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Comparative Study of Carbon Nanotubes and Lignosulfonate as Polyvinyl Acetate (PVAc) Wood Adhesive-Reinforcing Agents

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Abstract: This study aimed to reinforce a polyvinyl acetate-D3 (PVAc-D3) adhesive to improve its mechanical and thermal properties. The goal was to reach a polyvinyl acetate-D4 (PVAc-D4) adhesive performance that could make PVAc-D3 more attractive and add value to wood products. PVAc-D3 was modified by adding 0.05% and 0.5% (wt.) of multi-walled carbon nanotube particles (MWCNTs) as well as 0.5% and 2.5% (wt.) of lignosulfonate (LIGNO) particles. Adhesive blends were compared to neat PVAc-D3 and PVAc-D4, evaluating their physical–chemical properties. Also, they were analyzed using Fourier transform infrared spectroscopy (FT-IR) and mechanical dynamic analysis (DMA) with a storage module (E'). The blends were used to fabricate laminated wood pieces, pressed at 60 and 120 min (min), to be tested at shear strength under dry, elevated temperature and vacuum-pressure conditions. Delamination and adhesive penetration were determined by microscopy. Incorporating fillers into PVAc resulted in a decrease in viscosity. FT-IR evidenced that the PVAc-D4 adhesive had a bigger cross-linked degree than the other adhesive samples. The DMA showed that LIGNO and MWCNT fillers help increase E' at the bond line, reaching a higher stiffness level than neat PVAc-D3. In dry conditions, specimens glued with D3-LIGNO 0.5% at 120 min reached shear strengths that were 100%, 28%, and 3% higher than the standard requirement, PVAc-D4, and neat PVAc-D3, respectively. Also, those glued with D3-MWNTC 0.05% reached shear strengths that were 91%, 21%, and 3% higher than the standard requirement, D4, and neat D3, respectively. Only PVAc-D4 reached the standard requirement for elevated temperature and vacuum-pressure conditions. Delamination of $\leq$5% (standard requirement) was achieved by wood specimens glued with neat PVAc-D3, D3-MWNTC 0.5%, D3-LIGNO 0.5%, and PVAc D4 adhesive samples. In this study, it was found specific ranges of average penetration (AP) to ensure a glue line good quality. To conclude, LIGNO and MWCNT particles improved the PVAc-D3 adhesive's performance in dry conditions, but they were not very relevant to the D3 adhesive's behavior. At high temperatures, the LIGNO filler worked very well as a thermic stabilizer compared to the MWCNT filler. The solubility of the reinforcing agent can affect an adhesive's blend quality and its cohesion properties. An adequate penetration depth procures a good quality bond between an adhesive and substrate with less possibilities of delamination. An extensive pressing time may cause a weak interphase and poor mechanical properties in an adhesive bond in the presence of humidity.

Keywords: polyvinyl acetate wood adhesive; lignosulfonate; multi-walled carbon nanotubes (MWCNTs); thermal and mechanical properties

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1. Introduction

Polyvinyl acetate (PVAc) is a non-toxic wood adhesive alternative. It has several advantages, including a colorless gluing line, flexibility, water solubility, and a relatively low cost, among others [1]. However, its thermoplastic nature with a linear amorphous structure make it poorly resistant to temperature and relative humidity changes, which can affect the adhesive bond quality [2]. Therefore, its drawbacks include low high-temperature performance with a Tg close to 30 °C and weak hydrogen links, which are very susceptible to water and temperature [3]. Also, due to its poor thermal stability, with a heat presence, this adhesive can yield because of a continuous load effect over time [4,5].

There are different categories of PVAc depending on its application. In the wood adhesive market, it is possible to find D1, D2, D3, and D4 PVAc types, which improve in performance as the "D number" increases. PVAc-D1 is an indoor adhesive with low moisture content resistance (15% maximum); PVA-D2 is also an indoor adhesive that is able to withstand exposure to short moisture periods (18% maximum); the PVAc-D3 adhesive has a better performance against moisture than D1 and D2, and it can be used for outdoor applications but should not be directly exposed to weathering; D4 is on top of PVAc adhesives, and even though it is designed for indoor applications, it has high moisture resistance compared to the other categories due to its cross-linked degree [6], making it able to endure inclement weather under specific conditions [7,8].

Considering that PVAc is an adhesive oriented to manufacture engineering wood products (such as edge-glued panels (EGPs) formed by clear wood pieces jointed on its length and laterally with an adhesive), to conform a solid wood board [7], as well as in wooden molding and furniture, among other applications [9,10], the idea of modifying PVAc-D3 to have a similar behavior as the PVAc-D4 adhesive is the beginning of technologic development that promotes a PVAc performance improvement through a non-toxic reinforcement, which can be very attractive, especially to the wood manufacturing industry, because this modification could make a big economic difference. As reference information, PVAc-D4 may cost between 10% and 15% more than PVAc-D3, so obtaining an improved and more convenient D3 adhesive with similar characteristics to PVAc-D4 could add value to wood products. Several efforts have been carried out to reinforce PVAc adhesives to improve their thermal and mechanical properties using organic and inorganic fillers [1,11–14].

In this preliminary study, two reinforcing agents were chosen. Knowing that certain companies in the wood adhesive sector are interested in evaluating high-performance carbon-based reinforcing agents on the nanometric scale, and considering this scale makes it possible to work with small amounts to improve the materials' properties, PVAc reinforced with MWCNT particles was evaluated. Although it is an expensive compound, the fact that it could generate significant improvements in PVAc-D3 adhesives would allow us to assess if it is convenient or not in its application. For this reason, we also worked with lignosulfonate, which is much cheaper than MWCNTs but equally attractive as a reinforcing agent.

Multi-walled carbon nanotubes are based on graphene nanoplates, and they have the same physical and chemical compositions [15]. Their notable qualities include a special dimension, extraordinary mechanical strength, and physical properties that open a wide range of applications in different fields, such as biology/medicine, superficial coating, electronic devises, energy, and environmental technology [16]. Also, they have been used to develop new materials as well as composites with specific properties [17]. Moya et al. [18] incorporated MWCNTs into urea formaldehyde (UF) and polyvinyl acetate (PVAc), using different concentrations to improve the shear strength and wood failure, and evaluated it in several kinds of tropical laminated wood. According to the study, the PVAc adhesive did not show performance enhancement after MWCNTs were added, but UF showed significant strength and wood failure improvements in all glued wood species. Zafeiropoulou et al. [19] modified epoxy adhesives using nanofillers such as MWCNTs and used graphene nanoplatelets (GNPs) to modify specific characteristics. The nanofillers were added into the epoxy adhesive, where it was established that MWCNTs at 2% wt. and GNP at 8% wt.

increased the electrical and thermal conductivity, respectively, keeping the same glue bond mechanical properties as neat epoxy resin. ÇETİN [20] reinforced a polyurethane wood adhesive using MWCNTs to obtain a better impact behavior on aluminum honeycomb sandwich composite structures. The structure was formed by a carbon fiber composite (CFRC) glued with neat polyurethane (PU) and polyurethane blended with MWCNTs at a concentration of 0.1% and 0.2% wt. Reinforced samples by MWCNTs showed the best results, reaching the highest maximum load and impact resistance values at a concentration of 0.1% MWCNT. Ciritcioglu and G. Özbay [21] also modified phenol–formaldehyde (PF) wood resin by carbon nanotubes (CNTs), at concentrations between 1% and 5% wt. PF adhesives with CNTs incorporated showed higher thermal stability and bonding strength at dry and wet conditions than neat PF adhesives.

Lignosulfonate is originated from the pulp and paper process during sulfite treatment [22], where sulfonate groups are incorporated into lignin, making it soluble in water, which is possible because of the presence of sulfonate and carboxylic groups [23]. In addition, its aromatic and aliphatic elements play a fundamental role in obtaining a good relationship between the adhesive and surface, as well as interphases, which contribute to its good behavior as a surfactant [24,25], making it an efficient dispersant agent for the manufacture of several industrial products [22].

Applying lignosulfonate application to adhesives Lignosulfonate has been applied to improve the performance of wood adhesives. Da Silva et al. [26] developed a phenol–formaldehyde (PF) adhesive, incorporating from 20% to 100% of LIGNO on it, to manufacture particleboard panels. The study showed that mechanical properties were acceptable enough until 80% of LIGNO substitution, making it an interesting alternative for new wood adhesives generation. Magina et al. [27] modified polyurethane adhesive by LIGNO, where good adhesion strength was attributed to an efficient blend homogenization and a good polymeric cross-linked network, revealing a significant cure activation energy. Hellmayr et al. [28] developed a LIGNO-based wood adhesive by enzymatic polymerization. A wood solid adhesion test showed that LIGNO-based adhesives had similar mechanical properties as polyvinyl acetate adhesive (PVAc-D3), but it was observed that wood specimens glued with LIGNO adhesives failed into the glue line, and there was no wood failure. Balea et al. [29] developed different LIGNO-based adhesives to manufacture particle board panels with the presence of some cross-linking agents. Resistance to static bending results showed that most of the wood specimens glued with LIGNO-based adhesives reached the minimum value (0.35 N/mm^2) required by European standards.

