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Physico-mechanical properties of particleboards bonded with pine and wattle tannin-based adhesives

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Abstract—This study investigated the physical and mechanical properties of particleboards made using two types of tannin-based adhesives, wattle and pine, with three hardeners, paraformaldehyde, hexamethylenetetramine(hexamine) and TN (tris(hydroxyl)nitromethane), by measuring the physical (thickness swelling, linear expansion and water absorption) and mechanical properties (bending strength and internal bond strength). The performance of the particleboards made using tannin-based adhesives was influenced by physical conditions such as press time and temperature as well as by chemical conditions, such as the chemical structure of the tannin and the hardener. Wattle tannin-based adhesive being a thermoset, the wattle tannin-based particleboards were more influenced by physical conditions, while the pine tannin-based particleboards were influenced by the chemical structure of the pine tannin nuclei, which include phloroglucinolic A-rings. The reactivity of the hardener toward the tannin was in the order: paraformaldehyde > hexamine > TN for wattle tannin, while for pine tannin the order was hexamine > paraformaldehyde > TN.

Keywords: Wattle tannin; pine tannin; hardener; physical properties; mechanical properties; phloroglucinolic A-rings.

1. INTRODUCTION

As the standard of living increases, the more prosperous consumers, who are health conscious, are increasingly turning to natural wood-based materials as construction materials for interior decoration and flooring. As the consumption of wood-based raw materials has increased, the need for wood substitutes has also grown [1].

In the past, urea-formaldehyde and phenol-formaldehyde resin binders have contributed greatly to the progress made by the wood industry. These adhesives have

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been widely used as a major component in the production of building and furniture materials, such as medium density fiberboards, particleboards plywoods, etc. However, decreasing the emission levels of formaldehyde fumes from particleboards manufactured using urea-formaldehyde resins has now become one of the major concerns of the timber and wood adhesives industry, particularly in the case of adhesively-bonded wood products. Recently, attention has turned to other volatile organic chemicals (VOCs) that may be emitted from wood products. These VOCs include chemicals naturally present in the wood, as well as those added during processing. In new energy-efficient buildings, air exchange rates are low, permitting concentrations of VOCs to accumulate to detectable and possibly harmful levels. The adverse health effects associated with these increased VOC concentrations include eye and respiratory irritation, irritability, inability to concentrate and sleepiness. Moreover, health and the environment constitute two key concerns of the 21st century [2–4].

Furthermore, after the oil crisis in the early 1970s, increasing oil prices and the high energy requirements associated with the production of synthetic polymers prompted the use of renewable resources such as wood, tree bark, nut shells, etc., in material applications, rather than in energy production. A rise in the price of oil and the necessity to reduce fuel energy production have led to the development of replacement materials for petroleum-derived phenolic compounds from natural resources in the wood adhesive industry [5].

Amongst the possible alternatives, tannin is an excellent renewable resource which can be used for replacing petroleum-derived phenolic compounds. The major species from which it can be obtained are Mimosa, Quebracho and Radiata Pine. It is mainly concentrated in the inner layer of the bark and has been used in the adhesive industry in Africa, South America and Oceania to obtain the low formaldehyde emission levels required for environmental-friendly adhesives [6, 7].

Tannin is present predominantly as phloroglucinol or resorcinol A-rings and catechol or pyrogallol B-rings [8]. The chemical structures of wattle and pine tannins are shown in Fig. 1. The free C6 and C8 sites on the A-ring can react with formaldehyde because of their strong nucleophilicity to form the adhesive. The

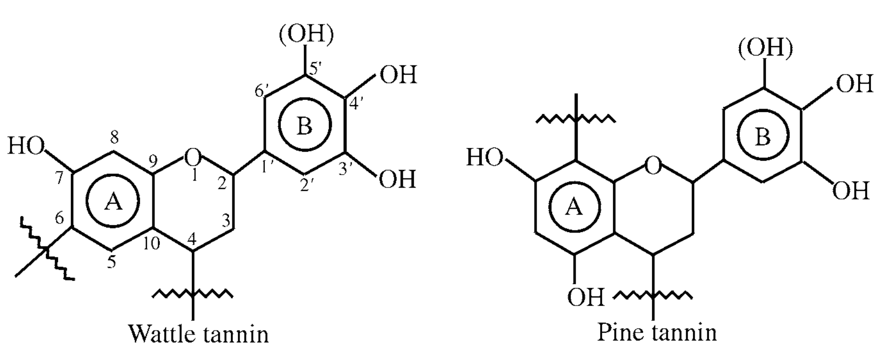


Figure 1. Basic structures of wattle and pine tannins.

