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Renewable Tannin-Based Adhesive from Quebracho Extract and Furfural for Particleboards

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Abstract: With increasing concerns about the production of sustainable materials, the field of wood-based materials still offers a critical challenge. Indeed, a close dependence on petroleum derivatives is still required, involving high consumption of non-renewable and toxic chemicals in the assembly of wooden parts. Herein, the aim of this research was to evaluate the potentiality of an entirely renewable tannin-based adhesive for particleboard production. Industrial quebracho (*Schinopsis balansae*) tannin powder was selected as a raw material and analyzed in terms of polyphenols, polysaccharides, and the total condensed amount. Furfural was proposed as a bio-sourced hardener to establish crosslinking between the flavonoid units and hence produce a resin. This formulation was analyzed in terms of viscosity and curing time and then applied to laboratory-scale single-layer particleboard production. The density, mechanical properties, and thickness swelling of the panels were investigated at different glue ratios and pressing conditions. It was observed that time has a higher impact than temperature on the internal bond, and panels pressed at 160 °C for a longer pressing time (>7 min) performed better than the boards obtained at a higher temperature. The registered values at 160 °C for 11 min of pressing of internal bond (0.37 MPa) and modulus of elasticity (1417 MPa) met the required standards for P1 panels according to European norms EN 312 (2010). Conversely, the modulus of rupture (4.9 MPa) did not satisfy the requirements suggesting the need for the use of additive or post-treatments. Considering the results achieved, quebracho–furfural adhesives are an interesting base for bio-based adhesive formulations.

Keywords: engineered wood products; condensed tannin; polyphenols; sustainable; eco-friendly; bio-materials

Citation: Cesprini, E.; Causin, V.; De Iseppi, A.; Zanetti, M.; Marangon, M.; Barbu, M.C.; Tondi, G. Renewable Tannin-Based Adhesive from Quebracho Extract and Furfural for Particleboards. *Forests* **2022**, *13*, 1781. https://doi.org/10.3390/f13111781

Academic Editor: Diego Elustondo

Received: 30 September 2022
Accepted: 25 October 2022
Published: 27 October 2022

1. Introduction

The world wood composites market has been increasing over the last decades without registering any drops until 2010, and recording a production of 420.3 million m^3 in 2017 [1]. Furthermore, since wood products enhance the carbon sink forest capacity by increasing the time that CO_2 is kept out of the atmosphere, a further increase in the wood product market to around 658.1 million m^3 by 2027 is foreseen [2]. In order to lead this large market to be more sustainable, new challenges for faster curing and lower formaldehyde emissions adhesives, as well as the inclusion of recycled material in the boards, have already been proposed [1,3–5]. However, engineered wood products heavily depend upon large amounts of synthetic derivates during the assembly process (~50 million tons of adhesives), despite

academia and industry making strong research efforts to get sustainable alternatives in recent decades [6–8]. Despite their environmental and human health threats, formaldehyde-based resins still dominate the wood adhesives markets (~95%) due to their excellent bonding performance and contained costs [9,10]. Nevertheless, the future scarcity of oil derivates and the related price increase, together with the increased concern for the environment by governments, continue to drive research toward more competitive green solutions. Within the wood-based material market, particleboard production accounts for half of the European wood product demand [11], covering a large share of adhesive consumption.

Before the rapid growth in the 1950s of synthetic derivatives, several bioresources were exploited, including polysaccharides, which are now re-purposed through implementations or modifications. For instance, Ningsi et al. extracted chitin from shrimp shells and converted it to chitosan, applying it as raw material for particleboard adhesives. The mechanical properties of these panels satisfied the requirements for the P2 panel type [12]. Starch extracted from palm oil was crosslinked with epichlorohydrin and applied to gluing rubberwood particleboards. In addition, in this study, the mechanical properties satisfied the standards for dry state requirements [13]. Among renewable resources, proteins of both animal and plant origin provided good potentialities, and several studies pointed to the revaluation of protein-based adhesives [14–16]. In particular, soy was deeply investigated and proposed for particleboards meeting the P2 requirements [17–19].

Moreover, similar results were obtained for formaldehyde-free adhesives consisting of soy flour, polyethyleneimine, and maleic anhydride, which were investigated for three-layer particleboard [20]. Due to the relevant protein and carbohydrate requests from the food and medicine sectors, the market is looking for non-food alternatives in order to avoid ethical conflicts. In this context, lignin plays a key role due to its great abundance and its polyphenolic nature [21,22]. Chen et al. [23] and El Mansouri et al. [24], for instance, exploited modified lignin for particleboard manufacturing, obtaining boards respecting the EN 312 (2010) for P2 requirements. In addition, magnesium sulfonate lignin added with a low amount of isocyanate was applied to obtain stable formaldehyde-free boards [25]. In order to limit the use of hazardous substances such as isocyanates as much as possible, appealing alternatives are proposed by exploiting the polyphenolic character of lignin. Thus, strong urethane bonds are proposed without the use of isocyanates [26]. Even though intensive lignin valorization research is ongoing [27,28], some drawbacks still limit industrial applications due to its high heterogeneity and low reactivity and solubility [29,30].

