IJFAC

Indonesian Journal of
Fundamental and Applied Chemistry

Article http://ijfac.unsri.ac.id

Synthesis and Characterization of Cellulose Acetate from α-Cellulose of Paper Waste

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Abstract

A cellulose derivative substance called cellulose acetate is frequently used in the manufacturing of photographic film, fiber, membranes, and bioplastics. However, the availability of sources for cellulose acetate's raw material does not support this demand. Paper waste has a high cellulose content. Therefore, the aim of this research is to synthesize cellulose acetate from α-cellulose waste paper. In order to separate alpha cellulose from waste paper in this study, the delignification process with NaOH solvent was used as a first step. After obtaining alpha cellulose, acetic anhydride was used to carry out the acetylation reaction. The yield of α-cellulose from paper waste is 51.8%. α-Cellulose is reacted with acetic anhydride through acetylation reactions and hydrolysis of acetyl groups. From this reaction, functional groups -OH, C=O ester, and C-O acetyl appeared from the FTIR spectra analysis which indicated that cellulose acetate had been successfully synthesized. The type of cellulose acetate produced is a type of cellulose monoacetate with an acetyl groups of 23% and a degree of substitution value of 1.17.

Article Info

Received 5 May 2023
Received in revised 15 June 2023
Accepted 16 June 2023
Available online 27 June 2023

Keywords: α-Cellulose; paper waste; cellulose acetate

Abstrak (Indonesian)

Selulosa asetat merupakan senyawa turunan selulosa yang sering digunakan sebagai serat, membran, bioplastik, dan film fotografi dalam industri. Namun kebutuhan tersebut tidak didukung oleh ketersediaan sumber bahan baku selulosa asetat. Limbah kertas memiliki kandungan selulosa yang tinggi. Oleh karena itu, penelitian ini bertujuan untuk mensintesis selulosa asetat dari limbah kertas. Penelitian ini dilakukan menggunakan metode delignifikasi dengan pelarut NaOH sebagai tahap awal pemisahan alfa selulosa dari limbah kertas. Setelah didapatkan alfa selulosa dilakukan reaksi asetilasi dengan anhidrida asetat. Rendemen α-selulosa dari limbah kertas sebesar 51,8%. α-Selulosa direaksikan dengan anhidrida asetat melalui reaksi asetilasi dan hidrolisis gugus asetil. Dari reaksi tersebut dan berdasarkan hasil spektroskopi FTIR muncul gugus fungsi -OH, C=O ester, dan C-O asetil yang menandakan bahwa selulosa asetat telah berhasil disintesis. Jenis selulosa asetat yang dihasilkan adalah jenis selulosa monoasetat dengan kadar asetil 23% dan nilai derajat substitusi 1,17.

Kata Kunci: α-selulosa, limbah kertas, selulosa asetat

INTRODUCTION

One of the derivatives of cellulose is cellulose acetate. The esterification of cellulose with acetic anhydride produces cellulose acetate. A few benefits of cellulose acetate include its favorable physical and optical characteristics. Moreover, cellulose acetate is environmentally friendly because it is quickly degradable, has high tensile strength, is thermoplastic, and stability [1]. As a result of these qualities, cellulose acetate is a substance that is frequently utilized in industry. The textile industry, cigarette filters, plastics, photographic films, and membranes all use cellulose acetate as a fiber [2,3].

Typically, high-quality wood pulp raw materials are used to create cellulose acetate. However, the low purity of the cellulose obtained when utilizing wood pulp is a drawback [4]. Paper is one of the byproducts of wood pulp, which contains a lot of cellulose. Inked paper has a cellulose level of 58.3%, while plain paper has a cellulose value of 60.5%, according to Ruseimy [5].

So far, the production of cellulose acetate has been carried out by several researchers using cellulose from various sources, such as kenaf pulp cellulose and wood sawdust waste. The use of different raw materials will affect the conditions for the stages of making cellulose acetate [17]. In this study, used paper waste was used as a raw material for cellulose which is easy to obtain, also contains high cellulose and is easily processed in cellulose refining. Paper is used widely and extensively in academia. Because all academic activities are very directly related to paper. The ensuing paper waste is directly impacted by this activity. Paper waste decomposes swiftly in the environment, giving the impression that it is safe.

