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Isolation of Cellulose Nanocrysral from Oil Palm Empty Fruits Bunches with Hydrolysis Method using H_2SO_4 54%.

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Abstract. Isolation and characterization of cellulose nanocrystal from oil palm empty fruit bunch (OPEFB), obtained from PTPN IV Adolina, by hydrolysis method using 54% sulfuric acid have been done. The isolation process was carried out in two stages; i.e. α-cellulose insulation from OPEFB, followed by isolation of cellulose nanocrystal from α-cellulose. OPEFB was de-lignification with 3.5% nitric acid and sodium nitrite, then the residue was treated with 17,5% sodium hydroxide, and bleached with H_2O_2 10%. Isolation of Cellulose nanocrystal was done using 54% sulfuric acid. The result of transmission electron microscopy (TEM) analysis shows that the diameter of cellulose nanocrystal is 66,6 nm. FTIR spectra show the C-O-C stretch of α-cellulose and cellulose nanocrystal at 1141 cm-^{1}, which indicates that there is glycoside bonding in the compound structure. The peak near 3200-3490 cm^{-1} is representative of the C-H and O-H groups. TGA curves show that α-cellulose occurs to decompose at around 315ºC, while cellulose nanocrystal occurs to decompose at 163ºC. The amount of char residue at 500°C in cellulose nanocrystal was remarkably higher compared to α-cellulose i.e. 30.5% and 7.2% respectively.

Keywords: Oil palm empty fruit bunch (OPEFB), α-cellulose, hydrolysis, characterization, cellulose nanocrystal,

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1 Introduction

Oil palm (*Elaeis guineensis Jacq*) is one of Indonesia's leading plantation commodities. Data shows that the area of oil palm plantations in Indonesia in 2009 reached 7.5 million hectares and is the largest oil palm plantation in the world (Badrun, 2010). The increase in the area of oil palm land, followed by an increase in the number of factories, is also followed by an increase in damage to the quality, quantity of natural resources (in the form of pollution and depletion), and the environment. This is due to the weight of palm oil processing waste being disposed of more and more. (Widhiastuti, 2001).

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During the processing of palm oil into palm oil, one ton of fresh fruit bunches (FFB) 0.21 tons of palm oil, and 0.05 tons of palm kernel will be produced, the rest is waste in the form of empty bunches, coir, and seed shells. Empty Palm Oil Bunches (TKS) is a solid waste produced from the processing of fresh fruit bunches (FFB) with an amount of 22-23% FFB. EFB contains 45.95% cellulose, 22.84% hemicellulose, 16.49% lignin, 1.23% ash, 0.53% nitrogen, and 2.41% oil (Darnoko, 1992).

The utilization of TKS as a ground cover or as a soil conditioner or organic fertilizer is less successful than its use even after going through composting. This is because TKS waste takes a long time to decompose, so it must be considered both in terms of cost, energy, and effectiveness. In the process of burning EFB, on the other hand, open pollution will be produced as a result of the production of carbon monoxide into the air (Suwadji, 2001).

Cellulose is a fibrous substance found in plants. Each large cellulose molecule contains several thousand -D-Glucose units linked together to form long chains with -1,4 bonds (McMurry, 1992). In each isolation method, cellulose cannot be obtained in a pure state, but only obtained as a less pure product which is usually called -cellulose. This term was defined by Cross and Bevan (1912) for wood cellulose which is insoluble in strong sodium hydroxide. The part that is soluble in alkaline media but can precipitate from the neutralized solution is called -cellulose. -cellulose is the name for the part that remains soluble even in a neutralized solution (Fengel, 1995).

Nanotechnology is the understanding and mastery of matter at dimensions around 0.2 - 100 nm, which will allow for new applications (Gardner, 2008). Cellulose nanocrystals are crystalline nanoparticles made of cellulose, which are very relevant for the development of biomaterials. These cellulose nanocrystals can be utilized in the preparation of biomedical devices, implants, and textiles given their biocompatible and non-toxic properties (Benavides, 2011). Recent research has shown that cellulose nanocrystals are suitable for use as reinforcement in thermoplastic composites (Postek, 2011).