These disadvantages of lignin do not frequently occur for polyphenolic tannins, which are the fourth most abundant biomass-extracted compounds right after cellulose, hemicellulose, and lignin [31]. Thus, as natural substitutes for synthetic resins, they are one of the most attractive candidates [32,33]. As in the case of lignin, new lines of research focus on the creation of urethane bonds without using toxic reagents and report promising results [34]. The copolymerization of tannin and urea-formaldehyde showed improved properties of particleboards, increasing the moisture resistance and decreasing the formaldehyde emissions [35]. Several types of hardeners have been proposed for tannin crosslinking [36,37], but a limited part of these formulations was investigated for particleboard production. Indeed, the major scientific works reported the combination of condensed tannins with formaldehyde and hexamine [38]. For instance, Anris et al. [39] and Valenzuela et al. [40] highlighted the good stability of tannin-hexamine formulation for fiber- and particleboard production. Alternative aldehydes, such as glyoxal, were proposed to replace formaldehyde, categorized as carcinogenic. Tannin-glyoxal resins reached an internal bond above 0.4 MPa [41]. In order to increase the sustainability of adhesive formulations, the use of bio-renewable hardeners is a viable path. Luckeneder et al. proposed furfuryl alcohol as a furanic derivate to produce engineered wood products, achieving the standard limit for P2 panel classification [42].

In the present study, the potential for an entirely renewable tannin-based resin to be used as an adhesive alternative to formaldehyde-based resins for the production of particleboards was assessed. The tannin-furfural formulation proposed in this study was

recently applied to plywood manufacturing with encouraging results [43] and hence here tested for the fabrication of particleboards. Furfural, belonging to the furan compounds and produced through the acid hydrolysis of biomass [44], is selected as a formaldehyde alternative. Industrial quebracho tannin extract was analyzed in terms of total polyphenols, condensed tannins, and polysaccharides contents and subsequently employed for adhesive formulations. The resin was characterized using gel time and viscosity tests, while the particleboards glued with the tannin-furfural resin were investigated for their physical properties in function of the processing parameters.

2. Materials and Methods

2.1. Materials

Quebracho tannin extract (Fintan 737B) was supplied by the company Silvateam (S. Michele Mondovì, Cuneo, Italy), and furfural (99%) was provided by International Furan Chemical IFC (Rotterdam, The Netherlands). Sodium hydroxide was purchased by Alfa Aesar (Thermo Fisher, Waltham, MA, USA). High purity (≥99%) ethanol, sodium carbonate, sulfuric acid, sodium acetate trihydrate, acetic acid, 2,4,5-tripyridyl-s-triazine, HCl, ferric chloride, ammonium formate, pectin, and dextran were purchased from Sigma-Aldrich (St. Louis, MO, USA). Folin-Ciocalteu's phenol reagent and vanillin were purchased from Merck (Darmstadt, Germany). Finally, the entirely recycled mixed wood species particles for industrial particleboard productions were provided by Fantoni spa (Osoppo, Udine, Italy).

2.2. Characterization of the Quebracho Extract

100 mg of tannin powder was dissolved in 5 mL of EtOH/ H_2O (80/20) and left under mechanical stirring for 30 min at 25 °C. The sample was then centrifuged for 15 min at 4 °C and 10,000 rpm to remove the insoluble fraction. The obtained extract was employed in the quantification of total polyphenols and condensed tannins.

The determination of total phenolic content (TPC) was performed using the Folin-Ciocalteu assay [45]. Briefly, 1 mL of diluted tannin extract, 1 mL of Folin reagent (diluted 1:10 with deionized water), and 0.8 mL of sodium carbonate solution at 7.5% were mixed. The solution was left in the dark at 40 °C for 30 min before the absorbance at 765 nm was measured. Each measurement was repeated three times. A serial dilution of gallic acid was used to create the calibration curve, and the results were expressed as μgGAE/mg.

The transformation of condensed tannins into anthocyanins using sulfuric acid and vanillin led to calculating the concentration of total condensed tannins (TCT) [46]. To sum up, 50 μL of the ethanol tannin solution was mixed with 2 mL of 4% methanol vanillin solution and 450 μL concentrated sulfuric acid. After 15 min, the absorbance was read at 527 nm, and the results were expressed as a relative ratio of equivalent catechin (μgCE/mg).

HRSEC was used for the quantification of the total polysaccharides and for the determination of their molecular weight distribution [47]. In brief, 1 mg of sample was dissolved in 1 mL of mobile phase (50 mmol/L aqueous solution ammonium formate) and sterile filtered (0.22 μm acetate cellulose filters, Millipore, Burlington, MA, USA) directly into HPLC glass vials. Then, 10 μL were injected into the chromatographic system with an Agilent 1260 series II quaternary pump LC (Agilent Technologies, Santa Clara, CA, USA) equipped with both DAD and RID detectors. Samples were kept at 4 °C before injection in a temperature-controlled auto-sampler. The separation was carried out at 20 °C with a gel permeation HPLC column (PL-Aquagel-OH 40, Agilent). The mobile phase was applied at a constant flow of 0.6 mL/min for 35 min, and the temperature of the RID cell was kept at 35 °C.

