THE EFFECT OF LIGNIN AS A NATURAL ADHESIVE ON THE PHYSICO-MECHANICAL PROPERTIES OF *VITIS VINIFERA* FIBERBOARDS

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Lignin was used as a natural adhesive to manufacture *Vitis vinifera* fiberboards. The fiberboards were produced at laboratory scale by adding powdered lignin to material that had previously been steam-exploded under optimized pretreatment and pressing conditions. The kraft lignin used was washed several times with an acidic solution to eliminate any contaminants and low molecular weight compounds. This research studied the effects of amounts of lignin ranging from 5% to 20% on the properties of *Vitis vinifera* fiberboards. The fiberboard properties evaluated were density, water resistance in terms of thickness swelling, water absorption, and the mechanical properties in terms of modulus of rupture, modulus of elasticity, and internal bond. Results showed that fiberboards made from *Vitis vinifera* without lignin addition had weaker mechanical properties. However, the fiberboards obtained using acid-washed kraft lignin as a natural adhesive had good mechanical and water resistance properties that fully satisfied the relevant standard specifications.

Keywords: Lignin; Natural adhesives; Fiberboards; Steam explosion; Vitis vinifera; Water resistance; Mechanical properties

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INTRODUCTION

Fiberboard, a structural and decorative material, is a fibrous-felted, homogeneous panel made from lignocellulosic fibers that are combined with a synthetic resin or other suitable bonding system and then bonded together under heat and pressure (ANSI Standards 1994). The manufacture of dry-process fiberboard is limited because the process involved requires the addition of resin binder. Efforts to produce dry-formed fiberboards without a resin binder have generally been unsuccessful. In recent decades an old process (Mason 1927) has been re-investigated (Suchsland et al. 1987; Susuki et al. 1998; Angles et al. 1999; Velasquez et al. 2003; Mancera et al. 2008). This process involves steam explosion of raw lignocellulosic material, thus hydrolyzing most of the hemicelluloses and plasticizing the lignin. The result of this pretreatment is a fiber that can be hot-pressed to produce fiberboard without the need for synthetic binders.

Due to the important role of lignin in fiberboard manufacture, several studies have investigated the use of lignin as a natural adhesive and the possibility of replacing fibers with lignin. Angles et al. (2001) tried to use lignin as a natural adhesive in fiberboard manufacture by adding different types of technical lignins. They found that replacing up to 20% of the fibers with kraft lignin improved the water resistance and mechanical properties of the boards without significantly affecting their density. Subsequently, Velasquez et al. (2003) studied the use of untreated or unpurified kraft lignin resulting from the kraft pulping process to steam exploded *Miscanthus sinensis*. They found that although increasing the quantities of lignin improved fiberboard properties, it also increased the presence of internal bubbles. This problem was somewhat reduced by mixing the *Miscanthus* fibers with the kraft lignin before the steam explosion. This reduced the amount of low molecular weight substances that are present in commercial kraft lignins (these being carbohydrates and inorganic and organic extractives) and caused the fibers and lignin to mix together more effectively.

Kraft lignin is a by-product of sulfate cooking wood chips, a process commonly known as kraft pulping. During sulfate cooking, the native lignin is degraded and dissolved from the wood. Almost all kraft lignins are burned to generate energy and recover chemicals. Only a small amount (1 to 2%) of the kraft lignin that is produced by the pulp and paper industry is commercially used, although it is employed in a wide range of products. Research into possible uses of lignin has focused, among other things, on the use of industrial lignins as binders or as phenolic wood adhesives for panel products. Thorough discussions of the development of lignin-based wood adhesives are given by Nimz and Pizzi (Nimz 1983; Pizzi 2004). Many patents have been lodged over the last few decades that use lignin as an adhesive for boards in place of conventional phenol-formaldehyde or urea-formaldehyde adhesives (Nimz 1983; Pizzi 1994). For various reasons these procedures have not yet led to any major application of lignin (Pizzi 1994).

The objectives of this study were to investigate the use of both acid-washed kraft lignin as a natural adhesive and *Vitis vinifera* fibers as raw material, for the first time, to produce fiberboards at laboratory scale. The effects of lignin ranging from 5% to 20% on the properties of fiberboards were studied.

