

Development of Self-Bonded Fiberboards from Fiber of Leaf Plantain: Effect of Water and Organic Extractives Removal

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Adhesive-free fiberboards can be self-bonded through high temperature thermo-compression processes. To achieve it, treatments such as steam explosion/injection, as well as chemical and enzymatic oxidation have been implemented. However, the role of extractive components in the structure and cohesiveness of fiberboards has not been fully understood. In this work fibers of leaf plantain were treated with organic solvents and with hot water to remove the extractives, and were then employed to produce self-bonded fiberboards. Treated fibers were characterized by thermogravimetric analysis, electronic paramagnetic resonance, and antioxidant capacity. The mechanical strength of the fiberboards evaluated by three point flexural tests, decreased when fibers were extracted with aqueous solvents, and increased after treatment with organic ones. This can be explained by the effect of water extractives in reducing the initial degradation temperature, and in retaining free stable radicals generated during thermo-compression. In the case of the organic extractive fraction, this inactivates the fibers, which impairs close contact between polar groups and thus decreases the mechanical properties of the fiberboards. According to the results, it is possible to increase the mechanical properties of self-bonded fiberboards by changing the concentration of polar and low molecular weight phenolic compounds.

Keywords: Extractive; Fiberboard; Lignocellulosic fiber; Self-adhesion

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INTRODUCTION

Fiberboards are composites produced from lignocellulosic fibers (usually from woody plants) with adhesives whose characteristics can be tuned to be suitable for selected applications (Nemli *et al.* 2006). Because of the world trend towards greener manufacturing processes and safer and healthier consumer demands, naturally occurring components are being considered as substitutes for currently employed, petroleum-derived adhesives (Okuda and Sato 2007). This stems from the fact that such synthetic molecules are difficult to degrade through natural processes, and they can be hazardous to humans upon exposure (the case of formaldehydes can be cited, for example) (Boran *et al.* 2011).

Adhesive-free fiberboards can be manufactured whereby bonding is achieved through self-adhesion (Widyorini *et al.* 2005a). During the fabrication process of such

composites, the lignocellulosic fibers are thermo-compressed at high temperatures, generally above 160 °C (Bouajila *et al.* 2005; Hunt and Supan 2006; Xu *et al.* 2006). Under these conditions, activation of the chemical components of the fibers occurs and radical species are formed (the onset of their formation can begin at temperatures as low as 70 °C) (Sivonen *et al.* 2002). Degradation of lignocellulosic fiber begins with the extractive fraction and it propagates until reaching the heteropolysaccharide and lignin components (Bourgois *et al.* 1989). Radical interactions trigger the formation of covalent bonds, which then leads to condensation reactions between lignin and/or lignin-heteropolysaccharides (Okuda and Sato 2004; Nuopponen *et al.* 2005; Okuda *et al.* 2006a). These reactions are responsible for increased inter-fiber adhesion, which is otherwise made possible by addition of synthetic adhesives. Radical species formation occurs either by depolymerization of phenolic compounds or from the degradation of other components such as the heteropolysaccharides, lignin and extractives present in the fibers. The lignin molecules and extractives become radicalized via their phenolic groups, while for heteropolysaccharides, due to their structure, the radicals formed during degradation are trapped by available phenolic compounds (Nuopponen *et al.* 2005; Fernández *et al.* 2006).

The activation of the chemical components in the fibers can be achieved by hot-pressing (Bouajila *et al.* 2005), and it can be improved by different treatments such as steam explosion, steam injection pressing (Widyorini *et al.* 2005b), and oxidative treatment (Felby *et al.* 2004). The steam-treated fibers are exposed to drastic pressure and temperature conditions. Steam treatment leads to the formation of acetic acid, which subsequently catalyzes the degradation of hemicellulose, lignin, and amorphous cellulose. Heteropolysaccharides degrade by hydrolysis of glucosidic bonds. This same process in lignin occurs through radical reactions (Focher *et al.* 1998). Degradation reactions of hemicellulose produce furfural products, which are believed to play an important role in bonding strength of self-bonded fiberboards, due to condensation reaction in lignin such as lignin-furfural (Suzuki *et al.* 1998). Furthermore, there is a thermal softening of lignin (Widsten 2002). A difference between steam explosion processes and steam injection pressing is that in the first case, the degraded components are solubilized in water and removed after processing, while in the second case, all fractions are formed during treatment and remain in the fibers.

