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Variation of Iodine Mass and Acetylation Time On Cellulose Acetate Synthesis From Rice Straw

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Abstract

Cellulose acetate is a membrane material that can be used in the sensor field. One source of cellulose acetate is from rice straw. This study aimed to study the effect of iodine mass and acetylation time on cellulose acetate synthesis from rice straw. The initial step is to isolate cellulose from rice straw, followed by cellulose acetate synthesis using iodine catalyst by varying the amount of iodine as much as 0.1-0.3 grams and acetylation time for 1until 5 hours. The cellulose acetate was characterized using an infrared spectrophotometer, and its viscosity was determined. The result shows that the cellulose 33.63%. The maximum time of cellulose acetate acetylation is 2 hours with a mass of iodine 0.2 g. The yield of cellulose acetate was 14.98%, with an acetyl value of 19.11% and a degree of substitution of 0.89. The cellulose acetate produced has a low viscosity. The FTIR characterization of cellulose acetate shows O-H functional groups at 3333 cm^{-1}, C-H functional groups at 2897 cm^{-1}, carbonyl functional groups at 1722 cm^{-1} C-O functional groups at 1029 cm^{-1} that were identical in cellulose acetate compounds. The amount of iodine and the acetylation time affected the cellulose acetate product.

Key words: Rice straw, cellulose, iodine mass acetylation time, cellulose acetate

INTRODUCTION

One of the technologies that have been developed rapidly for environmental monitoring is sensor technology. The main component in the sensor is the membrane. The membrane has an active ingredient in capturing the desired ion called ionophores. Several compounds that can be used as ionophores include humic acid and its derivatives in the form of humic amide compounds (Muhali, 2013), azocrown compounds and their derivatives (Purba, 2013), and cellulose acetate compounds (Mashuni, 2012). The advantages of cellulose acetate as a membrane material are that its raw material is a renewable source, has simple application, and is environmentally friendly.

Several researchers have researched the synthesis of cellulose acetate. Nurhayati and Rinta (2014) synthesized cellulose acetate from agar waste (Gracillaria sp) using a glacial acetic acid reagent, acetic anhydride, and with the help of a sulfuric acid catalyst. The yield of cellulose acetate was 26.19%. Seto and Sari (2013) synthesized cellulose acetate from nata de soya using a glacial acetic acid reagent, acetic anhydride, and with the help of a sulfuric acid catalyst. The yield of cellulose acetate was 67.93%. Fitriyano and Abdullah (2016) synthesized cellulose acetate from banana peel waste using a glacial acetic acid reagent, acetic anhydride, and with the help of a sulfuric acid catalyst. The yield of cellulose acetate was 50%. Susilowati (2003) synthesized cellulose acetate from rice straw waste using acetic anhydride, glacial acetic acid in benzene solvent and with the help of a perchloric acid catalyst. The yield of cellulose acetate obtained was 29.41%. Souhoka and Latupeirissa (2018) synthesized cellulose acetate from commercial α-cellulose using a glacial acetic acid reagent, acetic anhydride methanol reagent. The drawback of the method above uses an acidic catalyst that affects environmental pollution and can cause corrosiveness. Das et al. (2014) have conducted research related to cellulose acetate from rice husks, using acetic anhydride reagent and with the help of an iodine catalyst. The yield of cellulose acetate was 66%.

Therefore, based on the description above, it is interesting to research cellulose acetate synthesis from rice straw by studying iodine's mass variation as a catalyst and acetylation time. Iodine is used because it is more environmentally friendly than sulfuric and perchloric acid. Rice straw contains cellulose, which is the essential ingredient in the formation of cellulose

acetate. The main rice straw content is cellulose 34.2%, hemicellulose 26.1%, and lignin 11.71% (Fajar, 2015). This research will study the optimum amount of iodine and the optimum acetylation time to synthesize cellulose acetate from rice straw. The resulting cellulose acetate compounds were analyzed for their physical properties, including the solubility test with acetone, density,% acetyl, and functional groups using Fourier Transform Infrared (FTIR).

