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ORIGINAL ARTICLE

Shin-ichiro Tohmura

Acceleration of the cure of phenolic resin adhesives VII: Influence of extractives of merbau wood on bonding*

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Abstract The influence of merbau wood extractives on the gelation rate of a phenolic adhesive and the effects of some cure accelerators on the bond performance of merbau plywood were investigated. The addition of merbau wood extractives slightly increased the gelation rate of the phenolic resin. This increase in the gelation rate was revealed to be due to a fall in the resin pH caused by addition of the extractives. The addition of cure accelerators, sodium carbonate and propylene carbonate, caused a considerable reduction in the hot-pressing time required for the merbau plywood to achieve sufficient bond qualities. Brushing veneer surfaces caused an increase in bond qualities. The combination of the cure acceleration and the surface brushing greatly improved the bondability of merbau wood. The main factor of gluing difficulty is considered to be the poor wettability of the veneer surfaces resulted from the accumulation of migrating extractives.

Key words Phenolic resin · Cure-acceleration · Extractives · Merbau

Introduction

Merbau (*Intsia* sp.) is one of the trees that grow in tropical rain forests, mainly in New Guinea. Merbau wood is expected to be used not only as timber but also for structural panels because of its high density and durability in regard to fungi.[1–3] However, merbau plywood manufacture has had some gluing difficulties when phenol-formaldehyde (PF) resins were used. Similar problems have been reported when gluing hardwoods such as kapur,[4,5] blackbutt,[6] and turkey oak.[7] It is said that the acidic extractives such as ellagic acid, gallic acid, and ferulic acid lower the glue line pH, deteriorate the wettability of veneer surfaces, and retard the curing of PF resins.[8,9] However, no reports have been made on the influence of extractives of merbau wood on the gluing performance of PF resins.

Two methods have been reported for improving gluing performance. One is cleaning veneer surfaces with organic solvents,[10] and the other is wire-brushing the veneer surface.[11] Both treatments were successful in removing the extractives accumulated on the veneer surface, thereby improving the wettability and gluing performance.

We reported the catalytic actions of carbonates in previous papers.[12,13] Until now, improving the bondability of a difficult-to-glue wood by cure acceleration of PF resins has not been attempted. In this study, the influence of the merbau extractives on the curing rate of a PF resin, the effects of the addition of sodium carbonate (Na_2CO_3) and propylene carbonate (PC) to the PF resin on the bonding performance of merbau plywood, and the effects of combining cure acceleration and mechanical brushing of veneers on the bond qualities of plywood are discussed.

Experimental methods

Merbau wood extractives

Merbau wood powder was prepared by ball milling. The powder (30g) passed a 30-mesh screen was dispersed in water (1l) and stirred at room temperature for 24h. The mixture was filtered with a glass filter. The extract solution was concentrated with the use of an evaporator under a reduced pressure at 40°–50°C and was finally dried to powder. The extraction of merbau wood with methanol, hexane, an aqueous solution of sodium hydroxide, and hot water was undertaken during the same procedure. Three major extractives of merbau wood – robinetin, myricetin, resveratrol – were purified by Hayashi et al.[1] and provided for this study.

S. Tohmura (✉)
Forestry and Forest Products Research Institute, P.O. Box 16, Tsukuba Norin Kenkyu Danchi-nai, Tsukuba, 305-8691, Japan
Tel. +81-298-73-3211; Fax +81-298-73-3797
e-mail: tomura@ffpri.affrc.go.jp

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Measurement of gelation time of PF resin–extractives system

A commercial PF resin (Oshika Resin D-100) was used in this study. Aqueous solutions of extractives (1 ml) were added to 10 g of the PF resin. The additional level of the extractives was 0.2 wt% on the basis of the weight of the PF resin except for crude water extracts, which were added in amounts of 0.2, 0.3, and 0.5 wt%. Distilled water (1 ml) was added to 10 g of the PF resin to make the control system. PF resin additives–cure accelerator systems were prepared. In these systems 1 wt% of Na_2CO_3, PC, or both were added as cure accelerators.

