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Short Communication

Processing conditions analysis of *Eucalyptus globulus* plywood bonded with resol-tannin adhesives

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Abstract

Phenol-formaldehyde resol containing mimosa tannin extract was employed to produce plywood panels with two plies from *Eucalyptus globulus* veneers. The effect of processing conditions and tannin content on the gelation time of the adhesive in the glue line was evaluated by dynamic-mechanical analysis (DMA). These results were related with shear strength and wood failure of glue line in the final panels. Hazardous petrochemical phenol could be partially substituted in resols in industrial applications by addition of mimosa tannin extracts.

Keywords: Plywood; Adhesive resol; Tannin

1. Introduction

Phenol-formaldehyde (PF) resins are the most commonly used structural adhesives for outdoor purposes due to their good bonding ability with different lignocellulosic substrates, water resistance and low initial viscosity (Pizzi, 1993). The high fluidity of PF resols favors the spreading of the resin on the veneer surface with relatively low migration into the wood, thus enhancing the mechanical bond between the wood and adhesive (Vázquez et al., 1996; Gornik et al., 2000). Particularly, PF resols require veneer moisture content lower than 5% in order to avoid undesirable foaming process during industrial pressing operations (Vázquez et al., 1996; Gornik et al., 2000). Liu and Rials (1998) proposed that the lower bonding strength of such kind of wood with PF may be attributed to the migration of very small amounts of extractives, including saturated fatty acid and terpenes which are known to delay the curing and setting of phenolic and urea resins adhesives (Nussbaum, 1999; Aydin and Colakoglu, 2007).

Polyphenolic compounds of bark extracts have been used as accelerators of PF resins in particleboard and plywood manufacture due to their ability of reducing gelation and pressing time (Vázquez et al., 1996, 2002, 2006; Trosa and Pizzi, 1997; Nemli et al., 2004; Calve et al., 1996). Tannins are complex phenolic compounds of two main categories: hydrolysable and condensable tannins. Tannins have higher reactivity with formaldehyde than phenol, thus adhesives produced from tannin, if properly cured, give nearly zero formaldehyde emission (Bisanda et al., 2003; Joseph et al., 1996). This capability can be used to accelerate curing reactions and to reduce formaldehyde emission which is one of the major requirements for indoor grade panels (Kim and Kim, 2004). In addition, PF-tannin adhesives can reduce the tendency of resin to migrate to the

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interior of high-moisture veneers due to the broader molecular weight distribution of tannin-based adhesives (Steiner et al., 1993).

The aim of the present work is to substitute as much as possible phenol content in classic resol formulations by adding tannin extracts in order to use this tannin-based adhesive in the manufacture of two-ply panels based on high moisture content veneer (around 10 wt%) of *Eucalyptus globulus.* Bonding ability was evaluated from wood failure and shear strength measurements. The hardening reaction of adhesive in the wood joint was followed by dynamic-mechanical analysis (DMA).

2. Experimental

Commercial phenol-formaldehyde (PF) resol with F/P molar ratio 2.2, solid content 48 wt% and pH 12, was provided by Hexion Specialty Chemicals Ibérica S.A. (Spain). Wood tannin extract (*Acacia mearnsi,* mimosa) was supplied by Indunor, Argentina. Tannin extract was dissolved in 0.1 M NaOH solution to achieve 40 wt% solid. PF-tannin mixtures (PFT) were prepared from tannin solution and PF resol by mechanical stirring during 15 min at 25 °C in order to obtain tannin:resol solid ratios of 0:100, 15:85, and 30:70 (based on weight basis). The initial viscosity of the obtained PFT mixtures was determined at 25 °C with a Brookfield LV DV-I viscometer. Viscosity values determined at 30 rpm stirring rate were 510, 560 and 570 MPa s, respectively.

Two-ply panels were prepared using *E. globulus* veneer (Prodema, Spain), of dimensions 400 mm × 400 mm × 1.3 mm and 10 wt% moisture content (on dry basis). Tannin introduction in the formulation permits to increase moisture content with respect to neat phenolic resol resins. Approximately 16 g adhesive was spread with a brush on the single surface of each veneer. Mean adhesive consumption was 200 g/m^2. In order to prevent excessive losses of the adhesive by squeezing during the press stage, the impregnated veneers were exposed to two pre-assembly conditions: a) 24 h at 20 °C and b) 15 min at 70 °C. The veneers were joined together in the direction of the wood grains and pressed at 1.55 MPa during 20 min at two different temperatures: 130 and 160 °C. Three replicates of each PFT mixture, pre-assembly conditions and cure temperature were prepared.

