

EFFECTS OF DIFFERENT FLAVONOID EXTRACTS IN OPTIMIZING TANNIN-GLUED BARK INSULATION BOARDS

*G. Kain**

Researcher, Lecturer, PhD Student
E-mail: gkain.lba@fh-salzburg.ac.at

V. Güttler

Masters Student
E-mail: vguettler.htb-b2011@fh-salzburg.ac.at

B. Lienbacher

Masters Student
E-mail: blienbacher.htb-b2011@fh-salzburg.ac.at

M-C. Barbu

Professor for Wood Science and Technology
E-mail: marius.barbu@fh-salzburg.ac.at

A. Petutschnigg

Professor for Wood Science and Technology
Department of Forest Products Technology and Timber Construction
Salzburg University of Applied Sciences
Kuchl, Austria
E-mail: alexander.petutschnigg@fh-salzburg.ac.at

K. Richter

Professor for Wood Science
Holzforschung München
Technische Universität München
Munich, Germany
E-mail: richter@hfm.tum.de

G. Tondi

Senior Researcher in Wood Chemistry
Department of Forest Products Technology and Timber Construction
Salzburg University of Applied Sciences
Kuchl, Austria
E-mail: gianluca.tondi@fh-salzburg.ac.at

(Received February 2015)

Abstract. Efforts in decreasing energy consumption in buildings have created a market environment that favors insulation materials made from renewable resources. Tree bark is a naturally highly optimized material that can serve insulation needs. Thus, bark insulation panels have been produced from larch bark and bonded with a formaldehyde-free tannin-hexamine resin. Quebracho and mimosa tannins, containing different levels of hexamine, were mixed with bark particles at different ratios, and cured in a hot press for various press times. Mechanical and water-related board property evaluation showed mimosa tannins to be advantageous in terms of panel performance. This was supported by Fourier transform infrared (FTIR)

* Corresponding author

spectroscopic analysis of tannin polymers, which provided insight into the chemical activation by a hardener and possible rationale for the better performance of mimosa resin. Evaluating thermal conductivity of the panel showed that its dependence on temperature was comparable with commonly available insulation materials.

Keywords: Bark, tannin, insulation board, IR spectroscopy.

INTRODUCTION

Bark is a traditional byproduct in timber manufacturing. Typically, it is not widely used as a high-added-value product but has proved to be an interesting resource for insulation panel production (Kain et al 2013b). This might not be surprising because bark is naturally tailored to protect the sensitive vascular cambium of a tree against heat and frost, microorganisms, fire, and mechanical damage (Vaucher 1997). Thus, the obvious question arises as to if bark can be used as an exterior wall cladding element in building engineering. Although the thermal conductivity is not especially low, the main benefit of bark insulation is its excellent heat storage capacity (Kain et al 2013a).

For decades, synthetic resins have been extensively used in wood-based panel production. Some are problematic in that they emit formaldehyde (World Health Organization 2006) (eg urea formaldehyde, melamine urea formaldehyde, and phenol formaldehyde), whereas others, such as isocyanates, incur higher production costs because of the high price of the resin or equipment used, result in a hazardous workplace, or are completely synthetic-oil-based formulations. If bark insulation panels are to satisfy the needs of a market segment of environmentally friendly insulation materials, a resin system based on renewable resources is desirable.

Many studies have proposed natural adhesives suitable for the production of wood panels (Pizzi 1982; Tondi et al 2012; Umemura et al 2014), and one of the most promising lines exploits the tendency of flavonoid tannins to crosslink in an alkaline environment (Pena et al 2009).

Tannin resin formulations for the production of wood-based panels have a long history. The

most important species from which tannin can be extracted are mimosa, quebracho, and radiata pine bark (Moubarik et al 2010). The first attempt to produce industrially useful pine tannin resin formulations was made by Pizzi (1982). Optimized tannin resins with hexamethylenetetramine as a hardener were subsequently used (Pizzi et al 1997; Pichelin et al 2006). Further research showed alkaline conditions to be beneficial for autocondensation of mimosa tannins, with the chemical structures of tannin-hexamines being influenced by both the tannin structure and pH of the solution (Pena et al 2009). Tannin-formaldehyde resins have been used for manufacturing particleboards. However, these resins exhibited a greater variation in their internal bond (IB) strength than commercial synthetic resins, possibly because of their complex hardening mechanisms (Garnier et al 2002). Pasch et al (2001) compared quebracho and mimosa tannins and found that mimosa tannin was considerably branched, whereas quebracho tannin had a rather linear structure.

The use of hexamethylenetetramine (hexamine) as a hardener yielded very interesting results, and it was successfully applied to bark insulation panels. The resulting board characteristics were comparable with traditionally bound panel characteristics (Kain et al 2014, 2015).

Hexamine is widely used as a hardener for tannin-based resins (Pizzi 1994; Pichelin et al 1999; Pena et al 2009). In a hardening reaction, hexamine is principally decomposed to reactive imines. Decomposition products of hexamine react very readily with tannin (Pizzi 1994). Because hexamine is not decomposed to formaldehyde, panels with very low formaldehyde emissions ($E_0 = 0.6\text{--}0.8$ mg/100 g) can be produced (Pichelin et al 1999).

Natural bark panels were produced using quebracho tannin extract as a binder (Kain et al 2014). However, although it is very rich in condensed tannin (Tondi and Petutschnigg 2015), the quebracho tree grows very slowly and therefore its availability will decrease in the future. For that reason, the use of flavonoid extracts from fast growing plants is more appropriate and the replacement of quebracho with mimosa tannins strengthens the sustainable character of this innovative insulation material.

This study aims to determine if the performance of a mimosa-hexamine resin is superior to that of a quebracho-hexamine resin for binding bark insulation panels and also to evaluate the optimization potential in hardener amount and pressing time for limiting potential industrial production costs.