The resin systems (1 ml) were sealed in 2-ml glass ampuls and immersed in a constant-temperature (120°C) oilbath. The ampuls were turned upside down in the bath at intervals of 10 s. The time required for the resin systems to cease flowing was regarded as the gelation time.

Measurement of contact angle

Contact angles were measured with a contact angle meter (CA-Z, Kyowa Interface Science) goniometer five times for each veneer surface at 10-s intervals after a droplet of distilled water (10 μl) was dropped on the veneer surface.

Preparation of plywood and testing

Three adhesive systems were formulated from the commercial PF resin. A control system was prepared by mixing 100 g PF resin with 15 g wheat flour, 6 g filler (Oshika Hot P-5), and 10 g water. Two PF resin–cure accelerator systems were prepared by adding 1 g Na_2CO_3 or PC, respectively, to the control system.

Three-ply assemblies of the merbau veneers (300 × 300 × 1.8 mm) were bonded with these adhesive systems under the following conditions: moisture content of veneer 6.5%; glue spread 388 g/m^2 (double glue line); cold press under 0.98 MPa for 30 min; hot press under 0.98 MPa; 125° and 140°C for 1.5, 2.0, 2.5, and 3.0 min.

Thirty test specimens of Japanese Agricultural Standards (JAS) B type were cut from each panel. The share strength and wood failure were evaluated under dry conditions, after 60°C water soaking for 4 h, and after 72 h boiling water treatment for 10 specimens each.

Sugi (*Cryptomeria japonica*) plywood was prepared as a reference. Some of the merbau veneers were shaved (0.2 mm in depth) by a wire brushing machine (Syonai Tekko TS-350W with brush drum: φ 200 × 350 mm, wire φ 0.2 mm, density of wire 100 cm^2, drum rotation 1000 rpm, veneer carrying speed 10 m/min) and were subjected to the plywood preparation.

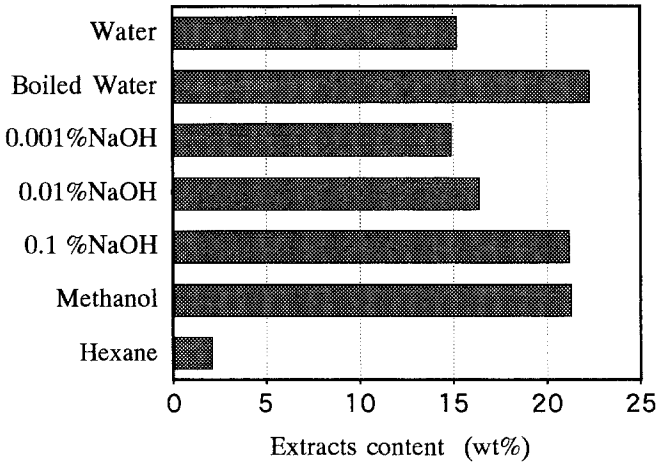

Fig. 1. Content of extracts in merbau wood

Results and discussion

Effects of merbau extractives on the gelation rate of PF resin

Merbau wood contains a considerable amount of extractives, especially water-soluble ones, as seen in Fig. 1. It is reported that the extractives of merbau wood consist mainly of flavonoids (e.g., robinetin, myricetin) and stylbenes (e.g., resveratrol).[1–3] Therefore, three purified compounds—robinetin, myricetin, resveratrol—in addition to crude water extracts and crude methanol extracts were added to PF resin, and their effects on the gelation rate were examined.

Figure 2 shows the gelation rates of the PF resin additive systems compared with that of the control system. The gelation rates were expressed as the reciprocals of gelation times (s^{-1}). The three purified compounds and the water–extract and methanol–extract solutions slightly increased the gelation rate. The cure accelerators (Na_2CO_3 and PC) increased the gelation rate by 1.3 and 2.0 times, respectively. For the combination of the merbau extractives and the cure accelerators, water extracts increased the gelation rate of the PF resin–Na_2CO_3 system but decreased that of the PF resin–PC system.