Shear test was performed by tension loading to failure to evaluate the bonding strength of the panels, using a testing machine Instron 4467 at a cross-head rate of 1 mm/min according to the procedure described in the ASTM D 2339-98 (2004). Bonding quality was evaluated from the percentage of wood failure at the bonding area (w) and the shear strength (f_v) of each specimen. Two different treatments were applied before testing. Treatment I: 7 days at 20 ± 2 °C and 65 ± 5% relative humidity (RH); treatment II: 7 days at 20 ± 2 °C and 65 ± 5% RH followed by 48 h of immersion in cold water (20 °C), followed by 7 days at 20 ± 2 °C and 65 ± 5% RH.

Dynamic mechanical properties were analyzed in a Metravib viscoanalyser using a bending device, at a frequency of 10 Hz and at constant amplitude of 0.1 V. An initial displacement of 100 μm was applied to ensure contact between sample and geometry. The hardening reaction of adhesive in the wood joint was evaluated by following the variation of the storage modulus (E') with time (t), according to a modification of the procedure reported elsewhere (Onic et al., 1998). Two plies of wood, each of dimension 60 mm × 10 mm × 1.3 mm were impregnated with PFT adhesive and exposed to the same pre-assembly conditions as those described for board manufacture. Normalized storage modulus (E'_n) was expressed as follows:

$$E'_n = \frac{E' - E'_{\min}}{E'_{\max} - E'_{\min}} \tag{1}$$

where $E'_{\min}$and ($E'_{\max}$) are the maximum and minimum value of storage modulus. For comparing purposes two parameters have been used: the gelation time (t_{gel}), which corresponds to the time at which the (E'_n) abruptly increases, and half-time of curing reaction ($t_{\mathrm{En}=1/2}$) determined at ($E'_n = 0.5$). Presented results are the average of three measurements.

3. Results and discussion

For traditional plywood manufacture with PF resols adhesive, required veneer moisture content must be lower than 5 wt% and fail with some relatively high density woods such as *Eucalyptus pilularis* and *E. globulus* (Vázquez et al., 1996; Gornik et al., 2000). In this work, veneer moisture is 10 wt%. Then, in order to reduce water content and avoid undesirable side-reactions during the press step, the impregnated veneers were pre-dried before pressing. The effect of the pre-assembly conditions on the gelation time was evaluated by measuring the variation of the storage modulus with time.

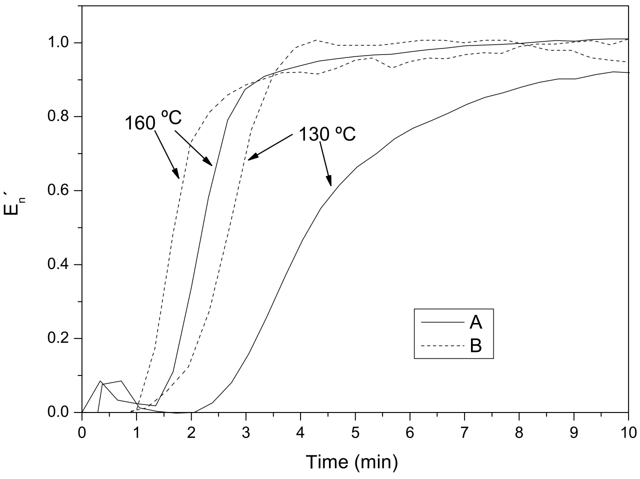

Fig. 1. Normalized storage modulus versus time of neat resol samples. Solid line: (A) pre-assembly condition – 24 h at 20 °C; Dash line: (B) pre-assembly condition – 15 min at 70 °C.

Table 1
Shear strength and wood failure for the two-ply boards bonded with resol as a function of different processing conditions

Pre-assembly conditions	Pressing conditions			Dry		Cold water	
	P (MPa)	T (°C)	t (min)	f_v (MPa)	w (%)	f_v (MPa)	w (%)
20 °C, 1440 min (resol)	1.55	130	20	7.6 ± 1.7	76	6.9 ± 0.6	90
	1.55	160	20	7.5 ± 1.8	75	5.9 ± 1.3	63
70 °C, 15 min (resol)	1.55	130	20	9.0 ± 1.1	62	8.2 ± 1.1	65
	1.55	160	20	8.0 ± 1.0	37	7.1 ± 1.5	66

f_v: shear strength mean value.
w: wood failure mean value.

Fig. 1 shows the normalized storage modulus determined for the two pre-assembly conditions followed by two isothermal treatments at 130 and 160 °C, which correspond to the press temperatures used for manufacturing the panels. All experimental curves show a similar behaviour: initially, E′ remains low due to the low viscosity of the adhesive. At this stage, the adhesive can not transfer the stresses applied from the lower to the upper layer of the joint and hence the overall rigidity observed is governed by the behaviour of the lower layer. At gelation time, E'_n increases up to reach a constant value at which vitrification of the adhesive takes place ($E'_n = 1$). The application of higher temperature and shorter time during the pre-assembly stage results in a reduction of t_{gel} and $t_{\mathrm{En}=1/2}$, when compared with values obtained by applying long open times and room temperature, i.e. $t_{\mathrm{En}=1/2}$ decreases from 250 to 160 s at 130 °C.