The presence of phenolic groups in lignin, in low-molecular weight compounds, and other phenolic substances, allows radicals to be formed on the fiber surfaces during oxidative treatment (Widsten 2002). Adhesion mechanisms involve formation of interfiber covalent bonds via coupling of radicals on adjacent fibers. Activation of wood particle surfaces can be achieved by ligninolytic enzymes, including laccase and peroxidases (Felby *et al.* 2002; Kudanga *et al.* 2011), inorganic oxidizing agents such as Fenton's reagent (H₂O₂/FeSO₄) (Riquelme-Valdés *et al.* 2008; Halvarsson *et al.* 2009), and γ -irradiation (Widsten 2002).

Self-bonded fiberboards can be developed without pre-treating the fibers. Chemical changes of the fiber occur during hot-pressing. For example, lignin and hemicelluloses are degraded, and condensation reactions can take place. Besides, low molecular weight components experience some chemical changes during hot-pressing and they form new chemical structures (Okuda *et al.* 2006b). The extent to which this so-called auto-adhesion takes place depends on the pressing conditions and the chemical and physical properties of the fibers. The effect of temperature, pressing, time, and moisture have been evaluated (Bouajila *et al.* 2005; Álvarez 2010). Other studies have been carried

out, for example to evaluate the effects of addition of acetic acid, vanillin, and organic extractives to fibers (Bouajila *et al.* 2005; Okuda *et al.* 2006b).

Few publications have shown the importance of low molecular weight components and extractives on the properties of particleboard. The effect of extractive removal from lignocellulosic fibers has been evaluated as far as the properties of traditional particleboard and the thermal stability of different wood species (Hashim *et al.* 2001; Shebani *et al.* 2008). Felby *et al.* (1997) reported that during development of self-bonded fiberboards, carbohydrates and lignin extractives that were generated during the pulping process interact as redox mediators with the surface-bound lignin and oxidative enzymes. Widyorini *et al.* (2005b) observed that all fractions formed during steam injection treatment contribute to the linkage between the particles. Moreover, Okuda *et al.* (2006b) evaluated the influence of removal and addition of methanol extractives of kenaf core fibers; the results showed that the IB values were almost identical to each other. In general, it has been shown that the presence of low molecular weight species and inorganic ions in the extractive fraction not only contributes to the formation and retention of free radicals, but also catalyzes the thermal degradation of lignocellulosic fibers (Bouajila *et al.* 2005; Yao *et al.* 2008). The removal of aqueous extractives increases the degradation temperature (Shebani *et al.* 2008) and therefore reduces the formation of radical species (Álvarez 2010). In contrast, the presence of non-polar extractives, usually present on the surface of the fibers, prevents close contact between polar groups, reducing reactivity, and bond strength, which negatively affects the mechanical properties of the material (Nielsen *et al.* 2009; Widsten *et al.* 2009). In spite of the above findings, more research is needed to understand the reasons why extractive components contribute to self-bonding of fiberboard.

This investigation addresses some of the key questions related to the use of green approaches to produce fiberboards. As such, thermogravimetric analysis (TGA), electronic paramagnetic resonance (EPR), antioxidant capacity, and mechanical tests were carried out in order to elucidate the effect of the extractive components from the fibers of leaf plantain on the properties of self-bonding fiberboards.

EXPERIMENTAL

Materials

Fibers were obtained from central vein leaf plantain. Samples were supplied by The Corbanacol Foundation (Colombia) and were extracted from commercial plantain plants (*Musa AAB*, cv. ‘Dominico Harton’) cultivated in the Urabá region (Colombia). The fibers were delivered in bales and were ground in a blender to *ca.* 2 mm particle size, and equilibrated with ambient air to moisture equilibrium of *ca.* 7 wt %.

