Physical and Chemical Characteristics of An Organic Nanoparticle Synthesized from Gmelina (Gmelina arborea Roxb) Wood Bark

Sutrisno¹, E M Alamsyah¹, T S Syamsudin¹, B S Purwasasmita², S Suzuki³ and H Kobori³
¹School of Life Sciences and Technology, Institut Teknologi Bandung, Jl. Ganesha 10 Bandung 40132, Indonesia
²Faculty of Industrial Technology, Institut Teknologi Bandung, Jl. Ganesha 10 Bandung 40132, Indonesia
³Faculty of Agriculture, Shizuoka University, Ohya-836, Suruga-ku, Shizuoka-shi, Japan 422-8529
sutrisno@sith.itb.ac.id

Abstract. The objective of this research is to investigate the characteristics of an organic nanoparticle produced from Gmelina wood bark using ball milling with liquid nitrogen treatment. In this study Gmelina wood bark was converted into nanoparticles using the ball milling method for 96 h and then filtered using four types of sieves (T77, T90, T120, and T200). These nanoparticles were characterized by particle size, morphology, chemical components, functional groups, and crystallinity using TEM, SEM, SEM-EDS, FTIR and XRD. The process resulted in nanosized organic material produced from Gmelina wood bark, with diameter sizes less than 1000 nm. The existence of carbon, oxygen, potassium, and calcium were observed from the SEM-EDS analysis. The FTIR analysis showed the presence of C-O-C in a plane and symmetric band at 829 cm⁻¹ for the nanoparticle produced from the T200 sieve type, while not observed in the nanoparticle produced from T77, T90 and T120 of sieve types. The crystalline structure as obtained from the XRD analysis contained calcium oxalate hydrate (C₂CaO₄·H₂O) with a 20 nm crystalline diameter size that was produced using the T77 and T200 sieve types.

Keywords: physical & chemical characteristics, organic nanoparticles, ball milling method, liquid nitrogen treatment, Gmelina wood bark

1. Introduction
West Java Province has 419,041.93 hectares of community forest with a timber potential of 12,005,551 m³ with an average timber potential 28.65 m³/ha. The community forests contain at least thirty-two species of wood, one of which is Gmelina (Gmelina arborea) [1]. To obtain the maximum benefits from community forests, it is not enough to use the timber only but to also find alternative uses for the wood bark waste. The volume of wood bark could be estimated in the range of 9-15% [2] or 10-25% [3] based on the volume of wood. If the average amount of wood bark would be estimated at 10% of the total wood volume and the potential timber of West Java’s community forests
is 12,005,551 m$^3$ [1], then the production of wood bark waste will be about 1,200.55 m$^3$. Wood bark has many uses, e.g., as adhesive filler [4-6], tannins adhesive [7-9], or wood preservative [10-12]. Today, wood bark waste is mostly used by wood processing industries as fuel for the boilers to produce steam for the drying process.

This research is essential to be done, especially to promote the use of wood bark nanoparticles as adhesive filler to improve the bonding properties of wood composites. This is because the adhesive better interacted with the wood on the nanometer scale level. Additionally, the adhesive penetration is resulted by the size and shape of the molecule and its solubility, whereas the process also will be occurred at the nanometer scale [13].

The definition of the term ‘organic nanoparticles’ is solid particles composed of organic compounds ranging in diameter from 10 nm to 1000 nm [14,15]. Similarly, nanoparticulate matter, including nanomaterials and nanoparticles, is defined as a collection of particles of at least one dimension smaller than 1000 nm [16]. Ball milling is one of several physical methods to produce nanoparticles with a broad size distribution (10-1000 nm) [17]. The advantages of this method are its simple operation, low cost, and the flexibility to produce large quantities of nanoparticulate matter. In the case of Pine, ball milled pine bark was applied for the heat and sound insulation material [18]. However, it is very difficult to produce ultrafine particles (1-100 nm) or this takes very long time [16,19]. Rajaonarivony et al. provided the Pine bark properties after two kinds of milling process and their energy consumption. They suggested that the particle agglomeration during milling process limited the possibilities for reaching ultrafine particles [20]. The final product quality of nanoparticles is affected by the type of mill, milling speed, container, time, and the weight ratio of ball to powder [19]. Therefore the objective of this study is to investigate the characteristics of an organic nanoparticle produced from Gmelina wood bark using ball milling with liquid nitrogen treatment.

