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Emerald Article: Eco-friendly tannin-phenol formaldehyde resin for producing wood composites

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Eco-friendly tannin-phenol formaldehyde resin for producing wood composites

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Abstract

Purpose – The purpose of this paper is to describe the development of an eco-friendly tannin-phenol formaldehyde resin (PFT) applicable in the wood composite industry.

Design/methodology/approach – The bark of oak (*Quercus castaneifolia*) contains a large amount of condensed tannin. Condensed tannin, with a large amount of Catechol groups was considered for reducing the formaldehyde emission level on the adhesive system. Physical characteristics of synthesized PFT resin were evaluated.

Findings – For optimal extraction, three solvents were used in the extraction process. The results showed that a mixture of water-methanol (1:1 v/v) as extracting solvent is the best solvent and yields about 14 per cent tannin based on dry weight of bark. For producing tannin phenol formaldehyde adhesive, 10 per cent, 20 per cent and 30 per cent (based on PF dry weight) of PF, substituted with natural extracted tannin. For evaluating PFT performance effects of percentage amount of substitution tannin content on the gel time, viscosity, pH, and density of adhesives were evaluated. Based on emission test (JIS A 1460-2001) formaldehyde emission of PFT 10 per cent, 20 per cent and 30 per cent were 1.13, 1.12 and 0.4 mg/100 g, which is very low compared with tannin-free PF.

Research limitations/implications – Tannin-PF adhesive compared to PF adhesive had lower PH, higher viscosity and shorter gel time.

Practical implications – The method developed provides a simple and excellent renewable resource "tannin" which can be used or partially substituted in phenol formaldehyde adhesive.

Originality/value – Results showed that replacing PF for tannin reduces modulus of rupture (MOR) and modulus of elasticity (MOE) slightly but has significant effects on IB, water absorption and thickness swelling.

Keywords Resins, Composite materials, Wood, Adhesives, Wood composite, Bark, Phenol formaldehyde, Extracted tannin

Paper type Research paper

Introduction

Phenol-formaldehyde (PF) resins are the most commonly used structural adhesive for producing exterior wood composites because of their good bonding ability with different lingo cellulosic substrates, water resistance and low initial viscosity (Pizzi, 1983). The high fluidity of PF resoles favors the spreading of the resins on the wood surface with relatively low migration into the wood, thus enhancing the mechanical bond between the wood and adhesive (Vazquez *et al.*, 1996; Gornik *et al.*, 2000). Many wooden flooring products containing formaldehyde-based resins release formaldehyde vapor, thus causing consumer's dissatisfaction and health-related complaints. Various symptoms such as the most common of which is irritation of the eyes and the upper respiratory tract are attributed to the emission of formaldehyde gases. These considerations have led to an intensified interest in the indoor environment. Residence products, especially construction materials are a major source of formaldehyde emission in the indoor environment (Kim *et al.*, 2007; Brown, 1999). Formaldehyde-based resins, however, has advantage super bonding properties and is inexpensive. Therefore, they are used extensively as the adhesive in manufacturing various household products. Several thin layers of wood are glued together by UF and PF resin to produce plywood. However, the toxicity of UF and PF resins bonded wood particles due to the emission of formaldehyde and associated possible health hazards, could act as promotion obstacle under the prevailing environmental concerns. Consequently, for reducing formaldehyde emission, there is a need for using replacement material in UF and PF adhesive. Several efforts have been made to reduce or replace formaldehyde contents in adhesive formulation (Mozaffar *et al.*, 2004; Nihat and Nilgul, 2002; Pizzi, 1977; Yoosup *et al.*, 2008; Eom *et al.*, 2006) or to develop adhesives from natural materials (Fuwap, 2003; Pizzi, 2006; Pichelin *et al.*, 2006; Yuan and Kaichang, 2007). More recent methods to decrease and minimize formaldehyde release are based on cornstarch and tannins were reported (Moubarik *et al.*, 2010; Tabarsa *et al.*, 2011). Among the possible alternatives, tannin is an excellent renewable resource which can be used for replacing. It could be partially substituted in industrial phenol formaldehyde adhesives. Because of their ability in reducing gel time and pressing time, polyphenolic compounds of bark extracts has been used as accelerators application of PF resins in particleboard and plywood manufacture (Vazquez *et al.*, 1996, 2002, 2003; Trosa and Pizii, 1997, 2001; Nemli *et al.*, 2004; Calve *et al.*, 1995). Tannins are complex phenolic compounds

