

Agglomeration Decrement from Nanocellulose Synthesis by adding PVA Capping Agent

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ABSTRACT

Indonesia is one of the largest palm oil productions in the world. In 2017, Indonesia was responsible for almost 50% of global palm oil production. The abundant availability of Oil Palm Empty Fruit Bunches (OPEFB) has become a potential resource to be further utilized in derivative products such as cellulose, hemicellulose and lignin. The demand for nanocellulose material from extracted cellulose fibers is increasing. In this study, nanocellulose synthesis was carried out in several stages namely hydrolysis (H₂SO₄ 64% (v/v) at 45°C for 45 minutes), delignification (NaOH 17,5% (w/v) at 80°C for 30 minutes), and bleaching (H₂O₂ 10% (v/v) at 60°C for 15 minutes). Then, nanocellulose was subjected to ultrasonication. It was proved that nanocellulose with 50.487 nm diameters resulted from ultrasonication 50% amplitude. Moreover, adding 5%-w PVA (polyvinyl alcohol) as capping agent obtained 36.635 nm average diameter of nanocellulose. It showed nanocellulose synthesis successfully lowering agglomeration and maintaining diameter size of nano size.

KEYWORDS

Hydrolysis
Empty fruit bunch
Delignification
Ultrasonication

INTRODUCTION

Nowadays, palm oil fulfil more than 30% of global demand for vegetables oil and 61% comes from Indonesia [1]. Since 2004, palm oil has contributed the highest in vegetables oil world market with total production of 30 million tons and an average growth rate of 8% per year [2]. Moreover, palm oil industry is one of the largest producers of residual solid biomass. This solid biomass is consist of 22-25%-w OPEFB, 12-14%-w fibers and 6-7%-w palm kernel shell from fresh fruit bunches [3]. The abundant availability of OPEFB has become a potential resource to be further utilized into derivative products such as cellulose, hemicellulose and lignin.

Generally, lignocellulose composition of OPEFB consists of cellulose (40-65%), hemicellulose (15-25%) and lignin (12-20%) [4]. OPEFB shaped oval and almost similar in dimension. The dimension such as diameter, wall thickness and length fiber cells are 8.3-20.5µm, 2.83-4.35µm and 0.33-50.31 mm respectively. It has porous and rough surface accompanied with silica-like bodies [5].

Cellulose is a high molecular weight homopolysaccharide composed of β-1,4-anhydroglucopyranose units and the glucose residues rotated through an angle of 180° about the molecular axis and hydroxyl groups in an equatorial position. High amount of hydroxyl groups

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makes cellulose molecules easy to form intermolecular or intramolecular hydrogen bonds. Cellulose consists of crystalline region with fewer hydrogen bonds compiled alternately [6]. Chemical formula of cellulose is similar across various plants and bacteria. However, the structural properties such as crystallinity and morphology may significantly differ [7].

In nature, the cellulose contents are normally embedded by the lignin and hemicellulose matrix via physical and chemical linkages to form a cellulose-hemicellulose-lignin complex. Pre-treatment stage must be implemented to solubilize the lignin and hemicellulose, and thus elevate the mass fraction of cellulose. The purpose of multiple pre-treatment steps are to disrupt the hemicellulose and the lignin structure in the biomass, and therefore maximize the accessibility of cellulose during the depolymerization process to produce nanocellulose from cellulose [4].

The demand of nanocellulose material from extracted cellulose fibers have escalated. This is due to the excellent structural characteristics including physical and mechanical properties (higher surface area, lower density, high aspect ratio, and tensile strength) of nano materials. Nanocellulose has been used as filler for example physical properties, thermo-physical and barrier properties of carboxymethyl cellulose (CMC) biopolymeric films, chitosan, agar, starch derivatives, polylactic acid and alginate films. Furthermore, nanocellulose materials used in enzyme immobilization, sensors technology, automotive, and electronic devices [8]. Nanocellulose applications for concrete, specialty paper, drilling fluids, electronic devices, food packaging and drug delivery [9]. Nanocellulose, which has two main forms, cellulose nanofiber and cellulose nanocrystal, has eminent properties, including high surface area, unique optical properties, high crystallinity and stiffness together with the biodegradability and renewability of cellulose for various fields [10]. Dimension of nanocellulose consist of lengths from several hundred nanometres up to micrometres, diameters range 5 up to 100 nm [11]. Furthermore, particular characterization such as large specific surface area (up to 250 m²/g), high tensile strength (7.5-7.7 GPa), low thermal expansion, high specific strength (up to 3000 kN m/kg) makes nanocellulose material used in wide range application [12].

