Tannin adhesive made from snakeskin fruit and its application for laminated wood

G F Virginia, S Suhasman*, and A Agussalim

Laboratory of Forest Product Utilization and Processing, Faculty of Forestry, Hasanuddin University, Makassar, Indonesia

*Email: suhasman@yahoo.com

Abstract. Snakeskin fruit called Salak is one type of tropical fruit that is widely grown in Indonesia. Salak fruit peels are known to contain a certain amount of tannin. This research explores the potential of rind salak fruit as the latest alternative adhesive. The extract from the rind had a tannin content of 1.85% and Stiasny number 76.67%. The results showed that the tannin extract of rind salak fruit was reactive to formaldehyde. Characteristics of Tannin Resorcinol Formaldehyde (TRF) adhesives with variation in resorcinol concentration have a significant effect on its viscosity, gelatinization, and solid content. Utilization of recorcinol 15% in TRF adhesive formula resulting a highest bonding strength of produced laminated wood. The value was 67.85 kg/cm³ with 53.3% wood failure on laminated wood. Those result indicated that utilization of tannin based adhesive from skin of salak fruit is very potential as an alternative raw material for bio adhesive.

1. Introduction

To reduce the utilization of synthetic adhesives, research on the development of natural-based adhesives was considered. Bio adhesive are frequently named as adhesive of natural origin from plants, animals, or another compound [1]. Tannins product from plants are compounds which usually have been developing natural adhesives. This compound was obtained from the extracts of plant body parts in the form of phenol compounds [2]. Tannin can be found on the rind, stems, leaves, fruit, and roots of the plants [3].

The types of plants used as raw materials for tannins are derived from woody plants such as Acacia mangium, Pinus merkusii, Rhizophora sp., and Intsia spp. Tannin extract was obtained from bark or part of wood species [4,5]. Since the beginning of the development of tannin as a natural adhesive in wood processing technology comes from wood parts. However, the use of wood and bark parts as tannin-producing materials will face several problems. If using wood parts can disrupt the supply of raw materials for the needs of the wood industry. While some tannin raw materials from agricultural products began to research to find out its potential. Pomace grapes which are processed wastes have tannins which have the potential to become raw materials for natural adhesives that are environmentally friendly [6].

The rind of salak fruit is one of the potential plants to be developed as a tannin based adhesive. Research that conducted by Umi Rahman [7] found tannin content in the extraction of salak fruit rind with a blackish color. Based on statistical data, in 2018, salak fruit production in Indonesia amounted to 896,504 tons [8]. These are interest information to produce the right tannin adhesive formulation.
Therefore, this study discusses the use of the rind of salak fruit rind as a source of tannin-producing raw materials to reduce the use of non-renewable adhesives.

2. Materials and Methods

2.1. Materials
Salak's rind as a main material for tannin adhesives was obtained from waste originating in Baraka Sub-district, Enrekang District, South Sulawesi Indonesia. The next adhesive was applied to lamina wood from Pinus merkusii and Paraserianthes falcatoria (L.) Nielsen. The two kinds of wood were taken from sawmills located in Tanralili, Maros Regency, South Sulawesi, Indonesia.

2.2. Methods

2.2.1. Tannin extraction
Chip-shaped Salak rind was first extracted in the water using a water bath with a ratio of 1:4 (w:v) at 70ºC of temperature for 4 hours. The tannin level was identified by weighing the extraction about 1-2 g and then put into a 100 mL beaker containing 50 mL of water. It was then heated at 40-60ºC for 30 minutes. The cold solution is filtered and put into a volumetric flask with addition water until reaching the target. The solution was put into an erlenmeyer and added with an indigo carmine solution to be titrated with 0.1N KMnO4 solution until the color was changed from blue to golden yellow. The second titration using indigo carmine solution was conducted until the color changes from blue to clearer yellow. The tannin level was then calculated using the following formula:

\[
\text{Tannin Levels} = \frac{d.f \times (a-b) \times 0.006235}{\text{sample weights}} \times 100\% \tag{1}
\]

where:
- \(a\) = mL number of KMnO4 0.1 N sample
- \(b\) = mL number of KMnO4 0.1 N blank
- \(d.f\) = dilution factor
- 1 mL KMnO4 0.1 N ~ 0.006235 g tannin

The tannin reactivity test of formaldehyde uses the Stiansny number test. Salak rind fruit extract around 0.1g was put into a 150 mL beaker containing 10 mL of air. Around 37% formaldehyde and 10 M HCl were added, respectively 2 mL and 1 mL. The formula was then put into the water bath for 30 minutes and then filtered. The filtrate was heated in the oven at 70-80ºC and then weighed [9]. The Stiasny number was calculated by using the following formulation:

\[
\text{Stiasny number} (%) = \frac{\text{sediment weights}}{\text{sample weight}} \times 100\% \tag{2}
\]

2.2.2 Adhesive characteristics
The tannin extract was made into an adhesive formulation by adding formaldehyde (RF) resorcinol solution to improve the adhesive quality. Tannin adhesives made from salak rind extract (T) was added with 50% (R) resorcinol solution, 37% (F) addition of formaldehyde and 40% NaOH. The adhesive ratio (v: v) of resorcinol formaldehyde (TRF) adhesive consists of 3 variations with different percentages of resorcinol, 100:5:10, 100:10:10, 100:15: 0.