2. Materials and Methods

2.1. Materials

Gmelina wood bark (GWB) was collected from a community forest in Cibugel District, Sumedang Regency, West Java Province, Indonesia. The sampling site is located at 6°44′-70°83′ south latitude and 107°21′-108°21′ east longitude. The wood bark was cut into small pieces (2 cm x 2 cm) using a cleaver and then solar dried until the moisture content was less than 5%. Then, the wood bark was powdered by pounding it using a pestle and filtered using a 60-mesh sieve.

2.2. Methods

2.2.1. Synthesis of Nanoparticles.

First, 0.383 kg of wood bark powder (60-mesh) was grounded by using the ball milling method for 48 h at 100 rev min$^{-1}$ with a 1.5:1 ratio of the weight of balls to powder. Secondly, wood bark powder was treated with liquid nitrogen with a 2:1 ratio of the volume of liquid nitrogen to powder and then grounded using the ball milling method for 48 h under same conditions. The wood bark powder was then filtered using four types of sieves (T77, T90, T120, and T200). The milling container was made of a PVC pipe with a 10.16 cm diameter and a length of 26.8 cm. Whereas the balls were made of alumina with diameter sizes in the range of 1.3-4.0 cm. Figure 1 presents a schematic overview of the synthesis of nanoparticles using the ball milling method with liquid nitrogen treatment. The nanoparticle synthesizing was conducted at the Advanced Materials Processing Laboratory, Engineering Physics Department, Faculty of Industrial Technology, Institut Teknologi Bandung.
Figure 1. Schematic overview of the synthesis of nanoparticles from Gmelina wood bark using ball milling and treatment with liquid nitrogen

2.2.2. Characterization.

After synthesizing the nanoparticles, they were characterized by their particle size, morphology, chemical components, functional groups, and crystallinity using transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning electron microscopy extended with energy-dispersive X-ray spectroscopy (SEM-EDS), Fourier Transform Infrared Spectroscopy (FTIR), and X-ray Diffraction (XRD)[21-26]. The characterization of nanoparticles was conducted at the Basic Science Center Laboratory, Institut Teknologi Bandung.

Morphology, particle size, and chemical components. Samples were taken and coated with platinum using an ion sputter coater. Then, the morphology and diameter size of the wood bark nanoparticles were characterized using SEM (JEOL-JSM-6510LV SEM type). Whereas the elemental composition of the wood bark was analysed using SEM extended with energy-dispersive X-ray spectroscopy (SEM-EDS). Especially for nanoparticles produced from T90 sieve type, the diameter size was analyzed using transmission electron microscopy (TEM) (JEOL-JEM-1400 TEM type).

Functional groups. The functional groups present in the Gmelina wood bark were examined using FTIR, (Prestige 21, Shimadzu, Japan). 5 mg of samples were mixed with 160 mg KBr (1:32) and then pressed into transparent thin pellets. An FTIR spectrum of the wood bark was obtained in the range of 4500 - 500 cm\(^{-1}\) and the spectral output was recorded in the transmittance mode as a function of wave number.

Crystallinity. The crystalline structure of the organic nanoparticles produced from Gmelina wood bark was identified using a powder X-Ray Diffraction (XRD) instrument (XRD, PW 1710, Philips analytical) that operated at 40 Kv and 30 mA with Cu/K\(\alpha\) (\(\lambda = 1.54060\) \(\text{Å}\)) radiation source. The diffractograms were scanned at a rate of 0.5° s\(^{-1}\) in steps of 0.02° from 5° to 65° (2 \(\theta\)) at room temperature. The crystalline size was determined from the X-ray diffraction peaks using Scherrer’s equation [27]:

\[
D = K \frac{\lambda}{\beta \cos \theta}
\]