Water extracts of wood consist mainly of polyphenols, which are usually weak acids.[9] The water–extract solution used in this study was acidic (pH 3.0). Therefore, it can be expected that the pH of the alkaline PF resin falls by adding the extractives. Because gelation rates depend strongly on the pH,[14,15] it is necessary to investigate the relation between the pH and the gelation rate in the PF resin–additives systems. Fig. 3 shows the gelation rates of the PF resin–additive systems plotted against the pH. The open circles and solid line represent the gelation rates of the control system, the pH of which was adjusted with aqueous hydrogen chloride and sodium hydroxide solutions. The gelation rate increased as the pH went down in this pH region (pH 11–12). Addition of the extractives caused a fall in pH and increased the gelation rate relative to the amount of extracts added. This result indicates that the water and

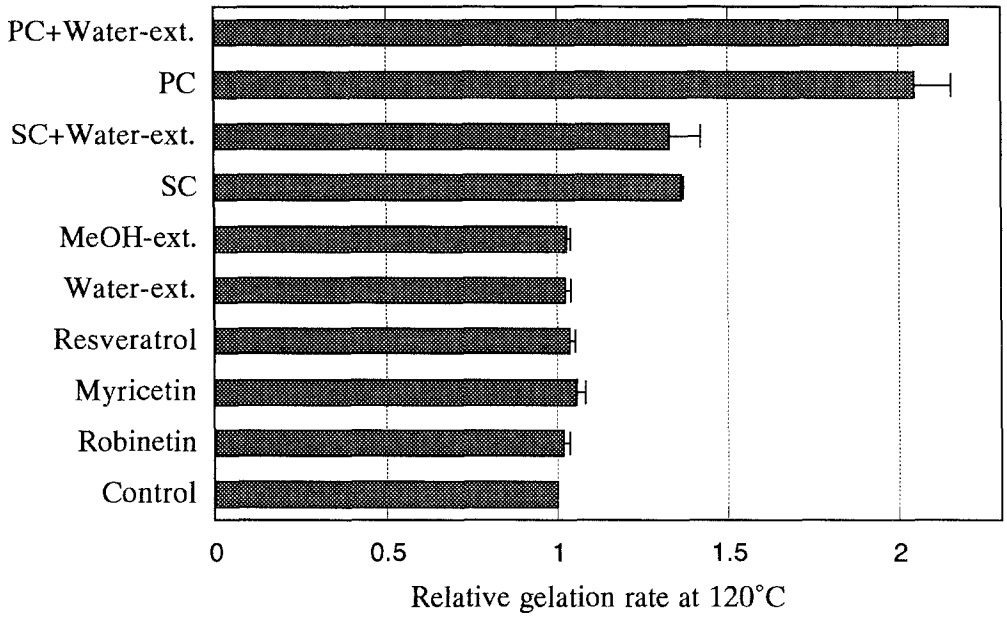

Fig. 2. Comparison of gelation rates of extractives (*ext.*) added to PF resin systems with those of control PF resin. Addition levels: extractives, 0.2 wt% to PF resin; *SC* (Na_2CO_3) and *PC* (propylene carbonate), 1 wt% to PF resin

