Jurnal Reaksi (Journal of Science and Technology)
Jurusan Teknik Kimia Politeknik Negeri Lhokseumawe
Vol. 17 No.01, Juni 2019 ISSN 1693-248X

SYNTHESIS OF ACETATE CELLULOSA FROM THE PALM OIL EMPTY FLOOR THROUGH THE REACTION OF ACTIVATION

Mauliana[1]*, Eka Kurniasih[1], Syafruddin[1]
[1]Jurusan Teknik Kimia, Politeknik Negeri Lhokseumawe
Email: maulianaa2308@gmail.com

ABSTRACT

Acetate cellulose is cellulose whose hydroxyl group is replaced by an acetyl group. Cellulose acetate has a high enough attractiveness because it is biodegradable so it is environmentally friendly. The purpose of this study is to increase the acetyl content of cellulose acetate by the acetylation reaction. This study uses 25 grams of empty fruit bunches to get cellulose, the delignification process is carried out for 30 minutes with NaOH solution, and the bleaching process for 1.5 hours with H2O2 solution. Next, as much as 5 grams of cellulose was carried out by the acetylation process by adding glacial CH3COOH solution, anhydrous CH3COOH solution with a ratio of 1:10, 1: 12.5 and 1:15 (w / v) and H2SO4 as a catalyst, with temperature variations of 40oC, 55oC and 70oC. Next, an acetyl concentration was analyzed by titration, and substitution degree analysis was carried out. The best results obtained from the two analyzes will be carried out the Fourier Transform Infrared (FTIR) test and the Scanning Electron Microscope (SEM) test. Acetyl content obtained was 8,152 - 24,58% and the degree of substitution obtained was 0,3 - 1,2%.

Keywords: *Acetylation, Bleaching, Cellulose, Cellulose Acetate, Delignification, Empty Fruit Bunches*

1. PRELIMINARY

Indonesia is currently one of the countries with the largest oil palm plantations in the world. The oil palm processing industry generates very large amounts of solid waste, one of which is oil palm empty fruit bunches. Only 10% of oil palm empty fruit bunches are used as compost and fuel. Besides that oil palm empty fruit bunches can also be used as raw material for making cellulose acetate.

Cellulose is a glucose polymer that is linear in shape and connected by β-1,4 glycosidic bonds. The linear structure causes cellulose to be crystalline and insoluble. Cellulose is not easily degraded chemically or mechanically. In nature, cellulose is associated with other polysaccharides such as hemicellulose or lignin forming the main skeleton of plant cell walls (Olievera et al, 2016).

Cellulose acetate application which is an important organic ester used as a fiber for textiles, cigarette filters, plastics, photographic films, paper coatings, and membranes. In general cellulose acetate is made from the waste of cassava stalks, nata de soya, water hyacinth, empty oil palm bunches, cotton, and sugarcane bagasse. In this study I used oil palm empty fruit bunches as the main raw material for making cellulose acetate. Because the cellulose content found in oil palm empty fruit bunches is 30-40%.

In previous studies, cellulose acetate was made using cellulose produced by oil palm empty fruit bunches (Gaol et al. 2013). Whereas in this study oil palm empty fruit bunches were used as raw material for the production of cellulose acetate in a two-step process, namely delignification using sodium hydroxide (NaOH) and continued with a bleaching process using hydrogen peroxide (H2O2).

Cellulose acetate is cellulose in which the hydroxyl group is replaced by an acetyl group. Cellulose acetate in the form of white solid, non-toxic, tasteless, and odorless (SNI 0444: 2009). Cellulose acetate is an artificial chemical compound which is a compound derived from cellulose. Cellulose acetate is often used as a fiber, membrane, and photographic film in the industry. Chemically, cellulose acetate is an ester of acetic acid and cellulose. This compound was first made in 1865 (Seto, et al, 2013).

Cellulose acetate is produced from the stages of cellulose acetate synthesis using glacial acetic acid, sulfuric acid, and anhydrous acetic acid. Glacial acetic acid serves as a pretreatment agent that aims to inflate the cellulose fibers to be more open so that it can accelerate the acetylation reaction with acetic anhydrous and increase cellulose reactivity and to reduce the degree of polymerization to a level suitable for acetylation. Sulfuric acid functions as a catalyst and anhydrous acetic acid functions as an acetyl donor (Widyaningsih and Radiman, 2007).

Cellulose acetate has a high enough attractiveness because it is biodegradable so it is environmentally friendly. The advantage of using cellulose acetate is that it is easily produced and the raw material comes from renewable natural sources (Iriyanti, 2016).

The degree of cellulose acetate substitution is 0 - 3.5 and increasing the degree of substitution will increase the melting point of cellulose acetate.