phenolic nuclei in tannins react with formaldehyde. This high reactivity of tannins towards formaldehyde is the result of their A-ring phloroglucinolic or resorcinolic nuclei, which have a 10–50-times higher reaction rate with formaldehyde than does phenol. Because of this characteristic, the resulting free formaldehyde emission is less than that from other wood adhesives, such as phenol-formaldehyde, urea-formaldehyde, etc. [9]. Additionally, in its use for the tanning of leather and shoes, tannin has better water-resistant properties than phenol-formaldehyde and urea-formaldehyde resins.

In this study, the physical properties (specific gravity, moisture content, linear expansion, thickness swelling and water absorption) and mechanical properties (3-point bending strength and internal bond strength) of particleboards manufactured using wattle and pine tannin-based adhesives with hardeners (paraformaldehyde, hexamethylenetetramine (hexamine) and TN(tris(hydroxymethyl)nitromethane)) were investigated at various press temperatures.

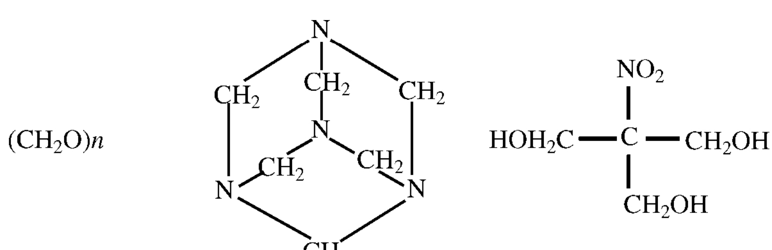
2. EXPERIMENTAL

2.1. Materials

2.1.1. Wood particles. The wood particles used for manufacturing particleboards were donated by Donghwa Enterprise (South Korea) and consisted of recycled chips used for core, which had a 3 wt% moisture content.

2.1.2. Tannin extracts. Two types of commercial tannin extracts, wattle and pine, were prepared. The wattle (*Acacia mearnsii*, mimosa) was supplied by Bondtite (Australia) and the pine (*Pinus radiata*, radiata pine) was supplied by (DITECO, Chile). These tannins were in the form of fine dark brown powder with a moisture content of 4 wt%.

2.1.3. Hardeners. The three hardeners, paraformaldehyde, hexamethylenetetramine (hexamine) and TN (tris(hydroxyl)nitromethane), were purchased from Aldrich. Their chemical structures are shown in Fig. 2.



Paraformaldehyde Hexamethylenetetramine TN (tris(hydroxyl)nitromethane)

Figure 2. Chemical structures of the three hardeners used.

2.2. Methods

2.2.1. Tannin-based adhesives. Aqueous tannin extracts with a 40 wt% concentration were prepared by dissolving the spray-dried powder of each tannin extract in water. To these solutions, 6.5, 8 and 10 wt% of each hardener, by weight of dry tannin extract, were added. Each hardener concentration was based on several results [10–12]. The pH ranged from 5.5 to 6. While paraformaldehyde and TN (tris(hydroxyl)nitromethane) were used in the pure solid state, hexamethylenetetramine was used as a 35 wt% hexamine solution [11].

For the determination and comparison of the effect of hardener content, paraformaldehyde for wattle and hexamethylenetetramine for pine tannin were selected. 0, 4, 8 and 12% of paraformaldehyde, by weight of dry tannin extract, were used for the wattle tannin, and 0, 3, 6.5 and 10% of hexamethylenetetramine for the pine tannin. The final adhesive systems are shown in Table 1.

2.2.2. Fabrication of particleboards and measurement of formaldehyde emission. The particleboards were fabricated using both pine and wattle tannin-based adhesives and three different hardeners to obtain a specific gravity of 0.8 and dimensions of 270 mm × 270 mm × 8 mm (length × width × thickness).

The wood particles were placed in a rotary drum mixer and the tannin-based adhesive used as the composite binder was sprayed onto them while rotating the mixer. The quantity of adhesive was calculated to be 14 wt% of the raw material based on the oven-dried weight. The mixture of particles and adhesives was cold pressed at 2 kg/cm^2 for 2 min, to ensure the stability of the mat and to obtain the proper density gradient of the composites prior to hot pressing.

