Effects of Citric Acid-Starch Composition Ratio and Pressing Temperature on Properties of Particleboard from Salacca (*Salacca sp.*) Frond

Ragil Widyorini[1,*], Ersadarita Sembiring[1], & Kenji Umemura[2]

[1]Faculty of Forestry, Universitas Gadjah Mada, Yogyakarta
[2]Research Institute for Sustainable Humanosphere, Kyoto University, Japan
**Email* : rwidyorini@ugm.ac.id

ABSTRACT

Development of eco-friendly biocomposite product has currently become an interesting topic in materials science. Characteristics of adhesive components can affect the optimal pressing temperature in the manufacture of particleboard. This study aimed to analyze the influence of pressing temperature and citric acid: starch adhesive composition on properties of the particleboard from salacca fronds. The compositions of citric acid: starch adhesive was set as follows, 100% : 0%, 75% : 25%, and 50% : 50%. In addition, the pressing temperature was set at 140°C, 160°C, and 180°C. Particleboards was produced by hot pressing at specific pressure 3.5 MPa for 10 minutes. Citric acid content was 20% based on dried particle, while the density target was set at 0,8 g/cm^3. Fourier Transform Spectophotometry (FTIR) analysis was conducted to analyze the bonding mechanism. Increasing of starch in adhesive composition affect on decreasing of physical properties of the boards. Interestingly, replacement of citric acid with starch until 25 wt% could increase the mechanical properties. However, 50 wt% of starch in adhesive composition caused decreasing of mechanical properties of the boards. Increasing of pressing temperature provided higher physical and mechanical properties of the boards. The infrared analysis confirmed the formation of the ester linkages at various manufacturing condition. Composition of citric acid: starch adhesive (%) 75 : 25 and press temperature of 180^{o}C produced the best properties of particleboard with the 0.93 g/cm^3 density, 9.85% moisture content, 28.20% thickness swelling, 52.73% water absorption, 8.83 MPa modulus of rupture,1.96 GPa modulus of elasticity, and 0.33 MPa internal bond strength.

Keywords: adhesive composition, citric acid, pressing temperature, Salacca frond, starch

Introduction

The development of the composite product made from wood or non-wood materials is greatly increased in recent years. Other materials such as concrete, plastic, and aluminum, could not replace the function of wood since they are non-biodegradable and non-renewable materials. Rowell et al. (1997) suggested some solutions to solve the wood demand problems, such as utilization of new plant for forest fast-growing species, recycling of wood and wood product, and utilization of lignocelluloses waste as the addition product from certain management agriculture such as cotton, corn, tobacco, sugar cane, jute, straw, and so on.

Snake fruit (*Salacca sp)* is popular tropical fruit, which it abundantly grows in Indonesia, mainly in Java and Sumatra. The potency of snake fruit is relatively high, around 862,465 ton in 2008 and increased to 1,030,401 ton in 2013 (BPS, 2014). This plant has a stem that usually covered by the frond. During maintenance, the frond is usually cut for 3-4 frond/plant/4 month. The frond is usually used as biomass waste and not utilized yet until now.

The formaldehyde-based adhesive is mainly used in composite production. Due to the increasing of environment concern, application of this adhesive is reduced. Many efforts have been done to reduce the emission, such as the development of natural adhesives (Pizzi 2006), or even binderless composite (Xu et al*.* 2003; Okuda & Sato 2006). However, during the manufacturing of natural adhesives such as lignin and chitosan, the small amount of formaldehyde was still added.

One potential natural materials that can act as binder or adhesive is citric acid, as natural polycarbocylic. This acid was usually used as absorption of Cu ion (McSweeny et al. 2006), crosslinking agent in starch film (Reddy & Yang 2010), as well as modification agent for beech wood (Despot et al*.* 2008). Addition of formaldehyde is not required to this adhesive. The researches on citric acid are still limited, such as *moulding* product made from acacia wood and bark (Umemura et al. 2011; 2012). The products had high mechanical properties and also high dimensional stability. Citric acid could act as a good binder in particleboard made from non-wood materials, such as bamboo, oil palm frond, and nypa frond (Widyorini et al. 2012a; 2012b; 2016a). Investigation of the effect of bamboo species, layer composition and amount of citric acid has also been done (Widyorini et al. 2016a). The results showed that the characteristic of the raw materials affected significantly the bonding properties of the particleboard. For getting the optimum properties, combination this polycarboxylic acid with other materials is also interesting to be done. Addition of sucrose until 75 %: 25% composition ratio could increase the mechanical properties of the particleboard (Umemura et al. 2013; Widyorini et al. 2016b). The results also showed that different adhesive compositions affected on required pressing temperature to get the optimum properties of the boards. Addition of starch also could increase the bonding properties of bamboo particleboard (Widyorini et al. 2017). However, the bonding mechanism of this adhesive is still unknown in detail.