Nanoparticles can be used for drug delivery purposes, both as drug formulations and as drug carriers. Current research is focused on cancer therapy and diagnosis, although many challenges need to be solved. Many different formulations involving nanoparticles have been used for drug delivery, namely: albumin, solid fat formulations, gelatins, hydrogels, and poly-alkyl cyanoacrylate composites. The purpose of drug adsorption in nanoparticles is to increase drug delivery and absorption by cells (Schenier, 2006).

The isolation process of cellulose nanocrystals can be carried out by two procedures, namely: The first procedure is by hydrolysis using H_2SO_4, while the second procedure is by dispersion in an organic medium (DMAc/LiCl). Acid hydrolysis is a process known to remove amorphous regions. This process will produce a stable suspension of cellulose nanocrystals in water (Bondeson, 2006). Based on the description above, the authors are interested in isolating cellulose nanocrystals from empty oil palm fruit bunches by acid hydrolysis method, using 54% sulfuric acid.

2 Materials and Methods

2.1 Equipments

In this study, a Shimadzu FTIR device, a JEOL JEM 1400, and a TGA Shimadzu TA 50 instrument were used. The glassware used was made of pyrex.

2.2 Materials

The materials used in this study were Empty Palm Oil Bunches (TKS) obtained from PTPN IV Adolina, nitric acid, sodium nitrite, sodium hydroxide, sodium sulfite, sodium hypochlorite, hydrogen peroxide, sulfuric acid, and Ammonium molybdate produced by Merck, as well as aqua dest. In this study, 25 dialysis membrane was also used.

2.3 Isolation of -Cellulose from EFB

A total of 75 grams of EFB powder was reacted with 1 L of 3.5% HNO_3 and 10 mg of $NaNO_2$, heated at 90°C for 2 hours to remove lignin which would dissolve to form nitro lignin. After washing the residue until neutral, it is digested with a solution containing 750 ml of 2% NaOH and 2% Na_2SO_3, heated at 50°C for 1 hour. The residue was washed until neutral, filtered, and bleached with 1.75% NaOCl at 100°C for 0.5 hours. The residue that has been washed and filtered is then reacted with 500 ml of 17.5% NaOH at 80°C for 0.5 hours. The bleaching process was carried out using 10% H_2O_2 at 60°C for 15 minutes. The cellulose obtained was washed and filtered, and dried in an oven at 50°C (Ohwoavworhua, 2005).

2.4 Spectroscopy Transmission Electron Microscopy (TEM) Analysis

Morphological analysis of cellulose nanocrystals was carried out using a Transmission Electron Microscopy JEOL JEM 1400 with a voltage of 120 kV.

2.5 Thermogravimetric Analysis (TGA)

Thermal degradation analysis was carried out using a Shimadzu TA 50. The temperature was programmed, from a temperature of 0°C to 500°C with a heating rate of 10°C/minute. This assay was carried out under a nitrogen atmosphere (20 ml/min) to prevent thermo oxidative degradation.

2.6 Infrared Fourier Transform (FTIR) Analysis

Functional group analysis was carried out using the Shimadzu IRPrestige-21. The result is displayed as a wavenumber curve from 4000-500 cm^{-1}.

3 RESULT AND DISCUSSION

3.1 TEM Analysis

The results of the analysis of the morphology of cellulose nanocrystals using TEM can be seen in Figure 1. From the image, it can be seen that crystalline particles are separated from each other. From the figure, the diameter size of the resulting nanocrystals can be obtained. Based on the measurements, the diameter length of the cellulose nanocrystals was 66.6 nm. From these results, it can be concluded that cellulose nanocrystals have been isolated from EFB because the range of nanoparticles is 0.2 nm – 100 nm.

