Determining Molecular Weight and Polymerization's Degree of α-Cellulose Isolated from Young Coconut Coir (Cocos nucifera L.) Using the Viscosity Method

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Abstract. Coconut coir is the largest component in coconut (Cocos nucifera L.) which contains 75% fiber and 25% cork. Coconut fiber contains cellulose as much as 54.3% with α-Cellulose 26.6% α-Cellulose is a polymer that is widely used in human life. The molecular weight and degree of polymerization are important because they directly affect the chemical properties of the polymer. The purpose of this study is to determine the molecular weight and degree of polymerization of α-Cellulose by viscosity method. The results showed that the molecular weight and degree of polymerization of α-Cellulose of young coconut coir (Cocos nucifera L.) were 3.0841 x10^4 g/mol and 171, respectively.

Keywords: Coconut, α-Cellulose, Molecular Weight, Polymerization's Degree

1 Introduction

Indonesia is a country rich in natural resources. One of them is young coconut. Coconut is a type of plant originating from the „aren-arenan" tribe or Arecaceae and the only member of the cocos genus. Young coconuts used are not limited to water and flesh, but the proportion of coconut fiber is not much and is effective and has economic value for use by the community. Every year, only about 15% of all coco coir waste is recycled by the community which proves that most of the coco coir waste is used to make doormats. This makes the coir fraction of young coconuts the largest component of waste that is dried and then burned [1]

Coconut husks occupy a sizable portion of the coconut fruit, accounting for about 35% of its total weight. Coconut coir is a valuable part of the coconut, consisting of fibers and cork that serve as an adhesive to hold one fiber to another. Each coconut contains 525 grams of fiber (75% of coir), and 175 grams of cork (25% of coir). Coconut fiber contains cellulose that is 54.3% with -cellulose 26.6% and 27.7% hemicellulose. In addition, it also contains 29.4% lignin which can be hydrolyzed into cellulose to increase the cellulose content of coir [2]. Coconut production in Indonesia averages 15.5 billion cocouts/year, which is equivalent to 1.8 million

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tons of coco fiber and 3.3 million tons of coir dust. So quite a lot of materials are available and can be processed as much as possible [3].

Cellulose is the main constituent of the plant cell wall organic compounds. In particular, cellulose has properties in the form of fibrous compounds, has high tensile strength, is insoluble in water, as well as organic solvents. Cellulose is commonly used as a reinforcing material in various polymer composites. The use of cellulose from coconut fiber is based on its high cellulose content, abundant availability, fast decomposition rate in soil, and excellent mechanical properties. Then cellulose will be further developed to meet human needs [4,5]. To obtain cellulose from lignocellulose, it is necessary to separate cellulose from hemicellulose and lignin. This is generally known as the delignification process which results in disruption of the lignocellulosic structure, where the cellulose will be more accessible and can also dissolve the lignin content of the fiber. The deligification process is generally used in alkaline solutions [6,7]. In this study we determined the molecular weight and degree of polymerization of α-Cellulose by viscosity method.

2 Experimental

Young coconut coir were taken at Medan Johor area, Medan City, North Sumatera, Indonesia, and chemicals used are Sodium Hydroxide (NaOH), Nitric Acid (HNO_3) 3.5%, Sodium Nitrite ($NaNO_2$), Sodium Sulfite (Na_2SO_3), Aquades, Sodium Hypochlorite (NaOCl) 1.75%, Hydrogen Peroxide (H_2O_2) 10%, Hydrochloric Acid (HCl) 2N; 2.5N; 3N, Acetonee (C_3H_6O).

2.1 Sample Preparation

Young coconut coir is first separated into small fibers, washed with running water and dried in direct sunlight. Dried young coconut coir cut into smaller pieces 1-2 cm. After obtaining a rough size, young coconut husks were ground using a grinding machine and sieved through a 60 mesh sieve. Young coconut powder is dried again using an oven for 1 hour at 60°C.