The objective of this research was to evaluate the physical and mechanical properties of biocomposite made from snake fruit (*Salacca* sp.) frond using citric acid-starch adhesive at different pressing temperature. To analyze the bonding mechanism, the functional groups were identified by Transform Infrared Spectrophotometry (FTIR).

Materials and Methods

Preparations of materials

The raw material used in this research was salacca (*Salacca* sp) frond, which was obtained from Yogyakarta province, Indonesia. The fronds were collected and were cut into 1 m length. Salacca frond particles were prepared using a chipper and knife ring flaker. The particles were screened into filter and those that passed 10 mesh-screen were used as raw material.

Citric acid (anhydrous) made from Weifang Ensign Industry Co. Ltd. China was used without further purification. Citric acid and arrow-root starch were dissolved in water under a certain ratio, and the solution concentration was adjusted to 59 ~ 60 wt%. The mixture ratios of citric acid/starch with were set as follows (wt%), 100 : 0, 75 : 25, and 50 : 50.

Manufacture of composite board

The citric acid was sprayed onto particles at 20 wt% resin content based on the weight of the dried fibers. The sprayed particles were then oven-dried overnight at 80^{o}C to reduce moisture content. The moisture content of the mat was around 3 - 5%. The particles were hand-formed into a mat by using a forming box, followed by hot pressing into particleboard. The dimensions of the boards were 25 x 25 x 1 cm, with the target board density was set at 0.8 g/cm^3. The pressing time was 10 min under a pressure of 3.5 MPa. The pressing temperatures were set at 140^{o}C, 160^{o}C, and 180^{o}C. Three replications of each manufacturing condition were applied in this study. Prior to the evaluation of the mechanical and physical properties, all of the boards were conditioned at ambient conditions for about 7-10 days.

Evaluation of board's properties

After being conditioned, the boards were then evaluated basically according to the Japanese Industrial Standard for Particleboards JIS A 5908-2003. Tests were carried out for its physical and mechanical properties. The thickness swelling (TS) as well as water absorption (WA) test were performed on a 50 x 50 x 10 mm specimen from each board after water immersion for 24 h at 20°C. The same size of the specimens of those used for the internal bond strength (IB) test. The bending properties of the boards, i.e. modulus of rupture (MOR), modulus of elasticity (MOE), were evaluated by conducting the static three-point bending tests on a 200 x 50 x 10 mm specimen for each board in dry and wet conditions. The effective span and loading speed were 150 mm and 10 mm/min, respectively. Before the bending strength test, the specimens were tested for their surface roughness using surface roughness SRG 400, where average roughness (Ra) was used to evaluate roughness characteristics of the particleboards. Six measurements were randomly taken from both surfaces of each sample. The MOR, MOE, and IB strength of the boards are values corrected for each target density based on specimen densities. Each experiment was performed in triplicate, and the average value and standard deviation were calculated.

Fourier Transform Infrared (FTIR) spectroscopy

After the MOR specimens were immersed in boiling water for 2 h and further immersing them in water of ordinary temperature for 1 h. The samples were then dried at 80°C overnight and ground into a powder. All infrared spectra were obtained with FTIR spectrophotometer (Shimadzu IR Prestige-21) using KBr disk method and were recorded by means of an average of 10 scans at a resolution of 16 cm^{-1}.

