Synthesis and Characterization of Bio-based Nanomaterials from Jabon (*Anthocephalus cadamba* (Roxb.) Miq) Wood Bark: an Organic Waste Material from Community Forest

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Abstract. The application of nanotechnology to produce nanomaterials from renewable bio-based materials, like wood bark, has great potential to benefit the wood processing industry. To support this issue, we investigated the production of bio-based nanomaterials using conventional balls milling. Jabon (*Anthocephalus cadamba* (Roxb.) Miq) wood bark (JWB), an organic waste material from a community forest was subjected to conventional balls milling for 96 h and was converted into bio-based nanomaterial. The morphology and particle size, chemical components, functional groups and crystallinity of the bio-based nanomaterial were evaluated using 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). The particle-sizes obtained for the JWB bio-based nanomaterial were between 43 nm to 469 nm and the functional groups were detected as cellulose. The chemical components found were carbon, oxygen, chloride, potassium and calcium, except for the sample produced from sieve type T14, which did not contain chloride. The crystalline structure was calcium oxalate hydrate ($C_2CaO_4.H_2O$) with crystalline sizes 21 nm and 15 nm, produced from sieve types T14 and T200 respectively.

Keywords: *bio-based nanomaterial; community forest; conventional balls milling; Jabon wood bark; organic waste material.*

1   Introduction

Wood from community forests is a good substitute for natural forest wood and is beneficial for the diversification of raw materials in the wood processing industry. A high potential of community forests is located on Java Island (55.73 million m^3) with a total area of 1.94 million hectare (ha) and a potential average of 28.73 m^3/ha. In West Java particularly, the area of community forests reaches

419,041.93 ha, with a timber potential of 12,005,551 m^3 or potential average of 28.65 m^3/ha. There are at least 32 species of woods [1].

The high economic potential of community forest timber in West Java can lead to the improvement of the people's economical situation. However, in order to obtain maximum benefit from the community forests it is not enough to simply make use of the timber. Alternative uses for the wood bark waste must also be developed. The wood bark volume can be estimated based on the wood volume, which ranges from 9-15% [2] to 10-25% [3]. Assuming an average wood bark volume of 10% and the area of community forests in West Java reaching 419,041.93 ha with a potential average of 12,005,551 m^3 [1], the production of wood bark waste would be about 1,200.55 m^3. In addition, wood bark waste could also have great economic potential for wood processing industries due to the large variety and high volume of wood processed. Currently, wood bark waste is mostly used in wood processing industries as a fuel source for boilers to produce steam for the drying process. Wood bark could also be used for many other purposes, such as filler material for adhesive formula [4-6]; certain species of wood bark containing condensate tannins can be made into tannin adhesive [7-11] or wood preservative [12-14].

According to Allouche [15], organic nanoparticles can be described as solid particles composed of organic compounds, ranging in diameter from 10 nm to 1000 nm. Bio-based nanomaterials can be defined as organic materials that have structured components of at least one dimension less than 1000 nm. In future nanotechnology research efforts, bio-based nanomaterials have a great potential for improving the forest processing industry in the form of coatings, biocides or modified resins [16]. This is due to the tendency of consumers, industry and the government to increasingly look towards products with raw materials derived from renewable natural resources that are sustainable, biodegradable and non-petroleum based, and have a small negative impact on the environment, animals and human health [17]. Besides that, bio-based nanomaterials lead to the emergence of new high-value bio-product applications [18].

The objective of this research was to produce bio-based nanomaterial from Jabon (*Anthocephalus cadamba* (Roxb.) Miq) wood bark (JWB) using conventional balls milling. The bio-based nanomaterial obtained from JWB was characterized using 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) according to Abdul Khalil, *et al*. [19] and Purwasasmita, *et al.* [20,21].

2   Materials and Methods

2.1   Preparation of Wood Bark Powder

Jabon wood bark (JWB) was collected from the community forest in Cibugel district, Sumedang regency, West Java province, Indonesia. Geographically, the sampling site is located at 6°44'-70°83' south latitude and 107°21'-108°21' east longitude. The JWB taken from the community forest was cut using a cleaver and broken into small pieces (2 x 2 cm^2), solar dried until the moisture content was less than 5%, and made into powder by pounding it using a pestle, and sieved by 60-mesh sieve.

