CHEESA: Chemical Engineering Research Articles
ISSN **2614-8757 (Print)**, ISSN **2615-2347 (Online)**
Available online at: http://e-journal.unipma.ac.id/index.php/cheesa

Research Article

The Effect of NaOH Concentration and Acetylation Time on Synthesis of Kepok Banana Peel Cellulose Acetate

Pengaruh Konsentrasi NaOH dan Waktu Asetilasi Terhadap Sintesis Selulosa Asetat Kulit Pisang Kepok

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Article History
Received: 23th July2023; Revised: 10th December2023; Accepted: 12th December2023; Available online: 04th January 2024; Published Regularly: December 2023

doi: 10.25273/cheesa.v6i2.17294.85-94

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Abstract

The high production of kepok banana is generating a significant amount of peel waste, contributing to environmental pollution. To address this issue, an innovative solution is the conversion of kepok banana peel into cellulose acetate as raw material for membrane production. Therefore, this research aimed to manufacture kepok banana peel cellulose acetate using varying concentrations of 1%, 1.5%, and 2% NaOH solvent, with acetylation times of 2 hours and 2.5 hours, respectively. The optimal results were achieved using 1% NaOH with kepok banana peel cellulose content of 56.07%. Furthermore, the best acetylation time occurred at a duration of 2.5 hours, producing a cellulose acetate content of 38.23% and a 2.3% degree of substitution (DS). These results suggested that the optimal combination for producing membrane from kepok banana peel is 1% concentration with an acetylation time of 2.5 hours, classifying it as cellulose diacetate.

Keywords: acetylation; cellulose; cellulose acetate; delignification; Kepok banana peel

Abstrak

Tingginya produksi kulit pisang kepok menghasilkan limbah kulit pisang yang mencemari lingkungan. Salah satu solusi dan inovasi untuk mengatasi permasalahan tersebut adalah dengan mengolah kulit pisang kepok menjadi selulosa asetat sebagai bahan baku pembuatan membran. Pembuatan selulosa kulit pisang kepok menggunakan variasi konsentrasi pelarut NaOH 1%, 1,5% dan 2%. Sedangkan pembuatan selulosa asetat dari kulit pisang kepok menggunakan variasi waktu asetilasi 2 jam dan 2,5 jam. Hasil penelitian terbaik terdapat pada pelarut NaOH 1% dengan kadar selulosa kulit pisang kepok sebesar 56,07%. Waktu asetilasi terbaik yaitu 2,5 jam menghasilkan kadar selulosa asetat sebesar 38,23% dan derajat substitusi sebesar 2,3%. Berdasarkan hasil penelitian, selulosa asetat 1% dengan waktu asetilasi 2,5 jam merupakan jenis selulosa diasetat untuk pembuatan membran selulosa asetat kulit pisang kepok.

***Kata kunci**: asetilasi; delignifikasi; kulit pisang kepok; selulosa; selulosa asetat*

1. Introduction

Indonesia is widely recognized for its extensive natural resources and holds a significant position as a leading banana producer globally. Generally, banana is a fruit plant, consisting of roots, stems, leaves, fruit flesh, and peel. The volume of banana production in the country from 2013 to 2017 was 6,279,279 tons, 6,862,558 tons, 7,299,266 tons, 7,007,117 tons, and 7,162,678 tons, respectively [1]. Among popular varieties, kepok banana (*Musa balbisiana*) is widely used for its meat as a processed food. However, the community has not fully optimized the use of kepok banana peel, resulting in immediate disposal as waste in the environment. This phenomenon contribute-s to environmental pollution and disrupts the aesthetics of the surrounding community. In order to address this issue, kepok banana peel is converted into cellulose acetate as raw material for membrane production.

Cellulose acetate membrane has become a significant technology in the field of renewable microfiltration membranes, currently gaining attention and rapid development globally [2]. This membrane is made of a natural polymer that has been developed as an alternative to conventional separation processes [3]. The natural polymer materials used in the manufacturing process are cellulose and cellulose acetate. Moreover, cellulose is obtained from kepok banana peel waste, which is used to manufacture membrane, consisting of 60-65% cellulose, 6-8% hemicellulose, and 5-10% lignin. Cellulose can be made into cellulose acetate through acetylation reactions [4]. Kepok banana peel waste is also processed into cellulose acetate by varying the speed of stirring through the acetylation process [5].

Cellulose acetate has distinct characteristics, including an asymmetric structure with an ultra-thin active layer, capable of retaining dissolved materials on a rough support layer. Furthermore, it is resistant to precipitation, producing biodegradable, hydrophilic, and hydrophobic properties for use as a raw material in membrane production. Cellulose acetate has a chemical property that allows it to dissolve in acetone [6][7]. The use of agar processing waste offers a viable pathway to produce cellulose acetate. This process uses various solvents such as NaOH at 3%, 6%, and 9% during isolation and variations in the ratio of cellulose acetate anhydride in the acetylation. The results showed that 6% NaOH could produce a hemicellulose content of 24.92% and the highest 53.33% alpha cellulose with a 24.92% yield value. The optimal ratio of cellulose and acetic anhydride to obtain cellulose acetate is 1:10, showing a whiter cellulose acetate color with a yield of 26.19% and an acetyl content of 43.5% [8]. The conversion of coconut coir into cellulose acetate has also been carried out, with varying volumes of acetic anhydride. The results showed that a maximum volume of 60 ml yielded an acetic anhydride with an acetyl content of 50.8737% and a Degree of Substitution (DS) of 3.8126% [9]. Another study has used empty palm fruit bunch pulp as a cellulose acetate product. The results obtained cellulose acetate levels ranging from 18-48% with an optimum acetylation time of approximately 2–3.5 hours [10]. Waste from cassava stems has been found effective in cellulose acetate production, yielding a content of 41.01%, and classified as cellulose diacetate [11].

