

Synthesis and Characterization of Cellulose Acetate and Nanocellulose Acetate from Sengon Agroindustrial Waste (*Paraserianthes falcataria*)

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ABSTRACT

Synthesis and characterization of cellulose acetate and nanocellulose acetate have been carried out. Cellulose was isolated from sengon wood powder waste using 6% NaOH solution and bleached with NaOCl. The cellulose was hydrolyzed with 60% formic acid to obtain nanocellulose. Cellulose and nanocellulose were then modified with acetic anhydride. The synthesized products were characterized by FTIR to identify organic functional groups, powder XRD to measure crystallinity, and SEM to observe surface morphology. Solubility tests in several types of solvents were also performed. The degree of substitution (DS) of cellulose acetate and nanocellulose acetate was carried out based on Indonesia's SNI 0444:2009 method. The DS calculation show that the cellulose acetate and nanocellulose have DS of 2.9 and 2.1, respectively.

Keyword: cellulose, nanocellulose, cellulose acetate, nanocellulose acetate

INTRODUCTION

Cellulose is one of the most abundant organic materials in nature [1]. Cellulose is found in nature, especially in the stems of plants. Cellulose is also found in an impure state, accompanied by lignin, hemicellulose, and others. Cellulose is insoluble in water and organic solvents, but soluble in certain ionic solution [2]. This makes cellulose difficult to use in industry. Hence, it is necessary to modify this polymer so that it is soluble in water and other solvents, and its derivatives can widely use in various fields.

All cellulose derivatives are based on replacing the hydroxyl group of celluloses with another functional group. To date, several modifications to cellulose have been carried out. This protection process can be carried out through esterification, etherification, and silicization reactions [3], formation of ketal compounds, and ionic interactions [4]. The use of modified cellulose has been widely explored, including for packaging [5], ink ingredient [6], antibacterial agent [7], textile [8], [9], tissue [10], and others.

Esterification reaction of cellulose can be done by sulfuric acid [11], citric acid [12], acetic acid [2], and etc. Cellulose acetate is a cellulose derivative in which the hydroxyl group of cellulose is protected by an acetate group. Cellulose acetate is a polymer, which obtained from esterification of the cellulose. Cellulose acetate can be obtained by reacting cellulose with acetic anhydride. Based on the number of acetate groups bound to cellulose, cellulose acetate

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is divided into three groups, namely cellulose monoacetate (CMA), cellulose diacetate (CDA), and cellulose triacetate (CTA). The type of cellulose acetate can be determined by the degree of substitution (DS). DS values are ranged from 0 to 3 [2].

Several studies on cellulose acetate have been reported previously. Souhoka and Latupeirissa (2018) have reported on the synthesis and characterization of cellulose acetate using commercial α -cellulose. The acetylation process involves glacial acetic acid, acetic anhydride, and sulfuric acid as catalysts. The reaction condition at 25°C for 2.5 hours had a DS value of 1.482, while the reaction condition at 40°C for 5 hours had a DS value of 2.295 [13]. The synthesis and characterization of cellulose acetate from royal palm tree agro-industrial waste were reported by Battisti, *et al* (2019). The highest yield of cellulose acetate was 99.5%, with DS values ranging from 2.08 to 2.82 [14]. Based on literature studies, there are still few reports on the synthesis of nanocellulose acetate.

Based on the background study above, research on the synthesis of cellulose acetate and nanocellulose acetate remains interesting. In this work, the cellulose was isolated from sengon wood saw waste. Sengon wood was chosen because it has a high cellulose content, reaching almost 41% [15].