2.2 Cellulose Synthesis

The synthesis of cellulose from young coconut coir is carried out using an alkaline pretreatment method. 75 grams of young coconut coir powder is added with 1L of a mixture of 3.5% HNO_3 solution and 10 mg $NaNO_2$, heated at 90°C for 2 hours, filtered and the residue is washed until the filtrate is neutral, then digested with 750 mL of a solution containing NaOH. 2% and 2% Na_2SO_3 at 50°C for 1 hour, filtered and the residue was washed until the pH of the filtrate was neutral, then bleached with 250 mL of 1.75% NaOCl solution at 70°C for 30 minutes, then filtered and the residue was washed until the filtrate neutral. The product formed is cellulose. Then characterized by FT-IR test [8].

2.3. α - Cellulose Isolation

Isolation of α-Cellulose was carried out using cellulose obtained from the previous step. Cellulose was put into a 1000 mL beaker glass and heated with 500 mL of 17.5% NaOH solution at 80°C for 30 minutes, filtered and the residue was washed until the pH of the filtrate was neutral. The neutral residue was followed by bleaching with 10% H_2O_2 at 60° C for 15 minutes, filtered and washed with distilled water. α-Cellulose produced was dried in an oven at 60°C.

2.4. Microcrystalline Cellulose (MCC) Synthesis

α-Cellulose which isolated from young coconut coir waste was hydrolyzed to obtain MCC with different times and concentrations of HCl. Where as much as 10 grams of Cellulose powder was hydrolyzed with 200 mL of 2N, 2.5N, 3N HCl solution, then each was refluxed at 100°C for 15, 30, 45 minutes. Then washed with distilled water until neutral, then dried in an oven at 60°C for 4 hours, cooled, mashed and sieved through a 60 mesh sieve.

2.5. Determination of Molecular Weight

Weighed 0.025 grams of the sample to be tested. Dissolved with 25 mL of acetonee in a beaker glass, and 10 mL of the solution was put into the Ostwald viscometer. The flow time of the mixture was recorded and carried out three times. The same procedure was carried out for each sample with variations in the concentration of the solution (0.025 gr/25 mL; 0.050 gr/mL; 0.075 gr/mL).

3 Results and Discussion

3.1. Cellulose Synthesis

The manufacture of cellulose from coconut fiber is carried out in several stages, are delignification, swelling, and bleaching. In the synthesis of cellulose used 75 grams of young coconut coir powder. The first stage is the delignification process using nitric acid to open and break down the lignocellulosic structure and remove lignin in the form of nitrolignin from young coconut coir. The purpose of removing lignin is because lignin can cause stiffness of a natural material and can inhibit acid penetration before hydrolysis takes place. Meanwhile, the addition of sodium nitrite aims to accelerate the lignin degradation process [9]. This stage produces a brownish yellow pulp which indicates that the lignocellulose has softened so that the lignin is slightly soluble in HNO_3 and the pulp is filtered and washed with distilled water so that the pH is neutral.

The bleaching or bleaching stage is carried out by adding 1.75% NaOCl to the brown pulp with the aim of removing the remaining lignin that is still present in the pulp [10]. This process produces a yellowish white pulp. The results of the research on the manufacture of cellulose from young coconut coir is grayish white after drying for 1 hour at a temperature of 60oC. The results of cellulose after the delignification, swelling and bleaching stages can be seen in Fig. 2.

Fig. 2. Cellulose produced from young coconut coir powder

3.2. α-cellulose Synthesis

Isolation of -cellulose was carried out from the advanced stages of making cellulose, namely delignification, swelling and bleaching. The steps taken were the separation of and cellulose using 17.5% NaOH. Where according to Nuringtyas, 2010 that and cellulose is soluble in 17.5% NaOH while α-cellulose is insoluble. The result of dissolving using 17.5% NaOH produces a yellow pulp. The next step is to bleach the pulp using 10% H_2O_2. This process aims to improve brightness, improve purity, minimize degradation of cellulose fibers and dissolve residual lignin compounds by degrading long lignin chains by bleaching chemicals into short lignin chains, so that lignin can be dissolved during washing in water or alkali [11].

