jriani_2020_IOP_Conf._Ser.__Mater._Sci._Eng._935_012032.pdf

by

Determination of optimum formulation of tusam (*Pinus merkusii*) tannin bark with resorcinol and formaldehyde

To cite this article: S Hajriani *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **935** 012032

Determination of optimum formulation of tusam (*Pinus merkusii*) tannin bark with resorcinol and formaldehyde

S Hajriani[1] A D Yunianti[2*], and S Suhasman[2]

[1]Magister Student of Forestry, Faculty of Forestry, Hasanuddin University, Makassar, Indonesia
[2]Laboratory of Forest Product Ulilization and Processing, Faculty of Forestry, Hasanuddin University, Makassar, Indonesia

*Email: dettiyunianti70@yahoo.com

Abstract. Adhesive is the one of main components that used for producing composite wood. The quality of the adhesive can affect the strength of the composite wood. However, adhesives which commonly used are synthetic adhesives that contain a lot of formaldehyde emissions and have negative impact on our health. To reduce its use, we need an alternative adhesive from natural raw materials. Tannin is a phenolic compound has been widely studied that can be used as a bio adhesive for wood composites. The main source of tannin for adhesive is derived from bark. One type of wood bark that contains tannins is tusam wood bark. Tannins have a high reactivity against formaldehyde. This study aims to determinate the optimum formula of tannin which is copolymerized with resorcinol and formaldehyde. Tannin is obtained by extracting wood bark with hot water. The optimum formula of tannins and resorcinol (TR) result is determined by the stiasny numbers, while the optimum formula of tannins and formaldehyde (TF) are determined by identification of solid content. The addition of resorcinol affects the percentage of stiasny number, the greater the formula of resorcinol added, the higher value of stiasny number, wherein the reactivity of tannin to formaldehyde increases. The addition of formaldehyde also affects the results of tannin formaldehyde solid content, the more addition of formaldehyde, the percentage of solid content decreases.

1. Introduction

Adhesive is the one of main components that required in composite wood industry. Adhesives that widely used are synthetic adhesives which are relatively expensive [1] because the raw material is derrivated from nonrenewable material, in addition to these adhesives also contain a lot of formaldehyde emissions which can negatively impact on health in the form of evaporated gas exposure at room temperature [2]. Adhesives are commonly commercialized by the most adhesive industries recently such as phenol formaldehyde and urea formaldehyde [3]. To reduce the use of synthetic adhesives, natural polymer compounds derived from plants and adapted for the same use as pure synthesis groups [4] are needed.

Tannin is one of the phenolic compounds that has great potential to produce bio adhesives because it has a high flavonoid content, especially in condensed tannins [5,6]. Tannins can be obtained in all parts of the plant, but the content of tannins in large quantities is obtained from wood bark extract which is studied as a bio adhesive. In recent years, condensed tannins have been widely studied as substitutes for phenol and resorcinol in their reactivity against formaldehyde [8,9]. Various types of pine bark have been studied and have tannin compounds that potential to be adhesives on composite wood [10-13].

Condensed tannins have a high affinity for resorcinol and formaldehyde so that they can copolymerize and used as adhesives [14]. Tannins have a high reactivity toward formaldehyde [15,16], but to reduce formaldehyde emission, the addition of resorcinol can be used to bind formaldehyde groups that do not react with tannins [17].

This study aims to react Tusam tannins with resorcinol and formaldehyde by determining optimum formulation of some modified ratios from several previous studies. Determination of the optimum tannin and resorcinol formulations based on stiasny number, and determination of tannin and formaldehyde formulations based on the percentage of solid content.

2. Materials and Methods

2.1. Bark extraction method
Tusam bark is prepared to be chips and then dried at air temperature until it reaches the moisture content of about 12%, then it extracted with hot water at bark and water ratio of 1:4 (g/mL) in a waterbath for 4 hours. Then it filtered to get tannin filtrate. tannin liquid is then dried using a spray dryer to get tannin powder.