2.3. Adhesive Preparation and Characterization

Quebracho tannin water solution was prepared at 45% w/w at room temperature under vigorous mechanical agitation. Once a homogenous solution was obtained, furfural was added to the solution at 10% with respect to the solid amount of tannin. The pH of the solution was adjusted from 6.7 to 8 by sodium hydroxide addition. The gel time was measured by placing 5.0 g of adhesive solution in a test tube and exposing it to 100 °C

in a water bath. The transition from liquid to a no longer workable viscous solution was observed, and gelation times were recorded using a stopwatch [48]. The test was repeated three times. The viscosity of the solution was analyzed with a Kinexus Lab rheometer from Malvern Panalytical (Malvern, UK). A cone-shaped geometry spindle with a diameter of 4 cm was used, and the gap between the plates was set at 0.15 mm. The experiment was conducted at 25 °C with a share rate between 10 s^{-1} to 300 s^{-1}.

2.4. Particleboard Production

A laboratory plowshare mixer (ETM-WHB75m) was used to mix the wood particles with the resin mixture. In the first step, the wood chips were put into the plowshare mixer, and then the adhesive was gradually added during vigorous mixing (approx. 100 rounds/min) for 1 min. The glued chips were evenly distributed in a 32 × 32 cm mold (Figure 1a). The panels were then pressed at a density target of 650 kg·m^{-3} and a final thickness of 1 cm with a Höfer (Taiskirchen, Austria) HLOP 280 laboratory press. Three pressing times (7, 9, 11 min) and temperatures (160, 180, 200 °C) at 15% gluing on dry wood particles were selected and initially investigated according to the typical particleboard reaction conditions. Subsequently, those parameters were optimized according to the results obtained. Specifically, lower temperature (140 °C), adhesive amount (10%), and longer pressing time (13 min) were tried. Afterward, the boards were stored at 25 °C and 65% humidity (Figure 1b), cut out of the side layers, and then the samples were prepared (Figure 1c).

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

Figure 1. (**a**) Cold pre-pressed wood particles mat glued with 15% of quebracho-furfural adhesives (**b**) Particleboards with 32 × 32 × 1 cm size pressed at different glue amounts (**c**) Panel cutting section for samples manufacturing used for physical and mechanical analysis.

2.5. Particleboard Testing

The density was calculated according to EN 323:2005 [49] for samples 1–10, while the density profile was measured with a DENSE-LAB X (EWS, Hameln, Germany) for specimens 1, 4, 5, 8, 9. Furthermore, the same specimens were analyzed for internal bond (IB) according to EN 319 [50], while modulus of rupture (MOR) and modulus of elasticity (MOE) were determined according to EN 310 [51] for samples A, B, C. Finally, the specimens 2, 3, 6, 7, 10 were tested for water absorption and thickness swelling following EN 3017 [52]. SEM analysis was performed with FEI Quanta scanning electron microscopy (variable pressure environmental E/SEM) for the morphological characterization of particleboards. The instrument was equipped with a tungsten filament for electron production, SED and LFD detectors for Everhart-Thornley, and large field secondary electrons, respectively, BSED/GAD for backscattered electrons, and EDX (EDAX Element-C2B) for X-ray detection. The image acquisitions were carried out in low vacuum at 20 kV.

2.6. Statistical Analysis

Analysis of variance (ANOVA) evaluated the significance of the difference between factors and levels. The means were compared using the Tukey multi-range test to identify

which groups were significantly different at a 95% confidence level. Statistical analysis was performed using RStudio Team (2021) [53].

3. Results and Discussion

3.1. Industrial Quebracho Extract Chemical Analysis

The chemical characterization enabled us to understand the tannin composition and thus obtain suitable information for further possible optimizations for the extraction process. The total phenolic content (TPC), total condensed tannins (TCT), and polysaccharide content (PS) of the extract are reported in Table 1.

Table 1. Total phenolic content, total condensed tannins, antioxidant capacity, and polysaccharide fraction of quebracho Fintan 737 industrial tannin extract.

Extract	TPC (µg GAE/mg)	TCT (µg CE/mg)	PS (mg/L)
Quebracho	646 ± 18	304 ± 65	552 ± 103

The measured values were similar to those previously reported for mimosa tannin extract [46,54]. The nature and extraction process may affect the reactivity of the polyphenols, influencing the effectiveness of the electrophilic substitution reactions involved with aldehyde based-hardeners. For instance, the presence of impurities, such as proteins or carbohydrates, and the establishment of non-covalent interactions, such as hydrogen bonds, hydrophobic interactions, and π-π stacking, should decrease the number of free positions on the aromatic ring [55]. In this view, the quebracho extract shows a moderate polysaccharide content [54,56], registering a value of 552 mg/L. Hence, the good purity combined with a high TCT/TPC ratio (0.47) promotes the quebracho industrial extract as an attractive polyphenol resource for the production of bio-resins [57].

3.2. Adhesive Characterization

The physical parameters of the adhesive were investigated in order to determine the processability of the resin. The resistance of the tannin-based adhesives to shear stress is expressed according to the physical parameter of viscosity expressed in mPa s and reported in Figure 2. A Non-Newtonian character was observed for the tannin-water formulation at pH = 8 (red curve). Conversely, the addition of furfural involved a lower drop when the shear stress increased (black curve) and lower viscosity due to its liquid character at room temperature. It has to be considered that the theoretical solid content of the resin without furfural is lower (45.0%) than that with furfural (47.4%), but because furfural is a liquid at room temperature, the viscosity of the tannin-furfural formulation was significantly lower.

