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Research Article
Effect of Tannin Addition in Phenol-Formaldehyde Adhesive on Reducing the Curing Temperature

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Abstract

Background and Objective: The plywood processing industry in Indonesia still uses synthetic adhesives which require high temperatures for the adhesive curing process. This study examined the effect of *Rhizophora* bark tannin on the reduction of adhesive curing temperature of Phenol-formaldehyde during the production of plywood. **Materials and Methods:** The dried bark was ground and sieved with a mesh size of 20-40. Tannin was extracted from the powdered bark by hot-water extraction at 70°C for 3 hrs with a water-to-bark ratio of 6:1 (w/w basis). The extracted tannin was filtered by using number 1 filter paper and mixed with Phenol-Formaldehyde (PF) resin at various ratios for the production of plywood. Delamination tests, bonding tests, adhesive curing analysis and Scanning Electron Microscopy (SEM) was used to observe the effects of *Rhizophora* bark tannin on the adhesive curing temperature during plywood production. **Results:** It was found that the rate of resin reaction increases when tannins are added to the PF resin which causes rapid drying. The addition of tannins to the PF resin reduced the delamination value and met the JAS test standards but it became negative if the amount of tannin added was higher (20%). The bond value in the wet cycle is quite good and has a relatively small reduction (23%). **Conclusion:** The addition of Rhizophora bark tannins to PF resin reduced the curing temperature of PF resin from 120-105°C. The addition of tannins up to 10% can be used to reduce temperatures up to 15°C in plywood production

Key words: Mangrove bark, tannin, plywood, bonding, crystallinity, volatile organic compound, wood composites

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Tannin is a complex polyphenolic material that is obtained from bark, roots, seeds or leaves by extraction with water, ethanol or acetone[1]. Mangrove species, especially the bark of *Rhizophora* spp., are one of many bio-resources containing tannin. Using this tannin as an adhesive for wood composites would reduce mangrove bark waste.

At present, 80% of wood applications need adhesive by any means[2]. In Indonesia, the wood composite industry uses synthetic formaldehyde-based adhesives such as Urea-Formaldehyde (UF) and Phenol-Formaldehyde (PF). These adhesives cause environmental problems by formaldehyde emission, which is harmful to human health. The synthetic adhesives UF and PF also require higher temperatures (110-140°C) for curing during composite production[3,4], thus, they potentially increase the effect of global warming and environmental burden. Natural adhesives could reduce the environmental load as well as make use of a natural renewable resource.

Tannin has been successfully applied in environmentally friendly adhesives[5] and used to replace UF resin to reduce formaldehyde and Volatile Organic Compound (VOC) emissions from adhesives[6,7]. Hafiz[8] reported that the curing reactions of PF resin could be improved by the addition of tannin. The addition of tannin to PF resin reduces the temperature during curing[9-12]. Along with lowering curing temperature, tannin also improves the durability of composites against termites and fungi. The polyphenolic compounds of tannin protect the composites against termite attack[13]. In a living tree, these polyphenols protect the tree against herbivore attacks and diseases[14]. Thus, it might be very helpful to use tannin with synthetic resin. However, there is very limited information on tannin-based adhesives, especially regarding optimum curing temperature and mixing ratio with PF resin.

Hence, the objective of this study was to determine the optimum temperature for adhesive curing by adding tannin extracted from *Rhizophora* spp. with PF resin for the production of plywood. Analyses of the mixing ratio and penetration of glue into the ply were also performed.

MATERIALS AND METHODS

The research was conducted at the Wood Technology Laboratory of the School of Life Sciences and Technology, Bandung Institute of Technology, Indonesia and the plywood industry "PT. Sumber Graha Sejahtera", Tangerang, Indonesia, from April-October, 2020, according to the following scheme.

Materials: *Rhizophora* spp. the bark was collected from a 30-year-old mangrove forest in West Java, Indonesia. Mangrove Wood Bark (MWB) was cut into samples of 20×20 mm. The samples were air-dried until the moisture content reached 5%. Dried MWB was ground in a Willey mill and sieved with 20-40 mesh sizes to separate debris such as sand, stones, etc. After sieving, the MWB was crushed to a particle size of 2-2.8 mm. Plywood was produced from rubber wood having a diameter of 20 cm and the commercial-grade PF resin was supplied by the Pamolite Adhesive Company, Probolinggo, Indonesia.

