The Effect of Delignification Time on % Yield of Alpha-cellulose from Bamboo Fiber (Bambuseae) Properties

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Keywords: Alpha-cellulose, Bamboo Fiber, Biocomposite, Biopolymer.

Abstract: Bamboo fiber (Bambuseae) has cellulose content that can be used as a filler in the composites. The objective of this study is to obtain alpha cellulose from bamboo fiber, through the isolation process. This study was carried out using the delignification method with NaOH solvent on temperature at 80°C and the time variations of 30, 60, 90, 120, 180 minutes as the first stage of separation of alpha cellulose from other compounds contained in bamboo fiber. The results showed that the optimum condition of delignification time was 60 minutes with yield of 55.26%. The FTIR spectra was performed to confirm the formation of the product (alpha cellulose) proved by spectrum indicating the presence of the cellulose compound characterized by peak formation in 1641 cm^{-1} absorption area by comparing the cluster on the reaction alpha cellulose with the cluster on the bamboo fiber. XRD result showed that the crystalline portion of alpha cellulose was higher than amorf portion of alpha cellulose itself with the total amount of crystallinity index was 93.3%.

1 INTRODUCTION

Bamboo is a plant of tropical and subtropical regions. Naturally, bamboo can growth in primer forest and also in secunder forest (former farm and grower). Bamboo is classified as a non-timber forest product, which is known by the community as a versatile plant. It is said like that because this plant can be used for various purposes, one of the benefits is as an alternative to wood. Bamboo is easily obtained at a relatively cheap price and the production age is relatively fast. Bamboo is included in natural fibers where natural fibers that can be directly obtained from nature. The amount of cellulose in fiber varies according to the source and it is usually related to materials such as water, wax, pectin, protein, lignin and mineral substances.

As a source of fiber, bamboo has a cellulose content of 60.8% and lignin 32.2% with mechanical strength ranging from 140-800 MPa (Liu et al., 2012). The high potential of bamboo causes bamboo fibers can be processed and developed into products with high economic value, one of them as a reinforcement in the composite. One of the cellulosic content is alpha-cellulose which has a high glossy fiber tensile strength and settles on a concentration of 17.5% NaOH solution. Cellulosecan be differentiated based on the degree of polymerization (DP) and solubility in the 17.5% sodium hydroxide compound (Klemm et al., 1998). Figure 1 and 2 show the cellulose and alpha-cellulosestructures.

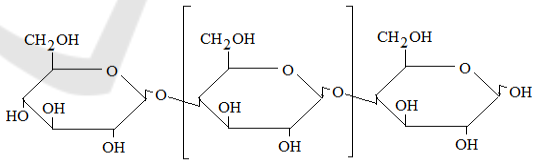

Figure 1: Cellulose Structure (Nuringtyas, 2010).

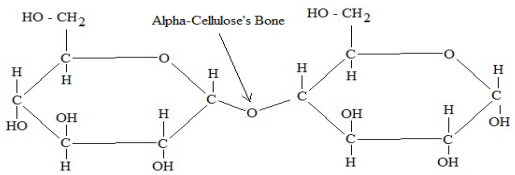

Figure 2: Alpha Cellulose Structure (Nuringtyas, 2010).

The previous research on the effect of delignification time on % yield alpha cellulose derived fromkepok banana peel showed the optimum condition was at 2 hours with yields of

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23.72% (Yannasandy et al., 2017). Moreover, klutuk banana stems (Musa Balbisiana Colla) showed the best % yield of alpha cellulose was 28.77% (Zulaekha et al., 2018)and the green coconut showed (Cocos Nucifera L.) the best % yield of alpha cellulose was 30.01% (Damanik et al., 2016).

The method that used to isolate alpha cellulose is the method of deposition of alpha cellulose with 17.5% NaOH solution by heating it in a magnetic stirred heater (Putri & Gea, 2018). In this study we tried to examine the effect of cooking time on % yield alpha cellulose from bamboo fiber.

2 METHODS

2.1 Materials

The chemicals that used in this study were aquadest, HNO_3, $NaNO_2$, NaOH, Na_2SO_3, NaOCl, NaOH, and H_2O_2which obtained as received. Bamboo fiber obtained from residential housing in Deli Serdang, North Sumatera.

2.2 Preparation of Fiber from Bamboo

Bamboo was cut into small pieces and washed with water then curled under the sun for 2 hours. The dried bamboo was mashed with a grinder to get 90 mesh. Fiber was carried out in three stages of the chemical process, namely delignification, alkalization, and bleaching to produce alpha cellulose.

2.3 Isolation Alpha Cellulose

2.3.1 Delignification Process

Delignification processaims to remove lignin which contained in the fiber.The bamboo fiber was weighed 75g and then put into a beaker. It was added 3.5% HNO_3 and 10 mg $NaNO_2$and stirring for 120 minutes at90^oC.