Furthermore, the reactivity of the resin was monitored using the gel time test performed at 100 °C. The registered value of 304 (±27) s was higher compared to that of commercial urea-formaldehyde (UF) (127 s), suggesting the need for a longer pressing time [58]. On the other hand, phenol-formaldehyde resins presented slower kinetics than UFs, recording a gel time five times higher [59]. Previous research showed that the addition of condensed tannins to PF led to 30% faster crosslinking [48]. This means that the polyphenolic characteristics of tannin, added to bio-based furfural hardener, could be an attractive alternative to phenol-based synthetic resins due to the reactivity and the sustainability of its reagents.

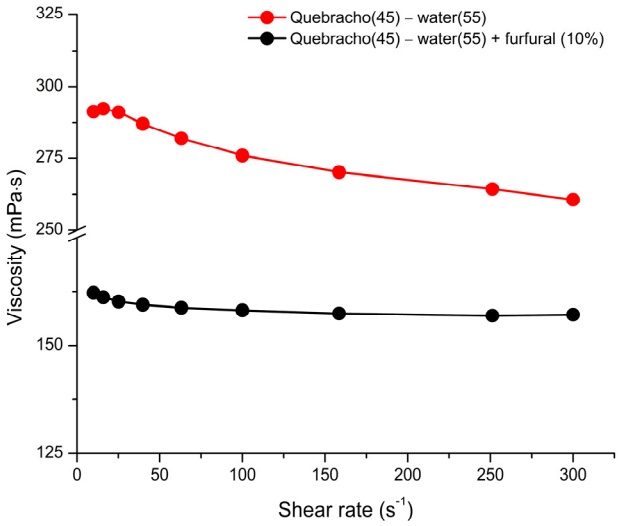

Figure 2. Viscosity of 45% tannin−water solutions at pH = 8 with (black) and without (red) furfural hardener.

3.3. Particleboard Characterization

3.3.1. Density Profile

Density is one of the major physical parameters influencing the mechanical properties of wood composites. Considering the prefixed density target of 650 kg·m^{-3}, the registered values reported in Table 2 are slightly higher, and a certain correlation between density and pressing time (p-value = 0.0661) was observed. Conversely, no correlation (p-value = 0.3194) with temperature was highlighted, as is visible in Figure 3. The higher values recorded were presumably correlated to the achieved board thicknesses, which were lower than the targeted 10 mm. Indeed, the pre-pressing at 9 mm could have caused the thickness decrease because of the rigidity of tannin-furanic adhesives [60], which did not allow the expected spring-back. Furthermore, the density profiles reported in Figure 4 show that 7 min at 160 °C reveals an irregular profile, with a sharp decrease in the middle (4–6 mm) due to the too-mild reaction conditions. As soon as the conditions became tougher, the typical "U-shape" [60] profile was observable, and in particular, the profiles recorded at 9 min all temperatures showed an "arc-shape". When too harsh conditions were applied, the core density decreased again. Thus, given that density was mostly affected by the pressing time showing irregular profiles, especially at 7 min, longer times will probably be necessary to guarantee the panel stability.

Table 2. Density and thickness values of particleboards glued with 15% tannin in function of the pressing parameters.

Temperature (°C)	Time (min)	Density (kg·m^{-3})		Thickness (mm)	
		Mean	SD	Mean	SD
160	7	663	21	10.1	0.19
	9	692	55	9.6	0.09
	11	701	46	9.3	0.08
180	7	659	40	9.4	0.10
	9	687	29	9.6	0.13
	11	698	40	9.3	0.05
200	7	696	37	9.4	0.07
	9	713	52	9.3	0.07
	11	685	39	9.5	0.10

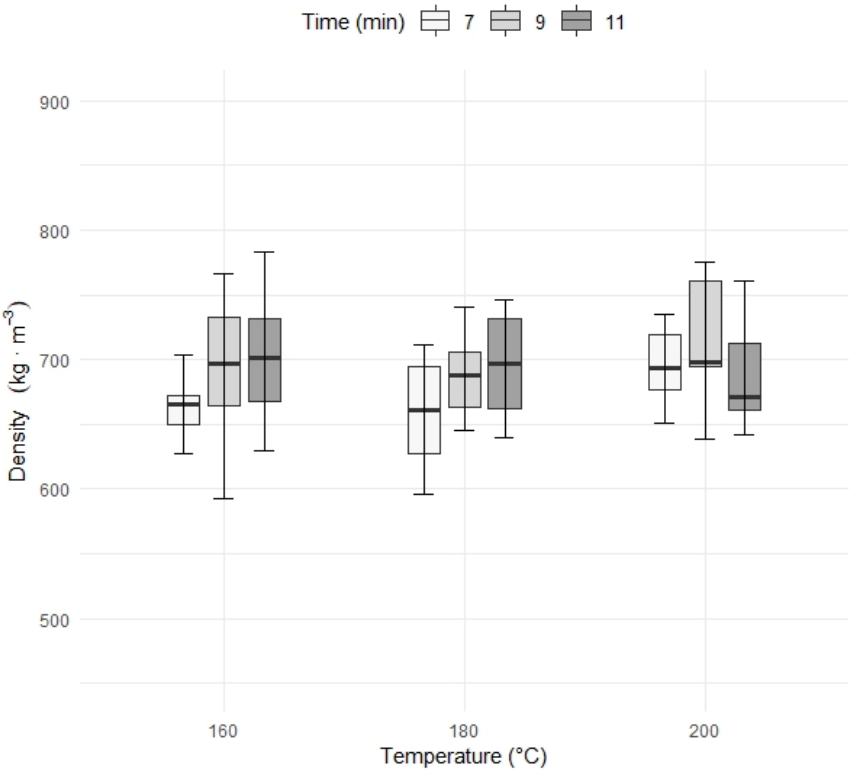

Figure 3. Density box char plot in function of pressing time and temperature. The whiskers represent scores outside the middle 50%, the median is represented by the line inside the box, while lower and upper quartiles are, respectively, the inferior and the bottom end of the box. Possible outsiders are indicated by asterisks.

