Tannin Adhesive from *Stryphnodendron adstringens* (Mart.) Coville in Plywood Panels

Amélia G. Carvalho, Antônio J.V. Zanuncio, Fábio A. Mori, Rafael F. Mendes, Marcela G. da Silva, and Lourival M. Mendes

The aim of this study was to evaluate the technical viability of using tannin adhesives derived from *Stryphnodendron adstringens* (Mart.) Coville barks in the production of plywood. 0, 25, 50, 75, and 100% tannin-based adhesives (TF) derived from barbatimão barks were combined with commercial phenol-formaldehyde (PF) adhesive. The properties of the adhesives were determined, and plywood was produced. The panels were produced with five crossed layers, an adhesive grammage of 360 g/m² (double line), and an assembly time of 10 min. A pressing cycle at a temperature of 150 °C, specific pressure of 12 kgf/cm², and duration of 10 min was used. With the exception of the parallel modulus of elasticity, panels produced with 25, 50, 75, and 100% barbatimão-derived tannin adhesive met NBR 31:000.05-001/2 standards (ABNT 2001). The tannin barbatimão adhesive proved feasible for use in plywood panels destined for both humid and dry environments.

Keywords: Tannin; Natural adhesives; Plywood

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INTRODUCTION

Gluing wood conserves forest resources because the yield obtained during the manufacturing of reconstituted wood products is higher than that in sawmills. Approximately 287,719,522 m³ of reconstituted wood panels were produced in 2011, representing an increase of 36.6% compared to the world production in 2001 (182,529,147 m³) (Food and Agriculture Organization 2013). This growth has simultaneously increased the consumption of adhesives, which are typically produced from oil and natural gas. The formaldehyde-based resins UF, MUF, and PF are the three most common adhesives used in the composite wood industry (Moubarik et al. 2010a). Phenol formaldehyde (PF) is the most used structural adhesive in the production of panels for outdoor use because of its good adhesion to different lignocellulosic substrates, high water resistance, and low initial viscosity (Pizzi 1983).

With dwindling oil resources and unstable oil prices, the future cost and availability of synthetic adhesives are uncertain. Highly priced synthetic adhesives increase the final cost of wooden panels. There are concerns about formaldehyde emissions from the very same adhesives. Research seeking to replace synthetic adhesives is needed to produce quality panels, with lower formaldehyde emissions, at a lower cost. The search for natural adhesives has recently been focused on the use of tar derived from carbonization on lignin, and on the use of tannins. Because it is an economically viable...
adhesive that uses abundant, renewable natural resources and meets the international standards for performance and emissions, plywood is economically and environmentally acceptable (Navarrete et al. 2010).

Tannins are phenolic compounds. They are secondary metabolites that help defend plants against solar radiation, herbivores, and pathogens. The concentration of phenolic compounds in a plant is influenced by the genetics of the species as well as the environmental conditions of the area in which it is located. The nature of phenolic tannins allows them to react with aldehydes under both acidic and alkaline conditions, which allows for their effective use as wood adhesives (Tondi and Pizzi 2009). The most common commercially-condensed tannins come from mimosa bark (Acacia mearnsii or mollissima), Quebracho wood (Schinopsis balansae and Schinopsis lorentzii), pine bark (Pinus radiata), and Gambier leaves (Uncaria gambier) (Tondi and Pizzi 2009). According to Santos et al. (2002), the condensed tannins from Stryphnodendron genus are formed with prodelphinidin units. Podelphinidins are formed by gallocatechin and/or epigallocatechin, which contain ortho-trihydroxyl groups in the B-ring.

Of the Brazilian Cerrado species that have the potential for tannin production, Stryphnodendron adstringens (Mart.) Coville, widely known as barbatimão, stands out. Its primary economic value comes from tannin extracts from its bark and leaves. The primary use of barbatimão is the extraction of tannins from its bark for use in tanning animal leather. It is also used in folk medicine.

According to Almeida et al. (2010), companies, government agencies, and NGOs (Non-governmental organizations) have stressed the importance of native forests to economic and social development. Interest in exploiting natural products as alternatives to synthetic products is constantly growing (Almeida et al. 2010).