Oil palm empty fruit bunches are one of the by-products in the form of solids from the palm oil processing industry. Oil palm empty fruit bunches (TKKS) are lignocellulosic materials produced from the processing of the palm fruit industry into crude palm oil (CPO). Oil palm empty fruit bunches also produce strong fibers that can be used for a variety of things including rubber fibers as a filling material for car seats and mattresses, poly pots (small pots, small boards, and industrial packing materials).

Delignification is a preliminary process of removing lignin in lignocellulosic material so that the results obtained from a process are already in the form of cellulose with high purity. The purpose of the delignification process is to eliminate lignin, can also reduce the cellulose crystallinity, and increase the priority of ingredients. The delignification process is often used with the use of a base solution. The use of alkaline or alkaline pretreatment solutions such as the use of NaOH can be used to help separate lignin from cellulose fibers (Kurniaty, et al, 2017).

The bleaching process is carried out to degrade the remaining lignin which is still present in the pulp. The bleaching process is expected to improve brightness, increase the purity of cellulose and cellulose fibers which are degraded to a minimum (Harpendi, et al, 2014).

Acetylation is the dissolution process by reacting cellulose which has been activated with glacial acetic acid as a solvent. In the case of acetylation required a large surface on cellulose fibers. This is because the reaction rate of the acetylation process is determined by the accessibility (ability to open the fiber surface) of cellulose, where the wider surface of the fiber, it will facilitate the absorption of acetic acid as a reactant (reactant) by cellulose fibers so that it is easier to react (Wahyusi, ddk, 2017).

2. RESEARCH METHODOLOGY

2.1 Material

Oil palm empty fruit bunches, NaOH, H2O2, glacial CH3COOH, CH3COOH anhydrous, sulfuric acid (H2SO4), methanol (CH3OH), ethanol (C2H5OH), HCl, sodium acetate (CH3COONa) and Aquades.

The stages of this study include several stages, namely: 1) α-cellulose preparation by carrying out the process of delignification and bleaching. 2) the acetylation process of cellulose acetate 3) the analysis process by analyzing the acetyl content and the degree of substitution. 4) characterization analysis.

2.2 α -Cellulose preparation

Oil palm empty fruit bunches are reduced by using a crusser, then washed. Furthermore, as many as 25 grams of oil palm empty fruit bunches were carried out by the Delignification process to obtain cellulose using 2% NaOH solution (1050 ml) with a temperature of 800C stirred for 30 minutes. Cool the material that has been mixed with NaOH solution, and filter it to get cellulose which is separated from the NaOH solution containing lignin.

Then the Bleaching process using H2O2 (10% w / v) with a temperature of 600C and stirred for 1, 5 hours. Next, wash cellulose using distilled water until it is white, filter and dry cellulose in an oven at 1000C, get α-cellulose ready for use for the acetylation stage.

2.3 Acetylate Cellulose Acetate

The acetylation process is carried out to obtain cellulose acetate, where 5 grams of cellulose is mixed and stirred with glacial CH3COOH (50 ml) stirring for 3 hours, adding anhydrous CH3COOH at 1:10, 1: 12.5 and 1:15 (b / v), and H2SO4 catalyst (3 drops) By varying the temperature of 400C, 550C and 700C the stirring was carried out for 2.5 hours, then added as much aquades (2 ml) and glacial CH3COOH (5 ml) and stirred for 30 minutes, then CH3COONa (5 ml) 1 gram) and stir for 5 minutes.

The cellulose acetate obtained was washed with distilled water to remove the aroma of acetic acid and soaked in methanol for 10 minutes. Next, cellulose acetate is filtered and dried in an oven at 500C, and then an analysis of acetyl content and the degree of substitution is carried out. After that, the best results obtained from the two analyses will be carried out the Fourier Transform Infrared (FTIR) test and the Scanning Electron Microscope (SEM) test.

2.4 Analysis Process

2.4.1 Acetyl Level Analysis

Inserting 1 gram of dry cellulose acetate sample into the enlemeyer then adding 40 ml of 75% ethanol to heat at 60oC for 30 minutes. Next, adding 0.5 N NaOH as much as 40 ml is heated for 30 minutes, allowed to stand for 72 hours. Titrate with 0.5 N HCl using the phenolphthalein indicator until the pink color disappears, the sample is allowed to stand for 24 hours. Re-titrate with 0.5 N NaOH until it turns pink.

2.4.2 Analysis of Degree of Substitution

Substitution degree analysis is carried out to determine the value of the amount of acetic acid esterified in the cellulose chain. The degree of substitution of cellulose acetate is between 0-3.5.

Formula:

$$DS = \frac{162\left(\frac{\%\,Asetil}{43}\right)}{100 - \left(\frac{42}{43} \times \%\,Asetil\right)}$$

2.5 Characterization Analysis

2.5.1 Fourier Transform Infrared (FTIR)

FTIR analysis is used to determine the presence of cellulose acetate or the success of the acetylation reaction is to identify changes in functional groups after the addition of acetyl groups.