EXPERIMENT

Chemicals and Instrumentations

Chemicals used in this research were sodium hydroxide (NaOH, 99% purity Merck, Germany), sodium hypochlorite (NaOCl, 99% purity Merck, Germany), formic acid (HCOOH, 99% purity Merck, Germany), acetic acid (CH₃COOH, 99% purity SMART LAB, Indonesia), sulfuric acid (H₂SO₄, 99% purity Merck, Germany), acetic anhydride (C₄H₆O₃, 99 % purity Merck, Germany), chloroform (CH₃Cl, 99 % purity Merck, Germany), *n*-hexane (C₆H₁₄, 99 % purity Merck, Germany) and distilled water. Meanwhile, the instruments used during the research were glassware, hot plate, magnetic stirrer, mercury thermometer, analytical balance, oven, ultrasonicator (DELTA D150H), suction pump, vacuum filter, FTIR (Shimadzu FTIR-8400S), powder XRD (PANalytical-type X'pert Pro), SEM (FEI SEM Inspect-S50), and DTA/TGA.

Procedure stages

This research consisted of several stages, namely: pretreatment, cellulose isolation, cellulose modification, cellulose hydrolysis, nanocellulose modification, determination of substitution degree, and solubility test.

Pretreatment

Sengon wood saw waste was dried by grinding using a grinder before being filtered using a 60-mesh sieve. The powder was washed using running water to remove dust and dirt. Next, the sengon wood powder was dried sun-dried.

Isolation of Cellulose

Isolation of cellulose from sengon wood powder was carried out by using alkaline and bleaching methods. This method refers to the research that has been successfully carried out on pine flower waste [16]. A total of 50 grams of sengon wood powder was placed in a 1000 mL beaker glass and then added to 6% NaOH solution. The ratio between sengon wood powder and NaOH was 1:10 (v/v). The mixture was then heated to 70°C for 4 hours. Next, the mixture

was filtered off by Buchner funnel and the solid was washed with distilled water until the filtrate reached a neutral pH. 50 grams of the alkalized powder was then bleached using 500 mL of 6% NaOCl solution. The mixture was heated to 70°C for 2 hours. This process was repeated several times until white cellulose is produced. The solid part was separated by filtration and washed with distilled water until the filtrate reached a neutral pH. Then the cellulose was dried by oven at 50°C overnight and homogenized.

Cellulose hydrolysis

Cellulose hydrolysis was carried out by mixing 2 grams of cellulose with 200 mL of 60% formic acid solution. The mixture was ultrasonicated at 45 °C for 300 minutes. The reaction was stopped, and the container was immersed in cold distilled water. The resulting solid was filtered off and washed until the filtrate reaches a neutral pH. Next, the solid was dried in an oven at 30-50 °C until obtain a constant weight.

Modification of cellulose and nanocellulose

Reaction method of cellulose acetate synthesis adopted from Tristantini (2018) with modifications [15]. The reaction was initiated by mixing 1 g of cellulose/nanocellulose with 25 mL of glacial acetic acid and stirred using a magnetic stirrer for 60 minutes at 35°C. Next, 0.125 mL of concentrated sulfuric acid as a catalyst was added and the mixture was stirred again for 45 minutes. Acetic anhydride was then added into the mixture with a ratio of cellulose to acetic anhydride of 1:10 (w/v), assisted by stirring for 60 minutes at 50°C. The mixture was then added with 5 mL of acetic acid and 2.5 mL of distilled water to stop the modification reaction. The filtrate was added dropwise with distilled water to form a precipitate. The precipitate was then filtered off and washed with deionized water until the filtrate reached a neutral pH. The solid was eventually dried in oven at 50°C for 6 hours.

Characterization

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The FTIR test was performed by mixing 5 mg of the sample with 95 mg of potassium bromide. The mixture is mashed and then made into a thin pellet. The thin plate that has been made is placed in a slit and the beam is passed through to form the FTIR spectrum [17].

X-Ray Diffraction (XRD) Analysis

Characterization of isolated cellulose, hydrolyzed nanocellulose, modified cellulose and modified nanocellulose using an XRD instrument with a rotation angle of 2θ by 10 to 90 and time of X-ray radiation every 2θ 0.02° for 46 seconds. The radiation source is obtained from Cu metal with a wavelength of $K\alpha_1$ of 1.540560 and a wavelength of $K\alpha_2$ of 1.54443. The results of the analysis are in the form of intensity reports and the response peaks of the particles after being irradiated with X-rays for measurements [18].