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of two main categories: hydrolysable and condensable tannins. Condenced tannins used in the previously described studies are very generally extracted from the bark of various trees: pine, pinus radiat and pinaster, grape pomace, mimosa, etc. (Fradinho *et al.*, 2002; Panamgama, 2007; Ping *et al.*, 2011; Stefani *et al.*, 2008). Tannins have higher reactivity with formaldehyde than phenol, thus adhesives produced from tannin, if properly cured; give nearly zero formaldehyde emission (Bisanda, 2003; Joseph *et al.*, 1996). This capability can be used to accelerate curing reactions and to reduce formaldehyde emission which is one of the major requirements for indoor grade panels (Kim and Kim, 2004). In addition PF-tannin adhesive can reduce the tendency of resin to migrate to the interior of high moisture veneers due to the broader molecular weight distribution of tannin-based adhesive (Steiner *et al.*, 1993). The aim of the present work is to substitute as much as possible phenol content in classic resoles formulation by adding tannin extracts of the bark of *Quercus castaneifolia*, as a component of a green adhesive formulation. In addition, the effect of tannin content in modified PF resin for reducing the formaldehyde emission level has been investigated by desiccator method.

Experimental

Materials

Fresh barks from 65 years old *Quercus castaneifolia* trees were obtained from Gorgan University educational forests. Bark consisted of a mixture on inner bark, outer bark and some woody materials of dimensions 250 mm × 25 mm × 10 mm and 12 per cent moisture content. All reagents were purchased from commercial suppliers and used without further purification.

Method for the extraction of tannin

Condensed tannin was extracted from the bark *Quercus castaneifolia* using TAPPI (T264-OM-97) standard as following procedure: the wood grounded to pass a 0.4 mm (40 mesh) screen. The grounded wood were added in the extraction thimble and placed in the Soxhlet apparatus. Place a small cone of thimble to prevent any loss of the specimen. Extract with 200 mL of solvent (methanol-water 50:50) for 6-8 h, keeping the liquid boiling briskly so that siphoning from the extractor in no less than four times per hour. After extraction with methanol-water solvents, transfer the wood to a Buchner funnel. Remove the excess solvent with suction and wash the thimble and wood with methanol. A gummy product was obtained after separating the extract from solvent in a rotary-evaporator under a reduced pressure at temperature 50°C. After being removed the solvent, 50 mL Et_2O (diethylether) was added to the extracted product. The separated compound (tannic acid) was analyzed by FT-IR and ^1H NMR spectroscopy after filtering. Tannic acid is a light to brown amorphous granular powder with the chemical formula of $C_{76}H_{52}O_{46}$ which decomposes at 210-215°C and it is soluble in water. The identification and quantitative analysis of tannic acid was performed by reversed-phase high performance liquid chromatography (HPLC) on a C18 column using a binary gradient elution with mobile phases consisting of an aqueous methanolic eluents at low pH. The gradient system consisted of solvent A (25 mL acetic acid and 975 mL distilled water) and solvent B (99.8 per cent methanol) pumped at 1 mL/min. The gradient started with 100 per cent solution A and ended with 100 per cent solution B at 30 min. A solution of 1g gummy product in 100 mL of absolute ethanol was injected at a volume of 20 μL and detected at the maximum wavelength of tannic acid (280 nm). The column temperature was maintained at 30°C. The sample peaks were identified by comparing to the standard solution of tannic acid. The percentage of tannic acid in the extracted product was determined based on the appropriate calibration curves. The correlation coefficient of the calibration curve of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 mmol/L of standard tannic acid in absolute ethanol was greater than 0.993. Also, we found the tannin content with considering of the solvent extraction in the extracted product is completely different, water extract: 7.3 per cent, methanol extract: 32.5 per cent and aqueous methanol extract (50:50 v/v) 70 per cent.