2.3.2 Alkaline Process

The alkalization process aims to remove impurities which contained in the fiber. Alkalization process consist of alkalization process I and II. Alkalization process I added 2% NaOH and Na_2SO_3 2% stirring for 60 minutes with temperature 50^oC. Alkalization process II added 17.5% NaOH and stirring for30 minutes at 80^oC.

2.3.3 Bleaching Process

The bleaching stage aims to remove the remaining lignin from the alkali. Bleaching process consists of bleaching process I and II. Bleaching process I used 1.75% of NaOCl with stirring process for20 minutes at 60^oC. The bleaching process II used 10% of H_2O_2 with stirring process for60 minutes at 60^oC.

2.4 Yield Calculation

The alpha cellulose results in the form of residual residue on boiling flask are then dried by using an oven at 80^oC for 1 hour. Weighing the weight of the fiber. Weighing the weight of the residue after extraction. Yields Percentage is calculated using equation (1).

$$Yield(\%) = \frac{Massof Residu}{Massof Sample} x\ 100\ \% \quad (1)$$

2.5 Lignin Content using Klason Method

The delignification time was made by using 17.5% of NaOH solution above the hot plate at 80^0C with variables of time are 30, 60, 90, 120, 180 minutes. The delignification process by the klason method aims to separate alpha cellulose from lignin. Chemicals added during the delignification process are expected to reduce % lignin.

Alpha cellulose was weighed 2g for samples (B) were put 500 ml glass beaker for alpha cellulose and then soaked in water that has been given ice for 20 minutes, then added 72% H_2SO_4 as much as 40 ml for alpha cellulose, stirred slowly while stirring for 2 hours then 400 ml of aquadest for alpha cellulose into 2000 ml for alpha cellulose. 1540 ml of water added for alpha cellulose. So the concentration of sulfuric acid becomes 3%. Then the solution is heated to boiling and left on a water bath for 4 hours with low heat. Allow the sample to stand until the lignin deposits settle completely. Then filtered with filter paper in a beaker glass that has been known the weight. The lignin wash deposits until acid free with hot water (test with litmus). The filter paper are dried in oven at 105^oC for 3 hours, cooled in a desiccator and weighed to a constant weight (A).Calculation of lignin content can be calculated with the equation below.

Calculation of Lignin Content:

$$X(\%) = \frac{A}{B} x\ 100\ \% \quad (2)$$

Information:

X = Value of lignin content,(%)
A = Weight of lignin precipitate, (g)
B = Weight of dry sample, (g).

2.6 Characterization of X-ray Diffraction (XRD) Analysis

The determination of the crystallinity index of cellulose material can be calculated through the segal method, with the equation below.
Segal method:

$$Crl = \left[\frac{I_{002} - I_{AM}}{I_{002}}\right] \quad (3)$$

Information:
I_{002} = The maximum intensity of the 002 diffraction pattern which is a representation of the two zones, namely the crystal zone and amorphous zone.
I_{AM} = The intensity of the diffraction in the same unit which is a representation of the amorphous zone.

2.7 Characterization of Fourier Transform Infrared (FTIR) Analysis

FTIR testing is carried out to determine the chemical bonds of alpha cellulose fibers at chemical treatment. The FTIR specification is Nicolet iS10 FT-IR Spectometer Instrument.

3 RESULT AND DISCUSSION

3.1 Effect of Delignification Time on the % Yield of Alpha Cellulose

The analysis was used to know the % yield of alpha cellulose obtained from bamboo fiber. The lignin content in bamboo fiber is 24.88%. Table 1 shows the effect of delignification time on the % yield of alpha cellulose and remaining of % lignin.

Table 1: Effect of Delignification Time on The %Yield of Alpha Cellulose and Remaining of %Lignin.

Delignification time	% Yield of Alpha Cellulose	% Lignin
30	49.56	1.65
60	55.26	1.62
90	50.54	1.58
120	48.41	1.55
180	46.17	1.45

From the table above, it can be seen that in general there is an increase in the % yield of 30 minutes to 60 minutes, but there is a decrease for 90 minutes. The % yield value at 30 minutes is 49.56%, increased to 55.26%, and decreased at 90 minutes to 50.54%. The increasing of the delignification time will affect the delignification process. Where an increase in delignification time will cause more dissolved lignin and the impregnation process between the solvent and alpha cellulose is more perfect (Sjostrom, 1995).

However, at the time of delignification that is long enough will trigger the degradation of alpha cellulose compounds that cause a decrease in the yield obtained (Daud et al., 2007). From the table above, it can be seen that the longer the delignification time, the lower of the lignin content. This proves that the longer delignification time will affect the level of lignin obtained (Jalaluddin & Rizal, 2005).