2.2   Synthesis of Bio-based Nanomaterials

In the first stage, 0.25 kg of the wood bark powder (60 mesh) was further ground by using a conventional balls mill for 48 h at 100 rev min^{-1} with a ratio weight of alumina balls to powder 2.9:1. In the second stage, the wood bark powder was treated with liquid nitrogen with a ratio volume of liquid nitrogen to powder 2:1, then ground using a conventional balls mill for 48 h under the same conditions as in the first stage. The wood bark powder was then filtered by a single sieve equipped with screen printing fabric type T14. For further evaluation, the wood bark powder was filtered again by four sieves equipped with screen printing fabric types T77, T90, T120 and T200 respectively.

The milling container was made of PVC pipe with a diameter of 10.16 cm and a length of 27.3 cm. The balls were made of alumina with a diameter size of 1.3-4.0 cm. Figure 1 shows a schematic diagram of the synthesis of bio-based nanomaterial using conventional balls milling.
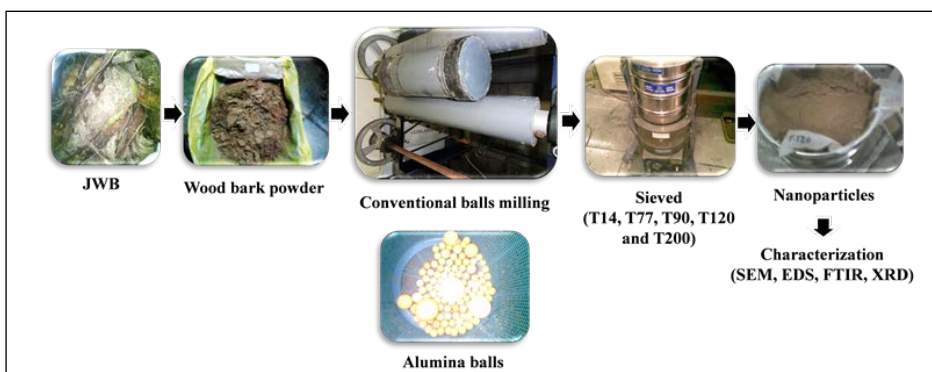

Figure 1 Schematic diagram of the synthesis of bio-based nanomaterial using conventional balls milling.

2.3   Characterization of Bio-based Nanomaterial

The morphology and diameter of the bio-based nanomaterial from JWB was characterized using SEM (JEOL-JSM-6510LV SEM type). Samples were taken and coated with platinum using an ion sputter coater. SEM analysis was extended to obtain the elemental composition of the JWB by means of energy dispersive X-ray spectroscopy analysis (SEM-EDS).

A Fourier transform infrared spectroscope (FTIR), Prestige 21, Shimadzu (Japan) was used to examine the functional groups present in the JWB. Five mg of samples were mixed with 160 mg KBr (1:32). They were then pressed into transparent thin pellets. An FTIR spectrum of the JWB was obtained in the range of 4500-500 cm^{-1}. The spectral output was recorded in the transmittance mode as a function of wave number.

The crystalline structure of the organic bio-based nanomaterial produced from JWB was identified using a powder X-ray diffraction instrument (XRD, PW 1710, Philips analytical), operating at 40 Kv and 30 mA with Cu/Kα (λ = 1.54060 °A) radiation source. The diffractograms were scanned using a scanning rate of $0.5°$ s^{-1} in steps of $0.02°$ from $5°$ to $65°$ (2 θ) at room temperature. The crystalline size was determined from the X-ray diffraction peaks using Scherrer's equation [22] as follows:

$$D = K\lambda / \beta \cos\theta \tag{1}$$

where D is the diameter of the crystalline size; K is the shape factor with a value of 0.9-1.4 or Scherrer's constant of the order of unity for usual crystals; λ is the wavelength of the X-rays (1.54060 Å); β is the value of the *full width at half maximum* (FWHM); and θ is the diffraction angle. XRD patterns were identified using the PDF2 CD-ROM (JCPDS-International Centre for Diffraction Data).

3   Results and Discussion

3.1   Diameter Size of Bio-based Nanomaterial

The diameter sizes of the particles from SEM analysis were 140-469 nm, 94-108 nm, 69-98 nm, 52-84 nm, and 43-57 nm produced from sieve types T14, T77, T90, T120 and T200 respectively with magnifications of 20,000-30,000 times. The morphology shows the formation of agglomerates among the particles (Figure 2). Therefore, the particles from the organic material of JWB can be considered nanoparticles since their size is in the range of 10-1000 nm [15]. The proportions of the nanoparticle sizes were 28.40%, 21.97%, 10.99% and 1.04% produced from sieve types T77, T90, T120 and T200 respectively

and the (37.61%) remaining nanoparticles were retained from sieve type T77 (Table 1).

Table 1   Sieve types and nanoparticles sizes.