METHODOLOGY

Materials and Instrumentals

The instrumentals used in this research are glassware (Pyrex) such as beaker, watch glass, glass stirrer, Erlenmeyer, measuring flask, volume pipette, spatula, burette, dropper pipette, thermometer, glass bottle, Lutron's CT pH meter, oven, magnetic stirrer, blender, 60 mesh sieve, analytical balance for OHAUSS model galaxy TM 160, mortar and pestle, Buchner filter, vacuum pump, petri dish, separating funnel, a set of soxhlets, scissors, hotplate stirrer; a set of Shimadzu 8201PC Fourier Transform Infrared (FTIR) viscometers and spectrophotometers.

The primary material in this research is rice straw waste. Other materials used with pro-analysis quality from Merck, namely acetic anhydride, iodine, sodium hydroxide, sodium thiosulfate, ethanol, methylene chloride, n-hexane, methanol, 30% peroxide acid, 96% sulfuric acid, distilled water, phenolphthalein indicator, indicators of methyl red, oxalic acid, HCl 37%, and filter paper

Procedure

Rice straw is collected in Mahang Barabai Village. Samples were cut ± 5cm, washed with water, and rinsed with distilled water for 1 hour to remove dirt. The samples were dried in the sun, then heated in an oven at 60 ^{o}C (Lamtiar, 2015). Dry samples were cut ± 1 cm, then blended. The composite sample was filtered with a 60 mesh sieve. The filtered powder samples were stored in air-free plastic bags.

Isolation of Cellulose from Rice Straw

Rice straw powder sample amount 50 g wrapped in filter paper and tied with twine. The sample was extracted with a mixture of hexane-methanol (2:1 v/v) using a soxhlet for 6 hours, and then the sample was dried. The extracted sample was weighed 10 g each, put in a beaker, and added 300 mL of NaOH solution with a concentration of 5%, then heated for 5 hours at 800 ^{o}C. The samples were cooled and acidified with 10% H_2SO_4 to pH 3-4 at 50 ^{o}C. The sample was separated from the filtrate using a Buchner funnel using a vacuum pump. The residue was placed into a beaker, and then 30 mL of 2% H_2O_2 solution added. The ratio of this mixture is 30:1. The mixture stirred for 5 hours. The residue obtained is filtered and washed with distilled water, then dried (Das et al., 2014). The dry precipitated cellulose obtained was weighed to constant weight.

Acetylation of Cellulose Acetate

The cellulose obtained was weighed as much as 0.2 g and put in a beaker equipped with a magnetic stirrer. 10 mL acetic anhydride is added to the beaker, then iodine is added to the beaker with a weight variation of 0.1; 0.15; 0.2; 0.25; and 0.3 g. The mixture was then heated for 60, 120, 180, 240, and 300 minutes at a temperature of 80 ^{o}C. In the final stage, 5 mL of sodium thiosulfate is added by stirring until the color changes from brown to transparent. The mixture was transferred to another beaker containing 30 mL of ethanol solution, then stirred for 60 minutes. The precipitate was filtered and washed with 75% ethanol and distilled water to remove unreacted acetic acid, then dried at 60 ^{o}C.

Cellulose Acetate Viscosity Test

A total of 0.1 g cellulose acetate was weighed and dissolved in 20 mL acetone. The mixture is stirred for 1 hour. The viscosity was determined by inserting the cellulose acetate solution, which was dissolved for 1 hour into the viscometer. The solution's time to fill the tube is calculated using a stopwatch starting from the lower limit line until it reaches the upper limit line. The recorded time is entered in Equation 1.

$$\text{Viscosity} = k.t \quad (1)$$

Where: k: viscometer constant, t: the time it takes for the solution to fill the tube.

Degree of Substitution (DS)

Cellulose acetate was weighed as much as 0.1 gram and put into a 100 mL Erlenmeyer flask. 4 mL of 75% ethanol were added, and the mixture was stirred at 50 °C for 30 minutes. A total of 4 mL of 0.5 M NaOH was added to the mixture and stirred for 15 minutes at 50-60 °C. The sample mixture was left to stand for 48 hours, then dripped with the phenolphthalein indicator. The excess NaOH was titrated with HCl (0.5 N), which had been standardized with oxalic acid until the titration's endpoint was marked with a color change. The titrated sample mixture is allowed to stand for one day to allow the NaOH to diffuse. The mixture is then titrated with NaOH (0.5 N) with a methyl red indicator

until the red color is formed. Blanks are carried out in the same way as samples. The acetyl content and degree of substitution are calculated based on Equations 2 and 3.