Methods

Fiber treatment

To evaluate the effect of removal of the extractives on the mechanical properties of fiberboard, dry fibers were exposed to two different treatments according to TAPPI standards 204 and 207: extraction with organic solvents (toluene:ethanol 2:1), and with hot water. After treatment, the fiber samples were filtered and dried in an oven at 40 °C for 24 h. The respective extractive-leaden solvent was evaporated, and the residual solids,

OE and WE for the organic and water extractives, respectively were dried at 40 °C until constant weight. Extractives and extracted fibers are labeled according to Table 1.

Characterization of extractives and fibers

The thermal stability of extractives and fibers was determined using a TA Instruments Q100 TGA. The tests were performed at a heating rate of 10 °C/min in a nitrogen atmosphere. The radical scavenging activity was measured with ABTS radicals. In order to oxidize the colorless ABTS to blue-green radical cation, ABTS^{•+}, 7 mmol/L of ABTS was mixed with potassium persulfate (for a final concentration of 2.42 mmol/L) and incubated for 12 to 16 h at room temperature in a container protected from light. Upon completion of the incubation time, the ABTS^{•+} solution was diluted with phosphate buffer (pH 7.4) to an absorbance of 0.70 (±0.02) at 734 nm. Afterwards, 5.0 mL and 990 µL ABTS^{•+} solution were added to 2 mg of ground fibers and to 10 µL of a solution of each component extractive, respectively. The extractive components were dissolved in aqueous and organic solvent to a concentration of 1.2 and 0.4 mg / mL, respectively. The mixtures were stirred for 30 s and the absorbance was monitored continuously for 30 min. The data were collected at 734 nm and room temperature (approx. 25 °C) using a Jenway 6405 UV–vis spectrophotometer.

The scavenging activity of the samples was determined from the reduction in ABTS absorption in Trolox units to verify that there was no influence of the sample mass used (Ugartondo *et al.* 2008) according to Eq. 1:

$$ABTSequi (mgTrolox / g_{Fibre}) = \left(\frac{0.2336 \times Absorbance + 0.8341}{Concentration_{sInABTS}} \right) \times 100\% \quad (1)$$

The amount of radicals formed on the treated samples was determined with the electronic paramagnetic resonance technique (EPR), using a Varian Century Series E-102 spectrometer at room temperature with a 100 KHz modulation frequency, a 1 G amplitude, a field center of 3385 G and a 9.51 GHz frequency. Ten 60-second sweeps were performed for each test, and the amount of radicals produced was determined according to the area under the spectrum curve per mass of sample (Zoia *et al.* 2007). 50 mg of fibers were deposited inside a quartz tube and were heated at 200 °C for 7 min to simulate the samples' thermo-compression process.

Manufacture of the fiberboards

The fiberboards were produced by pressing ground fibers in a circular mold at 200 °C and 3.0 MPa during 7 min. The process resulted in solid disks with an average diameter of 150 mm and a thickness of 1.5 mm, which were cut into 7 x 55 mm fiberboard samples (see Table 1 for nomenclature). The moisture content of fibers before the process was of ca. 7 wt %. The expected density of fiberboards was 1.0 g/cm³.

Characterization of the fiberboards

Modulus of elasticity (MOE) and modulus of rupture (MOR) were evaluated with a TA Instrument Q800 V20.6 with a Build 24 series 0800-0592 dynamic mechanical analyzer. Testing was performed at 30 °C using a dual cantilever clamp and a force ramp of 0.5 N / min. Tests were performed in triplicate.

Table 1. Nomenclature of Samples

Treatment	Nomenclature		
	Extractives	Fiber	Fiberboard
No treatment	-	F-NT	FB-NT
With organic solvents	OE	F-OE	FB-OE
With hot water	WE	F-WE	FB-WE

RESULTS AND DISCUSSION

The water and organic extractive contents of the fibers of leaf plantain were determined to be 15.0 and 2.5%, respectively. Figure 1a-b shows the thermal stability of the extractives. For water extractives (WE), an initial minor weight loss occurred up to a temperature of 80 °C, which is related with the evaporation of water from the samples. However, the non-polar organic extractives (OE) (Nielsen *et al.* 2009; 2010) did not present any weight loss at such temperatures. The OE degradation profile shows a small shoulder at *ca.* 250 °C, and a large peak between 120 and 520 °C approximately, with a maximum degradation temperature of 420 °C. In the case of the WE sample, three peaks associated to sample degradation are observed in the ranges 140 to 190 °C, 190 to 380 °C, and 380 to 540 °C. These peaks correspond to the degradation of the different components including those in the form of monomers, dimers, and polymers (Rowell *et al.* 2000).