Sieve type	Sieve designation (mesh)	Nominal sieve opening (microns)	Particles size (nm)	Proportion (%)	Remark
T14	95	151**)	140-469	-	Single sieve
T77	523	28**)	94-108	28.40	
T90	611	24**)	69-98	21.97	
T120	815	18**)	52-84	10.99	
T200	1358	10.6*)	43-57	1.04	
				37.61	Retained on sieve type T77

Note : *) based on SEM analysis; **) based on conversion from T200 sieve type
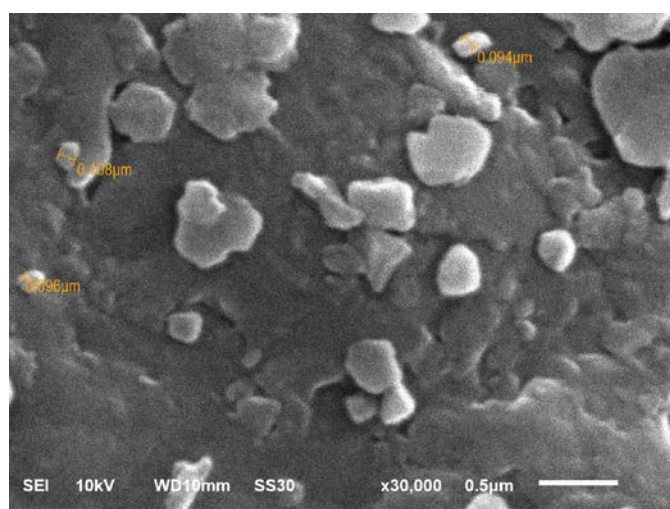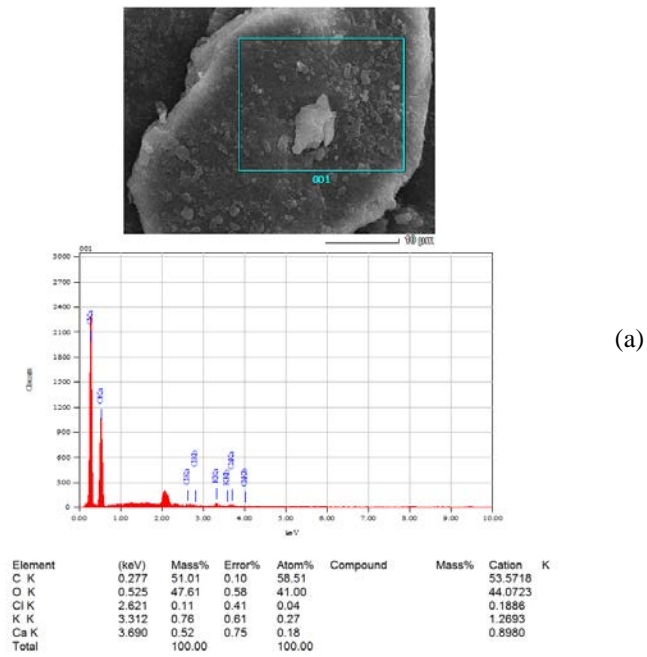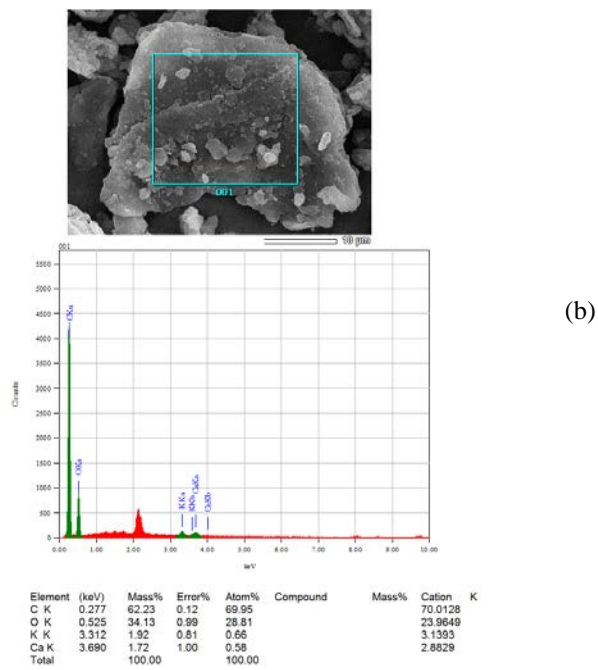

Figure 2   SEM analysis of JWB produced from sieve type T77.

