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Preliminary Studies on the Selection of Uruguayan Woods for the Production of Transparent Wood †

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Abstract: Transparent or translucent wood has garnered significant attention in recent years. In this preliminary work, the best delignification conditions for two wood species grown in Uruguay, *Pinus taeda* and *Eucalyptus bosistoana*, were determined. It was analyzed to determine which species is more suitable for the process. The effects of temperature and $NaCl_2$ concentration during delignification were the focus; delignified wood was impregnated with epoxy resin. Wood anatomy was observed with SEM and FTIR spectra were analyzed. The results suggest that the best delignification conditions were a reaction time of 300 min, a $NaClO_2$ concentration of 3.5% at a constant temperature of 80 °C, and bleaching with H_2O_2 for one hour at 80 °C. Both wood species are suitable for the development of transparent wood.

Keywords: wood modification; delignification; epoxy resin; *Eucalyptus bosistoana*; *Pinus taeda*

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1. Introduction

Construction is a main contributor to the social and economic development of any country. However, the long life cycle of the buildings involves potential economic losses and has a great impact on the environment. Energy consumption is huge during the whole cycle: the extraction of raw materials, their transportation, the use of them on the buildings and their modifications, and finally in their demolition. For this reason, cutting-edge sustainable technologies in the area of construction are being promoted to move towards meeting the UN Sustainable Development Goals. According to FAO [1], wood-based alternative products, such as those of wood engineering, are ever more used, as they can replace those based on fossil fuels [2,3]. Wood's physical–mechanical properties, anisotropy, and anatomical and ultra molecular structure make this renewable material of sustainable production an excellent candidate for modification and combination with other materials in the pursuit of new developments, one of which is transparent wood [4–6].

Transparent wood has garnered a lot of attention in the last few years for its high optical transmittance, high safety, light weight, excellent mechanical robustness and low thermal conductivity, which make it an energy-efficient material for construction and other applications [4,5].

Anisotropy, the presence of light absorbing chemical groups, and the complex structure of the wood make it opaque. To turn it transparent, it needs to be chemically bleached, a process by which the compounds which absorb or scatter light in the visible spectrum are removed. These, such as lignin and all of its associated chromogenic compounds (such as polyphenols and tannins, among others) are responsible for the characteristic brown

color. The most commonly used products in this stage are sodium chlorite, $NaClO_2$, or the mixture of sodium hydroxide, NaOH, and sodium thiosulfate, $Na_2S_2O_3$, along with peracetic acid [6–9].

After bleaching, a polymer must be included in the structure of the delignified wood to achieve new properties, which will depend on the incorporated polymer, and which determine the final application of the obtained material. If a monomer with high transmittance and a refractive index similar to that of cellulose and its surroundings (n = 1.56 [4]) is added, high optical transparency is achieved. This property allows light to pass through a material without observable scattering [7] meaning the material has a uniform refractive index. Commonly used resins include polymethyl methacrylate (PMMA) [10], epoxy resin [11], or compounds such as polyvinyl alcohol (PVA) [12], polyvinyl pyrrolidone (PVP), and polyester resin with MEKP catalyst (methyl ethyl ketone peroxide) [13].

Delignification of the wood must be controlled to reduce the degradation of the cell wall as much as possible [14]. At the delignification stage the integrity of polysaccharides must be preserved so that the native cell morphology is not altered by the treatment. The choice of wood species is vital to the whole process. In this preliminary work, the behavior of two wood species grown in Uruguay was compared: *Pinus taeda*, a low-density coniferous species with low extractive content, and *Eucalyptus bosistoana*, a hardwood species with high density and high extractive content. The best delignification conditions for both wood species were determined, and their overall suitability for the process was analyzed and compared. The results will be scaled up in a future phase, as life-cycle analysis of the product suggests that scaling up to an industrial level has less environmental impact than laboratory-scale production and according to the literature, it is favorable from an ecological perspective [15].

2. Materials and Methods

2.1. Wood Samples

A total of 240 samples of dimensions (50.0 mm × 50.0 mm × 3.0 mm) ± 0.5 mm were cut from *Pinus taeda* and *Eucalyptus bosistoana* wood (120 of each). *E. bosistoana* trees were chosen from a multispecies shelterbelt located in the Bernardo Rosengurtt Experimental Station of the Faculty of Agronomy of Universidad de la República (32°21′26″ S, 54°26′34″ W, Cerro Largo, Uruguay). *P. taeda* trees were chosen from a plantation in the same station. Half the samples were cut crosswise, and the other half lengthwise (tangentially). The basic density was calculated based on the weight and volume of each species. The samples were oven dried at 103 ± 2 °C for 24 h and kept in a desiccator. Based on bibliographical references [16,17] and setting up tests, the temperature was set at 80 °C, while $NaClO_2$ was chosen as the main bleaching agent as it is highly efficient in reproducible concentrations.