MATERIALS AND METHODS

Materials

Larch (*Larix decidua* Mill.) bark was sourced from Peter Graggaber GmbH (Unternberg, Salzburg, Austria). A four-shaft shredding system (RS 40) from Untha shredding technology GmbH (Kellau, Austria) was used to crush the bark before it was separated to obtain particles of 6-10 mm. The bark was dried in a vacuum dryer (Hildebrand-Brunner, Gehrden, Germany) at 60°C and an absolute pressure of 20-25 kPa for 2 wk until the particles had reached a final MC of <10%. The use of a vacuum dryer is industrially unusual for such purposes, but we used it because of its availability at our research facilities. A lower degree of the volatilization of bark extractives may be obtained via vacuum drying than via higher temperatures in a commercial drying kiln.

Mimosa (*Acacia mearnsii*) tannin extracts (Phenotan AG) from Tanac S.A. (Montenegro, Brazil) and quebracho (*Schinopsis balancae* spp.) tannin extracts (Colatan GT 10) from Markmann GmbH (Hamburg, Germany) were used to prepare the resins for the insulation boards.

Hexamethylenetetramine ($\geq 99\%$) and a solution of NaOH (32%) for resin preparation

were obtained from Merck Schuchardt OHG (Hohenbrunn, Germany) and Carl Roth GmbH & Co.KG (Karlsruhe, Germany), respectively.

Methods

Manufacturing of boards. For a resin, 50 wt% of tannin extract powder and 50 wt% of H₂O were mixed using a mechanical stirrer at 700-1500 rpm. The mixture was adjusted to pH 9 with a 32% NaOH solution. Mimosa and quebracho tannin formulations with 50% solid content (s.c.) and pH corrected to 9.0 were subjected to viscosity measurements. Viscosity was evaluated at room temperature (20°C) using a multispeed digital viscotester from Thermo Haake (Waltham, MA). Finally, the requisite amount ($w_{\text{hexamine}}/w_{\text{tannin}}$) of a 33% hexamine solution was added as a hardener.

The bark particles and the prepared tannin resin were mixed using a plowshare mixer and manually prepressed in a mold of 350 × 240 mm². With a Höfer (Taiskirchen, Austria) laboratory press with a plate temperature of 180°C, a mat was pressed for 5 min (0.25 min/mm), 6.5 min (0.33 min/mm), or 8 min (0.4 min/mm) in two steps to a final target thickness of 20 mm. Thereby, the press was closed in 60 s to an opening width of 19 mm and, after 60 s, was then opened to a final thickness of 20 mm at which it was held for the rest of the press time. In total, 22 boards were pressed with variations in tannin extracts and amount of hexamine at different press times (Table 1). For boards without a hardener, only one sample was produced because only a qualitative assessment was performed.

The boards were stored in a climate room at 20°C and 65% RH for 3 da before they were cut according to CEN (1994) into the required sizes for mechanical and physical tests. MC of boards during testing was determined in accordance with CEN (1993e).

Board properties. Bulk densities of boards and specimens were determined before the relevant tests in accordance with CEN (1993d). For two specimens of each board density, profiles

Table 1. Types of tannin, amount of hexamine as a hardener and press times with a constant target density of 350 kg/m³ (oven-dried weight) and resin content of 10% (based on the oven-dried weight of bark particles).

Tannin (kg/m ³)	Hexamine (%)	Press time (min)	No. of specimens
Quebracho	6	5.0	2
	6	8.0	2
	8	6.5	2
	10	5.0	2
	10	8.0	2
Mimosa	0	5.0	1
	0	8.0	1
	6	5.0	2
	6	8.0	2
	8	6.5	2
	10	5.0	2
	10	8.0	2

were generated with Dense-Lab X software (EWS, Beaverton, OR). Resulting profiles were averaged for every board type.

The two boards without any added hexamine were not considered and not measured because they showed poor cohesion of the bark particles, especially in their middle layers.

A Zwick Roell (Kennesaw, GA) Z 250 universal testing machine was used for the mechanical tests. For each of the 20 boards, five specimens were tested for IB according to CEN (1993b), and three-point bending tests to determine modulus of rupture (MOR) and modulus of elasticity (MOE) were performed for two specimens of each board in accordance with CEN (1993a). Furthermore, five specimens per board were tested for thickness swelling (TS) and water absorption (WA) after 2 and 24 h of immersion in water at 20°C and pH 7 according to CEN (1993c).

Thermal conductivities of three mimosa-bound and three quebracho-bound panels were measured according to CEN (2001) using an EP500 lambda meter (Lambda Measurement Technologies GmbH, Cincinnati, OH). The measurements were performed at average temperatures of 10°C, 25°C, and 40°C with a temperature difference of 15°C between the cooling plate (2.5°C, 17.5°C, and 32.5°C) and another plate (17.5°C, 32.5°C, and 47.5°C). The measuring

area was 200 × 200 mm². The six tested boards were 320 × 225 mm².

Evaluation of data. A unidimensional multivariate analysis of variance (ANOVA) was used to analyze the influences of independent variables (type of tannin, amount of hexamine hardener, and press time) on the material properties of the bark panels according to Eq 1.

