Horito *et al. J Wood Sci (2020) 66:13*
https://doi.org/10.1186/s10086-020-01858-3

Journal of Wood Science

NOTE

Open Access

Plywood adhesives using PF resin with fibrillated bark slurry from radiata pine (*Pinus radiata* D. Don): utilization of flavonoid compounds from bark and wood. IV

Masayoshi Horito[1*], Naoko Kurushima[1], Keiko Ono[1] and Yoshikazu Yazaki[2]

Abstract

In 2003, the first adhesives into which considerable amounts of bark particles (< 63 µm) were incorporated were developed using radiata pine bark. The quality of bark containing adhesives has now been substantially improved by fibrillating the bark. The finely ground bark (< 63 µm) was fibrillated using a disk mill and formulated into plywood adhesives. The adhesives contained different ratios of fibrillated bark, phenol–formaldehyde (PF) resin and water. The gluability of the fibrillated bark adhesives was evaluated according to the Japanese Agricultural Standard (JAS) for Plywood and was found to be excellent with the proportion of PF resin to bark being 6 to 4 and 5 to 5 on a solid basis. The bark was fibrillated with water (in the ratio 1 to 10), freeze-dried and used for the adhesive formulations. The freeze-drying process is extremely expensive and was considered inappropriate for the production of wood adhesives. However, it was found that when the ground bark (< 1 mm) was fibrillated with a bark to water ratio of 1 to 3, the resulting bark slurry was able to be directly incorporated into a PF resin to produce high performance plywood adhesives. This improved process is more economic because it requires neither further fractionation of the ground bark nor freeze-drying of the fibrillated bark slurry. The fibrillated bark slurry adhesives are able to produce a high quality of bonding in plywood samples from not only radiata pine, but also hinoki and karamatsu veneers.

Keywords: *Pinus radiata* bark, Fibrillated bark slurry, Plywood adhesives, Radiata tannin, Polyflavanoids, Hinoki (*Chamaecyparis obtusa*), Karamatsu (*Larix* species)

Introduction

The flavonoid compounds, which have been used commercially, are tannins derived from barks and woods. One of the most commonly used tannins is wattle tannin, which is obtained as a hot water extract from the bark of black wattle (*Acacia mearnsii* De Wild.) [1, 2].

The major components of wattle tannin are polyflavanoids consisting of flavan-3-ols as monomers and their polymers. Although the use of wattle tannin in leather tanning commenced in the early 1820s, the commercial use of wattle tannin as a major component in the manufacture of wood adhesives commenced only in the middle of the 1960s. A new approach to the use of the tannin in the bark without extraction, which was described as "bark adhesives" from radiata pine, was reported in 2011 [1, 3].

Since early 2000, cellulose nanofibers from wood have demonstrated superior properties such as light weight, high strength and low thermal expansion and so considerable attention has been focused on their use in next-generation industrial materials [4–6]. Attempts to obtain cellulose nanofibers from bark have been reported only from the bark of lodgepole pine (*Pinus contorta*) in Canada [7, 8]. However, the

*Correspondence: masayoshi.horito@woodone.co.jp
[1] WOOD ONE Co., Ltd, 1-12-1, Shimohera, Hatsukaichi-shi, Hiroshima 738-0023, Japan
Full list of author information is available at the end of the article

authors of that study were not interested in the tannin contained in the lodgepole pine bark but removed the tannin components from the bark as part of their investigation. Since radiata pine bark contains significant amounts of procyanidin polymers (polyflavanoids), which consist of linear chains of 3′,4′-dihydroxy flavan-3-ol units that have undergone varying degrees of condensation [9–11], the thought was that it may be possible to produce nano fibers for strength and reactive tannins by fibrillating radiata pine bark using a simple disk mill and formulating the product into a plywood adhesive. The gluability of the fibrillated bark adhesives was evaluated according to the Japanese Agricultural Standard (JAS) for Plywood [12] and found to be excellent, particularly with the proportion of a phenol–formaldehyde (PF) resin to bark being 6 to 4 and 5 to 5 on a solids basis. In the early trials, 1 kg bark was fibrillated with 10 L water, the product (bark slurry) freeze-dried to remove the water from the slurry and the dried material used in the adhesive formulations [13, 14].