The present work aims to Improve the mechanical and thermal properties of PVAc-D3 wood adhesives, since its low performance under adverse conditions restricts its industrial applications. This preliminary study is focused on finding an efficient alternative as a reinforcing agent to extend PVAc-D3 adhesive use fields. That is why, as a first approach to find a reinforcing filler for PVAc-D3 adhesive, it was sought to achieve an equal or similar performance as PVAc-D4 to study the glue line quality against moisture, and temperature variation, using non-toxic and convenient materials.

2. Materials and Methods

2.1. Adhesive Blends Preparation

Multi-wall carbon nanotubes were acquired from the international chemical input supplier company, Sigma-Aldrich from its sales branch located in Santiago, Chile. Their characteristics include a 90% purity, diameter between 110 and 170 nm and length between 5 and 9 µm.

Lignosulfonate (sodium lignosulfonate) was obtained from Grupo Transmerquim, S.A. (GTM), which is a Latino-American chemical company with a sales branch located in Santiago, Chile. This compound is a brown powder raw material, with 98% purity, whose particles have an approximate diameter of 32 (µm). PVAc-D3 blends were prepared by adding 0.05% and 0.5% (wt.) of MWCNT as well as 0.5% and 2.5% (wt.) LIGNO into 500 g of neat D3 adhesive.

The blend preparation is detailed below: reinforcing particles were pre-blended in 150 g of PVAc-D3, being incorporated during the stirring process at room temperature (25 °C). When the total volume of particles was applied into PVAc, the pre-blend was stirred for 30 min at 600 rpm. Finally, the pre-blend was mixed, incorporating it into the PVAc total amount and keeping the stirring process for another 30 min at 600 rpm and the same temperature condition.

Specific concentrations of MWCNT and LIGNO were established considering scientific bibliography (similar scientific works), previous academic studies, and applied confidential research projects in collaboration with companies in the wood adhesives sector, which were carried out at PRODIMA-LAB, University of Bío-Bío, Concepción City, Chile.

Also, neat PVAc-D3 and PVAc-D4 adhesives were prepared for comparison patterns.

All adhesive blends, as well as neat D3 and D4 adhesives, were characterized by their physical, chemical and electrical properties.

2.2. Adhesives Samples Characterization

The adhesive samples characterization included measurement of the following: viscosity (cP) at 25 °C, [30], pH by combined electrode pH meter at 25 °C [31]; solid content (%) by mass difference [32]; electrical conductivity (mS) by a multi-parameter meter, Water Quality Meter, AZ86031 at 25 °C, located at PRODIMA-LAB, Universidad del Bío-Bío Concepción, Chile, and density (g/cm) through the pycnometer technique [33]. All measurements were performed in triplicate to obtain an average of each property.

2.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Characterization was performed using an infrared spectrophotometer (Fourier Transform Infrared spectroscopy FTIR), Perkin Elmer Model Spectrum Two, with an ATR system (Total Attenuated Reflectance), located at Centro de Investigación de Polímeros Avanzados (CIPA) Concepción, Chile. The samples were prepared and analyzed directly on a diamond prism. The analysis was performed in a range of 4000–450 cm^{-1}, resolution of 4 cm^{-1} and laser incidence of 10 replicates. This analysis allowed characterizing the main polymer functional groups.

The adhesive samples studied by this analysis were neat D3 and D4 as well as adhesive blends with the highest filler concentration corresponding to D3-MWCNT 0.5% and D3-LIGNO 2.5% with the objective of observing the filler effect over chemical structures of adhesive samples. So, 4 adhesive samples in total were analyzed.

2.4. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis was carried out using a DMA analyzer Perkin Elmer 7e located at the Laboratorio de Adhesivos y Materiales Compuestos, Universidad del Bío-Bío, Concepción, Chile. Small laminated wood specimens were prepared, to be glued with neat D3 and D4, as well as adhesive blends with the highest filler concentration corresponding to D3-MWCNT 0.5% and D3-LIGNO 2.5% to observe the filler effect over wood–adhesive glue line bond stiffness. So, 4 adhesive samples in total were tested under the three-point flexion method.

The three-point flexion method applied over the wood sample was established with a range of temperature from 25 to 250 °C; temperature rate 10 (°C/min); static force 275 (mN); dynamic force 250 (mN); frequency 1 Hz [34–36]. DMA thermal conditions were set up from room temperature to 250 °C due to the neat PVAc-D3 decomposition temperature being approximately 220 °C and considering this adhesive was modified by fillers that could eventually improve its thermal performance; the polymer decomposition range was extended up to 250 °C of temperature. This way, it was checked that all adhesive samples completed their thermal cycle.

The following specimen dimensions were used: 1.1 (mm) of height, 5 (mm) of width, and 20 (mm) of length (see Figure 1). Three replicates were tested per each adhesive sample.

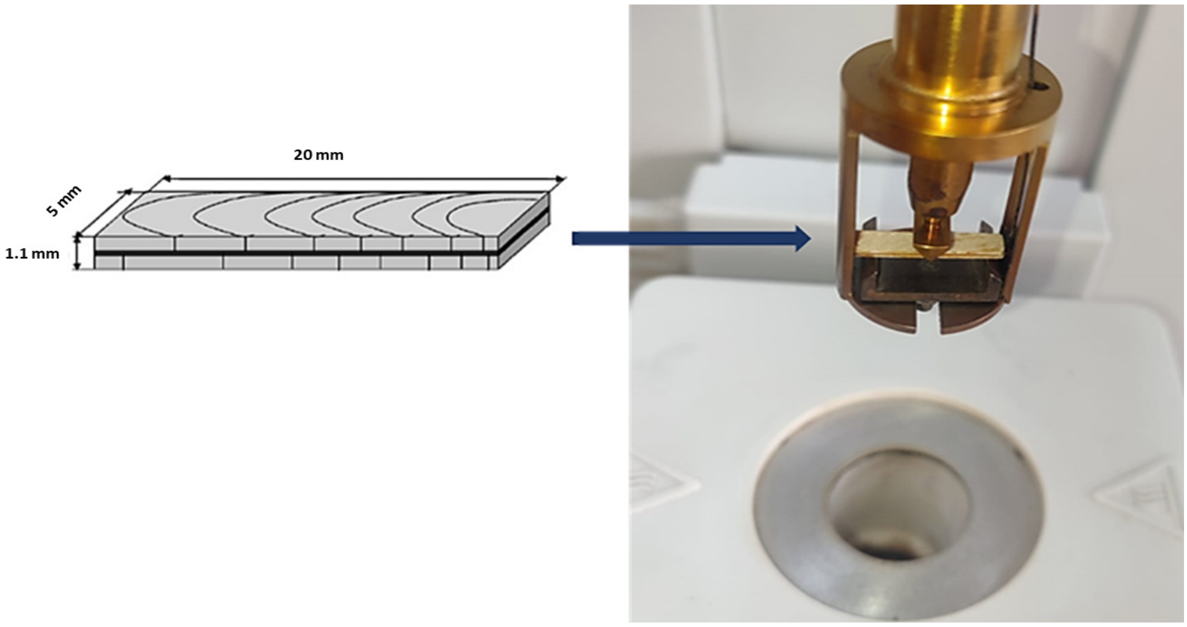


Figure 1. Specimen tested at DMA three-point flexion method.

2.5. Gluing and Wood Specimens Obtention

Once characterized, adhesive samples were used to elaborate Pine radiata glued laminated wood pieces. Wood pieces had a moisture content between 8% and 12% and a density between 470 and 545 kg/m^3.

Wood laminated specimens were elaborated by two lamellas, previously polished, having the dimensions of 19 (mm) × 100 (mm) × 450 (mm), to be glued adding 220 g/m^2 of adhesive on each wood surface with an open time of 5 min to be pressured later at 6 kg/cm^2. After being pressured, wood pieces were taken to a period of rest for 7 days under controlled conditions of temperature and humidity. After finishing this period, wood-laminated pieces were polished again on all their surfaces to reach a final dimension of 38.1 (mm) × 50.8 (mm) and 440 (mm).

For every adhesive sample, 25 glued wood laminated pieces, with a pressing time of 60 min, and others 25 at 120 min pressing time were obtained. These two pressing times were defined to observe any improvement related to bond line quality.

Every glued wood laminated piece was cut up according to Figure 2 to obtain 3 shear strength specimens, 3 microscopy specimens, and 1 delamination specimen, generating a total of 75, 75, and 25 specimens for shear strength (including dry, elevated temperature, and pressure-vacuum test) microscopy and delamination, respectively, for each pressing time. Then, 20 specimens glued with each adhesive sample were selected, considering the shear strength test at dry, elevated temperature, and vacuum-pressure conditions, with a total of 60 specimens. In the same way, 10 wood-glued specimens with each adhesive sample were selected for the delamination test. Finally, 3 wood specimens glued with each adhesive sample were selected to perform microscopy tests, reducing their sizes to cubic samples where each face had an area of 10 mm^2 to prepare later 3 wood tissue slices per specimen (see Figure 2).