2.2. Determination of stiasny number of tusam tannin bark
Determination of stiasny number aims to see the tannin reactivity toward formaldehyde which is shown based on the percentage of condensed tannins. Stiasny number is determinate by weighing the 2 g tannin powder sample then dissolved in 10 mL of water and reacted in a waterbath at 100° C with 37% formaldehyde (2 mL) that catalyzed by 10 N HCl 1 mL for 30 minutes. The resulting precipitate is accurately weighed and the Stiasny value is calculated as a percentage of the weight of dry extract [17].

2.3. Determination solid content of tusam tannin bark
A total of 2 g of the extract sample was weighed (W1) and dried for 24 hours in an oven at 100° C then cooled in a desiccator and weighed (W2) [18]. Solid content is calculated by the formula:

$$\text{Solid content (\%)} = \frac{W2}{W1}\ x\ 100\% \quad (1)$$

2.4. Determination of optimum tannin and resorcinol formulations
The optimum formulation is carried out to see the effect of resorcinol addition to stiasny number. The purpose of adding resorcinol is to activate phenolic compounds contained in tusam bark [14] so that it is expected to increase the tannin's reactivity to resorcinol. Ratio of tannin and resorcinol is showed in Table 1.

Table 1. Ratio of tannin resorcinol

Tannin	Resorcinol
1	0.000
1	0.025
1	0.075
1	0.125

2.5. *Determination of optimum tannin and formaldehyde formulations*

Addition of formaldehyde aims to react tannin with formaldehyde. The optimum formulation between tannins and formaldehydes is intended to see the effect of formaldehyde addition to the levels of solid content of tannins so as to form a new molecule comes from reaction of tannins with formaldehyde. Ratio of tannin and formaldehyde is determined from the results of modifications of previous studies [18-20] which are showed in Table 2.

Table 2. Ratio of tannin formaldehyde.

Tanin	Formaldehida
1	0.00
1	0.05
1	0.10
1	0.15

3. Results and Discussion

3.1. Optimum formulation of tannin resorcinol

The optimum formulation produced from Tusam tannin bark and resorcinol is shown in Figure 1

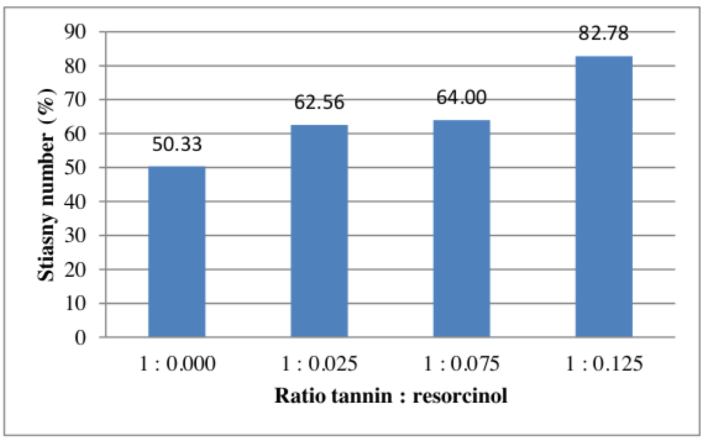

Figure 1. Results of solid content of tusam tannins bark and resorcinol

Figure 1 explains that the addition of resorcinol affects the percentage of the stiasny number where the stiasny number indicates the tannin reactivity of resorcinol. The higher levels of resorcinol are added, the greater the percentage stiasny number. The value of stiasny number of tusam tannin bark in figure 1 is 50.33%, but with the addition of resorcinol, the value is increase until the highest resorcinol addition reaches 82.78% whereas the resorcinol ratio which is the more reactive formulation of tannins. This result is almost same with previous research [1] on the percentage of the tannin stiasny number of 47.22% and after the addition of resorcinol, the percentage increased to 66.67%.

This also indicates that the addition of resorcinol to the adhesive can help increasing the complete copolymerization reaction, so that the molecules in resin are increasing [14]. In addition, resorcinol is also added with the aim to bind formaldehyde groups that do not react with tannins so as not to cause formaldehyde emissions [16].