EXPERIMENTAL

Raw Material Preparation

Vitis vinifera branches came from a plantation in Tarragona, Spain. They were air-dried and stored in jute bags. The branches were chipped into splinters smaller than 5 cm using a GA100 Black & Decker shredder. The average chemical composition of the initial material was 3.7% ash, 13.3% extractives, 24% lignin, 43.6% cellulose, and 19.1% hemicellulose. The sum of the chemical composition exceeds 100% (103.7%); this is a common result, due to the overlap of the testing parameters (Anglès et al, 1997). Softwood-derived kraft lignin was purchased from Ligno-Tech Iberica. This lignin was purified according to the method reported by Lin (1992). It was treated with sulfuric acid (1%) several times and washed extensively with hot water to solubilize the residual sugars. Its general features are: 3.9% moisture content, 0.5% ash content, 94.1% total

lignin, and 1.5% carbohydrates (El Mansouri and Salvado 2006, 2007). After drying the acid-washed kraft lignin at room temperature it was stored in plastic bags for use as a natural phenolic adhesive in *Vitis vinifera* fiberboards.

Steam Explosion

The *Vitis vinifera* chips (200g dry basis per batch) were subjected to a steam explosion pretreatment in an 8 L digester. The sample was steam exploded at a steam temperature of 218 ºC and a pretreatment time of 6 min. The material was rapidly depressurized in a 100 L vessel, which helped it to defibrillate. The pulps were filtered and washed with water.

Grinding

The air-dried steam-exploded pulps were ground and passed through a 4 mm sieve in a Retest cutting mill. This procedure increased the bonding area, thus improving the internal bond (Velasquez et al. 2002).

Board Production

The ground-pretreated material was air dried to 7% moisture content and mixed with lignin in different proportions (0%, 5%, 10%, 15%, and 20%). The testing boards were shaped from the previous mixture by hand using a forming box (150 mm in length and 50 mm in width). Boards were prepared with a target thickness of 3.0 mm. After the material was placed in the mold, it was hot pressed in a three-stage cycle (Angles et al. 1999), these stages involving: **(1)** pressing at the desired temperature and pressure for a given period of time (Pressing temperature=205ºC, Press pressure=12 MPa, and Pressing time=4 min), **(2)** a breathing period or pressure relaxation for 1 min, and **(3)** pressing at the desired temperature and pressure for a given period of time (205 ºC, 12 MPa, and 5 min).

Physical and Mechanical Characterization

The boards were characterized using European standards. The mechanical properties measured were: internal bond (IB) (EN319); modulus of elasticity (MOE), and modulus of rupture (MOR) (EN310). Dimensional stability was characterized by measuring: thickness swelling (TS), and water absorption (WA) (EN317). Additionally, the density of the boards was determined (EN323). Boards were conditioned at 20 ºC and 65% RH before any physical or mechanical tests were conducted, and the dimensions of the test pieces were determined on the basis of the EN 325 standard (EN325). European standards for these properties are as follows: Density>800 Kg/m^3, MOR≥40MPa, MOE≥3000MPa, IB≥0.7MPa, WA≤30%, and TS≤20%.

Experimental Design and Statistical Analysis

The experiment was designed to study the effect of one factor (percentage of added lignin) on four levels, and to compare binderless fiberboards with those made with acid-washed kraft lignin. These levels were chosen on the basis of the literature review and on the research group's previous experiences in producing fiberboards with externally added lignin (Angles et al. 1999; Velasquez et al. 2003). The responses

showed the physical and mechanical properties and were analyzed using the software Statgraphics Plus 5.0.

A variance analysis was carried out for each one of the response variables. All the hypotheses were tested at the 95% confidence level. In each case, the results of the ANOVA were explained by means of a plot showing the average value of the property for each level of lignin addition. The plots also showed an interval around each average. The intervals displayed were based on Fisher's least significant difference (LSD) procedure. They were constructed in such a way that if two averages are the same, their intervals will overlap 95.0% of the time. Any pair of intervals that does not overlap vertically indicates a pair of averages with a statistically significant difference.

RESULTS AND DISCUSSION

The results of the physico-mechanical properties of the fiberboards are shown in Table 1. The experimental factor studied was the percentage of added lignin. This was added in four quantities: 5%, 10%, 15%, and 20%. All the figures also include the results of adding 0% lignin, which corresponds to *Vitis vinifera* binderless fiberboards.

All the fiberboards obtained had densities of 1376 to 1386 Kg m^{-3} for control sample and from 1362 to 1982 Kg/m^{-3} for lignin-added fiberboards and were classified like High Density Fiberboard (HDF).