3.2   Chemical Components of Bio-based Nanomaterial

Figure 3 shows the energy dispersive X-ray spectroscopy analysis (EDS) spectra with the chemical composition of JWB. An essential observation is that all JWB nanoparticles produced from sieve types T77, T90, T120 and T200 contained carbon, oxygen, chloride, potassium and calcium. However, the sample produced from sieve type T14 contained only carbon, oxygen, potassium and calcium. For comparison, pine wood bark contains phosphorous, potassium, manganese, copper, calcium, magnesium, and zinc [23]. This corresponds with the nutrient content of wood bark differing between species, tree age, environmental factors, and growing site [23]; it contains about 60-70 percent glucose [2].

(a)

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	51.01	0.10	58.51			53.5718	
O K	0.525	47.61	0.58	41.00			44.0723	
Cl K	2.621	0.11	0.41	0.04			0.1886	
K K	3.312	0.76	0.61	0.27			1.2693	
Ca K	3.690	0.52	0.75	0.18			0.8980	
Total		100.00		100.00				

(b)

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	62.23	0.12	69.95			70.0128	
O K	0.525	34.13	0.99	28.81			23.9649	
K K	3.312	1.92	0.81	0.66			3.1393	
Ca K	3.690	1.72	1.00	0.58			2.8829	
Total		100.00		100.00				

Figure 3 EDS analysis of JWB produced from (a) T14 and (b) T77 sieve type.

### 3.3   Functional Groups of Bio-based Nanomaterial

The FTIR spectra of the JWB with diameters 140-469 nm, 94-108 nm, 69-98 nm, 52-84 nm, and 43-57 nm produced from T14, T77, T90, T120 and T200 sieve types respectively are similar, as illustrated in Table 2 and Figure 4. They are composed of cellulose, the main constituent in the cell wall of natural fibers [24-27].

In addition, the FTIR analysis shows the presence of a C=O stretching band at 1724 cm^{-1} in the nanoparticles of the JWB produced from sieve types T77 and T90 (Figure 4(b) and 4(c)) and a C=O stretching band at 1732 cm^{-1} of the JWB produced from sieve type T200 (Figure 4(e)), while no such structures were observed in the nanoparticles of the JWB produced from sieve types T14 and T120 (Figure 4(a) and Figure 4(d)). This result implies that the balls milling changed the presence of the functional groups of cellulose. Abdul Khalil, *et al.* [19] reported that the silanol (Si-OH) functional group was present after the oil palm ash was milled with high-energy ball milling for 30 h, due to the balls milling effect.

Table 2 Infrared spectrum of JWB.

| Sieve types and peak wave number (cm^{-1})					Assign ment	Reff.
T14	**T77**	**T90**	**T120**	**T200**		
3342-3368	3412-3356	3408-3352	3379	3383-3375	OH stretching	[24,25, 27,28]
2920-2850	2922-2852	2922-2852	2924-2856	2922	CH stretching	
2362-2343	–	–	–	–	OH stretching	
–	1724	1724	–	1732	C=O stretching	
1622	1624	1625	1624	1627	COO stretching	[26, 27]
1525	1514	1517	1519	1508	C=C stretching	[24, 25, 28]
1429-1259	1435-1257	1435-1257	1436-1257	1429-1249	C-H wagging	[26]
1153	1155	1155	1153	1157	C-C ring breathing, asymmetric	[25, 28]
1103-1028	1103-1031	1103-1031	1029	1105-1055	C-O-C glycosidic	
791-526	779-524	779-526	777-526	773-530	C-OH out-of-plane bending	[24]

Note : – = no data

(a)