The mixture was then hot pressed to form composite boards at a peak pressure of 30 kg/cm^2 and temperatures of 160, 170, 180 and 190°C. The press time was 5 min, with the pressure being released in two steps of 1 min each. A schematic diagram showing the multi-hot press schedule is shown in Fig. 3. The fabricated particleboards were pre-conditioned at 25°C and 65% RH for two weeks before testing.

Table 1.
Adhesive systems showing hardener content of in wt%

Hardener	Wattle tannin	Pine tannin
Paraformaldehyde	0 (wattle only)	8
	4	
	8	
	12	
Hexamethylenetetramine	6.5	0 (pine only)
		3
		6.5
		10
TN (Tris(hydroxymethyl)nitromethane)	10	10

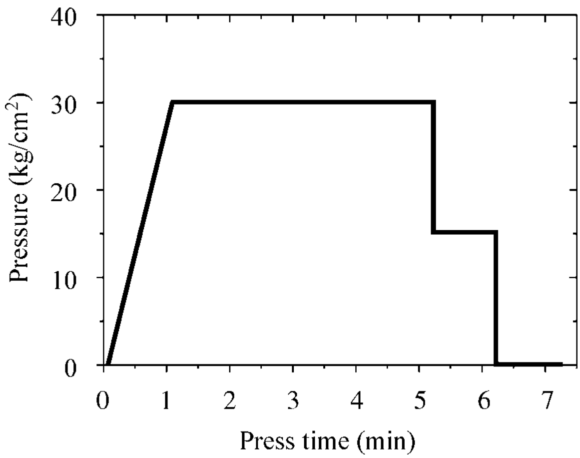


Figure 3. Multi-hot press schedule.

To measure the formaldehyde emission values of the fabricated particleboards, the perforator method was used.

2.2.3. Physical properties. Moisture content, specific gravity, linear expansion, thickness swelling and water absorption were examined using the ASTM D 1037-99 method. Specific gravity was controlled by quality control testing, wherein each value represents the average of five samples.

2.2.4. Mechanical properties. 3-point bending strength and internal bond strength were determined using a Universal Testing Machine (Zwick, NICEM at Seoul National University) using the ASTM D 1037-99 method. Each value represents the average of five samples. The results were compared with ANSI A208.1-1999 standard.

3. RESULTS AND DISCUSSION

3.1. Physical properties

No significant difference was found in the moisture content or specific gravity of the different particleboards made whether using wattle tannin-based or pine tannin-based adhesive or any of the hardeners investigated. The moisture content and the specific gravity of the wattle tannin-based adhesives were in the range of 6.14–8.43 wt% ($\pm$0.86) and 0.77–0.81 ($\pm$0.07), respectively, while that of the pine tannin-based adhesives were in the range of 5.96–8.82 wt% ($\pm$0.68) and 0.78–0.81 ($\pm$0.08), respectively.

The formaldehyde emission values of the fabricated particleboards are shown in Table 2. According to DIN EN 120, all particleboards bonded using wattle tannin-based adhesive of quality E1 can emit formaldehyde at <6.5 mg/100 g, as

Table 2.
Perforator values of the adhesive systems

	Adhesive system	Perforator value (mg/100 g)
Wattle tannin	Paraformaldehyde	3.36
	Hexamethylenetetramine	0.85
	TN (Tris(hydroxymethyl)nitromethane)	1.68
Pine tannin	Paraformaldehyde	12.81
	Hexamethylenetetramine	1.75
	TN (Tris(hydroxymethyl)nitromethane)	7.61