Tannin-PF resin preparation: Tannin was extracted from dried MWB by hot water extraction at 70°C for 3 hrs with a water-to-MWB ratio of 6:1 (w/w basis). After extraction, the material was filtered with number 1 filter paper to obtain the tannin (Fig. 1). Tannin powder was produced from the filtered extract after drying in an oven at 60°C temperature.

Powdered tannin was dissolved in water to achieve a tannin solution with a concentration of 41% (w/w basis). The commercial-grade phenol and formalin (41%) were placed into a laboratory reactor (phenol to formalin molar ratio of 1:2.2). Sodium hydroxide solution (50%) was added to the mixture until the pH of the mixture reached 11. The mixture was heated under reflux condition at 120°C. The boiling of the mixture started after half an hour. After boiling, the gel time of PF resin was measured continuously up to a gel time of 120 sec. The tannin solution was mixed with PF resin at different ratios while the mixture was stirring slowly (60 rpm). A small amount of ammonium chloride was added as a hardener. After 2 hrs, the tannin-Phenol-formaldehyde resin was ready. The synthesized resin was used for the manufacturing of plywood.

Board manufacture: Three-ply rubber plywood was manufactured using a hot press technique. Phenol-formaldehyde and tannin were used as glue to make the composites with the mixing ratio of 90:10 and 80:20 ratios. The layers were glued with different glue mixing ratios with a glue spraying rate of 180 g/m^2. The mould was cold-pressed for 10 min and later hot-pressed for another 5 min at 120 and 105°C with a constant pressure of 1.0 M Pa. After curing, the composites were stored in the conditioning room at 20°C and 12% relative humidity for at least 72 hrs before testing. At least 15 plywood's were manufactured for each category of glue and pressing temperature.

Analysis of adhesive properties

Delamination test: The delamination test was done following the in-house method of standard JAS[15]. The success ratio is presented in Eq. 1:

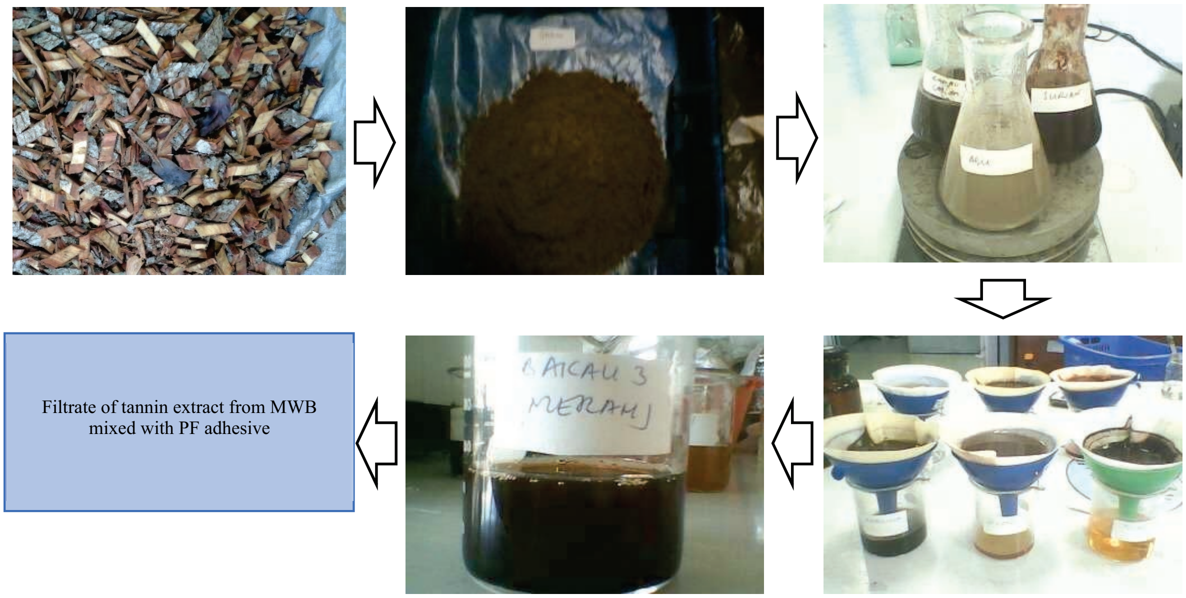

Fig. 1: Extraction process of MWB

$$S = \frac{N_s}{N_r} \times 100 \quad (1)$$

where, S is the success ratio, N_s is the number of successful specimens and N_T is the total number of test specimens.

Bonding test: The bonding test was conducted using a universal testing machine (Hounds Co., Seoul, Korea) in the tensile mode with a sample size of 5×5 cm and a crosshead speed of 2 mm/min[7].

Scanning electron microscopy (SEM): A scanning electron microscope (JEOL-JSM-6510LV SEM type) was used to analyse the morphology of the plywood produced. A thin section of the sample was mounted on an aluminium stub using conductive silver paint and sputter-coated with gold before the examination. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an acceleration voltage of 15 kV.

X-ray diffraction (XRD) analysis: The crystallinity of tannin liquid was carried out using an X-ray Diffractometer (XRD) (XRD, PW 1710, Philips analytical), operation at 40 kV and 30 mA with Cu/Kα (λ = 1.54060°A) radiation source. The diffractograms were scanned using a scanning rate of $0.5^\circ\ s^{-1}$ and in steps of 0.02° from 5-65° (2θ) at room temperature. The crystalline was measured by comparing the crystalline region with the amount of crystalline and amorphous regions[16], according to Eq. 2:

$$\text{Crystallinity (\%)} = \frac{\text{Crystalline region}}{\text{Crystalline + Amorphours region}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Adhesion properties: The assessment of ten specimens from each treatment revealed that all plywoods cured at 105°C passed the delamination test (Table 1). Observations were made on four sides of the glue line. All panels that passed the delamination test had a non-delamination percentage of less than 10% on four sides of the glue line[15].

Table 1 shows that the tannin 20/PFH120 failed the delamination test, while the tannin 20/PFH105 passed. Hoong *et al.*[17] investigated the delamination of *Acacia mangium* bark extracts co-polymerized with Phenol-formaldehyde (PF) for bonding mempisang (*Annonaceae* spp.) veneers. The authors reported that a high tannin percentage reduced the adhesion properties when mixed with PF resin. Furthermore, Kim[5] suggested that natural tannin was added to synthetic resin for increasing the viscosity of adhesive for better surface bonding. However, the use of a hardener in PF resin expands its ability to accommodate more tannin as a hardener facilitates the reaction and can improve the adhesion properties[8]. Temperature stimulates the pH of tannin, which has a positive impact on delamination and meets the test standards but it decreases at 20% tannin. Zhao *et al.*[18] reported that tannin reduced the curing temperature by promoting the curing reactions of adhesive during hot-pressing. Thus, the addition of tannin in PF resin reduced the curing temperature of PF resin from 120-105°C.

Table 1: Delamination test of plywood made using phenol-formaldehyde (pf) and tannin with different ratios at different curing temperatures

Additive (%)	Curing temperature (°C)	Adhesive (%)	Code treatment	Delamination (%)
0	105	PF+hardener	PFH105	Passed (100)
0	120	PF+hardener	PFH120	Passed (100)
Tannin (10)	120	PF+hardener	Tannin 10/PFH120	Passed (100)
	105	PF+hardener	Tannin 10/PFH105	Passed (100)
Tannin (20)	120	PF+hardener	Tannin 20/PFH120	Failed
	105	PF+hardener	Tannin 20/PFH105	Passed (100)

PF: Phenol-formaldehyde, hardener: Hexamine, PFH105: Adhesive with phenol-formaldehyde resin and hardener and curing temperature 105°C and tannin 10/PFH105: Adhesive with addition tannin 10% and phenol-formaldehyde resin that curing temperature at 105°C