To evaluate the influence of the relevant variables on panel properties, partial eta-squared values were determined. The amount of variance introduced by one variable in the model is thereby corrected by the effect of all the other factors in the model according to Eq 2 (Hartung et al 1995).

$$p_i(t, h, p) = \mu + \alpha_t + \beta_h + \gamma_p + (\alpha\beta)_{th} + (\alpha\gamma)_{tp} + (\beta\gamma)_{hp} + \varepsilon_{t, h, p} \quad (1)$$

$$\eta_i^2 = \frac{df_i \times F_i}{df_i \times F_i + df_{\text{error}}} \quad (2)$$

μ = average of main unit

p_i = panel property of factor i

t = tannin type (mimosa, quebracho)

h = amount of hexamine hardener (0%, 6%, 8%, 10%)

p = press time (5, 6.5, 8 min)

α_t = effect of tannin type

β_h = effect of hexamine amount

γ_p = effect of press time

$(\alpha\beta)_{th}$ = interaction effect between tannin type and hexamine amount

$(\alpha\gamma)_{tp}$ = interaction effect between tannin type and press time

$(\beta\gamma)_{hp}$ = interaction effect between hexamine amount and press time

$\varepsilon_{t, h, p}$ = random effects that are not controlled in the experiment

η_i^2 = partial eta-squared value for factor i

df_i = number of degrees of freedom of factor i

F_i = empirical F -value of factor i

df_{error} = number of degrees of freedom for unexplained residual variance

Fourier transform infrared spectroscopy. Samples (2 g) of each tannin extract (mimosa and

quebracho) powder were manually mixed with H₂O (10 g). Both mixtures were adjusted to pH 9 by adding a 32% NaOH solution. Finally, 10 wt% or 20 wt% of a 33% hexamine solution was added as a hardener. Thus, in total, six different formulations were prepared for Fourier transform infrared (FTIR) spectroscopy.

The resins were dried at 180°C for 16 h and then stored in a climate chamber at 20°C and 65% RH for 2 da. The hardened resins were ground to fine powders and then analyzed with an attenuated total reflectance (ATR)-equipped PerkinElmer (Waltham, MA) Frontier FTIR spectrometer. Spectra were obtained in the range of 4000-600 cm⁻¹ at a resolution of 4 cm⁻¹ from powder samples of a few milligrams by accumulating 32 scans. Each sample was scanned in triplicate, and spectra were baseline corrected and vector normalized using the software Unscrambler (Camo Software, Inc., Woodbridge, NJ) prior to averaging.

RESULTS

On average, density of the mimosa-tannin-bound boards was 408.63 kg/m³ (SD = 8.42 kg/m³) with an average (determined in accordance with CEN (1993e)) of 14.90% MC (SD = 0.43%), whereas that of quebracho-glued boards was

408.32 kg/m³ (SD = 9.10 kg/m³) on average, with an average of 14.79% MC (SD = 0.53%). Density, although showing minimal variation, was at least significantly ($p < 0.01$) positively correlated with MOR, MOE, and IB (shown by Pearson $R > 0.49$). Also, density did not show a significant influence on TS and was highly significantly ($p < 0.001$) negatively correlated with WA ($R = -0.52$).

Density distributions across the cross sections showed that for both resin types, density at the surface was on average 13% higher (average maximum density 460 kg/m³, SD = 40.37 kg/m³) than that at the core (average core density = 408.30 kg/m³, SD = 19.19 kg/m³). Although a distinct density profile was present, variation was high because of the coarse particles (Fig 1).

The complete set of boards produced with the target density of 350 kg/m³ (based on the oven-dry mass) presented a homogeneous and stable aspect on visual examination. Each board was tested for its mechanical and water behavior. The complete set of results is reported in Table 2.

Mechanical Characteristics

With regard to mechanical characteristics of the boards (Table 2), all except MOE showed

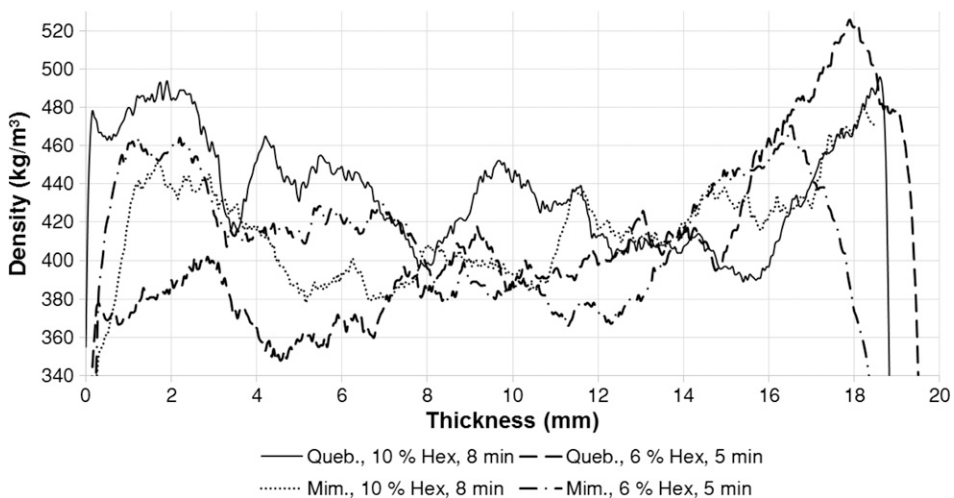


Figure 1. Density profiles for different bark panel variations.

Table 2. Mechanical board characteristics (mean value and standard deviation).