Morphological Analysis with Scanning Electron Microscope (SEM)

The process of taking an image is by attaching the sample to the SEM specimen holder using a carbon double type. Double type made of conductive carbon on both sides that serves to deliver all electrons that enter the sample out through grounding. The SEM is operated with the following standard operating parameters: High Voltage 20 kV, Spot Size 50, Work Distance (WD) 10 mm.

Determination of the degree of substitution (DS)

The method of determining DS is based on the Indonesia standard of SNI 0444:2009. A total of 1 gram of cellulose acetate (CA) or nanocellulose acetate (NCA) powder was put into an Erlenmeyer containing 40 mL of 75% ethanol. The mixture was heated in a 55°C bath for 30 minutes. Then, 40 mL of 0.5N NaOH was added and the mixture was heated again. The Erlenmeyer then removed from the bath and then covered with aluminum foil and stored at room temperature for 72 hours. Then, the solution was added 2 drops of PP indicator and titrated with 0.5N HCl. The Erlenmeyer was closed again with aluminium foil and stored for 24 hours at room temperature. Then titrated with 0.5 N NaOH. The same treatment was done for blank solution but without CA or NCA samples. The DS is calculated based on this equation:

$$DS = \frac{162 \times \left(\frac{\% \text{asetil}}{43} \right)}{100 - \left(\frac{42}{43} \times \% \text{asetil} \right)} \times 100\%$$

Solubility Test

Solvents used for the solubility tests of CA and NCA were water, chloroform, and n-hexane. The solvent used based on the level of its polarity. A total of 2 mL of solvent was placed in a test tube and then added with 0.1 grams of cellulose acetate or nanocellulose acetate. The mixture was shaken for a while and then it was observed.

RESULT AND DISCUSSION

Sengon Wood Cellulose and Nanocellulose Result

The raw material used in this research is sengon wood powder of sea sengon (*Paraserianthes falcataria*). Before use, the sengon wood powder was washed with running water and then dried. After obtaining dry powder, the powder is ready for delignification. First, 100 grams were weighed and then placed in a beaker, then added with 1L of 6% sodium hydroxide. The mixture was stirred for 4 hours. Stirring change the color of sodium hydroxide to dark brown, indicating that the lignin in sengon waste is dissolved in sodium hydroxide solution [19], [20]. Then the solids were separated and then washed with distilled water until reach neutral pH. After delignification, followed by repeated bleaching process used sodium hypochlorite to obtain white cellulose. The bleaching process was carried out 4 times with a ratio of solids and solutions of 1:10. The flow of cellulose isolation from sengon wood waste can be seen in Figure 1.

For every 100 grams of sengon wood powder that is reacted, 18-20 grams of cellulose are obtained (Figure 1c). The resulting dry cellulose is then hydrolyzed with formic acid solution using ultrasonication method to produce nanocellulose. The yield of synthesized nanocellulose was 87% (Figure 1d).



Figure 1. (a) sengon wood powder of sengon, (b) sengon bleached, (c) cellulose, (d) nanocellulose

Fourier Transform Infrared (FTIR) Analysis of Cellulose and Nanocellulose

Figure 2 shows the FTIR spectra of the sengon wood powder, cellulose, and nanocellulose. The spectra showed that there were several typical peaks, namely 3333 cm^{-1} (O-H Stretching), 2289 cm^{-1} (C-H cellulose), 1647 cm^{-1} (C=C lignin), 1165 & 1061 cm^{-1} (C-O and C-H cellulose), 1028 cm^{-1} (C-O-C pyranose ring), and 898 cm^{-1} (C-O and C-H cellulose). Compared to the IR spectra of the sengon wood powder, the IR spectra of cellulose shows a loss of intensity at 1700 cm^{-1} , but in the 1500 cm^{-1} region, peaks still appear with moderate intensity. This indicates that the cellulose is completely free from hemicellulose but not from lignin[16], [21]. The IR spectra of nanocellulose is considerably identical to that of cellulose, which shows that hydrolysis does not change the existing functional groups[22].