2.2.2.1. Visual appearance
The sample was poured on the object-glass and spread over to form a thin film layer. Observations were made visually by looking at the color and whether there are solid granules, coarse particles, or other foreign objects.
2.2.2.2. Viscosity
Viscosity testing uses a viscometer. A total 100 mL TRF adhesive was put into a 200 mL beaker with a temperature of 25°C, and then the tool was set at a rotor speed of 100 rad/min with a centipoise (cP) measurement unit. Viscosity values were displayed on the scale of the viscometer.

2.2.2.3 Gelatination
A total of 10 mL of salak rind tannin adhesive was put into a closed test tube, then it was placed around 2 cm below the water surface in the water bath at 100ºC. Gelatinization time was obtained by noting the time needed by adhesive to get hard.

2.2.2.4 pH
pH of the tannin adhesive was measured by using a pH meter at a temperature of 25°C.

2.2.2.5 Solids content
Determination of solids content was conducted by weighing the dry weight of an empty Petri dish (B1), then weighing 10 mL of TRF and then placing it in the cup (B2), then the cupped containing TRF is put into the oven at 103 ± 2ºC for 24 hours. The cup was taken out of the oven and put in a desiccator for 15 minutes then was weighed (B3).

\[ SC(\%) = \frac{B3 - B1}{B2} \times 100 \]  

(3)

2.2.3. Adhesive application
The lamina produced is made from types of *Pinus merkusii* wood and *Paraserianthes falcataria* (L.) Nielsen. The lamina is then dried conventionally to ± 12% moisture content. The weight of the labor for lamina wood is 200 g/m² with the application of TRF 0.55 g/surface adhesive called the double spread method. The adhesive that has been applied to the lamina wood is then pressed using a cold press for 24 hours at a pressure of 8 kg/cm². At this stage also observed the percentage of wood failure.

3. Results and Discussion

3.1. Tannin extraction
The results of the quote from the content of the tannin extract of salak fruit peel obtained 1.42-2.62%. The extraction result does not produce high tannin content, due to there are also other compositions outside of tannin. Other compounds contained from the salak rind fruit were as alkaloid secondary metabolites, polyphenols, flavonoids, quinones, monoterpenes, and sesquiterpenes [10]. Meanwhile, the results of the Stiasny number test on salak rind were at obtained 76.67%. This value is fulfilling the standard Stiasny FAO [11] yields 75-100%. This value shows the extract of salak rind is quite reactive with formaldehyde.

| Parameter                  | Score of salak rind tannin extract (%) |
|----------------------------|----------------------------------------|
| Tannin content             | 1.85 ± 0.66                            |
| Stiasny numbers            | 76.67 ± 5.77                           |

3.2. Characteristic of tannin adhesive
The variation of resorcinol levels from the adhesive ratio consists of 5%, 10%, and 15%. Like appreciating resorcinol and formaldehyde, each of which has a concentration of 50% and 37% in this TRF ratio, the rind of salak fruit contributes ratio consists are 1.85%. This value was based on the evaluation results of tannin extract obtained from testing tannin levels in salak rind. The results of the physical properties of tannin adhesives made from salak rind extract for the characteristic features of adhesives were presented in Table 2.
Table 2. Analysis of characteristics of tannin adhesive

| Physical base       | Tannin Resorcinol Formaldehyde (%) Resorcinol levels | SNI [18]                        |
|---------------------|-----------------------------------------------------|---------------------------------|
|                     | 5%                                                  | 10%                              | 15%                              | Liquid and free of impurities |
| Visual appearance   | Reddish brown                                       | Brownish yellow                  | Reddish brown                    | 100-150                        |
| Viscosity (cP)      | 1.79                                                | 2.27                             | 2.57                             | 60                              |
| Gelatinization (minute) | 109                                                | 62                               | 45                               | 7.6 – 8.6                       |
| pH (cP)             | 7.63                                                | 7.33                             | 7.40                             |                                  |
| Solid content (%)   | 5.38                                                | 7.70                             | 9.83                             | 49 – 51                         |

3.2.1. Visual appearance

Usually, the base color of tannins is a brownish yellow, but in this study, the color varies according to formaldehyde [12]. Another factor for color variation from tannin adhesives made from salak rind is NaOH added from every adhesive. It's known that tannin adhesive colors with a concentration of resorcinol 5% and 15% both have a pH of 10.28. Whiles the resorcinol 10% concentration has a pH of 10.02%. The other visual appearance of the three formulations is free from dirt and foreign matter.