However, after the bark was fibrillated with water, it was necessary to remove the water or at least to concentrate the bark content from about 10% up to 45%, which is the approximate solids concentration in PF resins. Thus, it was necessary to remove 10 L or up at least 8.8 L water from the fibrillated bark slurry (1 kg/10 L water). Since much of the radiata tannin is dissolved in the liquid portion of the bark slurry, a simple filtration could not be used due to the loss of tannin in the filtrate. Additionally, to prevent chemical changes of the fibrillated bark components, freeze-drying was the best option at that stage. However, freeze-drying is extremely expensive. For example, although there are no direct references showing the cost difference with or without freeze-drying for radiata pine bark, after the harvest, raw cones of hop were dried using three different drying methods. The results showed that freeze-drying by far required the most energy, followed by microwave vacuum drying and hot-air drying, which are 8.42 and 5.96% of freeze-drying requirement [15]. Consequently, freeze-drying could not be considered for a commercial operation for drying bark.

Hence, the simplest way to reduce the water content of the final fibrillated slurry is not to put excess water there in the first place, so that the slurry could be added directly to the PF resin. This paper describes how plywood samples using veneers of radiata pine, hinoki (*Chamaecyparis obtusa*) and karamatsu (*Larix* species) were produced using adhesives made from blended fibrillated radiata pine bark and PF resin and the resulting bonding qualities of the samples evaluated.

Materials and methods

Radiata pine bark

The bark used was obtained from 30- to 35-year-old radiata pine logs (*Pinus radiata* D. Don) from Kaitaia in New Zealand and collected from the debarkers. It was dried at 100 °C for 24 h, and then sent to WOOD ONE CO., LTD. in Hiroshima, Japan.

Fibrillated bark slurry

The dried radiata pine bark was roughly ground using a garden shredder, and then further size reduced using a hammer mill having a screen opening of 1 mm. 2 kg of fine bark (< 1 mm) was soaked in 6 L water for 24 h and then fibrillated using a disk mill (Supermasscolloider MKZA10-15 J; MASUKO SANGYO CO., LTD., Japan) at 1800 rpm. Bark slurry was fed continuously to the disk mill which contained two grinding disks positioned on top of each other. The fibrillation was operated in three passes at contact grinding with the gap between the two disks being 80, 60 and 40 μm. The fibrillated bark was collected as a bark slurry after these three passes.

Phenol–formaldehyde resole (PF) resin

A commercially available PF resin was used. The properties of the PF resin used are shown in Table 1.

Adhesives formulations

Commercial formulation

The commercial formulation consisted of the phenolic resin (100 parts by mass), wheat flour (10 parts), calcium carbonate (17 parts), sodium bicarbonate (3 parts), bark extract (2 parts) and water (10 parts).

Fibrillated bark slurry adhesives

Formulations, total solids contents and viscosities of the adhesives are shown in Table 2. Fibrillated bark slurry adhesives were prepared by mixing the fibrillated bark with a PF resin at a solids content ratio as shown in Table 3. The

Table 1 Properties of PF resin

	PF resin
Solids content (%)	44.8
Viscosity (Pa s) (23 °C)	0.33
pH[1]	11.3
Gelation time (min) (100 °C)[1]	24
Molecular weight[2]	
Number-average molecular weight (*Mn*)	1237
Weight-average molecular weight (*Mw*)	2993
Polydispersity (*Mw*/*Mn*)	2.42

[1] Catalogue spec

[2] The molecular weight was determined by measuring the acetylated phenolic resin by gel permeation chromatography (GPC)

Table 2 Fibrillated bark slurry adhesive composition and bonding quality of radiata pine plywood from the continuous 72-h boiling test (JAS)