Result and Discussion

Table 1 shows the physical properties of salacca frond particleboard using various citric acid-starch compositions. It clearly showed that increasing pressing temperature significantly affected on decreasing of thickness swelling and water absorption values. This result consistent with other researches using bamboo particles (Widyorini et al. 2016a). It also showed that increasing starch in composition with citric acid tends to decrease the dimensional stability. It may due to starch has strong hydrophilic characteristic (Averous & Boquillon 2004). Compared to bamboo particleboard at the same condition (Widyorini et al. 2016a), this particleboard has lower properties. This is supposedly due to the characteristics of differences between salacca frond and bamboo, especially for its chemical composition. More analyses will be done to make a clear discussion on the bonding properties of those materials.

Table 1. Physical properties of salacca frond particleboard using various citric acid-arrowroot starch composition

CA:AS (%)	Pressing Temperature (°C)	Physical properties			
		Moisture content (%)	Thickness swelling (%)	Water adsorbtion (%)	Surface roughness (μm)
100:0	140	14.7±0.26	54.24±7.89	93.30±3.77	14.31±1.04
75:25		12.4±0.61	68.22±6.67	114.21±4.96	12.52±1.54
50:50		11.4±0.91	79.7±10.81	155.99±13.99	10.33±1.29
100:0	160	14.8±0.66	45.53±5.41	59.73±5.15	12.82±1.26
75:25		10.6±0.58	61.97±1.75	85.95±0.48	9.30±0.87
50:50		10.2±0.41	63.02±5.87	99.11±6.83	9.85±1.81
100:0	180	10.6±0.90	26.59±3.91	50.80±3.45	12.45±1.09
75:25		9.8±0.74	28.10±4.14	52.73±5.94	10.32±2.37
50:50		9.4±1.63	40.44±5.13	74.12±9.57	10.33±1.20

The average surface roughness (Ra) values of salacca frond have been measured, and the result could be shown in Table 1. It clearly showed that increasing of pressing temperature did not significantly improve on the Ra values. Interestingly, addition of starch in adhesive composition affected on the surface roughness. The surface roughness values of the particleboards in this study were range from 9.7 – 14.3 μm, which it was higher than Widyorini et al. (2016a). This range was out from average Ra values for commercially manufactured particleboard, which is 3.67 – 5.46 μm (Hiziroglu & Suzuki 2007) or particleboard made from rubberwood (Hiziroglu et al. 2004).

Figure 1, 2, and 3 shows mechanical properties of salacca frond particleboard using various citric acid-starch compositions. It showed that pressing temperature was more significantly on the mechanical properties, compared to adhesive composition. According to Figure 1, it shows that the MOE values of salacca frond boards is between 0.26 – 1.96 GPa. The highest value of MOE could be reached at the manufacturing condition of citric acid-starch (75:25 wt%) at 180°C pressing temperature condition. Effect of pressing temperature was dominant on the MOE values at various adhesive composition. It is due to the pressing temperature affected on the reaction. The decreasing of citric acid content on the adhesive composition affected the decreasing of carbonyl groups that it ester linked with hydroxyl groups from starch and the raw materials.

Figure 2 shows that the MOR of the boards were the range at 0.77 – 8.83 MPa. Based on this data, the particleboard bonded with citric acid-starch (75 : 25 wt%) and pressed at 180°C pressing temperature met the requirement of JIS A 5908 type 8. The effect of pressing temperature and composition ratio of citric acid-starch on MOR was similar compared to MOE. The bending properties of the boards were relatively low compared to bamboo using the same adhesive composition (Widyorini et al. 2017). It showed that the characteristic of the materials affected the properties of the boards.

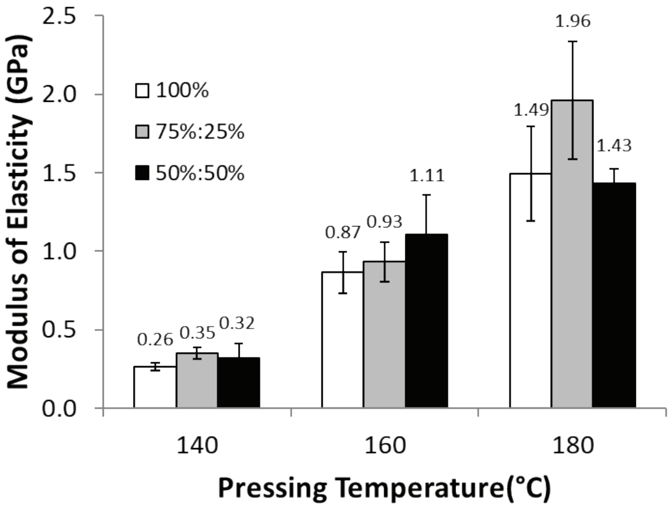

Figure 1. Modulus of elasticity of salacca frond composite board at various adhesive compositions (citric acid-starch) and pressing temperature. *Vertical lines through the bars* represent the standard deviation from the mean.