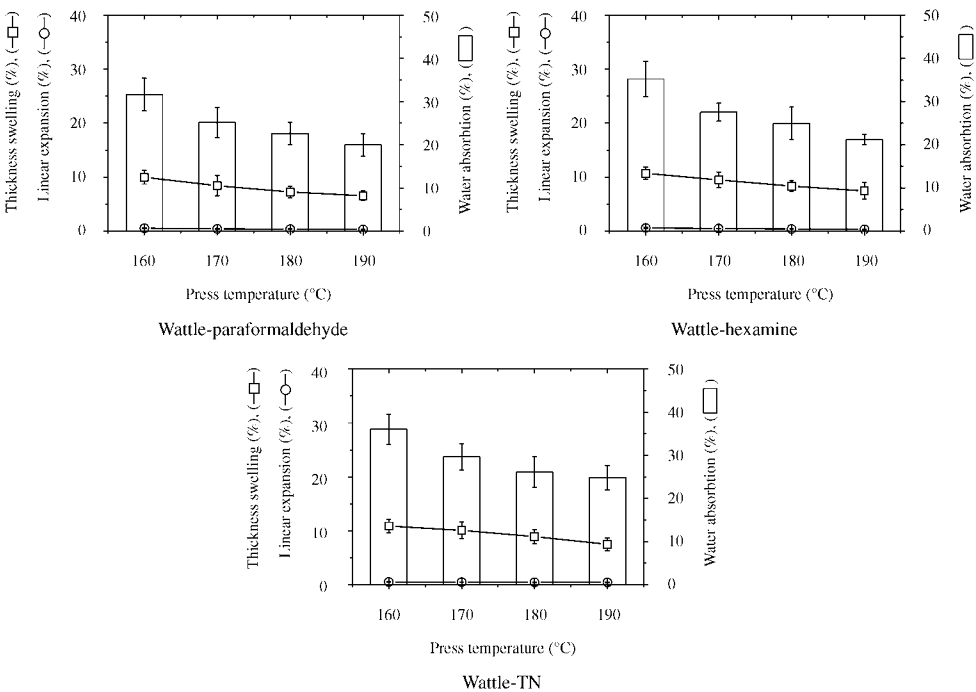


Figure 4. Physical properties of particleboards bonded with wattle tannin-based adhesives.

determined using the dry product and the perforator method, while only hexamethylenetetramine can be emitted in the case of pine tannin.

The physical properties (thickness swelling, linear expansion and water absorption) of the particleboards made using both the wattle and pine tannin-based adhesives and with the three different hardeners are shown in Figs 4 and 5. In Fig. 4, the thickness swelling of the wattle tannin-based adhesive with paraformaldehyde at 160°C is 9.98%, and then decreases with increasing press temperature to 6.55% at 190°C. This same trend is shown in the case of hexamine and TN, with the only difference being the degree of thickness swelling, which varies for the different hardeners. In the case of wattle tannin-based adhesive, the thickness swelling is 10.71% for hexamine at 160°C and for TN the corresponding value is 10.90%. Thus, the

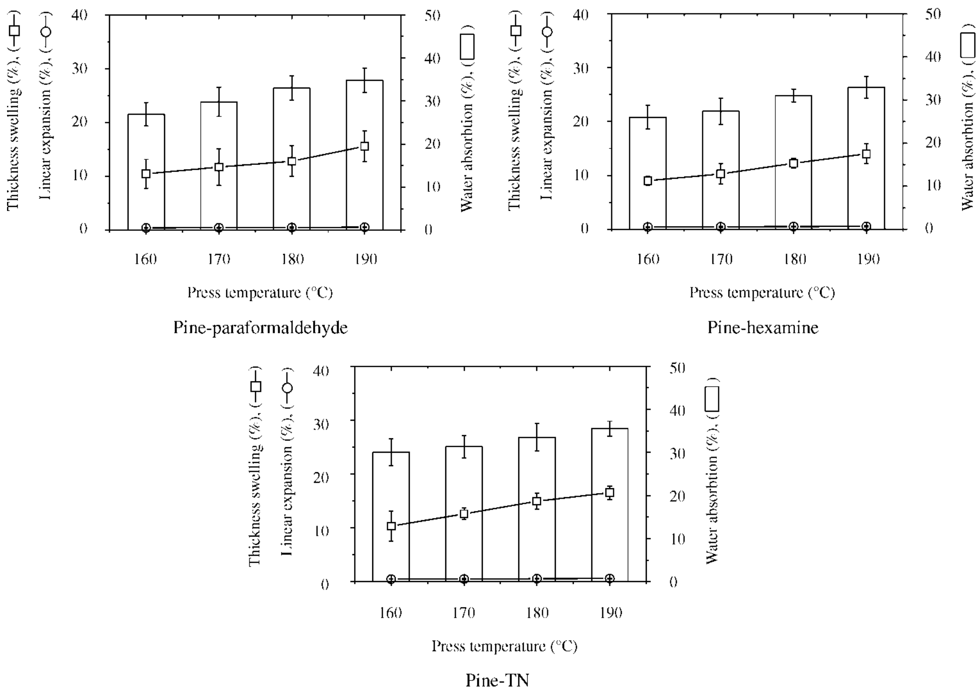


Figure 5. Physical properties of particleboards bonded with pine tannin-based adhesives.