Method for the synthesis of resin

Extracted tannin (from bark of *Quercus castaneifolia*) was used for producing tannin-phenol formaldehyde formulation. Extracted tannin was dissolved in water to achieve a tannin solution with concentration of 41 per cent. Commercial phenol was melted, and then melted phenol and formalin (41 per cent) were placed into a laboratory (phenol to formalin molar ratio of 1-2) reactor with capacity of capacity 80 kg. Hydroxide sodium solution (50 per cent concentration) was added to the mixture until the pH of mixture reached 11. The mixture was heated under reflux condition (120°C). Boiling of mixture started after half an hour. After boiling, gel time of PF rein was measured continuously up to a gel time of 120 s. Then, resin was cooled to 25°C. According to experimental design, PF substituted with tannin solution at 10, 20 or 30 per cent levels based on dry weight of PF while mixture was stirring slowly (60 rpm). After 2 h, PFT resin was ready. Synthesized resin is used for manufacturing particleboard to evaluate performance of it. For this purpose, wood particles were provided from a local particleboard mill. Three levels of substitution percentage of PF for tannin and two press time used as variables and with three replicates 18 experimental boards with nominal density of 0.7 g/cm^3 were fabricated. Physical and mechanical properties of experimental boards were evaluated after 15 days.

Methods for the characterization of extracted tannin and PFT resin

FT-IR spectroscopic analysis

FT-IR spectrum of extract of oak bark between KBr discs was obtained with a Perkin 100 FT-IR spectrometer.

HPLC analysis

HPLC system consisted of a diode array (UV) detector, a SC-04 (125 × 4.0 mm) PRONTOSIL 120-5-C18-H 5.0 μm column.

Physical characteristics of manufactured PFT resin were examined by measuring density, viscosity, gel time and solidity based on DIN 16485. Physical and mechanical properties of experimental boards were evaluated based on DIN 68763 and DIN 52364. The test performed on the specimens were internal bond strength perpendicular to the plane of the board (IB), static bending (modulus of rupture (MOR) and modulus of elasticity (MOE)), water absorption (WA) and thickness swelling (TS). The WA and TS samples were fully immersed in distilled water at 250°C for 2 h and 24 h period of time. Emission of formaldehyde was evaluated according to JIS A 1460-2001 method. Data was analyzed using ANOVA and SPSS software.

Measuring formaldehyde emission by desiccator method

Typical methods for evaluation of formaldehyde emission are desiccator, perforator and 20 L small chamber.

In desiccator test, emission of formaldehyde is determined by placing test samples in a desiccator at a controlled temperature and measuring the quantity of emitted formaldehyde absorbed in a specified volume of water for 24 h. The related formaldehyde was caught in the distilled water and analyzed using a UV spectrometer after treatment with acetylacetone.

Results and discussion

Effect of solvents on the amount of extraction is shown in Figure 1, and the maximum extraction attributes to water (25.27 per cent). Methanol and water-methanol had lower extracts 19.33 and 17.93 per cent, respectively. The reason for this phenomenon is that bark extractives such as simple sugars and hemicelluloses are hydrolyzed during extraction, but fatty acids, proteins, and mineral salts are solved in water easily.

FT-IR spectrum of extract of oak bark in range of 400-4,000 cm^{-1} is shown in Figure 2, strong attractive band is seen in the area 3,400 cm^{-1} which relates to (O—H) group. Aromatic group of (C—H) is seen in area of 3,000 cm^{-1} which is located under wide band of hydroxyl group. Tensile vibration of aromatic ring (C—C) is located in area of 1,617.65 cm^{-1}.