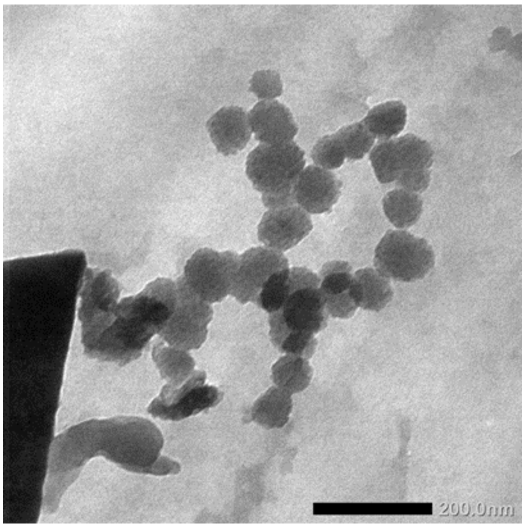

Figure 1.The morphology analysis of nanocrystal cellulose by TEM

3.2 FTIR Analysis

Functional group analysis with FTIR has been carried out using the Shimadzu IRPrestige-21 tool. The samples analyzed were α-cellulose and cellulose nanocrystals obtained from EFB fibers. The spectrum of samples of α-cellulose and cellulose nanocrystals in the wavelength range of 4000-500 cm^{-1} can be seen in Figure 2. The peak around 3200-3490 cm^{-1} indicates the presence of C-H and O-H groups in -cellulose and nanocrystal cellulose. The peak around 1640 cm^{-1} indicates the presence of water absorption. The absorption area at wave number 2893 cm^{-1} and fingerprint area 894 cm^{-1} indicate absorption from the C-H (1H) or alkane group. The presence of an absorption area at 1141 cm^{-1} indicates the presence of C-O-C groups in the sample. This absorption is derived from the glycoside bonds contained in the structure of cellulose and nanocrystal cellulose compounds.

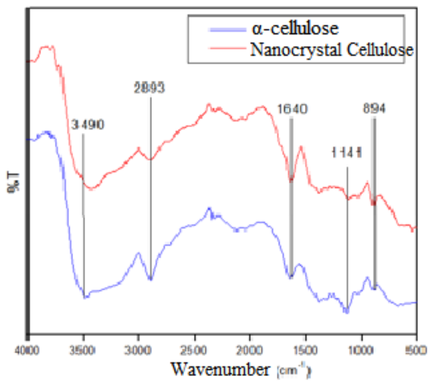

Figure 2. FTIR Spectrum of α-Cellulose and Cellulose Nanocrystals

3.3 TGA Analysis

TGA analysis aims to compare the thermal stability between -cellulose and cellulose nanocrystals. The results of the TGA analysis can be seen in Figure 3. The initial mass decrease occurs at temperatures below 100°C. This decrease was caused by the evaporation of water from the sample because α-cellulose and cellulose nanocrystals were hygroscopic. Decomposition of α-cellulose began to occur at a temperature of 315°C to 400°C. The maximum mass decrease occurs at a temperature of 380°C. On the TGA curve of cellulose nanocrystals, it can be seen that there are three decomposition points. The initial decomposition process occurs at a temperature of 163°C, then occurs at a temperature of 259°C and 350°C. Cellulose nanocrystals showed a much larger residual mass than -cellulose, which were 30.5% and 7.2%, respectively, at 500°C.

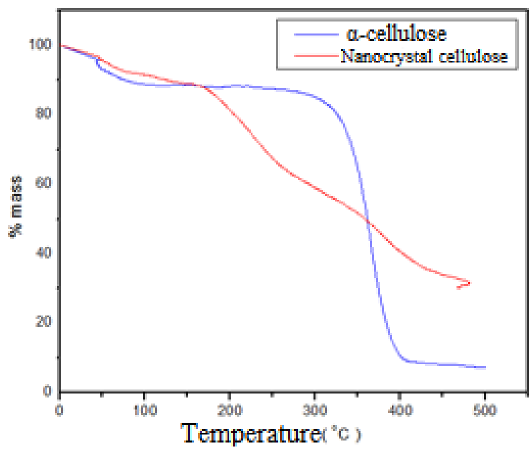

Figure 3 TGA curves of -Cellulose and Cellulose Nanocrystals

4 Conclusion

Based on the results of the research, it can be concluded as follows:

The research obtained nanocrystals in the form of clear needle crystals as much as 35% of the initial mass of cellulose. The results of morphological analysis using TEM showed that the length of the diameter of the cellulose nanocrystal was 66.6 nm. Functional group analysis by FTIR showed the presence of C-H and O-H groups as well as C-O-C groups. The results of TGA analysis showed that -cellulose began to decompose at a temperature of 315oC, while cellulose nanocrystals began to decompose at a temperature of 163oC.

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