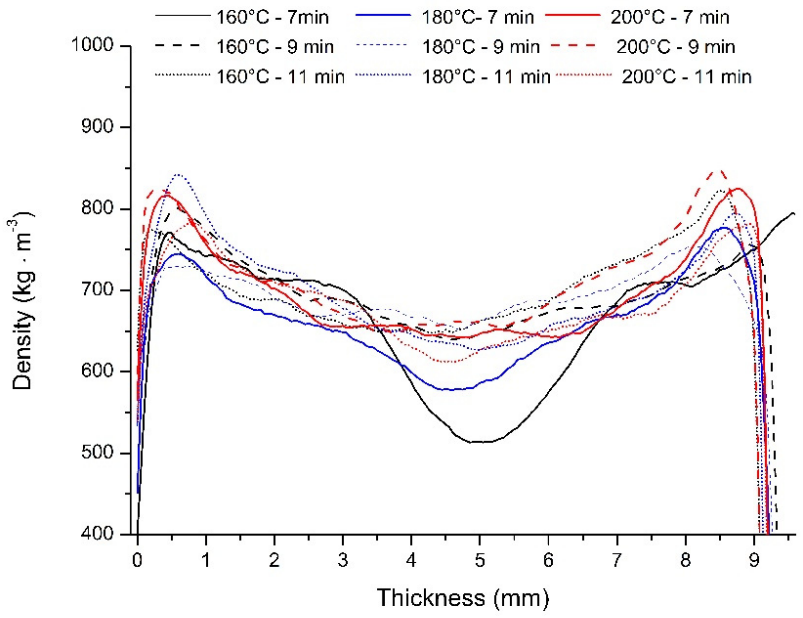

Figure 4. Density profile for particleboards manufactured at different pressing times (7, 9, 11 min) and temperatures (160, 180, 200 °C).

3.3.2. Mechanical Properties

Internal bond (IB), modulus of elasticity (MOE), and modulus of rupture (MOR) were studied to understand the mechanical behavior of the boards (Figure 5).