Figure 1 Effect of solvent on amount of extract of oak bark

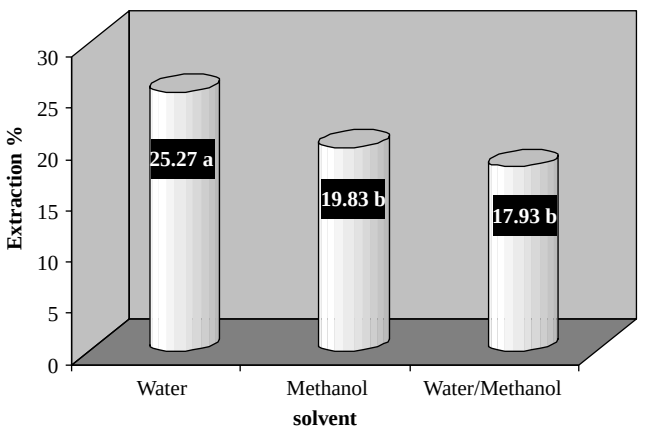
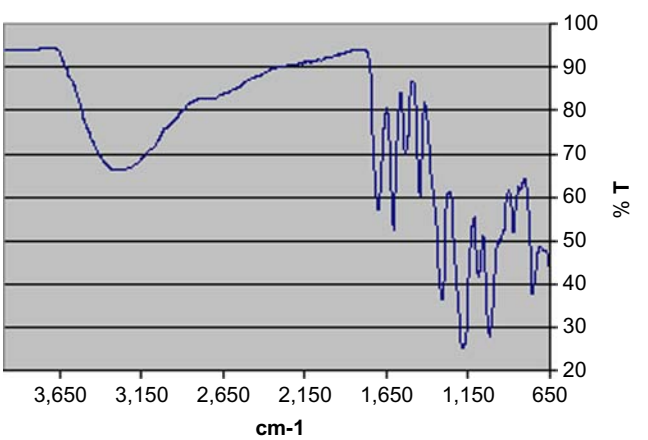


Figure 2 FT-IR spectrum of oak extract



Attractive band in area of 1,325-1,448 cm^{-1} relates to the bending vibration of methyl group. Attractive band in area of 1,718.09 cm^{-1} relates to ester carbonyl group. Tensile band (C—O) appears in the area of 1,033-1,203 cm^{-1}. Resulted spectrum is similar to one presented by Turley *et al.* (1990). Lee and Lan (2006) observed OH group in area of 1,330-1,420 cm^{-1}.

Amount of tannin present in extracts by different solvents (Figure 3) was calculated using calibration curve of standard tannin and HPLC chromatogram of extracted tannin which is shown in Figure 4. We see that the highest tannin is found in extract by water-methanol solvent and the lowest tannin is seen in extract by water. Since tannin has phenolic compounds and they are highly polarity therefore polar solvents like water cannot extract them. For these reason, tannin in extract by water is low but solvent of water-methanol cause swelling in wood and increases contact between alcohol, composed of medium polarity, and matrix so more tannin is extracted (Chirinos *et al.*, 2007).

Figure 3 Amount of tannin in extract of different solvents

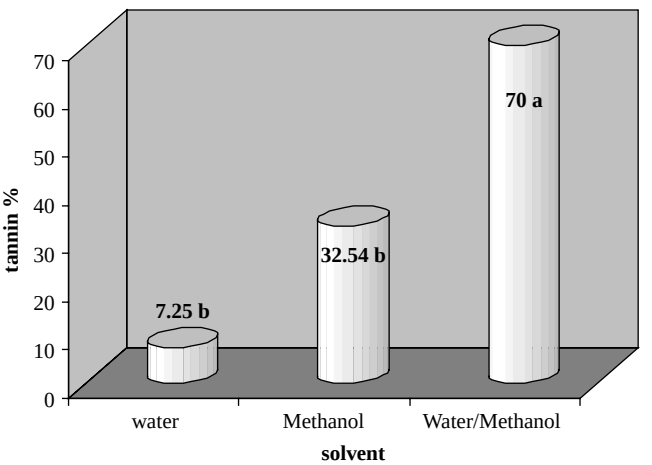
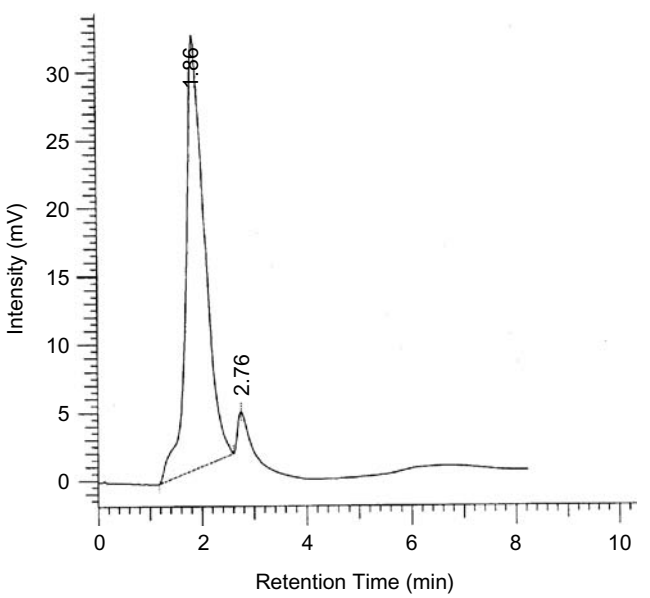


