Investigation of eco-friendly plywood bonded with citric acid – starch based adhesive

S S Kusumah\textsuperscript{1}, Jayadi\textsuperscript{1}, D T Wibowo\textsuperscript{1}, D A Pramasari\textsuperscript{1}, B A Widyaningrum\textsuperscript{1}, T Darmawan\textsuperscript{1}, Ismadi\textsuperscript{1}, W Dwianto\textsuperscript{1}, and K Umemura\textsuperscript{2}

\textsuperscript{1}Research Center for Biomaterials, Indonesian Institute of Sciences (LIPI)
Jalan Raya Bogor Km. 46, Cibinong, Jawa Barat, Indonesia 16911
\textsuperscript{2}Laboratory of Sustainable Materials, Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
Email: sukma.surya@biomaterial.lipi.go.id

Abstract. Concerning the environmental issues, the eco-friendly panel product has been developed by using natural based adhesive to ensure safe product application for human health. In this study, \textit{Paraserienthes falcataria} veneer and citric acid – starch were used in the manufacturing of plywood. The 30 wt\% concentration of citric acid – starch-based adhesive was prepared and it was spread to each veneer with 150 g/m\textsuperscript{2} of glue spread. The plywood was constructed by 3 layers of veneers. The dimension of each veneer was 30 x 30 x 0.2 (cm). The effect of composition ratio between citric acid (CA) and starch (St) as natural sources of adhesive on delamination and shear strength of the plywood was investigated. The plywood was produced under pressing conditions of 180°C for 10 min with 5 MPa of pressure. The variation of compositions ratio (CA:St) were 90:10, 80:20, 70:30, 60:40, 50:50. The research results showed that the plywood with 50 wt\% additional of starch had the lowest delamination and highest shear strength. The shear strength of plywood satisfied Standard National Indonesia (SNI) of plywood for general use. Infrared (IR) spectral analysis demonstrated the presence of ester linkage, indicating that the carboxyl groups of citric acid reacted with the hydroxyl groups of the wood veneer. Therefore, 50:50 of composition ration between CA and St was effective composition ratio in the manufacturing of eco-friendly plywood.

Keywords: Eco-friendly plywood, citric acid, starch

1. Introduction

Incline demand for furniture industry across the globe and massive growth urbanization has fostered the growth of the plywood in the construction sector \cite{1}. The plywood is used in the construction of marine decks. Further, it has uses in the construction of light partition or external walls, furniture particularly in cupboards, kitchen cabinets, light doors, and shuttles. Likewise, plywood is also used in commercial constructions for temporary flooring, detached garages, and sheds. Moreover, the softwood plywood is used beyond the construction of homes, skateboard ramps, and work tables. The environmentally friendly plywood is yet another factor that has led to a higher demand for plywood market expansion all over the world. Moreover, the middle-class population, especially in Asian countries, has led to increase in the growth of plywood markets such as Indonesia, Malaysia, and India, etc. \cite{1}. Recently, fast-growing species of wood is used as raw material in the manufacturing of...
plywood. Nowadays, Sengon wood (*Paraseriethes falcata*) which is fast-growing species is an important source of veneer and plywood due to easy to feel or slice. The tree has high diameter of stem in short harvesting. Moreover, plywood uses adhesive to bond the veneers which make it water-resistant and reach high mechanical properties. However, formaldehyde and petroleum-based adhesives such as phenol-formaldehyde (PF), urea-formaldehyde (UF), and isocyanate are used as common adhesive in the manufacturing of plywood. Unfortunately, their use will be inescapably restricted in the future due to decreases in fossil resources. Moreover, the formaldehyde emission cause disorder in human health [2, 3, 4]. In recent years, scientists and industries pay attention to find and use free formaldehyde emission adhesives. Citric acid had been used as bio-adhesive in the manufacturing of particleboard [5-10] and obtained good physical properties. Furthermore, Kusumah [9] has enhanced particleboard physical properties by adding sucrose. Same as sucrose, starch is polysaccharide that consists of huge number of glucose. The derivative compound of starch such as maltodextrin can be produced by acid hydrolysis. Furthermore, the maltodextrin has anomeric carbon which reacts easily with hydroxyl group of Sengon wood. Accordingly, starch has potential as alternative raw material for environmentally friendly adhesive in the manufacturing of plywood.

Therefore, this study investigates the application of the bio-adhesive which composed of citric acid and starch in the manufacturing of plywood made from Sengon wood veneer. The effect of composition ratios between citric acid and starch on the physical and mechanical properties of the plywood was observed.

2. Materials and Methods

Sengon wood veneers which have a thickness of 2 mm were collected from the plywood industry in Tangerang, West Java, Indonesia. The citric acid (anhydrous) of extra purity grade was purchased from MERCK and was used without further purification. The starch of food-grade was purchased from PT. Umas Jaya Agrotama (Lampung, Indonesia).