Some of the remaining wood specimens were discarded and others were kept in case additional information is required. Table 1 is directly related to Figure 2; it summarizes the experimental design of glued wood cutting and specimen kinds obtained with neat and modified adhesive blends (type of filler and concentration), reporting specimens number per test type, such as shear strength (3 conditions: dry, elevated temperature, and pressure-vacuum), microscopy and delamination, which were obtained by two pressing times (60 and 120 min).

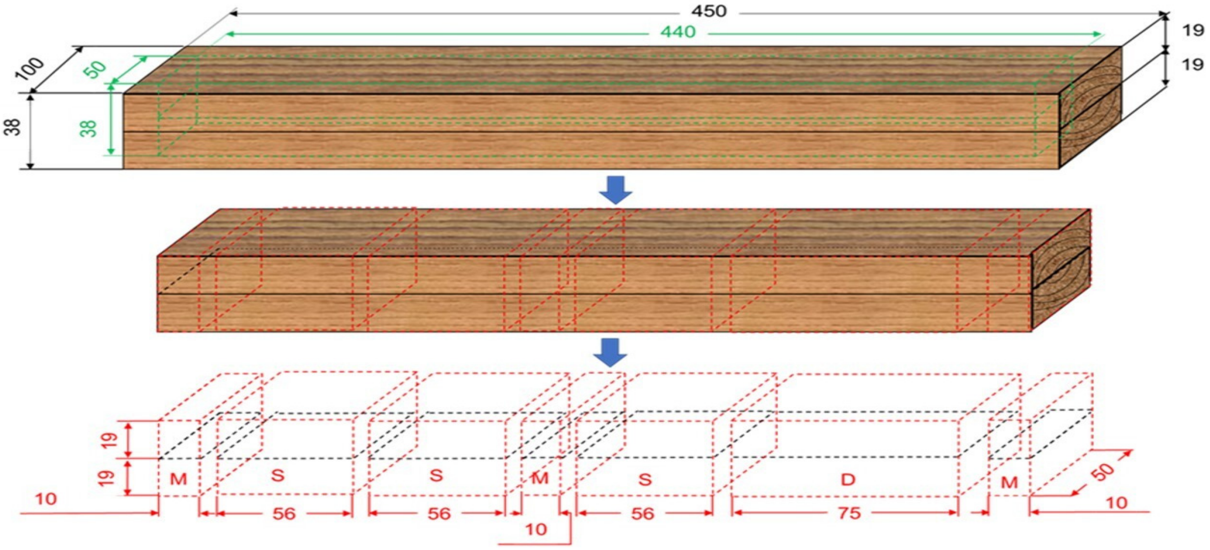


Figure 2. Wood specimens extraction scheme for shear strength, delamination, and microscopy test (dimension in millimeters). M: wood piece for microscopy test. D: wood piece for delamination test. S: wood piece for the shear strength test.

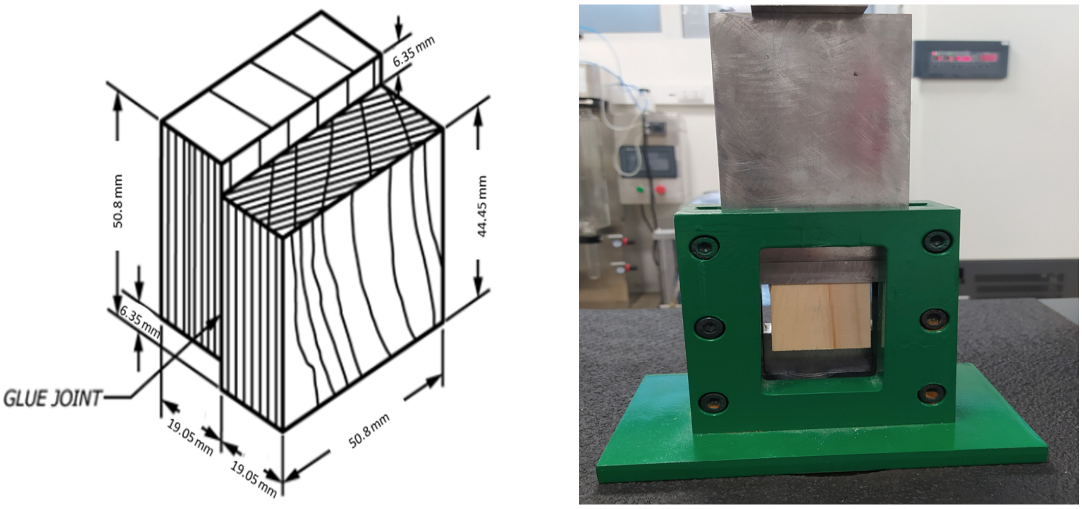
Table 1. Experimental design glued wood pieces.

Samples ID	MWCNT (%)	LIGNO (%)	Number of Specimens Tested					
			Shear Strength (3 Conditions)		Microscopy		Delamination	
			Pressing Time (min)					
			60	120	60	120	60	120
D3	-	-	60	60	3	3	10	10
D3-MWCNT	0.05	-	60	60	3	3	10	10
D3-MWCNT	0.5		60	60	3	3	10	10
D3-LIGNO	-	0.5	60	60	3	3	10	10
D3-LIGNO	-	2.5	60	60	3	3	10	10
D4	-	-	60	60	3	3	10	10

The test standard [37] considers an average (group specimens) and individual values (each specimen) of shear strength and wood failure requirement (see Figure 3). According to this standard, the requirement for radiata pine solid wood at dry, elevated temperature and vacuum-pressure test are established, as it is shown in Table 2.

Table 2. Standard requirement for shear strength and wood failure.

Condition Test	Shear Strength (MPa)		Wood Failure (%)	
	Group Specimens (Average)	Individual Each Specimen	Group Specimens (Average)	Individual Each Specimen
Dry	6.22	3.11	≥60	≥30
Elevated temperature	4.15	2.07	≥40	≥20
Vacuum-pressure	5.19	2.59	≥50	≥25



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

Figure 3. Shear strength wood specimen, for dry, elevated temperature and vacuum-pressure test. (**a**) Specimen dimensions. (**b**) Shear strength test.

2.6. Dry Test

Glued wood specimens at 12% moisture content at room temperature were evaluated by being subjected to a continuous shear loud at a rate of 0.5 in (12.8 mm)/min 610% to determine shear strength in the glue joint.

2.7. Elevated Temperature Test

Wood specimens were taken to an oven at 104 ± 3 °C for 6 h. After that period, the temperature was increased to 110 ± 3 °C for 22 min. The shear test was running at the same speed as the dry test within 30 min after the wood specimens were removed from the oven.

2.8. Vacuum-Pressure Test

Wood specimens were immersed in water at room temperature; then, a vacuum was applied at 25 Hg in (84.45 kPa) for 30 min. Finishing that period, wood samples were subjected to 75 ± 2 psi of pressure for 30 min. Specimens were tested by shear load at the same speed as the dry test. Specimens were tested in wet conditions within the next hour.

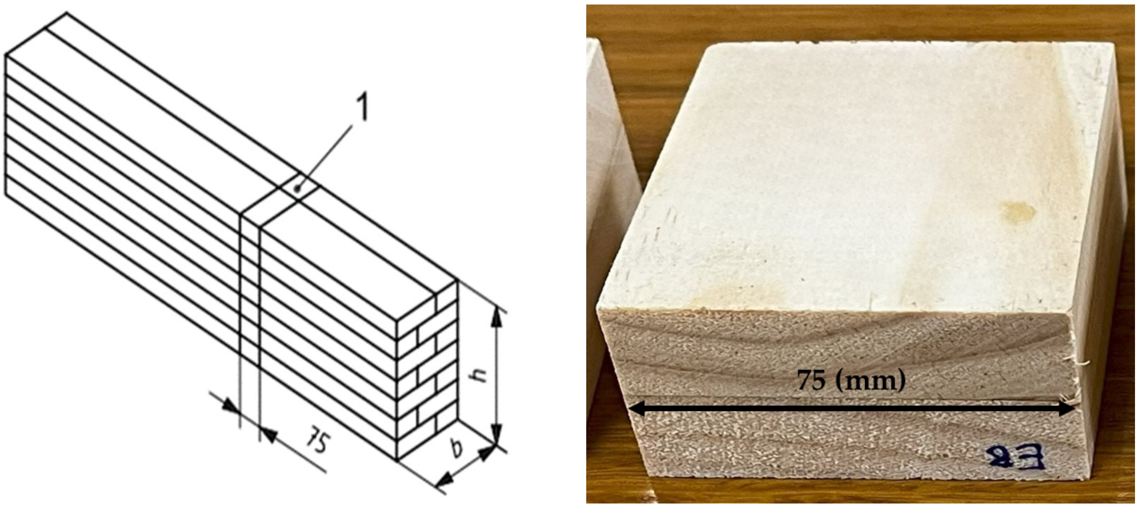
2.9. Delamination Test

The wood delamination test [38] was carried out through an accelerated aging cycle into the impregnation cylinder. The specimens were dimensioned at 75 (mm) (glue line length) × 50 (mm) × 38 (mm). Before a cycle, specimens were weighted to register the initial mass, and we determined the initial glue line length on each of its heads (see Figure 4).