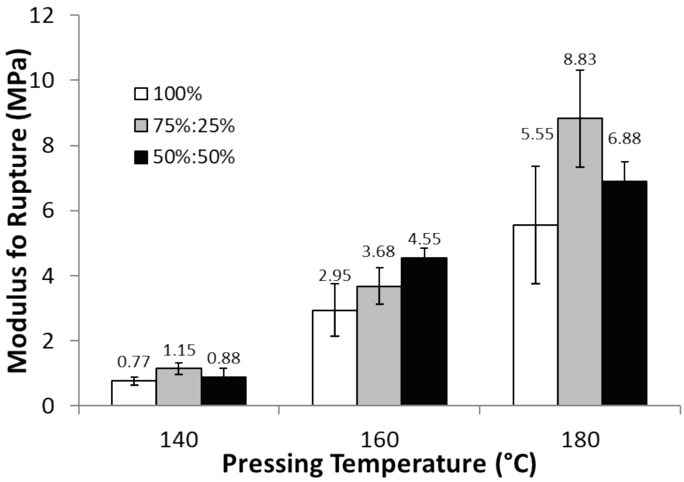

Figure 2. Modulus of rupture of salacca frond compositeboard at various adhesive composition (citric acid/starch) and pressing temperature. *Vertical lines through the bars* represent the standard deviation from the mean.

Figure 3 shows that the value of the internal bonding strength of boards was 0.01 – 0.33 MPa. The highest IB value was obtained when the manufacture condition was 180°C of pressing temperature with the adhesive composition of citric acid-starch was 75 : 25. Another result from Ghanbarzadeh et al. (2011) showed that citric acid could be acted both as a plasticizer and a crosslinking agent in the starch film. Based on the results in this study, it was clarified that the hydroxyl groups from starch reacted with carboxyl groups from citric acid, providing the good performance of the boards. However, if the starch composition was 50 wt% in adhesive, the bonding properties become low. It due to the number of carboxyl groups of citric acid was also decreased. Compared to bamboo (Widyorini et al. 2017), the internal bond strength of the boards in this study was relatively low. It may due to the salacca frond has higher extractives than bamboo, that could affect the bonding mechanism with citric acid/starch adhesive.

To investigate the bonding mechanism of the board, FTIR analysis were measured, as shown in Figure 4. After addition of 20 wt% of citric acid, the peak of the absoption band at around 1734 cm^{-1} (4a, b, c) that it was ascribed to C=O stretching derived of carbonyl groups was appeared (Umemura et al. 2011). The peak was hardly recognized on the salacca frond. This peak was attributed to the formation of ester linkages (Umemura et al. 2012; Widyorini et al. 2016), resulting from the reaction between the carboxyl groups from citric acid and the hydroxyl groups from salacca frond and starch in this study. The effect of pressing temperature could be seen at Figure 5. The effect of pressing temperature more remarkable than composition ratio on peak at 1734 cm^{-1}.

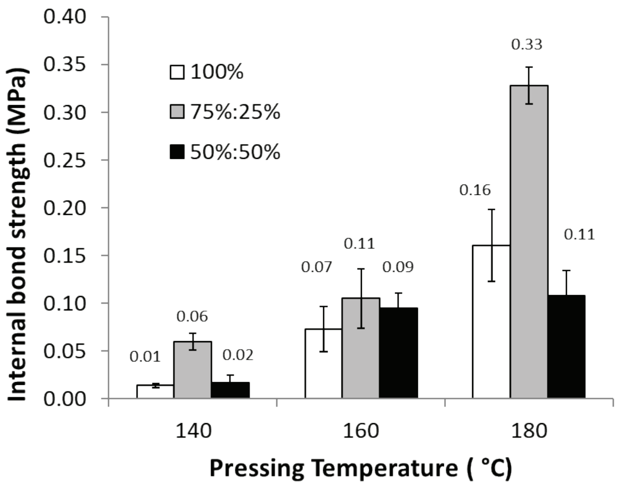

Figure 3. Internal bond strength values of salacca frond compositeboard at various adhesive composition (citric acid/starch) and pressing temperatures. *Vertical lines through the bars* represent the standard deviation from the mean.