Tannin	Hardener (%)	Press time (min)	Density MOR (kg/m ³)	MOR (N/mm ²)	MOE (N/mm ²)	Density _{IB} (kg/m ³)	IB (N/mm ²)	Density TS/WA (kg/m ³)	TS 2 h (%)	TS 24 h (%)	WA 2 h (%)	WA 24 h (%)											
Mimosa	6	5.0	425.00	10.00	183.50	26.36	405.85	21.59	0.16	0.03	395.20	22.20	11.69	1.09	13.55	2.07	50.68	2.64	73.41	3.42			
		8.0	422.50	9.57	141.50	10.61	402.64	22.87	0.16	0.03	401.93	27.54	11.85	1.14	13.57	2.11	48.96	2.95	72.34	4.02			
	8	6.5	430.00	8.16	1.09	190.50	42.88	404.71	17.54	0.17	0.03	406.62	21.36	11.33	1.79	12.55	2.35	47.93	2.18	71.23	2.81		
		10	5.0	432.50	12.58	1.13	176.75	29.98	419.08	18.56	0.19	0.03	417.03	25.21	11.19	1.87	12.85	2.83	48.11	2.83	71.61	2.73	
	Quebracho	6	5.0	420.00	8.16	0.99	0.13	150.00	46.03	410.39	18.59	0.17	0.03	411.26	20.29	11.33	2.37	13.22	2.69	48.01	1.58	70.78	2.49
			8.0	402.50	5.00	0.50	0.09	91.95	6.72	393.73	15.77	0.05	0.01	393.17	16.63	24.03	15.15	23.49	3.33	54.35	2.54	77.22	1.72
	8	5.0	420.00	0.00	0.85	0.01	95.85	3.89	412.75	20.06	0.14	0.02	405.41	24.23	14.72	2.19	18.60	2.94	51.32	4.10	78.42	3.08	
		6.5	412.50	5.00	0.64	0.07	142.00	7.07	415.10	20.88	0.14	0.02	409.58	13.02	12.90	2.17	15.95	1.85	48.00	2.26	73.29	2.03	
	10	5.0	430.00	14.14	0.55	0.46	144.80	87.96	406.20	15.41	0.13	0.03	403.73	23.84	13.07	1.36	16.33	2.81	50.44	3.21	75.74	1.62	
		8.0	410.00	33.67	0.62	0.43	177.00	33.94	417.33	16.56	0.16	0.03	410.61	23.64	12.00	1.12	14.57	3.28	48.26	1.97	75.89	3.14	

significance ($p < 0.01$) in the applied model (Table 3). The tannin type used accounted for 50% of the variation in MOR. The mimosa-bound panels with an average MOR of 1.03 N/mm² (SD = 0.15 N/mm²) showed a 69% higher MOR than the quebracho-bound panels (0.61 N/mm², SD = 0.29 N/mm²) (Fig 2). Of the scatter in IB, 65% can be explained by the model, with the greatest contribution (41%) being caused by the different tannin types. Hardener amount and press time also greatly significantly influenced IB. The mimosa resin resulted in an average IB of 0.17 N/mm² (SD = 0.03 N/mm²), which is 31% higher than quebracho resin (average = 0.13 N/mm², SD = 0.04 N/mm²). When amount of hexamine hardener was increased from 6 to 10%, increases in IB of 13% for mimosa and 50% for quebracho were achieved. With quebracho tannin, a press time of 5 min resulted in an IB of 0.09 N/mm² (SD = 0.05 N/mm²), whereas a press time of 8 min for the same panels led to an average IB of 0.17 N/mm² (SD = 0.03 N/mm²), a trend that was not observed with mimosa (Fig 3).

Behavior in Water

TS after 2 h of water immersion was significantly ($p < 0.01$) affected by tannin type and hardener amount. This was also the case for TS after 24 h, whereas press time had a contributory power of 7%. Panels with a mimosa tannin resin showed 13.15% (SD = 2.36%) swelling after 24 h of water immersion, compared with an average of 17.79% (SD = 4.21%) for those with quebracho tannin resin, which corresponds to a decrease of 26%. With regard to swelling properties, a greater amount of hexamine hardener was not beneficial for mimosa tannin, whereas with quebracho tannin, a greater hardener content led to slightly better results. Extending the press time was not found to improve the swelling properties (Fig 4). WA was clearly determined by tannin type, which accounted for almost 35% of the variation after a longer immersion time. Thus, it was clearly shown that greater density is associated with decreased WA and that mimosa-bound boards

Table 3. Partial eta-squared values for single factors of a multivariate unidimensional ANOVA.

	MOR	MOE	IB	TS 2 h	TS 24 h	WA 2 h	WA 24 h
Coefficient of determination	0.589**	0.533	0.645***	0.370***	0.617***	0.375***	0.475***
Tannin	0.500***	0.280*	0.406***	0.117**	0.426***	0.078**	0.347***
Hardener	0.000	0.189	0.254***	0.105**	0.226***	0.172***	0.087**
Press time	0.001	0.013	0.142***	0.052*	0.071*	0.085**	0.001
Tannin*hardener	0.035	0.182	0.078**	0.080**	0.167***	0.022	0.001
Tannin*press time	0.162*	0.122	0.232***	0.058*	0.088**	0.021	0.018
Hardener*press time	0.010	0.023	0.069*	0.035	0.023	0.011	0.001
N	38	27	100	100	100	100	100

Significance levels: *** = <0.001, ** = <0.01, * = <0.05.

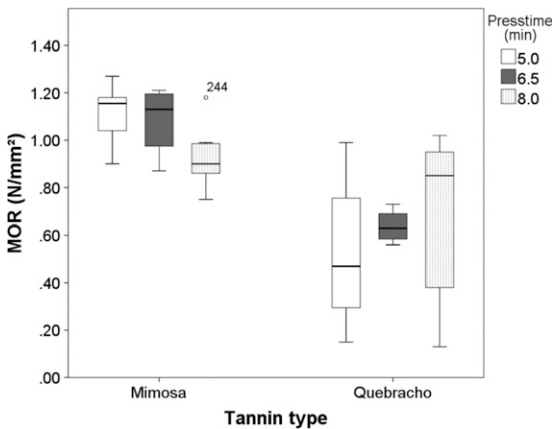


Figure 2. Effect of pressing time on MOR for different tannins.

(average 71.88%, SD = 3.15%) took up on average 6% less water than equivalent quebracho-bound panels (average 76.11%, SD = 2.89%) (Fig 5).