2.1. Preparation of materials

The Sengon wood veneers were cut into 30 x 30 cm of width and length, respectively. The veneers were dried in an oven at 80 °C for 12 h to obtain a moisture content of less than 10%.

Citric acid and starch were dissolved in water at a concentration of 59 wt% under several composition ratios of citric acid (CA) and starch (St), and this solution was used as the adhesive. Those composition ratios (CA:St) were 90:10; 80:20; 70:30; 60:40; 50:50 wt%.

2.2. Plywood production

Plywood was composed of three layers of veneer. Each veneer was spread by citric acid-starch based adhesive with 150 g/m² of glue spread under several composition ratios between CA and St. Three veneers were laminated in perpendicular directions to each other. The laminated veneer was pressed under pressing conditions of 180 °C for 10 min. and 5 MPa of pressure. Three plywood were manufactured under each manufacturing condition.

2.3. Evaluation of the plywood properties

2.3.1 Physical property: Delamination test. The delamination test was done following the standard SNI of plywood for general use [11] and previously reported work [12]. It measured the perimeter of failed glue line over the total perimeter of glue line available. The estimation of delamination is presented in the following equation:

\[
D = \frac{P_{gl}}{P_{gl} \times N} \times 100
\]
3. Results and Discussion

3.1. Delamination of plywood

The delamination of plywood bonded with CA-St based adhesive shown in Fig. 1. The delamination of plywood was not significantly different when the starch was added from 10 to 30 wt% and declined sharply when the additional starch achieved 40 to 50 wt% as shown in Fig. 1. The delamination of plywood with 50:50 wt% composition ratio between CA and St was lower than that of the plywood with other composition ratios. This means that 50 wt% of starch addition is the effective utilization of starch as a filler of adhesive to obtain good bonding quality of plywood. The phenomenon was occurred due to the viscosity of adhesive solution increased by adding high content starch hence the starch was hydrolyzed by citric acid as acid compound into dextrin, then anomeric carbon of dextrin was attacked by hydroxyl group of wood compounds to form a glycosidic linkage. Moreover, the other linkage was formed such as ester linkage since the reaction between carboxyl group of citric acid and hydroxyl group of wood [13].
3.2. Shear strength of plywood

The shear strength of the plywood is almost similar except for the plywood with 50 wt% of starch addition as shown in Fig. 2.

The plywood bonded with 50:50 wt% composition of CA – St based adhesive have higher shear strength (12.9 Kg/cm²) than that of the other plywood. According to the SNI 01-5008.2-2000 standard for plywood for general use, the shear strength should be higher than 7. Exception for plywood with 10 wt% of additional starch, all of the plywood bonded with CA-St based adhesive satisfied with the SNI 01-5008.2-2000 with higher shear strength than the requirements (7.5 to 12.9 Kg/cm²).
enhancement in the shear strength can be explained as follows. The hydroxyl groups of wood chemical compounds build a strong chemical interaction with both the carboxyl groups of citric acid and anomeric carbon of dextrin as a derivative compound of the starch [14].

3.3. Wood failure of plywood
The wood failure of plywood with 50 wt% of starch addition (50:50) was higher than that of the other plywood as shown in Fig. 3. These mean that adding starch less than 50 wt% was not effectively increased the mechanical properties of the plywood. Same as the shear strength of the plywood, this phenomenon has happened due to such a reaction between citric acid, starch and wood components have occurred. In addition, the plywood with 50 wt% of starch addition has higher value of wood failure that the minimum requirement of the SNI 01-5008.2-2000 (more than 50%).

![Figure 3. Effect of citric acid – starch ratio on the wood failure of plywood](image)

3.4. Functional groups in plywood
The infrared (IR) spectra of sengon plywood bonded with a varied composition ratio of citric acid – starch-based adhesive is presented in Fig. 4. An absorption peak at 1720 cm\(^{-1}\) appeared clearly in all of the plywood. The peak at 1720 cm\(^{-1}\) was typically assigned to C=O stretching due to carbonyl groups and/or the C=O ester groups [15, 16]. In addition, appearance of absorption peak at 1195 cm\(^{-1}\) and 1120 cm\(^{-1}\) was typically assigned to C-O-C glycoside bond angle [17]. The appearance of ester groups in the IR spectra indicates that the carboxyl groups of citric acid reacted with hydroxyl groups of lignocellulose chemical compounds from wood sengon to form ester linkages.
Figure 4. Fourier transform infrared spectra of wood (a), starch (b), and plywood with varied additional of starch content: 50 wt% (c), 40 wt% (d), 30 wt% (e), 20 wt% (f), 10 wt% (g).