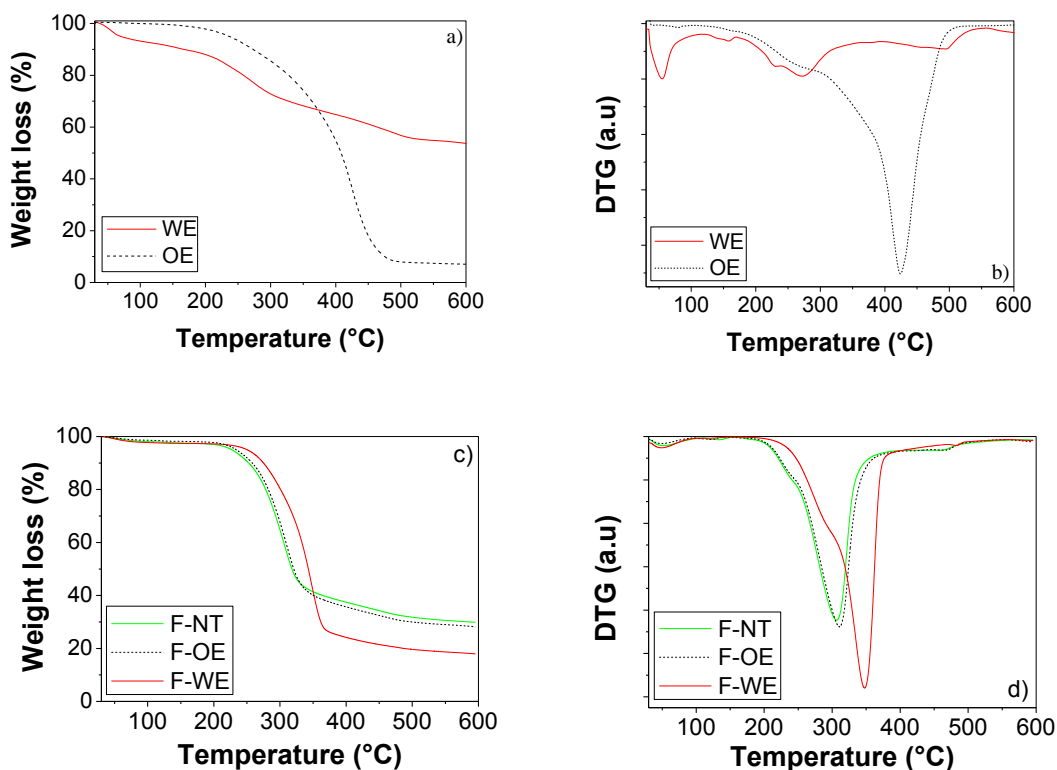


Fig. 1. Thermogravimetric analysis of water and organic extractives, and fibers of leaf plantain: a) TGA and b) DTG of water and organic extractive; c) TGA and d) DTG of treated and non-treated leaf plantain fibers.

Compared to OE samples, WE was subject to a greater degradation below 380 °C; above this temperature WE samples showed a higher thermal stability, perhaps due to the residual ash present (35%).

Figure 1c-d shows the thermal stability of fibers before and after extraction. All samples experienced a weight loss below 100 °C, due to water evaporation (Spinacé *et al.* 2009). Weight loss due to thermal decomposition of cellulose and hemicelluloses (Shebani *et al.* 2008) in the F-NT and F-OE samples began at about 200 °C and ended at 390 °C, with the maximum degradation temperature recorded at approximately 300 °C. The lignin degradation was observed between 390 and 490 °C. The sample treated with hot water (F-WE) was more thermally stable. The initial and maximum degradation temperatures were 240 °C and 350 °C, respectively, and the lignin degradation was observed at approximately 470 °C. The higher degradation temperature of the F-WE samples is attributed to the removal of the extractive components, and the presence of inorganic ions, which play a catalytic role in the thermal degradation (Bouajila *et al.* 2005; d'Almeida *et al.* 2006; Yao *et al.* 2008). The results are in agreement with several investigations that indicate that the removal of extractives from lignocellulosic fibers increases the fiber degradation temperature, especially after water extraction (Shebani *et al.* 2008). The samples treated with hot water presented a significant reduction in ash content, since salts were lost in the WE.