Adhesives	CF[1]	1-1	1-2	1-3	1-4	1-5	1-6
Mass ratio							
PF resin (solids)	100	70	60	50	40	30	20
Fibrillated bark slurry (solids)	0	30	40	50	60	70	80
Wheat flour	24	0	0	0	0	0	0
Other solid components	22	0	0	0	0	0	0
Total solids content (%)	55	36	35	30	27	24	21[2]
Viscosity (Pa s) (23 °C)	1.4	1.7	1.6	2.0	1.9	2.0	2.9
Reactive components in adhesive (%)							
PF resin contents	32.0	25.2	21.0	15.0	10.8	7.2	4.2
Polyflavanoids contents	0.0	5.7	7.4	7.9	8.5	8.8	8.8
Bonding test results							
Number of panels	4	4	4	4	6	4	4
Number of specimens	32	32	32	32	48	32	32
Average of shear strength (MPa)[3]	0.84 ± 0.21b	1.06 ± 0.25a	1.07 ± 0.32a	0.88 ± 0.25b	0.82 ± 0.21b	0.81 ± 0.19b	0.77 ± 0.22b
Average wood failure ratio (%)[3]	87.2 ± 9.9a	72.2 ± 35.3abc	76.9 ± 27.2ab	65.3 ± 37.6bc	56.0 ± 26.0bc	52.2 ± 39.0c	78.1 ± 20.7a
Judgment of test results (JAS)[4]	PASS	PASS	PASS	PASS	PASS	PASS	PASS

[1] "CF" means "Commercial formulation" refers to a composition of a commercial adhesive using PF resin for plywood

[2] This value was not determined but estimated on the basis of the viscosity in the previous study [13]

[3] Results are given as the mean ± standard deviation. ANOVA for analysis of variance showed that the means are significantly different ($p < 0.001$). Same letters within a row are not significantly different as determined by the Tukey's test ($p < 0.05$)

[4] "PASS" means met the criteria of JAS

Table 3 Fibrillated bark slurry adhesive composition and bonding qualities of hinoki and karamatsu plywoods from the continuous 72-h boiling test (JAS)

Adhesives	CF[1]	1	2	3	CF[1]	1	2	3
Mass ratio								
PF resin (solids)	100	60	50	40	100	60	50	40
Fibrillated bark slurry (solids)	0	40	50	60	0	40	50	60
Wheat flour	15	0	0	0	15	0	0	0
Other solid components	22	0	0	0	22	0	0	0
Total solids content (%)	55	34	30	27	55	34	30	27
Viscosity (Pa s) (23 °C)	1.6	1.9	1.6	2.1	1.7	1.9	1.6	2.1
Bonding test results								
Plywood species	**Hinoki (Japanese cypress)**				**Karamatsu (*Larix* species)**			
Number of panels	4	4	4	4	4	1	2	3
Number of specimens	32	32	32	32	32	8	16	24
Average of shear strength (MPa)[2]	1.02 ± 0.37a	1.18 ± 0.28a	1.24 ± 0.37a	1.17 ± 0.39a	1.05 ± 0.33a	0.98 ± 0.34a	0.86 ± 0.36a	0.87 ± 0.24a
Average wood failure ratio (%)[2]	93.8 ± 5.5a	23.1 ± 33.2c	21.9 ± 25.3c	47.5 ± 35.6b	94.4 ± 8.4a	95.0 ± 8.7a	21.8 ± 17.6b	47.5 ± 30.3b
Judgment of test results (JAS)[3]	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS

[1] "CF" means "Commercial formulation" refers to a composition of a commercial adhesive using PF resin for plywood

[2] Results are given as the mean ± standard deviation. ANOVA for analysis of variance showed that the means are significantly different ($p < 0.001$). The same letter within a row are not significantly different as determined by the Tukey's test ($p < 0.05$)

[3] "PASS" means met the criteria of JAS

viscosity of each adhesive was adjusted to be in a range from 1 to 3 Pa s (23 °C) by adding water as shown in these tables.

Veneers

Veneers (250 mm × 250 mm × 3 mm) of radiata pine (*Pinus radiata*), hinoki (*Chamaecyparis obtusa*) and karamatsu (*Larix* species) were conditioned to 4% moisture content. The oven-dry densities of the veneers were 0.43, 0.43 and 0.60 g/cm^3, respectively.

