

# ALKALINE TREATMENT OF SULFITED TANNIN-BASED ADHESIVE FROM MANGROVE TO INCREASE BOND INTEGRITY OF BEECH SLIPS

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Received April 2005

**PARIDAH, M. T. & MUSGRAVE, O. C. 2006. Alkaline treatment of sulfited tannin-based adhesive from mangrove to increase bond integrity of beech slips.** Sulfited tannin solutions were prepared by extracting *Rhizophora mucronata* and *R. apiculata* barks with 4% aqueous sodium sulfite and 0.4% aqueous sodium carbonate at 100 °C for two hours. The sulfited tannin solutions were pre-treated with 50% sodium hydroxide at various amounts, and kept at 1 min, 5 min, 60 min or 24 hours prior to mixing with phenol resorcinol formaldehyde (PRF) resin for bonding beech slips. Two types of bonding techniques were used: (1) normal, one-component and (2) honeymoon, two-component adhesive mixtures. The adhesive mixtures were evaluated for pH, water resistance property and gel time. The bond integrity of the jointed beech slips was assessed based on shear strength and wood failure percentage. The study showed that the amount of aqueous sodium hydroxide added to the sulfited-tannin solution had significant effects on viscosities of the final adhesive mix, consequently influencing the penetration of the adhesive into the wood surface. The amount of sodium hydroxide used depended on the type of tannin; *R. mucronata* tannin adhesive required 2–4% and *R. apiculata* 0–2%. However, the viscosity of adhesive made from mixed *R. mucronata*-*R. apiculata* tannin was not affected by the amount of sodium hydroxide added. The pre-treatment with sodium hydroxide had successfully increased the gel time of this adhesive to an acceptable working condition for honeymoon bonding technique. This technique improved the gluebond quality of the PRF-sulfited tannin-bonded joints by at least 20%.

Keywords: Alkaline sulfited tannin, honeymoon joints, gel time, lapse time, water resistance

**PARIDAH, M. T. & MUSGRAVE, O. C. 2005. Rawatan alkali terhadap perekat sulfit tanin daripada bakau bagi menambah integriti rekatan kepingan bic.** Tanin sulfit disediakan melalui pengekstrakan kulit pokok *Rhizophora mucronata* dan *R. apiculata* menggunakan 4% natrium sulfit akues dan 0.4% natrium karbonat akues pada suhu 100 °C selama dua jam. Larutan tanin sulfit kemudiannya dicampurkan 50% natrium hidroksida pada jumlah yang berbeza dan disimpan selama 1 minit, 5 minit, 60 minit dan 24 jam sebelum dicampurkan dengan perekat fenol resorsinol formaldehid (PRF) bagi ujian rekatan menggunakan kayu bic. Dua teknik rekatan digunakan iaitu campuran perekat (1) biasa yang mempunyai satu komponen dan (2) honeymoon dengan dua komponen. Integriti rekatan kayu bic yang telah direkat dinilai dengan menguji sifat ketahanan terhadap air, kekuatan ricih dan peratusan kegagalan kayu. Kajian menunjukkan bahawa jumlah akues natrium hidroksida yang dicampurkan itu memberi kesan signifikan terhadap kelikatan akhir campuran perekat, seterusnya mempengaruhi penembusan perekat ke dalam permukaan kayu. Jumlah natrium hidroksida yang dicampurkan bergantung pada jenis tanin yang digunakan: perekat berasaskan tanin *R. mucronata* memerlukan 2–4% dan *R. apiculata* 0–2%. Sementara itu, kelikatan perekat yang diperbuat daripada campuran tanin *R. mucronata*-*R. apiculata* tidak dipengaruhi oleh jumlah natrium hidroksida yang dicampurkan. Rawatan awal menggunakan natrium hidroksida telah berjaya menambah masa gel bagi perekat ini ke tahap yang bersesuaian dengan teknik rekatan honeymoon. Teknik ini telah meningkatkan kualiti rekatan PRF-sulfit tanin sebanyak sekurang-kurangnya 20%.