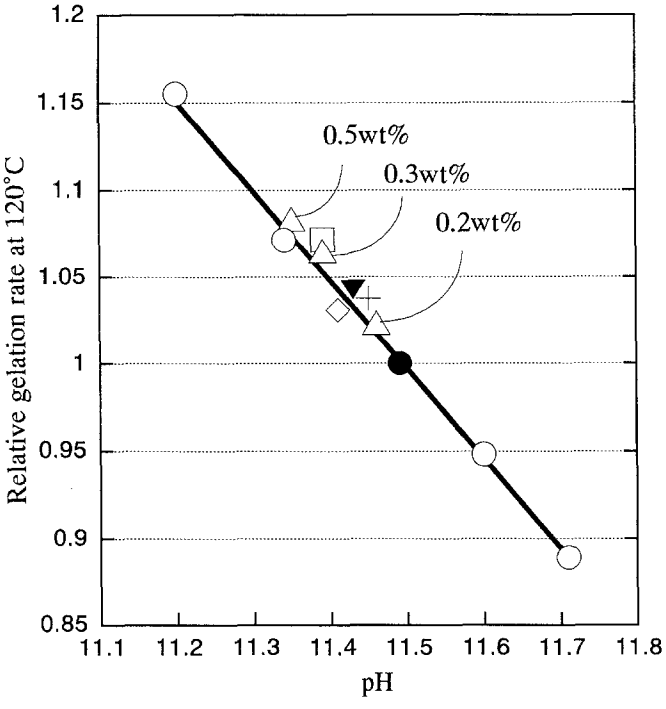

Fig. 3. Relation between pH and gelation rate. *Open diamond*, robinetin; *open square*, myricetin; *cross*, resveratrol; *open triangle*, water extracts; *filled triangle*, MeOH extracts; *filled circle*, control; *open circles*, control (adjusted pH). Addition levels of water extract to PF resin: 0.2–0.5 wt%

methanol extracts of merbau wood have no essential effects other than the alkali-consuming effect on the gelation rate of the PF resin.

Effects of cure accelerators on bonding properties

In a previous paper[12] we showed that the catalytic activities of Na_2CO_3 and PC were ascribed to the particular molecular structure of the hydrogen carbonate ion formed from Na_2CO_3 and PC. The effects of these cure accelerators on bond performance are unknown, although they have been used practically. Therefore, Na_2CO_3 and PC were added to PF resin and applied to the bonding of merbau wood, which is known to be difficult to glue.

Table 1 summarizes the result of shearing tests on plywood. Sugi plywood showed enough shear strength under the ordinary pressing condition for PF resins (140°C, 1.5 min = 16.6 s/mm). Merbau plywood blew under those pressing conditions when the control adhesive was applied. A pressing time longer than 2.5 min is needed when making merbau plywood at 140°C. The addition of either of the cure accelerators to the PF resin enabled formation of merbau plywood under the pressing conditions of 125°C for 2 min. That is, the cure accelerators not only accelerated curing of the PF resin but also contributed to the bonding performance of this difficult-to-glue species. Moreover, the use of the cure accelerators reduced the hot-pressing time and temperature for the manufacture of plywood.

Brushing the veneer also made formation of plywood with enough bond strength possible under pressing conditions of 125°C for 2 min. One of the reasons brushing improves bonding performance is that it improves the wettability of the veneer surfaces. Figure 4 shows the effect of brushing on the contact angles between water and the veneer surfaces. It is clear that brushing cut off the extractive-stained surfaces and generated new, rough surfaces. In Table 2 it is noted that the percentages of wood failure of panels made with brushed veneers are remarkably high, suggesting that the adhesive penetrated the brushed

Table 1. Average shear strength of sugi and merbau plywoods

Hot press time and aging[b]	MPa at 140°C		MPa at 125°C					
	Sugi (control)	Merbau (control)	Sugi (control)	Merbau			Brushed merbau[a]	
				Control	PF–Na_2CO_3	PF–PC	Control	PF–Na_2CO_3	PF–PC
1.5 Minutes									
Dry	0.79 (0.20)		0.94 (0.19)					1.49 (0.19)	1.39 (0.15)
Hot water	0.83 (0.18)	Blow	0.23 (0.11)	Blow	Blow	Blow	Blow	0.99 (0.11)	1.15 (0.08)
Boiling	0.78 (0.19)		0.35 (0.14)					0.90 (0.17)	1.08 (0.11)
2.0 Minutes									
Dry						1.68 (0.13)	1.62 (0.26)	1.53 (0.16)	1.52 (0.33)
Hot water	–	–	–	Blow	Delaminated	1.31 (0.09)	1.32 (0.24)	1.02 (0.13)	1.27 (0.11)
Boiling						1.31 (0.14)	1.28 (0.13)	0.96 (0.32)	1.34 (0.10)
2.5 Minutes									
Dry	0.85 (0.22)	2.24 (0.29)	0.88 (0.22)		1.49 (0.45)	2.33 (0.18)	1.62 (0.25)	2.06 (0.19)	1.56 (0.15)
Hot water	1.05 (0.24)	1.66 (0.16)	0.84 (0.14)	Blow	1.11 (0.17)	1.75 (0.13)	1.28 (0.18)	1.40 (0.19)	1.27 (0.06)
Boiling	0.73 (0.30)	1.40 (0.15)	0.87 (0.17)		0.94 (0.15)	1.63 (0.16)	1.25 (0.13)	1.29 (0.18)	1.23 (0.11)
3.5 Minutes									
Dry				1.87 (0.21)	2.00 (0.19)	2.17 (0.26)	1.62 (0.25)	2.32 (0.17)	
Hot water	–	–	–	1.51 (1.53)	1.49 (0.14)	1.95 (0.15)	1.41 (0.26)	1.56 (0.19)	–
Boiling				1.40 (0.14)	1.35 (0.21)	1.68 (0.07)	1.42 (0.11)	1.44 (0.10)	