$$\frac{[(D-C)N_a + (A-B)N_b]\, x\, 4{,}305}{W\ sample} \quad (2)$$

$$DS = \frac{BM \times \%Asetil}{4300 - (42 \times \%asetil)} \quad (3)$$

Note:
X = acetyl content
A = V NaOH for sample titration (mL)
B = V NaOH for blank titration (mL)
C = V HCl for sample titration (mL)
D = V HCl for blank titration (mL)
N_a = Normality of HCl
N_b = Normality of NaOH

Data analysis

Data analysis was carried out by displaying the data obtained from this study. The data are percentage of acetyl, degree of substitution, viscosity, and infrared spectrum. These data are performing in tables or graphs, then analyzed descriptively. The analysis to see the effect of iodine mass and acetylation time cellulose acetate from rice straw and previous research references.

RESULTS AND DISSCUSION

Rice Straw Preparation

Rice is a plant that is planted every year by the Barabai people, especially Mahang Village. The rice planted in local rice, where the harvest age is six months. The rice that has been harvested by the community leaves straw. The straw is taken by cutting rice stalks, then collected in one sack.

The pretreatment of rice straw includes washing, drying, milling, and sieving. Washing is carried out to remove materials contained in rice straw such as soil and other impurities. Drying is done using direct sunlight. Drying is carried out to facilitate milling rice straw because, in a humid state, rice straw is difficult to mash. The coarse straw is mashed and then sifted to a size of 60 mesh to get a uniform straw size.

Isolation of cellulose from rice straw

The adequate sample was extracted using a soxhlet device. The purpose of extraction is to remove extractive rice straw levels such as pectin, wax, and protein. The solvents used in the extraction process are n-hexane and methanol, with a ratio of 2:1 (v/v). This solution is because rice straw contains non-polar and polar compounds that will dissolve with each other, where the *n*-hexane compound is non-polar, and methanol is polar.

The extractive free sample was delignified with 7% NaOH. This process aims to remove the lignin content bound to rice straw fibers to obtain a high cellulose purity level. Immersion in 7% NaOH causes swelling of the cellulose structure. The swelling that occurs will open the cellulose fibers. The swollen structure of cellulose causes the –OH group in cellulose to be reactive so that the reagent's penetration into the cellulose interior becomes easier (Pasla, 2006). The mixture is hydrolyzed by adding 10% H_2SO_4 solution. The purpose of hydrolysis is to dissolve hemicellulose and lignin. So, dark brown cellulose deposits are obtained in the filtering stage and hemicellulose and lignin as filtrate. The final stage of cellulose bleaching is obtained by adding 2% H_2O_2 solution with a ratio of 30:1 (v/w). The cellulose obtained was dried in an oven at 60 ^oC for 6 hours. The physical results of cellulose can be seen in Figure 1.

Figure 1. Isolated cellulose from rice straw

Based on Figure 1, the isolated cellulose is white. Cellulose levels were obtained by comparing the amount of cellulose isolated from the initial amount. The cellulose content of rice straw obtained in this study was 33.63%. Research conducted by Alighiri et al. (2015) with a particle size of 100 mesh, using 15% NH_3 and immersion for 24 hours, showed cellulose from rice straw isolation with a yield of 49.38%. Nur et al. (2016) researched with a particle size of 20 mesh, using 12% NaOH and soaking for 2 hours, showed rice straw isolation results with a yield of 20.37%. The difference in yield of cellulose was due to differences in particle size, extracting solution, and soaking time with the cooking solution.

Acetylation of Cellulose Acetate

The cellulose is then acetylated to produce cellulose acetate. Acetylation is carried out by dissolving iodine with acetic anhydride. This process causes one of the carbonyl bonds in acetic anhydride to be iodinated, resulting in the carbon in the carbonyl

group having room to bind with the cellulose compound. Cellulose with an active OH group will react with the carbonyl group carbon that binds to iodine, forming new bonds and rearranging the new compounds to have a stable bond to cellulose acetate acetic acid compounds are formed as side products. The physical results of cellulose acetate can be seen in Figure 2.