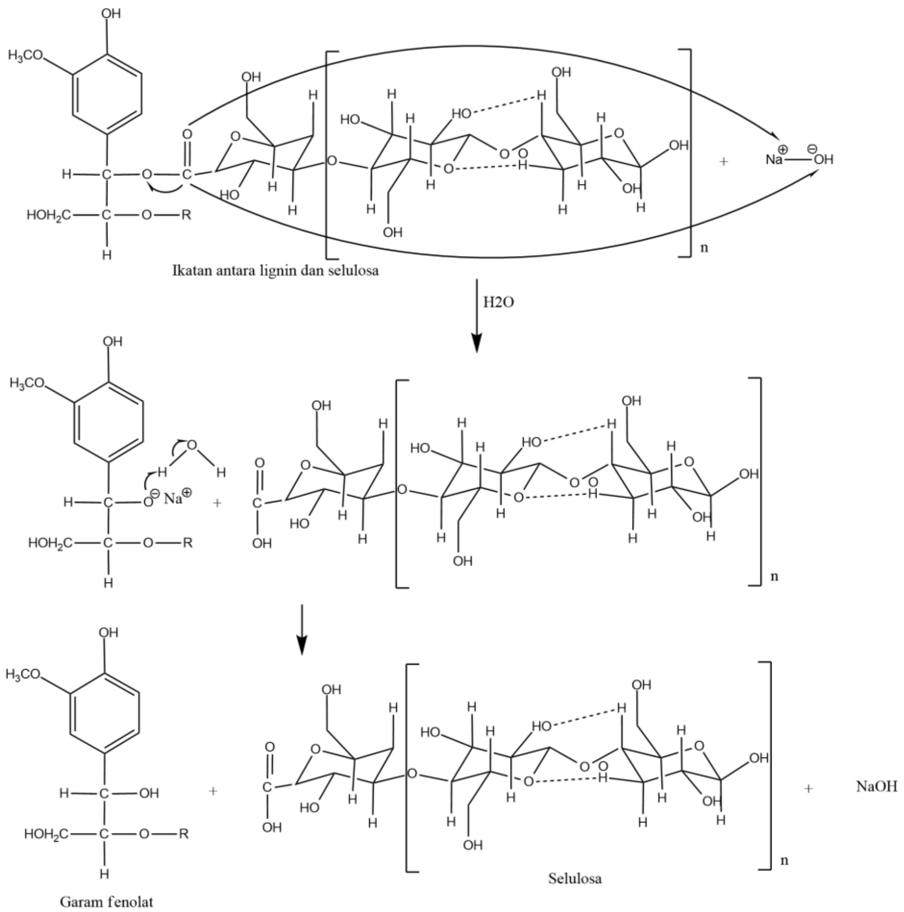

Figure 1. Mechanism of separation of lignin and cellulose

MATERIALS AND METHODS

Materials

Paper trash gathered from the Universitas Bangka Belitung environment, distilled water, $NaOCl_2$ (Merck), NaOH (Merck), PP indicator, acetic anhydrous, glacial acetic acid, H_2SO_4 (Merck), acetone, and ethanol are the components utilized.

Methods

Extraction of α-Cellulose from Paper Waste

The paper waste is cleaned using the bleaching agent $NaOCl_2$, then the pH is balanced with distilled water before being dried in an oven at 50 °C. By adding 1000 mL of 17.5% NaOH solution, up to 40 grams of paper waste from the bleaching process that had a pH of neutral were then delignified. Then, it was roasted on a hotplate for three hours at 80 ºC. After that, the delignified paper waste underwent pH neutralization using distilled water before being placed in an oven to dry at 50 ºC until the weight remained constant and the yield was measured [18].

Synthesis of Cellulose Acetate

A three-neck flask was filled with 5 grams of delignified paper samples, 50 mL of glacial acetic acid, and 50 mL of 98% sulfuric acid. The flask was then sealed at room temperature. Add 50 mL of acetic anhydrous and 20 mL of glacial acetic acid to continue the acetylation procedure. To create primary cellulose acetate, heat in a water bath at 50 °C (Primary Cellulose Acetate). Then, to the primary cellulose acetate that has been prepared, add glacial acetic acid

DOI: 10.24845/ijfac.v8.i2.82

and sulfuric acid. For one hour, the reaction takes place at 80 ºC. Then, 1 L beaker was filled with the solution, 500 ml of distilled water was added while it was being stirred, and the cellulose acetate was allowed to solidify. after which it was neutralized with distilled water and filtered through a Buchner funnel. Following neutralization, cellulose acetate was dried at 50 ºC until it reached a consistent weight [18].