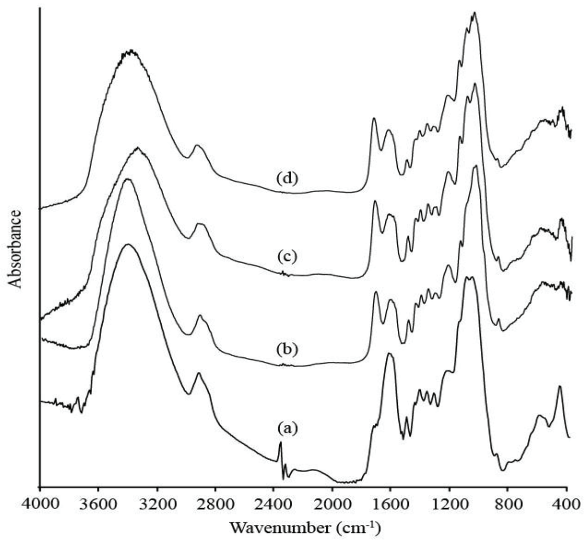

Figure 4. Fourier transform infrared (FTIR) spectra of (a) salacca frond particles (b) citric acid/starch (50/50)-bonded board, (c) citric acid/starch (75/25)-bonded board, (d) citric acid/starch (100/0)-bonded board at pressing temperature of 180 °C.

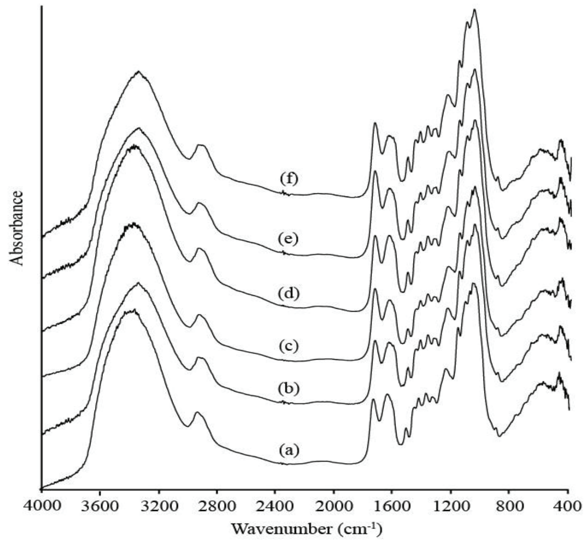

Figure 5. Fourier transform infrared (FTIR) spectra of particleboards (a) citric acid/starch (50/50) and 140 °C, (b) citric acid/starch (50/50) and 160 °C, (c) citric acid/starch (50/50) and 160 °C, (d) citric acid/starch (75/25) and 140 °C, (e) citric acid/starch (75/25) and 160 °C, (f) citric acid/starch (50/50) and 180 °C

Conclusion

The effects of citric acid-starch composition ratio and pressing temperature on the properties of particleboards made from salacca frond were investigated in this study. Increasing starch in composition ratio until certain ratios could increase the mechanical properties. Pressing temperature affected more remarkable on physical and mechanical properties of the boards.The infrared analyses indicated that carboxyl groups of citric acid could react with the hydroxyl groups of the starch and salacca frond. Composition of citric acid-starch adhesive (%) 75 : 25 and press temperature of 180°C produced the best properties of particle board as follows 28.20% thickness swelling, 52.73% water absorption, 8.83 MPa modulus of rupture, 1.96 GPa modulus of elasticity, and 0.33 MPa internal bond strength.

Acknowledgments

The authors are grateful to Ministry of Research, Technology and Higher Education of the Republic of Indonesia for funding this project under research grant scheme of the International Research Collaboration and Scientific Publication (2016-2017) and was supported by SPIRITS 2017 of Kyoto University.