Table 1. Results of Physico-Mechanical Properties of Fiberboards

(%) Lignin Added	MOR (MPa)	MOE (MPa)	IB (MPa)	WA (%)	TS (%)
0	24	4331	0.14	12.6	8.8
0	25	3876	0.12	13.1	9.1
0	26	4198	0.15	11.8	9.0
5	40	5073	0.33	12.2	9.1
5	41	4940	0.24	12.3	9.3
5	43	5135	0.27	11.6	8.5
10	42	5671	0.53	9.0	7.1
10	43	5334	0.49	8.8	7.4
10	44	5436	0.53	9.5	6.8
15	48	6014	0.70	9.0	4.0
15	45	6481	0.67	9.5	4.2
15	46	6219	0.62	10.3	4.3
20	50	5665	1.09	3.9	2.1
20	52	5610	1.12	3.3	1.6
20	55	5592	1.06	4.2	1.7

Effects on Water Absorption and Thickness Swelling

Water absorption (WA) and Thickness swelling (TS) are physical properties related to the dimensional stability of the boards. These properties give us an idea of how the boards will behave when used under conditions of severe humidity and are especially

important regarding boards that are to be used externally. WA and TS were analyzed together because they came from the same assay. The plots for WA and TS are shown in Figs. 1 and 2, respectively.

For WA it can be seen that the intervals do not overlap vertically, except for the pair of intervals 0%-5% and 10%-15%. Figure 1 shows the decrease in the fiberboards' water absorption as the percentage of incorporated lignin increases. The incorporation of 20% lignin has significantly decreased water absorption and thus improved the water resistance of the fiberboards.

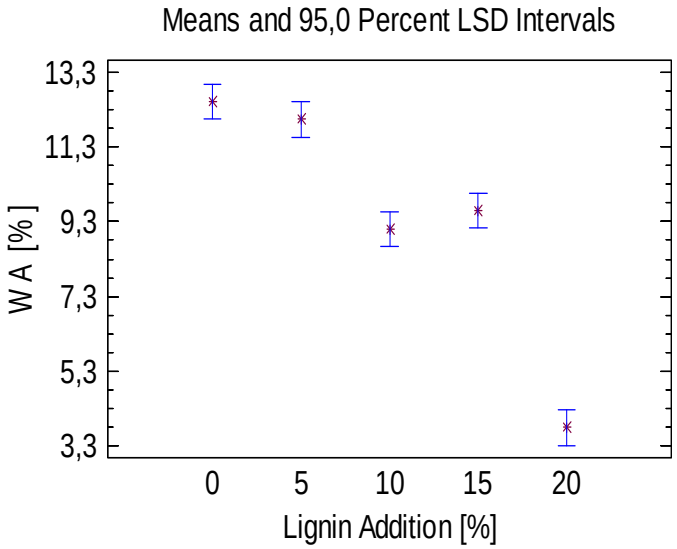

Fig. 1. Average and 95.0 percent LSD intervals for WA

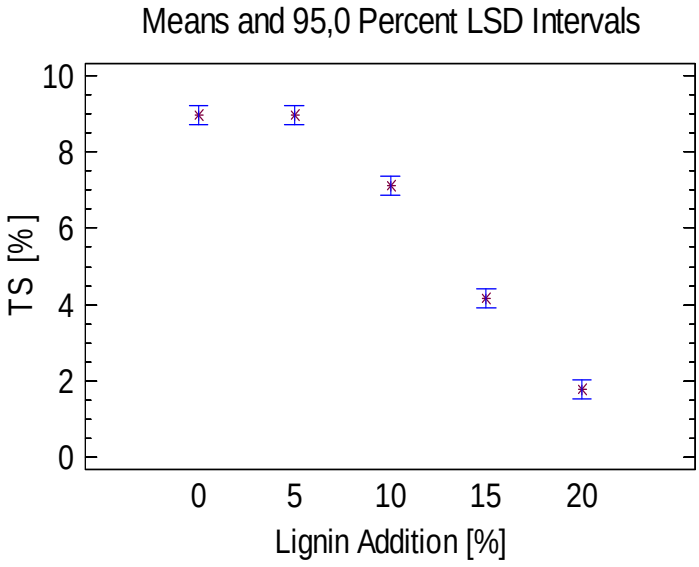

Fig. 2. Average and 95.0 percent LSD intervals for TS

It is well known that lignocellulosic materials absorb water by forming a hydrogen bond between water and hydroxyl groups of cellulose, hemicellulose, and lignin in the cell wall (Rowell et al. 1976). However, the lignin added externally was able to reduce the water absorption of *Vitis vinifera* fibers, possibly because of the non-polar hydro-carbon chains and aromatic rings in the lignin molecules (Rozman et al. 2000). On the other hand, there are two possible ways in which the lignin could reduce water absorption: (1) by bulking the cell wall and (2) by plugging the lumen of the cell wall. The first possibility is likely because if the cell wall is bulked by lignin; this makes it hydrophobic and water cannot enter and swell up the cell wall. The second possibility is unlikely because the lignin is too big to enter into the cell wall.