Acetyl Analysis and Degree of Substitution

The Erlenmeyer was filled with up to 1 g of cellulose acetate and 40 mL of 70% ethanol. In a bath, the mixture was heated for 30 minutes at 55 ºC. The mixture was then heated in a water bath at 55 ºC for 15 minutes after 40 mL of 0.5 N NaOH was added. then wrapped with aluminum foil and left for 72 hours. Following the addition of 2 drops of pp indicator, the mixture was covered once again and left for 24 hours before being titrated with 0.5 N HCl (the volume of HCl required for the titration was recorded). Titrate with 0.5 N NaOH after adding a further 2 drops of pp indicator. Secondly, determine the degree of substitution (DS) and the acetyl groups (AG) (%).

$$\%AG = \frac{[(Vbi+Vbt)\mu b\text{-}Va]43}{mca} \times 100 \quad (1)$$

$$DS = \frac{3{,}86\ \%AG}{(102{,}4\text{-}\%AG)} \quad (2)$$

% AG = percentage of acetylated groups
V_{bi} = volume of NaOH added to the system
V_{bt} = volume of NaOH lost in the titration
μ_b = NaOH concentration
V_a = volume of HCl added to the system
μ_a = HCl concentration
43 = molecular mass of the acetyl groups
M_{ca} = weight of the cellulose acetat sample

RESULTS AND DISCUSSION

Extraction of α-Cellulose from Paper Waste

Bleaching, delignification, and refining operations are the three stages that make up the extraction of cellulose from waste paper. Impurities detected in paper waste are to be removed using the bleaching procedure (such as ink to ensure that the cellulose produced is highly pure [6]. Because it can harm the hemicellulose and cellulose chains, this bleaching technique shouldn't be done for an extended period of time [7]. Although the goal of the NaOH-based delignification procedure is to eliminate hemicellulose from waste paper [8]. The alkali cleaves the intramolecular crossed bonds between lignin and hemicellulose through solvation and saponification reactions, increasing the material porosity and the alkali access to the lignin. The remaining hemicellulose residue is intended to be eliminated during the purifying procedure. Mechanism of separation of lignin and cellulose are presented in **Figure** 1. The product of cellulose extraction from waste paper is a white, odorless substance [9]. The yield of cellulose produced is 51.8%.

Analysis using FTIR spectroscopy is required to determine whether the cellulose extraction process from paper waste was successful. Dewi [10] claim that the standard functional groups in conventional cellulose are the repeating -OH, C-O-C-, and C-O- groups. The presence of the OH group, which is the primary functional group of cellulose, is indicated by the absorption of wave number 3626 cm^{-1}. Wave number 2880 cm^{-1} is the -CH group, and wave number 1440 cm^{-1} shows the presence of the $-CH_2-$ group by its adsorption [11]. Additionally, a glycosidic C-O group is present, as shown by the wave number of 1051 cm^{-1}. And the presence of an absorption peak at 1155 cm^{-1} shows the presence of -C-O-C- (ether) groups [12,19].

Synthesis of Cellulose Acetate

In the cellulose acetate synthesis process, the removal of most of the lignin is very important because lignin competes with cellulose for acetylation reactants. During the process, fiber swelling occurs, thereby increasing the accessibility of acetic anhydride to the OH groups of cellulose and increasing the activation of cellulose pulp for acetylation reactions. The majority of the hydroxyl groups are replaced by acetyl groups during this acetylation process (**Figure** 3). The majority of groups after full esterification have dihydroxy bonded primer on cellulose.

Figure 4 displays the findings of a functional group study using FTIR on cellulose acetate. The absorption of 1728 cm^{-1}, which is a carbonyl group (C=O) ester, indicating in a qualitative manner that cellulose has experienced an esterification reaction and has transformed to cellulose acetate. Moreover, there is a very prominent peak in the IR spectra for the group (C-O) of the acetyl group, which is a typical group of cellulose acetate.