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## INTRODUCTION

Sulfited condensed tannins are potentially useful in wood adhesives. The sulfite treatment improves extraction yield by removing nonphenolic materials such as uronic acids and fats, waxes that adversely affect the adhesive properties. They are more water-soluble and are less viscous. The resulting tannins are reactive in condensations with formaldehyde and could, in principle, replace some of the phenol in phenol formaldehyde resins and some of the resorcinol in phenol resorcinol formaldehyde (PRF) resins.

Conifer tannins are noted for their extremely high reactivity toward formaldehyde. Application of tannin-based cold-setting adhesives was made possible when the concept of 'honeymoon' adhesives (i.e. two-component adhesives) was applied to laminating and end-jointing adhesives using this class of tannin. Similar applications can be envisaged for mangrove bark extracts since it belongs to the same class as conifer tannin, i.e. having a 5,7-dihydroxylated A-ring.

Mangrove trees, in particular *Rhizophora mucronata* and *R. apiculata*, have substantial amount of tannin. Barks of these trees can yield 26% tannin using sulfite as extraction medium (Paridah & Musgrave 1999). This amount is comparable with those obtained from quebracho (26–29%), mimosa (30–33%) and radiata pine (13–15%) tannins (Pizzi 1989). These tannins have been extensively studied and some, namely, mimosa and pine tannins, have gained commercial importance as wood adhesives.

### Alkaline treatment of sulfited tannin

The use of sulfited pine tannins in wood adhesives is often considered to result in poor water resistance of gluelines because of the presence of sulfonic acid groups at C-4 of the phenolic A-ring. However, this C-4 sulfonic acid group can be removed by a base-catalyzed desulfonation reaction (i.e. alkaline treatment) to produce an intermediate functional group in the adhesive system that will give water-resistant gluelines. The reaction is rapid and can be carried out at pH 8.0–10.0 at ambient temperature. Such reaction reduces the molecular weight and improves the viscosity and solubility of the resulting tannin solution through removal of the sulfonic acid function. The final tannin solution could then easily react with

formaldehyde to give materials that are more insoluble in water (Hemingway 1989, Bae *et al.* 1994). Mangrove tannin, having a similar type of structure, except for the extra hydroxy group present in the B-ring, behaves in a generally similar manner because the B-ring does not play an important part in these reactions (Laks 1989).

Viscosity of alkaline tannin solution was found to be the dominant factor affecting the wetting, spreading and transfer of adhesive on wood surfaces. Viscosity is markedly influenced by the alkali mix lapse time, i.e. the period between the addition of aqueous sodium hydroxide to the solution of the sulfited tannin and the addition of PRF resin, hardener and paraformaldehyde to that solution. It has been reported that the ideal lapse time for conifer tannin should be between 1 and 24 hours and that the sodium hydroxide concentration should be below 13% in order to produce an alkaline sulfited tannin adhesive having an acceptably long gelation time (McGraw *et al.* 1988). Using lapse times of < 20 min, the viscosities of the 2% alkaline sulfited tannin for *Rhizophora mucronata*, *R. apiculata* and *R. mucronata-R. apiculata* mixture increased to 1500, 950 and 1000 cP (Paridah 1995). These values increased between 7 to 12 times when the amount of caustic was increased to 6% (w/w). This experiment was thus carried out to determine the effects of sodium hydroxide addition on the final viscosity of the adhesive mixtures and bond integrity of beech slips bonded with them. The present work also examined the effects of alkaline treatment on gel time of sulfited mangrove tannin and on water resistance of the resulting glue bond. The effect of alkaline mix lapse time was also discussed.

## MATERIALS AND METHODS

### Preparation of sulfited tannin

Finely ground barks (100 g) from 15-year-old *R. mucronata* and *R. apiculata* trees were boiled with water (600 g) containing anhydrous  $\text{Na}_2\text{SO}_3$  (4.0 g) and anhydrous  $\text{Na}_2\text{CO}_3$  (0.4 g) for two hours (Paridah & Musgrave 1999). Bark particles of diameters > 0.075 mm and < 0.8 mm were used. The tannin solutions were filtered under reduced pressure using sintered glass filters (porosity 3). Portions of the resulting solutions were then evaporated under reduced pressure using a rotary evaporator at 50 °C and 20 mm Hg until

the concentration of the sulfited tannin solution reached approximately 30–40%. The solution was then spray dried and kept in an air tight plastic container.