Gluing conditions

Gluing conditions for plywood production were not optimized for each adhesive, but were set at the conditions assumed that the adhesive would completely cure. Three-ply plywood samples were prepared by bonding veneers of three wood species conditioned to 4% moisture content. Each of the adhesives was applied at a spread rate of 200 g/m^2 in a single glue line. The spread panels were prepressed at room temperature at 1.0 MPa for 30 min. All panels were then pressed at 135 °C for 9 min (60 s/mm) at 1.0 MPa.

Assessment of bonding quality

The assessment of the bonding quality was made to meet the criteria for an adhesive bonding level of "Type special" as defined in the JAS for Plywood [12]. "Type special" is the type of plywood the main purpose of which is for use outdoors or in places (environments) where conditions are continuously wet. The plywood samples were tested according to the "Continuous Boiling Test" defined in the JAS. Bonding strength tests on all specimens were carried out in the wet state after 72-h immersion in boiling water and the average of shear strength and average wood failure ratio determined. The bonding quality was regarded as "PASS" if shear strength (MPa) and average wood failure ratio (%) were not less than the values in the following combinations: 0.7 MPa—(no limit) %, 0.6 MPa—50%, 0.5 MPa—65% and 0.4 MPa—80%.

General methods

The viscosity of each of the adhesives was determined at 23 °C using a coaxial cylinder rotational viscometer (HAAKE Viscotester 550 (VT 550); Thermo Electron Co., Germany) with a SV-DIN type measuring system.

The solids content (%) of the adhesives was calculated using the equation indicated as follows:

$$\text{Solids content (\%)} = (\text{weight after drying} / \text{weight before drying}) \times 100.$$

Statistical analysis

The data obtained from the bonding quality test (shear strength and wood failure ratio) were analyzed by one-way analysis of variance (ANOVA) and Tukey's test. The statistical analyses were performed using the R open-source statistical software package (version 3.5.1; R Development Core Team, Austria).

Results

Fibrillated bark slurry adhesives

Radiata pine plywood

Plywood adhesives were formulated with a PF resin and fibrillated bark slurry (fibrillated bark slurry adhesives) in which the mass ratios of the PF resin to the fibrillated bark ranged from 70:30 (Adhesive 1-1) to 20:80 (Adhesive 1-6). Bonding quality (shear strength and wood failure ratio) of plywood samples, which were bonded with these adhesives, were assessed again using the JAS continuous 72-h boiling tests for plywood adhesives. The adhesive composition and results from the 72-h boiling tests are summarized in Table 2.

The ratios of PF resin (solids) and fibrillated bark slurry (solids) in Adhesives 1-1 to 1-6 are shown in Table 2. The solids content of Adhesives 1-1 to 1-6 decreased from 36 to 21%. However, even with the low total solids content compared to that of commercial PF formulation (55%) (CF), the gluing properties of all the adhesives were able to achieve a "PASS" on the basis of the JAS continuous 72-h boiling test. The results of statistical analysis both on shear strength and wood failure ratio showed that the shear strength of Adhesives 1-1 and 1-2 were significantly different from the other adhesives ($p < 0.05$) including CF and that those of Adhesives 1-3 to 1-6 were equivalent to CF whilst the average of the wood failure ratios of CF and Adhesive 1-6 were not significantly different from Adhesives 1-1, 1-2 and 1-3 but were significantly different from Adhesives 1-4 and 1-5. Consequently, it can be concluded that Adhesives 1-1 and 1-2 were superior in both the shear strength and the average of wood failure ratio to CF and Adhesives 1-3 to 1-6. These results strongly indicate the great gluability of the fibrillated bark slurry adhesives.

The results from the JAS continuous 72-h boiling test shown in Table 2 confirmed that adhesives containing 30 to 80 parts by mass of fibrillated bark slurry provided excellent glue bonding.