Figure 4 HPLC profile of tannic acid extracted from *Quercus castaneifolia*



Condensed polyflavonoid tannins of the bark of *Quercus castaneifolia*, due to their phenolic nature, can undergo some of the typical reactions of phenol such as reacting rapidly with formaldehyde under acid and alkaline condition. Condensed tannins are oligomers constituted by flavonoid repeating units as shown in Figure 5, mostly linked 4-6 or 4-8 to each others.

The addition of formaldehyde produce hydroxymethyl groups mainly at the free C8 or C6 sites.

Therefore, synthesis of PFT copolymer resins could be carried out at two stages. It should be formed the PF prepolymer by reacting the phenol with formaldehyde at the first stage and then bark extracts added and underwent the copolymerisation reaction at the second stage. Three synthesized tannin phenol formaldehyde and phenol formaldehyde resin properties are shown in Table I.

These properties were compared statistically. As we can see differences between pH of different resins are significant at 99 per cent confidence. pH of PF resin is 11 when 10, 20 and 30 per cent PF substitute for tannin pH decreased to 8.5, 8.36 and 5.87, respectively. This result shows that tannin provides an acidic condition in resin system.

Effect of tannin on the density of resins is not significant however, when tannin penetration into resin system density increases somewhat. Gel time of PF is affected by substitution of tannin significantly. When tannin is added to PF resin system as much as 10, 20 and 30 per cent gel time decreases from 120 s to 70, 67 and 80 s, respectively, (Figure 6).

Since tannin molecules are big, with increasing the content of tannin in PF resin accessibility of radical groups of both material (tannin and phenol) reduce so some part of lignin and some part of tannin train unreacted. Thus, gel time increases because

Figure 5 Precursor of condensed tannin and reaction sites with formaldehyde

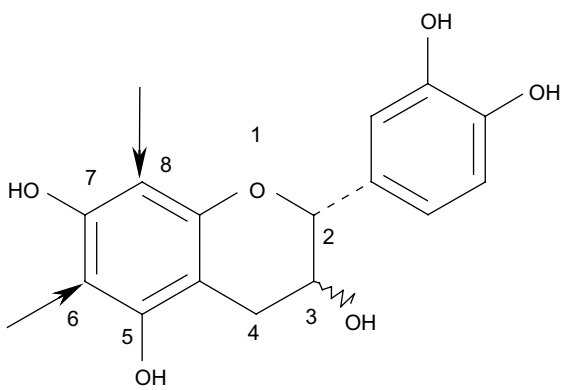
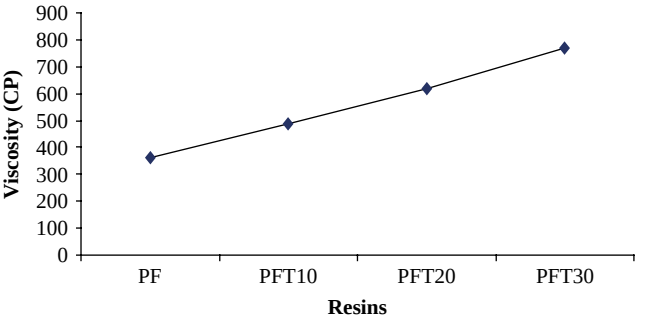


Table I Properties of PF and three types of PFT resins

Resins	pH	Density (g/cm^3)	Gel time (s)	Viscosity (cps)	Nonvolatile (%)
PF	11	1.18	120	360	55
$PFT_{10\%}$	8.3	1.185	70	480	55
$PFT_{20\%}$	8.36	1.19	67	610	55.5
$PFT_{30\%}$	5.87	1.2	80	760	60
Significance	*	ns	*	*	ns

Notes: *Analysis of variance showed that means are significantly different at: $p = 0.05$; ns – no significance

Figure 6 Effect of substitution tannin on viscosity of PF resin



of reaction between tannin and formaldehyde, and it then reduces because of the reduced reaction rate. Tannin affects the viscosity of PF resin significantly. When tannin comes into PF resin system viscosity increases from 360 centi pose to 480, 610 and 760 centi pose, respectively, (Figure 7).