jt77
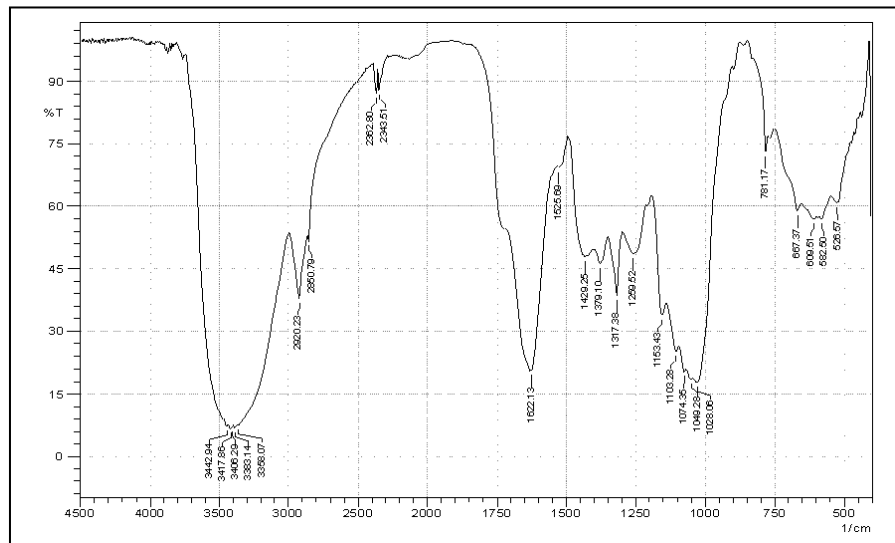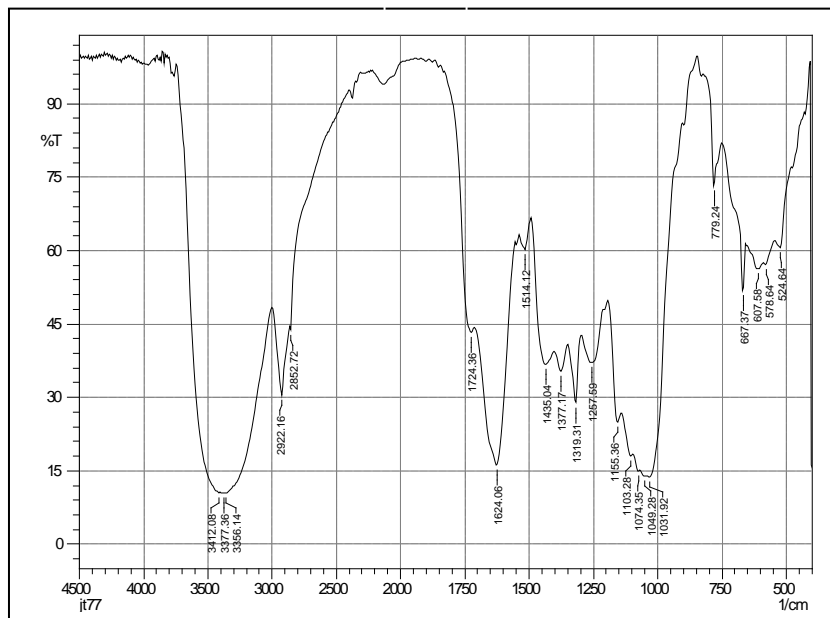
(b)

Figure 4 *Continued.* FTIR analysis of JWB produced from five sieve types: (a) T14, (b) T77, (c) T90, (d) T120 and (e) T200.
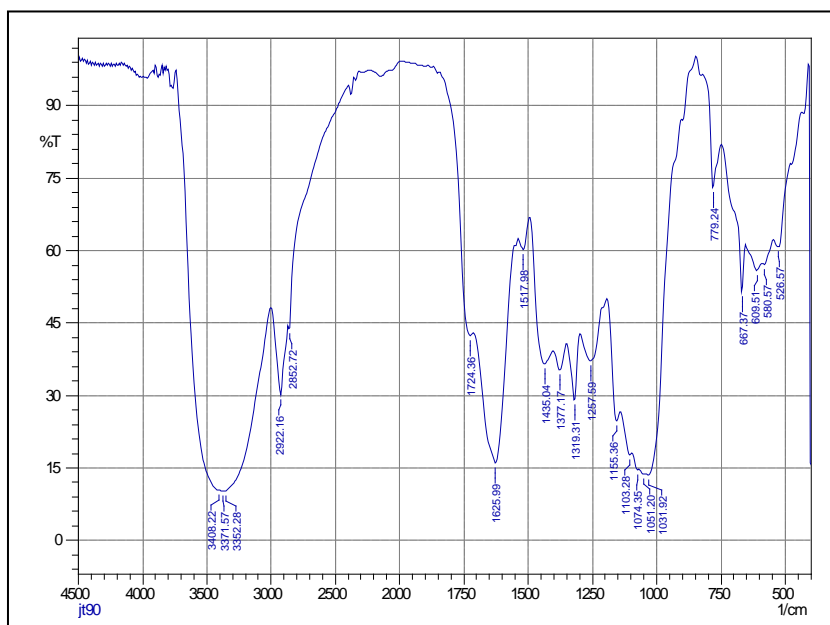
(c)
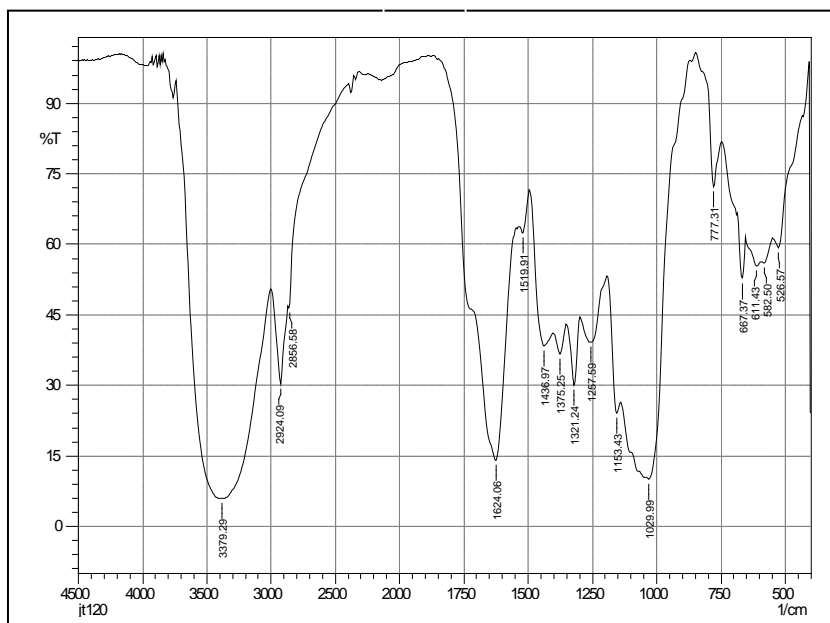
(d)