Hinoki and karamatsu plywoods

Fibrillated bark slurry adhesives were formulated with a PF resin and fibrillated bark slurry in which the mass ratios of the PF resin to the fibrillated bark ranged from 60:40 (Adhesive 1), 50:50 (Adhesive 2) to 40:60 (Adhesive 3). Bonding quality (shear strength and wood failure ratio) of plywood samples from hinoki and karamatsu, which were bonded with these adhesives, were assessed again using the JAS continuous 72-h boiling tests for plywood adhesives. The adhesive composition and results from the 72-h boiling tests are summarized in Table 3.

The ratios of PF resin (solids) and fibrillated bark slurry (solids) in Adhesives 1, 2 and 3 are shown in Table 3. The solids contents of these Adhesives were 34, 30 and 27%, respectively. The gluing properties of the adhesives were able to achieve a "PASS" on the basis of the JAS continuous 72-h boiling test. The results of statistical analysis on shear strength showed that the shear strength of all hinoki and karamatsu plywoods bonded with Adhesives 1 to 3 were very similar to those of control plywoods ($p < 0.05$), which were bonded with the commercial formulation. However, the average of wood failure ratio of all the plywood samples appeared to be variable, this may be due to variable quality veneer samples.

The results from the JAS continuous 72-h boiling test shown in Table 3 confirmed that although this was a preliminary experiment, adhesives containing 40 to 60 parts by mass of fibrillated bark slurry to 60 to 40 parts PF resin provided good glue bonding for hinoki and karamatsu plywoods.

Discussion

Bonding quality of fibrillated bark slurry adhesives

The previous paper [13] reported that ground radiata pine bark (< 1 mm) was sieved to obtain bark powder (< 63 μm), which was fibrillated with water and the fibrillated bark freeze-dried for use in adhesive formulations. However, in this current set of experiments the ground bark (< 1 mm) was directly fibrillated with water and the fibrillated bark slurry itself was used as a component of the adhesive formulations. Thus, the presently described process has removed two process steps sieving the ground bark and freeze-drying the fibrillated bark slurry. Since these steps add substantially to the process cost [15], their removal by using the fibrillated bark slurry directly into the adhesive formulations greatly reduces costs.

The results of this study showed that the fibrillated bark slurry adhesives provided excellent glue bonding meeting the criteria of the JAS. The fibrillated bark slurry adhesives, even with the low total solids content, the gluing properties of the adhesives were able to achieve a "PASS" on the basis of the JAS continuous 72-h boiling test. The results from the statistical analysis and the JAS tests showed that the best gluing properties were obtained with the Adhesives 1-1 and 1-2 when adhesives containing fibrillated bark were considered.

This study showed that fibrillated bark slurry adhesives gave excellent bonding qualities which satisfy the requirements of the JAS for exterior use of plywood, despite the fact that they contained low total solids contents. Adhesives containing fibrillated bark slurry contained much lower total solids contents and were simple formulations in that they contained only PF resin, fibrillated bark and water.

As the previous paper [13] reported, the gluing conditions used in this study are our laboratory standard, which assesses the gluability of adhesives for plywood. The hot pressing time of 9 min at 135 °C is quite a long time for a 3-layered plywood and would not be economic in commercial practice. The next stage in this study for the commercial application of bark adhesives will be to optimize the gluing conditions. Since a preliminary experiment showed that the hot pressing time of 5 min provided good gluing properties, we are confident that the 10-min hot pressing time can be substantially reduced.

Comparison between fibrillated bark slurry adhesives and fibrillated and freeze-dried bark adhesives

In order to compare the results obtained from the fibrillated bark slurry adhesives and from the previous fibrillated and freeze-dried bark adhesives [13, 14], a statistical analysis was conducted using the results from all 13 adhesives test (Adhesives 1-1 to 1-6, Adhesives 2-1 to 2-6 which are described in the previous paper [13] and CF). The results of the statistical analysis are summarized in Table 4.

It appeared that the gluing property, particularly the average of shear strength of the bark slurry adhesives was higher than that of the fibrillated and freeze-dried bark adhesives. However, the results from the statistical analyses showed that there was no significant difference between them. As far as the average shear strength, all the bark adhesives performed better or same as the commercial formulation (CF), whilst as far as the average of wood failure ratio, CF performed better than the bark adhesives. Therefore, the wood failure of the bark adhesives should be improved before the bark adhesives are commercialized and used in the plywood industry.