2.6.2 Scanning Electron Microscope (SEM)

Morphological analysis with SEM is carried out with the aim to see the appearance of the surface structure of particles contained on the surface of cellulose acetate.

The first major component of this SEM tool is with the help of three pairs of electromagnetic lenses whose function is to focus the electron beam into a small dot, then by two pairs of scan coil scanned with a variable frequency on the surface of the sample. The second is an electron source, which can usually provide a beam of electrons that theoretically has single energy. The third is the Imaging Detector, which functions to change the electron signal into an image. The morphological analysis will be compared with previous studies (Gaol et al. 2013).

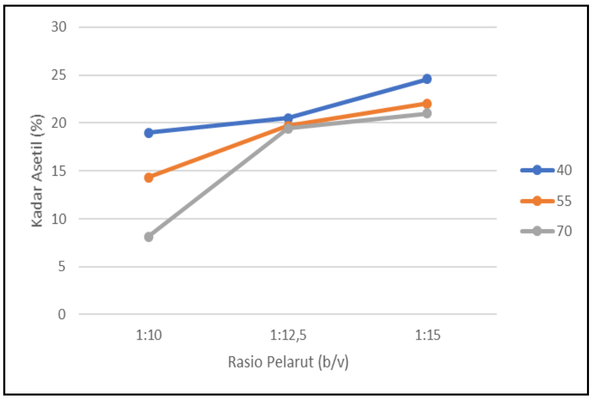
3. RESULTS AND DISCUSSION

3.1 Research result

Ratio of Anhydrous Acetic Acid and α-Cellulose (b/v)	Acetylation Temperature(^{0}C)	Analisys	
		Acetyl Levels (%)	Degree of Substitution
1 : 10	40	18,982	0,877
	55	14,305	0,626
	70	8,152	0,333
1 : 12,5	40	20,516	0,966
	55	19,711	0,919
	70	19,433	0,903
1 : 15	40	24,58	1,218
	55	22,036	1,057
	70	21,025	0,996

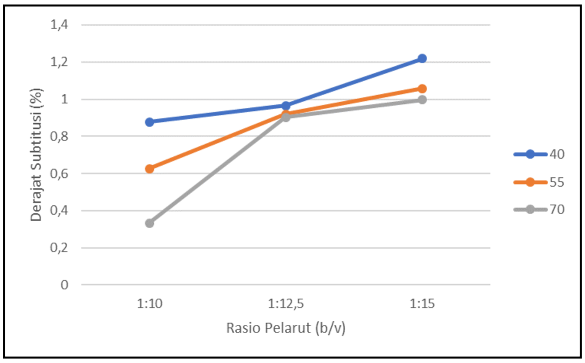
3.2 Discussion

The highest acetyl content was obtained at a solvent ratio of 1:15 with a temperature of 40oC as much as 24.58%. Can be seen in the graph below:



Picture 1. Graph of Acetyl Cellulose Acetate

The highest degree of substitution was obtained at a solvent ratio of 1:15 with a temperature of 40oC as much as 1.218%. Can be seen in the graph below:

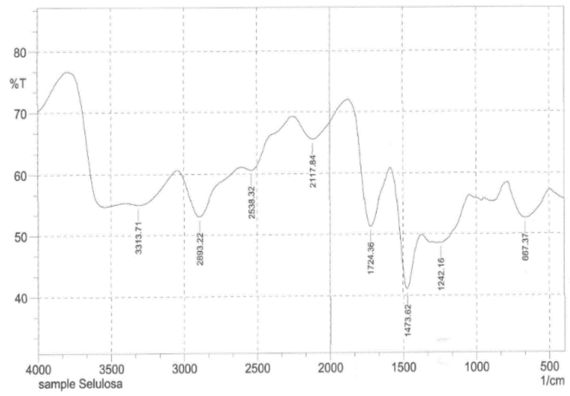


Picture 2. Graph of Cellulose Acetate Substitution Degree

3.3 Characterization Analysis Results

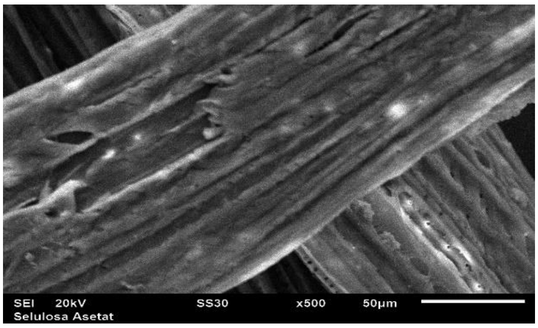
The results of the Characterization Analysis were performed on the best sample results obtained from Cellulose Acetate at the CH3COOH Anhydrous 1:15 Ratio with 40^{O}C temperature.