Fig. 3. α-Pure cellulose produced from young coconut coir powder

In the bleaching process, two reactions occur, namely chlorination and oxidation. This reaction causes a change in the color of the cellulose from grayish white to white and the lignin becomes easily soluble in water so that when washing, the lignin will be carried away by water and the remaining -cellulose. The resulting α-cellulose is white. In the -cellulose isolation process, 75 grams of young coconut coir powder were used to produce cellulose, then the α-cellulose isolation process was carried out and at the end of the process 22.715 grams of -cellulose were produced or about 30.285% of the initial weight of coconut coir powder. These results were obtained after the removal of several substances such as lignin, hemicellulose and others contained in young coconut coir during the refining of α-cellulose. The results obtained were not much different from the α-cellulose composition of coconut coir which should have been around 34.9% [12]. The difference in yield of different yields may be due to the different compositions of natural fibers due to the cultivation method and environmental conditions such as soil, water and air and the chemicals used in the manufacture of alpha cellulose greatly affect the yield. α-cellulose obtained from the study can be seen in Fig. 3.

3.3. Microcrystalline Cellulose (MCC) Synthesis

The synthesis of Microcrystalline cellulose (MCC) is prepared by acid hydrolysis using reflux. The mineral acid used in this study is hydrochloric acid. The choice of hydrochloric acid is because HCl has a low price and is easy to obtain. In addition, HCl has better reactivity in the hydrolysis process when compared to other acids such as nitric acid and sulfuric acid [13]. In the hydrolysis process, there is a partial separation in the composition of cellulose microfibres where the amorphous form will break and will leave a crystalline form, namely areas of regularly arranged cellulose molecules. In the process of making Microcrystalline cellulose, 10 grams of -cellulose were used and hydrolyzed with each different concentration of HCl and at different times. variations in concentration (2N, 2.5N, 3N) and three variations in time (15 min, 30 min, 45 min).

3.4. Determination of Molecular Weight

The determination of the average molecular weight (Mv) of -Cellulose and Microcrystalline Cellulose was carried out based on the calculation of their viscosity. Viscosity was measured using Ostwald viscometry with acetonee as solvent. To determine the viscosity of the polymer, the polymer flow time was first measured at various concentrations. The polymer flow time was measured at a constant temperature of ± 25°C. And to obtain the average molecular weight can be obtained by calculations through the following Mark and Houwink equation:

$$[\eta] = k(Mv)^a \qquad (1)$$

Where :

$[\eta] = Intrinsic\ Viscosity$

$k = 13.3 \times 10^{-4}\ mL/g$

a = 0.616

3.5. α-Cellulose Molecular Weight Determination

Polymer characterization is generally carried out to evaluate the quality of synthesis or substitution products, one of which is the determination of molecular weight. Determination of the molecular weight of -cellulose was first carried out by testing the flow time with three different concentrations used. The use of three concentrations so that the required flow time of -cellulose is more specific. The following in Table 1. shows the flow time data for α-Cellulose at each concentration in acetonee solvent obtained with the Ostwald Viscometer.

Table 1. The flow rate time of -Cellulose obtained with the Ostwald viscometer

Solution	t_1 (s)	t_2 (s)	t_3 (s)	t_{ave} (s)
Acetone	0.86	0.84	1.01	0.903
α-Cellulose 0.625 g/mL	1.23	1.26	1.27	1.253
α-Cellulose 1.25 g/mL	1.28	1.27	1.31	1.286
α-Cellulose 1.875 g/mL	1.32	1.33	1.30	1.316

It can be determined the values of η_{sp} sp and η_r which are specific viscosity and relative viscosity which can be determined from the formula below:

$$\eta r = \frac{\text{tsample}}{\text{tsolvent}} \times \eta_{\text{solvent}} \quad \text{and} \quad \eta sp = \frac{\eta r - \eta \text{acetone}}{\eta \text{acetone}} \qquad (2)$$