To determine the kind of tannin, HPLC chromatogram was usually used to monitor the tannic acid or disappearance of tannin and to identify fermentation and products after hydrolysis. Results from the hydrolysis of purpose tannin indicate that it is not able to hydrolyze into gallic acid. Therefore, this isolated tannin was considered as condense tannin.

Effect of tannin substitution on the physical and the mechanical properties of particleboard manufactured using PF and PFT resin are presented in Table II.

As it can be seen, tannin replaced with PF has significant effect on all physical and mechanical properties. Formaldehyde is the major part of PF resin which actively reacts with radical groups of wood substrate and produce strong bond with substrate. Since tannin has also very active

Figure 7 Effect of substitution tannin on gel time of PF resin

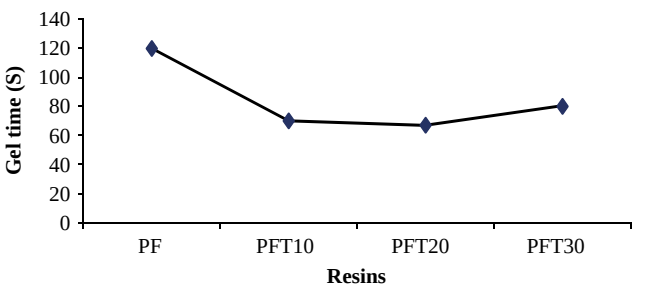


Table II Properties of particleboards manufactured using PF and three types of PFT

Resins	MOR (Mpa)	MOE (Mpa)	IB (Mpa)	Water absorption 2 h	Water absorption 24 h	Thickness swelling 2 h	Thickness swelling 24 h
PF	18.8^{a}	3,210^{a}	1.26^{a}	34.42^{a}	54.51^{a}	7.25^{a}	10.08^{a}
$PFT_{10\%}$	17.04^{b}	2,980^{b}	1.13^{b}	35.17^{a}	55.06^{a}	7.29^{a}	10.29^{a}
$PFT_{20\%}$	16.69^{bc}	2,940^{b}	1.08^{c}	36.44^{b}	63.32^{b}	8.64^{b}	10.86^{b}
$PFT_{30\%}$	15.51^{c}	2,930^{b}	0.89^{d}	53.03^{c}	70.03^{c}	11.91^{c}	15.28^{c}
Significance	*	*	*	*	*	*	*

Note: $^{a-d}$ The data were grouped by Dancan's test

radical groups which react with formaldehyde. When tannin involves in resin system part of formaldehyde radical groups react with tannin so less free radical groups in resin system are available to react with wood substrate radical groups. For this reason, tannin replaces with PF reactivity of resin decreases. It may also be related to the size of tannin molecules. So mechanical properties such as MOR, MOE and IB are reduced and physical properties such as WA and TS are increased. All these reductions are due to less availability free formaldehyde in the system to provide strong bond between resin and wood substrate. Based on emission test, as the amount of tannin additive in PFT increased 10, 20 and 30 per cent, formaldehyde emission of PFT decreased to 1.13, 1.12 and 0.4 mg/100 g, respectively, which is very low compared with tannin free PF and provided environmental friendly adhesive.

Conclusions

Results of this study indicate that from a quantity point of view, solvent of water had the highest amount of extracts because most of simple sugars and hemi-cellulosed are hydrolyzed. But regarding the content of tannin in the extracted product was shown, solvent of water-methanol showed to have the highest value of tannin. Tannin substituted PF as much as 10, 20 and 30 per cent for phenol and resulted PTF had higher viscosity, lower gel time and lower pH. Evaluating of physical and mechanical properties of manufactured boards showed that replacing tannin up to 30 per cent decreases MOR, MOE and IB and increases WA and TS significantly. In spite of such reduction values of these properties are still higher than EN standard for exterior particleboard. In desiccator test, formaldehyde emission of adhesive system decreased, when amount of tannin additive increased. In conclusion, PFT resins were successfully applied as environment-friendly adhesive of surface bonding for manufacturing particleboard.

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