The lignocellulosic materials contain abundant hydroxyl groups derived from lignocellulosic components such as cellulose, hemicellulose, and lignin [18]. Besides that, hydroxyl group of sengon wood attacked the anomeric carbon of derivative compound of starch i.e. dextrin that was resulted by hydrolysis due to acid compound from citric acid and heat from hot pressing process during plywood manufacturing [13]. The consequent formation of ester and glycoside linkages would improve the adhesiveness. As a result, the physical and mechanical properties of sengon plywood bonded with citric acid-starch based adhesive were improved.

4. Conclusion
In this study, the bio-adhesive formulated from citric acid was applied firstly in the manufacturing of plywood. The additional starch in the manufacturing of plywood bonded with citric acid-based adhesive enhanced the physical and mechanical properties of plywood. The additional starch of 50 wt% has effectively improved the plywood properties and it passed the SNI standard of plywood for general use. The ester and glycoside linkages were formed by interaction between hydroxy group of sengon wood, carboxyl group of citric acid, and anomeric carbon of derivative starch, hence the plywood obtained good bondability. Therefore, the plywood earned superior physical and mechanical properties. The addition of starch higher than 50 wt% with the 59 wt% of concentration could not be investigated due to the higher viscosity will be obtained and couldn’t apply for the manufacturing of plywood. Thus, adding starch more than 50 wt% with low concentration of adhesive solution will be investigated in future studies.
References

[1] FAO 2017 Global Forest Products: Fact and Figure 2016 Food and Agriculture Organization of The United Nation. USA.
[2] National Cancer Institute 2012 Formaldehyde and cancer risk
[3] Roffael E 2006 Volatile organic compounds and formaldehyde in nature, wood and wood based panels *Holz als Roh und Werkstoff* **64**(2) 144-149
[4] Salthammer T, Mentese S, Marutzky R 2010 Formaldehyde in the indoor environment *Chem Rev.* **110**(4) 2536-2572.
[5] Umemura K, Ueda T, Munawar S S, Kawai S 2012 Application of citric acid as natural adhesive for wood *Journal of Applied Polymer Science* **123**(4) 1991-1996.
[6] Widyorini R, Yudha A P, Adifandi Y, Umemura K, Shuichi K 2013 *Wood Research Journal* **4**(1) 31-35
[7] Liao R, Xu J, Umemura K 2016 BioResources **11**(1) 2174-2185
[8] Kusumah S S, Umemura K, Yoshioka K, Miyafuji H, Kanayama K 2016 *Industrial Crops and Products* **84** 34-42
[9] Kusumah S S., Arinana, Hadi YS, Guswenrivo, I., Yoshimura, T., Umemura, K., Tanaka S and Kanayama, K. 2017. *BioResource* 12(4), 7498-7514. DOI: 10.15376/biores.12.4.7498-7514
[10] Kusumah S S, Umemura K, Guswenrivo I, Yoshimura T, Kanayama K 2016 *J Wood Sci* DOI: 10.1007/s10086-016-1605-0
[11] SNI 2000 SNI 01-5008.2-1999: Kayu lapis dan papan blok penggunaan umum. Standar Nasional Indonesia. Jakarta.
[12] Larsson P, Mahlberg R, Vick C, Simonson R, Rowell R. Adhesive bonding of acetylated pine and spruce. Chemical modification of lignocellulosics, New Zealand Forest Research Institute, Rotoura, New Zealand, 1992. p. 16–24.
[13] Onusseit, H., 1993 Starch in industrial adhesives, *Industrial Corps and Products*, vol 1, p. 141-146
[14] Kang H, Wang Z, Wang Y, Zhao S, Zhang S, Li Z 2019 *Industrial Corps and Products*, vol 133, p. 10-17.
[15] Yang CQ, Xu Y, Wang D 1996 FT-IR spectroscopy study of the polycarboxylic acids used for paper wet strength improvement *Ind Eng Chem Res* **35** 4037–4042
[16] Žagar E, Grddolnik J 2003 An infrared spectroscopic study of H-bond network in hyperbranched polyester polyol. *J Mol Struct* **658** 143–152
[17] Sekkai M., Dincqb V., Legrandb P., Huvenneb J.P. 1995. Investigation of the glycosidic linkages in several oligosaccharides using FT-IR and FT Raman spectroscopies. *J. Molecular Structure* 349, 349 – 352 DOI: 10.1016/0022-2860(95)08781-P
[18] Zhang D, Zhang A, Xue L 2015 *Wood Science and Technology* **49** 661-679 DOI:10.1007/s00226-015-0728-6

Acknowledgments
Authors wishing to acknowledge financial support from an annual research project of Biomaterial Engineering and Modification Laboratory and Ministry of Research, Technology, and Higher Education.