Up to this time, there has been a lack of studies related to the use of tannin adhesive from barbatimão in plywood panels; thus, the goal of this study was to evaluate the technical viability of a tannin-based adhesive derived from Stryphnodendron adstringens (Mart.) Coville bark in the production of plywood.

**EXPERIMENTAL**

**Methods**

*Extraction of tannin and preparation of tannin adhesive*

Barbatimão bark was collected from a Cerrado fragment area located at 919 m altitude and at coordinates 21°15'56,97 S and 44°58'34,65 W. After collection, the bark was mixed and fragmented, and the chopped material was air-dried and triturated in a hammer mill with a sieve opening size of 2 mm².

Polyphenols were extracted from Stryphnodendron adstringens (Mart.) Coville with 3% (dry basis) sodium sulfite at 70 °C for 3 h with a 15:1 liquor:bark (volume:mass) ratio. At the end of the extraction, the material was filtered using a 1-mm²-sized mesh. The material was then filtered again with a vacuum pump and sintered glass crucibles (porosity2). Extracts were poured in glass trays and placed in an oven at a 40 °C until they were completely dry. They were then manually ground with a porcelain mortar and pestle.

The tannin-based thermosetting adhesives were synthesized by mixing the tannin powder with water at a concentration of approximately 50% total solids with an agitator.
rotating at a speed of 3000 rpm. After 24 h of hydration, 8% (dry basis) paraformaldehyde (a binder) was added.

**Characterization of adhesive**

The viscosity, gel time, solids content, and pH of the pure tannin, phenol-formaldehyde adhesives, and mixtures of the two were determined. The viscosity was determined using a Ford cup viscometer (Universal) and following the parameters stipulated by ASTM D-1200 (ASTM, 1994). The determination of solids content was performed by weighing 1 g of the adhesive, then drying in an oven at 103 ± 3 °C until constant weight. The pH values of the adhesives were determined by pH meter, until stabilization was achieved.

**Production of plywood panels**

To produce the panels, five treatments were used. Three samples of each type of panel were created. The concentrations of the tannin compounds in each type of adhesive are shown in Table 1. The plywood panels were produced using 30-year-old *Pinus oocarpa* wood. The felled trees were cut into discs and logs. The discs were used to determine the wood’s density according to NBR 11941 (ABNT 2003). The *Pinus oocarpa* logs were immersed in water at 66 °C and heated for 24 h. The plies were created in a rolling mill. Their nominal thickness was 2 mm, and they were sliced to dimensions of 480 x 480 mm.

The plies were allowed to dry naturally in a covered locale. Subsequently, the layers were dried in an oven with forced air circulation to 8% moisture content.

The final panels were produced with five crossed layers, an adhesive grammage of 360 g/m² (double line), and an assembly time of 10 min. The pressing cycle used took place at 150 °C, under 12 kgf/cm² pressure, for 10 min.

**Evaluation of physico-mechanical properties**

The apparent density and water absorption (WA) after 24 h of immersion in water were determined according to the Brazilian Association of Technical Standards NBR 9485 (ABNT 1986). The thickness swelling (TS) after 24 h of immersion was determined according to NBR 9535 (ABNT 1986). The moduli of rupture and static bending elasticity (both parallel and perpendicular) were determined according to standard EN 310 (1993). The glue-line shear was determined according to standard EN 314-1 (1993).

**Statistical analysis**

A completely randomized design (CRD) was used in the study. To differentiate between treatments, ANOVA and regression analysis were performed at a 5% significance level. The Tukey test was performed at a 5% significance level to differentiate between the densities of each treatment.

Before the analysis of variance, the Bartlett test of homogeneity of variances (5% significance) and the Shapiro-Wilk normality test (5% significance) were conducted.
RESULTS AND DISCUSSION

Properties of the Adhesives

As shown in Table 1, the viscosity of the tannin-based barbatimão adhesives was higher than that of pure phenol-formaldehyde adhesives (PF). Replacement of 25% of the PF adhesive with the tannin adhesive caused a measurable increase in viscosity. The same increase occurred with 50 and 75% substitution; however, the increase in viscosity was so large that it was impossible to measure using the Ford viscosity cup.

