefulness of lignin as a particle board adhesive and to find the optimal pH range for its oxidation through an evaluation of the E-modulus, internal bond strength, and swelling properties of boards glued with unmodified and oxidized Kraft-lignin adhesives.

MATERIAL AND METHODS

For the tests a powdered Kraft lignin and core layer wood chips were used. Two series of boards were prepared using modified lignin adhesives: (a) lignin oxidized with hydrogen peroxide (H_2O_2) and the Fenton reagent ($FeSO_4$) under acidic conditions, and (b) lignin oxidized with hydrogen peroxide (H_2O_2) in the alkaline pH range. The purpose of the first tests was to determine how changing the pH affected the efficiency of the Fenton reagent. The second tests were made to observe the oxidation behaviour in a higher pH range for future tests with dissolved Kraft lignin. Modifications were made in aqueous suspensions and the pH was adjusted with sodium hydroxide (NaOH). The lignin was oxidised with 30 % hydrogen peroxide (H_2O_2) and the final H_2O_2 content was 5.7 % of the resin weight. Commercial UMF adhesive with ammonium sulfate as hardener and an unmodified lignin adhesive were used as reference.

In the production of particle boards, 10 % of adhesive was used. The dimensions of the single layer particleboards were 500x500x16 mm and the target density was 620 kg/m^3. The press factor was 20 s/mm and the press temperature 210°C. From each board, two samples were taken for bending strength and E-modulus measurements and five samples for the internal bond measurements. The absorption of water was tested by 2 hours swelling tests at 20°C.

RESULTS

Table 1 shows the results from the tests. The lignin board with pH 8.1 failed already during cutting. As expected, the boards glued with lignin showed poor mechanical and moisture properties compared to the board glued with the reference UMF adhesive. All the samples were close to falling apart after the 2h swelling test. The performance of an adhesive is shown by the internal bond (IB) test that was better for the oxidized lignin samples than for the unmodified reference material that failed all five IB tests. The E-modulus was slightly higher for the oxidized lignin boards. The variation in density is explained by the fact that some of the boards cracked slightly from the core after pressing due to insufficient adhesive bonding. The best pH range for oxidation was between 3 and 4.

Table 1. Results of the mechanical tests on the reference and modified lignin boards

Adhesive	pH	Density (kg/m^3)	Bending (N/mm^2)	E-modulus (N/mm^2)	IB (N/mm^2)	Swelling 2 h (%)
UMF reference	-	615	3.9	1232	0.25	50.6
Unmodified lignin ref	-	576	1.8	441	0	84.0
Lignin+H_2O_2	2.8	562	1.6	554	0.02	52.3
Lignin+Fe+H_2O_2	2.8	549	1.2	438	0.02	72.3
Lignin+NaOH+Fe+H_2O_2	3.0	609	1.8	556	0.03	failed
Lignin+NaOH+Fe+H_2O_2	4.1	613	2.2	735	0.02	94.6
Lignin+NaOH+Fe+H_2O_2	6.0	593	1.7	489	0.01	86.2
Lignin+NaOH+Fe+H_2O_2	8.1	-	-	-	-	-
Lignin+NaOH+H_2O_2	9.0	583	1.7	604	0.03	96.6
Lignin+NaOH+H_2O_2	9.8	567	1.5	527	0.01	94.9

DISCUSSION

The results presented are limited, but they give a good indication of which full-scale tests should be conducted. The low adhesion of the core of the oxidized lignin boards indicates poor dispersion of the powdered lignin, too low a temperature and too short a time for the lignin to crosslink. Modified lignin adhesives could perhaps be used in the surface layers of the particle boards where the press conditions are more severe. Applying the lignin to the wood chips and obtaining a good dispersion is difficult when the lignin is in a powder form, even if the dry chips absorb moisture during the mixing in a aqueous suspension. Powdered lignin does not provide sufficient tackiness for the mat. It is well known that the adhesive needs to form molecular level contact with the surface of the wood to form a good bond. For this the adhesive should be in a liquid form. Solubilizing Kraft-lignin adds another step in the modification process.

The press factor of 20 s/mm used in the experiments is high compared to that used in the particle board industry. Industrially the greatest problem is the low reactivity of lignin that is a consequence of its crowded molecular structure. Even if all the reactive sites in lignin could be activated, steric hindrances would still lower its reactivity. Residual lignin from pulping processes can be used as a filler and partial replacement in adhesives, and such industrial applications do exist. In applications where the press time is a critical factor, as in particleboard manufacture, an industrially viable and cost-effective method would need a dramatically new point of view for the application and the modification.