This cycle is based on room temperature water immersion with a vacuum at 70 to 85 kPa for 30 min and pressure at 500 kPa for two hours. When the vacuum-pressure cycle finished, specimens were dried at 65 °C, 8% relative humidity, at 2 m/s circulating speed air, until specimens reached initial weight. The total delamination percentage was calculated on both heads of each specimen as follows (Equation (1)):

$$D = \frac{\mathrm{T_L}}{\mathrm{L}} \times 100\ (\%) \tag{1}$$

where D is delamination in %; $\mathrm{T_L}$ is the total delamination in mm, and L is the glue line length on specimen head in mm.



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

Figure 4. Delamination test. (**a**) Wood specimen according to ISO 12580 standard [38]. (**b**) Delamination line on specimen head.

2.10. Microscopy Test

A microscopy test was accomplished to study the wood–adhesive interphase. Three specimens in total were obtained from wood-laminated pieces from their extremes and center (see Figure 1). Then, every wood specimen was reduced to a cube of 10 mm^2 per face, where we took one slice with 30 to 35 µm of thickness from the transversal section by each cube over the glue line area. Finally, 3 sheets of the cross-sectional region corresponding to one laminated wood piece glued with every adhesive sample were obtained. The average values of the parameters to study were determined from these sheets for each kind of glue bond analyzed by images. A total of 150 wood tissues were studied to quantify penetration over the interphase area.

Slices were cut by using a Leica SM2000R sliding microtome with horizontal displacement located at Centro de Biotecnología, Universidad de Concepción, Concepción Chile. Later, slices were placed into a glass plate, making it easy to obtain pictures through a fluorescence Leica DM 2000 LED optical microscope, located at PRODIMA-LAB Universidad del Bío-Bío, Concepción, Chile. Every glue line slice was pictured and analyzed taking three images sections to calculate an average of interest parameters, as it is shown in Figure 5. Every picture was processed by ImageJ software 1.8.0, using a grid to calculate distances and area capture, with a similar method as Nuryawan et al. (2014) to analyze the glue line [39].

The effective penetration (EP) and average depth penetration (AP) were calculated according to Sernek et al. 1999 [40] and Qin et al. 2016 [41].

EP was obtained by calculating the total area observed adhesive penetration within the interphase region; then, that value was divided by the glue line length (*Xo*) (see Equation (2)). *AP* was calculated considering the farther area of tracheids with adhesive inside their lumens within the interphase region width (see Equation (3)).

$$EP = \sum_{i=1}^{n} Ai/Xo \tag{2}$$

where *EP* is the effective penetration depth in µm; *Ai* is the penetration adhesive areas in µm^2; and *Xo* is the length of glue line into the established area in mm.

$$AP = \sum_{i=1}^{N} Yi/N \tag{3}$$

where *AP* is the average penetration depth in µm; *Yi* is penetration from farther adhesive areas within the interphase region width in µm; and *N* is the farther total area of tracheids with adhesive inside their lumens within the interphase region width in µm.

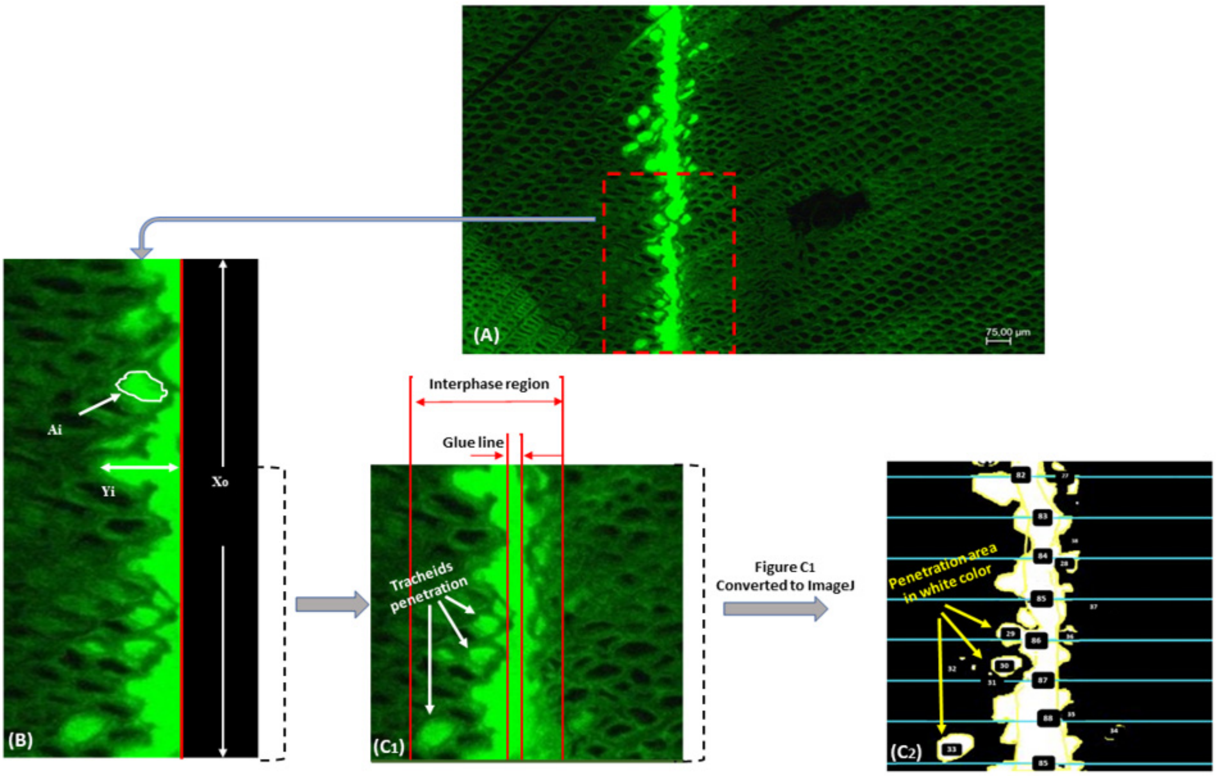


Figure 5. Image process to obtain EP and AP parameters. (**A**) Fluorescence Leica DM 2000 LED microscope picture. (**B**) Studied section. Variables definition: (*Ai*), (*Yi*), (*Xo*). (**C$_1$**) Areas of the section studied. (**C$_2$**) Image (**C$_1$**) converted by ImageJ software.

3. Results

3.1. Adhesives Characterization

Adhesive samples exhibited viscosity values between 994.67 and 3171.67 cP. The range of pH fluctuated from 2.5 to 3.3. Density varied between 1.09 and 1.12 g/cm^3. The solids content range fluctuated from 40% to 52%. Finally, electrical conductivity exhibits values between 8.12 and 12.97 mS (see Table 3).

Table 3. Adhesive samples characterization.

Samples ID	Viscosity (cP)	pH	Density (g/cm^3)	Solid (%)	Electrical Conductivity (mS)
D3	2668.33	3.2	1.10	45	8.12
D3-MWCNT 0.05%	1549.00	3.1	1.10	43	8.52
D3-MWCNT 0.5%	994.67	3.3	1.09	40	8.33
D3-LIGNO 0.5%	1486.00	2.9	1.10	44	8.37
D3-LIGNO 2.5%	1719.00	3.3	1.10	45	8.97
D4	3171.67	2.5	1.12	52	12.97

In general, PVAc-D3 and PVAc-D4 adhesives showed similar physical and chemical properties as those reported on their technical manufacturing data sheet.

The PVAc-D4 adhesive presented higher values of viscosity, total solids and electrical conductivity.

Also, the D3-MWCNT and D3-LIGNO adhesive blends showed a lower viscosity compared to the neat PVAc-D3 adhesive.

3.2. FTIR Analysis

FTIR analysis shows a first transmittance band at 3325 cm^{-1} corresponding to O-H groups associated with PVAc adhesive conformation and water presence. This peak did not exhibit an important difference among adhesive samples, except for the PVAc-D4 adhesive, with a weaker intensity in this area compared to the neat PVAc-D3 and PVAc-D3 adhesive blends.

C-H aliphatic groups ubicated between 3001 and 2851 cm^{-1} bandwidth exhibited a low vibration as was expected.

At 1734 cm^{-1}, one of the characteristic PVAc peaks appears, which represents the initial harmonic stretching vibration of ester carbonyl O–C=O chains being notorious on the PVAc-D4 spectrum. Over the 1700 to 500 cm^{-1} transmittance band, it is found in the PVAc fingerprint region, where we observed -C-O stretching, several kinds of -CH$_2$ groups vibration and also -CH groups at a bending vibration out of plane as well as a polymer chain stretching vibration. D3-MWCNT 0.5% adhesive blends and PVAc-D4 adhesive presented an intensity increase in bandwidths corresponding to the said region (see Figure 6).