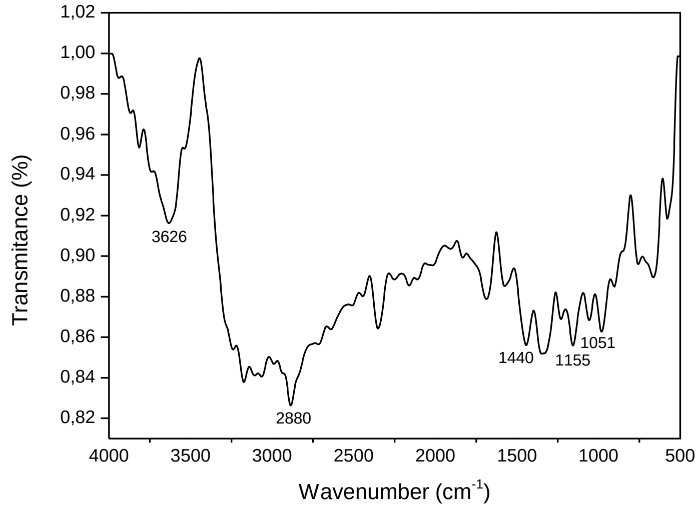

Figure 2. FTIR spectrum of α-cellulose waste paper

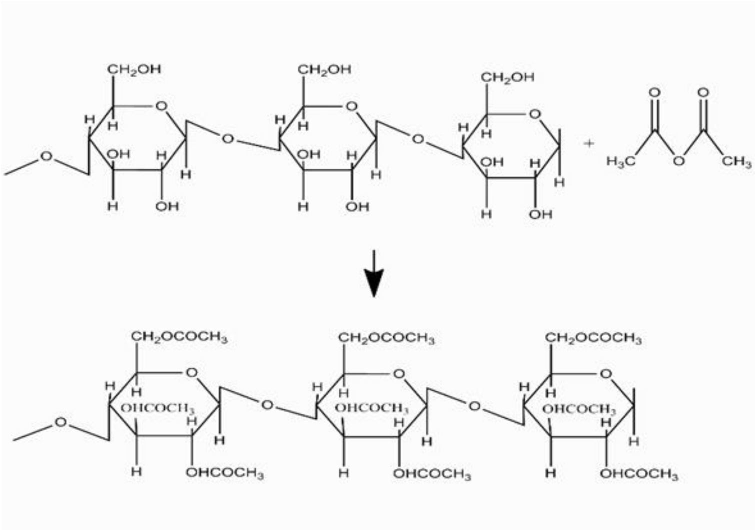

Figure 3. Mechanism of Acetylation reaction

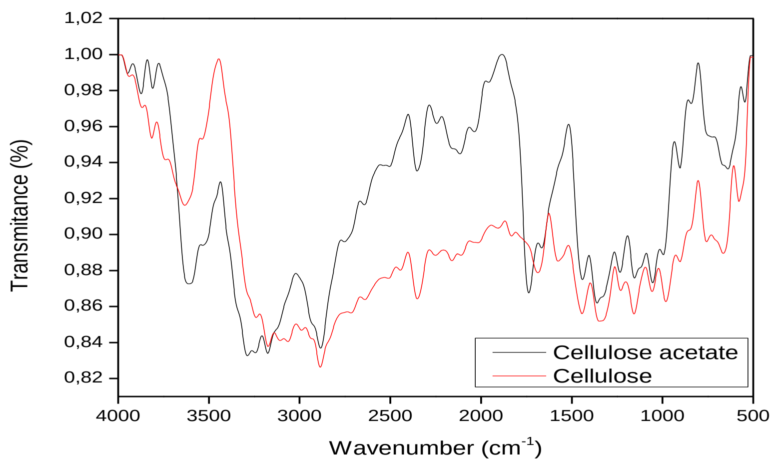

Figure 4. FTIR spectra of synthesized and commercial cellulose acetate are compared

According to the FTIR spectrum in **Figure** 4, the O-H function is present in the selulosa acetate that originates from the waste paper at the 3593 cm^{-1} adsorptivity limit. This is because there is still a lot of gugus O-H that hasn't been replaced by acetyl groups. Due to the presence of air in the material, drying throughout the process is not always successful [13]. Carbonyl groups presents at 1682 cm^{-1} band; this indicates that celulose acetate is essentially constant. Absorption band at 1728 cm^{-1} in accordance with the oscillation of C=O bond from carbonyl ester group and an increase at 1360 cm^{-1} in accordance with C-H vibration [14,16].

The degree of substitution in this investigation was 1.17, and the 23% acetyl groups showed that the cellulose acetate produced was cellulose monoacetate. Cellulose monoacetate has a degree of substitution (DS) 0-2 with acetyl groups < 36.5%. One hydroxyl group in cellulose acetate is changed to one acetyl group to create cellulose monoacetate [20]. Souhuka [15] claim that cellulose monoacetate can be used as a bioplastic and membrane.

CONCLUSION

This research showed that paper waste has the potential to be used as a raw material for the production of cellulose acetate, namely cellulose monoacetate, which has a 23% acetyl groups and a 1.17 degree of substitution value. It is possible to use this cellulose monoacetate as a bioplastic and membrane. To ascertain the precise process for synthesizing specific forms of cellulose acetate, further research is required to conduct experiments with different concentrations of the acetic anhydride employed and reaction times.

ACKNOWLEDGMENT

Authors thanks to Universitas Bangka Belitung for research funding through Penelitian Dosen Tingkat Universitas scheme in 2022.

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