Thermal Characteristics

Thermal conductivities of the panels were evaluated as 77.23 mW/(m·K) (SD = 1.46 mW/[m·K]), 81.55 mW/(m·K) (SD = 1.33 mW/[m·K]), and 86.90 mW/(m·K) (SD = 1.53 mW/[m·K]) at measuring temperatures of 10°C, 25°C, and 40°C, respectively. The thermal conductivity of the bark panels was found to increase by 6% with a 15°C temperature rise in the investigated temperature range (Fig 6). This trend was highly significant ($p < 0.001$). The average density of the investigated boards was 407 kg/m³ (SD = 24.10 kg/m³). The type of tannin used did not have a significant influence on thermal conductivity of the investigated samples.

FTIR Spectroscopy

Figures 7 and 8 show very similar trends for the two tannin extracts. The signals that were

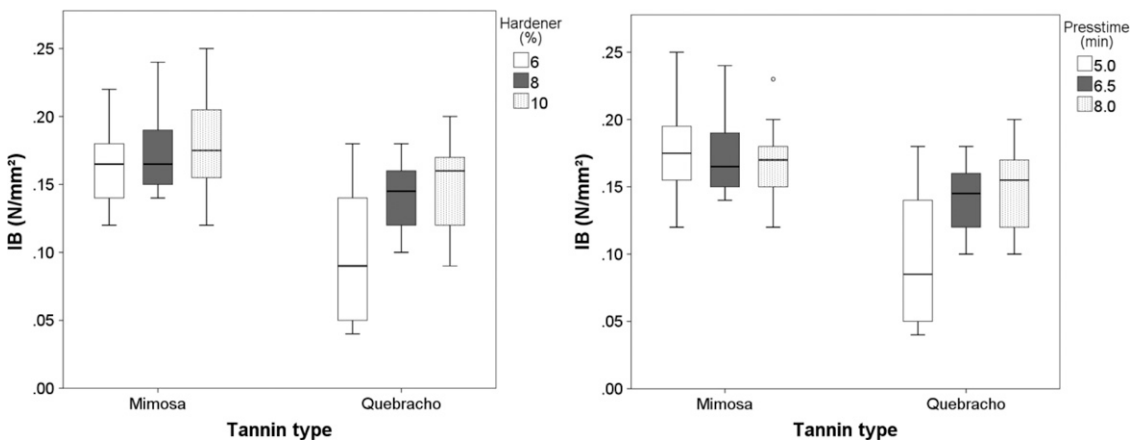


Figure 3. Effect of hardener and pressing time on IB for different tannin types.

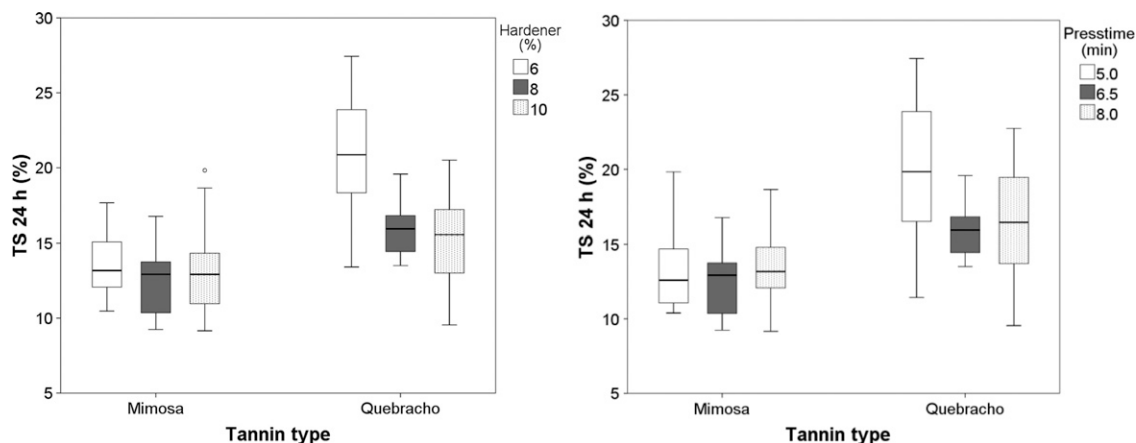


Figure 4. TS after 24 h of water immersion dependent on tannin type, hardener amount, and press time.

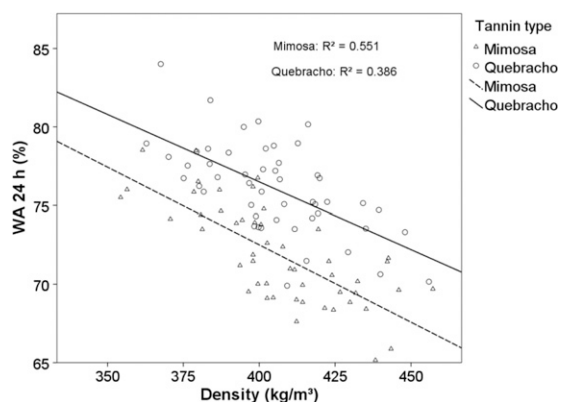


Figure 5. WA after 24 h of water immersion dependent on density and tannin type.

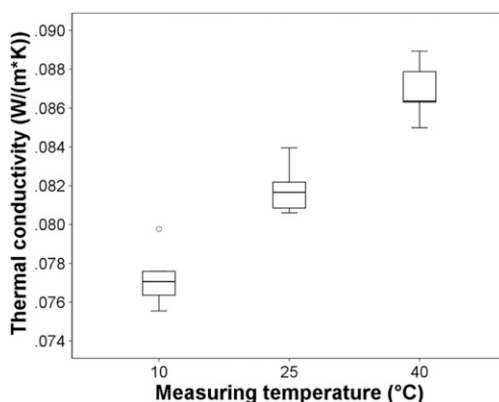


Figure 6. Dependence of thermal conductivity on measuring temperature.

modified during hexamine activation are summarized in Table 4.