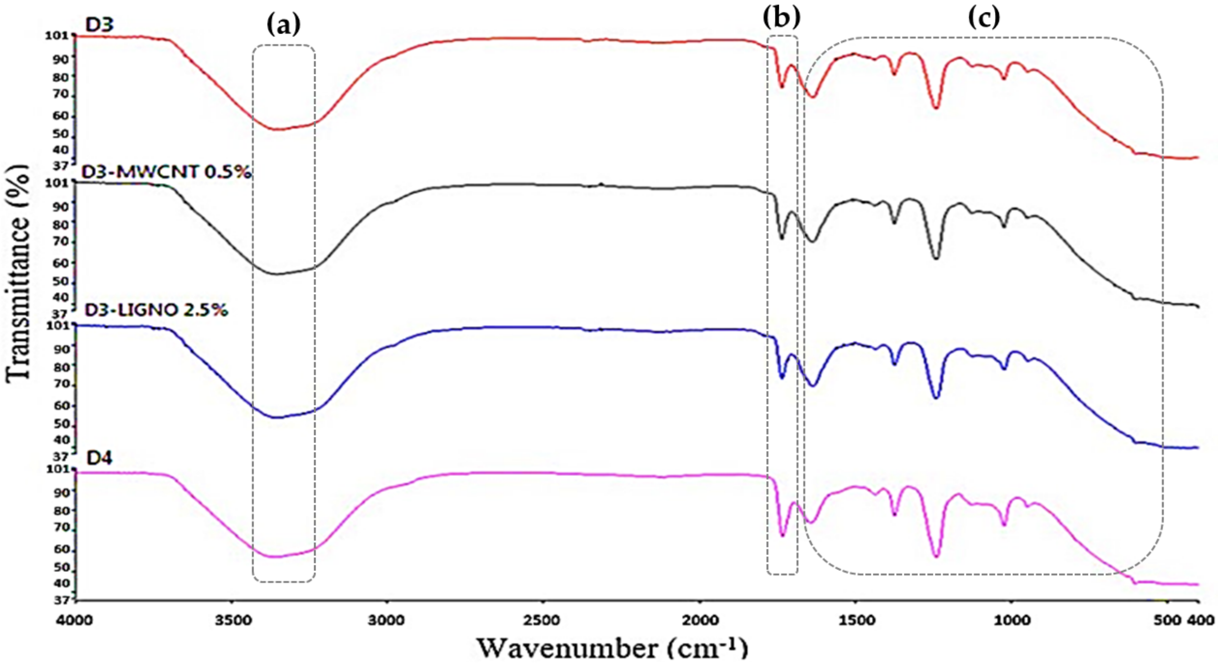


Figure 6. FTIR analysis of adhesives samples. (**a**–**c**) Bandwidth identification. (**a**) Bandwidth: 3325 cm^{-1}; (**b**) bandwidth: 1734 cm^{-1}; (**c**) bandwidth: fingerprint PVAc.

3.3. Dynamic Mechanical Analysis (DMA)

The storage modulus (E′), related to the stiffness degree of the adhesive bond, varied between 1.49×10^9 Pa and 4.43×10^9 Pa. The PVAc-D4 adhesive presented the maximum E′ value (4.43×10^9 Pa), which was followed by D3-LIGNO 2.5% (2.57×10^9 Pa) and D3-MWCNT 0.5% (2.09×10^9 Pa), where the lowest glue line stiffness value (E′) was exhibited by a neat PVAc-D3 adhesive (1.49×10^9 Pa). Results indicate that MWCNTs and LIGNO fillers work as effective reinforcement agents, increasing neat PVAc-D3 stiffness by 40% and 72%, respectively. Figure 7 graphs this statement.

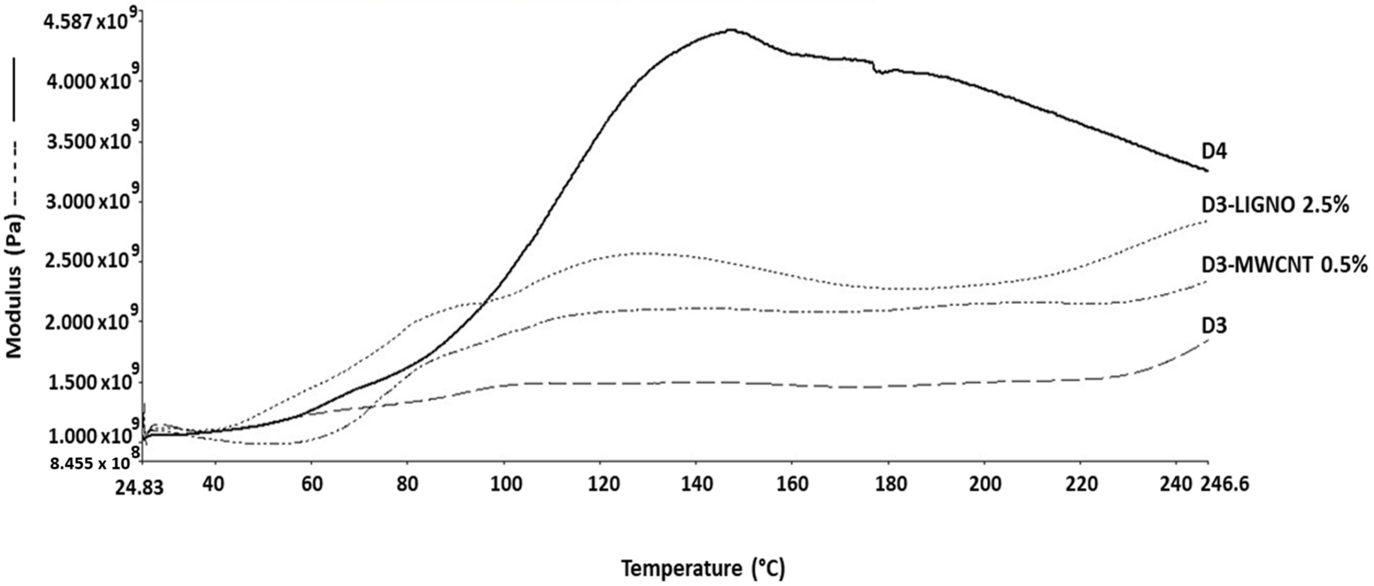
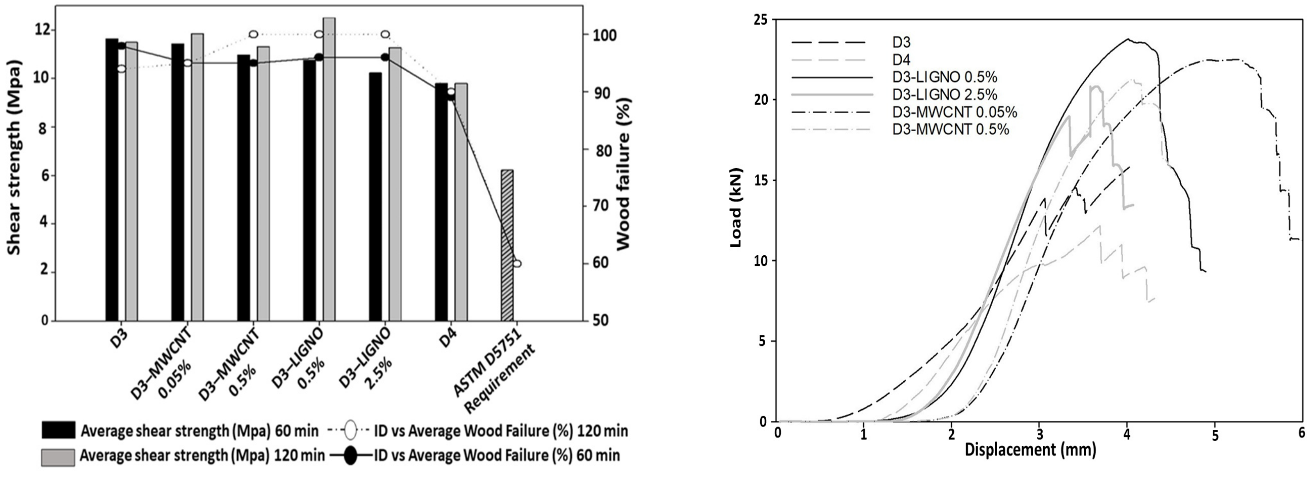


Figure 7. DMA, three-point flexion method, wood–adhesive glue line bond stiffness (E′).

3.4. Mechanical Properties Test

It was observed that all specimens bonded with D3 adhesive blends showed a good performance in dry conditions (see Figure 8). The shear strength values obtained from the dry test fluctuated between 9.8 and 12.51 MPa. In the same way, wood failure varied between 90 and 100%. This behavior was shown by pressed wood specimens at 60 min and 120 min, achieving the standard requirements.



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

Figure 8. Shear strength test at dry condition. (**a**) Average shear strength and wood failure. (**b**) Loud vs. displacement at 120 min pressing time.

According to the dry test, the average (wood specimen group evaluated) as well as single values (each specimen tested) of shear strength and wood failure reached the standard requirement.