Figure 4 *Continued.* FTIR analysis of JWB produced from five sieve types: (a) T14, (b) T77, (c) T90, (d) T120 and (e) T200.
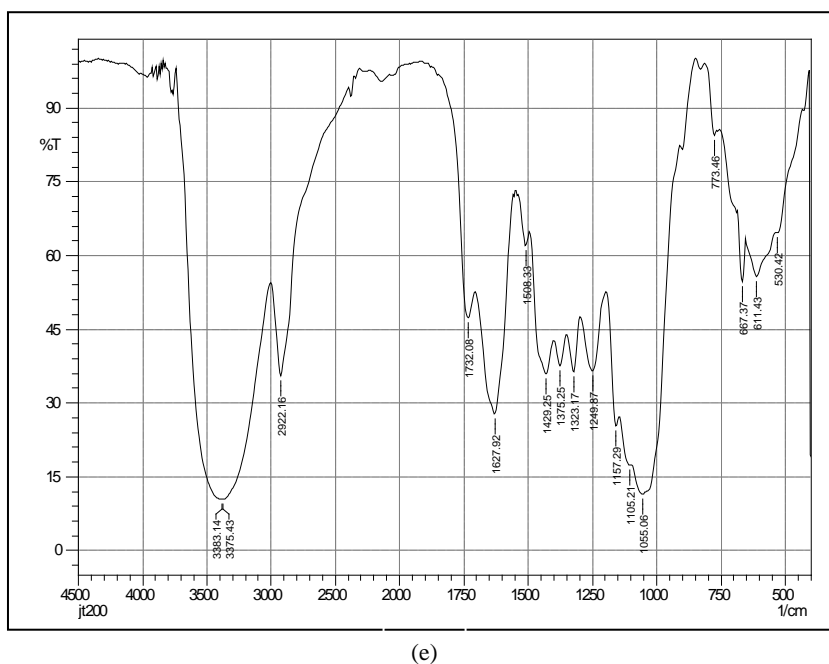
(e)

Figure 4 FTIR analysis of JWB produced from five sieve types: (a) T14, (b) T77, (c) T90, (d) T120 and (e) T200.

3.4   Crystallinity of Bio-based Nanomaterial

As comparison of crystalline size, the crystallinity was studied from the bio-based nanomaterial with the largest and smallest nanoparticle size, produced from sieve types T14 and T200 respectively. The crystalline structure was explained by the presence of peaks after the samples were scanned using X-ray in a range of diffraction angles. The XRD analysis (Figure 5) shows the crystalline structure of calcium oxalate hydrate ($C_2CaO_4.H_2O$). This is due to the essential chemical composition of the bio-based nanomaterial, consisting of carbon, oxygen, chloride, potassium and calcium, except for the sample produced from sieve type T14 (which contained no chloride). In a previous research, hexagonal calcium oxalate crystals were also obtained from bark of basswood (*Tillia americana*) [27]. The reflecting peaks at $2\theta = 14.94°$, $24.44°$, $30.14°$ and $38.32°$ were used to estimate the average crystalline size produced from sieve type T14, which was calculated to be 21 nm (Figure 5(a)). The reflecting peaks at $2\theta = 14.98°$, $20.27°$, $22.92°$, $24.36°$ and $29.48°$ were used to estimate the average crystalline size produced from sieve type T200, which was calculated to be 15 nm (Figure 5(b)). Crystallinity is one of several factors that affect the accessibility of cellulose; other factors