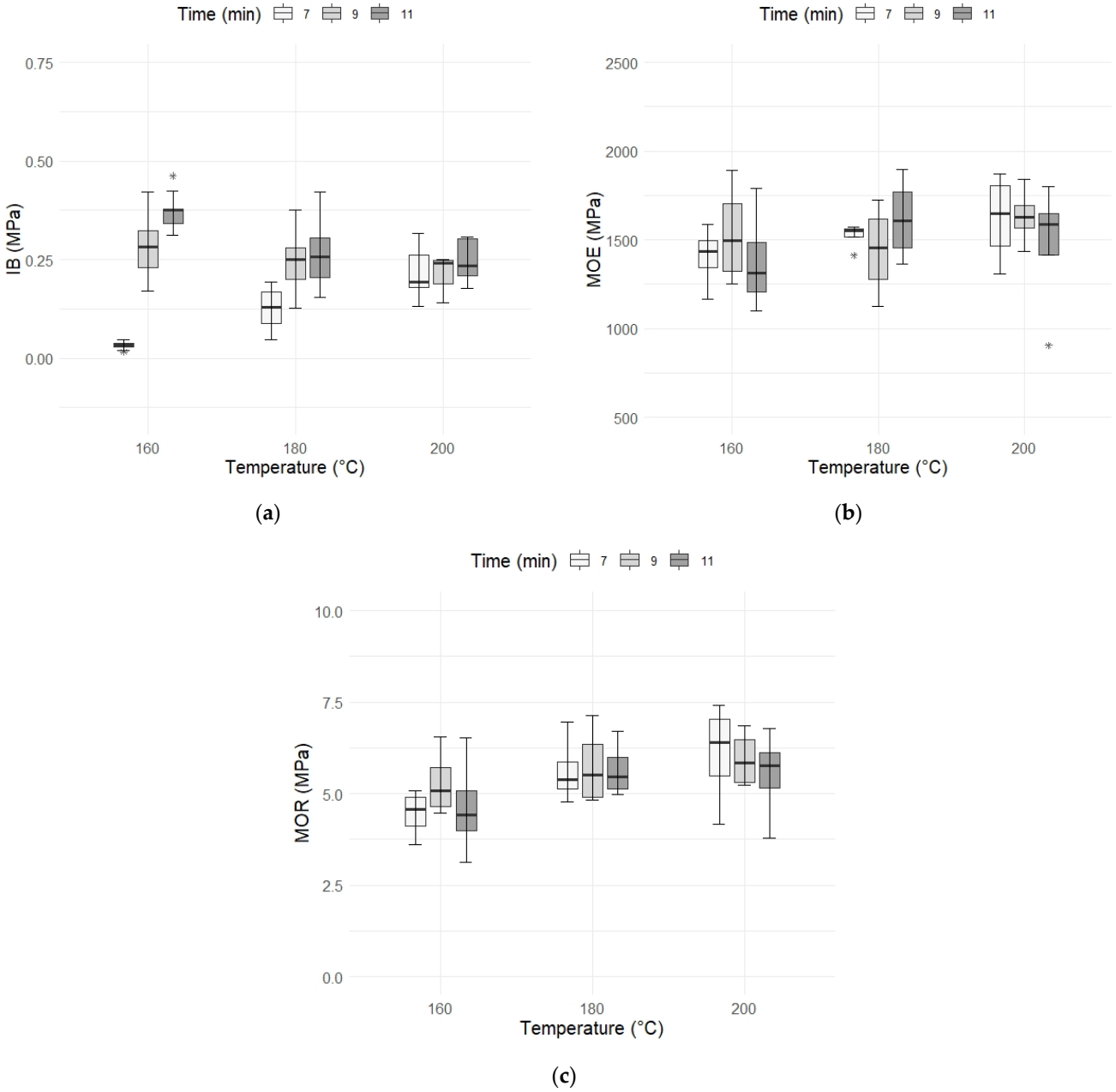

Figure 5. Influence of pressing parameter on (**a**) Internal Bond, (**b**) Modulus of elasticity, (**c**) Modulus of rupture. The whiskers represent scores outside the middle 50%, the median is represented by the line inside the box, while lower and upper quartiles are, respectively, the inferior and the bottom end of the box. Possible outsiders are indicated by asterisks.

Internal bond is often considered one of the more significant mechanical properties of particleboards. It was observed that, on the one hand, a high direct correlation between pressing time and internal bond was observed, reporting a p-value equal to 2×10^{-16}, as represented in Figure 5a. On the other hand, the pressing temperature showed a limited influence on the final value of cohesion, showing a p-value equal to 0.685, while a combination of both press parameters significantly affected the final internal bond value (p-value = 1.37×10^{-10}). It can be observed that increasing the temperature allowed for reducing the pressing time, reaching a similar final value of internal cohesion. The boards pressed at 160 °C for 9 and 11 min were characterized by the highest value of an internal bond (0.32 MPa and 0.37 MPa, respectively), exceeding the P1 limit standard requirement of 0.28 MPa for general purposes. The results of the bending tests are reported in Figure 5b,c.

MOE resulted in parameters unaffected by a reaction, recording a *p*-value of 0.906 and 0.430 for pressing time and temperature, respectively. Meanwhile, a slightly significative correlation between MOR and temperature was found (*p*-value 0.0491) and using a posthoc Tukey test, a significative difference between 160 and 200 °C was highlighted. Although no standard minimum MOE value was given for P1 general dry applications, the values of MOR obtained were moderately lower than the standard requirements for boards, with thickness ranging between 6 and 13 mm [61]. However, these bending properties can both be significantly improved by coating with melamine-impregnated paper, which is a common praxis in modern furniture.

3.3.3. Thickness Swelling

Thickness swelling was also investigated, and the results are presented in Figure 6. The panels pressed at milder conditions (160 °C, 7 min) did not resist the dipping in water for 24 h, while all the other combinations resisted the test. However, thickness swelling was significantly influenced by pressing temperature (*p*-value = 0.045) as well as by pressing time (*p*-value < 0.01). Indeed, harsher reaction conditions involved panels with lower water affinity, and also for this feature, pressing time plays a major role. Observing the thickness swelling behavior from 160 °C to 200 °C for 11 min of pressing, a decrease in swelling of around 30% was detected. Although an increase in reaction parameters led to a low water affinity, the registered values did not satisfy the requirement for wet application, and additional treatments would be necessary to increase the moisture resistance properties of the particleboard.

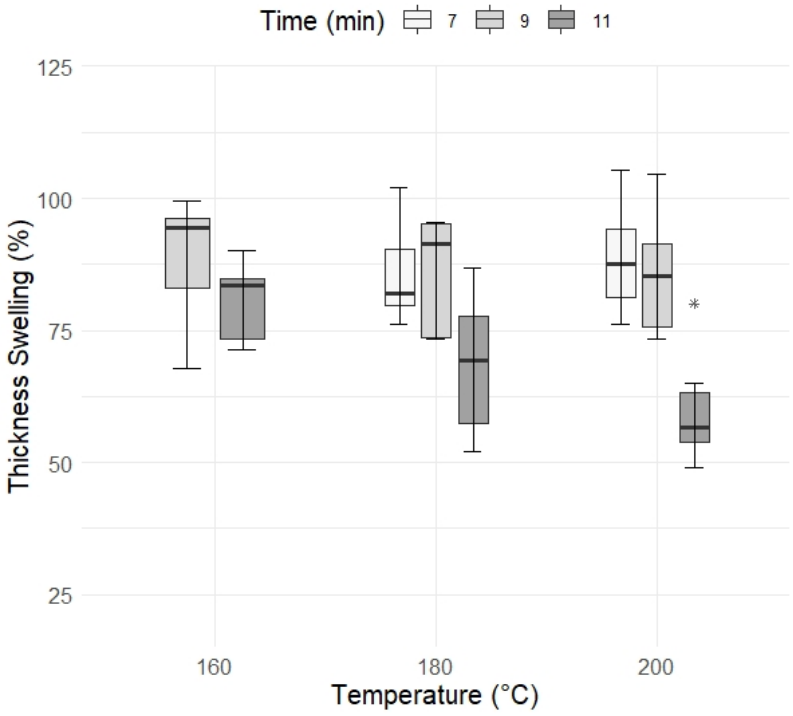

Figure 6. Thickness swelling after 24 h of the produced particleboards in function of the pressing parameters. * $p < 0.05$.