Table 2 includes values of the antioxidant capacity of fibers before and after extraction. The removal of the extractable components reduced the antioxidant capacity of the samples; this effect was more notorious in the F-WE sample. The antioxidant capacity of F-NT was 63% and that of the F-WE and F-OE samples was 36 and 53%, respectively. Compared with the water extractives, the organic extractives have a greater antioxidant capacity (80.5%) (Álvarez 2010); however, the greater concentration of water extractives in the fibers (15%), explains their more significant effect in the fibers. These results were corroborated by the reduction in ABTS absorption in Trolox units, where a similar trend was observed.

The results for antioxidant capacity were corroborated with electron paramagnetic resonance (EPR) experiments after treatment at 200 °C for 7 min. Radical retention capacity on fibers decreased after treatments. Table 2 indicates a lower content of free radicals for the F-WE samples relative to that of samples after organic solvent extraction.

Table 2. Antioxidant Capacity of Treated and No Treated Fibers

Sample	Scavenging capacity (%)	Trolox Equivalent ($\mu\text{molTrolox/g-fibre}$)	Free radicals (area/mg)
F-NT	63.3 \pm 4.4	2.79 \pm 0.2	15.1 \pm 0.4
F-OE	53.2 \pm 4.9	2.60 \pm 0.4	13.0 \pm 0.4
F-WE	36.1 \pm 3.0	2.44 \pm 0.1	11.1 \pm 0.3
OE	80.5 \pm 2.2	216.8 \pm 2.4	-
WE	22.1 \pm 1.2	79.3 \pm 1.4	-

The presence of phenolic units in extractives and lignin present in fibers contributes to their antioxidant capacity, allowing the retention of stable free radicals, which are generated due to degradative processes during hot-pressing (Sun and Tomkinson 2003; d'Almeida *et al.* 2006; Shebani *et al.* 2008). According to Bourgois *et al.* (1989), during the degradation process of lignocellulosic fibers, radical species are

formed, beginning with the extractives, which have the lowest thermal stability (70 °C), and followed by heteropolysaccharides and lignin. These radicals increase the reactivity of the samples and lead to the formation of covalent bonds (radical-radical reactions). These covalent bonds facilitate self-adhesion of the fibers and thus improve the mechanical properties of the agglomerated boards (Felby *et al.* 2004; Yelle *et al.* 2004). The activation of the fibers and, therefore, the material properties are directly related to the processing temperature. Enzymatic and chemical oxidation treatments have been used by different authors to probe the effect of stable free radicals on mechanical properties of self-bonded fiberboards. Brown-rot fungi, phenol oxidase enzyme such as laccase (Felby *et al.* 2004; Widsten and Kandelbauer 2008) and Fenton's reagent (Widsten and Laine 2002) are some examples of this treatment.

Figure 2a-b includes the modulus of elasticity (MOE) and modulus of rupture (MOR) of particleboards from un-extracted and extracted fibers, respectively. An increase in MOE and MOR by *ca.* 30 and 35% was measured for FB-OE particleboards compared to those of FB-NT. As shown in other studies, the fiber surface is inactivated by accumulation of non-polar extractives, which impairs a close contact between polar groups, producing a weak adhesion (Frihart 2005; Nielsen *et al.* 2010). Therefore, the removal of the OE allows a higher formation of hydrogen bonding, creating a better contact between the fibers (Xu *et al.* 2006). According to these results, the adverse effect that could be causing the reduction in the antioxidant capacity of the fibers on the mechanical properties of the agglomerate boards is offset by the reduced content of non-polar groups on the surface of the fibers. It is noted that the thermal stability was not affected by the respective treatments.