Due to the large potential application of nanocellulose, while agglomeration is still a problem in nanocellulose research, this study aims to reduce agglomeration by adding process ultrasonication and capping agents.

LITERATURE REVIEW

Hydrolyzing methods, such as acid hydrolysis and alkaline hydrolysis as well as catalytic routes like delignification via oxidation, organosolv pre-treatment, and ionic liquid (IL) pre-treatment, are studied extensively for increasing cellulose extracted. Chemical treatments are the most popular pre-treatment technology which extracts cellulose fibers into nanocellulose [10]. Most nanocellulose syntheses are produced by sulfuric acid hydrolysis of lignocellulose. The use of sulfuric acid imparts a negatively charged surface group, acidic sulphate ester (-OSO₃-H⁺), onto the cellulose nanocrystals (CNC. surface. This acidic sulphate ester group can provide stable dispersibility of the nanocellulose in a pristine condition without dehydration [13]. Furthermore, sulfuric acid is the most frequently used acid for producing nanocellulose because its good solubility in water [12]. Nanocellulose obtained from sulfuric acid hydrolysis disperse readily in water in consequence of the abundance of negatively charged sulfate ester groups on their surface [14].

Production of nanostructured cellulose from OPEFB via one-pot oxidative-hydrolysis process using 30% hydrogen peroxide, $\text{Cr}(\text{NO}_3)_3$ solution and 8% H_2SO_4 obtained nanocellulose with an average diameter range $51,6 \pm 15,4$ nm [4]. Nanocellulose extraction from *cocos nucifera* used various chemical such as $\text{C}_2\text{H}_5\text{OH}-\text{C}_7\text{H}_8$, 0.7 wt% of NaClO_2 in an acetic solution (pH 4-4,5), 17,5% (wt/v) NaOH , 80% CH_3COOH and 70% HNO_3 , mechanic by ball mill and ultrasonication obtained nanocellulose with an average diameter range 55-64 nm [15]. Another nanocellulose extraction from empty fruit bunch using various chemical such as 2% (w/v) NaClO_2 (at pH 4), 4% (w/v) NaOH solution, 56-60 wt% H_2SO_4 , dialyzed with membrane and ultrasonication resulted nanocellulose 69.22 nm hydrodynamic diameter [16]. Nanocellulose extraction from rice husk using various steps and chemicals has been done. Rice husk with particle size of 100-240 nm delignified with 3% NaOH , bleached with 65% acetic acid, 20% H_2O_2 and hydrolyzed with 65% H_2SO_4 . Finally, it treated by sonication followed by freeze drying resulted nanocellulose 11.7-48.3 nm diameter particle size [17]. Production of cellulose nanofiber from OPEFB by steam exploded with saturated steam at 20 bars, bleached using 5% (w/v) sodium chlorite followed with grounded by nano-grinder resulted nanocellulose with average diameter 17.85 nm [18]. Nanocellulose from palm residues has been done by pulping process with 10% (wt/wt) NaOH 160 °C 2 h then acidic hydrolysis with 20% (v/v) H_2SO_4 . It resulted nanocellulose with 42-82 nm spherical particles [19]. In addition, nanocellulose production from OPEFB by delignification using alkaline NaOH (w/v) at 80°C for 30 minutes, bleaching with H_2O_2 (v/v) at 70°C for 15 minutes, acid hydrolysis 64% for 45 minutes and followed by freeze drying for 6 hours resulted nanocellulose with size 86.8 nm [20].