Table 2: Bonding properties at 105°C

				Bonding (N/mm^2)		
Wood species*	Adhesive**	Thickness (mm)	Ply	Wet cycle	Air dry	Wet/dry cycle ratio (%)
Rubber	PF 90%	5	3	1.26	1.64	0.77
		Tannin 10%		Passed (>0.65 N/mm^2)		
Rubber	PF 80%	5	3	1.09	1.57	0.69
		Tannin 20%		Passed (>0.65 N/mm^2)		

*Veneer, **Weight based ratio

Based on the analysis of curing temperature, bonding tests were conducted for samples cured at 105°C to identify the effects of tannin addition in PF resin. Bonding tests were performed in both air dry (dry test) and wet cycle conditions (Table 2). The air-dry testing condition gives a higher value compared to the same wet cycle for all the cases. Furthermore, the increased addition of tannin reduced the bonding properties for both air-dry and test cycle conditions. The value of the test cycle to air-dry ratio was 0.77, indicating that the binding was reduced by only 23%. However, the ratio decreased when more tannin was added to PF resin.

Curing behaviour and SEM analysis: Pressing time is another important parameter for hot pressing. Generally, plywood specimens made with a long pressing time gain improved mechanical properties when PF resin is used. The data of Fig. 2(a-b) shows the SEM analysis and curing behaviour of PF resin with and without tannin and its crystallinity during the production of plywood.

Based on the X-ray diffraction analysis, PF resin without tannin (Fig. 2a) showed an amorphous XRD pattern because it had a hump[19]. Whereas after PF resin added tannin and hardener at 105°C curing temperature (Fig. 2b), PF resin added hardener (Fig. 3a) and PF resin added tannin and hardener at 120°C curing temperature (Fig. 3b), were shown some of the sharp peaks, which resulted as characteristics of crystalline compounds[20]. The addition of MWB tannin to PF resulted in the increased crystallinity degree, due to the higher intensity and the narrower of the half-width peak at 2, 12 and 25°C as shown in Fig. 2b and 3b, respectively. The intensity of crystalline after PF resin added tannin and hardener at 105°C curing temperature were 229 and 200 counts at 2, 12 and 25°C, respectively (Fig. 2b).

On the other hand, the intensity of crystalline after PF resin added hardener at 120°C curing temperature was 286 and 304 counts at 2, 12 and 25°C, respectively (Fig. 3a), while the values were increased into 487 and 412 counts after PF resin added tannin at 2, 12 and 25°C, respectively (Fig. 3b).

SEM analysis also confirmed the result of XRD analysis when the examination was done at the transverse direction of the plywood thickness. SEM analysis confirmed that resin penetrated up to 44 and 69 μm for PF resin with tannin and PF resin, at 105°C curing temperature (Fig. 2b) respectively. This higher penetration of PF resin into wood might result in a lower crystallinity degree for PF resin impregnated plywood.

Together, these results may be due to the addition of tannin in PF resin, which increases the rate of curing reactions, resulting in faster drying of resin. Tannin as an additive to PF resin accelerates the reactivity of the tannin-formaldehyde matrix with wood, hence decreasing the curing time[17]. Thus, the addition of tannin in PF resin decreases the drying time by increasing the reactivity, which ultimately decreases the curing time and increases the crystallinity degree.

The increase of crystallinity degree is attributed to the amorphous regions being preferentially attacked and rapidly hydrolyzed below the gelatinization temperature, increasing the decomposition temperature of native starch[21]. This result was also supported by the SEM analysis where resin penetrated wood to 48 and 25 μm for PF resin and PF resin with tannin, at 120°C curing temperature (Fig. 3b)