Figure 2. Cellulose acetate from rice straw

Figure 2 shows the color of cellulose acetate obtained yellowish white. According to Fengel and Wegener (1995), cellulose acetate changes are caused by oxidative changes in cellulose molecules resulting in colored compounds during the acetylation process. This condition occurred in this study, where the white cellulose turned into a dark brown solution after adding iodine catalyst and acetic anhydride reagent. However, during the distilled water and 75% ethanol during the deposition process, the residue becomes yellowish white. The cellulose acetate obtained was then calculated for acetyl content and degree of substitution (DS). Based on the calculation results, the maximum acetyl cellulose acetate content was obtained at 2 hours acetylation time with iodine concentration 0.2 g with an acetyl value of 19.11% and a DS value of 0.89. The results of the calculation of acetyl and DS levels can be seen in Table 1.

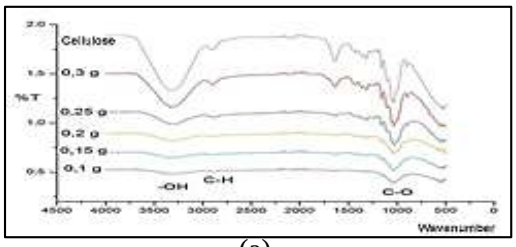
Table 1. Calculation results of acetyl content and degree of substitution (DS) of cellulose acetate.

Number	Time (hour)	Iodine mass (g)	Acetyl Percentage	DS
1	1	0.1	9.09	0.38
		0.15	10.97	0.46
		0.2	11.52	0.49
		0.25	8.95	0.37
		0.3	9.65	0.40
2	2	0.1	12.43	0.52
		0.15	9.91	0.41
		0.2	19.11	0.89
		0.25	7.35	0.30
		0.3	11.46	0.49
3	3	0.1	11.56	0.49
		0.15	11.70	0.50
		0.2	9.76	0.41
		0.25	9.13	0.38
		0.3	8.55	0.35
4	4	0.1	6.32	0.26
		0.15	12.76	0.55
		0.2	10.85	0.46
		0.25	12.34	0.53
		0.3	10.82	0.46
5	5	0.1	9.46	0.40
		0.15	14.01	0.61
		0.2	10.91	0.46
		0.25	10.47	0.44
		0.3	12.42	0.53

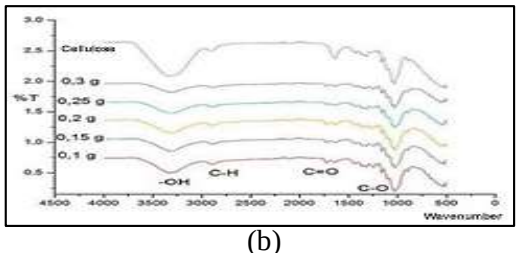
Based on Table 1, it can be seen that the optimum acetylation time is at 2 hours with an acetyl value of 19.11% with an amount of iodine as much as 0.2 grams. The value of the degree of substitution obtained from the acetylation time of 1 hour to 5 hours ranged from 0.26 to 0.89. These numbers indicate that the cellulose acetate produced is a monoacetate group. The results of acetylation of cellulose acetate follow the theory of Gaol et al. (2013). This theory tells that cellulose acetate with a DS 0-2.0 and acetyl content 13-18.6% is classified as cellulose monoacetate. Cellulose diacetate has a DS 2.0-2.8 with an acetyl content of 35-43.5%, while cellulose triacetate had a DS of 2.8-3.5 and an acetyl content of 43.5-44.8%.

Functional Cluster Analysis (FTIR)

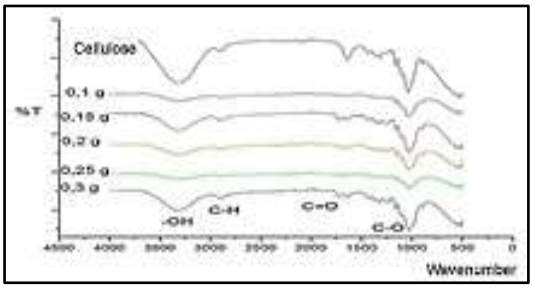
The synthesized cellulose acetate was characterized using an FTIR spectrophotometer. The FTIR spectrum of cellulose and cellulose acetate with the amount of iodine 0.1 - 0.3 grams and acetylation time of 1 until 5 hours can be seen in Figure 3.