2.2. Delignification Process

A 2^3 factorial design was carried out. Three independent variables were studied at two levels: the concentration of $NaClO_2$ (from Sigma-Aldrich, Saint Louis, MO, USA), at 2% and 3.5%; the delignification time, at 180 and 300 min; and the cutting plane of the sample, lengthwise and crosswise. The temperature was maintained at 80 °C. Table 1 shows the experimental conditions of the delignification tests.

Six samples of the same species, three cut lengthwise and three crosswise, were placed in 250 mL bohemian glasses. A measure of 100 mL of $NaClO_2$ was added to each glass, which was then heated on a heating iron without stirring for the times laid out in the experimental design. The tests were performed twice. The response variable was the qualitative observation of the samples, looking out for discoloration and degradation.

Table 1. Experimental conditions of the delignification tests on *P. taeda* and *E. bosistoana* samples according to the experimental design.

Test Number	Cutting Plane	$NaClO_2$ (%)	Time (min)
1	Lengthwise	3.5	180
2	Crosswise	2	300
3	Crosswise	2	180
4	Lengthwise	3.5	300
5	Crosswise	3.5	180
6	Lengthwise	2	300
7	Lengthwise	2	180
8	Crosswise	3.5	300

After delignification, half the samples were bleached for a second time with a H_2O_2 solution for 60 min at 80 °C. All samples were washed with deionized water and stored in absolute ethanol until impregnated. Absolute ethanol removes residual water and improves the penetrability of the wood.

2.3. Impregnation Process

Impregnation was carried out in an acrylic desiccator, connected to a vacuum pump and a pipe to let the resin in. Inside the desiccator, the samples were placed in glass lids. The resin flowed through the pipe to the lids. Firstly, the effect of the level of vacuum on the delignified wood was analyzed, so that it was neither so excessive that it would make the wood collapse, nor so insufficient the resin would not get inside the wood.

Once the samples were placed inside, the desiccator vacuum was set at −70 kPa and maintained for 20 min. The vacuum allows the resin, with their respective accelerators, to seep through the microstructure of the wood; 5-min cycles of vacuum-atmospheric pressure were repeated twice. The epoxy resin EpoKukdo YD 128, a liquid-type standard resin derived from Bisphenos A, was used. The curing agent was DOCURE KH-816, a modified cycloaliphatic amine. The samples were kept immersed for 2 min and then removed from the resin, placed between glass, and placed in an oven at 45 °C for 48 h to curate the resin.

2.4. SEM Analysis

SEM analysis was performed with a JEOL JCM-6000 PLUS (Jeol USA, Peabody, MA, USA) scanning electron microscope in high vacuum mode with an accelerating voltage of 10 kV and SE detector.

2.5. FTIR Analysis

Fourier-transform infrared spectroscopy (FTIR) was performed with an IR Prestige-21 Shimadzu spectrometer (Kyoto, Japan), working at a 5 cm^{-1} resolution and running 32 scans per sample.

3. Results and Discussion

Density is a very important characteristic of wood which determines its physical and mechanical properties. It depends on many factors: age, growth site, and environmental conditions, among others. Density is influenced by the wood's anatomy, affecting the final product [18]. The total lignin content of the wood, its location in the cell wall (middle lamella–secondary wall), the syringyl/guaiacyl (S/G) unit ratio, and the corresponding degree of condensed linkages between units [19], are factors that, in turn, determine how easily the lignin can be removed without damaging the remaining cellulose matrix. These factors also vary with species. Hardwoods have a lignin content ranging from 20% to 25%, consisting of S and G units, while conifers have a lignin content ranging from 26% to 32%, mainly composed of G units [18,19].

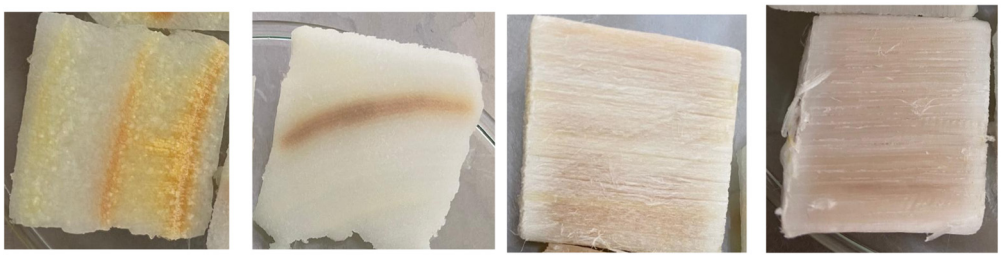
Results show that the basic density of *Eucalyptus bosistoana* was 0.826 g/cm^3, double that of *Pinus taeda* at 0.41 g/cm^3. The removal of the lignin and chromophoric compounds affects cellulose and hemicellulose, which can make the structure of the wood so frail it collapses. This is especially critical for species of low density such as *P. taeda*. However, under the same reaction conditions, *P. taeda* yielded better results because its lower density improves the diffusion of the reagent inside its structure and the removal of chromophore compounds.