Numbers in parentheses are the standard deviation.
MPa, shear strength.
Adhesives: PF–Na_2CO_3, sodium carbonate–added PF resin; PF–PC, propylene carbonate–added PF resin. Addition level of the cure-accelerator: 1 wt% to PF resin.
[a] Merbau veneers brushed by the wire-brushing machine.
[b] Hot water: wet after 4 h immersed in 60°C water. Boiling: wet after 72 h immersed in boiling water.

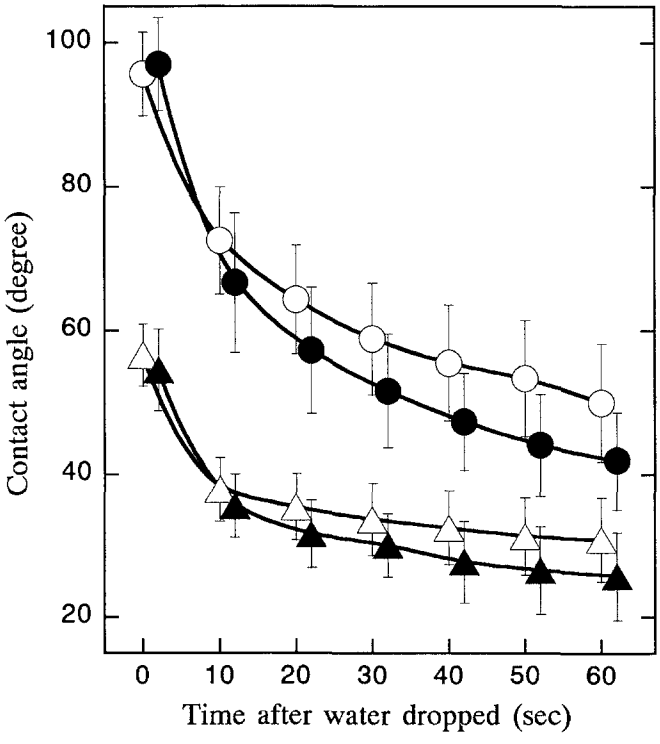

Fig. 4. Effect of brushing on the contact angle between water and the surface of the veneer. *Open circles*, control face; *filled circles*, control back; *open triangles*, brushed face; *filled triangles*, brushed back

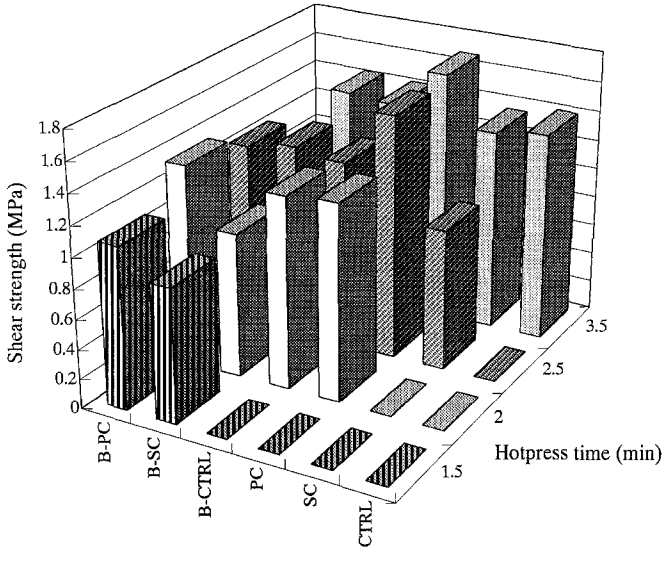

Fig. 5. Relation between shear strength after 72 h of boiling and the hot press time, addition of cure accelerator (*SC*, Na_2CO_3; *PC*, propylene carbonate), and brushing treatment (*B*). *CTRL*, control

veneers more easily and formed an anchor structure to create a tough bond. A combination of adding a cure accelerator and brushing the veneers was successful in reducing of the pressing time up to 1.5 min at 125°C without deteriorating the bond quality (Fig. 5).