Mechanical process in nanocellulose synthesis is the isolation of cellulose fibrils by applying high shear force to cleavage the cellulose fibers in longitudinal axis. The most used mechanical approaches consist of high-pressure homogenization, ultrasonication and ball milling methods. However, high energy consumption is the main drawback. Therefore, mechanical process is usually mixed with other pre-treatment for decreasing energy [21]. Most cellulose extraction through multiple steps such as acid and or alkaline hydrolysis accompanied with mechanical processes such as ultrasonication has been successfully resulted nano-sized cellulose.

In fact, cellulose is sensitive to moisture owing to the rearrangement of the hydrogen bonds according to the hydration and dehydration processes. The hydrogen bonding during dehydration is irreversible or partially reversible, which may cause a morphological change or agglomeration of the nanocellulose [13]. Research by Tang et al (2013) showed that the increasing of pre-treatment level such as esterification due to increasing agglomeration. [22] In addition, strong intermolecular hydrogen bonding interaction and the high surface energy of nanocellulose make it tend to aggregate in many media [14]. Moreover, aggregation of nanoparticles could occurred when solvent were removed during purification [5]. Modification by additives which are called capping agent can hinder hydrogen bond formation in nanocellulose.

Polyvinyl alcohol (PVA) with molecular formula CH_2CHOH is a vinyl polymer linked by only carbon-carbon linkages. It is water soluble and biodegradable which is used to make water soluble and biodegradable carriers. Manufacture of delivery systems use it for chemicals such as fertilizers, pesticides and herbicides [23]. Polyvinyl alcohol (PVA) is a material that was appropriated by the Food and Drug Administration for its use in humans and food. It has been reported that during dehydration, cellulose nanofiber (CNF) without PVA resulted in larger agglomeration compared to CNF overlaid with PVA as capping agent. The result showed that PVA can be used as capping agent to hinder the formation of hydrogen bonds between nanocellulose [9]. Moreover, PVA is a semi-crystalline, non-toxic and has possibility to interact with hydrophilic

surfaces of the biomaterials in consequence of the strong hydrogen bonding [24]. Indeed, nanocellulose tremendously as an active agent in PVA (biodegradable polymer for food packaging) could extend food quality and safety [12]. In addition, dispersion stability of nanocellulose in water indicated by value of zeta potential greater than 30 mV [6] Nanocellulose obtained by mixed acid hydrolysis and ultrasonication resulted zeta potential -12 to -44 mV [25]. Herein, mixed acid hydrolysis and ultrasonication is not adequate to fulfill stable dispersion of nanocellulose in water.

Through literature study that has been explored, this study was carried out comprehensively via various step series such as hydrolysis, delignification, bleaching, ultrasonication and adding PVA as capping agent. Capping agent addition would decrease agglomeration and increase the dispersion stability through storage, transportation, and usage in diverse application.

RESEARCH METHOD

Material

OPEFB was purchased from a local plantation in Bogor. Sodium hydroxide pellets technical grade and hydrogen peroxide 30%-v solution were purchased from local chemical mart. Sulfuric Acid (H_2SO_4 , 95-97%) pure analyzed grade were purchased from Merck. PVA (polyvinyl alcohol) was commercial grade and purchased from a local chemical store.

Methods

Preparation

OPEFB washed thoroughly with deionized water for removing impurities. Afterwards, it dried in the open air. It was then chopped into pieces around 5 cm. After that, OPEFB milled using grinder and sieved through strainer of 200 mesh size.

Procedures

Multistep processes such as hydrolyzing, delignifying, bleaching, ultrasonication and adding capping agent were carried out respectively to synthesis nanocellulose from OPEFB. OPEFB was hydrolyzed with 64% (v/v) H_2SO_4 at 45°C for 45 minutes. Subsequently, it washed with deionized water until reached neutral pH. Afterwards, the delignification process was carried out with 17.5% (w/v) NaOH at 80°C for 30 minutes. After that, it washed with deionized water until neutral pH was attained. Next, the delignified OPEFB bleached with 10% (v/v) H_2O_2 at 60°C for 15 minutes. It was repeated two times to remove the remaining lignin. Nanocellulose which was obtained from these processes washed until pH 7 reached. The washed pulp was filtered with filter paper by vacuum pump.