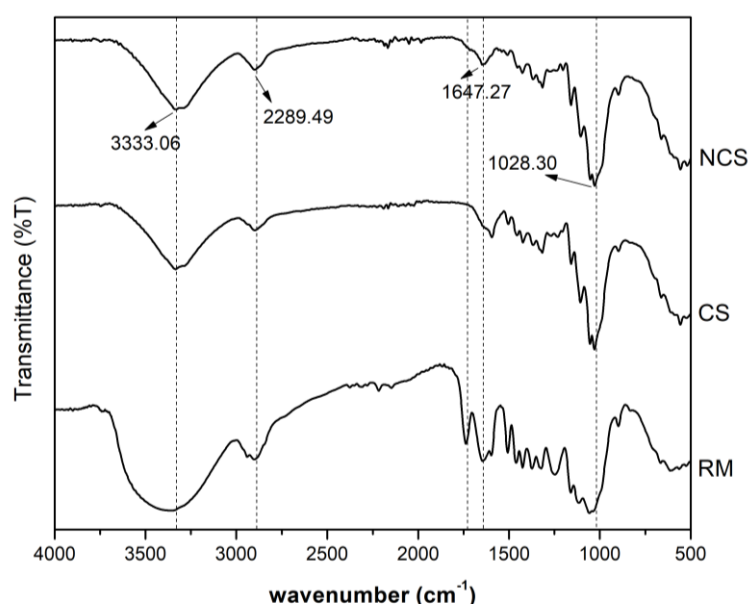


Figure 2. FTIR spectra of sengon wood powder (RM), Cellulose (CS), and Nanocellulose (NCS)

X-Ray Diffraction (XRD) Analysis of Cellulose and Nanocellulose

The XRD diffractogram shows the appearance of peaks at $2\theta\ 11^\circ$ and 22° for cellulose and nanocellulose. The peak at $2\theta\ 11^\circ$ indicates an amorphous region while at $2\theta\ 22^\circ$ is crystalline. This indicates that the cellulose sample is more crystalline than amorphous which is known from the dominant peak at $2\theta\ 22^\circ$. Based on the Beghal equation, the crystallinity value of isolated cellulose was 66.56% and 72.79% for nanocellulose. This shows that the hydrolysis process makes the crystallinity higher (Figure 3) [16], [21], [22].

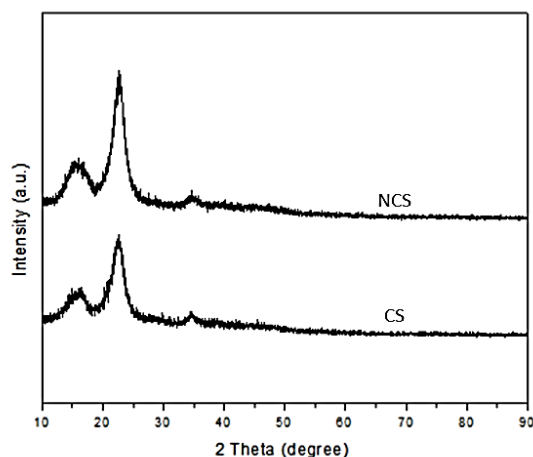


Figure 3. XRD diffractogram of cellulose (CS) and nanocellulose (NCS)

Table 1. Crystallinity Index of cellulose and nanocellulose

	CS	NCS
Yield (%)	20	98
CI (%)	66.59	72.79

Characterization by Scanning Electron Microscopy

SEM images of cellulose and nanocellulose are presented in Figure 4. Based on the SEM characterization, the synthesized cellulose and nanocellulose are in the form of crystalline, in which the nanocellulose fibers has smoother appearance than the cellulose. Based on the results of the analysis using imageJ software [23], the average diameter and length of cellulose were 55.78 nm and 125.52 nm, and nanocellulose was 13.41 nm and 82.35 nm. These results indicate that hydrolysis changes the size of the cellulose particles to be smaller.