In equation (1), \(D\) is the diameter of crystallites; \(K\) is a shape factor with a value of 0.9-1.4 or the Scherrer’s constant of the order of unity for usual crystals, \(\lambda\) is the wavelength of the X-rays (1.54060 \(\text{Å}\)); \(\beta\) is the value of the full width at half maximum (FWHM); and \(\theta\) is the diffraction angle. The XRD patterns were identified using the PDF2 CD-ROM (JCPDS-International Centre for Diffraction Data).
3. Results and Discussion

3.1. Nanoparticles size and morphology

The TEM analysis found that the particle size of Gmelina wood bark was 60.78 nm produced from the sieve type T90. Additionally, the SEM analysis found that the particle size was 104-254 nm, 71-104 nm, 33-47 nm, and 33-38 nm produced using the T77, T90, T120, and T200 sieve types, respectively. The particles had magnifications of SEM of 30,000 times and the particles were seemed agglomeration. Figure 2 and 3 shows the morphology of these particles. From these observations, the process obtained nanosized organic materials from Gmelina wood bark, because the particles' size is in the range of 10-1000 nm [14,15] or less than 1000 nm [16]. This result is in line with previous research using jabon and surian wood bark [24,25]. As a comparison, high-energy ball milling of oil palm ash for 30 h produced particles with diameter sizes of up to 50 nm [21]. Whereas this is contradictory with non-organic materials synthesized from wood waste ash which forms no agglomeration among particles [26].

The proportion of nanoparticle sizes was 11.2%, 82.9%, 3.5%, and 0.6% produced using the T77, T90, T120, and T200 sieve types, respectively and the last 1.8% of nanoparticles was retained on the T77 sieve type (table 1). The nominal sieve opening of the T200 sieve type was 10.6 micron on average based on the SEM analysis as presented in figure 4.
Figure 3. SEM analysis of nanoparticles size produced from four of sieve types: (a) T77, (b) T90, (c) T120, and (d) T200

Table 1. Sieve types and nanoparticle size

| Sieve Type | Sieve designation (mesh) | Nominal sieve opening (microns) | Nano particles size (nm) | Proportion (%) |
|------------|--------------------------|---------------------------------|--------------------------|---------------|
| T77        | 523                      | 28**)                          | 93-110                   | 11.2          |
| T90        | 611                      | 24**)                          | 67-165                   | 82.9          |
| T120       | 815                      | 18**)                          | 68-93                    | 3.5           |
| T200       | 1358                     | 10.6*)                         | 42-114                   | 0.6, 1.8***   |

Note: *) based on SEM analysis  
**) based on a conversion from the T200 sieve type  
***) retained on the T77 sieve type

Figure 4. The average nominal sieve opening of the T200 sieve type based on SEM analysis
3.2. Chemical Components

Figure 5 shows the SEM-EDS spectra with the chemical composition of Gmelina wood bark containing carbon, oxygen, potassium and calcium. Wood bark consists of about 60-70 percent glucose [28] and it's nutrient content depends on species, tree age, environmental factors, and growing site [29]. As a comparison, pinewood bark contains phosphorous, potassium, manganese, copper, calcium, magnesium, and zinc [29]. Whereas Falah et al. have studied the potential uses of the bark of G. arborea Roxb. as an antioxidant activity and investigated their 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging activity [30].

![SEM-EDS spectra with chemical composition of Gmelina wood bark.](image)

**Figure 5.** SEM-EDS analysis of nanoparticles produced from the T90 sieve type

3.3. Functional Groups

FTIR analysis showed that the transmission spectrum of the Gmelina wood bark was composed of cellulose, the main constituent of natural fibres that acts as the reinforcing material in the cell wall [31-35] (Table 2; Figure 6). Also FTIR analysis showed the presence of C-O-C in a plane and symmetric band at 829 cm\(^{-1}\) in the nanoparticles produced using the T200 sieve type due to balls milling effect, while not observed in the nanoparticle produced from T77, T90 and T120 of sieve types. There is a correlation between the morphology and chemical composition of wood from the bark through the cambium [34].