CONCLUSIONS

The results show that using lignin as an adhesive in an insoluble form results in poor adhesion and too long a press time. This is also supported by results presented in the literature. The results indicated that the best working pH for Fenton reaction is between 3 and 4. However, as the pH of the unmodified Kraft-lignin is about three, the need for pH adjustment is still unclear.
An adhesive system consisting mainly of lignin would need a radically new approach. However, plenty of unexplored modifications, hardeners, and ways to use lignin exist.

REFERENCES

Benar, P., Goncalves, A.R., Mandelli, D. & Schuchardt, U. 1999. Eucalyptus organosolv lignins. Study of the hydroxymethylation and use in resols. Bioresource Technology 68:11-16.

Cetin, N.S. & Özmen, N. 2002. Use of organosolv lignin in phenol–formaldehyde resins for particleboard production I. Organosolv lignin modified resins. International Journal of Adhesion & Adhesives 22:477–480.

da Silva, C.G., Grelier, S., Pichavant, F., Frollini, E. & Castellan, A. 2013. Adding value to lignins isolated from sugarcane bagasse and Miscanthus. Industrial Crops and Products 42:87– 95.

Danielson, B. & Simonson, R. 1998. Kraft lignin in phenol formaldehyde resin. Part 1. Partial replacement of phenol by kraft lignin in phenol formaldehyde adhesive for plywood. Journal of Adhesion Science and Technology 12:923-939.

El Mansouri, N-E. & Salvado, J. 2006. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. Industrial Crops and Products 24:8–16.

Goncalves, A.R. & Benar, P. 2001. Hydromethylation and oxidation of organosolv lignins and utilization of the products. Bioresource Technology 79:103-111.

Heitner, C., Dimmer, D. & Schmidt, J. 2010. Lignin and Lignans: Advances in Chemistry. CRC Press Boca Raton LF, USA.

Hu, L., Pan, H., Zhou, Y. & Zhang, M. 2011. Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: a brief review. BioResources 6(3).

Imam, S.H., Gordon, S.H., Mao, L. & Chen, L. 2001. Environmentally friendly wood adhesive from a renewable plant polymer: characteristics and optimization. Polymer Degradation and Stability 73:529-533.

Khan, M.A., Ashraf, S.M. & Malhotra, V.P. 2004. Development and characterization of a wood adhesive using bagasse lignin. International Journal of Adhesion & Adhesives 24:485–493.

Lora, J.H. & Glasser, W.G. 2002. Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials. J. of Polymers and the Environment 10:39-48.

Mankar, S.S., Chaudhari, A.R. & Soni, I. 2012. Lignin in phenol-formaldehyde adhesives. International Journal of Knowledge Engineering 3:116-118.

Mansouri, H.R., Navarette, P., Pizzi, A., Tapin-lingua, S., Benjelloun-Mlayah, B., Pasch, H. & Rigolet, S. 2011. Synthetic-resin-free wood panel adhesives from mixed low molecular mass lignin and tannin. European Journal of Wood and Wood Products 69:221-229.

Pizzi, A. 2006. Recent development in eco-efficient bio-based adhesives for wood bonding: opportunities and issues. Journal of Adhesives Science and Technology 20:829-846.

Rowell, R.M. 2012. Handbook of wood chemistry and wood composites. Bio-based Adhesives. CRC Press.

Sarkar, S. & Adhikari, B. 2000. Lignin-modified phenolic resin: synthesis optimization, adhesive strength, and thermal stability. Journal of Adhesion Science and Technology, 14(9):1179–1193.

Tejado, A. Kortaberria, G., Peña, C., Labidi, J., Echeverria, J.M. & Mondragon, I., 2008. Isocyanate curing of novolac-type ligno-phenol–formaldehyde resins. industrial crops and products 27:208–213.

Windsten, P. & Kandelbauer, A. 2008. Adhesion improvement of lignocellulosic products by enzymatic pre-treatment. Biotechnology Advances 26 (2008) 379–386.

Zhang, Y., Yang, D-Q., Wang, X-M., Feng, M. & Brunette, G. 2012. Process for fungal modification of lignin and preparing wood adhesives with the modified lignin and wood composites made from such adhesives. Patent: WO 2012/113058 A1.

Zhang, W., Ma, Y., Wang, C., Li, S., Zhang, M. & Chu, F. 2013. Preparation and properties of lignin–phenol–formaldehyde resins based on different biorefinery residues of agricultural biomass. Industrial Crops and Products 43:326– 333