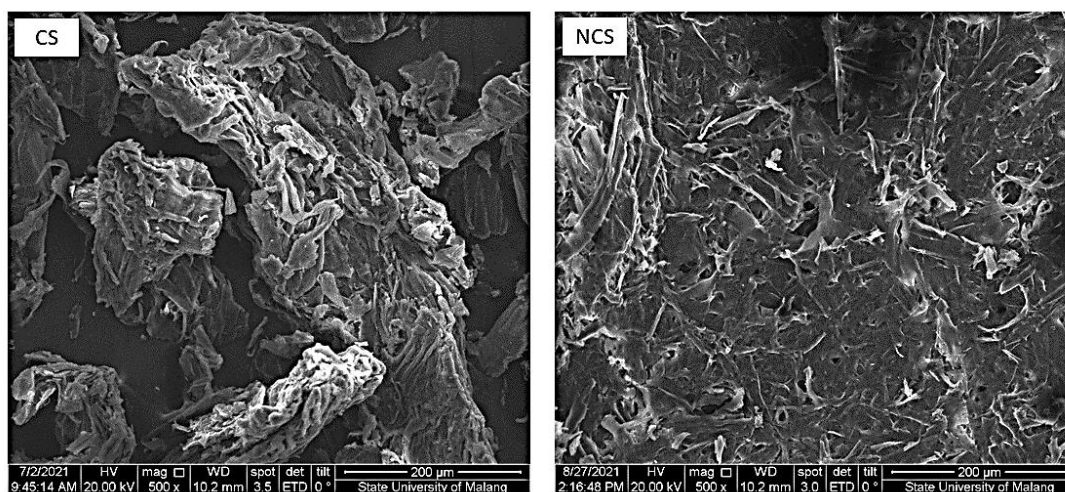


Figure 4. SEM images of cellulose (CS) and nanocellulose (NCS)

Fabrication of cellulose acetate and nanocellulose acetate

Both cellulose and nanocellulose synthesized were further modified with acetic anhydride to become cellulose acetate (Figure 5a) and nanocellulose acetate (Figure 5b). The schematic reaction of cellulose and acetic anhydride is shown in Figure 6. The resulting cellulose acetate and nanocellulose acetate are in the form of a pure white slurry. After the slurry was dried, brownish powder was obtained. reduced water content causes cellulose acetate and nanocellulose acetate to change color. Cellulose acetate and nanocellulose acetate were characterized by FTIR, XRD, SEM, DS, and solubility test.