3.3.4. SEM Analysis

In order to investigate the morphological features of the produced particleboard, a representative section was selected for SEM analysis and reported in Figure 7.

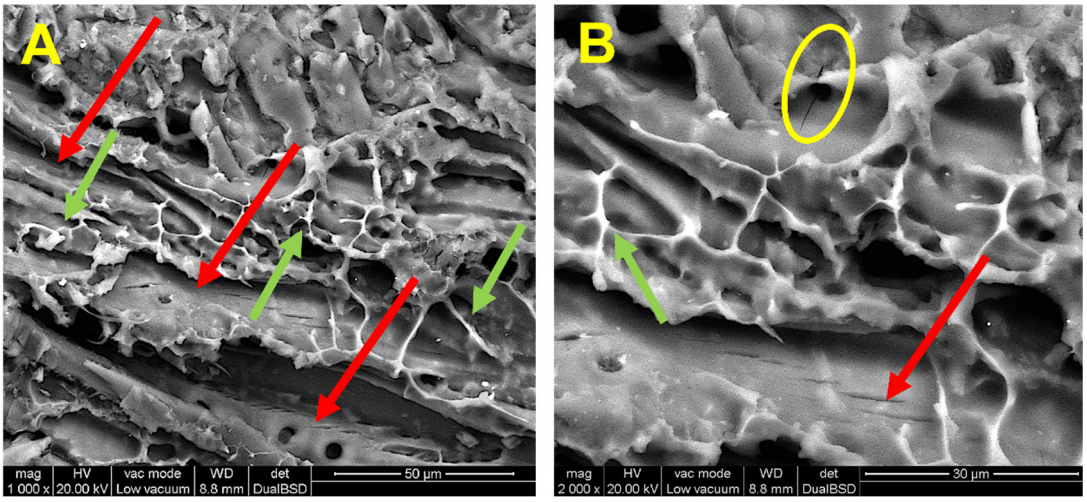

Figure 7. Scanning electron microscopy images of particleboard glued with 15% of adhesive formulation. Different magnifications of the same representative area are proposed: (**A**) 1000× (**B**) 2000×. Red arrows identify the wooden matrix; green arrows identify the tannin-furfural adhesive.

Although the fibers in the wood matrix were not easy to identify, the SEM images allowed us to observe: (i) the wood fiber structure, constituted of parallel fibers (red arrows), and (ii) the adhesive distributed in a networked morphology, which accumulated in the white areas (green arrows).

Notwithstanding the presence of visible pits, this microscopic analysis suggests a relatively homogenous distribution of the adhesive within the woody matrix. At a higher magnification (Figure 7B), the presence of sharp breaks (yellow area), which can be due to the rigidity of the furanic adhesive, can also be noticed.

3.4. Optimization of Pressing Parameters

Further investigations extending the processing conditions were also performed. In particular, we tried to consider extended conditions such as temperature (140 °C), pressing time (13 min), and adhesive amount (10%). The results of these tests are summarized in Table 3, where they are compared with the reference measurement (in bold) and the most promising series at 160 °C with the lower pressing time (in italics).

Table 3. Physical and mechanical outcomes from the optimization of process parameters at 160 °C.

Samples			IB	MOE	MOR	T-Swelling
Temperature (°C)	*Pressing Time* (min)	*Adhesive Amount* (%)	(MPa)	(MPa)	(MPa)	(%)
140	11	15	0.16	1453	4.8	82
160	13	15	0.35	1560	5.5	77
160	11	10	0.31	1083	5.5	82
160	**11**	**15**	**0.37**	**1417**	**4.9**	**80**
160	*9*	*15*	*0.32*	*1542*	*5.3*	*90*
160	*7*	*15*	*0.03*	*1417*	*4.5*	*n.a.*

According to what was observed in the literature [62], the pressing temperature is a fundamental parameter also for tannin-furfural bonded particleboard. The panels produced at 140 °C showed less than half the internal bond of the reference formulation, clearly highlighting the need for a higher temperature (>140 °C). Extending the pressing time to 13 min did not lead to a substantial increase of internal bond, but the panels improved their bending strength MOE and MOR by 10%, but still did not completely meet the required standards. Further, a slightly lower tendency to absorb water was recorded. This observation further highlights the importance of the pressing time for the properties of the tannin-furfural panels because of the contained reactivity of this

bio-based adhesive. We also tested the performance of the boards using less adhesive (10% in place of 15%), and it led to a reduction in board elasticity, registering a lower MOE (around 30%). However, no considerable differences were found for IB and MOR. In addition, the high thickness swelling was related to the adhesive itself and not influenced by its amount, and no substantial differences were found for thickness swelling. To sum up, the increase in pressing temperature and time mainly affected the internal cohesion of the boards. Under more severe conditions, the diffusion of water in the wood was favored, and consequently, the resin was able to penetrate easily into the voids (mechanical interlocking) [63]. Furthermore, at higher temperatures, a chemical change in the woody substrate is promoted, such as the overcoming of the glass transition of lignin and the breaking of hydrogen bonds, which allows chemical interlocking, too.

