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ORIGINAL ARTICLE

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Bondability of tropical fast-growing tree species III: curing behavior of resorcinol formaldehyde resin adhesive at room temperature and effects of extractives of *Acacia mangium* wood on bonding

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Abstract The effects of curing time at room temperature and methanol extracts from *Acacia mangium* on the curing behavior of resorcinol formaldehyde (RF) adhesive were examined by using the thermomechanical analysis spring method. For a specimen that was cured for 3 months at room temperature, the relative elasticity (E_r) curve did not change to a hard glass state from room temperature to 200°C and the adhesive had cured completely. The initial temperature of the reactive zone for chemical and mechanical changes was 15° and 25°C higher than that for the control when 10 and 15 parts by weight methanol extract was added to the liquid adhesive, respectively. It appears that the extractives of *A. mangium* in RF adhesive interferes with the chemical cure of the adhesive. It is suggested that a combination of curing time and sweeping by methanol on the laminae surface can improve the bonding performance of *A. mangium* laminates bonded with RF at room temperature.

Key words Bondability · Curing behavior of RF · *Acacia mangium* bonding

Introduction

Our previous study[1] indicated that the bonding performance of *Acacia mangium* laminates that bonded with resorcinol formaldehyde (RF) resin adhesive at room temperature [20°C and 65% relative humidity (RH)] was distributed in bad and the worst categories. One of the reasons given was that the adhesive did not cure completely during the first week of curing under the condition of 20°C and 65% RH. Results similar to those of our study were reported by Taki et al.[2] and Liu,[3] for studies that used selangan batu and hinoki, respectively. To clarify this indication, an investigation on the curing behavior of RF using the thermomechanical analysis (TMA) spring method has been conducted. This method has been used to study the curing behavior of some thermosetting resins such as phenol–formaldehyde (PF) and RF.[4–7] It is reported that this method is suited to studying curing reaction behavior as the thermosetting resin progresses from liquid to gel and to the solid state. Previously, many investigators have studied the curing behavior of thermosetting resin by dynamic mechanical analysis methods [dynamic mechanical analysis (DMA), torsional braid analysis (TBA), etc.].[8–13] However, TMA with a wire spring method had not been widely used to determine mechanical properties of RF resin adhesive.

Acacia mangium is one of the most popular fast-growing wood species in Indonesia. This wood is expected to be used not only as raw material for pulp and paper but also for glulam production because of its high bond strength[1] and good mechanical properties.[14,15] However, *A. mangium* lamination manufacture has had some bonding difficulties especially in the case of bonding with RF resin. Wood components, probably extractives, appear to affect curing of RF resin and deteriorate the wettability of the wood surface as shown by low wood failure values.[1] The presence of wood extractives as inhibitory components on the curing of resin and the bonding performance has been reported in many previous studies.[16–23] However, no report has examined the influence of extractives of *A. mangium* on the curing behavior of RF resin adhesive. In this report, the effects of curing time and methanol extracts on the curing behavior of RF and the effects of sweeping by methanol on the wood surface for improving wettability and bonding performance of *A. mangium* are discussed.

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Materials and methods

Measurement of curing behavior of RF resin

A commercial RF resin adhesive (J-6000, Dainippon Ink and Chemicals) with solid content of 58% ± 3% and viscosity of 6.0 ± 2 Pa.s was used in this study. Liquid adhesive specimen was 100 parts by weight (pbw) resin mixed with 15 pbw paraformaldehyde (TD-473) as a catalyst. Fifteen pbw methanol, 10 and 15 pbw methanol extracts were added into liquid to investigate the effect of methanol and methanol extracts on the curing behavior. The total amount of liquid specimen that inserted into the small wire spring was 10 mg. The heating rate was 10°C/min. The amplitude cycle was 0.1 Hz and the tensile amplitude load was 1.96×10^{-2} N. The curing behavior of resin was analyzed in an elevating temperature condition (20°–200°C). In order to clarify whether the resin had cured completely, specimens were cured at room temperature for 1 week, 2 weeks, 1 month, 2 months, and 3 months.