Moreover, nanocellulose was subjected to Hielscher ultrasonication with a sonication probe at amplitude 30% and 50% for 6 hours. After ultrasonication, nanocellulose with the lowest diameter size is treated with capping agent. PVA which is used as capping agent varies from 1%, 3% and 5% (w/v). PVA was dissolved in deionized water for 4 hours at 80°C with constant stirring. Furthermore, nanocellulose mixed with PVA solution (ratio 1:1) under constant stirring at 80°C for 3 hours [26]. The mixture was then carried out in ultrasonication for 30 minutes.

Characterization of EFB and nanocellulose

The data used in this research are primary data and secondary data. Primary data were obtained from direct interviews with the government and randomly selected residents, including farmers, private employees, entrepreneurs, public employees, and civil servants. Apart from interviews, data was also obtained from Focus Group Discussions. The parameters used in the interviews related to people's income, education, age, home ownership status, the impact of tidal floods related to health, clean water quality, infrastructure, sanitation, and tidal flood disaster management.

(i) Moisture content

Moisture content was analyzed by gravimetric method. One gram of OPEFB was subjected into evaporating dish then dried in oven at 110°C for 3 hours. After that, it cooled at room temperature for 5 minutes then put into desiccators for 10 minutes. Subsequently, it was measured until the weight was constant. The moisture content was calculated by measuring the loss weight of OPEFB.

(ii) SEM Analysis

The morphological structure of nanocellulose was analyzed using Zeiss Evo 10 Scanning Electron Microscope (SEM) at 10kV with 10.00K magnification. The sample was placed on the sample holder and imaged directly without pretreatment although the sample is not completely dry.

DISCUSSION

Before pretreatment, OPEFB is grinded and sieved at 200 mesh. The untreated OPEFB showed in Figure 1. The moisture content was 8.85%-w.



Figure 1. (a) The untreated OPEFB before, and (b) after grinding and sizing

Acid hydrolysis was the first step. The result of the hydrolysis and delignification is shown in Figure 2. Visually, the color of pretreated OPEFB was black and like mud. This is due to high lignin content. This shows that the lignin is tightly bound yet in the OPEFB or the lignin that has been released is still attached to the cellulose solid and cannot dissolved into the acid solvent.

Acid hydrolysis is used to release the amorphous region of cellulose. It yielded elongated fibrillar or defect-free rod-like crystalline particles having at least one nanoscale dimension [6]. Alkali pretreatment used to remove lignin and hemicellulose from cellulosic fibers [12].



Figure 2. (a) Hydrolyzed OPEFB (b) delignified OPEFB

The liberation of lignin and hemicellulose was carried out by delignification using 17.5% (w/v) NaOH. The delignified cellulose brownish color is presented in Figure 2b. It showed that color change indicates the alleviation of lignin content. Afterwards, it was bleached using H₂O₂ to remove remaining lignin. The bleached cellulose is shown in Figure 3.

The brownish color of nanocellulose was caused by the presence of lignin. Nanocellulose showed in whitish appearance indicated lignin content is very low [27]. In fact, the lignin removal or liberation in this study has not been maximized. This relates to the sequence of nanocellulose synthesis in which the delignification and bleaching process should be carried out first before hydrolysis. Hydrolysis process is not effective because hindered by the lignin layer.