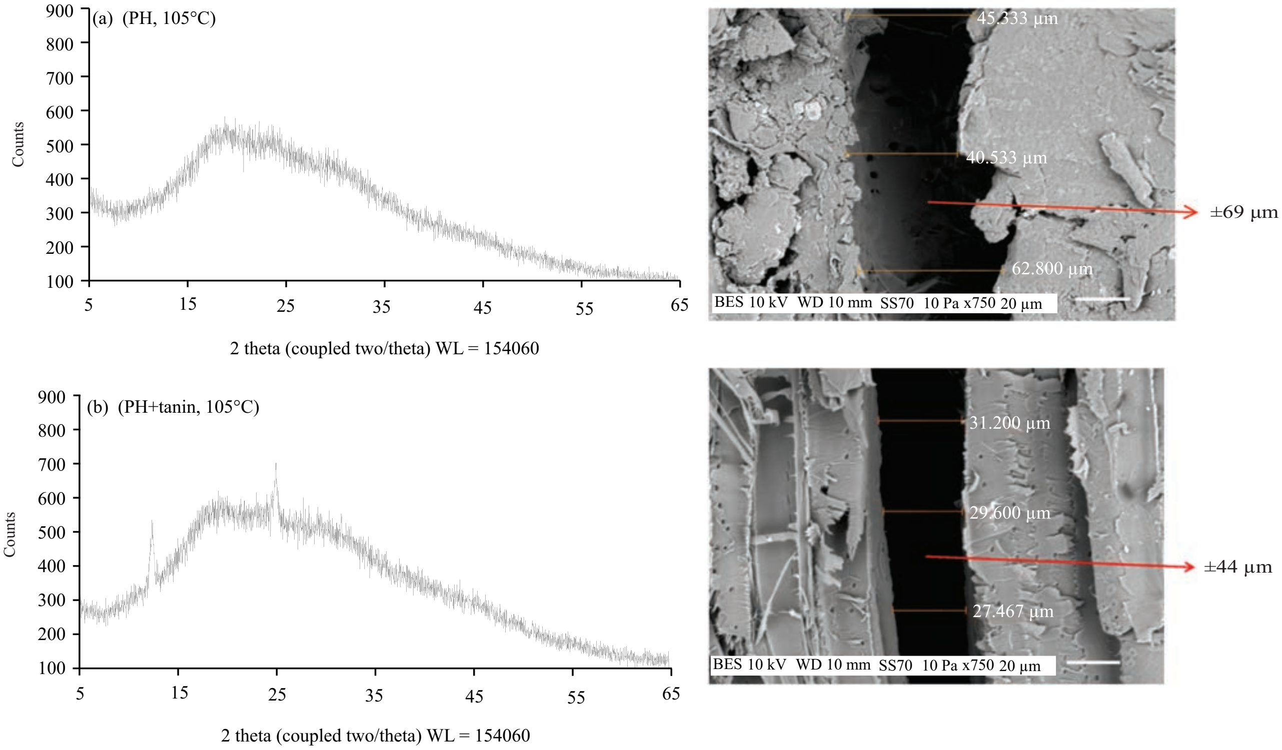

Fig. 2(a-b): XRD and SEM analysis of plywood

(a) PF resin and (b) PF resin added tannin (10%) and hardener (8%) at 105°C curing temperature

