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RESEARCH NOTE

Isolationand Characterization of Nanocrystal from Corncob Waste Using H_2SO_4 Hydrolysis Method

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ABSTRACT

Corncob is one of the industrial waste has cellulose content of 39.1 wt%, which makes it has high potential to be a raw material in the production of cellulose nanocrystal. Corncob was delignificated with 3.5 wt% HNO_3 and $NaNO_2$ 10 mg, precipitated process with 17.5 wt% NaOH, and bleached with 10 wt% H_2O_2. Cellulose nanocrystal was obtained by hydrolysis using 45 wt% H_2SO_4. Corncob and cellulose nanocrystal was characterized by Fourier Transform Infra Red (FTIR) and showed that the absorption peak indicated the presence of cellulose clusters was obtained from corncob and cellulose nanocrystal has many similarities and there was no new bond formation. Cellulose nanocrystal particle size was observed by Transmission Electron Microscopy (TEM) and the result showed the size of cellulose nanocrystal was 9-29 nm. Crystallinity index of cellulose nanocrystal from corncob determined by X-Ray Diffraction (XRD) was 70%. This showed the atomic structure of cellulose nanocrystal quite regular so obtained a high crystallinity index.

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1. INTRODUCTION

Cellulose is the abundant organic compound which can be found in plants, animals, and some bacteria. One of material contains cellulose is corncob, where corncob has lignocellulose consists of cellulose, hemicellulose, and lignin [1]. Corncob has around of 39.1% cellulose, 42.1% hemicellulose, 9.1% lignin, 1.7% protein and 1.2% ash [2]. Corncob has cellulose can be utilized as additional material or filler that processed further to be cellulose nanocrystal (NCC).

Cellulose nanocrystal (NCC) is nanoparticle was obtained by sulfuric acid hydrolysis [3]. NCC is easy to find and overflow in nature, has very small size and typical properties, such as the ratio of surface to the large volume and high crystallinity [4, 5]. These properties make NCC has an advantage when used as filler on polymer material because it can improve mechanical properties and better stress transfer [6].

Many researchers have utilized organic material to be made as additional material or filler. NCC can be produced from some sources such as switchgrass [7], kenaf bast fibers [8], cellulose microcrystal (MCC) [9], cotton [10], softwood [11], and even office waste paper [12].

The production of NCC has been done by many previous researchers with various processes and methods. One of the methods that can be used to produce NCC is by sulfuric acid hydrolysis. As for some previous research have used this method; as did by Meng et al. [7] used this method to produce NCC from switchgrass; which was hydrolyzed by sulfuric acid 60 wt% at 45 ºC for 60 minutes under constant stirring. Mariano et al. [13], hydrolyzed sisal fiber by sulfuric acid 64 wt% at 50 ºC for 40 minutes. Orue et al. [12], hydrolyzed office waste paper by sulfuric acid 64 wt% at 45 ºC for 30 minutes. The NCC was obtained from that processes can be utilized or applicated as filler on polymer product, such as filler on natural rubber latex film [14], as filler on nanocomposite [15], and filler on bioplastic [16]. Using NCC as filler in polymer material has many advantages especially to increase the mechanical properties of polymer-based products.

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In this research, NCC was processed by cellulose hydrolysis method from corncob waste using sulfuric acid 45 wt% at 45 ºC for 45 minutes. The result of hydrolysis process produces NCC that used as filler in natural rubber latex product, where the resulting NCC will be analyzed first according to criteria of the nanoparticle.

2. RESEARCH METHOD

2. 1. Materials Corncob as the raw material was obtained from the local market at Jalan Dr. Mansyur, Universitas Sumatera Utara (USU), Medan, North Sumatera. Aquadest (H_2O), nitric acid (HNO_3), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium hypochlorite (NaOCl), hydrogen peroxide (H_2O_2), sodium nitrite ($NaNO_2$), sodium sulfite (Na_2SO_3) were obtained from CV. Multi Kreasi Bersama, Medan, Indonesia.

3. RESEARCH PROCEDURE

3. 1. Corncob Preparation Corncob was washed and soaked for 2 hours. Then was dried in the sun for two days. After that, it was battered and blended until soft fibers were obtained [17].

3. 2. α-Cellulose Isolation from Corncob The corncob fiber much as 75 gram was put in beaker glass, then it was being added to 1 L mixture of 3.5 wt% HNO_3 and 10 mg of $NaNO_2$, after that it was heated on a hot plate at 90 ºC for 2 hours. Then, it was filtered and the fiber was washed until the filtrate is neutral. Next, it was heated with 750 ml of 2 wt% NaOH and 2 wt% Na_2SO_3 solution at 50 ºC for 1 hour. After that, bleaching was conducted with 250 ml solution of 1.75 wt% NaOCl at boiling temperature for 30 minutes. It was filtered and the fiber was washed until the filtrate was neutral. Then, the α-cellulose purification from the sample was undertaken with 500 ml of 17.5 wt% NaOH solution at 80 ºC for 30 minutes. After that, it was filtered and washed again until the filtrate was neutral. The bleaching process was taken with 10 wt% H_2O_2 at 60 ºC in the oven for 1 hour. Then, it was filtered and washed until the filtrate was neutral [17].