The most important band after hexamine activation appears at approximately $\nu = 1650 \text{ cm}^{-1}$ (Figs 7 and 8). This absorption can be attributed to N–H bending in the nitrogen-containing adducts formed during the activation of the flavonoids. The presence of these species provides insight into the crosslinking mechanism of the polymers that occurs after activation of the aminomethylene bridges. The other signals at $\nu = 1505$, 1150 , 1110 , 1040 , and 980 cm^{-1} decreased during activation and present a smoother profile when hexamine was added. The only signal showing a different trend was that at $\nu = 1420 \text{ cm}^{-1}$,

which arose only when 10% hexamine was added. This signal might be attributed to many vibrations, but in tannins, it is probably caused by the C–H deformation of aromatic rings or the stretching of the benzene ring.

DISCUSSION

Mechanical measurements showed that mimosa tannin use resulted in higher quality board properties (MOR, IB, TS, and WA) than quebracho-tannin-bound panels. Panels using quebracho-based resin had the same IB (main characteristic for panel stability) values than those from a previous study ($\text{IB} > 0.15 \text{ N/mm}^2$

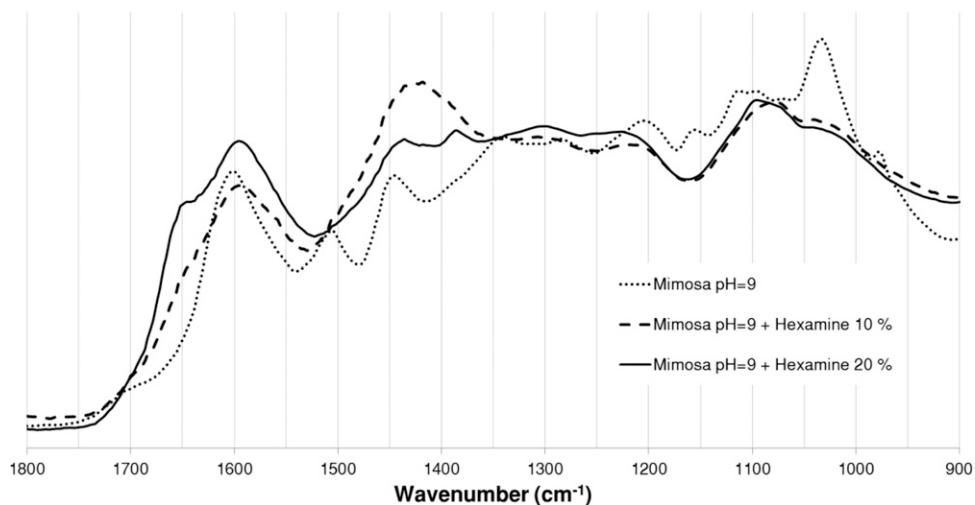


Figure 7. Absorption spectra of mimosa tannin resin at different polymerization steps.

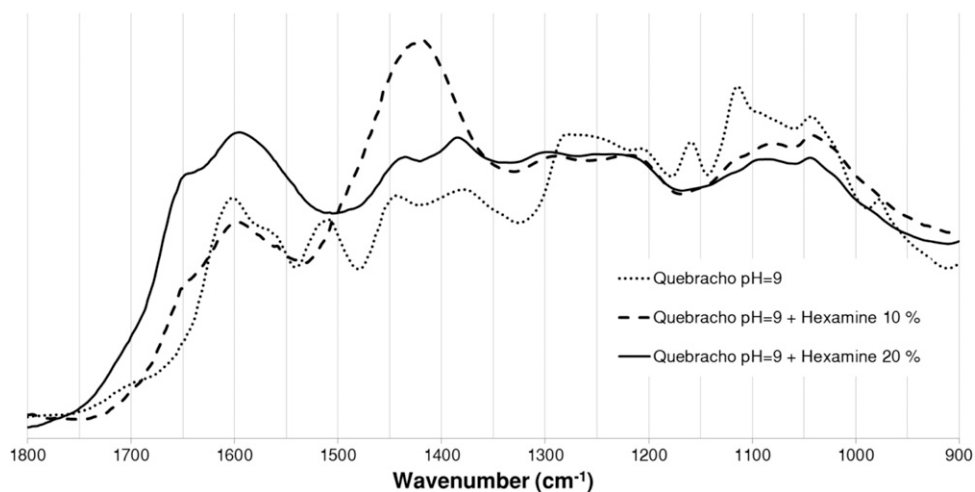


Figure 8. Absorption spectra of quebracho tannin resin at different polymerization steps.

Table 4. Band modification during hexamine activation.

Wave number (cm ⁻¹)	Mimosa			Quebracho			Attribution
	pH 9	10% hexa	20% hexa	pH 9	10% hexa	20% hexa	
1650	—	M	L	—	M	L	N-H-bend secondary amines or amides or imines (eg CH ₂ -NH-CH ₂ -; -NH-CH ₂ -NH; -NH-C(=O); -C=N-H)
1505	M	—	—	M	—	—	C=C-H str. asym. arom.
1425	—	L	—	—	L	—	C-H deform., C-C str., NH-CH ₂ -arom.
1150	S	—	—	S	—	—	C-O str. ring A, C-C bend ring A
1110	S	—	—	M	—	—	C-O str. arom.
1040	M	S	S	S	S	S	C-H bend. arom. symm. in-plane
980	S	—	—	S	—	—	C-H bend. asym. out-of-plane

L, large; M, medium; S, small.

with density of 350 kg/m^3) (Kain et al 2014), whereas mimosa resin resulted in roughly 20% greater IB values. This was probably caused by the lower viscosity of the mimosa resin (mimosa 1310 mPa and quebracho 9630 mPa initial viscosity) and a subsequently greater particle wetting.