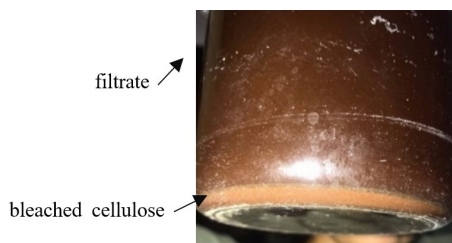


Figure 3. Bleached cellulose and filtrate

The cellulose content in OPEFB ranges from 40-65% [4], meanwhile yield of bleached nanocellulose is 36.5%-w. This value is quite good, but it seems that not only cellulose but also parts of lignin remain. The brown color indicates the lignin presence in the cellulose. Furthermore, the low yield of cellulose can be caused by exceptionally acidic conditions that decompose cellulose into individual sugar molecules [27].

Then, synthesis of nanocellulose was carried out using ultrasonication. SEM analysis of nanocellulose is presented in Figure 4.

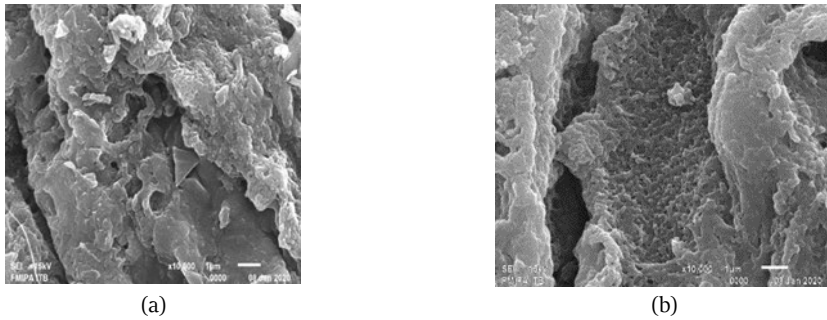


Figure 4. SEM analysis of nanocellulose by ultrasonication amplitude (a) 30% and (b) 50%

Ultrasonication principle is that the cavity in the cellulose cell absorbs energy from high-intensity ultrasonic waves which are influenced by temperature, concentration, amplitude, size, time, and distance from the probe tip so that it can break down the cellulose into small size. Ultrasonication in this study was carried out at an amplitude of 30% and 50%. This refers to previous studies. Ultrasonication with an amplitude of 30% produces nanocellulose with an average diameter of 100.137 nm, while at 50% the amplitude was 7.69-76.28 nm [28]. This shows that the amplitude of 50% can reduce agglomeration because mechanical movement can break up agglomeration. Whereas in other previous study, ultrasonication carried out at an amplitude of 40% and 60%. Ultrasonication at 40% amplitude produces nanocellulose with diameter range of 17-148 nm. Meanwhile at an amplitude of 60% it produces nanocellulose with diameter of 32.7-121.7 nm [29]. This shows that the amplitude of 60% produces larger sized nanocellulose. Therefore, in this study the amplitude is limited to 30 and 50%.

Figure 4 shows a large agglomeration of nanocellulose both from nanocellulose by ultrasonication amplitude 30% and 50%. This indicates that additional processes such as ultrasonication are not strong enough to prevent agglomeration although it obtained cellulose in nano sized. The SEM results show that the nanocellulose particles have not been well dispersed even though the SEM magnification is large enough. It showed that intermolecular hydrogen bonding interaction is robust constantly through ultrasonication. The drying process of the solvent also contributed to the agglomeration of nanocellulose.

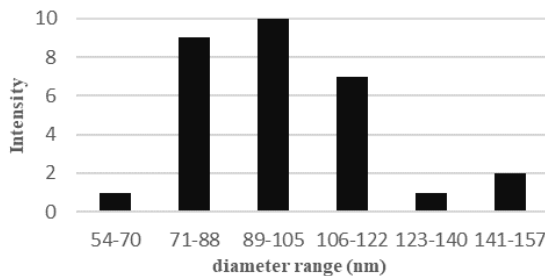


Figure 5. Diameter size distribution of nanocellulose by ultrasonication amplitude 30% (nanocellulose A)

Image J tool was used to determine the size of nanocellulose. Diameter size distribution of nanocellulose A and B was presented in Figure 5 and 6. Nanocellulose A has a diameter of size range of 54.24-156.25 nm with an average diameter of 100.137 nm. Meanwhile, nanocellulose B has a particle size range of 7.686-76.281 nm with an average diameter of 50,487 nm. Nanocellulose B has the lowest diameter particle size. The diameter particle range of nanocellulose

which is quite wide shows not only because the nanocellulose synthesis obtained large particle size, but also due to agglomeration nanocellulose.