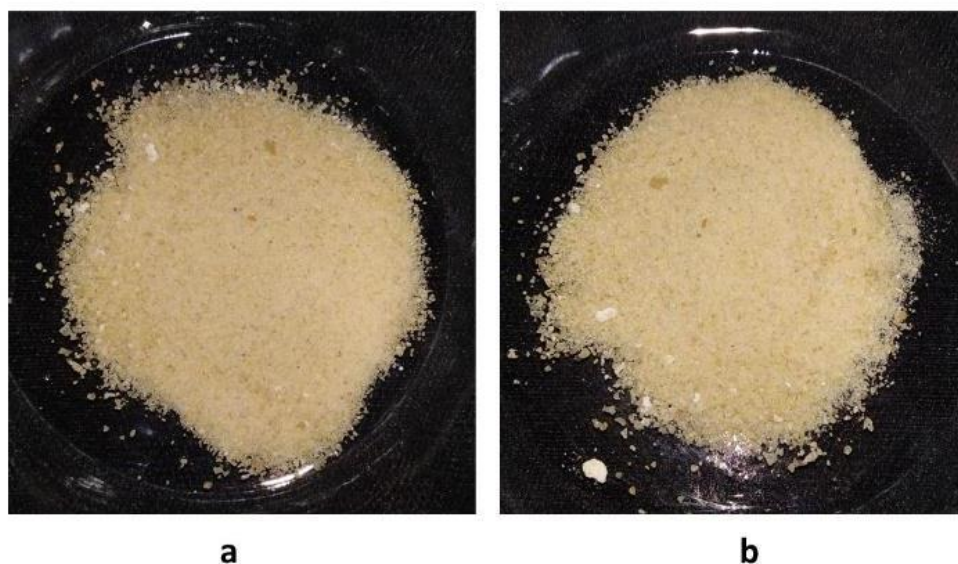


Figure 5. Cellulose acetate (a) and nanocellulose acetate (b)

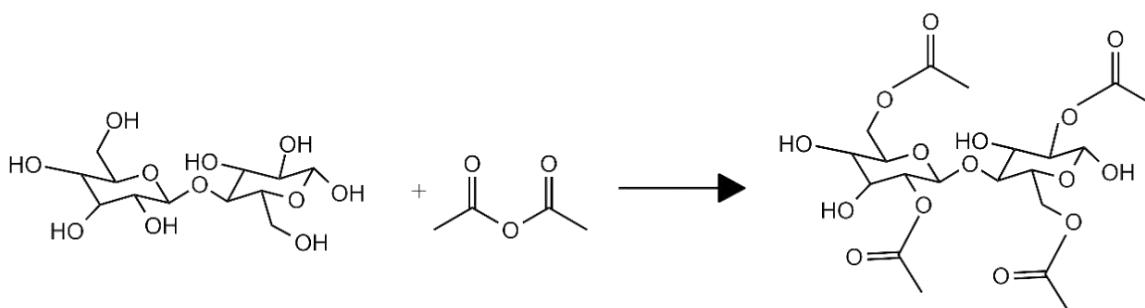


Figure 6. The schematic reaction of cellulose acetate reaction

FTIR Spectra of Cellulose acetate and Nanocellulose acetate

Two distinctive peaks appeared in the modified cellulose and nanocellulose, in the 3300 cm^{-1} and 1700 cm^{-1} regions [13]. The reduced intensity in the 3300 cm^{-1} regions indicates the success of the substitution of the -OH group with other functional groups. Followed by the strengthening of the peak intensity of 1755 cm^{-1} which indicates the presence of C=O bonds that support the success of the cellulose and nanocellulose acetylation processes.

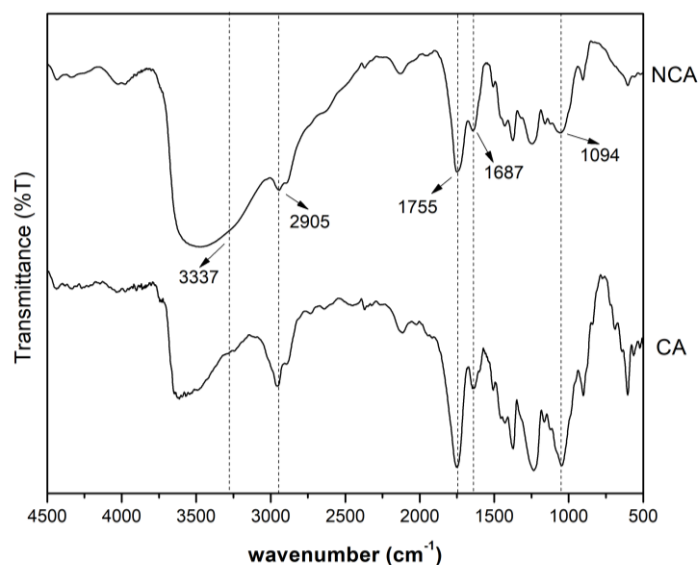


Figure 7. FTIR spectra of cellulose acetate (CA) and nanocellulose acetate (NCA)