Pichelin et al (1999) previously detailed the importance and partial problems of particle wetting using tannin-hexamine resins, which form an essentially stiff gel at ambient temperatures. This study suggests that the steric hindrance of the original quebracho flavonoid was higher than that of mimosa. This led to greater viscosities in the quebracho-glued boards and hence lower penetration into bark chips and inferior mechanical performances.

The spectroscopic study explains why no adhesion occurred when no hardener was added because the following spectra differences could be detected. The signal at $\nu = 1650 \text{ cm}^{-1}$ was typical of amino-methylene activation, and hence, it became more pronounced as hexamine was added (Pichelin et al 1999). This suggests that a higher number of crosslinks were formed when more hardener was added. The signal at $\nu = 1425 \text{ cm}^{-1}$ can also be partially attributed to the presence of amino-methylene-activated rings (Kinugasa et al 2013). The increased intensity of this signal for 10% activated substrates can be explained as a superposition of the Ar-CH₂-NH bending signal with other signals of the tannins, whereas in the spectrum of the sample containing 20% hexamine, the intensity of this band was lower because of the tightening of the structure caused by the larger number of crosslinks. When the flavonoid units were closely packed, the partial conversion of the amino-methylene bridges to simple methylene bridges (with the release of NH₃) has to be considered.

The decreases in the signals at $\nu = 1505, 1150, 1110, 1040,$ and 980 cm^{-1} can be attributed to the networking of the tannin molecules, which weakens the vibrations of the C–O and C–H bonds. The only notable difference between the two tannin species was observed at $\nu = 1040 \text{ cm}^{-1}$.

This signal can be attributed to the aromatic in-plane bending of flavonoids (Tondi and Petutschnigg 2015). Here, mimosa showed a higher absorbance than quebracho because there was more free space for vibrations of the Ar–H bonds between the flavonoid units. This can be explained by the higher degree of C4–C8 bonding in quebracho, which resulted in a more compact oligomer. This effect completely disappears after networking because the C–H in-plane bending is similarly hindered.

Macroscopically, this feature results in the lower viscosity of the mimosa tannin because of its less compact structure. The more linear quebracho tannin molecules (Pasch et al 2001) may produce a higher amount of secondary forces, resulting in a higher initial viscosity. The lower initial viscosity of mimosa tannins may result in a better penetration of wood and hence greater adhesive performance.

In panel production, the necessary press time in hot presses needs to be limited because it limits production capacities and requires a high energy input (Thoemen and Humphrey 2006). In this study, a press time of 8 min instead of 5 min was not beneficial for MOR. For IB and TS, this was also confirmed for the mimosa tannin resin, whereas the quebracho tannin resin slightly profited from a longer press time. Therefore, mimosa tannin may have had a higher reactivity.

Hexamine as a hardener is a potential source of formaldehyde emission and also is the only synthetic component in the material investigated. Therefore, minimizing the amount used without detriment to the bonding was desirable. Attempts to orient samples without hexamine showed that polymerization required it as a hardener. Although MOR was not significantly affected by different amounts of hardener, IB properties were significantly enhanced with 10% instead of 6% hexamine. Coarse particles cause a filigrane structure with low board densities, which results in a limited in-plane compression tension resistance caused by small in-plane particle contact area (Kain et al 2013b). Subsequently, MOR is not affected by better resin performance to the same

extent that IB is. For TS, an increased amount of hexamine was only beneficial for the quebracho-bound panels. This further corroborated the assumption of mimosa showing a higher reactivity toward the hardener.

Overall, the most important factor among those studied (ie tannin type, amount of hardener, and press time) was the tannin type, which accounted for between 10 and 50% of the variation in panel properties.

Thermal properties were evaluated for three mimosa-bound and three quebracho-bound boards to confirm the panel's potential for insulation use. With an average sample density of 407.07 kg/m³ (SD = 24.10 kg/m³), thermal conductivity was measured as 81.85 mW/(m·K) (SD = 1.33 mW/[m·K]). These findings are consistent with those of previous studies in which thermal conductivity values less than 0.08 W/(m·K) with densities less than 450 kg/m³ were achieved (Kain et al 2013b, 2014). With regard to temperature dependence, across the investigated range (10-40°C), thermal conductivity was shown to be significantly ($p < 0.001$, coefficient of correlation = 0.90) correlated with panel temperature. The gradient of the linear regression function for temperature-dependent thermal conductivity was 0.32. This is comparable with the slope for wood wool (0.31, 348 kg/m³) but greater than that for mineral wool (0.13, 145 kg/m³) (Abdou 2005). This finding is important because the effectiveness of insulation layers applied to limit the thermal load of, eg, buildings is also a function of the ambient temperature. From this viewpoint, the studied bark panels showed a satisfactory rather than an excellent performance.

CONCLUSIONS

Mimosa-hexamine resin was compared with quebracho-hexamine resin for potential use in binding bark insulation panels. With regard to MOR, IB, TS, and WA, mimosa tannin showed better results. This was supported by IR spectroscopic results, which indicated that the mimosa-based polymers showed a higher degree of in-plane bending and hence presumably a lower

viscosity, thereby enabling better particle wetting during resination.

For the mimosa-bound panels, a press time of 5 min (0.25 min/mm) was sufficient because the properties were not significantly improved by pressing for 6 or 10 min. In the case of quebracho tannin, the mechanical properties of the board were slightly improved with a longer press time. The amount of hexamine hardener may be maintained at 6% for mimosa tannin because no significant improvement in board properties occurred with adding 8% or 10% of hexamine. Furthermore, slight benefits from an increased amount of hardener were shown for the quebracho tannin resin.