Table 1. Properties of the Adhesives

<table>
<thead>
<tr>
<th>Treatment No</th>
<th>Adhesive Formulation</th>
<th>Viscosity (cP)</th>
<th>Gel time (s)</th>
<th>Solids content (%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100% TF*</td>
<td>494</td>
<td>53</td>
<td>50.7</td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>100% PF</td>
<td>150</td>
<td>279</td>
<td>46.8</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>25% TF / 75% PF</td>
<td>188</td>
<td>50</td>
<td>49.0</td>
<td>12.2</td>
</tr>
<tr>
<td>4</td>
<td>50% TF / 50% PF</td>
<td>-</td>
<td>44</td>
<td>47.9</td>
<td>10.5</td>
</tr>
<tr>
<td>5</td>
<td>75% TF / 25% PF</td>
<td>-</td>
<td>40</td>
<td>46.8</td>
<td>9</td>
</tr>
</tbody>
</table>

*TF: tannin formaldehyde, PF: phenol formaldehyde

One of the biggest difficulties in the production of tannin adhesives is maintaining the viscosity necessary for different uses, especially when the adhesive is applied by spray nozzles (requiring low viscosity). Because of the reaction occurring within the mixtures of 50:50 and 75:50 barbatimão:PF, it was impossible to apply these mixtures to particle boards.

The low gel time of the tannin adhesive shows the high reactivity of the tannins relative to that of paraformaldehyde, which promotes faster curing and reduces the adhesive’s shelf life. Lower average values for the gel time were observed in the TF adhesive as compared to the PF adhesive, which may be due to the high pH of the PF adhesive. According to Pizzi (1983), the tannin adhesive polymerizes faster in a high pH medium, because both the A and B groups of the tannin flavonoid unit take part in the curing reaction, accelerating curing.

Because they can reduce the gel time and thus, the pressing time, polyphenolic compounds extracted from bark have been widely used as a PF resin accelerator in the production of particleboard and plywood (Trosa and Pizzi 1997; 2001).

The solids content indicates, in general, the percentage of reactive sites within the binding agent. Usually, a higher adhesive solids content is better and makes the glue line durable. However, certain limits are in place, since too high a solids content also complicates the application of the adhesive via spraying. This is due to its increased viscosity. High solids content also hinders the penetration and spread of adhesives across wood veneers during plywood production.
The tannins were hydrated to generate an adhesive with a solids content of 50%. In general, both the mixtures and the PF adhesive had solids contents close to 50%, which is an adequate level for the production of laminated panels.

It is possible to verify the acidic character of tannin adhesives and the basic character of phenol formaldehyde adhesives based on their pH. As the degree of barbatimão substitution was increased, the pH of the mixtures decreased.

Jahanshaei et al. (2012) evaluated the properties of PF adhesive and of mixtures of 10, 20, and 30% *Quercus castaneifolia* derived tannin adhesive with PF. They observed gel time values of 120, 70, 67, and 80 s; viscosities of 360, 480, 610, and 760 cP; pH values of approximately 11, 8.3, 8.36, and 5.87; and solid contents of 55, 55, 55.5, and 60% for the PF adhesive and the mixtures with 10, 20, and 30% tannin adhesive, respectively.

Replacement of PF adhesive with a tannin adhesive derived from *Stryphnodendron adstringens* showed similar behavior to replacement within an adhesive derived from *Quercus castaneifolia*: both substitutions decreased the pH and gel time and increased the viscosity.

### Physical Properties of the Plywood Panels

#### Apparent density

The density of *Pinus oocarpa* wood, a species used for the fabrication of three types of panels, was 0.42 g/cm³. There was no statistical difference in the densities of the panels generated with different treatments (see Table 2).

**Table 2. Apparent Density of the Plywood Panels**

<table>
<thead>
<tr>
<th>Treatment Conditions</th>
<th>Apparent density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1. 0% TF / 100% FF</td>
<td>0.516</td>
</tr>
<tr>
<td>T2. 25% TF / 75% FF</td>
<td>0.530</td>
</tr>
<tr>
<td>T3. 50% TF / 50% FF</td>
<td>0.523</td>
</tr>
<tr>
<td>T4. 75% TF / 25% FF</td>
<td>0.524</td>
</tr>
<tr>
<td>T5. 100% TF / 0% FF</td>
<td>0.524</td>
</tr>
</tbody>
</table>

The apparent densities of the plywood panels were between the minimum (0.476 g/cm³) and average (0.552 g/cm³) densities required by the Brazilian Association of Mechanically Processed Timber (ABIMCI 2007) for five-layer *Pinus* sp. Commercial plywood panels.