Hence, for the same reaction time, less reagent was needed for *P. taeda*. The time required for total delignification was 300 min for both species; in the case of *P. taeda*, the wood weakened but did not collapse. In the future, partial delignification [7] for a shorter time (between 180 and 300 min) will be considered. Partially delignified *P. taeda* retains its distinct growth rings, which many authors describe as "aesthetic transparent wood" [3].

Some authors have identified time as a key factor in how it interacts with different wood species. For instance, balsa [17] and poplar [20] wood have shown improved results when delignified with $NaClO_2$ for longer reaction times (6 and 24 h, respectively).

The better performance of the crosswise-cut samples in both species can be explained by the increased availability of empty spaces for diffusion. Another critical factor observed was the importance of maintaining homogeneous wood width. Any spot that is wider, even by a few millimeters, will delignify slower and produce darker areas.

To further enhance the appearance of the wood, some samples were bleached for a second time with H_2O_2, which improves the final product without damaging the wood. Figure 1 shows delignified samples after bleaching with H_2O_2.



(**a**) (**b**)

Figure 1. Samples bleached with H_2O_2 after delignification: (**a**) *P. taeda* and (**b**) *E. bosistoana.*

Once a cellulose-rich white template was obtained, the empty spaces left by the removed lignin allowed resin to penetrate the polymer matrix. The results depended on the level of vacuum applied and the even distribution of resin throughout the structure. Polyester resin was discarded in favor of epoxy resin, which distributed more easily throughout the wood. Samples cut crosswise impregnated better than those cut lengthwise, indicating that resin primarily spread through the lumens, as supported by the literature.

3.1. SEM Analysis

Figure 2 shows the wood appearance after delignification with 3.5% $NaClO_2$ for 300 min for *P. taeda* (a, b) and *E. bosistoana* (c, d). Crosswise-cut *P. taeda* shows enlarged and deformed cell lumens and a thinned cell wall due to the loss of its structural polymers. Delignification did not significantly damage the structure of eucalyptus' cell wall. After impregnation, the epoxy resin occupies both the empty cellular lumens and the cell wall with a heterogeneous distribution (Figure 2e,f). As with Pinus wood, the epoxy resin distributes heterogeneously both in the lumens and the walls.

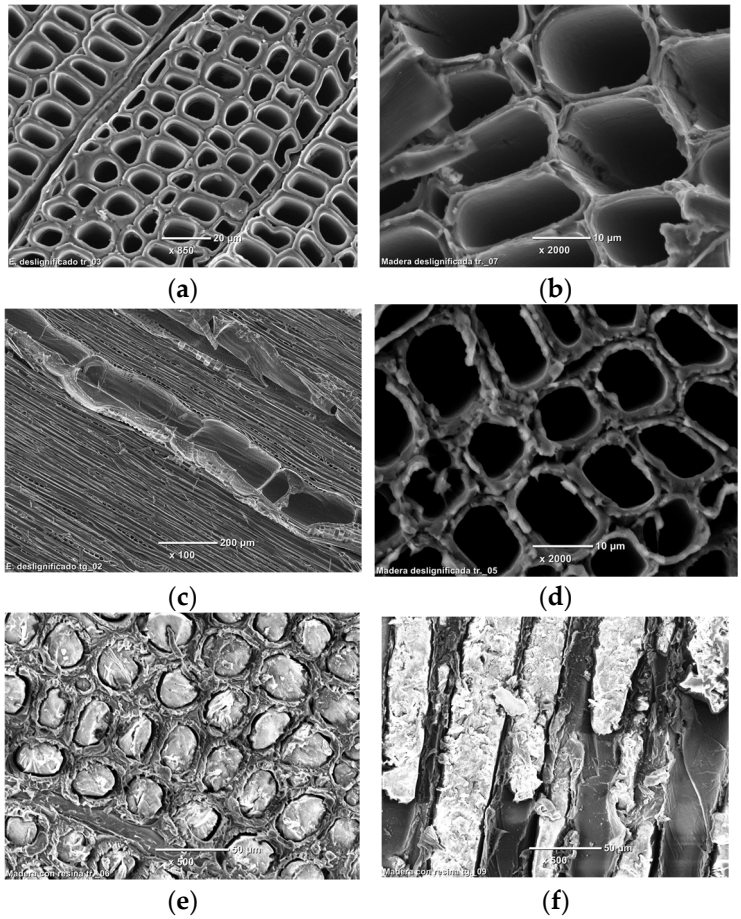


Figure 2. Cut wood: (**a**) cut crosswise normal pine wood, (**b**) cut crosswise delignified pine wood, (**c**) cut lengthwise delignifiedeucalyptus wood, (**d**) cut crosswise delignified eucalyptus wood, (**e**) cut crosswise pine wood impregnated with epoxy resin, (**f**) cut lengthwise eucalyptus wood impregnated with epoxy resin.