Table 2. Average wood failure of sugi and merbau plywoods

Hot press time and aging[b]	Wood failure (%) at 140°C		Wood failure (%) at 125°C						
	Sugi (control)	Merbau (control)	Sugi (control)	Merbau			Brushed merbau[a]		
				Control	PF–Na_2CO_3	PF–PC	Control	PF–Na_2CO_3	PF–PC
1.5 Minutes									
Dry	100 (0)		100 (0)					42 (21)	65 (32)
Hot water	52 (27)	Blow	0 (0)	Blow	Blow	Blow	Blow	27 (14)	71 (14)
Boiling	74 (23)		1 (3)					54 (33)	86 (15)
2.0 Minutes									
Dry						90 (6)	45 (32)	73 (25)	82 (30)
Hot water	–	–	–	Blow	Delaminated	45 (22)	34 (11)	25 (19)	72 (23)
Boiling						89 (22)	84 (15)	85 (13)	87 (11)
2.5 Minutes									
Dry	100 (0)	38 (21)	100 (0)		23 (29)	52 (23)	64 (32)	56 (29)	86 (13)
Hot water	53 (29)	19 (8)	19 (25)	Blow	10 (7)	45 (15)	40 (18)	36 (19)	82 (16)
Boiling	77 (25)	17 (8)	33 (39)		22 (11)	29 (12)	72 (18)	49 (15)	100 (0)
3.5 Minutes									
Dry				94 (18)	45 (24)	85 (9)	88 (9)	73 (28)	
Hot water	–	–	–	71 (65)	21 (31)	29 (9)	45 (14)	44 (13)	–
Boiling				76 (20)	51 (32)	44 (20)	85 (17)	64 (19)	

Numbers in parentheses are the standard deviation.
Adhesives: PF–Na_2CO_3, sodium carbonate–added PF resin; PF–PC, propylene carbonate-added PF resin. Addition level of the cure-accelerator: 1 wt% to PF resin.
[a] Merbau veneers brushed by the wire-brushing machine.
[b] Hot water: wet after 4 h immersed in 60°C water. Boiling: wet after 72 h immersed in boiling water.

Cause of gluing difficulties of merbau plywood

Difficult-to-glue wood species with high extractive content have been reviewed by Hse and Kuo.[16] It is said that extractives, migrating on drying and contaminating the surface of wood, cause gluing difficulty and low bond qualities; moreover, the accumulation of extractives on the surface blocks the reaction sites and prevents the anchoring of adhesives. The results of this study regarding the effects of veneer brushing support the above description and indicate that the surface wettability is a significant factor for gluing merbau wood. No inhibiting effects of the extractives were found during the curing reaction of the PF resin. Therefore, the primary factor of the gluing difficulty of merbau wood is the poor wettability of the wood surface. Because PF resins are highly sensitive to moisture content (MC), veneers usually need to be dried below 6% MC. This thorough drying presumably make the extractives migrate more easily to the surface of the veneer.

Conclusion

The extractives in merbau wood slightly increased the gelation rate of an alkaline PF resin. It was revealed that the increase was caused by a fall in the pH of the resin system, and the extractives had no essential effect on the curing of the PF resin.

The addition of cure accelerators (sodium carbonate and propylene carbonate) to the PF resin resulted in an increased gelation rate and a shortened hot-pressing time required for producing plywood with sufficient bond properties. Wire-brushing treatment of veneers improved the wettability of the surfaces and led to enhancement of bonding. A combination of cure accelerators and brushing is effective for faster bonding of merbau wood. The primary factor contributing to the gluing difficulty of merbau wood is believed to be the poor wettability of the surfaces due to the migration and accumulation of extractives.

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