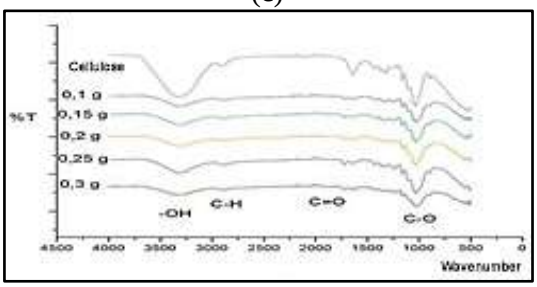
(a)



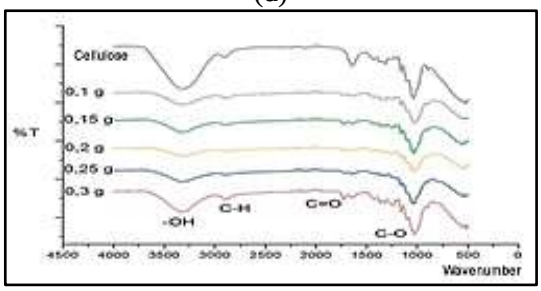
(b)



(c)



(d)



(e)

Figure 3. IR spectrum of cellulose, cellulose acetate with variations in the amount of iodine 0.1 - 0.3 grams at time a (1 hour), b (2 hours), c (3 hours), d (4 hours), e (5 hours)

Based on Figure 3, it can be seen the difference in the peaks of cellulose and cellulose acetate, wherein cellulose there is no peak at the wave number 1722 cm^{-1}. Based on the FTIR comparison of cellulose and cellulose acetate, acetylation has been successful with the presence of –OH group vibrations in the 3333 cm^{-1} regions, CH vibrations in the 2897 cm^{-1} region, the vibration of carbonyl groups in the 1722 cm^{-1} region, and CO vibrations. in the area of 1029 cm^{-1}. The higher the mass of iodine used, the sharper the –OH and carbonyl groups produced.

Cellulose acetate viscosity test

The viscosity test's purpose is to determine the level of viscosity of the cellulose acetate solution dissolved previously with acetone solvent. Viscosity indicates the ability of cellulose acetate to immobilize in acetone. The results of the viscosity can be seen in Figure 4.

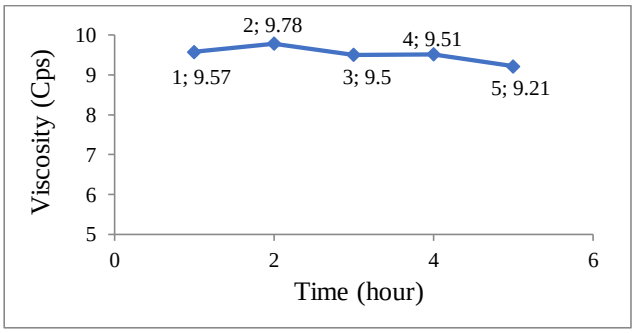


Figure 4. The viscosity of cellulose acetate

Based on Figure 4, the viscosity of cellulose acetate at one hour is 9.57 Cps. The viscosity is increasing at 2 hours of acetylation, about 9.78 Cps. The viscosity decreases at 3 hours to 9.50 Cps, increases at 4 hours of acetylation by 9.51, and decreases at 5 hours of acetylation of cellulose acetate to 9.21 Cps. The viscosity measurement decreases with the length of the acetylation time. This condition is because the resulting cellulose acetate has a low degree of polymerization. The shorter the cellulose acetate chains that are bound will cause the viscosity value to decrease.

CONCLUSION

The synthesis of cellulose acetate from rice straw was carried out at an optimum acetylation time of 2 hours with 2 grams of iodine. The IR spectrum of cellulose acetate shows vibrations of –OH, C-H, C = O groups, and C-O bonds. The resulting cellulose acetate viscosity decreased with increasing acetylation time. This result is because the degree of polymerization produced in cellulose acetate is short.

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