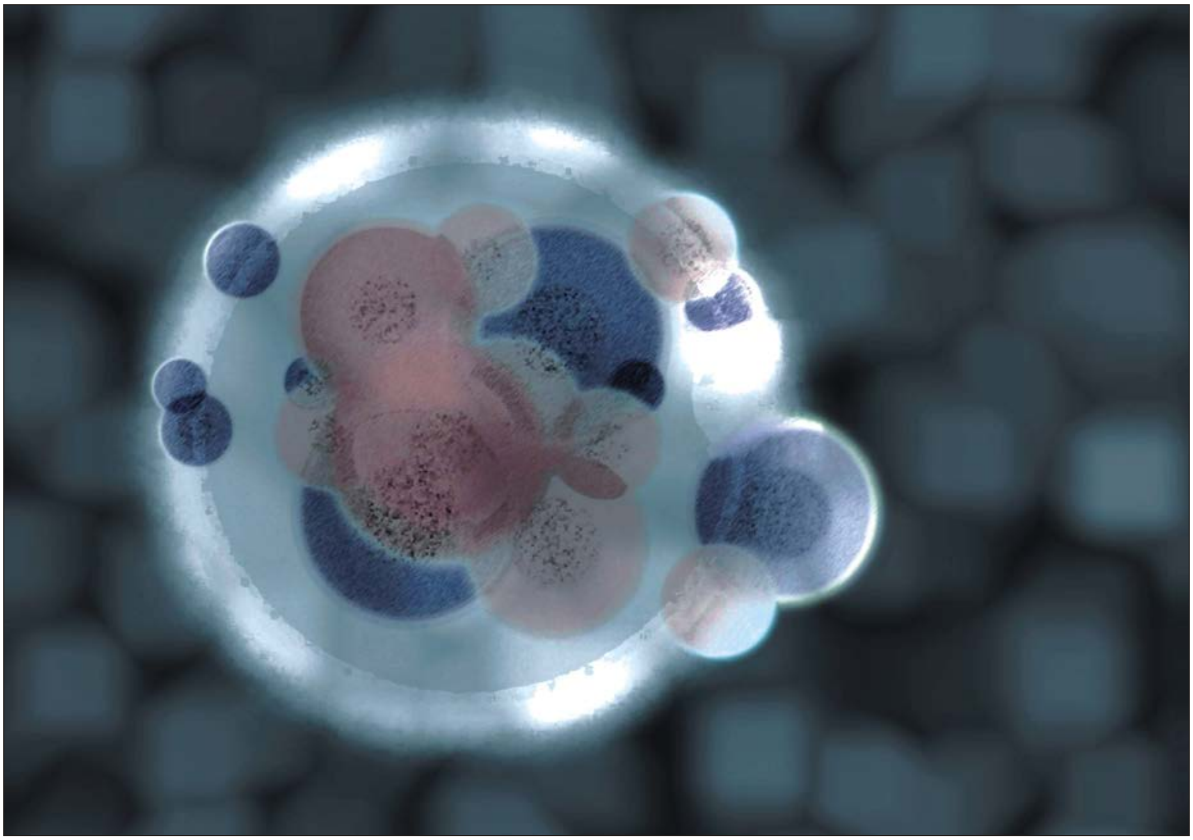

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Synthesis of Bio-based Nanomaterial from Surian (*Toona sinensis* Roem) Wood Bark Using Conventional Balls Milling Method and its Characterization

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Abstract: The objective of this research was to produce a bio-based nano material from surian (*Toona sinensis* Roem) wood bark (SWB) using conventional balls milling and four of sieve types (T77, T90, T120 and T200). SWB is an organic material waste from community forest was subjected to conventional balls milling for 96 h and was converted into bio-based nanomaterial. Bio-based nanomaterial was characterized for its particle size, chemical components, functional groups and crystallinity by using Scanning Electron Microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). The particle size obtained from SEM analysis were found to be 93-110, 67-165, 68-93 and 42-114 nm produced from T77, T90, T120 and T200 of sieve types, respectively. The nanoparticle of organic material from SWB was obtained with the size in diameter was less than 1000 nm. The proportion of nano particle size were 39, 29, 24 and 2% produced from T77, T90, T120 and T200 of sieve types respectively and the last (6%) of nano particle retained on T77 of sieve type. The chemical components found in bio-based nano material from SWB obtained from EDS analysis were carbon, oxygen, potassium and calcium. The FTIR analysis shows the presence of C = O stretching band at 1735 cm^{-1} in the nanoparticle of SWB produced from T90 and T120 of sieve types, respectively and C = O stretching band at 1734 cm^{-1} of SWB produced from T200 of sieve type, due to balls milling effect while the nanoparticle of SWB produced from T77 of sieve type not observed. Whereas the crystalline structure was found calcium oxalate hydrate ($C_2CaO_4.H_2O$) with diameter of crystalline size were 26 and 14 nm produced from T77 and T200 of sieve types, respectively.