| Sieve types and peak wavenumber (cm\(^{-1}\)) | Assignment | References |
|---------------------------------------------|------------|------------|
| T77 | T90 | T120 | T200 |
| 3406-3352 | 3408-3354 | 3412-3375 | 3412-3371 | O-H stretching | [26,27,31] |
| 2920-2852 | 2920-2850 | 2922-2852 | 2920-2852 | C-H stretching | |
| 1726 | 1724 | 1728 | 1724 | C=O stretching | |
| 1633-1625 | 1633 | 1633 | 1635 | COO stretching | [27,29] |
| 1514 | 1512 | 1514 | 1514 | C=C stretching | [26,27,31] |
| 1425-1263 | 1425-1265 | 1425-1263 | 1427-1263 | C-H wagging | [29] |
| 1155 | 1155 | 1153 | 1153 | C-C ring breathing, asymmetric | |
| 1053-1037 | 1055-1037 | 1053 | 1055 | C-O-C glycosidic | |
| - | - | - | 829 | C-O-C in plane, symmetric | |
| 779-522 | 779-520 | 779-520 | 779-520 | C-OH out-of-plane bending | [26] |

Note: - no data
3.4. Crystallinity

The study also assessed the crystallinity of nanoparticles produced using the T77 and T200 sieve types. The XRD analysis (see figure 7) shows the crystalline structure of calcium oxalate hydrate ($\text{Ca}_2\text{CaO}_4\cdot\text{H}_2\text{O}$). The reflecting peaks at $2\theta = 14.98^\circ$, $24.40^\circ$, $30.14^\circ$ and $38.22^\circ$ were used to estimate the average of crystalline size produced from T77 of sieve type, which was calculated to be 20 nm (figure 7(a)). Whereas the reflecting peaks at $2\theta = 14.96^\circ$, $24.44^\circ$, $30.12^\circ$, and $38.20^\circ$ were used to estimate the average crystalline size produced using the T200 sieve type, which was calculated to be 20 nm (figure 7(b)). Thus, the T77 and T200 sieve types produced similar average crystalline sizes. The accessibility of cellulose is affected by crystallinity, lignin, and hemicellulose contents as well as its distribution, porosity, and particle size [36].
Figure 7. XRD analysis of the nanoparticles produced from sieve types (a) T77 and (b) T200

Note: The arrow indicates the similarity of crystalline features of calcium oxalate hydrate according to data from the powder diffraction file from The International Center for Diffraction Data (Powder-X version 2004.04.07 Pro).

4. Conclusions
The TEM analysis found that the particle size of Gmelina wood bark was 60.78 nm produced from the sieve type T90. Additionally, the SEM analysis found that the particle size was 104-254 nm, 71-104 nm, 33-47 nm, and 33-38 nm produced using the T77, T90, T120, and T200 sieve types, respectively. Thus, the study produced nanosized organic material from Gmelina wood bark, as its size in diameter is in the range of 10-1000 nm or less than 1000 nm. The chemical composition of the nanoparticles produced from Gmelina wood bark contained carbon, oxygen, potassium, and calcium. The study also found the presence of the functional group of cellulose in the wood bark. Furthermore, the FTIR analysis showed the presence of C=O-C in a plane and symmetric band at 829 cm\(^{-1}\) for the nanoparticles produced using the T200 sieve type, while the nanoparticle produced from T77, T90 and T120 of sieve types not observed. The study concludes that the ball milling effect has altered the functional groups of cellulose. Lastly, the crystalline structure of the nanoparticles contains calcium oxalate hydrate (C\(_2\)CaO\(_4\)H\(_2\)O) with a crystalline size of 20 nm, as was produced using the T77 and T200 sieve types.