3.2.2. Viscosity

The results of viscosity the tannin adhesives from salak rind using a viscometer continue to increase along with the increase in resorcinol concentration. The addition of resorcinol accompanied requires monomers in adhesive formulations [13]. The condition of liquid adhesive is also the life of the pot period of adhesive of salak rind [5].

3.2.3. Gelatinization

The condition of the adhesive so liquid that it affects the age of tannin adhesive seen from the results of the gelatinization adhesive. The concentration of resorcinol also affects the time of adhesive gelatination. The more resorcinol added faster the tannin adhesive gelatinization time [5].

3.2.4. pH

The rind of salak fruit extract added with 50% resorcinol solution with 37% formaldehyde has a neutral pH containing acid. NaOH as a catalyst is starting to be used to convert the pH of the adhesive into a base for longer service life with the adhesive polymerization process continues [12]. Because of the pH tannin adhesive, the hydrogen bonding reaction is inhibited [14].

3.2.5. Solid content

The result of this study indicated that the solid content of adhesives formulation tends to increase when the resorcinol content increases. Meanwhile, the relationship between formaldehyde content with solid content of adhesives formulation indicated that the solid content will decrease when formaldehyde content decreases. The trend that found in this study similar with Rachmawati et al. [15] that using mangium bark.

3.3. Adhesive application

The tannin adhesive made from salak rind is applied to lamina Pinus merkusii lamina wood and Paraserianthes falcataria (L,) Nielsen which uses stickiness and failure of the wood. The value of the constancy check is presented in Figure 1 as follows:
Three variations of resorcinol levels, namely 5%, 10%, and 15%, were applied to Pinus merkusii and Paraserianthes falcataria (L.) Nielsen, which have varying average results. The highest bonding strength value is held by Paraserianthes falcataria (L.) Nielsen with 15% resorcinol content and then followed by Pinus merkusii wood with the same resin. Based on JAS 234-2007 [16], only tannin adhesives with 15% resorcinol content in wood in Pinus merkusii and Paraserianthes falcataria (L.) Nielsen meets the minimum lamina wood bonding standard of 54 kg/cm³. In general, the addition of resorcinol to adhesives give an effect on its application. Where more concentrations of resorcinol were added, the quality of the adhesive increases [15].

Looking at the results of bonding strength testing of tannin adhesives, the highest percentage of wood failure that reached 53.3% is based on the wood of Paraserianthes falcataria (L.) Nielsen from a resorcinol concentration of 15%. The wood density of Pinus merkusii is relatively higher compared to Paraserianthes falcataria (L.) Nielsen is also one of the factors that influence the percentage of wood hardness Paraserianthes falcataria (L.) Nielsen is higher. Figure 2 shows the visual damage from wood using tannin adhesives made from the rind of salak fruit.

Figure 1. Histogram of bonding strength

Figure 2. Wood damage after wood density testing; a. Pinus merkusii and b. Paraserianthes falcataria (L.) Nielsen
The results of the study show that tannin extracts up to its application on lamina wood have the potential of salak rind fruit as a tannin adhesive. On a laboratory scale, salak bark as a natural adhesive raw material has relatively high results that meet the standards for the use of adhesives and wood production. This standard then becomes the main requirement for potential adhesive production including its application. By fulfilling the existing standard, the tannin adhesive from salak rind is feasible to be accepted.

The feasibility of further adhesive production for production potential can be looking from the availability of raw material for salak fruit rind. Based on the Badan Pusat Statistik [8] data in catalog No. 5205010 salak products reached 896.504 tons in Indonesia with total rinds of 77.099 tons where the yield of salak rind was 8.6%. From the results of tannin levels from salak rind obtained with the total in Indonesia in 2018, it can be appraiser that the resulting tannin extract is around 2.282 tons in doses. Looking further, the results of tannin extract from salak can produce plywood suitable for production using natural salak rind adhesives as much as 33.064 m$^3$. Indonesia's total plywood production in 2018’s according to the BPS [17] 4,213,557 m$^3$ can support 0.7% production using tannin adhesives made from salak leather. Thus, the potential for salak rind as environmentally friendly is quite potential to be used as a natural adhesive. From this good potential, its production strategy does not only prioritize the use of its fruit, including snakeskin.

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