Key words: Bio-based nanomaterial, conventional balls milling, surian wood bark

INTRODUCTION

Mechanical milling or conventional balls milling is one of several physical methods for the synthesis of nanoparticles. In the milling process, different types of mechanical mills are categorized according to their capacities and applications (Umer *et al*., 2012). The methods involve braking the larger materials (macro or micro scale) into nanoparticles called top-down method, including mechanical attrition or ball milling methods (Overney, 2013). The resulting particles had broad size distribution (10-1000 nm), varied particle shape or geometry, impurities and used for nanocomposites or nano-grained bulk materials (Overney, 2013).

The advantages of mechanical milling are simple operation, low cost of production of nanoparticles and the possibility to scale it to produce large quantities. On the other hand it is very difficult to produce ultrafine particles using these techniques or it takes very long times (Umer *et al*., 2012). In terms diameter size of nanoparticles, fine particles cover a range of 100-2500 nm while ultrafine particles size of 1-100 nm (Buzea *et al*., 2007). The important factors affecting the quality of the final product are type of mill, milling speed, container, time and weight ratio of ball to powder (Umer *et al*., 2012).

The size range in diameter for nano organic materials was 10-1000 nm (Allouche, 2013). Whereas nanoparticulate matter, including nanomaterials and nanoparticles, defined a collection of particles with at least one dimension smaller than 1000 nm (Buzea *et al*., 2007). Bio-based nanomaterial can be defined as organic materials which have structured components with at least one dimension less than 1000 nm.

An alternative using of bio-based nanomaterial is to be used as adhesive filler for improved forest products industry. The bark powder can be used also as extender phenolic-resin glues or an inert filler due to it flows under heat and pressure and actually undergoes chemical reaction during hot pressing (Harkin and Rowe, 1971).

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The using of wood bark powder with 200 mesh size for adhesive filler or filler in thermoplastic composites has been studied (Eberhardt and Reed, 2005, 2006; Eberhardt *et al*., 2009). The effect of filler size has not been studied before, whereas the size of filler affect on the penetration of adhesives (Sellers *et al*., 2005) and the adhesive molecules need to interact with the wood in nanometer scale (Frihart, 2004, 2005). On the other hand, bio-based nanomaterial lead the emergence of new high-value of bio-product applications (Missoum *et al*., 2013).

The objective of this research was to produce a bio-based nanomaterial from surian wood bark using conventional balls milling and four of sieve types equipped with various size of fabric screen printing (T77, T90, T120 and T200). The bio-based nanomaterial obtained from SWB will be characterized by using Scanning Electron Microscopy (SEM), energy dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) (Abdul Khalil *et al*., 2011; Purwasasmita *et al*., 2013a, b).

MATERIALS AND METHODS

Materials: Surian Wood Bark (SWB) was collected from community forest at Cibugel District, Sumedang Regency, West Java Province, Indonesia. Geographically, sampling site is located at 6°44'-70°83' south latitude and 107°21'-108°21' east longitude.

Methods: SWB was collected from community forest then cut using cleaver into small pieces measuring length by width about 20 by 20 mm and then solar dried until moisture content less than 5%. SWB was made into powder by pounded using a pestle and sieved by 60 mesh size.

Synthesis of bio-based nanomaterial was conducted by two step. First, 0.22 kg of wood bark powder (60 mesh) was further ground by using conventional balls milling for 48 h at 100 rev min^{-1} with a ratio of balls to powder of 3.2:1. Second, wood bark powder treated by liquid nitrogen with a ratio of volume of liquid nitrogen to powder of 2:1, then ground using conventional balls milling for 48 h under condition as same as before. Wood bark powder then sieved by four of sieve types equipped with various size of fabric screen printing was called T77, T90, T120 and T200 of sieve types, respectively.