### Preparation of alkaline sulfited tannin-PRF adhesive

Three types of alkaline sulfited tannins were prepared: *R. mucronata* (MU), *R. apiculata* (AP), and *R. mucronata-R. apiculata* (MA) mixture. Sulfited tannin solution (40%, w/w) was prepared by mixing sulfited tannin powder in water. The alkaline sulfited tannin was prepared by adding 0, 4, 8 and 16% aqueous sodium hydroxide (50%, w/v) to the sulfited-tannin solution. The alkali sulfite-tannin solutions were then kept for 5 min lapse time prior to mixing with PRF (56% solids) resin and hardener (named as Formulation 1). The adhesive mixtures were evaluated for gel time, pH, water resistance and pot life. The pot life was recorded at 22 °C by measuring the time (min) for the adhesive to harden.

### Gluing of beech slips

The alkaline sulfited-tannin solutions were prepared according to the methods described earlier, but the amounts of sodium hydroxide added were varied from 2 to 8%. European beech (*Fagus sylvatica*) was used to measure the performance of the sulfited tannin-based adhesive joints according to BS 1204 1979. Two types of bonding techniques were used to bond the beech slips: (1) normal, i.e. having one component only and (2) honeymoon, two-component adhesive mixtures. The adhesive (i.e. Formulation 2) for normal, one-component bonding technique was prepared by mixing all the ingredients after 1 min, 60 min or 24 hours alkali lapse times. The adhesives used for the honeymoon gluing study (i.e. Formulation 3) were prepared in two components: (1) Component A (comprising alkaline sulfited tannin and paraformaldehyde) and (2) Component B (phenol resorcinol formaldehyde resin and hardener). The amount of paraformaldehyde was about 50% w/w of the hardener. In honeymoon jointing, the alkaline sulfited tannin solutions were kept for 1 min, 60 min or 24 hours lapse time prior to mixing with paraformaldehyde

(Component A). Following this, Component B was prepared by mixing PRF resin (56% solids) and hardener. The alkali lapse time was measured from the time the alkaline sulfited tannin was prepared to the time when both wood surfaces (each was spread with either component A or B) were clamped. Details of the variables used in the study are summarized in Table 1.

Four types of adhesives (PRF, PRF-MU, PRF-AP, and PRF-MA) were used to make the glue joints. The moisture content of the beech slips (thin strips of wood measuring 12.5 × 2.5 × 0.3 cm) was maintained at about 10% and glued with a 2.5 × 2.5 cm overlap parallel to the timber grain. The adhesive was spread at a rate of 340 g m<sup>-2</sup> (double glue line) and the assembly time was set at 10 min after which the joints were clamped at finger tight for 20 hours at 18–20 °C. The glued slips were conditioned for a week at 20 °C and 65% relative humidity. The joints were tested according to procedures specified in BS1204 1979 (Synthetic resins for wood. Phenolics and Aminoplastics Part 2: Close contact adhesives). The gluelines were cured using two curing temperatures, namely 20 and 40 °C. Components A and B were applied on separate surfaces at a spread rate of 170 g m<sup>-2</sup> (single glue line). Five replicates were produced for each type of adhesive. The performance of the adhesives and the effects of alkali mix lapse time on shear strength and wood failure percentage were examined. The shear reduction was then calculated as follows:

$$\text{Shear reduction} = \frac{(\text{Initial shear strength} - \text{final shear strength})}{\text{Initial shear strength}} \times 100$$

### Determination of gel time

Gel time of the adhesive were determined by stirring the adhesive mixture with a glass rod until it became a smooth syrup and was then kept at room temperature (25 °C). The gelation time, i.e. the time required for the adhesive to gel or harden was taken; this would be when the glass rod could not be pulled out of the mixture.