are contents and distribution of lignin and hemicellulose, porosity, and particle size [29].
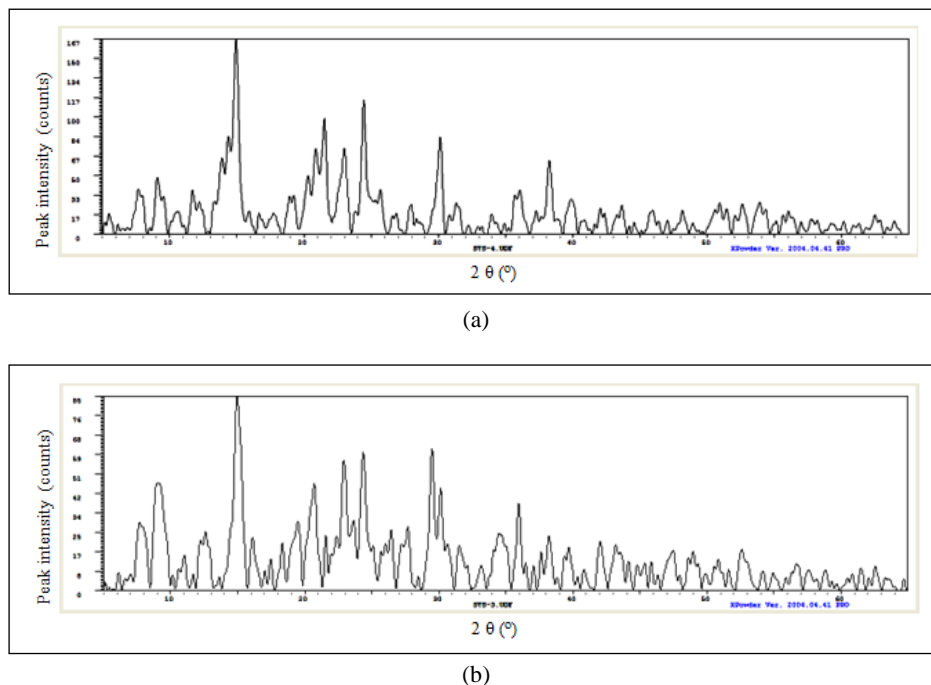

(a)

(b)

Figure 5 XRD analysis of JWB produced from (a) T14 and (b) T200 sieve type.

4 Conclusions

Bio-based nanomaterial from Jabon wood bark was produced using conventional balls milling with a diameter of about 140-469 nm, 94-108 nm, 69-98 nm, 52-84 nm and 43-57 nm from sieve types T14, T77, T90, T120 and T200 respectively. It is concluded that the particles of the bio-based material from JWB can be considered nanoparticles since their size is in the range of 10-1000 nm.

The chemical composition of the JWB contained carbon, oxygen, chloride, potassium, and calcium, except for the sample produced from sieve type T14, which did not contain chloride. The functional groups that exist in the JWB were detected as cellulose. Additionally, conventional balls milling changed the presence of functional groups of JWB's cellulose.

The crystalline structure of the bio-based nanomaterial produced from JWB was calcium oxalate hydrate ($C_2CaO_4.H_2O$) with crystalline size 21 nm and 15 nm

produced from sieve types T14 and T200 respectively.

Acknowledgments

References

[1]   Ministry of Forestry Republic of Indonesia, *Opportunities of Community Forest Investment in Java*, Directorate General for Development of Watershed Management and Social Forestry, Jakarta, 2010. (Text in Indonesian)

[2]   Harkin, J.M. & Rowe, J.W., *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, 1971.

[3]   Miles, P.D. & Smith, W.B., *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, 2009.

[4]   Eberhardt, T.L. & Reed, K.G., *Grinding and Classification of Pine Bark for Use as Plywood Adhesive Filler*, Peer reviewed, Appita Pre Symposium, pp. 109-113, 2005.

[5]   Eberhardt, T.L. & Reed, K.G., *Strategies for Improving the Performance of Plywood Adhesive Mix Fillers from Southern Yellow Pine Bark*, Forest Products Journal, **56**(10), pp. 64-68, 2006.