The milling container was made of PVC pipe with diameter size of 101.6 mm and length size of 275 mm. Balls were made of alumina with diameter size of 13-40 mm. Fig. 1 shows the schematic of synthesis of bio-based nanomaterial by using conventional balls milling.

Bio-based nanomaterial was evaluated using Scanning Electron Microscopy (SEM), energy dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD). The morphology and diameter size of bio-based nanomaterial from SWB was characterized by using SEM (JEOL-JSM-6510LV SEM type). Samples were taken and coated with platinum with an ion sputter coater. The chemical composition of the SWB was analyzed using SEM that extended with energy dispersive X-ray spectroscopy analysis (SEM-EDS).

The functional groups present in the SWB was examined using Fourier Transform Infrared Spectroscopy (FTIR), Prestige 21, Shimadzu (Japan). Five miligram of samples were mixed with 160 mg KBr (1:32). They were then pressed into transparent thin pellets. A FTIR spectrum of SWB was obtained in the range of 4500 to 500 cm^{-1}. Spectral output was recorded in the transmittance mode as a function of wavenumber.

The crystallinity and its size of bio-based nanomaterial from SWB was identified by powder X-Ray Diffraction (XRD) instrument (XRD, PW 1710, Philips analytical) operation at 40 kV and 30 mA with Cu/Kα (λ = 1.54060 °A) radiation source. The diffractrograms were scanned using a scanning rate of 0.5° sec^{-1} and in steps of 0.02° from 5° to 65° (2 θ) at room temperature.

The crystalline size of nanoparticle of SWB was determined from the X-ray diffraction peaks using Scherrer's equation (Patterson, 1939), after correction for instrumental broadening as follow:

$$D = K\lambda/\beta\cos\theta \quad (1)$$

In the Eq. 1, D is the diameter of crystalline size, 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, λ is the wavelength of the X-rays (1.54060 °A), θ is the diffraction angle and β is the value of the full width at half maximum (FWHM). XRD patterns were identified using the PDF2 CD-ROM (JCPDS-International Centre for Diffraction Data).

RESULTS AND DISCUSSION

Diameter size of bio-based nanomaterial: The particle size obtained from SEM analysis was found to be 93-110, 67-165, 68-93 and 42-114 nm produced from T77, T90, T120 and T200 of sieve types respectively with magnifications of 30,000 times and its morphology seemed the formation of agglomeration among particles (Fig. 2).

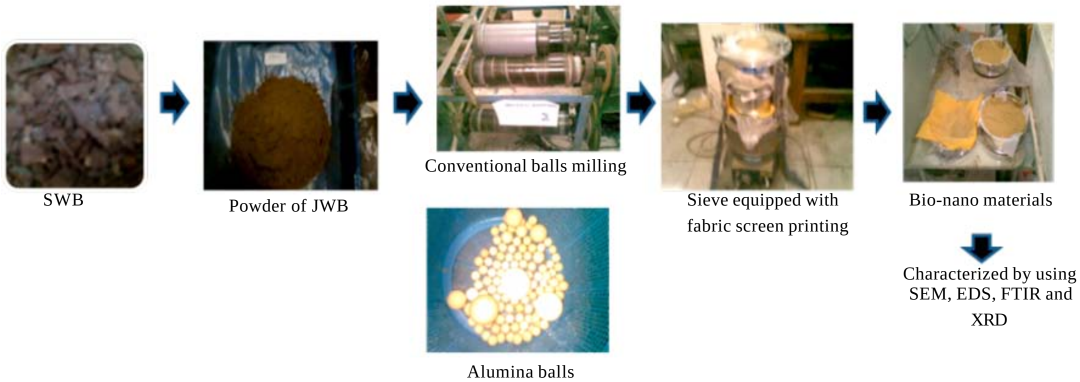


Fig. 1: Schematic diagram of synthesis of bio-based nanomaterial using conventional balls milling