The curing behavior of resin was analyzed by using a TMA apparatus (TMA-4000, Mac Science). The top of the spring was caught in the hook of the terminal of the detector, and a container was fixed on the support tube with the hook as shown in Fig. 1. Then a fixed vibration load was applied at the spring in every constant period with the temperature of the specimen controlled through the atmosphere in the electric oven. When the load was applied, the spring caused a change in volume. The quantity of change in volume (amplitude) greatly depends on hardness of the specimen. The modulus of elasticity (E') and loss energy of each period were analyzed by vibration load (stress) and the delay of the phase of the vibration of the spring (strain). Curing behavior is expressed in relative elasticity (E_r), which is calculated using the following equation:

$$E_r = \frac{(E_x - E_{min})}{(E_{max} - E_{min})}$$

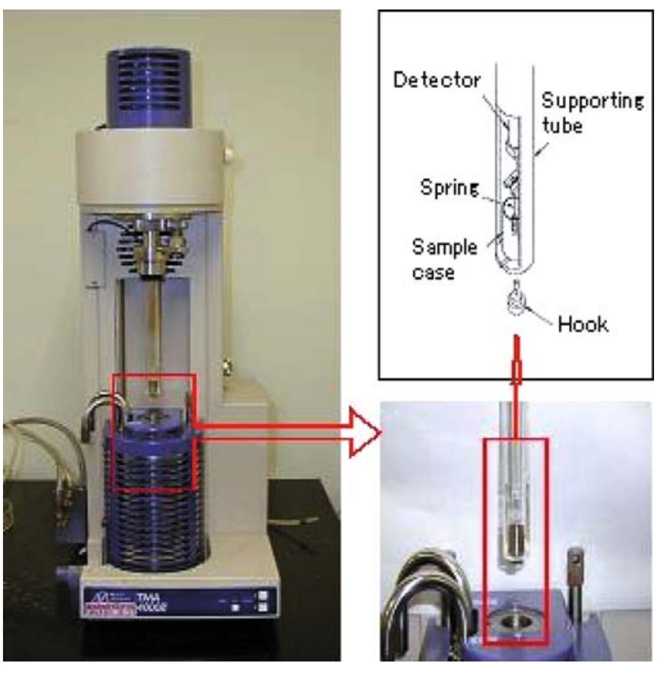

Fig. 1. Thermomechanical analysis apparatus

where E_r is the relative elasticity, E_x is the modulus of elasticity (E') at x°C, E_{min} is the minimum modulus of elasticity, and E_{max} is the maximum modulus of elasticity.

Acacia mangium wood extracts

Acacia mangium wood particles and laminae were obtained from Winaya Mukti University, Indonesia. One hundred grams of particles was dispersed in 3 l of methanol in a shaker and stirred at room temperature for 8 h. The methanolic extracts were filtered through an Advantec No. 2 filter paper. The extract solution was concentrated with the use of an evaporator (EYELA, CA-1111) under reduced pressure at 40°–45°C, and then placed under vacuum (0.005 MPa) with the use of an aspirator (ULVAC, MDA-050) for 20 min. The total yield of methanolic extract obtained from the sample was 3% (w/w).

Measurement of contact angle

Contact angle changes were measured at 20°C and 65% RH with a contact angle meter apparatus (CA-DT type A)[24] five times for each laminae surface [9% moisture content (MC)] at 10-s intervals for 120 s after a droplet of distilled water (0.20 cm^3) was dropped on the laminae surface. as the sample included a control (C) and treatments B (boiled for 3 h, dried at room temperature for 24 h), AS (swept six times by acetone), and MS (swept six times by methanol).

Bonding performance

Two-ply laminations of six-year-old *A. mangium* Willd with 0.54 g/cm^3 air-dry density and 9% MC were bonded with RF resin adhesive (spread rate 250 g/m^2) with a roller. Pressure was applied at 1.18 MPa at 20°C and 65% RH for 24 h (cold-pressing time). Then the laminates were reconditioned at 20°C and 65% RH for 1 week as a control (C), 2 weeks (W2), 1 month (M1), 2 months (M2), and 3 months (M3). The specimens were also prepared for the laminae surface swept six times by acetone (AS) and methanol (MS) before adhesive was spread on it for 1 week for comparison with the control specimen. Ten small block-shear specimens ($20 \times 25 \times 30$ mm, thickness × width × length) for each treatment were cut from the two-ply lamination. In block-shear testing, an Amsler machine was used with a load rate of about 9.8 kN/min. Bond strength and wood failure under normal condition (N) were measured according to Japan Agricultural Standard for Structural Glued Laminated Timber (shear area about 6.25 cm^2).[25] Bond strength and wood failure for wet conditions were also measured after accelerated aging tests described below, which were used for delamination testing of glulam:

1. Cyclic boiling (CB) test: specimen submerged in boiling water for 4 h, submerged in cold tap water for 1 h, dried at 70° ± 3°C for 18 h, submerged in boiling water for 4 h, and then tested when wet.