3. 3. Cellulose Nanocrystal Isolation from α-Cellulose One gram of α-cellulose was dissolved in 25 ml of 45 wt% H_2SO_4 at 45 ºC for 45 minutes. After cooled down, it was added with 25 ml of aquadest and left out for one night, until the suspension was formed. The suspension was centrifuged at the speed of 10,000 rpm for 25 minutes until pH was neutral. Then, it was ultrasonicated for 10 minutes, put in dialysis membrane and soaked in 100 ml of aquadest. It was left out for 4 days while stirred. After that, aquadest was being evaporated at 70 ºC to obtain the cellulose nanocrystal [17].

4. RESULT AND DISCUSSION

4. 1. Fourier Transform Infra-Red (FTIR) Characterization FTIR characterization from corncob waste and cellulose nanocrystal (NCC) can be seen in Figure 1.

Figure 1 shows the result FTIR analysis of corncob and NCC where spectrum peaks indicate the existence of alcohol O-H, alkane C-H, alkene C=C, aldehyde C=O and ether C-O clusters, which are clusters of cellulose. The absorption peak at the wave number 3394 cm^{-1} indicates existence of -OH cluster (3300-3500 cm^{-1} refer to -OH stretching), the absorption peak at the wave number 2893 cm^{-1} indicates existence of C-H cluster [18], and the absorption peak at the wave number 1639 cm^{-1} shows similar results with the previous research that at this wave number states the presence of the -OH cluster of water absorption [7].

Figure 1 shows that the characteristics of corncob and NCC obtained by chemical treatment have many similar, but there are some cluster changes from FTIR test results from corncob and NCC, that is at the absorption peak with the wave number 1246 cm^{-1} indicates the existence of the ether C-O cluster which shows the existence of lignin and hemicellulose in corncob. Other than at the absorption peak with the wave number 1720 cm^{-1} indicates the cluster C=O which is a typical cluster existing in lignin. The loss of absorption peak at the wave number 1246 and 1720 cm^{-1} in the result FTIR analysis of corncob and NCC showed that the existence of lignin and hemicellulose were well finished by the delignification process with acid treatment, and bleaching that works to remove lignin and hemicellulose from lignocellulose [19].

4. 2. Transmission Electron Microscopy (TEM) Characterization TEM characterization of NCC was aimed to analyze the size of NCC particle resulted from acid hydrolysis process and ultrasonication.

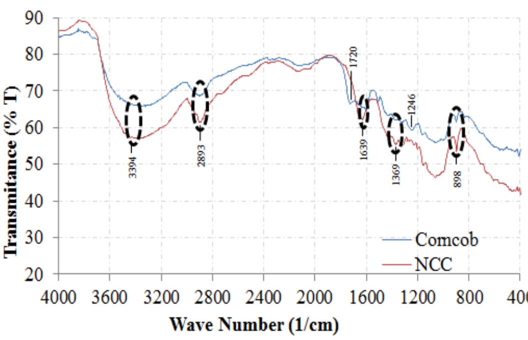

Figure 1. FTIR Analysis of Corncob and NCC

TEM characteristics of NCC are shown in Figure 2. Figure 2 shows that the NCC resulted is the particle with a spherical shape, with irregular position and non-uniform size. From the figure, can be calculated the size of NCC with average particle size of 9-29 nm. It is evident that NCC results processed by strong acid hydrolysis from corncob waste obtained have met the criteria of nanoparticle size, where nanoparticle is a particle with the size of 1-100 nanometers [20]. The size was obtained by acid hydrolysis process using sulfuric acid as hydrolysis agent, and the breaking of cellulose bond by the ultrasonic wave at ultrasonication process. In acid hydrolysis, the hydrolysis reaction that occurs produces hydro cellulose with a low degree of polymerization, but higher crystallinity. This is the cause of the change in cellulose particle size [21]. After the hydrolysis process is complete, the excess of sulfuric acid in the suspension should be discarded using centrifugation. During the centrifugation process, the precipitate is taken and separated, then neutralized. To obtain the more stable dispersion, ultrasonication process is done on the cellulose nanocrystal suspension. Then, the suspension separated using dialysis membrane. At the time of separation, the NCC will out of the membrane and the cellulose not nano-size will stuck on the membrane. The average size of cellulose nanocrystal from TEM analysis can be calculated from Equation (1) [22].

$$x = \frac{scale\ size \times diameter\ of\ picture}{scale\ lenght} \quad (1)$$

In the previous research by Harahap et al. [23] NCC produced from bagasse waste as raw material that processed by sulfuric acid hydrolysis and resulted NCC has a rod shape with the average size of 40-160 nm. It is shown that the NCC obtained from corncob has the average particle size smaller than NCC obtained from bagasse waste.