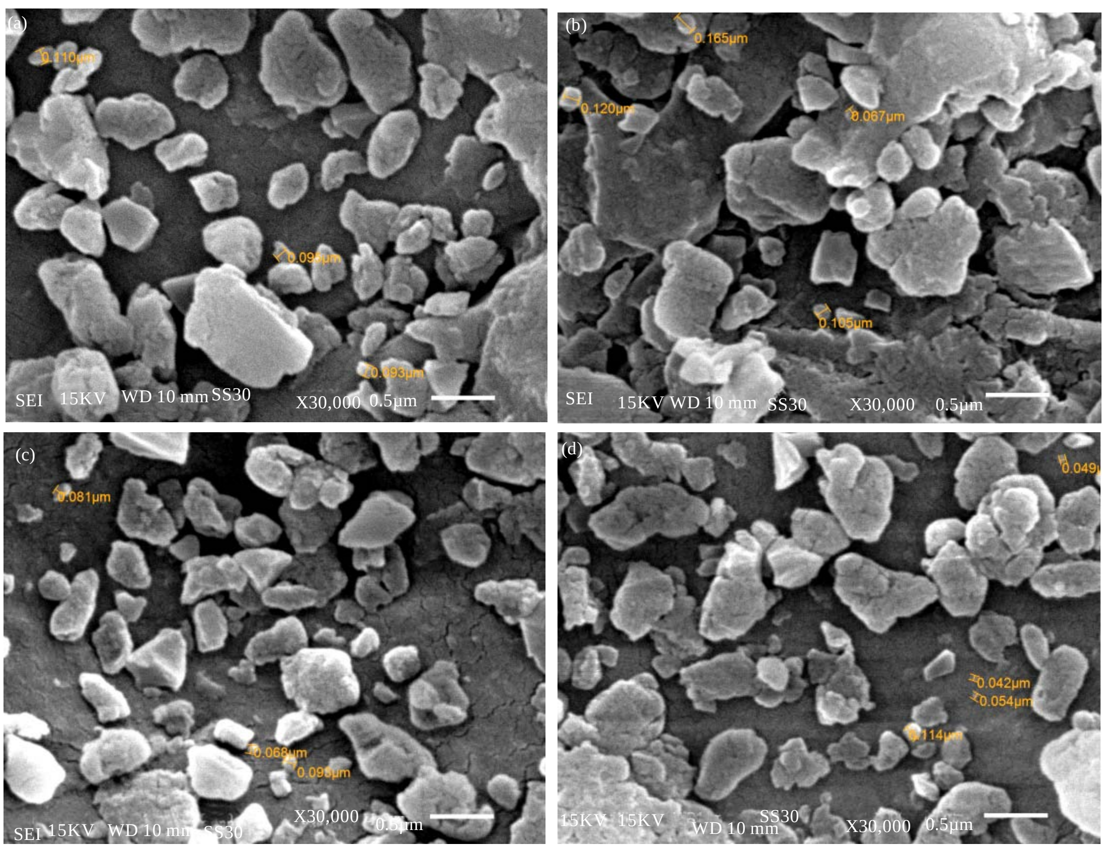


Fig. 2(a-d): SEM analysis of particle size were produced from four of sieve types: (a) T77, (b) T90, (c) T120 and (d) T200

Therefore, the nanoparticle of organic materials from SWB was obtained, because their size in the rang e of 10-1000 nm (Allouche, 2013). For comparison, Abdul Khalil *et al*. (2011) reported that after the oil palm ash milled with high-energy ball milling for 30 h, the diameter size of particles up to 50 nm.

The proportion of nanoparticle size were 39, 29, 24 and 2% produced from T77, T90, T120 and T200 of sieve

Table 1: Sieve types and nanoparticle size

Sieve type	Sieve designation (mesh)	Nominal sieve opening (microns)	Nanoparticle size (nm)	Proportion (%)
T77	523	28**	93-110	39
T90	611	24**	67-165	29
T120	815	18**	68-93	24
T200	1358	10.6*	42-114	2 6***)

*: Based on SEM analysis, **: Based on conversion from T200 of sieve type, ***: Retained on T77 of sieve type

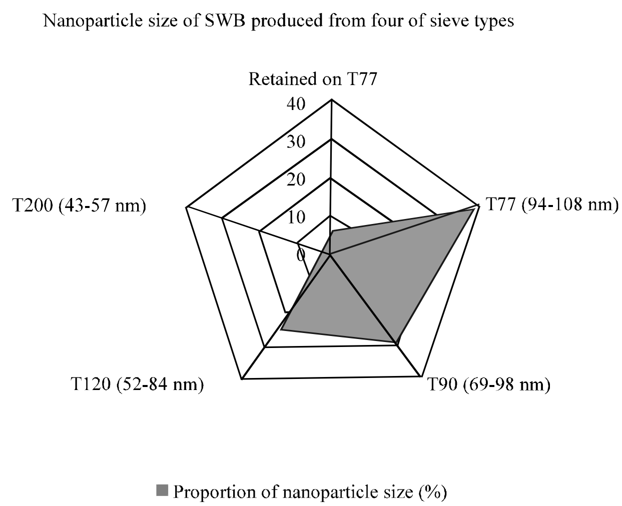


Fig. 3: Proportion of nanoparticle size

types, respectively and the last (6%) of nanoparticle retained on T77 of sieve type (Table 1; Fig. 3).