Gluability of fibrillated bark slurry adhesives for plywood production of hinoki (*Chamaecyparis obtusa*) and karamatsu (*Larix* species)

According to the Japanese Ministry of Agricultural, Forestry and Fishery statistics [16], the supply of various woods to the plywood manufacturing industry in 2018

Table 4 Comparison between fibrillated bark slurry adhesives and fibrillated and freeze-dried bark adhesives

Adhesives		Fibrillated bark slurry adhesive						fibrillated and freeze-dried bark adhesive[2]					
	CF[1]	1-1	1-2	1-3	1-4	1-5	1-6	2-1	2-2	2-3	2-4	2-5	2-6
Total solids content (%)	55	39	33	30	27	24	21	36	35	30	27	24	21
Reactive components in adhesive (%)													
PF resin content	32.0	27.3	19.8	15.0	10.8	7.2	4.2	25.2	21.0	15.0	10.8	7.2	4.2
Polyflavanoid content	0.0	6.2	6.9	7.9	8.5	8.9	8.9	5.7	7.4	7.9	8.5	8.8	8.8
Bonding test results													
Average of shear strength[3]	0.84 ± 0.21c	1.06 ± 0.25ab	1.07 ± 0.32a	0.88 ± 0.25bc	0.82 ± 0.21c	0.81 ± 0.19c	0.77 ± 0.22c	1.04 ± 0.28ab	1.13 ± 0.30a	0.74 ± 0.15c	0.71 ± 0.13c	0.74 ± 0.24c	0.70 ± 0.13c
Average wood failure ratio[3]	87.2 ± 9.9ab	72.2 ± 35.3abc	76.9 ± 27.2abc	65.3 ± 37.6bcd	56.0 ± 26.0cde	52.2 ± 39.0de	78.1 ± 20.7abc	89.1 ± 15.5ab	90.9 ± 13.3a	72.0 ± 33.3abcd	32.5 ± 35.3ef	21.9 ± 25.6f	27.8 ± 28.6f
Judgment of test results (JAS)[4]	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS

[1] "CF" means "Commercial formulation" refers to a composition of a commercial adhesive using PF resin for plywood

[2] All the results are described in the previous paper [13]

[3] ANOVA for analysis of variance showed that the means are significantly different ($p < 0.001$). The same letter within a row are not significantly different as determined by Tukey's test ($p < 0.05$)

[4] "PASS" means met the criteria of JAS

was 5.29 million m^3 in Japan, of which Japanese domestic woods was 4.49 million m^3 (85%), whilst imported woods was 0.80 million m^3 (15%). The Japanese domestic softwoods consisted of sugi (*Cryptomeria japonica* D, Don): 63.5%, karamatsu: 17.9%, hinoki: 8.0%, ezomatsu (*Picea jezoensis* Carr. var. *hondoensis* Rehd.)·todomatsu (*Abies firma* Sieb. et Zucc): 5.4% and akamatsu (*Pinus densiflora* Sieb. et Zucc)·kuromatsu (*Pinus thunbergii* Parl): 4.2%, which occupies 99% of the total domestic woods for plywood production.

In this study, gluability of the fibrillated bark slurry adhesives were tested only with plywoods from hinoki and karamatsu. This was due to the availability of veneers for testing. Since the production of sugi plywood is a major industry in Japan, the gluability of the fibrillated bark slurry adhesives should be conducted in the production of sugi plywood and this will be undertaken.

Reactive components and their roles in gluing

The fibrillated radiata pine bark slurry adhesives contain a PF resin and polyflavanoid compounds from the radiata tannin as principal reactive components, which provide excellent gluing properties.

PF resins consist of methylol phenol monomers, dimers, oligomers and polymers, which will crosslink on heating so that glue bonding can be made. However, radiata tannin does not crosslink on heating without crosslink reagents such as paraformaldehyde. For example, the fibrillated bark slurry without any PF resin (total solids content: 22.5%, viscosity: 2.27 Pa s) was able to provide a high-quality bonding when tested under dry but when the plywood samples were heated in boiling water, the bonding was completely destroyed.