Table 1 summarizes the bonding quality of PF bonded panels obtained under the pre-assembly conditions, press temperatures and treatments before testing. Pre-assembly at 70 °C and 15 min conducts to panels with improved shear strength. The f_v values increase about 19% for panels cured at 130 °C exposed to both treatments (dry and cold water), whereas f_v and wood failure values slightly decrease at 160 °C. This may be ascribed to the short t_{gel} (lower than 1 min) at the higher cure temperature. This condition restricts the mechanical anchorage of the adhesive into the substrate during the press stage lowering its bonding ability. As a consequence of higher shear strength of glue line by using the pre-assembly condition of 70 °C during 15 min, this last was selected to produce panels with PF adhesive modified with different amounts of mimosa tannin.

The addition of tannins resulted in increase of the curing rate as evidenced by DMA results (see Fig. 2). Indeed, the addition of tannins produce a decrease in $t_{\mathrm{En}0.5}$ from 162 s for neat PF to 130 s for 30% PFT. However, the increase in press temperature up to 160 °C did not show a noticeable effect in t_{gel} and $t_{\mathrm{En}=1/2}$. This fact may be ascribed to the increased reaction rate due to the combined effect of rising temperature and adding tannins.

The addition of tannins does not have a significant effect on the final properties of PFT bonded panels, as concluded from the analysis of Table 2. For 130 °C, PFT bonded panels show f_v values similar to those obtained for PF panels. As a general trend, shear strength decreased as the severity of the test treatment increased from dry to cold water, meanwhile there were no significant differences between boards as regards the average extent of wood failure at the bonding area. The main difference observed for PFT bonded samples pretreated at 160 °C was the drop in the wood failure at the bonding area whatever the treatment applied. As it can be observed in Fig. 2, the $t_{\mathrm{En}0.5}$ at 160 °C is lower than 1 min. This condition restricts the diffusion of PFT adhesive into the wood microstructure,

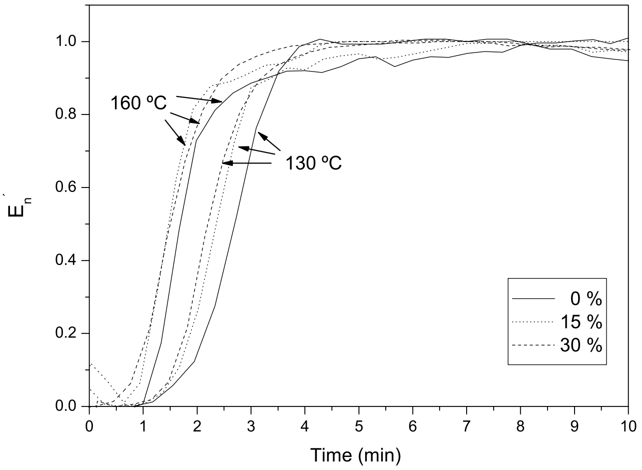

Fig. 2. Normalized storage modulus versus time of samples prepared with tannin content at different curing temperatures. In all samples the B pre-assembly condition was used – 15 min at 70 °C.

Table 2
Shear strength and wood failure for the two-ply bonded PFT boards as a function of different processing conditions and tannin content

Pre-assembly conditions	Pressing conditions			Dry		Cold water	
	P (MPa)	T (°C)	t (min)	f_v (MPa)	w (%)	f_v (MPa)	w (%)
70 °C, 15 min (15% tannin)	1.55	130	20	8.7 ± 1.0	66	7.8 ± 1.8	60
	1.55	160	20	8.1 ± 1.1	14	6.7 ± 1.7	44
70 °C, 15 min (30% tannin)	1.55	130	20	8.6 ± 0.5	69	7.7 ± 0.6	72
	1.55	160	20	7.8 ± 1.8	26	6.9 ± 2.1	18

reducing the adhesion through mechanical interlocking, resulting in a lower glue line strength.

4. Conclusions

Tannin–phenol-formaldehyde mixtures were successfully used to bond together two-ply panels based on *E. globulus*. The addition of mimosa tannin extract to phenol-formaldehyde resol induced a reduction in gelation time with comparable final properties to those obtained for PF-bonded panels.

On the other hand, using of isothermal DMA measurements for determination of gelation time and half-time of adhesive in the wood joint from isothermal DMA measurements resulted to be an efficient technique for evaluating the rate of curing reactions under assembly conditions currently used in industrial applications.

The results obtained therein allow one to conclude that wood panels with similar properties may be obtained by replacing hazardous phenol by tannins, with the additional advantage of leading more eco-friendly products.

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