order of swelling is paraformaldehyde < hexamine < TN. The tendency towards decreasing thickness swelling both with increasing press temperature and the order paraformaldehyde < hexamine < TN were confirmed by the results of linear expansion and water absorption. The overall physical properties of wattle tannin-based adhesives decrease with increasing press temperature and are in the order paraformaldehyde < hexamine < TN. In contrast, the pine tannin-based adhesives showed the opposite behavior. As shown in Fig. 5, the thickness swelling, linear expansion and water absorption of the particleboards made using pine tannin-based adhesives with the three different hardeners increased with increasing press temperature. The thickness swelling of the particleboards made using the pine tannin-based adhesive with hexamine at 160°C is 9.04%, while at 190°C the corresponding value is 14.01%. Why do these physical properties show opposite behaviors? Tannin-based adhesives, especially those based on wattle tannin, are thermosetting adhesives, like phenol-formaldehyde and urea-formaldehyde adhesives. Accordingly, composites made using tannin-based adhesives show this kind of trend. As the press temperature increases, molecules of the tannin prepolymer and functional groups are cross-linked with each other and are hardened [13, 14]. Higher temperature means more energy to cross-link, and that is why the physical properties improve with increasing press temperature. However, pine tannin-based adhesive is not only a thermosetting adhesive, but can also act as a fast reacting cold-setting adhesive [12, 15, 16]. This can be explained by the faster reactivity and shorter pot-

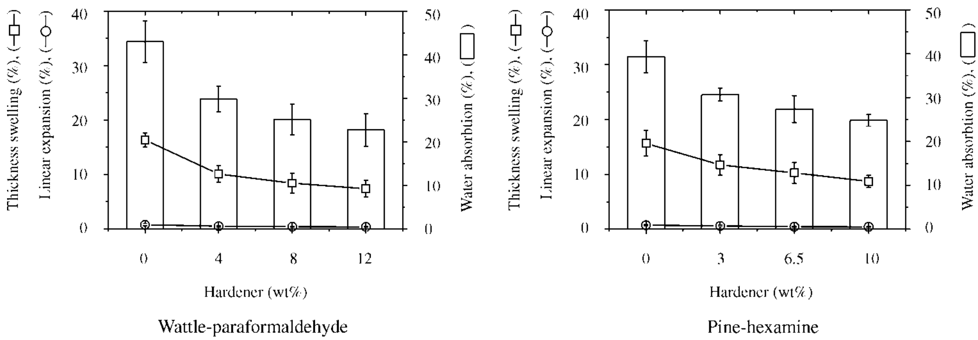


Figure 6. Physical properties of particleboards with tannin-based adhesives as a function of the amount of hardener.

life of pine tannin, while hexamine acts as an accelerator. Assuming the reactivity of phenol towards formaldehyde to be 1, and that of resorcinol and phloroglucinol to be 10 and 100, respectively, the flavonoid resorcinolic A-rings have a reactivity of about 8–9, while the phloroglucinolic A-rings have a reactivity of well over 50 [9]. The pine tannin-based adhesives are already cured at 160°C or below. Accordingly, when the press temperature is increased, the surface of the particleboards tends to suffer from thermal degradation, because curing has already taken place. The particleboard made using the wattle tannin-based adhesive with paraformaldehyde showed the best physical properties, while hexamine was the best hardener for pine tannin, as these adhesive systems were investigated in several studies [10, 11, 17]. From Fig. 6, it can be seen that, as the amount of hardener is increased, the thickness swelling, linear expansion and water absorption all are decreased. It was shown that increasing the amount of hardener led to higher degree of curing.