The size of particle resulted is highly influential on the further utilization of NCC, which the impact can be seen on the quality of the products produced. Like the application of NCC as a filler of polymer products, the small particle size produces a large surface area which can to bind and spread equally and expand the contact area, so produced the product that has better mechanical properties.

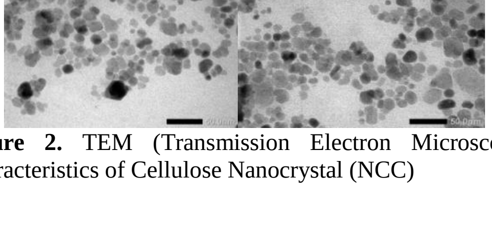

Figure 2. TEM (Transmission Electron Microscope) Characteristics of Cellulose Nanocrystal (NCC)

4. 3. X-Ray Diffraction (XRD) Analysis X-Ray Diffraction (XRD) was used to analyze crystallinity of NCC. The result from crystallinity test using XRD is shown in Figure 3.

From Figure 3, can be seen the absorption peak that resulted are at 2θ = 12,34°, 20,18° and 22,14°. Base on the absorption peak the crystallinity index of NCC that resulted from corncob can be calculated. Crystallinity can be determined by various methods, one of them is X-ray diffraction (XRD), that based on the system of crystalline and amorphous diffraction spectrum [24]. The crystallinity of NCC can be calculated by using Segal method from Equation (2) [25]:

$$CrI = \frac{I_{002} - I_{AM}}{I_{002}} x\ 100\% \quad (2)$$

From Figure 3, it can be known that crystallinity index of cellulose nanocrystal by Segal method is 70%, indicated by sharp absorption peak from spectra produced by cellulose nanocrystal sample. The resulted absorption peak from cellulose nanocrystal sample. If viewed from the previous research, the crystallinity index of NCC resulted from bagasse waste is 92.33% [23]. It is indicated that the NCC resulted from corncob waste and bagasse waste have the high of crystallinity index. The high crystallinity index indicates that the hemicellulose and lignin in the amorphous part have been successfully removed by delignification process and bleaching, where the high crystallinity index has good reinforce effect on the polymer material, so it can improve the mechanical properties and thermal resistance of the material [14, 26].

5. CONCLUSION

NCC was obtained by hydrolysis method using sulfuric acid 45 wt% at 45 °C for 45 minutes from corncob waste shows the peaks of the spectrum have the existence of cellulose clusters from FTIR analysis. It is also visible that the existence of lignin and hemicellulose in the NCC have been well ended by delignification process and bleaching.

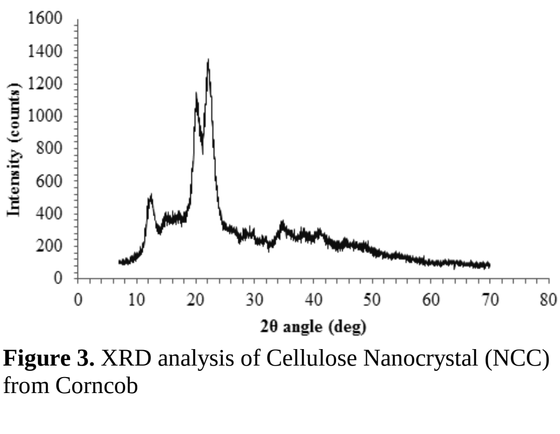

Figure 3. XRD analysis of Cellulose Nanocrystal (NCC) from Corncob

NCC that resulted has the spherical shape with the average size of 9-29 nm and the crystallinity index of 70%. This result shows that the very small sized of NCC and high crystallinity index has a good impact when used as a filler in polymer-based products.

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چکیده

تفاله ذرت یکی از ضایعات صنعتی است که حاوی 39 درصد سلولز است، ماده اولیه مناسبی برای تولید نانوکریستال سلولز محسوب می شود. تفاله ذرت با استفاده از محلول 3/5 درصد وزنی اسید نیتریک و 10 میلی گرم نتریت سدیم و محلول سود 17/5 درصد لیگنین زدائی شده است سپس با محلول اب اکسیژنه 10 درصد وزنی سفید شده است. نانوکریستال سلولز با هیدرولیز اسید سولفوریک 45 درصد انجام شده است. مشخصات تفاله ذرت و نانوکریستال سلولز با استفاده از FTIR تعیین گردید. طیف های جذب بدست آمده نشان داده است که توده های سلولز از تفاله ذرت با نانوکریستال سلولزتشابه مطلوبی داشته است و پیوند جدید تشکیل نشده است. اندازه ذرات نانوکریستال سلولز توسط TEM مشاهده گردید در محدوده 29–9 نانومتر بوده است. اندیس و درجه کریستالی نانوکریستال سلولزاز تفاله ذرت با استفاده از اشعه ایکس و XRD بمیزان 70 درصد تعیین گردید. این نتایج نشان میدهد که ساختار اتمی نانوکریستال سلولز کاملا متعارف بوده که از اندیس کریستالی مطلوبی برخوردار است.

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