Based on the above formula, the relative viscosity and specific viscosity data of α-Cellulose are obtained in Table 2 below:

Table 2. Relative and Specific Viscosity Data for α-Cellulose

Concentration (C)	Relative Viscosity (kg/ms)	Specific Viscosity (η_{sp})
α-Cellulose 0.625 g/mL	4,342	0.387
α-Cellulose 1.25 g/mL	4,457	0.423
α-Cellulose 1.875 g/mL	4,561	0.457

Where from the specific viscosity (η_{sp}) obtained above will be obtained the value of the reduction viscosity (ηred) with the formula:

$$\eta \text{red} = \frac{\eta_{sp}}{\text{C}} \qquad (3)$$

Then, the reduction viscosity value (ηred) is obtained in Table 3 below:

Tabel 3. Reduction Viscosity (η_{red})

Concentration (C)	Reduction Viscosity (η_{red})
α-Cellulose 0.625 gr/mL	0.6192
α-Cellulose 1.25 gr/mL	0.3384
α-Cellulose 1.875 gr/mL	0.2437

The intrinsic viscosity value is obtained from the resulting linear graph, where the intercept value from the plot is the intrinsic viscosity value and the intercept value is 0.7759. Based on the formula for determining molecular weight through the Mark and Houwink equations, the molecular weight value of -cellulose is obtained at **3.0841×10^4 g/mol.**

3.6. Molecular Weight of Microcrystalline cellulose (MCC) 3N and 15 Min

The molecular weight of MCC can be obtained from the intrinsic viscosity value of Microcrystalline cellulose (MCC) 3N 15 Minutes carried out the same thing as the calculation for -Cellulose. That is, first record the MCC flow time three times and take the average time obtained through the Ostwald viscometry test.

Table 4. Time flow rate of MCC 3N 15 minutes obtained with Ostwald Viscometer

Solution	t_1 (s)	t_2 (s)	t_3 (s)	t_{ave} (s)
Acetone	0.86	0.84	1.01	0.903
MCC 0.625 g/mL	1.03	1.06	1.01	1.033
MCC 1.25 g/mL	1.1	1.11	1.11	1.106
MCC1.875 g/mL	1.11	1.12	1.15	1.316

Based on the above formula, the relative viscosity and specific viscosity data obtained from MCC 3N 15 Minutes in Table 5 below:

Table 5. Relative and Specific Viscosity Data for α-Cellulose

Concentration (C)	Relative Viscosity (η_r) (kg/ms)	Specific Viscosity (η_{sp})
MCC 0,625 g/mL	3,580	0.1437
MCC 1,25 g/mL	3.833	0.2246
MCC 1,875 g/mL	3.902	0.2466

Where from the specific viscosity (η_{sp}) or the increase in the fraction (part) in the viscosity obtained above, the reduction viscosity value (ηred) can be obtained. The calculation results can be seen in Table 6 below :

Tabel 6. Reduction Viscosity (η_{red})

Consentration (C)	Reduction Viscosity (η_{red})
MCC 0.625 g/mL	0.2299
MCC 1.25 g/mL	0.1796
MCC 1.875 g/mL	0.1315

The intrinsic viscosity value is obtained from the resulting linear graph, where the intercept value from the plot is the intrinsic viscosity value, which is 0.7759. Based on the formula for determining molecular weight through the Mark and Houwink equation, the molecular weight value of MCC 3N 15 Minutes is 0.5853×10^4 g/mol

3.7. Molecular Weight of Microcrystalline cellulose (MCC) 3N and 45 Min

Determination of the molecular weight of MCC to obtain the intrinsic viscosity value of Microcrystalline cellulose (MCC) 3N 45 minutes is carried out in the same way as the calculation for -Cellulose, namely first recording the MCC flow time three times and taking the average time obtained through the Ostwald viscometry test. And the calculation is done looking for the value of specific viscosity, viscosity reduction and the last is intrinsic viscosity. In table 7 is the result of measuring the flow time of MCC 3N 45 minutes.