Chemical components of bio-based nanomaterial: The chemical c ompositions of the SWB were studied by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy analysis (SEM-EDS). Figure 4 shows the energy dispersive X-ray spec-troscopy analysis (EDS) spectra with the chemical composition of SWB. An essential ob-servation is that the SWB contained of carbon, oxygen, potassium and calcium.

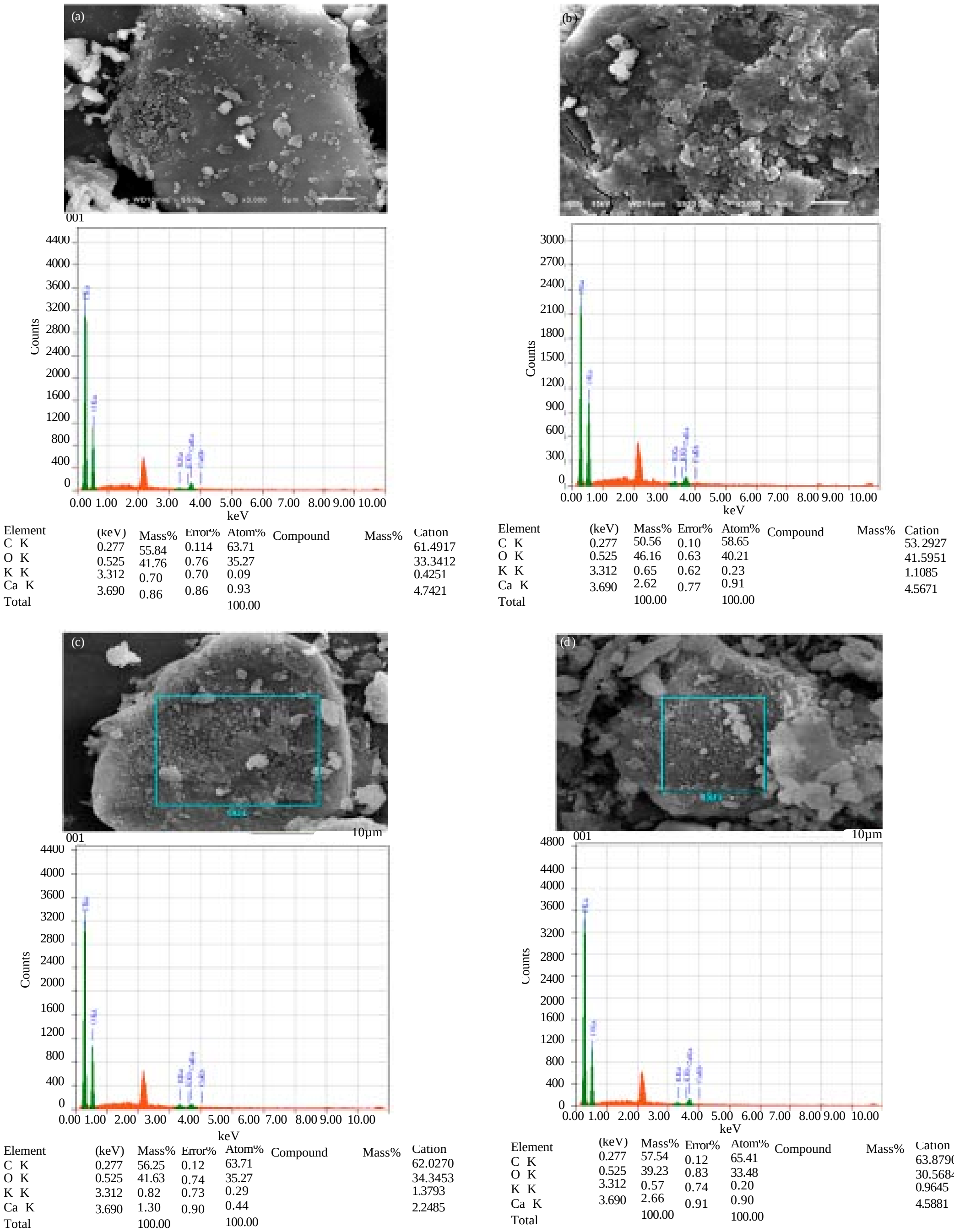
Wood bark containing about 60-70% of glucose (Harkin and Rowe, 1971) and its nutrient depend on species, tree age, environmental factors and growing site (Buamscha *et al*., 2007). For comparison, pine wood bark contained of phosphorous, potassium, manga-nese, copper, calcium, magnesium and zinc (Buamscha *et al*., 2007).