X-Ray Diffractogram (XRD) of Cellulose acetate and Nanocellulose acetate

Figure 8 is an XRD diffractogram of cellulose acetate and nanocellulose acetate. Unlike the cellulose and nanocellulose diffractograms, the modified diffractograms are more amorphous. It is indicated by the disappearance of sharp peaks at 11° and 22° and changes to weak absorption in the 10.6° regions. This results in weak crystallinity of cellulose acetate and nanocellulose acetate caused by the replacement of the hydroxyl group with acetate (larger group) which can damage inter and intramolecular hydrogen bonds [24].

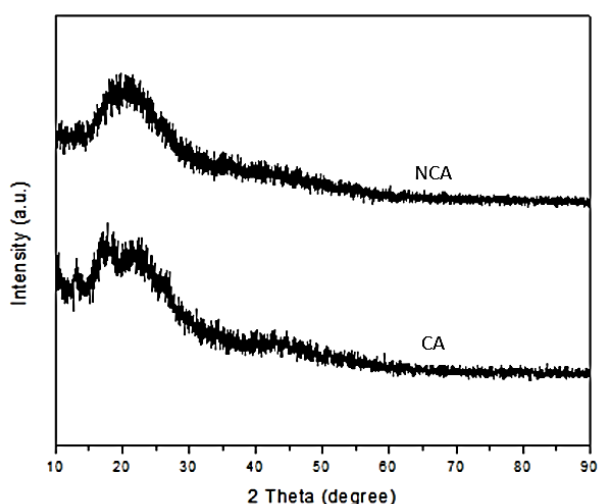


Figure 8. XRD Diffractogram of cellulose acetate (CA) and nanocellulose acetate (NCA)

Morphological of Cellulose Acetate and Nanocellulose Acetate using SEM

The results of SEM characterization of cellulose acetate and nanocellulose acetate showed that the surface of the two samples was shaped like hills and valleys, and the surface of hills and valleys on nanocellulose acetate was more evenly distributed than cellulose acetate (Figure 9). Meanwhile, the effect of particle size resulted in a more uniform surface. More peaks and valleys formed resulting in a larger surface area.

Meanwhile, the cellulose acetate and nanocellulose acetate showed different morphology. Both has uneven surface with many “hills and valleys”, in which the uneven surface on the nanocellulose acetate was more evenly distributed than on the cellulose acetate. Rivera (2021) reported about a film synthesized from a mixture of commercial cellulose acetate and Bombyx Mori silk fabrics with various blending variations. The synthesis results showed that the greater the concentration of cellulose acetate added, the film with a rougher surface was produced [2].