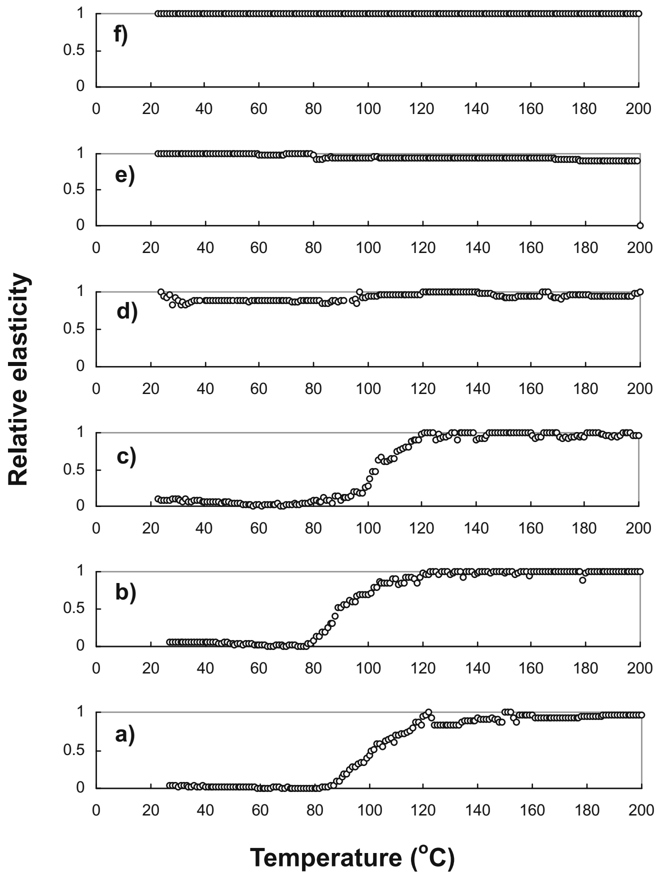

Fig. 2a–f. Effects of curing time at room temperature on the curing behavior of resorcinol formaldehyde (RF) resin adhesive. **a** Liquid; **b** 1 week; **c** 2 weeks; **d** 1 month; **e** 2 months; **f** 3 months

2. Vacuum pressure soaking (VPS) test: specimen submerged in cold tap water for 1 h, evacuated at 0.085 MPa for 5 min, pressurized at 0.51 ± 0.03 MPa for 1 h, these steps repeated, and tested when wet.

Results and discussion

Curing behavior of RF resin

The effect of curing time on the curing behavior of RF at room temperature is shown in Fig. 2. At the beginning of the test, the initial relative elasticity (E_r) of adhesive compounds is assumed to be 0 and is assumed to be 1 when the adhesive had cured completely. In liquid state and specimens cured for 1 and 2 weeks, the curve of relative elasticity (E_r) was flat from room temperature to 85°C. Beyond 85°C the E_r curve increased up to near 120°C, and the E_r curve did not change in a hard glass state up to 200°C. It seemed that the reactive zone of the chemical and mechanical changes of liquid and specimen that cured for 1 and 2 weeks was in the temperature range of 85° to 120°C, and over 120°C the adhesive had cured completely. The initial temperature of the reactive zone in this study was 20°C higher than that in a previous study.[4] This may be caused by differences in the adhesive formulation. For the specimens that cured for 1, 2, and 3 months, the E_r curve was almost flat from room temperature to 200°C. However, the E_r curve in specimens cured for 1 and 2 months seemed change to a hard glass state to 200°C. In the specimen cured for 3 months, the E_r curve did not change to a hard glass state from room temperature to 200°C and the adhesive had cured completely. A previous study has also reported that more than 1 month is needed for RF adhesive to cure completely when it is applied at room temperature.[4]