References
[1] The Ministry of Forestry of the Republic of Indonesia 2010 Opportunities of Community Forest Investment in Java. (text in Indonesian). Directorate-General for Development of Watershed Management and Social Forestry, Jakarta, 66 p.
[2] Harkin J M and Rowe J W 1971 Bark and Its Possible Uses. Res. Note FPL-091. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wis. In Cooperation with the University of Wisconsin, 56 p.
[3] Miles P D and Smith W B 2009 Specific Gravity and other Properties of Wood and Bark for 156 Tree Species Found in North America. Res. Note NRS-38. Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northern Research Station 35 p.
[4] Eberhardt T L and Reed K G 2005 Grinding and Classification of Pine Bark for Use as Plywood Adhesive Filler. Peer-reviewed. *Appita Pre Symposium* pp. 109-113.
[5] Eberhardt T L and Reed K G 2006 Strategies for Improving the Performance of Plywood Adhesive mix Fillers from Southern yellow pine Bark. *Forest Prod. J.* 56 (10), 64-68.
[6] Eberhardt T L, Reed K G and So C L 2009 Partitioning of Pine Bark Components to Obtain a Value-Added Product for Plywood Manufacture in Advanced Biomass Science and Technology for Bio-Based Products, ed Hse CY, Jiang Z. and Kuo M L Developed from a
Symposium sponsored by the Chinese Academy of Forestry & USDA Forest Service, Southern Research Station pp. 302-309.

[7] Pizzi A 1994 Tannin-Based Wood Adhesives. In Advanced Wood Adhesives Technology, ed Pizzi A. Marcel Dekker Inc, New York, pp. 149-215, 289 p.

[8] Subyakto and Prasetya B 2003 Direct Utilization of Acacia Wood Bark Powder as an adhesive of Particle Board. Journal of Tropical Wood Science and Technology, 1 (1), 20-25.

[9] Subyakto, Suryanegara L, Gopar M and Prasetyio K W 2005 Utilization of Acacia Wood Bark (Acacia mangium Willd) for Particle Board with Low Levels of Phenol Formaldehyde. Journal of Tropical Wood Science and Technology 3 (2) 20-23.

[10] Carter F L, Cario A M and Stanley J B 1978 Termiticidal Components of Wood Extracts: 7-Methyljuglone from Diospyros virginia. Journal Agriculture Food Chemistry 26 (4), 869–873.

[11] Jasni, Pari G, Ruliadi, Kosasih K and Sutrisno 2001 The Potential Use of Tannin as a Preservative for Wood and Rattan. Proceedings of the Fifth International Conference on the Development of Wood Science, Wood Technology and Forestry (ICWSF), Ljubljana, Slovenia, pp. 61-67.

[12] Hagerman A E 2012 What is Tannin? The Tannin Handbook. http://chemistry.muohio.edu/hagerman. Accessed February 15, 2012.

[13] Frihart C R 2004 Adhesive Interactions with Wood in Winandy J E and Kamke F A, Eds., Fundamentals of Composite Processing. Proceedings of a workshop; November 5-6, 2003; Madison, WI. Gen. Tech. Rep. FPL-GTR-149. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 118 p.

[14] Allouche J 2013 Synthesis of Organic and Bioorganic Nanoparticles: An Overview of the Preparation Methods. Nanomaterials: A Danger or a Promise? In A Chemical and Biological Perspective ed Brayner R, Fivet F and Coradin, Springer-Verlag London, 2013, pp. 27-74.

[15] Drexler K E 1981 Molecular engineering: An approach to the development of general capabilities for molecular manipulation. Proc. Natl Acad. Sci. USA, 78 (9), pp 5275-5278.

[16] Buzea C, Pacheco I I and Robbie K 2007 Nanomaterials and nanoparticles: Sources and toxicity. Biointerphases 2 MR17-MR172.

[17] Overnay R 2013 Nanothermodynamics and nanoparticle synthesis part 1: Nanoparticles and synthesis. NME 498.

[18] Danilov V E and Ayzenshtadt A M 2019 The Use of Modified Scots Pine Bark as Filling Material of Heat and Sound Insulation. Lesnoy Zhurnal-Forestry J., 2 pp. 111-118.

[19] Umer A, Naveed S, Ramzan N and Rafique M S 2012 Selection of a suitable method for the synthesis of copper nanoparticles. Brief Rep. Rev 7 p 1-18. http://www.worldscientific.com/doi/pdf/10.1142/S1793292012300058. Accessed August 15, 2013.

[20] Rajaonarivony K, Rouau X, Lampoh K, Delenne JY and Mayer-Laigle C 2019 Fine Comminution of Pine Bark: How Does Mechanical Loading Influence Particles Properties and Milling Efficiency? Bioengineering, 6, 102, doi:10.3390/bioengineering6040102.