### Assessment of water resistance of adhesive

The cured resin (1 g) was finely ground, mixed with 5 ml water, and kept for five days. Water resistance property was judged by the appearance

**Table 1** Adhesive formulations and parameters used according to the types of adhesive prepared

Type of adhesive mixture	Ingredient parts by weight				Added 50% sodium hydroxide (%)	Alkali lapse time (min)
	Alkaline sulfited tannin, 40%	Para-formaldehyde	PRF, 56%	Hardener		
Formulation 1 PRF-sulfited tannin (One component)	35	-	25	2.4	0, 4, 8, 16	5
Formulation 2 PRF-sulfited tannin (One component)	15	1.1	10.7	2.1	2, 4, 5, 6, 8	1, 60, 1440
Formulation 3 PRF-sulfited tannin (Two component)	15 (Component A)	1.1 (Component A)	10.7 (Component B)	2.1 (Component B)	2, 4, 5, 6, 8	1, 60, 1440

of water whether clear (1), traces of colour(2), slight coloration (3), or brownish colour (4). Discoloration in the cured resin solution shows that the resin has not been fully cured and that the phenolic resin is being solubilized in the water. Darker colour indicates the extent of the uncured resin being solubilized.

## RESULTS AND DISCUSSION

### Effects of sodium hydroxide on the properties of PRF-sulfited tannin adhesives

The study indicated that the amount of aqueous sodium hydroxide added to the tannin solution greatly influenced the viscosities of resulting adhesives and that this amount depended on the type of tannin used (Table 1). *Rhizophora mucronata* tannin adhesive required an addition of 2–4% aqueous alkali to produce workable viscosities (< 1000 cP) while *R. apiculata* tannin adhesive needed < 2%. The viscosity of *R. mucronata-R. apiculata* tannin adhesive was less affected by the alkali added. Both *R. mucronata* and *R. mucronata-R. apiculata* tannins gave smooth syrups while *R. apiculata* tannin produced a lumpy paste. The adhesive mixtures prepared from the former had very high viscosities (> 5000 cP) while that from the latter had low, about 2200 cP.

The effects of the amount of sodium hydroxide on pH and pot life of the adhesive mixture and water resistance of the cured resin are shown in Table 2. There was no apparent effect on pH of the alkaline tannin solution when  $\geq 8\%$  sodium hydroxide was added to the

aqueous tannin solution. The pH values increased markedly (from pH < 6.0 to > 9.0) as 4% sodium hydroxide was added but beyond this, marginal increments in pH were recorded. The final pH values after 16% sodium hydroxide was added for all three types of tannin solutions were 10.8, 10.9 and 10.6 for *R. mucronata*, *R. apiculata* and *R. mucronata-R. apiculata* mixture respectively.

Similar effects were noted for pot life of the tannin adhesives. For instance, at  $\leq 4\%$  sodium hydroxide, pot life values of the tannin adhesives were longer than 240 min whilst at  $\geq 8\%$  pot life of the adhesives was markedly shortened, i.e. average of 180 min (Table 2).

The use of larger (8 and 16% w/w) concentrations of sodium hydroxide did not appreciably improve water resistance of the joints which utilized *R. mucronata* and *R. mucronata-R. apiculata* tannins. With *R. apiculata* tannin, the improvement was more apparent. Treating the 40% *R. apiculata* tannin solution with at least 8% sodium hydroxide improved water resistance of glued joints from rank 4 (brownish) to 2 (traces of colour) (Table 2).

The effects of alkali mix lapse time on the gelation times of the sulfited tannin adhesives are shown in Table 3. At higher sodium hydroxide concentrations, namely, 6 and 8%, the gelation times were much shorter for all the adhesives, especially those prepared using the one-minute lapse time. One-hour lapse times produced marked increase in gelation times but 24-hour lapse times resulted only in small further changes. With sodium hydroxide concentration of 4% or less, *R. mucronata* tannin produced the longest gelation time and *R. apiculata* tannin, the

**Table 2** Effects of aqueous sodium hydroxide on the physical properties of PRF-sulfited tannin adhesive

Adhesive type <sup>1</sup>	Amount of added aqueous sodium hydroxide (50%)											
	0%			4%			8%			16%		
	pH	PL (min)	WR <sup>2</sup>	pH	PL (min)	WR	pH	PL (min)	WR	pH	PL (min)	WR
PRF-MU	5.4	462	2	9.2	470	2	10.6	188	3	10.8	177	2
PRF-AP	6.1	465	4	9.0	305	4	10.6	217	2	10.9	203	3
PRF-MA	5.7	460	2	9.1	241	2	10.7	185	3	10.6	174	2