All density values were between a minimum of 0.516 g/cm³ and an average of 0.565 g/cm³ for panels produced from pine wood, as required for five-layer, 9 mm thick panels by standard NBR 31:000.05 001/2 of the Brazilian Association of Technical Standards (ABNT 2001).

#### Water absorption

The relationship between the percentage of tannin adhesive used and the water absorption of the plywood after 24 h of immersion (WA 24h) yielded a significant quadratic regression (Fig. 1). Mixing the adhesives promoted an increase in the water absorption. The treatments with 100% phenol formaldehyde (PF) and 100% barbatimão
absorbed less water than the treatments with mixtures of the tannin adhesive and phenol formaldehyde.

Silva et al. (2012) produced plywood with layers of Pinus taeda using PF adhesive and a tannin adhesive from Pinus oocarpa var. oocarpa. The adhesives were applied at a grammage of 320 g/m². The authors determined that the water absorbance values after 24 h of immersion were 107.6 and 63.8% for panels with 100% PF adhesive and 100% pine tannic adhesive, respectively. Thus, the average values obtained in this work were lower for both adhesives than those obtained by Silva et al. (2012).

![Graph](image)

**Fig. 1.** Water absorption of plywood after 24 h of immersion in water; *:significant at 5% level

**Thickness swelling**

The association of the tannic adhesive with the phenol-formaldehyde adhesive did not yield significant thickness swelling (Fig. 2).

![Graph](image)

**Fig. 2.** Thickness swelling values of plywood after 24 h of immersion in water

The average water absorption and thickness swelling values for the plywood treated with 100% barbatimão tannic adhesive were lower than those of the panels treated with phenol-formaldehyde adhesive.

Almeida et al. (2004) produced plywood with five 2 mm thick layers. The authors used wood from a clone of a Eucalyptus grandis x E. urophylla hybrid and urea-
formaldehyde adhesive applied at a grammage of 360 g/m². The authors determined 24-h thickness swelling values of 7.0 and 7.3% following 8 and 12 min pressing times, respectively.

Silva et al. (2012) produced plywood with three 2 mm thick layers of *Pinus taeda* with a tannin adhesive derived from *Pinus oocarpa* var. *oocarpa*. The adhesive was applied at a grammage of 320 g/m². ATS value of 8.7% was observed.

Overall, the PF and TA adhesives and mixtures had average 24-h TS values lower than those reported in other literature.

**Mechanical Properties of Plywood Panels**

*Shear strength on the glue line*

There was no significant relationship between the shear strength and the degree of substitution of the tannic adhesive (Fig. 3).

![Graph showing shear strength values](image_url)

**Fig. 3.** Average shear strength values of dry plywood panels

A cubic regression provided a significant fit for the shear test results after 24 h of water immersion. The shear strength decreased initially then increased with increasing substitution of the barbatimão adhesive. The panels produced with 100% tannic adhesive had lower values than those of the other treatments, as shown in Fig. 4.

![Graph showing predicted and observed shear strength values](image_url)

**Fig. 4.** Shear strength of plywood after 24 h of immersion in water; *: significant at 5% level
Hoong et al. (2009) tested the dry and wet shear strengths of plywood panels produced with *Canarium* spp. wood. An adhesive grammage of 300 g/m² (double line) was used with three different adhesive formulations. The three formulations used were pure PF adhesive, 90% *Acacia mangium* derived tannic adhesive (TA) and the balance PF, and a mixture of 10:80:10 parts PF:TA:LPF, respectively. The LPF is a phenolic adhesive with low molecular mass. Their dry shear strength test results ranged from 2.22 to 1.86 MPa and their wet shear strength test results ranged from 2.16 to 1.77 MPa.

Hoong et al. (2011) produced three-layer Memisang (*Annonaceae* spp.) plywood with an adhesive grammage of 250 g/m² (double line). The adhesives used were PF and an *Acacia mangium* derived tannic adhesive with 7% added paraformaldehyde (dry basis). The pressing cycle took place at 130°C, at a pressure 15 kg/cm², for 4 min. The authors reported values of 2.29 and 2.03 MPa for the dry shear strength and wet shear strength ratios of 1:14 and 1:32 MPa for the PF adhesive and the tannic adhesive, respectively.