References

Averous L, Boquillon N. 2004. Biocomposites Based on Plasticized Starch: Thermal and Mechanical Behaviours. Carbohyd. Polym. **56:** 111–122.

Badan Pusat Statistik (BPS). 2014. Luas Panen, Produksi, dan Produktivitas Salak. Departemen Pertanian.

Despot R, Hasan M, Jug M, Sefc B. 2008. Biological Durability of Wood Modified by Citric Acid. Drvna Industrija **59**(2) : 55-59.

Ghanbarzadeh B, Almasi H, Entezami AA. 2011. Improving the barrier and mechanical properties of corn starch-based edible films: Effect of citric acid and carboxymethyl cellulose. Ind. Crop. Prod. **33**(1): 229-235.

Hiziroglu S, Suzuki SV. 2007. Evaluation of surface roughness of commercially manufactured particleboard and medium density fiberboard in Japan. J. Mater Process Technol **184**: 436 – 440.

Hiziroglu S, Jarusombuti S, Fueangvivat V. 2004. Surface characteristics of wood composites manufactured in Thailand," Build. Environ. **39**(11): 1359-1364

Japanese Industrial Standard (JIS), 2003. JIS A 5908-2003. Particleboard. Japanese Standard Association, Tokyo, Japan.

McSweeny JD, Rowell RM, Min SH. 2006. Effect of Citric Acid Modification of Aspen Wood on Sorption of Copper Ion. Journal of Natural Fiber **3**(1) : 43 – 58

Okuda N, Sato M. 2006. Water Resistance Properties of Kenaf Core Binderless Boards. J Wood Sci **52**: 422-428

Pizzi A. 2006. Recent Developments in Eco-efficient Bio-Based Adhesives for Wood Bonding: Opportunity and Issues. J. Adhesion Sci. Technol. **20**(8) : 829-846

Reddy N, Yang Y. 2010. Citric acid cross-linking of starch films. Food Chemistry **118** : 702-711

Rowell RM, Young RA, Rowell JK. 1997. Paper and Composites from Agro-based Resource. CRC Lewis Publishers, Boca Raton Florida. p. 69.

Umemura K, Ueda T, Munawar SS, Kawai S. 2011. Application of Citric Acid as Natural Adhesive for Wood. J. Appl. Polym. Sci. **123**:1991-1996

Umemura K, Ueda T, Kawai S. 2012. Characterization of wood-based molding bonded with citric acid. J. Wood Sci. **58:**38–45

Umemura K, Sugihara O, Kawai S. 2013. Investigation of a new natural adhesive composed of citric acid and sucrose for particleboard. J Wood Sci. **59**:203–208

Widyorini R, Yudha AP, Ngadianto A, Umemura K, Kawai S. 2012a. Development of Bio-based Composite Made From Bamboo And Oil Palm Frond. Proceedings of BIOCOMP 2012 (11th Pacific Rim Bio-Based Composite Symposium). Shizuoka. Japan

Widyorini R, Prayitno TA, Kurniawan BA, Wicaksono BH. 2012b. Pengaruh Konsentrasi Asam Sitrat dan Suhu Pengempaan Terhadap Kualitas Papan Partikel dari Pelepah Nipah. Jurnal Ilmu Kehutanan **6**(1): 61-70

Widyorini R, Umemura K, Isnan R, Putra DR, Awaludin A, Prayitno TA. 2016a. Manufacture and properties of citric acid bonded particleboard made from bamboo materials. Eur. J. Wood Prod. **74:** 57-65.

Widyorini R, Rahman MZA, Nugraha PA, Prayitno TA. 2016b. Bonding Ability of a New Adhesive Composed of Citric Acid-Sucrose for Particleboard. BioResources **11**(2): 4526-4535.

Widyorini R, Umemura K, Kusumaningtyas AR, Prayitno TA. 2017. Effect of Starch Addition on Properties of Citric Acid-bonded Particleboard made from Bamboo. BioResources **12**(4): 8068-8077.

Xu J, Han GP, Wong ED, Kawai S. 2003. Development of Binderless Particleboard From Kenaf Core Using Steam-Injection Pressing. J Wood Sci **49**:327–332