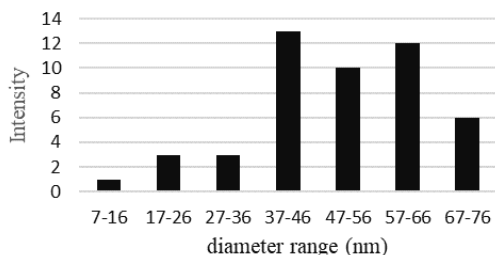


Figure 6. Diameter size distribution of nanocellulose by ultrasonication amplitude 50% (nanocellulose B)

The range of diameter particle size is quite close to the nanocellulose of Nagarajan et al (2019) which obtained 55-64 nm nanocellulose at amplitude ultrasonication 60% for 10 minutes. In addition, particle size diameter in this study was also near with nanocellulose from Foo, et.al [16] which obtained 69.22 nm nanocellulose at amplitude ultrasonication 60% for 5 minutes. The duration of ultrasonication is quite different compared with this study because Nagarajan, et.al [15] and Foo, et.al [16] combined with others pretreatment before ultrasonication. Nagarajan, et.al [15] used various chemicals whereas Foo, et.al [16] using dialyzed membrane process. It showed that ultrasonication plays an important role in nanocellulose synthesis.

In ultrasonication process, defibrillation occurs of cellulose fiber with the hydrodynamic forces of the ultrasound. The mechanical oscillating power is produced, resulting in the formation, expansion, and implosion of microscopic gas bubbles when the liquid molecules absorb ultrasonic energy [21]. Moreover, the energy provided by cavitation (10-100 kJ/mol) is the hydrogen bond energy range. Therefore, the ultrasonic impact can effectively disintegrate amorphous region of cellulose and giving access to enter the interior of cellulose fibers [22]. Indeed, the duration time of ultrasonication affects reduction size of cellulose.

Agglomeration alleviation is carried out by adding PVA after ultrasonication. PVA was used as a filler in the amorphous site that is broken during hydrolysis and prevents collisions among nano particles. PVA is added into nanocellulose B (nanocellulose with lowest diameter particle size). SEM analysis of nanocellulose B is shown in Figure 7 and 8.