Functional groups of bio-based nanomaterial: The presence of the functional groups that exist in the SWB were detected by fourier transform infrared spectroscopy (FTIR). The FTIR transmission spectrum of the SWB with size in diameter were 93-110, 67-165, 68-93 and 42-114 nm, produced from T77, T90, T120 and T200 of sieve types respectively composed of cellulose, the main constitute in natural fibers that acts as the reinforcing material in the cell wall (Fan *et al*., 2012; Garside and Wyeth, 2003; Kampeerapappun, 2012; Marchessault, 1962; Poletto *et al*., 2012) (Table 2; Fig. 5).

On the other hand the FTIR analysis shows the presence of C = O stretching band at 1735 cm^{-1} in the nanoparticle of SWB produced from T90 and T120 of sieve types (Fig. 5b, 5c) and C = O stretching band at 1734 cm^{-1} of SWB produced from T200 of sieve type (Fig. 5d due to balls milling effect while the nanoparticle of SWB produced from T77 of sieve type not observed (Fig. 5a).

Marchessault (1962) reported that there are correlation between morphology and chemical composition of wood from the bark through the cambium. Whereas Abdul Khalil *et al*. (2011) reported that the silanol (Si-OH) functional group presented after the oil palm ash milled with high-energy ball milling for 30 h.

Crystallinity of bio-based nanomaterial: According to the XRD results (Fig. 6), samples of bio-based nanomaterial produced from T77 and T200 of sieve types shows the crystalline structure of calcium oxalate hydrate



(a)

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation
C K	0.277	55.84	0.114	63.71			61.4917
O K	0.525	41.76	0.76	35.27			33.3412
K K	3.312	0.70	0.70	0.09			0.4251
Ca K	3.690	0.86	0.86	0.93			4.7421
Total				100.00			

(b)

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation
C K	0.277	50.56	0.10	58.65			53.2927
O K	0.525	46.16	0.63	40.21			41.5951
K K	3.312	0.65	0.62	0.23			1.1085
Ca K	3.690	2.62	0.77	0.91			4.5671
Total		100.00		100.00			

(c)

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation
C K	0.277	56.25	0.12	63.71			62.0270
O K	0.525	41.63	0.74	35.27			34.3453
K K	3.312	0.82	0.73	0.29			1.3793
Ca K	3.690	1.30	0.90	0.44			2.2485
Total		100.00		100.00			

(d)

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation
C K	0.277	57.54	0.12	65.41			63.8790
O K	0.525	39.23	0.83	33.48			30.5684
K K	3.312	0.57	0.74	0.20			0.9645
Ca K	3.690	2.66	0.91	0.90			4.5881
Total		100.00		100.00			

Fig. 4(a-d): EDS analysis of nanoparticle were produced from four of sieve types: (a) T77, (b) T90, (c) T120 and (d) T200

($C_2CaO_4.H_2O$). The reflecting peaks at 2 ϑ = 15.02, 24.46, 30.20, 36.04, 38.30 and 39.90° were used to estimate the average of crystalline size produced from T77 of sieve type which was calculated to be 26 nm (Fig. 6a). Whereas the average of crystalline size produced from T200 of sieve type had smaller size. The reflecting peaks at

2 ϑ = 15.10, 24.58, 30.28, 36.18, 38.38 and 43.68° were used to estimate the average of crystalline size produced from T200 of sieve type which was calculated to be 14 nm (Fig. 6b). According to Park *et al.* (2010) accessibility of cellulose affected by crystallinity, lignin and hemicellulose contents and its distribution, porosity and particle size.