3.2. Mechanical properties

3.2.1. Bending strength. The bending strengths of the particleboards fabricated using both the wattle and pine tannin-based adhesives with the three different hardeners at press temperatures of 160, 170, 180 and 190°C are shown in Fig. 7. The bending strength of the particleboards made using the wattle tannin-based adhesives with all three hardeners increased slightly as the press temperature increased, while in the case of pine tannin a marked decrease in bending strength with increasing press temperature was observed. Based on ANSI [18], the bending strengths of all the adhesive systems for all press times are over Grade M-3. As regards the hardeners, the bending strength in the case of wattle tannin-based adhesives was in the order paraformaldehyde > hexamine > TN. From these results, it can be seen that wattle tannin is cured best with paraformaldehyde, then with hexamine and finally with TN. In the case of pine tannin the opposite behavior is observed. The bending strength increases with increasing press temperature. The order of bending strength of the pine tannin-based adhesive system, for different hardeners, was found to be hexamine > paraformaldehyde > TN, in contrast to that of wattle

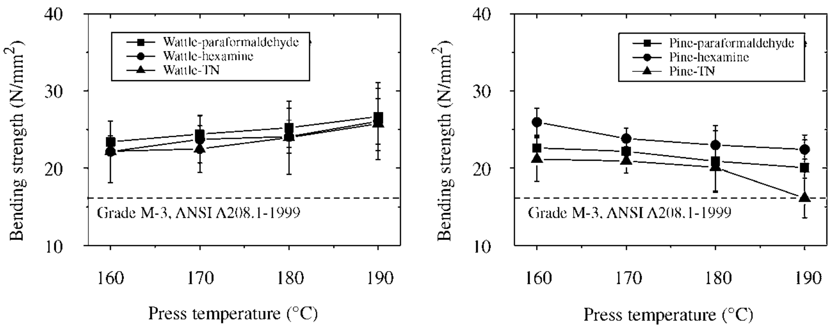


Figure 7. Bending strength of particleboards with tannin-based adhesives at various press temperatures.

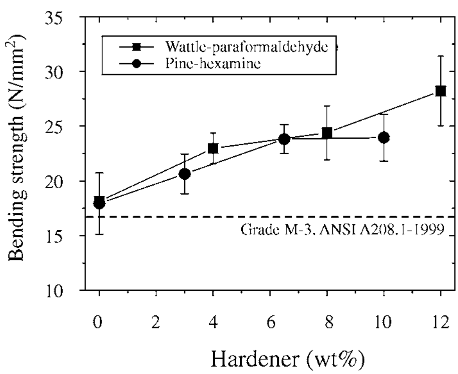


Figure 8. Bending strength of particleboards with tannin-based adhesives as a function of the amount of hardener.

tannin. These results showed the same tendency as the physical properties results. Increasing the amount of hardener caused the bending strengths of both the pine and wattle tannin-based particleboards to increase, as shown in Fig. 8. This was also found in another study [19]. As for physical properties results, it is understandable that the particleboard properties were improved by increasing the press temperature and time, because wattle tannin-based adhesive is thermosetting. When the press time was increased to 170°C, the bending strength of the particleboards, made using the wattle tannin-based adhesives, slightly increased, while those made using the pine tannin-based adhesives decreased, as shown in Fig. 9. These results can be explained by the reactivity of the resorcinol A-ring and phloroglucinol A-ring toward formaldehyde, and thus it can be understood that wattle tannin-based adhesives are cured to a higher degree by increasing temperature and time, while in the case of pine tannin-based adhesive, it is already cured at low temperature and at an earlier time.

The typical stress-strain curves for the particleboards made using the wattle and pine tannin-based adhesives are shown in Fig. 10. The bending modulus of elasticity (MOE) is the slope of the tangent line at the stress point of proportional limit [1].

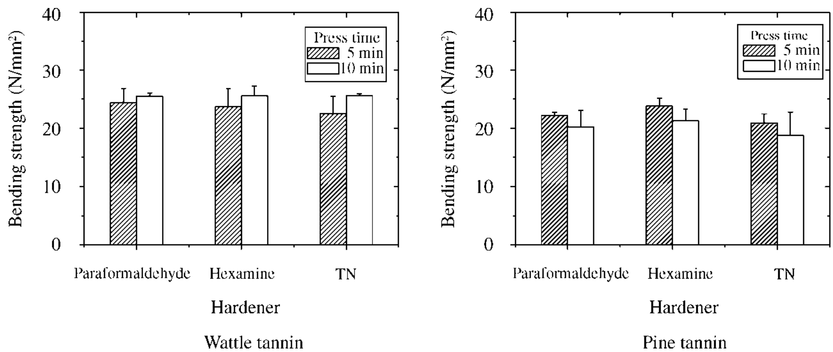


Figure 9. Bending strength of particleboards with tannin-based adhesives for two different press times.