The results of all treatments in this study were consistent with data reported in other literature, in that all values were greater than 1 MPa. This is the minimum required by the European standard EN 314-2 (1993).

**Moduli of rupture and static bending**

There was no significant relationship between the degree of substitution of the phenolic adhesive and the MOR // or the MOR ⊥ (Fig. 5).

![Graph showing modulus of rupture parallel and perpendicular to static bending](image-url)

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**Moubarik et al. (2009)** produced five-layer pine plywood with both commercial PF adhesive and a mixture of corn starch, quebracho tannins, and PF (15:5:80). The adhesives were applied at a grammage of 225 g/m² (single line). The authors found MOR values of 41 and 70 MPa for the pure adhesive (PF) and the mixture, respectively.

**Iwakiri et al. (2012)** produced plywood from *Pinus caribaea* and varieties *caribaea* (Pcc), *hondurensis* (Pch), and *bahamensis* (Pcb) using phenol-formaldehyde adhesive applied at a grammage of 380 g/m² (double line). The authors determined values of 61.0 (Pcc), 75.2 (Pch), and 84.1 MPa (Pcb) for MOR // and average values of 34.9 (Pcc), 33.2 (Pch), and 34.6 MPa (Pcb) for MOR ⊥.

Generally speaking, the average values for MOR // and ⊥ obtained for all treatments in this study were consistent with those obtained in other literature.
treatments met the requirements of standard NBR 31:000.05-001/2 (ABNT 2001), in which the requirements are 30.9 MPa for MOR // and 14 MPa for MOR ⊥.

Increasing the amount of tannic adhesive in the mixture significantly reduced the MOE ⊥ of the panels. Treatments with a mixture of adhesives yielded the lowest MOE ⊥ values (Fig. 6).

![Graph showing MOE ⊥ observed and estimated](image)

**Fig. 6.** Modulus of perpendicular elasticity of the plywood panels

Figure 7 shows the average values of the parallel elastic modulus (MOE //). No significant relationship between the amount of tannic adhesive added and the MOE // was observed.

![Graph showing MOE // observed and estimated](image)

**Fig. 7.** Modulus of parallel elasticity of the plywood

Moubarik *et al.* (2010b) evaluated the mechanical properties of five-layer, pine plywood panels joined with commercial PF adhesive and tannin-cornstarch adhesive. The authors obtained MOE values of 3122 and 3310 MPa for the PF adhesive and the tannic adhesive, respectively.

Iwakiri *et al.* (2009) produced five-layer *Pinus oocarpa* plywood. The five 2-mm layers were joined using phenol-formaldehyde adhesive applied at a grammage of 360 g/m². The authors obtained an MOE // value of 5195 MPa.
Moubarik et al. (2009) produced plywood panels with a commercial PF adhesive and a mixture of corn starch, quebracho tannins, and PF (15:5:80) at an applied grammage of 225 g/m² (single line). They obtained MOE values of 2958 and 4271 MPa for the pure adhesive (PF) and the mixture, respectively. Thus, the values for the MOE⊥ and //rigidity obtained in this study were near or above those reported in other literature. All treatments met the minimum MOE⊥ required (1485 MPa), as per standard NBR 31:000.05-001/2 (ABNT 2001). Despite having similar or superior values to those reported in other literature, the MOE// did not meet the minimum requirement of 5223 MPa set by the standard, except in those panels made with pure phenol-formaldehyde adhesive.

CONCLUSIONS

1. There is potential for the use of barbatimão tannins in plywood panel production, possibly without any phenol-formaldehyde adhesive. The tannin barbatimão adhesive tested in this study proved feasible for use in plywood panels destined for both humid and dry environments.

2. The substitution of phenol-formaldehyde adhesive with barbatimão tannin adhesive during plywood production had a significant effect on the water absorption, wet shear strength, and modulus of perpendicular elasticity. The highest water absorption values and lowest modulus of perpendicular elasticity values were found in the panels made with mixtures of the adhesives.

3. The panels produced with 25, 50, 75, and 100% added barbatimão tannic adhesive did not meet standard NBR 31:000.05-001/2 (ABNT 2001) because their modulus of parallel elasticity values did not satisfy the requirements.

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