<sup>1</sup>MU = *R. mucronata*, AP = *R. apiculata*, MA = *R. mucronata-R. apiculata*<sup>2</sup>WR = Water resistance. 1 = clear; 2 = traces of colour; 3 = Slight coloration; 4 = brownish colour**Table 3** Effects of aqueous sodium hydroxide and lapse times on pH and gelation time of PRF-sulfited mangrove tannin adhesives<sup>1</sup>

Sodium hydroxide (%)	Lapse time	PRF-MU		PRF-AP		PRF-MA	
		pH	Gel time (min)	pH	Gel time (min)	pH	Gel time (min)
2	1 min		250		123		103
	60 min	7.4	273	7.4	278	7.2	172
	24 hours		300		293		192
4	1 min		216		101		104
	60 min	7.6	240	7.8	201	7.8	160
	24 hours		262		253		180
5	1 min		110		90		90
	60 min	8.2	138	8.3	140	8.2	138
	24 hours		152		160		150
6	1 min		90		75		64
	60 min	8.3	140	9.0	88	8.8	70
	24 hours		160		95		84
8	1 min		61		72		63
	60 min	9.0	88	9.4	85	9.2	82
	24 hours		79		91		91

<sup>1</sup>MU = *R. mucronata*, AP = *R. apiculata*, MA = *R. mucronata-R. apiculata*

shortest but this order was not maintained at higher alkali concentrations. In the presence of 5% aqueous sodium hydroxide, all lapse times used in this study produced gelation times of less than three hours. Longer gel times were recorded when lower concentrations were used. The results suggest that for successful incorporation of sulfited tannins into adhesives, it is essential to keep careful control of the pH of alkaline tannin solutions and of the lapse times in order to restrict the extent of rearrangement of phloroglucinol groups. If treated appropriately the tannin will retain sufficient phloroglucinol functionality to permit rapid cross-linking with

the PRF resin. The pH values of the various adhesive mixtures are in agreement with previous observations by Kreibich (1992). At pH > 8.0 with lapse times of one hour or more, mangrove tannin sulfonates lost their sulfonate groups and the products then polymerized rapidly. Subsequent addition of aqueous to the PRF resin or paraformaldehyde mixture led to further condensation, producing water-insoluble adhesive.

The concentration of aqueous sodium hydroxide present in alkaline sulfited tannin solutions also greatly influenced the gelation rate of the resulting PRF-sulfited tannin adhesives.

The addition of 5% aqueous sodium hydroxide lowered the rate of gelation so that efficient use of such tannin extracts in wood adhesives was possible. The effects of lapse time on gelation time of sulfited tannin from mangrove bark were more noticeable when aqueous sodium hydroxide with concentrations of 4% and lower were used.

In summary, two factors that caused the viscosity of sulfited tannin adhesives to be particularly high are (1) the amount of aqueous sodium hydroxide added during the preparation of alkaline tannin solution, and (2) the alkali mix lapse time. In this study, addition of 5% w/w aqueous sodium hydroxide with one hour lapse time increased the pH of sulfited tannin adhesives to slightly above 8.0, giving an acceptably slow desulfonation rate as reflected by the relatively low viscosity obtained (Table 3). We conclude that this solution, upon mixing with PRF, hardener, and paraformaldehyde in the two-component gluing technique produced an adhesive with a viscosity suitable for wood gluing. The average shear strength and wood failure values for different sulfited adhesives produced in this study are shown in Table 4. All the PRF-sulfited tannin adhesives improved the shear strength values of beech slips after being cured at 40 °C, especially for those tested under dry conditions. At this temperature, the strengths of glue joints of alkaline sulfited tannin adhesives were comparable with that of PRF except for those containing *R. apiculata*.