Finally, resin formulations and press parameters can represent important aspects for optimization in the context of tannin-bound bark insulation boards. This is especially pertinent to industrial applications because decreases in resin amount and press time will directly influence the profitability of production.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Peter Graggaber Corporation (sawmill Unternberg, Austria) and UNTHA Shredding Technology Corporation (Golling, Austria).

REFERENCES

- Abdou AA (2005) Comparison of thermal conductivity measurements of building insulation materials under various operating temperatures. *J Build Phys* 29(2):171-184.
- CEN (1993a) EN 310. Engineered wood products: Determination of the modulus of rupture and the modulus of elasticity. European Committee for Standardization, Brussels, Belgium.
- CEN (1993b) EN 319. Fiberboards and particleboards: Determination of the internal bond. European Committee for Standardization, Brussels, Belgium.
- CEN (1993c) EN 317. Fiberboards and particleboards: Determination of the thickness swelling after water storage. European Committee for Standardization, Brussels, Belgium.
- CEN (1993d) EN 323. Wood-based panels: Determination of density. European Committee for Standardization, Brussels, Belgium.
- CEN (1993e) EN 322. Wood-based panels: Determination of moisture content. European Committee for Standardization, Brussels, Belgium.

- CEN (1994) EN 326-1. Engineered wood products: Sampling, blanking and supervision, part 1: Sampling and cutting of specimens and analysis of results. European Committee for Standardization, Brussels, Belgium.
- CEN (2001) EN 12667. Determination of the thermal resistance with the panel and heat flow panel measuring device. European Committee for Standardization, Brussels, Belgium.
- Garnier S, Pizzi A, Huang Z (2002) Dry I.B. forecasting of commercial tannin adhesives-bonded particleboard by TMA bending. *Eur J Wood Prod* 60(5):372.
- Hartung J, Elpelt B, Klösener K (1995) Statistik. 10th ed. R. Oldenbourg, München, Germany.
- Kain G, Barbu M, Hinterreiter S, Richter K, Petutschnigg A (2013a) Using bark as heat insulation material. *Bioresources* 8(3):3718-3731.
- Kain G, Barbu M, Teischinger A, Musso M, Petutschnigg A (2013b) Substantial bark use as insulation material. *Forest Prod J* 62(6):480-487.
- Kain G, Charwat-Pessler J, Barbu M, Plank B, Richter K, Petutschnigg A (2015) Analyzing wood bark insulation board structure using X-ray computed tomography and modeling its thermal conductivity by means of finite difference method. *J Composite Mater* (in press).
- Kain G, Güttler V, Barbu M, Petutschnigg A, Richter K, Tondi G (2014) Density related properties of bark insulation boards bonded with tannin hexamine resin. *Eur J Wood Prod* 72(4):417-424.
- Kinugasa S, Tanabe K, Tamura T (2013) Spectral database for organic compounds SDBS, National Institute of Advanced Industrial Science and Technology. http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_search.cgi (12 May 2015).
- Moubarik A, Charrier B, Allal A, Charrier F, Pizzi A (2010) Development and optimization of a new formaldehyde-free cornstarch and tannin wood adhesive. *Eur J Wood Prod* 68(2):167-177.
- Pasch H, Pizzi A, Rode K (2001) MALDI-TOF mass spectrometry of polyflavonoid tannins. *Polymer (Guildf)* 42(18):7531-7539.
- Pena C, Caba K, Retegi A, Ocando C, Labidi J, Echeverria J, Modragon I (2009) Mimosin and chestnut tannin extractives reacted with hexamine in solution. *J Therm Anal Calorim* 96(2):515-521.
- Pichelin F, Kamoun C, Pizzi A (1999) Hexamine hardener behavior: Effects on wood glueing, tannin and other adhesives. *Eur J Wood Prod* 57:305-317.
- Pichelin F, Nakatani M, Pizzi A, Wieland S, Despres A (2006) Structural beams from thick wood panels bonded industrially with formaldehyde-free tannin adhesives. *Forest Prod J* 56(5):31-36.
- Pizzi A (1994) Hardening mechanism of tannin adhesives with hexamine. *Eur J Wood Prod* 52:229.
- Pizzi A (1982) Pine tannin adhesives for particleboard. *Eur J Wood Prod* 40:293-301.
- Pizzi A, Stracke P, Trosa A (1997) Industrial tannin/hexamine low-emission exterior particleboards. *Eur J Wood Prod* 55:168.
- Thoemen H, Humphrey PE (2006) Modeling the physical processes relevant during hot pressing of wood-based composites. Part I. Heat and mass transfer. *Eur J Wood Prod* 64(1):1-10.
- Tondi G, Petutschnigg A (2015) Middle infrared (ATR FT-MIR) characterization of industrial tannin extracts. *Ind Crops Prod* 65:422-428.
- Tondi G, Wieland S, Wimmer T, Schnabel T, Petutschnigg A (2012) Starch-sugar synergy in wood adhesion science: Basic studies and particleboard production. *Eur J Wood Prod* 70(1-3):271-278.
- Umamura K, Sugihara O, Kawai S (2014) Investigation of a new natural adhesive composed of citric acid and sucrose for particleboard II: Effects of board density and pressing temperature. *J Wood Sci* 61(1):40-44.
- Vaucher H (1997) Baumrinden: Aussehen, Struktur, Funktion, Eigenschaften. Naturbuch-Verlag, Augsburg, Germany.
- World Health Organization (2006) IARC monographs on the evaluation of carcinogenic risks to humans. Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxypropan-2-ol. Vol. 88. WHO Press, Geneva, Switzerland.