Table 2: Infrared spectrum of bio-based nanomaterial produced from SWB

Sieve types and peak wavenumber (cm^{-1})				Assignment	References
T77	T90	T120	T200		
3419-3356	3414-3373	3415	3414-3375	OH stretching	(Fan *et al.*, 2012; Garside and Wyeth, 2003; Kampeerapappun, 2012; Marchessault, 1962; Poletto *et al.*, 2012)
2924-2854	2922-2856	2924-2854	2922-2854	CH stretching	
-	1735	1735	1734	C = O stretching	
1620	1622	1622	1622	COO stretching	(Kampeerapappun, 2012; Marchessault, 1962)
1519	1510	1516	1512	C = C stretching	(Fan *et al.*, 2012; Garside and Wyeth, 2003; Poletto *et al.*, 2012)
1448-1280	1456-1263	1448-1261	1448-1261	C-H wagging	(Kampeerapappun, 2012)
1149	1155	1153	1153	C-C ring breathing, asymmetric	(Garside and Wyeth, 2003; Poletto *et al.*, 2012)
1101-1050	1105-1037	1051	1051	C-O-C glycosidic	
887-819	896-819	894-819	894-821	C-O-C in plane, symmetric	
779-518	779-520	779-520	779-520	C-OH out-of-plane bending	(Fan *et al.*, 2012)