For dry conditions, the wood specimens glued with D3-LIGNO 0.5% at 120 min of pressing time reached an average shear strength that was 100%, 28%, and 3% higher than the standard requirement, PVAc-D4 and neat PVAc-D3, respectively (see Figure 8a). On the other hand, wood specimens glued with D3-MWNTC 0.05% at the same pressing time reached an average shear strength that was 91%, 21% and 3% higher than the standard requirement, PVAc-D4 and neat PVAc-D3, respectively. Always, at 120 min pressing time, wood specimens glued with D3-MWCNT 0.5%, D3-LIGNO 0.5% and D3-LIGNO 2.5%, achieved 100% wood failure under shear load.

The load vs. displacement behavior of specimens glued with D3-MWCNT (0.05% and 0.5%) adhesive blends showed a balanced behavior between load resistance and ductility, followed by D3-LIGNO (0.5% and 2.5%), which confirms that this kind of reinforcing worked very well in dry conditions (see Figure 8b).

ANOVA data analysis complemented with the Fisher (LSD) method of minimum significant difference indicated a statistically significant difference between the shear strength of specimens glued with D3-LIGNO 0.5% at 120 min pressing time and those glued with neat D3 and D4 adhesive for both pressing times (see Table 4), which indicates that lignosulfonate could be a very good alternative to reinforcing the D3 adhesive.

Table 4. Average shear strength and wood failure of specimens glued with adhesive samples.

ID SAMPLES	Dry Test		Elevated Temperature Test		Vacuum-Pressure Test	
	Shear Strength (MPa) *	Wood Failure (%) *	Shear Strength (MPa) *	Wood Failure (%) *	Shear Strength (MPa) *	Wood Failure (%) *
D3 (1)	11.64^{ab}	98^{ab}	5.6^{ab}	5^{a}	1.53^{b}	5^{ab}
D3 (2)	11.55^{abc}	94^{abc}	3.65^{ab}	5^{a}	0.92^{ab}	0^{a}
D3-MWCNT 0.05% (1)	11.43^{abc}	95^{abc}	3.70^{ab}	10^{a}	0.83^{a}	0^{a}
D3-MWCNT 0.05% (2)	11.85^{bc}	95^{abc}	2.60^{ab}	5^{a}	0.77^{a}	25^{b}
D3-MWCNT 0.5% (1)	10.97^{abc}	95^{abc}	2.16^{a}	0^{a}	0.96^{ab}	5^{a}
D3-MWCNT 0.5% (2)	11.32^{abc}	100^{b}	3.14^{ab}	5^{a}	1.13^{abc}	20^{bc}
D3-LIGNO 0.5% (1)	10.76^{abc}	96^{abc}	7.83^{b}	19^{b}	1.39^{bc}	1^{a}
D3-LIGNO 0.5% (2)	12.51^{b}	100^{b}	6.26^{b}	7^{a}	1.11^{abc}	0^{a}
D3-LIGNO 2.5% (1)	10.24^{ab}	96^{abc}	6.44^{bc}	3^{a}	1.11^{abc}	0^{a}
D3-LIGNO 2.5% (2)	11.28^{abc}	100^{b}	5.39^{bc}	1^{a}	0.93^{ab}	0^{a}
D4 (1)	9.80^{a}	89^{a}	5.81^{bc}	50^{b}	5.48^{b}	70^{c}
D4 (2)	9.80^{a}	90^{ab}	4.06^{bc}	20^{b}	4.98^{b}	45^{c}

(1) 60 min pressing time; (2) 120 min pressing time. *: averages. Super index letters reflect significant differences according to LSD test with confidence interval of 95% (there are not statistically significant differences among levels that share the same column). Software Statgraphics Centurion XVII 19-X 64.

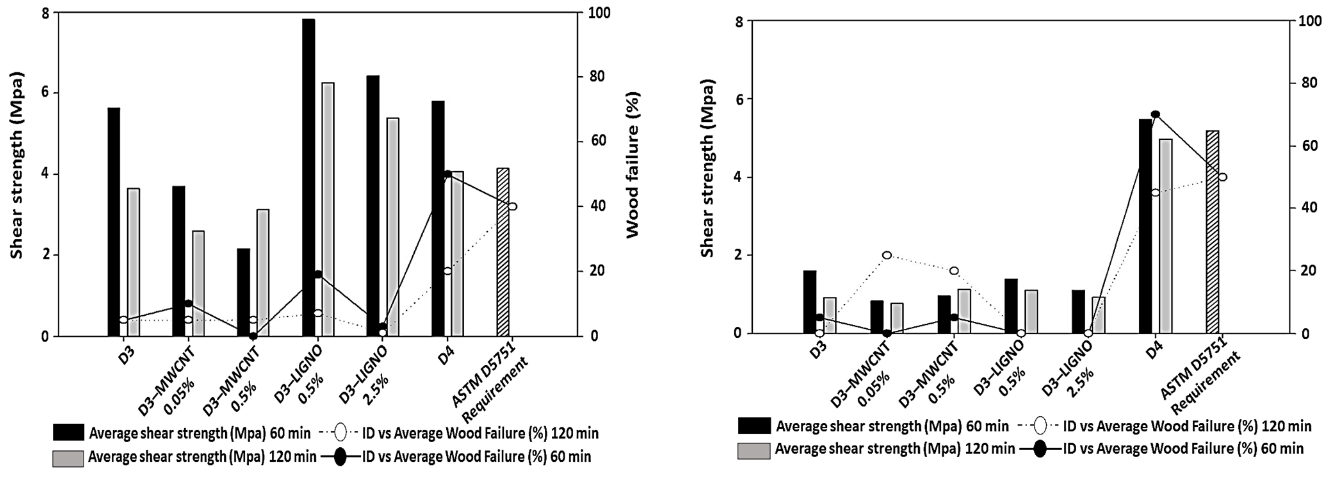
The values of shear strength obtained from an elevated temperature test fluctuated between 2.16 and 7.83 MPa. Specimens glued with the neat D3 adhesive and D3-MWCNT (0.05% and 0.5%) adhesive blends, pressed at 60 min and 120 min, did not reach the standard average shear strength value, and neither did the individual one. Likewise, for the average and individual wood failure values, specimens glued with neat D3 and D3-MWCNT (0.05% and 0.5%) at 60 min and 120 min pressing times did not achieve standard requirements.

Specimens glued with D3-LIGNO (0.5% and 2.5%) reached the highest values of average shear strength for the elevated temperature test with an even better result than D4 adhesive at 60 min of pressing time, achieving the standard request. Specifically, D3-LIGNO 0.5% reached an average shear strength of 89%, 40%, and 35% higher than a standard requirement, neat PVAc-D3 and PVAc-D4 adhesives, respectively.

As shown in Table 4, the shear strength values of specimens glued with D3-LIGNO 0.5% and D3-MWCNT 0.5% at 60 min of pressing time presented statistically significant differences, confirming that D3-LIGNO blends, for this condition, have a better performance than D3-MWCNT blends.

The average wood failure values were not very concordant with shear strength, varying between 0% and 50%. Specimens glued with D3-LIGNO blends showed quite good performance at shear strength in group (average) and individual ways. However, these specimens did not obtain the average and individual wood failure standard requirements.

Finally, the average shear strength values obtained from the vacuum-pressure test of wood specimens fluctuated between 0.77 and 5.48 MPa, and average wood failure varied from 0% to 70%. The vacuum-pressure test evidenced that only wood specimens glued with the D4 adhesive at 60 min of pressing time reached average and individual shear strength standard requirements. Specimens glued with the other adhesive blends showed similar average and individual shear strength values, all of them under the standard requirement limit. The same phenomenon was observed for average and individual wood failure values (see Figure 9).



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

Figure 9. Shear strength test at temperature and humid conditions. (**a**) Average shear strength and wood failure. Elevated temperature test. (**b**) Average shear strength and wood failure. Vacuum-pressure test.

At vacuum-pressure conditions, it is clear that the D4 adhesive presented a superior behavior of the overall adhesive samples for shear strength and wood failure, especially at 60 min of pressing time, which was corroborated by statistical analysis (see Table 4).

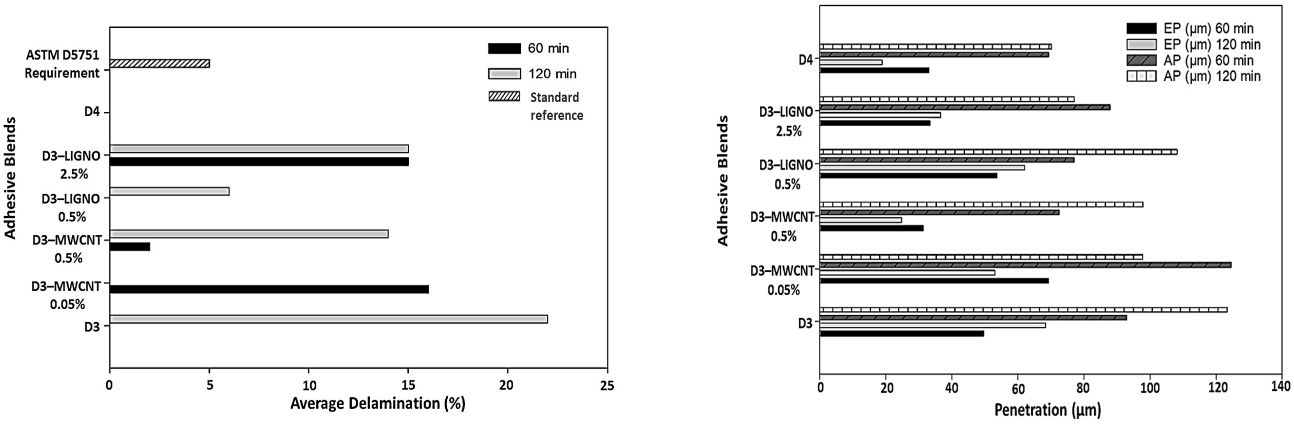
Mechanical resistance tests evidenced that wood specimens pressed at 120 min showed a bond line performance lower than those pressed at 60 min. Only in the dry condition did the specimens pressed at 120 min reach shear strength values and wood failure higher than those pressed at 60 min.