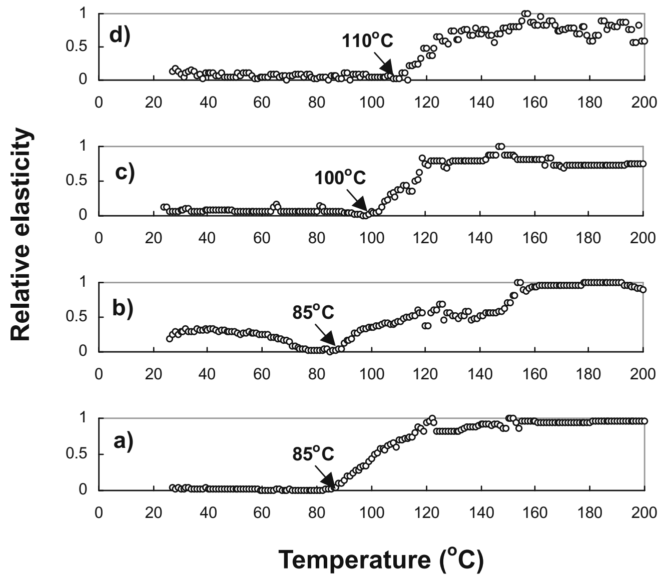

Fig. 3a–d. Effects of methanol extracts on the curing behavior of RF resin adhesive. **a** Liquid (control); **b** 15 parts by weight (pbw) methanol; **c** 10 pbw methanol extracts; **d** 15 pbw methanol extracts

The effects of methanol and methanol extracts of *Acacia mangium* wood on the curing behavior of liquid RF adhesive are shown in Fig. 3. In liquid that contained 15 pbw methanol, the E_r curve was flat from room temperature to 85°C. Beyond 85°C, the E_r curve increased up to near 120°C, and the E_r curve did not change to a hard glass state up to 200°C, which is the same as the results of the control specimens. These results indicated that there was no effect of methanol on the reaction zone temperature for chemical and mechanical changes of liquid RF adhesive. For liquid that contained 10 pbw methanol extracts, the E_r curve was flat from room temperature to 100°C. Beyond 100°C, the E_r curve increased up to near 130°C, and the E_r curve did not change to a hard glass state up to 200°C. It seemed that the reactive zone for the chemical and mechanical changes of this specimen was in the temperature range of 100° to 130°C; over 130°C the adhesive had cured completely. For liquid that contained 15 pbw methanol extracts, the E_r curve was flat from room temperature to 110°C. Beyond 110°C the E_r curve increased up to near 140°C, and the E_r curve did not change to a hard glass state up to 200°C. It seemed that the reactive zone for the chemical and mechanical changes of this specimen was in the temperature range of 110° to 140°C; over 140°C the adhesive had cured completely. These results indicated that the initial temperature of the reactive zone for the chemical and mechanical changes of RF adhesive containing 10 pbw and 15 pbw methanol extracts were 15° and 25°C higher than that of the control specimen. It seemed that the presence of extractives of *A. mangium* in the RF adhesive interfered with the chemical cure of the adhesive. However, to complete this study it is necessary to identify major extractive components from *A. mangium* that interfere with the curing behavior of RF adhesive. The effects of extracts of *A. mangium* on the bonding performance was specifically reported by Tachi et al.,[20] when they used *A. mangium* for wood–cement board production. They reported that cement-hardening inhibitory components from *A. mangium* led to the isolation of two flavonoids. An inhibitory index confirmed that a major component, teracidin, with a 7,8-dihydroxyl group in a leucoanthocyanidin structure has a strong inhibitory effect. Furthermore, some previous study on the effects of wood extractives on the curing reaction of the resol showed that the acidity of the wood extractive is the one of the chemical factors that affects the curing behavior of the resol. The resol was changed from weak basic to neutral by adding the inhibitory components, and resulted in the formation of a large quantity of dimethylene ether linkage.[16,17]

Wettability

Wettability of a wood surface refers to the rate at which a liquid can wet and spread over it.[26] It is a quick method for predicting the gluability of unknown species, and can be measured by determining the contact angle between the solid–liquid interface and the liquid-air surface.[27] Data of the contact angle changes during 2 min of observation time are shown in Figs. 4 and 5. After the water was dropped, the average contact angle at 20 s in the control (C) was 73° in the heartwood and 61° in the sapwood. In B, AS, and MS samples, the averages were 66° in the heartwood and 58° in the sapwood, 64° in the heartwood and 56° in the sapwood, and 46° in the heartwood and 37° in the sapwood, respectively. Results showed that the contact angle of laminae surface swept by methanol was about 25° lower than the control for both heartwood and sapwood. It seemed that sweeping by methanol could improve the wettability of laminae surfaces more than sweeping by acetone or boiling treatment. Another method for improving the wettability of the wood surface has been reported by Tohmura.[22] It is said that brushing the veneer surface improves the wettability and bonding properties in merbau wood that contains high extractives content. Sakuno and Moredo[23] reported that hexane treatment effected a general improvement of the dry strength properties of some tropical wood that contained high extractives when bonded with aqueous polymer isocyanate (API) and RF adhesive.