The first proposal that tannin could be used as a curing accelerator for phenol formaldehyde resins [17] was made in 1918. However, it was not until the later 1940s that tannin research for use in wood adhesives seriously was undertaken by Dalton [18]. In 1966, the use of wattle tannin had been established by Plomley for the production of water-resistant tannin adhesives [19] and the world's first commercial use of wattle tannin for plywood adhesives occurred in Australia. The use of radiata tannin in wood adhesives has not been universally accepted, the rate of its reaction with formaldehyde was 10 times faster than that of wattle tannin with formaldehyde. In addition, radiata tannin reacts with crosslink reagents such as formaldehyde and methylol phenols at lower temperatures than those for PF resins.

Since the chemical composition of the fibrillated and freeze-dried bark is the same as that of the bark in the fibrillated bark slurry, the amounts of reactive components (PF resin and polyflavanoid) in the fibrillated bark slurry adhesives have been calculated in the same way as was used in the previous experiments which was described in the first paper [13].

As shown in Table 2, the PF contents in fibrillated bark slurry adhesives decreased from 25.2% for Adhesive 1-1 to 4.2% for Adhesive 1-6 whilst the polyflavanoid contents increased from 5.7 to 8.8% while the total solids contents decreased from 36 to 21%.

Since radiata tannin in the fibrillated bark slurry can react with the PF resin, when the PF resin exists as the major component (Adhesive 1-1), the radiata tannin acts as a curing accelerator for the PF resin, so that the PF adhesives can cure faster and also at lower temperatures than PF adhesives without the tannin. When radiata tannin exists as the major component, (Adhesive 1-6), the PF resin acts as a hardener crosslink reagent for the tannin adhesive as well as a PF adhesive.

Considering that the contents of the reactive components in radiata tannin adhesives and also in commercial PF resin adhesives should be approximately 30% in order to produce high-quality plywood gluing [20, 21], the amount of the reactive components of 13.0% (less than half that of the commercial PF resin adhesives) in the fibrillated bark slurry Adhesive 1-6 is small indeed to produce a similar shear strength to that of the commercial PF resin adhesive.

This indicates that in addition to polyflavanoid tannin, other chemical components such as cellulose, lignin, hemicellulose, neutral solvent extractives and phenolic acid (1% NaOH solubles) [9] are likely to play an important role in producing good quality plywood gluing. Since the first paper described the existence of nano-sized fibers in the fibrillated and freeze-dried bark, those nano-sized fibers may have an important role in the gluing.

Conclusions

This study showed that the gluability of fibrillated bark slurry adhesives, which were formulated with PF resin, fibrillated bark slurry and water only, gave an excellent quality of gluebonds despite the fact that gluing conditions were not optimized. These fibrillated bark slurry adhesives have a number of advantages in that there is no requirement for tannin extraction, there is a total use of bark, it is a very economical process without requiring sieving the ground bark nor freeze-drying of the fibrillated bark slurry and there is a high gluebond quality.

The results from the JAS continuous 72-h boiling test confirmed that adhesives containing 40 to 60 parts by mass of fibrillated bark to 60 to 40 parts PF resin provided good glue bonding for hinoki and karamatsu plywoods.

These results may suggest the possibility of fibrillated bark slurry adhesives to be used not only for plywood production, but also for the other wood-based panels (fiberboard, particleboard, strand board, etc.), and so further research is anticipated.

Acknowledgements
The authors would like to thank Hidetaka Nogami at Okayama Prefectural Research Institute for Forest and Forest Products for producing fibrillated bark slurry samples and Frank Lawson from Monash University for his critical reading of this manuscript.

Authors' contributions
MH, KO and YY conceived and designed the experiments; MH performed the experiments and analyzed the physical test data, and NK analyzed chemical components; MH, NK, KO and YY wrote the paper. All authors read and approved the final manuscript.

Funding
Not applicable.

Availability of data and materials
All data generated or analyzed during this study are included in this published article.

Competing interests
The authors declare that they have no competing interests.