3.5. Delamination Test and Microscopy

Delamination values obtained from specimens glued with the neat D3 adhesive, D3 adhesive blends, and D4 adhesive fluctuated between 0% and 22%, where neat D3 at 60 min of pressing time, D3-MWCNT 0.05% and 0.5% at 120 min and 60 min pressing time, respectively, as well as D3-LIGNO 0.5% at 60 min pressing time, D4 at 60 min and 120 min pressing time, reached delamination $\leq$ 5% as is required by the Standard reference [38]. It must be noted that wood specimens glued with PVAc-D3 MWCNT blends for both pressing times showed a better response under humid conditions than those glued with PVAc-D3 LIGNO blends.

The D4 adhesive exhibited the best behavior under this condition, without any delamination evidence, which is concordant with the shear strength result. In general, most of the wood specimens pressed at 60 min time showed less delamination than those pressed at 120 min, obtaining values smaller than 5% (see Figure 10a).

The effective penetration (EP) values of adhesive samples fluctuated between 31 and 69 µm for wood glued and pressed at 60 (min), D3-MWCNT 0.05% being the blend that obtained the highest value (see Figure 10b). At the pressing time of 120 (min), we observed a range of EP between 19 and 68 µm, where the highest PE value was achieved by the neat D3 adhesive. None of these two adhesive samples showed a remarkable shear strength or delamination performance. However, an interesting phenomenon was detected in this study, which was related to a certain range of penetration depth, where for example, a high penetration does not mean necessarily less delamination. Indeed, the average penetration (AP) for pressing times at 60 min and 120 min reached values of 70–77 µm and 93–98 µm of depth, respectively, which included adhesives samples such as neat D3, D3-NTC 0.5%, D3-LIGNO 0.5% and D4, which exhibited percentages delamination values under the 5% (standard limit) in most of the cases. On the contrary, depth values higher than 98 µm did not reach the delamination value standard.



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

Figure 10. Adhesive bond line quality. (**a**) Delamination test. (**b**) Penetration. Microscopy study.

4. Discussion

Adhesive characterization indicated that the PVAc-D4 adhesive presented the highest value of viscosity, total solids, and electrical conductivity. Clearly, this was because of its specific use and method of cure. It is important to mention that wood products bonded with D4 adhesive, most of the time, are pressed using radiofrequency technology, which accelerates cured and production times. Therefore, electrical conductivity is a quite relevant property for adhesives cured under this technique [42,43].

On the other hand, it is observed that D3 adhesive blends modified by the fillers MWCNT and LIGNO particles, applied in different concentrations, showed a lower viscosity compared to the neat D3 adhesive. This effect can be attributed to the filler condition, which means that the interlinkage between the particles and adhesive is not totally efficient [44], since the particles' presence in a polymeric matrix may drop the flow friction decreasing viscosity [45].

In general, fillers to reinforce PVAc tend to reduce blend viscosity. The particle size and filler geometry influence must be considered as well as their chemical effect within the system. The filler chemical effect drastically influences the blend viscosity even more than geometry, since water-insoluble fillers form isolated particle structures within the blend without interacting with matrix polymeric chains. This decreases the blend viscosity, being even more evident at higher filler concentrations, which would explain why the PVAc-MWCNT 0.5% blend presented a lower viscosity compared to PVAc-MWCNT 0.05%.

Instead and under the same logic, water-soluble fillers also form isolated groups of particles, but some of them do interact with the polymer chains matrix, which is favored by a higher filler concentration. The above could explain why the PVAc-LIGNO 2.5% blend presented a higher viscosity than D3-LIGNO 0.5%.

FTIR analysis evidenced the first transmittance peak at 3325 cm^{-1} (O-H groups), which was very similar among neat D3, D3-MWCNT 0.5%, and D3-LIGNO 2.5%; only the D4 adhesive showed a lower intensity than other samples at that bandwidth. This can be related to D4 polymer morphology, since commercial PVAc-D4 has incorporated a hardener agent to increase cross-linked points, which means its structure presents fewer free groups available, within them OH groups, than a regular thermoplastic adhesive [46]. On the other hand, the D3-MWCNT 0.5% adhesive blend exhibited a slightly bigger intensity at 1734 cm^{-1} transmittance than neat D3 and D3-LIGNO 2.5%, which could be a consequence of the abundant C-C links originated by the presence of MWCNT particles [47]. However, the D4 adhesive showed the biggest intensity at this transmittance band, observing a strong stretching vibration of ester carbonyl C=O groups.

From 1700 to 500 cm^{-1}, the D4 adhesive was the only sample that exhibited an intensity increase on its fingerprint transmittance zone, which could be mainly attributed to a generous presence of C-C, C-O, C-H links and CH_2 groups, confirming that the D4 adhesive has a higher cross-linked degree than D3 blends, vibrating in different ways (rocking, wiggling and twisting), at the same time [48].

The lack of vibrational signal from D3 adhesive blends could be related to the small amounts of fillers used as reinforcement into PVAc D3, generating weak vibrations of bandwidth.

DMA analysis aimed to observe the stiffness degree of the adhesive bond on the wood substrate and the effect of temperature on it. This phenomenon can be studied by the storage module (E′), which is evaluated through the transition from fluid to solidification of the adhesive in intimate interaction with wood. Then, E′ is associated with the material elastic component and is defined as its storage energy, which is equivalent to the elasticity modulus or Young's modulus (E) in elastic material studies. [49].

Considering the maximum storage modulus (E′) of the wood–adhesive glue line bond, for PVAc-D3 adhesive blends, D3-LIGNO 2.5% could have achieved the highest stiffness degree due to its composition. As a derivative of lignin, lignosulfonate is a polyphenolic compound with important volumes of available hydroxyl groups, which can form hydrogen bonds with matrices rich in OH groups [50], such as PVAc, working very well as a cross-linking agent. This could have caused D3-LIGNO 2.5% to have the highest stiffness value (E′) among the PVAc-D3 samples at the solid glue line.

It is well known that lignin and its derivatives are capable of acting as cross-linking agents, replacing phenol in phenol–formaldehyde resins with good results, since their high volume of aliphatic and phenolic hydroxyl groups favors their reactivity and reticular structure when interacting with some kind of adhesive [51].

In the same way, the adhesive–wood bond with D3-MWCNT 0.5% in the solid state indicated that the carbon nanotubes can stiffen the glue line with a lower concentration than PVAc D3-LIGNO. In this case, the solid state of the glue line was achieved because of solvent (water) loss or evaporation by temperature rise (DMA test), where PVAc-D3 adhesive fusion causes an intimate approach with carbon nanotubes, generating a composite, which in the solid final state remained embedded in the thermoplastic matrix [52].

Both reinforcing agents (LIGNO and MWCNT) presented a higher stiffness degree at the adhesive bond line than the neat PVAc-D3 adhesive, which shows that both reinforcements significantly improve its performance. However, they did not exceed the E′ value at the glue line solid state achieved by the PVAc-D4 adhesive, which is concordant with the evaluation carried out by FTIR analysis.

According to the results of the mechanical properties, LIGNO and MWCNT fillers improve PVAc-D3 performance at dry conditions. However, D3-LIGNO blends at elevated temperature conditions had a better performance than D3-MWCNT blends. This behavior could be related to the lignosulfonate thermal stability that, as a lignin-derived compound, has exhibited extraordinary thermal stabilizer properties evaluated in different thermoplastic polymers with interesting results [53–55].

Lignin is a cross-linked bio-polymer with some amorphous zones, which is formed by phenylpropane units bound to ether and carbon–carbon links. Its chemical structure based on aromatic compounds and carbon–carbon groups makes it quite thermally stable, generating considerable char remains in the combustion process [56].