3.2. The optimum formulation of tannin formaldehyde

The optimum formulation in tannin formaldehyde is shown in Figure 2. The results in Figure 2 show that the addition of formaldehyde affects percentage of formaldehyde tannin solid content. The higher addition of formaldehyde, the solid content decreases. The result of solid content in tusam tannin bark is 13.83%, but with the addition of formaldehyde by 5% of the amount of tannin, the value of solid content increased to 16.86%, but in the addition of formaldehyde 10% and 15%, the percentage of solid content decreased respectively also became 15.86 and 14.12%. This effect is not much different from tannin in research [18] whereas the level of solid content increases with the addition of formaldehyde by 5% and decreases with the increase in the addition of a number of formaldehydes. The same thing happened in mahogany tannins in the study [20] where an increase in solid content to 18.15% occurred in the addition of formaldehyde by 5% and decreased with the addition of formaldehyde by 20% to 17.77%.

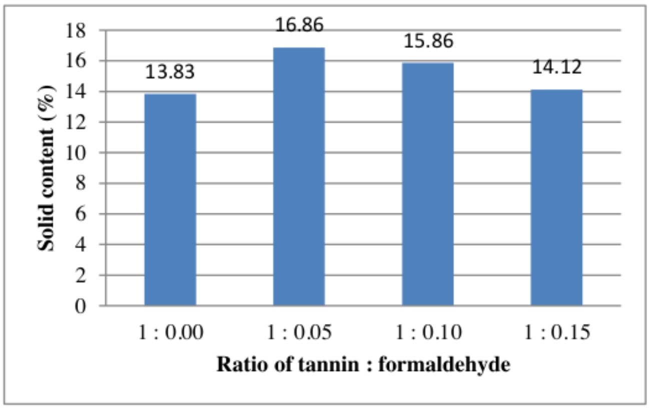

Figure 2. Results of optimum formulation of tannin and formaldehyde

The addition of formaldehyde to make polymerization bridges whose bonds tend to be more stable so that it increases the adhesion strength, but the addition of formaldehyde with high levels will cause the crosslinking process being weak and imperfect because there are a number of formaldehyde groups which do not react with tannin [18,20].

References

[1] Dradjat and Santoso A 2017 Identification of optimum formula on tannin adhesive by xrd and dta methods *Jurnal ITEKIMIA* **2**(1)1-14

[2] Raharyaningsih MA and Azizah R 2017 Formaldehyde emission levels and eye irritation in workers in the production area of wood adhesives industries in Surabaya *Enviromental Health Journal* **9**(2) 191-9

[3] Moubarik A, Allal A, Pizzi A, Charrier F, and Charrier B 2011 Characterization of a formaldehyde free cornstarch tannin wood adhesive for interior plywood *Eur. J. Wood and Wood Product* **68**(4) 427-33

[4] Santoso A 2005 Utilization of lignin and tannin as substitute alternative of glue raw material for wood composite *Proceedings of the national polymer symposium* 155-64

[5] Li T, Cao M, Liang J, Xie X, and Du G 2017 Mechanism of base-catalyzed resorcinol formal dehyde and phenol resorcinol formaldehyde condensation reactions: a theoretical Study *J. Polymers* **9** 426