3.2. FTIR Analysis

The absorption peaks characteristic of natural wood and those of the delignified and later impregnated wood were compared by FTIR analysis. Delignification can be analyzed not only through the loss of lignin itself but on the damage to the structural carbohydrates.

In accordance with the literature [14,17,21], the considered absorption peaks were the following: 3417 cm^{-1} assigned to the vibrational narrowing of the O-H bond in cellulose, 2920 cm^{-1} assigned to the vibrational narrowing of the C-H bond, 1735 cm^{-1} assigned to the acetyl site of the hemicellulose, 1504 cm^{-1} assigned to vibrational narrowing of the aromatic skeleton of lignin, and 1165 cm^{-1} assigned to C-O-C vibrational tapping of cellulose.

In *E. bosistoana*, the absorption peaks at 3417 cm^{-1} and 1165 cm^{-1} corresponding to cellulose decrease sharply with a longer reaction time or a higher $NaClO_2$ concentration. This means that increasing both factors degrade cellulose. This happens regardless of the cut, although the tangential cut seems to be more sensitive to changes in time or concentration, as suggested by the sharper decrease in the peaks at 1765 cm^{-1} assigned to hemicellulose and 1504 cm^{-1} assigned to lignin; the fluids diffuse through empty spaces rather than through the cell walls. Figure 3 shows the comparison of FTIR graphics.

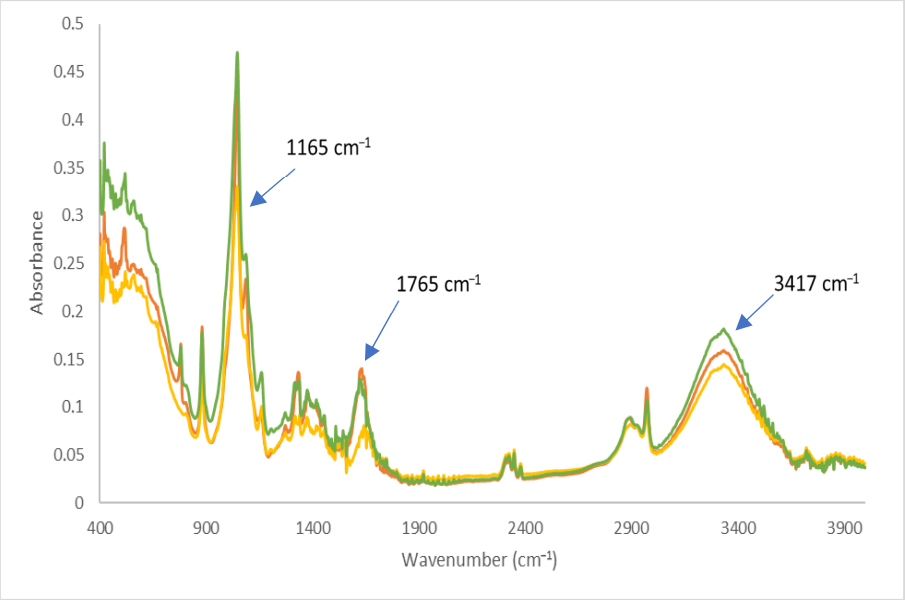


Figure 3. FTIR graphic for tangential cut of E. *bosistoana*: green line is 180 min, 2% $NaClO_2$; red line is 180 min, 3.5% $NaClO_2$; orange line 300 min, 3.5% $NaClO_2$.

In the case of lengthwise-cut *P. taeda*, the intensity of the peaks does not respond to changes in time or concentration. Cut crosswise, it is more sensitive to changes in reaction time.

4. Conclusions

Both wood species grown in Uruguay are suitable for the development of transparent or translucent wood.

The best delignification conditions were a reaction time of 300 min, and a $NaClO_2$ concentration of 3.5% at a constant temperature of 80 °C. A second round of bleaching with H_2O_2 for one hour at 80 °C improves the results.

Delignification conditions turned out to be the most consequential factor. Wood density has no impact on the process. A higher extractive content may increase the consumption of reactive chemicals during the process.

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