Note: - no data

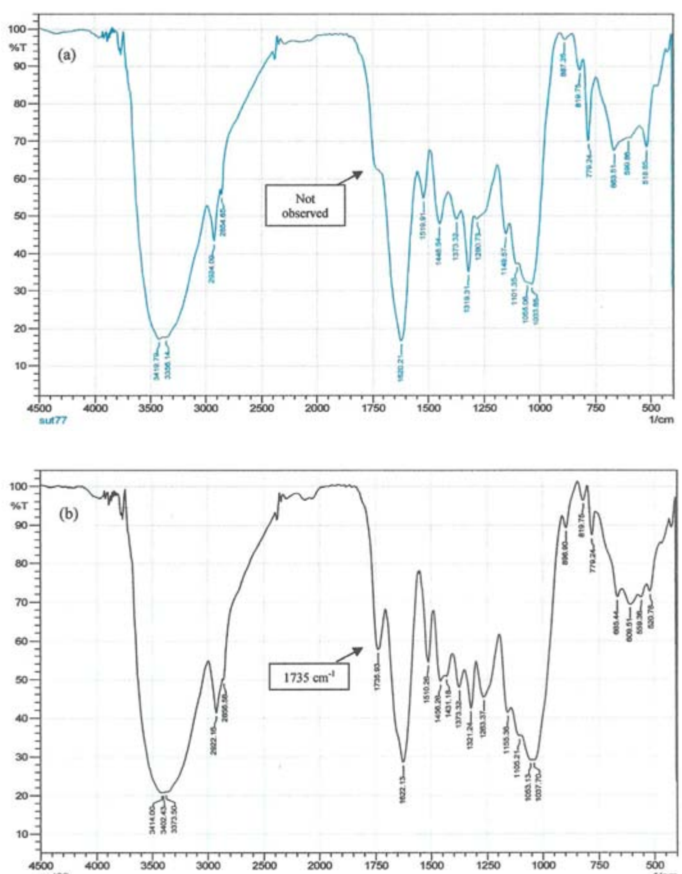


Fig. 5(a-d): Continue

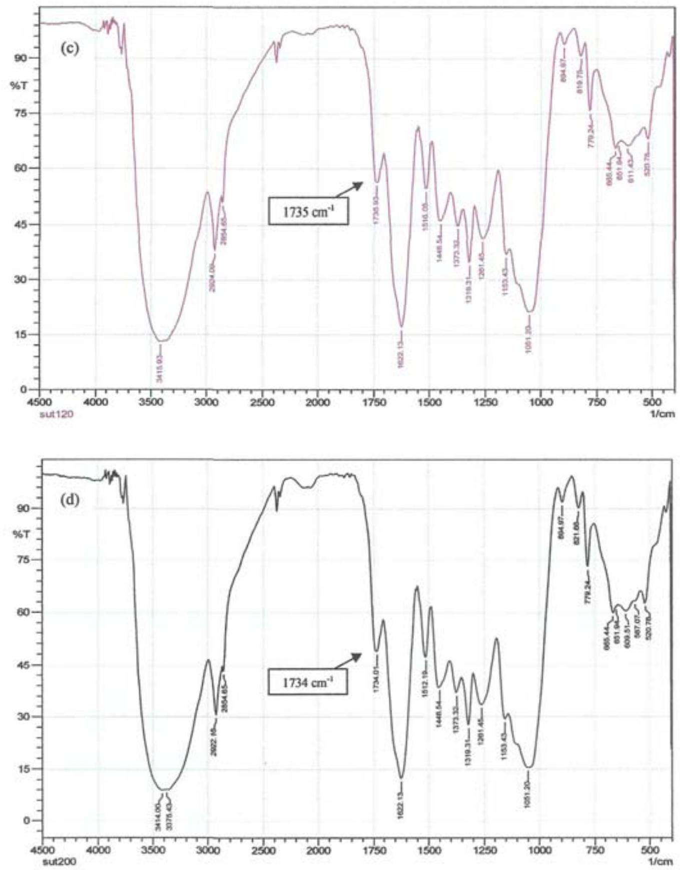


Fig. 5(a-d): FTIR analysis of nanoparticle were produced from four of sieve types: (a) T 77, (b) T 90, (c) T 120 and (d) T200

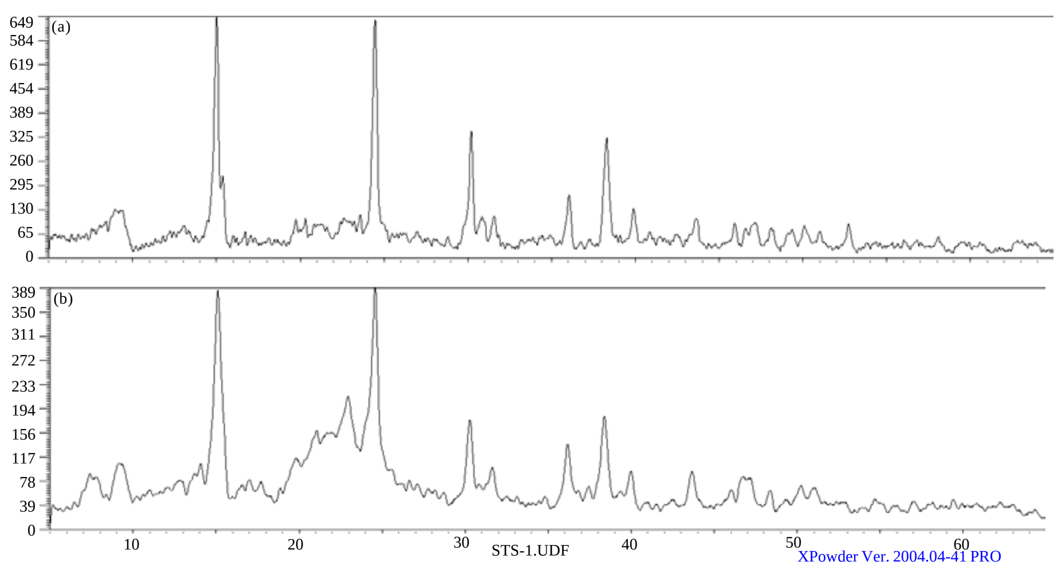


Fig. 6(a-b): XRD analysis of nanoparticle were produced from : (a) T 77 and (b) T200 of sieve types

CONCLUSION

- The bio-based nanomaterial from surian wood bark were produced using conventional balls milling with size in diameter were 93-110, 67-165, 68-93 and 42-114 nm produced from T77, T90, T120 and T200 of sieve types, respectively. It was concluded that the nanoparticle of organic material from SWB was obtained with the size in diameter was less than 1000 nm
- The chemical composition of bio-based nanomaterial from SWB contained of carbon, oxygen, potassium and calcium which was confirmed by SEM-EDS analysis
- The presence of the functional groups that exist in the SWB were detected by FTIR resulted that SWB is composed of cellulose. The FTIR analysis shows the presence of C = O stretching band at 1735 cm^{-1} in the nanoparticle of SWB produced from T90 and T120 of sieve types and C = O stretching band at 1734 cm^{-1} of SWB produced from T200 of sieve type due to balls milling effect while the nanoparticle of SWB produced from T77 of sieve type not observed. This research was indicated that conventional balls milling has changed the functional groups of cellulose of SWB
- The crystalline structure of bio-based nanomaterial from SWB was found calcium oxalate hydrate ($C_2CaO_4.H_2O$) with crystalline size were 26 and 14 nm produced from T77 and T200 of sieve types, respectively.

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