[6] Yang I, Ahn S, Choi I, Kim HY, and Oh S 2009 Adhesives formulated with chemically modified okara and phenol resorcinol formaldehyde for bonding fancy veneer onto high-density fiberboard *Journal of Industrial and Engineering Chemistry* **15** 398-402
[7] Grisby W and Warnes J 2004 Potential of tannin extracts as resorcinol replacements in cold cure thermoset adhesives *J. Biomaterial Engineering* **62** 433-8
[8] Yang T, Dong M, Cui J, Gan L, and Han S 2019 Exploring the formaldehyde reactivity of tannins with different molecular weight distributions: bayberry tannins and larch tannins *Holzforschung* 1-10
[9] Pizzi A 1982 Pine tannin adhesives for particle board *Holz als Roh-und Werkstoff* **40** 293-301
[10] Gaspar F, Cruz H, Gomes A, and Nunes L 2009 Production of glued laminated timber with copper azole treated maritime pine *Eur.J. Wood Prod.* **68** 207-18
[11] Saad H, Khoukh A, Ayed N, Charrier B, and Charrier F 2014 Characterization of Tunisian Aleppo pine tannins for a potentialuse in wood adhesive formulation *Industrial Crops and Product* **61** 517-25
[12] Derkyi NSA, Sekyere D, and Darkwa NA 2014 Effect of extraction solvent on tannin-formaldehyde adhesives for plywood production *JENRM* **1**(2) 120-6
[13] Santoso A, Pari G, and Jasni 2015 Quality of laminated boards glued with resorcinoladhesive from merbau wood extracts *J. Forest Product research* **33**(3) 253-60
[14] Santoso A and Abdurachman 2016 Characteristics of mahogany bark extract as wood adhesive *J. Forest Product research* **34**(4) 269-84
[15] Yusro F 2013 Active Tannin Concentration of jengkol bark (*PithecellobiumJiringa Jack*) extract and its reactivity to formaldehyde *J. Vokasi* **9**(1) 21-6
[16] Hernawati A and Sutoyo S 2018 Characteristics of adhesive firmness of tannin resorcinol formaldehyde from johar sawdust extract as adhesive on lamina wood *Proceedings of national seminar on chemistry* **171** 111-5
[17] Elbadawi M, Osman Z, Paridah T, Nasroun T, and Kantiner W 2015 Mechanical and physical properties of particleboards made from Ailanthus wood and UF resin fortified by Acacias tannins blend *J. Mater. Environ. Sci.* **6**(4) 1016-21
[18] Rachmawati O, Sugita P, and Santoso A 2018 Synthesis of tannin resorcinol formaldehyde adhesive from mangium bark extract for improving quality of oil palm trunks *J. Forest Product Research* **36**(1) 33-46
[19] Jessica 2018 Characterization and development of mangium (*acacia mangium* Willd.) extract tannin as an adhesive of laminated wood [Dissertation] Pascasarjana Institut Pertanian Bogor
[20] Lestari ASRD 2018 Mahogany tannin adhesive for glued laminated lumber [Dissertation] Pascasarjana Institut Pertanian Bogor

Acknowledgement
We acknowledge to the sponsorship of the Ministry of Research, Technology, and Higher Education for supporting this research well through the Master Thesis Research Grant Scheme 2020.

jriani_2020_IOP_Conf._Ser.__Mater._Sci._Eng._935_012032.pdf

ORIGINALITY REPORT

%11	%9	%10	%8
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Submitted to University of Greenwich Student Paper	%7
2	Submitted to Universitas Samudra Student Paper	%2
3	www.degruyter.com Internet Source	%1
4	N. Saito, M. Reilly, Y. Yazaki. "Chemical Structures of (+)-Catechin-Formaldehyde Reaction Products (Stiasny Precipitates) Under Strong Acid Conditions: Part 1. Solid-State 13C-NMR Analysis", Holzforschung, 2001 Publication	<%1
5	F. C. Jorge, C. Pascoal Neto, M. A. Irle, M. H. Gil, J. Pedrosa de Jesus. "Wood adhesives derived from alkaline extracts of maritime Pine bark: preparation, physical characteristics and bonding efficacy", Holz als Roh- und Werkstoff, 2002 Publication	<%1
	link.springer.com	

6	Internet Source	<1%
7	Makkarennu, O Katsuya, AR Kadir. "Business development strategy of sago for food security", IOP Conference Series: Earth and Environmental Science, 2018 Publication	<1%
8	S H Larekeng, R Dermawan, H Iswoyo, K Mustari. "RAPD primer screening for amplification on Katokkon pepper from Toraja, South Sulawesi, Indonesia", IOP Conference Series: Earth and Environmental Science, 2019 Publication	<1%

EXCLUDE QUOTES	ON	EXCLUDE MATCHES	< 5 WORDS
EXCLUDE BIBLIOGRAPHY	ON		