[21] Abdul Khalil H P S, Fizree H M, Jawaid M and Alattas O S 2011 Preparation and characterization of nano-structured materials from oil palm ash: A bio-agricultural waste from oil palm mill. BioResources, 6 pp 4537-4546.

[22] Purwasasmita B S, Tafwidli F and Septawendar R 2013 Synthesis and characterization of carbon nanocoil with catalytic graphitization process of (Oryza sativa) pulp precursors. J. Aust. Ceramic Soc., 49 (1), pp 119-126.

[23] Purwasasmita B S, Larasati L D, Septawendar R, Nugraha A B, Aufan M R and Sosiati H 2013 Synthesis and characterization of zirconia crystal using base hot water treatment (BHWT) method. J. Aust. Ceramic Soc. 49 (2) p 89-94.

[24] Sutrisno, Samsudin T S, Alamsyah E M and Purwasasmita B S 2014 Synthesis of Bio-based Nanomaterial from Surian (Toona sinensis Roem) Wood Bark Using Conventional Balls
Milling and its Characterization. *J Biol Sci* **14**(3), pp. 204-212.

[25] Sutrisno, Syamsudin T S, Alamsyah E M, and Purwasasmita B S 2015 Synthesis and characterization of bio-based nanomaterials from Jabon (*Anthocephalus cadamba* (Roxb.) Miq) wood bark: an organic waste material from community forest. *J Math Fund Sci* **47**(2) pp. 205–218.

[26] Sutrisno, Alamsyah E M, Sulistyawati E and Suheri 2018 The potential use of wood waste ash nanofiller for improvement of laminated veneer lumber production made from Jabon (*Anthocephalus cadamba*). *J Indian Acad Wood Sci* **15**(2) pp. 126–131.

[27] Patterson A L 1939 The Scherrer formula for X-ray particle size determination. *Phys. Rev.* **56** pp. 978-982.

[28] Harkin J M and Rowe J W 1971 Bark and its possible uses. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wis. In Cooperation with the University of Wisconsin.

[29] Buamscha M G, Altland J E, Sullivan D M, Horneck D A and Cassidy J 2007 Chemical and Physical Properties of Douglas Fir Bark Relevant to the Production of Container Plants. *HortScience* **42**(5) pp. 1281-1286.

[30] Falah S, Katayama T and Suzuki T 2008 Chemical constituents from *Gmelina arborea* bark and their antioxidant activity. *J Wood Sci* **54** pp 483–489.

[31] Fan M, Dai D and Huang B 2012 Fourier Transform Infrared Spectroscopy for Natural Fibres, Fourier Transform - *Materials Analysis*, ed Salih S ISBN: 978-953-51-0594-7, InTech, pp. 45-68.

[32] Garside P and Wyeth P 2003 Identification of cellulosic fibres by FTIR spectroscopy: Thread and single fibre analysis by attenuated total reflectance. *Studies in Conservation* **48**(4) pp 269-275.

[33] Kampeerapappun P 2012 Preparation Characterization and Antimicrobial Activity of Electrospun Nanofibers from Cotton Waste Fibers. *Chiang Mai J. Sci.* **39**(4), pp 712-722.

[34] Marchessault R H 1962 Application of Infra-red Spectroscopy to Cellulose and Wood Polysaccharides. *Pure Appl. Chem* **5**(1-2) pp 107-130.

[35] Poletto M, Zattera A J and Santana R M C 2012 Structural Differences Between Wood Species: Evidence from Chemical Composition, FTIR Spectroscopy, and Thermogravimetric Analysis. *Journal of Applied Polymer Science* **126** E336–E343.

[36] Park S, Baker J O, Himmel M E, Parilla P A and Johnson D K 2010 Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnol. Biofuels*, Vol. 3.

**Acknowledgements**

The authors would like to thank the Directorate of Research and Community Services, Ministry of Research Technology and Higher Education of the Republic of Indonesia for their financial support under the research scheme of Basic Research for the Fiscal Year 2019.