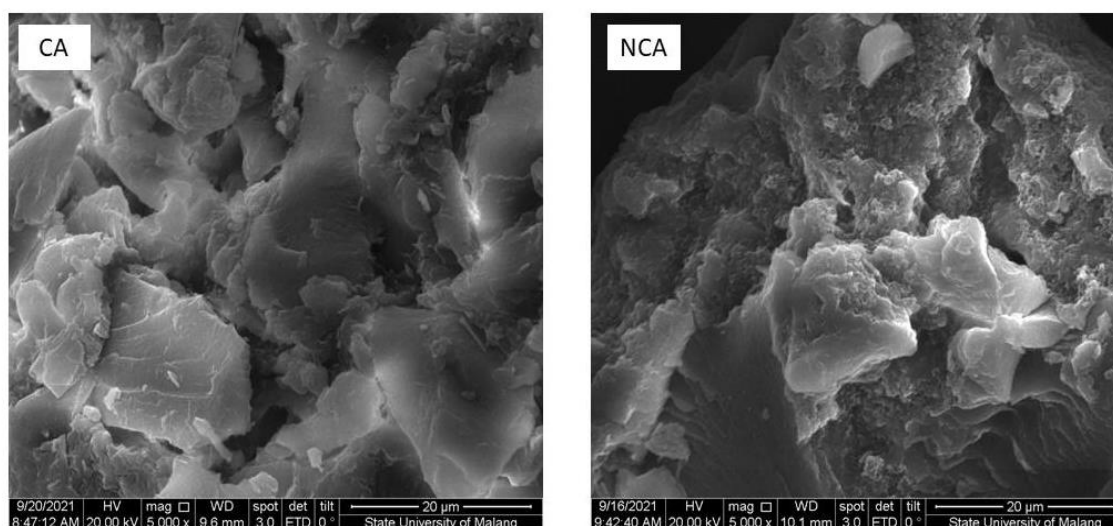


Figure 9. SEM images of cellulose acetate (CA) and nanocellulose acetate (NCA)

Degree of Substitution

Degree of substitution (DS) is the average number of hydroxyl groups that were replaced by a particular substituent in each repeating unit. This number is determined by the number of hydroxyl groups that can be chemically modified in each repeating unit [25], [26]. In this study, DS was determined according to Indonesia's SNI 0444:2009 method. The DS values of CA and NCA are shown in **Table 2**. DS of CA is greater than NCA, this shows that the surface area is more responsible. The wider the area of cellulose, the better the chemical replacement reaction will work.

Table 2. Degree of substitution of CA and NCA

Sample	DS
CA	2.9
NCA	2.1

Solubility Tests

Figure 10 shows the appearance of the solubility test of cellulose acetate and nanocellulose acetate with various types of solvents that have different polarities. Based on the results of the solubility test for water, acetic acid, chloroform and n-hexane, cellulose acetate and nanocellulose acetate are soluble in water and acetic acid, slightly soluble in chloroform and insoluble in n-hexane. Both cellulose acetate and nanocellulose acetate are perfectly distributed to form a turbid solution in water, completely soluble in acetic acid, separate to form two layers in chloroform and insoluble in n-hexane. Based on the results of solubility test, these results are accordance with the DS value and the expected result.

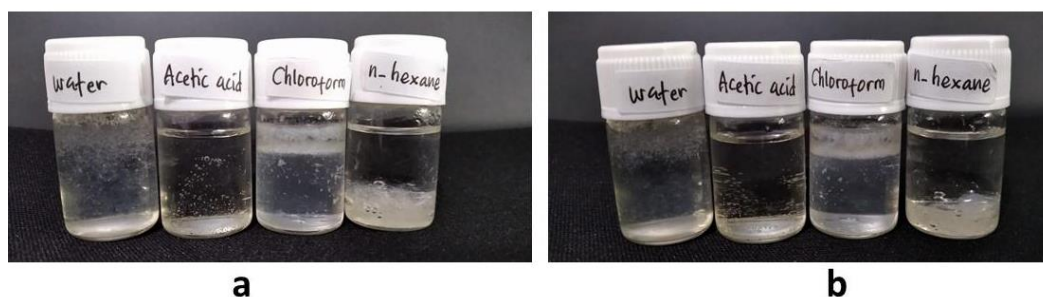


Figure 10. Solubility test of cellulose acetate (a) and nanocellulose acetate (b) in water, acetic acid, chloroform, and n-hexane

CONCLUSION

Based on the results of research and discussion, it can be concluded that cellulose was successfully isolated from sengon wood. hydrolysis of the synthesized cellulose using 60% formic acid solution produces nanocellulose with a diameter of 13.41 nm and a length of 82.35 nm. Cellulose acetate and nanocellulose acetate can be synthesized through the esterification reaction of sengon wood cellulose using glacial acetic acid, acetic anhydride, and sulfuric acid as catalysts. The degree of substitution of cellulose acetate was 96%, while the degree of substitution of nanocellulose acetate was 68%. The results of the solubility test showed that cellulose acetate and nanocellulose acetate were soluble in water and acetic acid, slightly soluble in chloroform and insoluble in n-hexane.

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