## CONCLUSIONS

The addition of sodium hydroxide into aqueous tannin solution prior to adhesive preparation was able to control the viscosity of the resulting tannin adhesives within a workable range. It also controlled the pH and thus, was responsible for the shorter pot life and greater water resistance properties of the adhesive. The extent of the effects, however, varied among the types of tannin used. Tannins from *R. mucronata* and the mixture of *R. mucronata* and *R. apiculata* were more sensitive toward the alkali addition while that of *R. apiculata* was less affected.

The amount of aqueous sodium hydroxide added during preparation of the alkaline tannin solution, and the lapse time, i.e. the period between the addition of the aqueous sodium hydroxide and the addition of the PRF resin and hardener, were the two main factors that influenced the properties (viscosity, pH, gel time, pot life and glue bond integrity) of the resulting tannin adhesive.

## REFERENCES

- BAE, Y. S., MALAN, J. C. S. & KARCHESY, J. J. 1994. Sulfonation of procyranidin polymers: evidence of intramolecular rearrangement and aromatic ring substitution. *Holzforschung* 48: 119–123.
- HEMINGWAY, R.W. 1989. Reaction at the interflavanoid bonds of proanthocyanidins. Pp. 265–284 in Hemingway, R. W. & Karchesy, J. J. (Eds.) *Chemistry and Significance of Condensed Tannins*. Plenum Press, New York.

**Table 4** Average shear strength and wood failure values of beech joint glued with PRF-sulfited mangrove tannin adhesives at 20 and 40 °C curing temperature

Adhesive type <sup>1</sup>	Curing temperature (°C)	Dry condition	After 24-hours	After 6-hours boiling	Shear reduction (%)
		Shear WF <sup>2</sup> (kN) (%)	soaking in cold water Shear WF (kN) (%)	in water Shear WF (kN) (%)	
PRF	40	3.2 15	2.6 83	2.5 92	20
PRF	20	3.2 0	2.8 73	2.6 78	13
PRF-MU	40	3.2 0	2.6 84	2.5 89	18
PRF-MU	20	2.1 0	1.7 12	1.8 86	18
PRF-AP	40	3.1 0	2.4 51	2.6 75	25
PRF-AP	20	2.4 0	2.0 22	2.2 21	16
PRF-MA	40	3.1 0	2.5 92	2.3 78	18
PRF-MA	20	2.7 0	2.1 74	2.2 62	20

<sup>1</sup>MU = *R. mucronata*, AP = *R. apiculata*, MA = *R. mucronata-R. apiculata*

<sup>2</sup>WF = Wood failure

- KREIBICH, R. E. 1992. *Use of Bark Tannins in End-jointing Adhesives for Wood*. Final Report Phase 11 SBIR-88-33610-4171. USDA Forest Service, Pineville.
- LAKS, P. E. 1989. Chemistry of the condensed tannin B-ring. Pp. 249–263 in Hemingway, R.W. & Karchesy, J. J. (Eds.) *Chemistry and Significance of Condensed Tannins*. Plenum Press, New York.
- MCGRAW, G. W. HEMINGWAY, R.W. & LAKS, P. E. 1988. Condensed tannins: desulfonation of hydroxy benzylsulfonic acids related to proanthocyanidin derivatives. *Journal of Wood Chemistry and Technology* 8: 91–109.
- PARIDAH, M. T. & MUSGRAVE, O. C. 1999. Sulfited mangrove tannin for wood adhesives. *Journal of Tropical Forest Products* 5(1): 46-57.
- PARIDAH, M. T. 1995. Utilisation of Mangrove Bark Extracts in Cold-Setting Wood Adhesives. Ph.D. thesis, University of Aberdeen, Arberdeen.
- PIZZI, A. 1994. Tannin-based wood adhesives. Pp. 149–218 in *Advanced Wood Adhesives Technology*. Marcel Dekker, New York.
- PIZZI, A. 1989. Research versus industrial practice with tannin-based adhesives. Pp. 254–270 in Hemingway, R. W., Conner, A. H. & Branham, S. J. (Eds.) *Adhesives from Renewable Resources*. American Chemical Society Symposium Series No. 385. American Chemical Society, Washington, D.C.