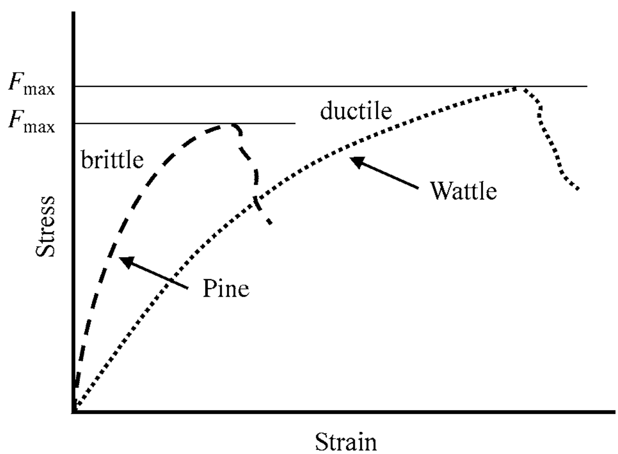


Figure 10. Typical stress–strain curves of wattle and pine tannin-based adhesives. F_{max} is the maximum load to break.

The strain (bending modulus of elasticity) in the particleboards made using the wattle tannin-based adhesives was higher than that of the particleboards made using the pine tannin. Greater strain means that the particleboard is more ductile. Because the pine tannins were cured early, due to the fact that the phloroglucinolic A-rings reacted faster with formaldehyde, the resulting particleboards were brittle and had lower strain values.

3.2.2. Internal bond strength. The internal bond strength provides an overall measure of the board's integrity, which defines how well the core material is bonded together, and this property is influenced directly by the board density, resin content, particle geometry, and raw material type [20]. As can be seen in Fig. 11, the wattle tannin-based adhesives were more affected by the type of hardener than the pine tannin-based adhesives. All wattle tannin-based adhesive systems satisfied Grade M-2 of ANSI. Furthermore, in the case where paraformaldehyde or hexamine

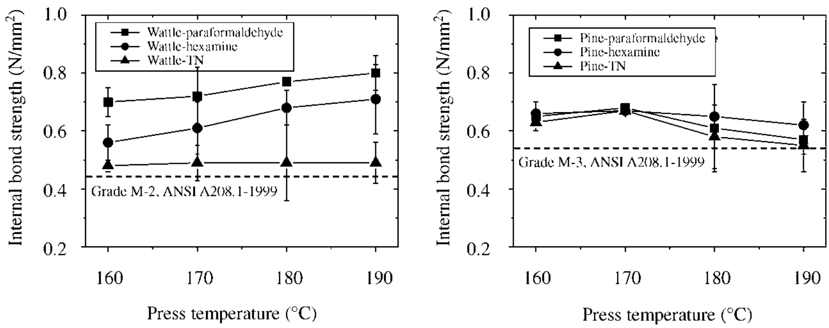


Figure 11. Internal bond strength of particleboards with tannin-based adhesives at various press temperatures.

were used as a hardener, the adhesive system also satisfied Grade M-3. From a dynamic mechanical thermal analysis of tannin-based adhesives, the reactivity of the hardener toward the tannin was found to be in the order paraformaldehyde > hexamine > TN for wattle tannin; while for pine tannin the order was hexamine > paraformaldehyde > TN. It was also found that pine tannin-based adhesive showed faster initial reactivity than wattle tannin-based adhesive. These results were obtained from the storage modulus (E') and loss modulus (E''), which form part of the DMTA data. From the loss modulus (E'') of the DMTA data, the modulus value of wattle tannin with the paraformaldehyde system demonstrated the lowest temperature, at 102.89°C, with wattle tannin with hexamine and TN being next, in that order, while the lowest temperature of the loss modulus (E'') in the case of pine tannin was obtained with hexamine. In general, as regards the hardener, the adhesive system cured at a lower temperature showed better internal bond strength.

Increasing the press temperature from 160°C to 190°C caused the internal bond strength of the particleboards to increase. On the other hand, in the case of the pine tannin-based adhesives, the choice of the hardener had little influence on the internal bond strength. Because pine tannin has the above-mentioned phloroglucinolic A-rings, this has an effect on the performance. It can be said that pine tannin nuclei include phloroglucinolic A-rings which take part in the reaction. This behavior is also shown in Fig. 12. As the amount of hardener was increased in the case of wattle tannin the internal bond strength markedly increased, while it increased only slightly in the case of pine tannin. Figure 13 shows the difference in internal bond strength as a function of press time for all tannin-based adhesive systems. This tendency was the same as that observed for the bending strength. When the press time was increased from 5 min to 10 min at 170°C, the internal bond strength of the particleboards made using the wattle tannin-based adhesives slightly increased, while that of the particleboards made using the pine tannin-based adhesives decreased.