Characteristics analysis includes the Fourier Transform Infrared (FTIR) test and the Scanning Electron Microscope (SEM) test.

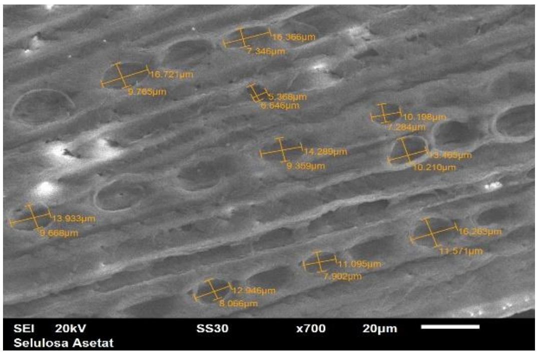


Picture 3. Graph of FTIR Analysis Results on Cellulose Acetate

Based on the results of FTIR analysis for cellulose acetate can be seen in Figure 3 where the functional groups of cellulose acetate that are read in accordance with the results of research by Lia Lismeri (2016) the functional groups owned by cellulose acetate are -OH, C-H, C = O, C-H, and C-O.



Picture 4. Morphological Structure of Cellulose Acetate at 500x Magnification



Picture 5. Morphological Structure of Cellulose Acetate at 700x Magnification

From figures 4 and 5, it can be seen that the results of the SEM morphological structure of cellulose acetate from solvent variations of 1:15 with a temperature of 400C indicate that cellulose acetate is a cavity in size between 5.3μm-16.7μm. This shows that the surface structure of cellulose acetate with the addition of CH3COOH Anhydrous which is produced is rarely shaped. When compared with the study of Lindu, M, et al, (2010) in Figure 4.4, namely cellulose acetate from nata de coco which has a pore size between 0.009 μm to 0.04 μm, the resulting surface structure is in the form of a tight cavity.

CONCLUSION

The highest acetyl content was obtained at a solvent ratio of 1:15 with a temperature of 40oC as much as 24.58%. While the highest degree of substitution obtained at a solvent ratio of 1:15 with a temperature of 40oC as much as 1.218%. The cellulose acetate function group obtained from the FTIR analysis is a C-O carbonyl group at a wavelength of 1724.36 cm-1 and a C-O ester group at a wavelength of 1242.16 cm-1. The surface structure of cellulose acetate tested with SEM at 700x magnification has a pore size ranging from 5.3μm to 16.7μm.

REFERENCE

[1] Oliviera, F. B. (2016). Production Of Cellulose Nanocrystals From Sugarcane Bagasse Fibers And Pith. *Industrial Crops and Products*, 48-57.

[2] Gaol, M. R., Sitorus, R., Sitorus, Y., Surya, I., & Manurung, R. (2013). Pembuatan Selulosa Asetat dari α-Selulosa Tandan Kosong Kelapa Sawit. *Jurnal Teknik Kimia USU*, 33-39.

[3] BSN. (2009). Cara Uji Kadar Selulosa Alfa, Beta, Gamma. *SNI 0444 : 2009*.

[4] Seto, A. S., & Sari, A. M. (2013). Pembuatan Selulosa Asetat Berbahan Dasar Nata De Soya. *Konversi*.

[5] Widyaningsih, S., Radiman, & Cynthia, L. (2007). Pembuatan Selulosa Asetat Dari Pulp Kenaf (Hibiscus Cannabinus). *Jurnal Molekul*, 13-16.

[6] Iriyati, A. (2016). Sintesis Membran Elektrolit Selulosa Asetat Dari Daun Pandan Laut (Pandanus Tectorius) Dengan Pemlastis Dimetil Ftalat Untuk Aplikasi Baterai Ion Litium (Skripsi). *Universitas Negeri Yogyakarta*.

[7] Kurniaty, I., H Habibah, U., Yustiana, D., & M Fajriah, I. (2017). Proses Delignifikasi Menggunakan NaOH Dan Amonia (NH3) Pada Tempurung Kelapa. *Jurnal Integrasi Proses*, 197-201.

[8] Harpendi, R., Padil, & Yelmida. (2014). Proses Pemurnian Selulosa Pelepah Sawit Sebagai Bahan Baku Nitrokesulosa Dengan Variasi pH Dan Konsentrasi H2O2. *Laboratorium Dasar Teknik, Jurusan Teknik Kimia, Fakultas Teknik, Universitas Riau*.

[9] Wahyusi, N. K., Siswanto, & Utami, I. L. (2017). Kajian Proses Asetilasi Terhadap Kadar Asetil Selulosa Asetat Dari Ampas Tebu. *Jurnal Teknik Kimia*.