The decreased percentage of lignin inside alpha cellulose is affected by temperature. Lignin will dissolve at high temperatures in the black leachate because the hydroxyl phenolate lignin group is in an ionized state to form its salt and. This treatment will break lignin into smaller particles (Ariani & Idiawati, 2011).

Lignin levels decrease with the addition of NaOH. The addition of an alkaline base in the form of NaOH will make it easier to break the bonds of lignin compounds. Figure 3 show reaction of lingocellulose bonds breaking using NaOH.

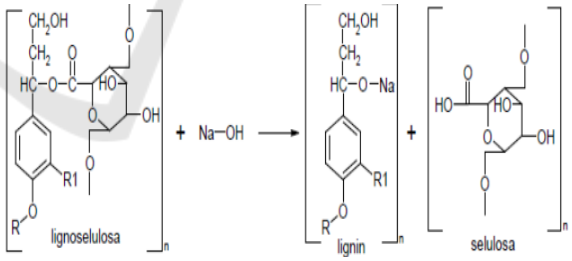

Figure 3: Reaction of Lignocellulose Bonds Breaking Using NaOH (Fengel & Wegener, 1989).

NaOH molecules will enter the lignocelluloses and break down the structure of lignin (Elwin et al., 2013). So that lignin is more soluble which results in decreased levels of lignin.

3.2 Results and Discussion of X-ray Diffraction (XRD) Analysis

The more orderly arrangement of atoms in a material is directly proportional to the higher level of

crystallinity. The determination of crystallinity of alpha cellulose was carried out by the X-ray Diffraction (XRD) method based on the amorphous crystal diffraction spectrum pattern. The results of the crystallinity test using XRD can be seen in Figure 4 below.

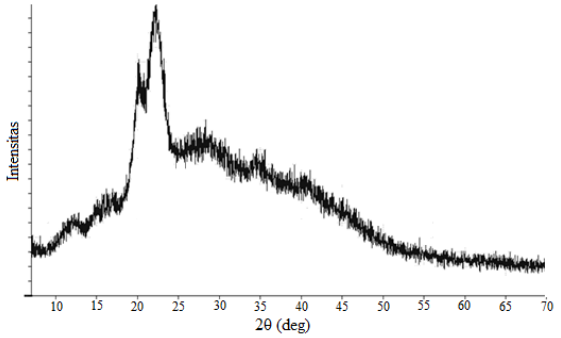

Figure 4: Alpha Cellulose XRD Spectrum Results from Alpha Cellulose.

The crystallinity index of alpha cellulose for bamboo fiber was calculated using the Segal method. The peak absorption of the spectra produced by alpha cellulose samples from bamboo fibers is at $2\theta = 22°$ and I_{AM} at $2\theta = 16°$ indicating the crystalline portion of cellulose. From the peak of the absorption can be determined the crystallinity index of alpha cellulose.

From the Segal method, the crystallinity index of alpha cellulose for bamboo fiber is equal to 93.3%, it indicated by the sharp peak absorption (sharp peak) of the spectrum produced in the alpha cellulose for bamboo fiber samples. High crystallinity shows that the arrangement of the polymer chains in the material is arranged regularly or the crystalline portion is more perfect (Lu & Hsieh, 2010). This increase in crystallinity is caused by a decrease in the amorphous fiber composition due to chemical treatment. Chemical treatment is directed at removing hemicellulose, lignin, pectin, which are fiber components that contribute to the amorphous part of the fiber (Susheel et al., 2009).

The amorphous part is more easily hydrolyzed compared to the crystalline part, so the hydrolysis treatment causes the fibers to become more crystalline (Elanthikkal et al., 2010). Alpha cellulose for bamboo fibers obtained has a high crystallinity index where the crystallinity index of alpha cellulose is usually in the range of 55-80% (Zeinali et al., 2014).

3.3 Results and Discussion of Fourier Transform Infrared (FTIR) Analysis

Bamboo fiber has components, namely lignin, hemicellulose and cellulose. The three components are composed of alkanes, esters, aromatics and alcohol (Gian et al., 2017). The characterization of Fourier Transform Infra Red (FTIR) is to identify the functional groups that exist in the alpha cellulose and compared with bamboo fiber as raw material for alpha cellulose. The characterization of FTIR and functional group absorbance regions of alpha cellulose and bamboo fiber fillers can be seen in Figure 5 and Table 2 below:

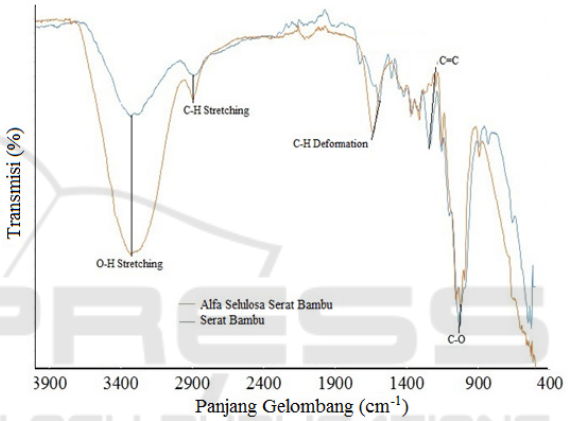

Figure 5: FTIR Spectrums of (a) Bamboo Fiber(b) Alpha Cellulose Bamboo Fiber.

Table 2: TheAbsorption peak of Bamboo and Alpha Cellulose Bamboo Fiber.

Bond Type	Wave Number (cm^{-1})	
	Bamboo Fiber(cm^{-1})	Alpha Cellulose Bamboo Fiber(cm^{-1})
O-H Stretching	3331	3334
C-H Stretching	2891	2905
C-HDeformation	1602	1641
C=C	1241	1225
C-O	1031	1024

The figure above shows the absorption peak of bamboo and alpha cellulose bamboo fibers. In the process of alkalization reduced the hydrogen bonds due to the removal of hydroxyl groups by reacting with sodium hydroxide. The results of the alkalization process showed the concentration of the -OH stretching group. The wave frequency of 3350-

3175 cm^{-1} indicates the presence of OH bonds (Zhbankov, 1966).

As seen in bamboo fibers with an absorption peak of 3346 cm^{-1} whereas in alpha cellulose bamboo fibers showed an area of absorption that was sharper at 3341 cm^{-1}. It indicates that the O-H bond was stretching due to the influence of alkalization. Alkalization reduces hydrogen bonds because the hydroxyl group reacts with sodium hydroxide which causes an increase in the concentration of -OH when compared to bamboo fibers (Łojewska et al., 2005).

Furthermore, wave frequencies from 3000-2850cm^{-1} indicates the presence of CH stretching groups (Zhbankov, 1966). Bamboo fibers are shown in the absorption area of 2891cm^{-1} and in alpha cellulose bamboo fibers appear sharper absorption area at 2905 cm^{-1}. The absorption peak shows the stretching of the C-H aliphatic group where the residual hemicellulose from the delignification process and the structural changes of the C-H bond cause the peak to shift toward the maximum (Zhbankov, 1966).

Concentration of $-CH_2$ deformation bonds was shown in bamboo fibers with an absorption area of 1602cm^{-1}. Whereas the alpha cellulose bamboo fiber looks sharper with the absorption area of 1641 cm^{-1}. It shows the crystalline area, where the absorption area will increase along with the purification process (Alves et al., 2014)

The double bond C=C of aromatic compounds is shown to have a peak at susceptible 1200-1300 cm^{-1}. The uptake of the 1241cm^{-1} area in the bamboo fiber looks sharper compared to the alpha cellulose bamboo fiber in the absorption area of 1225cm^{-1}. In the aromatic group C=C, it can be seen that lignin is still present, which means that the alkaline treatment has not completely eliminated lignin but only reduced the level of lignin (Han, 2015).

In the picture above it can also be seen that there are concentrations of C-O groups in the absorption area between 1000-1200cm^{-1}. In bamboo fiber, it can be seen that the absorption peaks appear sharper at 1031cm^{-1}, whereas in alpha cellulose bamboo fibers have absorption peaks at 1024cm^{-1}. Both samples are thought to originate from the vibration of the pyronose ring group on the cellulose unit (1035–1170cm^{-1} referring to the pyronose ring) where the absorption peak indicates enrichment of cellulose fibers and it can be proven that the sharp peak absorption of the C-O group contained in the alpha cellulose of bamboo fiber further indicate the presence of a pyronese ring which is a typical group that only belongs to the cellulose unit and is not owned by the lignin and hemicellulose components (Peng et al., 2011).

4 CONCLUSION

Alpha cellulose had been obtained succesfully from bamboo fibers by using sodium hydroxide (NaOH) solvent. It was revealed that the longer the delignification time, the higher of the yield of alpha cellulose up to 60 minutes. However, the longer delignification time up to 180 minutes, the lower of the yield of alpha cellulose. It was caused by the degradation of alpha cellulose to glucose molecules. FTIR showed that alpha cellulose from bamboo fibers have the similar structure with cellulose structure. XRD result showed that the crystalline portion of alpha cellulose was higher than amorf portion of alpha cellulose itself with the total amount of crystallinity index was 93.3%.

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