[6]   Eberhardt, T.L., Reed, K.G. & So, C.L., *Partitioning of Pine Bark Components to Obtain a Value-Added Product for Plywood Manufacture in Advanced Biomass Science and Technology for Bio-Based Products,* Hse, C.Y., Jiang, Z. & Kuo, M.L. (eds.). Developed from a Symposium sponsored by Chinese Academy of Forestry & USDA Forest Service, Southern Research Station, pp. 302-309, 2009.

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

[8]   Santoso, A. & Sutigno, P., *Effect of Bio-Adhesive Urea Formaldehyde Composition to the Bonding Strength of Meranti Plywood,* Jurnal Penelitian Hasil Hutan, **13**(3), pp. 87-93, 1995. (Text in Indonesian)

[9]   Linggawati, A., Muhdarina, Erman, Azman & Midiarty, *Utilization of Tanin from Wood Waste of Plywood Industry for Modified Phenol Formaldehyde Resin,* Jurnal Natur Indonesia, **5**(1), pp. 84-94, 2002. (Text in Indonesian)

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

[11] Subyakto, Suryanegara, L., Gopar, M. & Prasetiyo, K.W., *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), pp. 20-23, 2005.

[12] Carter, F.L., Cario, A.M. & Stanley, J.B., *Termiticidal Components of Wood Extracts: 7-Methyljuglone from* Diospyros Virginia, Journal Agriculture Food Chemistry, **26**(4), pp. 869-873, 1978.

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

[14] Hagerman, A.E., *What is Tannin?* The Tannin Handbook. (http://chemistry.muohio.edu/hagerman), (15 February 2012).

[15] Allouche, J., *Synthesis of Organic and Bioorganic Nanoparticles: An Overview of the Preparation Method,*Nanomaterials: A Danger or a Promise? A Chemical and Biological Perspective. Brayner, R., Fievet, F. and Coradin, T. (eds.), Springer-Verlag London, pp. 27-74, 2013.

[16] Gardner, D.J. & Han, Y., *Nanotechnology Applications in Forest Products: Current Trends,*55th International Convention of Society of Wood Science and Technology, August 27-31, 2012, Beijing, China AP2-7, pp.1-4, 2012. (Conference proceeding)

[17] Moon, R.J., Martini, A., Nairn, J., Simonsenf, J. & Youngblood, J., "Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites." *Chemical Society Review*s, **40**, pp. 3941-3994, 2011.

[18] Missoum, K., Belgacem, M.N. & Bras, J., *Nanofibrillated Cellulose Surface Modification: A Review*, Materials, **6**(5), pp. 1745-1766, 2013. doi:10.3390/ma6051745

[19] Abdul Khalil, H.P.S., Fizree, H.M., Jawaid, M. & Alattas, O.S., *Preparation and Characterization of Nano-Structured Materials from Oil Palm Ash: A Bio-Agricultural Waste from Oil Palm Mill*, BioResources, **6**(4), pp. 4537-4546, 2011.

[20] Purwasasmita, B.S., Tafwili, F. & Septawendar, R., *Synthesis and Characterization of Carbon Nanocoil with Catalytic Graphitization Process of* Oryza sativa *Pulp Precursors,* Journal of the Australian Ceramic Society, **49**(1), pp. 119-126, 2013a.

[21] Purwasasmita, B.S., Larasati, L.D., Septawendar, R., Nugraha, A.B., Aufan, M. R. & Sosiati, H., *Synthesis and Characterization of Zirconia Crystal using Base Hot Water Treatment (BHWT) Method*, Journal of the Australian Ceramic Society, **49**(2), pp. 89-94, 2013b.

[22] Patterson, A.L., *The Scherrer formula for X-ray Particle Size Determination*, Physical Review, **56**, pp. 978-982, 1939.

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

[24] Fan, M., Dai, D. & Huang, B., *Fourier Transform Infrared Spectroscopy for Natural Fibres, Fourier Transform - Materials Analysis*, Salih Salih (ed.), ISBN: 978-953-51-0594-7, InTech, pp. 45-68, 2012. (http://www.intechopen.com/books/Fourier-transform-materials-analysis/Fourier-transform-infraredspectroscopy-for-natural-fibres). (17 March 2013).

[25] Garside, P. & Wyeth, P., *Identification of Cellulosic Fibres by FTIR Spectroscopy: Thread and Single Fibre Analysis by Attenuated Total Reflectance,* Studies in Conservation, **48**(4), pp. 269-275, 2003.

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

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

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

[29] Park, S., Baker, J.O., Himmel, M.E., Parilla, P.A. & Johnson, D.K., *Cellulose Crystallinity Index:Measurement Techniques and their Impact on Interpreting Cellulose Performance*, Biotechnol. Biofuels, **3**, 2010.