On the other hand, MOR and MOE are slightly affected by the pressing parameters. In fact, those properties are mostly influenced by the nature of the resin itself and the size and geometry of the wood particles [64,65].

However, a literature comparison between bio-sourced adhesives is not simple due to the broad system of variables. A general overview is presented below and compared to the presented formulation.

In particleboard with a density of 650 kg m^{-3} bonded by oxidized base lignin resin, the authors registered an internal cohesion strength of 0.10 MPa, while the modulus of elasticity and modulus of rupture were respectively 1847 and 8.1 MPa. Adding different amounts of isocyanate from 1 to 3%, increases of up to 0.40, 2900, and 15 MPa, respectively, were observed [25].

When a mixture of corn starch and mimosa tannin was applied at 22% for a three-layer laboratory scale particleboard pressed for 7 min at 200 °C, this led to IB, MOR, and MOE of 0.98, 10.36, and 2220 MPa, respectively [66]. In another study, bio-based dextrin adhesive was synthesized and applied to particleboard production [67]. Despite a pressing time of 30 min, low-quality mechanical properties are reached, recording an MOE, MOR, and IB of 915, 5.68, and 0.11 MPa.

Additionally, chestnut tannin extract crosslinked with different hardeners was considered an adhesive [68]. Here the boards were pressed at 195 °C for 7.5 min and registered a final dry IB of 0.4–0.6 MPa, and a wet IB of 0.06–0.15 MPa. Mechanical properties are not as sensitive as water resistance for particleboards glued with bio-based adhesives. Moisture and water resistance can be considered the main drawback of bio-based adhesives, which often limit the application to dry conditions only.

For instance, Zhao et al. applied a tannin-sucrose formulation to the production of particleboard, registering a thickness swelling of around 30% [69]. Slightly higher values were registered by Ghary and Pizzi [70] using a soy flour-tannin-based adhesive.

Casein-based adhesives were used to glue other agroforestry resources for boards [71], and in this case, values between 18 and 53% of thickness swelling were measured.

However, the quebracho-furfural resin has been shown to be more stable for gluing particleboard than plywood, regardless of process parameters [43].

A final consideration is that the use of recycled particles was observed to lead to a significant reduction of mechanical properties [72]. In this study, a decrease of 38% for IB, 28% for MOR, and 18% for MOE, was observed using UF adhesives.

In this context, the quebracho-furfural formulation presented in this work offers comparable mechanical properties to other bio-sourced adhesives. Internal bonds of 0.37 MPa satisfy the European standard for a P1 panel type, and an increase in density allows an enhancement of cohesion, thus broadening the potential fields of application [23]. Like the vast majority of natural-based resins, the presented resin does not offer sufficient moisture resistance, requiring the addition of some reinforcing component such as other phenolics (PFs, RFs) or isocyanates. It has to be considered that the industrial conditions for particleboard production consist of higher pressing temperatures (200–230 °C) but far lower pressing times (1–2 min). This means that important enhancements have to be achieved in order to speed up the crosslinking kinetic of the tannin-furfural resins

(tailored catalysis), but on the other hand, the lower temperature applied may contribute to containing energy costs.

4. Conclusions

In this work, the efficacy of quebracho tannin-furfural adhesive for particleboards was studied by modifying pressing temperature (140, 160, 180, and 200 °C), pressing time (7, 9, 11, and minutes), and adhesive content (10, 15%). A preliminary chemical characterization of industrial quebracho extract highlighted high condensed tannin content and a limited sugar portion, confirming its suitability as a building block for adhesives. The tannin-furfural resins at 45% tannin content were tested, showing good processability and stability but also a longer gel time than typical UF synthetic resins. According to density profile analysis, the pressing time plays a major impact on the final mechanical board properties. Finally, the most effective pressing parameters for particleboards were identified: (i) Pressing temperature must be higher than 140 °C, (ii) a pressing time of 9 min at least, and (iii) 15% adhesive content. In particular, the particleboards produced at 160 °C for 9 and 11 min at 15% of tannin adhesive content registered, respectively, 0.32 MPa and 0.37 MPa of internal bond, satisfying the requirement for interior conditions according to EN 312 (2010). Ultimately, this work sheds new light on the totally renewable, sustainable, and formaldehyde-free wood adhesive for the manufacture of interior-grade particleboard.

Author Contributions: Conceptualization, G.T. and E.C.; methodology, G.T., M.C.B. and M.M.; software, E.C.; validation, G.T. and E.C.; formal analysis, G.T., investigation, E.C. and A.D.I.; resources, M.C.B., V.C., M.M. and M.Z.; data curation, E.C. and A.D.I.; writing—original draft preparation, E.C. and G.T.; writing—review and editing, G.T., M.M., V.C., M.Z. and M.C.B.; visualization, E.C.; supervision, M.Z., G.T. and M.C.B.; project administration, G.T.; funding acquisition, M.Z., V.C., M.M. and M.C.B. All authors have read and agreed to the published version of the manuscript.

Funding: The project was supported with the funds of TESAF department and of the doctoral school LERH.

Data Availability Statement: The original data are available from the corresponding author.

Acknowledgments: The authors gratefully acknowledge the TESAF department of the University of Padua for the support of the project BIRD 2021 and the doctoral school LERH.

Conflicts of Interest: The authors declare no conflict of interest.

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