The overall performances with respect to the bending strength and internal bond strength of the particleboards made using the wattle and pine tannin-based adhesives

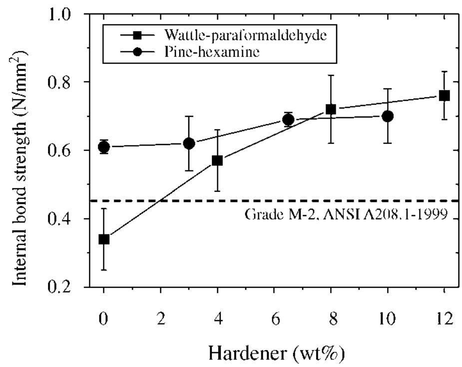


Figure 12. Internal bond strength of particleboards with tannin-based adhesives as a function of the amount of hardener.

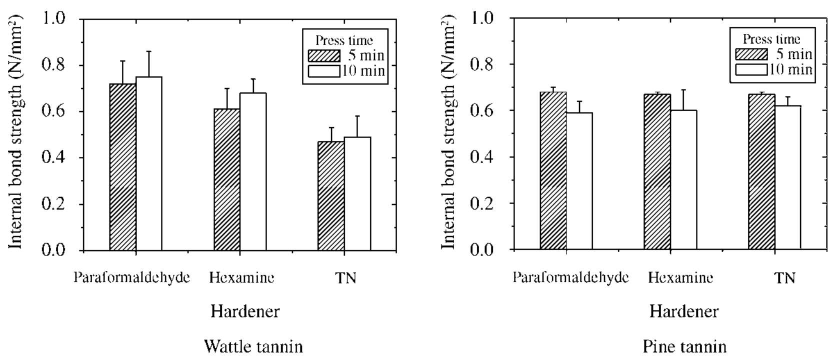


Figure 13. Internal bond strength of particleboards with tannin-based adhesives for two different press times.

can be summarized as follows:

$$
\begin{array}{ll}
P_{\mathrm{w}} \propto T^{a} & a \geqslant 1 \\
P_{\mathrm{p}} \propto T^{a} & a \leqslant 1 \\
P_{\mathrm{w}} \propto t^{b} & b \geqslant 1 \\
P_{\mathrm{p}} \propto t^{b} & b \leqslant 1
\end{array}
\quad
\left(
\begin{array}{l}
P = \text{performance (bending strength or internal bond strength)} \\
T = \text{press temperature} \\
t = \text{press time} \\
\mathrm{w} = \text{wattle tannin-based adhesive} \\
\mathrm{p} = \text{pine tannin-based adhesive}
\end{array}
\right),
$$

where P represents the performance, such as the bending strength or internal bond strength. The performance of the particleboards made using the wattle tannin-based adhesives is directly proportional to both press time and temperature, while that of the particleboards made using the pine tannin-based adhesives is inversely proportional to both press time and temperature.

4. CONCLUSION

As wattle tannin-based adhesives are thermoset in nature, the performances of the different particleboards showed a similar pattern of behavior, with both the bending strength and internal bond strength increasing with increasing press time and temperature. However, in the case of the pine tannin-based adhesives the results were different. Because pine tannin nuclei include phloroglucinolic A-rings, which have a reactivity of well over 50, these adhesive systems were cured early, so that the press time and press temperature did not have as much effect as in the case of the wattle tannin-based adhesives. From the physical (thickness swelling, linear expansion and water absorption) and mechanical properties (bending strength and internal bond strength), it can be characterized that the reactivity of the hardener toward the tannin was in the order paraformaldehyde > hexamine > TN for wattle tannin, while for pine tannin the order was hexamine > paraformaldehyde > TN. The performance of the particleboards made using the tannin-based adhesives is influenced by both physical and chemical conditions. The physical conditions involved are the press time and temperature, while the chemical conditions involved are the chemical structure of the tannin and the choice of hardener.

Acknowledgements

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