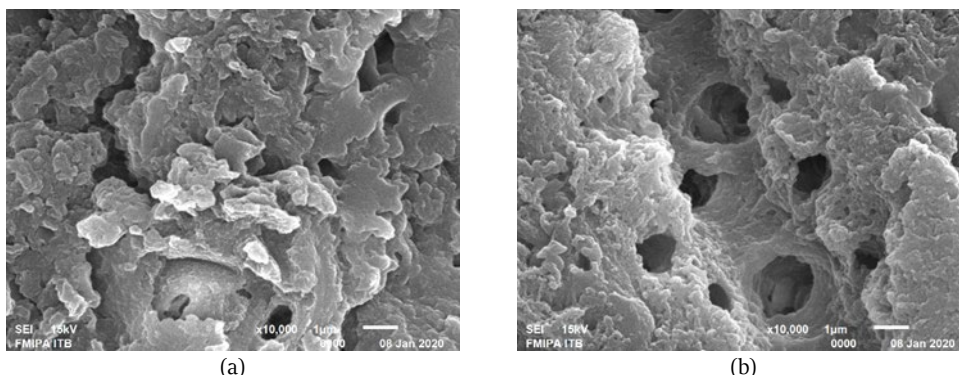


Figure 7. Nanocellulose B with (a) 1%-w and (b) 3%-w PVA capping agent

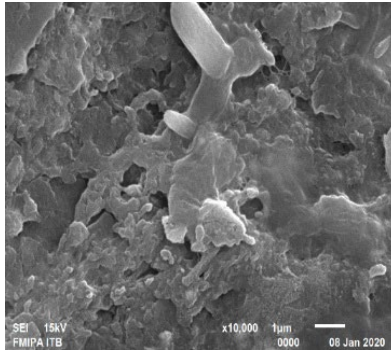


Figure 8. Nanocellulose B with 5%-w PVA capping agent

Figures 7 and 8 represent that nanocellulose is more porous than that of without PVA (Figure 4). This indicates that the agglomeration is reduced. Data of nanocellulose particle size diameter from SEM was analyzed using image J tools. Diameter range of 42.949 – 136.500 nm with an average diameter of 89.954 nm for nanocellulose B (adding 1%-w PVA), 31.250 – 127.152 nm with an average diameter of 72.015 nm for nanocellulose B (adding 3%-w PVA) and 11.409 – 91.837 nm with an average diameter of 36.635 nm for nanocellulose B (adding 5%-w PVA). The average diameter of each nanocellulose without (0%-w PVA) and with PVA capping agent (1-5%w PVA) is presented in Figure 9.

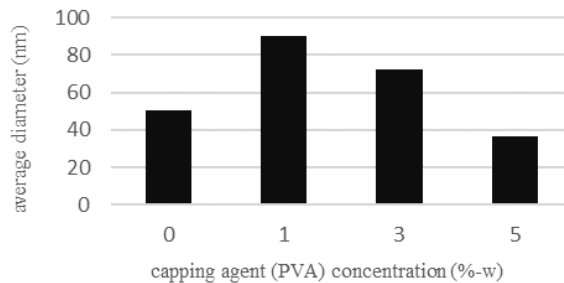


Figure 9 Nanocellulose before and after adding PVA as capping agent

Figure 9 shows nanocellulose with 5%-w PVA as a capping agent could maintain the diameter of the nanocellulose. In contrast, diameter size of the nanocellulose became larger after adding capping agent at 1%-w and 3%-w PVA. It is caused the PVA with these concentrations could not fulfill amorphous region that was broken during the hydrolysis process. Hence, nanocellulose particles collide and form a larger diameter. It is indicated that the enhancement of PVA affects lower agglomeration.

Exceptionally, addition of 5% PVA into nanocellulose lead to lower diameter particle which is from 50.487 nm to 36.635 nm. The presence of capping agent can redisperse the agglomerate nanocellulose which previously formed. Apart from the presence of PVA, this could also be a consequence of the ultrasonication which was carried out after the addition of PVA. The ultrasonication process strengthens the bond between nanocellulose and PVA.

Nanocellulose obtained by acid hydrolysis followed by freeze drying resulted higher diameter particle of nanocellulose (51.5-66.5 nm) [20] compared to this study. The difference is the hydrolysis temperature in this study was lower than the previous study and the difference of nanocellulose final treatment. It is proven that the synthesis of nanocellulose by acid hydrolysis

continued by ultrasonication and followed by the addition of the capping agent PVA produces nanocellulose in particle sizes of lower diameter and decreased agglomeration compared to our previous research. The previous study was synthesis of nanocellulose by acid hydrolysis followed by freeze drying. This indicates that ultrasonication step and addition of capping agent play an important role in the synthesis of nanocellulose. Nevertheless, it needs higher energy due to the high cost in using ultrasonication process.

This indicates that ultrasonication step and addition of capping agents play an important role in the synthesis of nanocellulose.

CONCLUSION

The multistep process of nanocellulose has been successfully carried out consists of acid hydrolysis, delignification and bleaching followed by ultrasonication and adding capping agent respectively resulted cellulose in nano sized. PVA as capping agent at 5%-w concentration successfully decreasing agglomeration, maintaining, and reducing diameter size of nanocellulose. The lowest average diameter size of nanocellulose resulted from this study is 36.635 nm. In the future, it is necessary to carry out more research related to improving the hydrolysis and bleaching processes not only to reduce but also prevent agglomeration.

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