Author details
[1] WOOD ONE Co., Ltd, 1-12-1, Shimohera, Hatsukaichi-shi, Hiroshima 738-0023, Japan. [2] Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia.

Received: 16 July 2019 Accepted: 7 February 2020
Published online: 26 February 2020

References

1. Yazaki Y (2015) Utilization of flavonoid compounds from bark and wood: a review. Nat Prod Commun 10(3):513–520
2. Ogawa S, Yazaki Y (2018) Tannins from *Acacia mearnsii* De Wild. bark: tannin determination and biological activities. Molecules 23(4):837. https://doi.org/10.3390/molecules23040837
3. Nakamoto Y, Tsunoda T, Ono K, Yano H, Yazaki Y, Jian H, Lawson F, Uhlherr PHT (2011) A method for the production of powder with high tannin content and its use (in Japanese). JP Patent 4683258
4. Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 40:3941–3994
5. Isogai A (2013) Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials. J Wood Sci 59(6):449–459
6. Nakagaito AN, Yano H (2014) Cellulose-nanofiber-based materials. In: Hinestroza JP, Netravali AN (eds) Cellulose based composites: new green nanomaterials. Wiley-VCH, Weinheim, pp 3–25
7. Nair SS, Yan N (2015) Effect of high residual lignin on the thermal stability of nanofibrils and its enhanced mechanical performance in aqueous environments. Cellulose 22(5):3137–3150
8. Nair SS, Yan N (2015) Bark derived submicron-sized and nano-sized cellulose fibers: from industrial waste to high performance materials. Carbohydr Polym 134:258–266
9. Yazaki Y (1985) Extraction of polyphenols from *Pinus radiata* bark. Holzforschung 39(5):267–271
10. Yazaki Y, Hillis WE (1977) Polyphenolic extractives of *Pinus radiata* bark. Holzforshung 31(1):20–25
11. Yazaki Y, Hillis WE (1980) Molecular size distribution of radiata pine bark extracts and its effect on properties. Holzforschung 34(4):125–130
12. Japanese Agricultural Standard (2014) Japanese Agricultural Standard (JAS) for Plywood (in Japanese), Notification No. 303 of the Ministry of Agriculture, Forestry and Fisheries of Japan. Japan Plywood Inspection Corporation, Tokyo, Japan
13. Matsumae T, Horito M, Kurushima N, Yazaki Y (2019) Development of bark-based adhesives for plywood: utilization of flavonoid compounds from bark and wood. II. J Wood Sci 65:9. https://doi.org/10.1186/s10086-019-1780-x
14. Horito M, Kurushima N, Matsumae T, Yazaki Y (2018) ADHESIVE. International Patent Publication WO 2018/199190 A1, 1 Nov 2018
15. Ferenezi S, Molnár H, Adányi N, Cserhalmi Z (2018) Comparison of microwave vacuum-, freeze- and hot-air drying by energy efficiency and aroma composition of dried hop (*Humulus lupulus*). Int J Food Eng 4(2):136–139
16. Japan Ministry of Agriculture, Forestry and Fisheries (2019) Wood Statistics in 2018 (Heisei 30). http://www.maff.go.jp/j/tokei/kouhyou/mokuzai/attach/pdf/index-103.pdf. Accessed June 24 2019
17. McCoy JPA (1918) Process of hardening phenolic condensation products. U.S. Patent 1,269,627, June 18 1918
18. Dalton LK (1950) Tannin-formaldehyde resin adhesives for wood. Aust J Appl Sci 1:54–70
19. Plomley K (1966) Tannin-formaldehyde adhesives for wood. Division of Forest Products Technological Paper, No 39, pp 1–16
20. Yazaki Y, Collins PJ (1994) Wood adhesives from *Pinus radiata* bark. Holz Roh-Werkst 52(3):185–190
21. Yazaki Y, Collins PJ (1998) A novel tannin extraction from Radiata pine bark for high quality wood adhesives. In: Proceedings of the Fourth Pacific Rim Bio-Based Composites Symposium, Bogor, Indonesia, 2–5 November 1998, pp 19–26

Publisher's Note