It is relevant to mention that the lignosulfonate structure is formed by 0.4 to 0.7 sulfonate groups and two times methoxyl groups per unit of phenyl propane than neat lignin (mostly hydrophobic), making it soluble in water [24,57,58]. This could have an effect on adequate affinity and cohesion between lignosulfonate particles and the PVAc-D3 adhesive, as well as good particles dispersion into the adhesive matrix, causing a near interaction with the hydroxyl groups (-OH) of the wood and adhesive, which generate a strong glue bond associated with its polar condition [58]. In addition, its negative charge and alkaline pH (>9) allow a good dissociation of phenolic hydroxyl groups, increasing its structural strength. The same as lignin, lignosulfonate is formed by a cross-linked molecular structure [24], which could obtain a reinforced linear-amorphous PVAc polymer due to its various functional groups that may interact with the adhesive matrix available molecules, stiffening blends structure. Because of these reasons, specimens glued with D3-LIGNO blends at dry conditions showed close values of shear strength and wood failure to the D4 adhesive. Even though shear strength reached values very close to the D4 adhesive, D3-LIGNO blends probably did not obtain a structure cross-linked enough and as chemically stable as the D4 adhesive, yielding because of the load applied after temperature and humidity treatments [1]. This can explain the low wood failure exhibited by species glued with D3-LIGNO blends at elevated temperature and vacuum-pressure conditions, where failure happens in the adhesive itself and not over the substrate.

This study considered carbon nanotube particles as an interesting option to improve the mechanical properties of the PVAc-D3 adhesive. Due to its nanometric scale which increases its specific surface, is possible to use small amounts and obtain excellent results, making it an attractive resource as a reinforcing agent. Taking advantage of its high strength, carbon nanotube particles have been used to reinforce different kinds of materials [16]. Its stiffness, for example, can reach 1250 GPa, outperforming high-strength steel which can obtain 200 GPa, where its hexagonal structure formed by carbon–carbon links is the cause of its outstanding mechanical performance [15]. However, it must be considered that carbon nanotube particles are used as fillers to improve the thermal properties of the polymeric matrix because they have excellent thermal conductivity [59], working very well as a heat dissipater in integrated electronic circuits [60,61]. Then, in an elevated temperature test (104 ± 3 °C), MWCNT particles could have transmitted heat all over the adhesive matrix, making it flow because of high temperature, losing stiffness and mechanical strength. It has been reported that PVAc adhesive bond strength can be affected by temperatures over 70 °C [6]. Also, it is important to indicate the hydrophobic nature of carbon nanotube particles, which make its appropriate dispersion into a polymeric matrix difficult [62]. The lack of hydroxyl groups (-OH) on its superficial structure does not allow homogeneous distribution and effective miscibility with polar polymeric matrices, such as the PVAc adhesive [18]. In other words, the MWCNT structure is constituted by pure carbon, presenting high Van der Waals traction forces causing particles agglutination, hindering their dispersion and homogeneous distribution in aqueous or organic systems. This limits carbon nanotubes use, reducing their application potential [63]. Surface modification can correct the solubility lack, ensuring they can interact intimately with different types of molecules [64]. In this sense, the functionalization technique enables functional groups formation on the carbon nanotubes surface, restricting Van der Waals traction forces; this causes a greater intermolecular approach between carbon nanotubes and the polymeric matrix or solvent (according to the case), which leads to an efficient dispersion and good solubilization of them. Carbon nanotube functionalization promotes improvements in: reactivity, solubility, chemical modification (adsorption), metal deposition, and grafting, among others [63]. Chemical oxidation, for example, generates the appearance of functional groups, such as carboxylic acids, amines, amides, and covalent aryl radicals (diazonium chemistry) [65].

Therefore, considering that the MWCNTs used in this study were applied without any previous functionalization treatment, it is quite probable that its dispersion and solubilization into the PVAc matrix were unable to reach satisfactory results, obtaining as a consequence a low cohesion adhesive blend, poor adhesive–substrate interphase, as well as a weak glue bond at high-temperature conditions and in the presence of water.

Another relevant factor to consider is the adhesive samples' viscosity degree. The viscosity of PVAc-D3 blends was lower than that of neat PVAc-D3 and PVAc-D4 adhesives, which could have influenced the shear strength results. A low viscosity can facilitate penetration into wood, causing better adhesion between the adhesive and substrate, but also, an overpenetration can lead to a poor adhesive bond and consequently a low mechanical resistance of the glue line [66–68].

Delamination and microscopy tests indicated that a range of EP and AP values could be adequate to procure a good glue line quality, which is directly related to adhesive viscosity, as it was mentioned above. In this study, it can be established that no adhesive that penetrates deeply into wood will have a better effect of fixing or strong glue bond. The quality of the glue line bond depends on several properties such as the wood density, physical and chemical wood properties, adhesive characteristics, pressing cycle (temperature and time), and use conditions, among others [8,69].

It is important to mention that adhesive penetration must be enough, which means an overpenetration can affect negatively the glue line: this is why finding an adequate penetration range is very relevant to procure a good-quality bond between the adhesive and substrate [70].

At pressing times of 60 min and 120 min, it must be indicated that wood specimens glued with adhesive samples in dry conditions showed an expected trend, since a longer pressing time led to higher strength values. While wood failures were obtained, tests that involved high temperature and humidity (elevated temperature and vacuum-pressure conditions) did not present this pattern. At elevated temperature and vacuum-press test, all strength shear and wood failure values were smaller at 120 min pressing time than 60 min. This could be explained due to the elastic recovery of wood, which can be observed as “shape memory effect” or “spring-back”.

Even though both “shape memory” and “spring-back” effects are similar, the first one occurs when a piece of wood was already deformed (environmental factors). After a pressing period, wood can keep a new shape for a while as long as the environment stays the same as the beginning, which means dry conditions [71]. When conditions change, wood tends to recover its original shape [72]. The second one happens specifically in wood boards, generating an irreversible thickness swelling as soon as the pressure load is removed, causing strength loss in the adhesive bond [71,73].

According to the present results, elastic recovery is closer to the “shape memory effect”, which could be occurring in a directly proportional way to pressing time, where a longer pressing time is applied on wood specimens, the greater its elastic recovery and its elastic recovery is bigger, affecting negatively the glue line strength. The elastic recovery phenomenon is favored by humidity, steam water (elevated temperature test), and direct water contact (vacuum-press test). So, a more extensive pressing time may imply a higher potency of elastic recovery released, causing greater weakness in the adhesive bond [73].

This could be the reason why wood specimens glued and tested at elevated temperature and vacuum-pressure conditions showed a lower mechanical performance at 120 min pressing time than at 60 min.

5. Conclusions

The chemical effect of the reinforcing agent drastically influences the viscosity of the adhesive blends, which depends on its nature and its solubility. A filler's lack of solubility can affect the adhesive blend quality, cohesion properties, and glue line mechanical properties.

The FTIR analysis indicates that the D3-MWCNT 0.5% adhesive blend showed a small intensity increase at 1734 cm^{-1} transmittance because of the presence of MWCNT particles. Also, the PVAc-D4 adhesive evidenced a marked intensity on the fingerprint zone, indicating a higher cross-linked degree than other adhesive samples.

DMA analysis indicated that LIGNO and MWCNT fillers help to increase the E' value at the wood–PVAc adhesive bond line, working better than neat PVAc-D3, showing that both reinforcements significantly improve their performance.

The dry condition wood specimens glued with D3-LIGNO 0.5% at 120 min of pressing time reached a higher average shear strength than the standard requirement, PVAc-D4 and neat PVAc-D3 adhesives. However, this improvement was quite significant, according to the standard requirement and D4 adhesive performance, but it was not very relevant, concerning the D3 adhesive behavior.

Specimens glued with D3-MWCNT (0.05% and 0.5%) adhesive blends showed a balanced behavior between load resistance and ductility in dry conditions.

Also, specimens glued with D3-LIGNO 0.5%, at 60 min of pressing time, under elevated temperature conditions achieved an average shear strength higher than the standard requirement, neat PVAc-D3 and PVAc-D4 adhesives.

LIGNO and MWCNT particles improved the PVAc-D3 adhesive performance in dry conditions. At high temperatures, the LIGNO filler worked very well as a thermic stabilizer, being a promising alternative as a PVAc adhesive-reinforcing agent.

For future works, we will consider tests using functionalized MWCNTs, which could improve significantly these filler performances at elevated temperatures and vacuum-pressure conditions, into a water-soluble polymeric matrix, such as PVAc leading to a water-soluble polymeric matrix, as seen with PVAc.

The D4 adhesive presented the best performance at the delamination test, which was followed by neat D3 at 60 min pressing time, D3-MWCNT (0.05% and 0.5%) at 120 min and 60 min pressing time, respectively, as well as D3-LIGNO 0.5% at 60 min pressing time and the D4 adhesive at 60 min and 120 min pressing time.

In general, for the delamination cycle, the wood specimens glued with PVAc-D3 MWCNT blends for both pressing times showed better performance than those glued with PVAc-D3 LIGNO blends at humid conditions.

The average penetration (AP) at 60 min and 120 min pressing times suggests that the optimal adhesive depth range is 70–77 µm and 93–98 µm, respectively, to procure a good-quality bond between the adhesive and substrate with delamination $\leq$5%.

The wood elastic recovery or "shape memory effect", produced by a long pressing time, can affect negatively the glue line strength, because a more extensive pressing time may imply a higher release of elastic recovery potency in the presence of humidity, causing a weak interphase and an adhesive bond with poor mechanical properties.

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