Bonding performance

The effect of curing time on the shear strength and wood failure of *A. mangium* bonded with RF at room temperature is shown in Fig. 6. Under normal conditions, higher shear strength and wood failure were achieved by M2 and M3 (around 14 MPa and 80%). After CB treatment, higher shear strength was achieved by M3 (9.3 MPa) while higher wood failure was achieved by M1 and M3 (80%). In VPS treatment, higher shear strength was achieved by M3 (10.8 MPa) while higher wood failure was achieved by M2 (65%). Results further showed that in *A. mangium* laminates bonded with RF at room temperature, at least 1 month of curing time is required to meet 60% wood failure as a minimum requirement for a good bonding performance classification, as described in our previous study.[1]

The effect of acetone and methanol sweeping on the bonding performance is shown in Fig. 7. In normal treatment and after accelerated aging treatment, higher shear strength with higher wood failure was achieved by MS specimens. Shear strength were 0.75%, 44%, and 26% greater than the control in the normal treatment and after CB and VPS treatments, respectively. Wood failures were 20%, 15%, and 14% greater than the control in the normal treatment and after CB and VPS treatments, respectively. It seemed that sweeping by methanol could improve the good bonding performance of *A. mangium* because wood failure

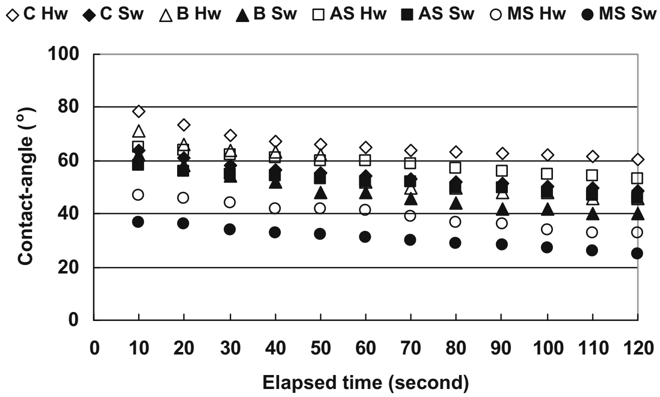

Fig. 4. Effects of boiling (*B*), acetone (*AS*), and methanol (*MS*) treatments on the contact angle changes of laminae surfaces. *C*, Control; *Hw*, heartwood; *Sw*, sapwood

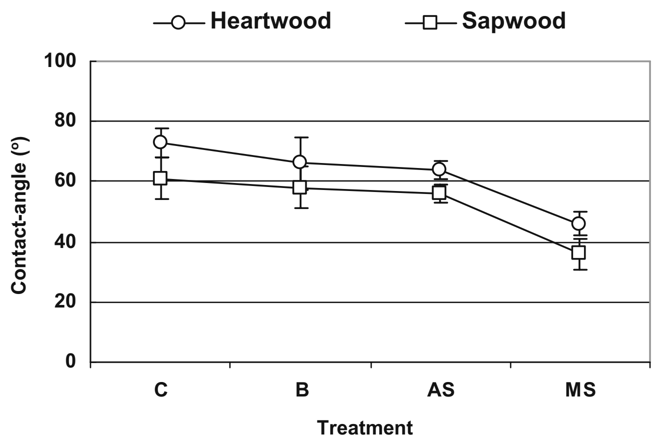

Fig. 5. Effects of boiling (*B*), acetone (*AS*), and methanol (*MS*) treatments on the average contact angle changes of laminae surfaces at 20-s measurement