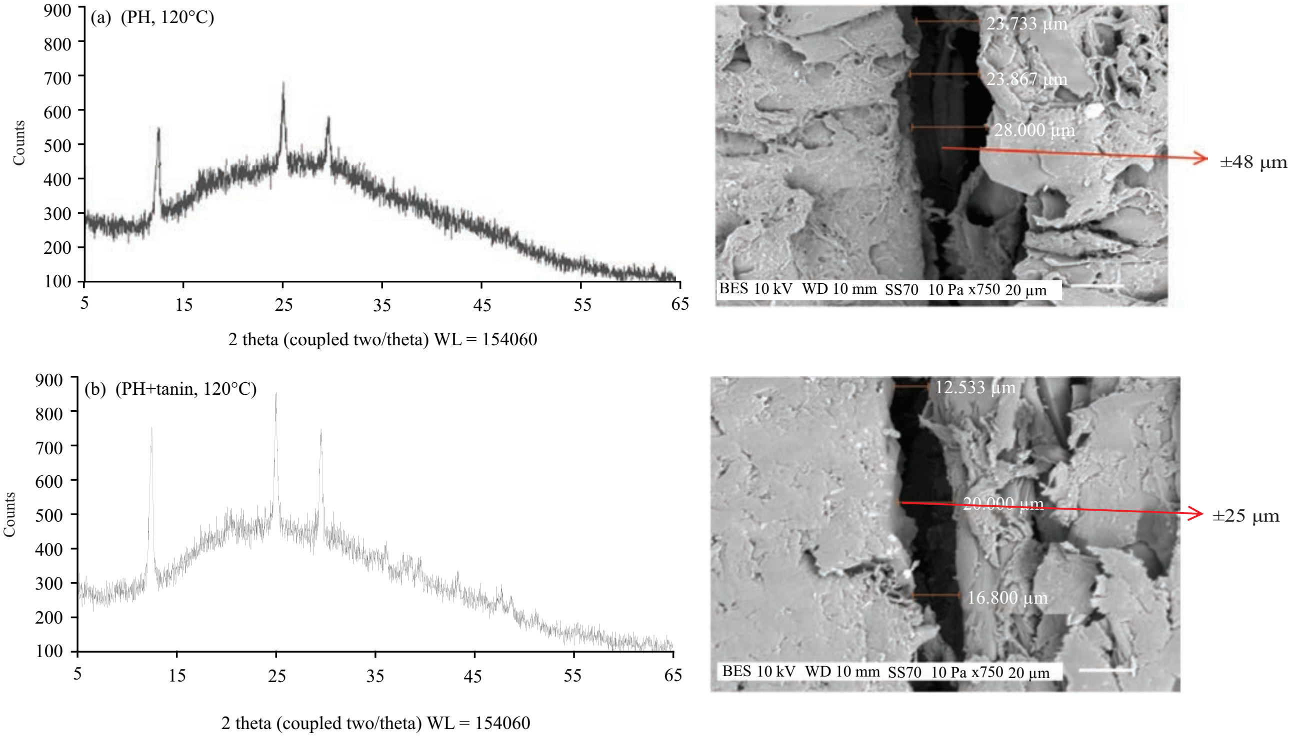

Fig. 3(a-b): XRD and SEM analysis of plywood

(a) PF resin added hardener (8%) and (b) PF resin added tannin (10%) and hardener (8%) at 120°C curing temperature respectively. Higher reactivity and quick-drying might be the cause of this higher crystallinity degree when tannin is added to PF resin.

Generally, the temperature changes in adhesively bonded joints cause a wide variety of different stress states. The viscosity of the adhesive is reduced with the heating of the adhesive, which enables it to flow and wet the surfaces. However, the temperature rise also leads to curing when the polymer develops cross-links and changes from a liquid to a solid. In the process of solidifying, the cold-curing adhesives also shrink. The curing shrinkage induces stresses in the adhesive by reaction against the adherents.

The degree of crystallinity is positively correlated with intimate contact of adhesive in Fig. 3b. The glue line at 120°C is thinner than that of 105°C temperature. Tannin as an additive in Phenol-formaldehyde can reduce the curing temperature and can increase the intensity of crystalline up to 12-46% when the temperature drops from 120-105°C. The results of this study show that the optimum curing temperature for plywood manufacturing with tannin (10%) and PF resin is 105°C.

CONCLUSION

The reaction rate of resin was increased when tannin was added to PF resin which also induced quick drying. The addition of tannin in PF resin reduced delamination value and meet test standards, however, it was negative when a higher amount of tannin (20%) was added. The bonding values of the wet cycle was quite well and had a relatively small reduction (23%). The addition of tannin from MWB in PF resin reduced the curing temperature from 120-105°C and increased the crystallinity index. The optimum temperature for plywood manufacturing is 105°C when 10% tannin would be added to PF resin.

SIGNIFICANCE STATEMENTS

This study discovers the addition of tannins from mangrove bark (MWB) to Phenol-formaldehyde adhesive was able to reduce the curing adhesive temperature of the plywood. In addition, it can increase the crystallinity area in the adhesive line and meets JAS standards in plywood applications. This study can also help the plywood industry in Indonesia to reduce the cost of PF adhesives through the use of tannins as a PF adhesive extender for plywood applications.

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