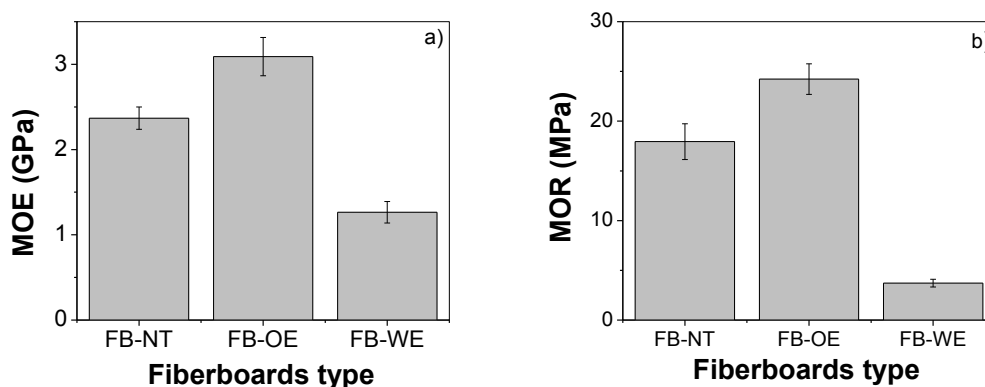


Fig. 2. Mechanical strength, a) MOE and b) MOR of particleboards from un-extracted and extracted fibers

Removal of water extractives produced negative effects in the mechanical properties of the particleboards: the MOE and MOR of the FB-WS were 1.1 GPa and 14.6 MPa, respectively, which is lower than those of the FB-NT. This corresponds to a 45% and 80% reduction. In this case, the thermal stability of the fibers increased (see Figure 1c), and as a consequence, the formation of free radicals decreased (see Table 2). The reduction of the antioxidant capacity produced a lower activation of the fibers, which consequently led to a decreased formation of covalent bonds during the thermo-compression process, which reduced the mechanical properties of the produced fiberboards.

Different authors have examined the effect of temperature on the properties of self-bonded fiberboards (Bouajila *et al.* 2005; Nonaka *et al.* 2013). It has been evaluated within the temperature range of 180 to 280 °C using different plant sources. The results show that by using higher temperatures (above 240 °C) mechanical properties increase. The results are associated with the production of furan monomers during thermo-compression process at high temperatures, which have the potential for promoting self-bonding of the wood fibers (Tshabalala *et al.* 2012). Furthermore, partial degradation of fiber allows for the formation of low molecular weight components with high reactivity. The degradation also leads to the formation of radical species, which can be captured by the phenolic hydroxy groups present in the fibers (lignin and extractable components), as some authors report (Boustingorry *et al.* 2005; Nuopponen *et al.* 2005; Boonstra *et al.* 2007).

The chemical composition of the fibers plays a critical role in the development of self-bonded agglomerate boards. First of all, lignin links the particles through covalent lignin-lignin and lignin-heteropolysaccharide bonds (Windeisen and Wegener 2008), while the polysaccharides contribute with secondary bonds such as hydrogen bonds and van Der Waals forces (Pohjamo *et al.* 2003; Mohan *et al.* 2006). Even though the effect of extractable components has not been directly studied, some reports have indicated that they play a critical role in the development of self-bonding in lignocellulosic fibers (Bouajila *et al.* 2005; Álvarez 2010). This is also observed in the present work, where the mechanical properties of fiberboards decrease if fibers are water-extracted. In contrast, if the organic extractives are removed, the mechanical properties are improved.

CONCLUSIONS

1. The extractable components present in non-wood fibers play a critical role in the development of mechanical strength of self-bonded fiberboards. The water extractive components serve as catalysts of fibers' degradation reactions, aiding in the formation of stable free radicals at lower degradation temperatures, which lead to the formation of covalent bonds that facilitate inter-fiber bonding. Therefore, the presence of water extractives increases the mechanical properties of the materials upon thermo-compression. Because of the non-polar nature of organic extractives, they decrease the reactivity of the surface of the fibers, limiting their bonding ability, and resulting in a reduction of the mechanical properties of the self-bonded fiberboards.
2. Water extractives, which are low molecular weight and have antioxidant capacity, activates the fibers during thermo-compression, allowing for better bonding, and increasing the mechanical properties of the materials.

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