Table 7. 10 MCC 3N 45 minute flow rate obtained with Ostwald Viscometer

Larutan	**t_1 (s)**	**t_2 (s)**	**t_3 (s)**	**t_{ave} (s)**
Acetone	0.86	0.84	1.01	0.903
MCC 0.625 g/mL	0.90	0.89	0.87	0.906
MCC 1.25 g/mL	0.91	0.91	0.92	0.913
MCC 1.875 g/mL	0.94	0.90	0.95	0.93

Based on the above formula, the relative viscosity and specific viscosity data obtained after the calculation of the MCC 3N 45 Minutes. Then the calculation data can be seen in Table 8.

Table 8. Relative and Specific Viscosity Data for α-Cellulose

Concentration (C)	**Relative Viscosity (η_r) (kg/ms)**	**Specific Viscosity (η_{sp})**
MCC 0.625 g/mL	3,140	0.0031
MCC 1.25 g/mL	3.164	0.0108
MCC 1.875 g/mL	3.223	0.0297

Where from the specific viscosity (η_{sp}) obtained above, the value of the reduced viscosity (η_{red}) can be obtained in Table 9 below:

Tabel 9. Reduction Viscosity (η_{red})

Concentration (C)	**Reduction Viscosity (η_{red})**
MCC 0.625 g/mL	0.00496
MCC 1.25 g/mL	0.00864
MCC 1.875 g/mL	0.0158

The intrinsic viscosity value is obtained from the resulting linear graph, where the intercept value from the plot is the intrinsic viscosity value, which is 0.001. Based on the formula for determining molecular weight through the Mark and Houwink equations, the molecular weight value of MCC 3N 45 minutes is **0.00069×10^4 g/mol.**

3.8. Molecular Weight Average of α-Cellulose and Microcristalline cellulose (MCC)

Based on the calculations that have been made regarding the determination of the average molecular weight of α-Cellulose and Microcristalline cellulose (MCC) using the Mark and Houwink equation, the data obtained in Table 10 is as follows:

Table 10. Average molecular weight of α-Cellulose and Microcyistalline cellulose (MCC

Polymers	Molecular Weight Average (Mv)
α-Cellulose	3.0841×10^4
MCC 3N 15 Menit	0.5853×10^4
MCC 3N 45 Menit	0.00069×10^4

Table 10 shows that there has been a decrease in molecular weight after the hydrolysis process using HCl where there has been a cutting of the α-Cellulose molecular chain and also proves that the longer the time used for hydrolysis, the molecular weight will decrease. Based on the data obtained from the results of research that the manufacture of Microcrystalline Cellulose (MCC) is good at a concentration of 2.5N HCl with a long time of 30 minutes.

4 Conclusion

The synthesis of MCC was obtained from -Cellulose isolated from 75 g of young coconut coir (Cocos nucifera L.) obtained as much as 22,712 g or about 30, 279% of the initial weight and as much as 10 grams of α-Cellulose of young coconut coir (Cocos nucifera L.) hydrolyzed with HCl to become Microcrystalline cellulose. The effect of the best concentration of hydrochloric acid on the characteristics of microcrystalline cellulose is at the time of hydrolysis is 2.5N with the highest percentage of crystallinity of 50.52%. While the higher the concentration used, the color produced from white to brownish white, in the form of a fine powder, decreased pH value, increased water solubility, decreased drying shrinkage. Molecular weight determination was carried out using the viscosity method and the molecular weight of α-Cellulose was 3.0841×10^4 g/mol. And after being hydrolyzed into Microcrystalline cellulose, the molecular weight decreased over time, namely MCC 3N 15 minutes 0.5853×10^4 g/mol while MCC 3N 45 minutes had a molecular weight of 0.00069×10^4 g/mol.

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