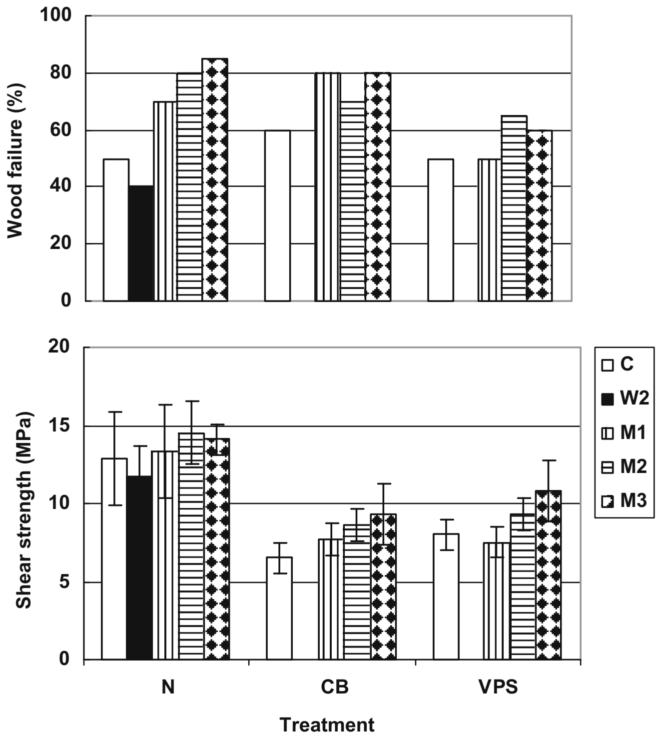

Fig. 6. Effects of curing time on wood failure (*upper*) and shear strength (*lower*) of *Acacia mangium* laminates bonded with RF. *N*, Normal; *CB*, cyclic boiling; *VPS*, vacuum pressure soaking. *C*, Control; *W2*, 2 weeks; *M1*, 1 month; *M2*, 2 months; *M3*, 3 months. CB and VPS data for W2 specimen was not available. *Error bars* indicate standard deviations

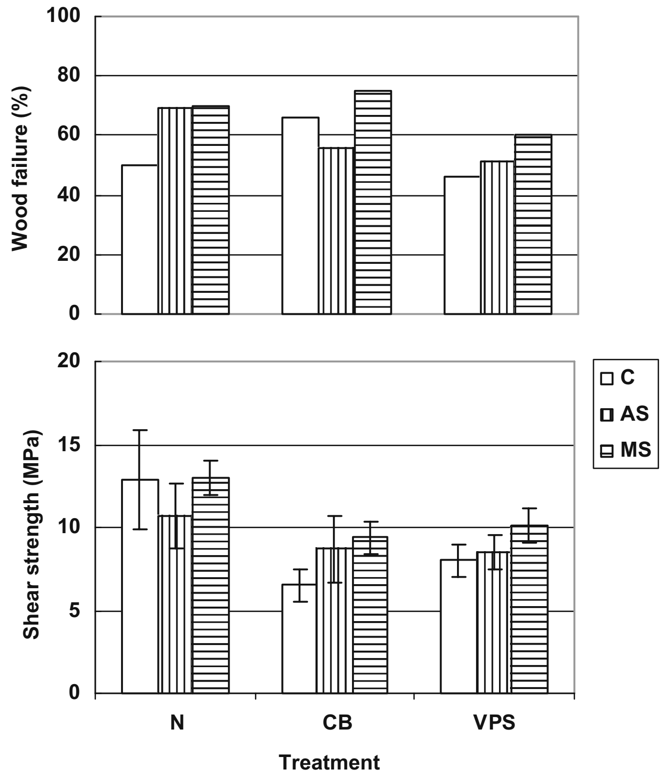

Fig. 7. Effects of acetone (*AS*) and methanol (*MS*) treatments on wood failure (upper) and shear strength (*lower*) of *A. mangium* laminates bonded with RF. *Error bars* indicate standard deviations

of more than 60% was achieved in all treatment conditions. Difficult-to-glue wood species with high extractive content have been reviewed by Hse and Kuo.[18] It is said that extractives, migrating on drying and contaminating the surface of the 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. A similar result to the above study was also reported by Tohmura[22] for merbau wood. Hence, the results of this study regarding the effects of the laminae sweeping support the above description and indicate that the surface wettability is a significant factor for bonding of *A. mangium* wood.

Conclusions

In specimens cured for 3 months, the relative elasticity (E_r) curve did not change to a hard glass state from room temperature to 200°C and the adhesive had cured completely. It is clear that at room temperature, RF adhesive that cured for 1 week did not cure completely. For RF adhesive that contained 10 and 15 pbw methanol extracts, the starting temperature of the reactive zone for chemical and mechanical changes was 15° and 25°C higher than that of the control, respectively. It seemed that the presence of extractives of *Acacia mangium* in RF adhesive interfered with the chemical cure of the adhesive.

In the wettability test, results showed that the contact angle of laminae surfaces swept by methanol was about 25° lower than that for the control for both heartwood and sapwood. It appears that sweeping treatment by methanol can improve the wettability of the laminae surface. It is suggested that a combination of curing time and sweeping by methanol on the laminae surface can improve the bonding performance of *A. mangium* laminates bonded with RF at room temperature.

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