The only intervals that overlap vertically for TS are the pair of 0%-5% intervals. Thickness swelling of lignocellulosic material occurs when the cell wall is bulked by water. Figure 2 clearly shows that fiberboards with no lignin or with just 5% added lignin had higher TS than those made with 10% and 15% lignin. Of particular note are the results found for fiberboards made of 20% externally added lignin, which show 4 times less TS than binderless fiberboards. Thus, it is clear that externally added lignin was able to reduce the extent of swelling in fiberboards, because swelling was reduced as lignin levels increased. These results clearly indicate that lignin is able to reduce the amount of water that enters and swells the cell wall. This finding is similar to the results found for water absorption.

Effects on Modulus of Rupture and Modulus of Elasticity

The modulus of rupture (MOR) and modulus of elasticity (MOE) were analyzed together because they came from the same bending assay. The plots of MOR and MOE are shown in Figs. 3 and 4, respectively. For MOR it can be seen that the intervals do not overlap vertically except for the pair of intervals at the 5% and 10% addition levels.

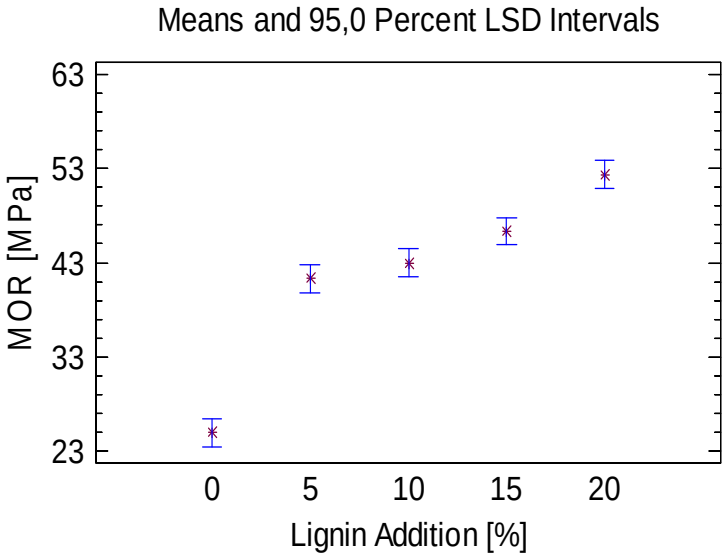

Fig. 3. Average and 95.0 percent LSD intervals for MOR

Figure 3 shows that the fiberboard increased in strength as the amount of lignin was increased. Fiberboards made with lignin had higher strength values than binderless fiberboards. It is particularly interesting to note that the strength of fiberboards made with just 5% lignin was almost the double of that of binderless fiberboard. More interesting are the results for fiberboards made with 10% added lignin, which show MOR values that passed the relevant standard specifications. The incorporation of 20% lignin resulted in fiberboards with MOR values (52MPa) that were two times higher than those obtained for binderless fiberboards (25MPa). This provides a good indication that the incorporation of lignin is able to improve the MOR of fiberboards made from *Vitis vinifera*. Indeed, it can be seen that the incorporation of lignin overcame the discontinuity in the fiber matrix caused by the poor adhesion between the fibers. This may be because the lignin causes better adhesion at the fiber-fiber interface. Lignin is a polymeric material that consists of non-polar and polar substituents. The former come from the polymeric networks consisting of benzene rings, hydrocarbon linkages and so on, and the latter come from the phenolic hydroxyl groups. Thus, the hydrophilic quality of lignin may contribute to the improved fiber-fiber adhesion.

For the MOE it can be seen that the intervals do not overlap vertically. Generally, the MOE of *Vitis vinifera* fiberboards increased as the percentage of lignin increased (Fig. 4). The results show that incorporating lignin stiffened the fiberboards. A similar trend has been observed by other authors (Velasquez et al. 2003). Figure 4 also shows that the MOE of the fiberboards significantly increased as the lignin loading increased to 15%. Thus, the results illustrate that lignin enhances the stiffness of fiberboards. This may be because lignin improves the compatibility between fibers, resulting in increased strength and stiffness.

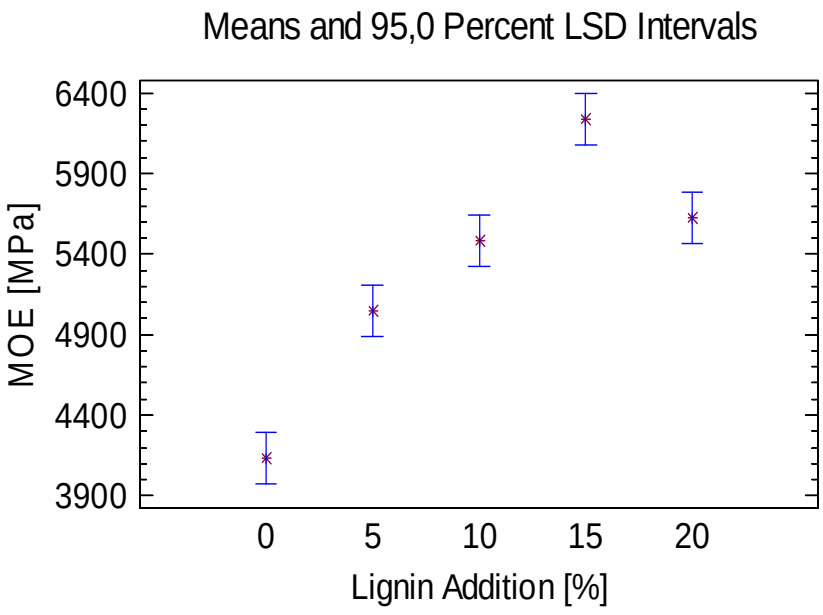

Fig. 4. Average and 95.0 percent LSD intervals for MOE

Effects on the Internal Bond

The plot for the internal bond (IB) is shown in Fig. 5. It can be seen that the intervals for the IB do not overlap vertically. The internal bond refers to the strength of the bond between fibers, which is important because it ensures that the boards will not delaminate during post-processing. Overall, the internal bond of the fiberboards was improved with the incorporation of lignin. It is interesting to note that fiberboards made with 15% and 20% acid-washed kraft lignin had an IB which meets the relevant standard specifications. The results also show that the effect of lignin on the IB became more evident as more lignin was added. Thus, the results indicate that lignin plays a positive role in improving the IB of fiberboards made from *Vitis vinifera*. This improvement is because the lignin melts well at the selected pressing temperature, and is then able to flow over the fiber surface and form strong inter-fiber bonds (Back 1987).

Velasquez et al. (2003) found that increasing the amount of crude kraft lignin increased the presence of internal bubbles which affect the final properties of the fiberboards. However, in the present study, acid-washed lignin overcame this problem. The crude kraft lignin was acid-washed to hydrolyze the organic compounds, such as carbohydrates organic extractives, which are responsible for (1) water absorption, and (2) forming bubbles inside the fiberboards during hot pressing (Velasquez et al. 2003). Therefore, the use of acid-washed lignin improved the mechanical properties and water resistance of *Vitis vinifera* fiberboards.

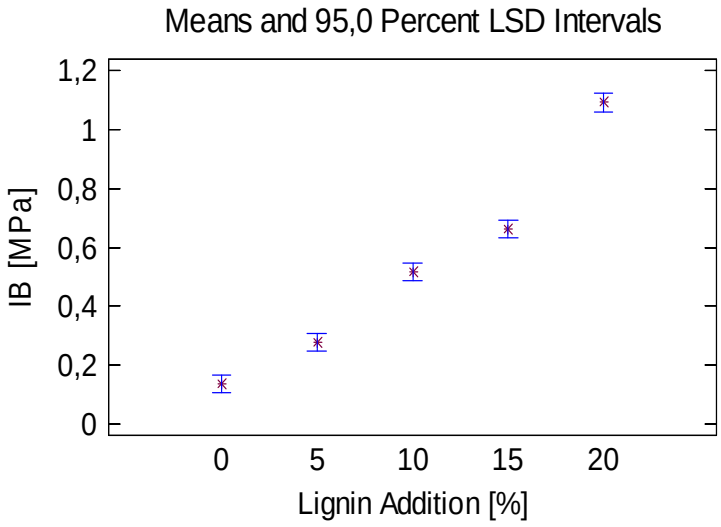

Fig. 5. Average and 95.0 percent LSD intervals for IB

CONCLUSIONS

The effect of adding lignin to fiberboards was investigated to determine the effects on the fiberboards' physico-mechanical properties and to explore the potential use of acid-washed kraft lignin as an alternative to synthetic adhesives for binderless fiberboards made from *Vitis vinifera*. It was found that *Vitis vinifera* fiberboards made

without lignin had weaker mechanical properties. However, fiberboards containing 15% acid-washed kraft lignin had good mechanical and water resistance properties that fully satisfied the relevant standards specifications.

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