Based on the problems above, this research aimed to apply kepok banana peel waste in the manufacturing of cellulose acetate as a raw material for membrane production. The novelty is variations in the concentration of NaOH solvent (1%, 1.5%, and 2%) in the delignification process and acetylation time. A NaOH solvent with a higher concentration causes the degradation of cellulose, leading to a decrease in cellulose levels in the delignification process. The percentage of cellulose acetate content increased to a maximum at an acetylation time of 2.5 hours. However, prolonged acetylation reaction time results in decreased cellulose acetate content, showing a direct proportionality to the DS [12][13]. This research is anticipated to minimize kepok banana peel waste and obtain optimal cellulose acetate as a raw material for cellulose acetate membrane production.

2. Research Methods

2.1 Instruments and Materials

The kepok banana peel was obtained from a fried banana seller in Cilacap. The chemicals used include NaOH, CH_3COOH, $(CH_3CO)_2O$, and H_2SO_4 obtained from Merck, while NaOCl and Aquadest were collected from Brataco. The instrument was glassware, sieve 60 mesh, analytical balance, Fourier Transform Infra-Red (FTIR) specification Bruker Alpha II Platinum-ATR, and Scanning Electron Microscope (SEM) merk Tescan.

2.2 Preparation of Cellulose

The preparation of kepok banana peel cellulose commenced with a delignification process to remove the lignin and hemicellulose content, obtaining a high cellulose content. Kepok banana peel measuring 60 mesh and 50 grams was added to a 1% NaOH solution and refluxed at 70^{o}C for 2 hours. The precipitate of kepok banana peel was filtered and washed using distilled water to achieve a neutral pH of 6.5–7.5. This was followed by bleaching the delignified peel with a 1.75% NaOCl solution, using a sample-to-NaOCl solution ratio of 1:25, and heating at 70^{o}C for 1 hour. Subsequently, filtration and neutralization were carried out using distilled to obtain a neutral pH. The cellulose content and functional groups were analyzed using the FTIR instrumentation and the surface structure with the SEM on delignified kepok banana peel.

2.3 Preparation of Cellulose Acetate

The preparation of cellulose acetate was carried out by mixing 75 grams of wet cellulose powder with 150 ml of a 30% glacial acetic acid solution, followed by heating, and stirring at 38^{o}C for 60 minutes. Approximately 1 ml of a 2% sulfuric acid solution was added, heated, and stirred at the same conditions. Furthermore, the acetylation process was carried out by adding 40 ml of a 30% acetic anhydride solution, heating, and stirring at 38^{o}C, with variations lasting for 2 and 2.5 hours, respectively. This was followed by the addition of 10 ml of distilled water and 20 ml of a 30% glacial acetic acid solution, which was heated and stirred at 50^{o}C for 30 minutes. The solution was allowed to stand, forming a precipitate, which was placed in 500 ml of distilled water to achieve white cellulose acetate flakes. The cellulose acetate was filtered and neutralized using distilled water until the sour smell disappeared. Subsequently, cellulose acetate content and Degree of Substitution (DS), functional groups were also analyzed using the FTIR, and the surface structure of the cellulose acetate was measured with SEM instrumentation.

3. Results and Discussion

3.1 Kepok Banana Peel Cellulose

In this research, kepok banana peel cellulose was produced through delignification, bleaching, and washing processes. The delignification process using NaOH solvent was carried out to reduce the lignin and hemicellulose content. Delignification produced cellulose, which was distinguished by a blackish brown color, as moist powder kepok banana peel. The bleaching process was performed to whiten the cellulose content, which has a blackish-brown color from the results of delignification. After the cellulose was washed with distilled water to neutralize its pH, which ranged from 6.5 to 7, a white, odorless product was produced. Figure 1 shows the results of delignification and bleaching in the form of cellulose from kepok banana peel waste.

(a) **(b)**

Figure 1. Delignification of kepok banana peel cellulose a) before bleaching; b) after bleaching

The analysis of the cellulose content of kepok banana peel was carried out using the Chesson method [13]. Based on the results, the cellulose content was found to be 56.07%, 46.54%, and 44.54%, in 1%, 1.5%, and 2% NaOH solvent. This showed that the interaction between lignin compounds and NaOH solvents produced the best results at a concentration of 1%. The lignin content in the kepok banana peel was degraded due to an increase in the cellulose content of the kepok banana peel. This suggested that NaOH with a higher concentration would cause the degradation of cellulose, thereby leading to a decrease in the cellulose content obtained in the extraction results [12][13].

Functional group analysis was carried out to identify the presence of functional groups and wave numbers based on the bonds contained in the cellulose of the kepok banana peel. Subsequently, tests were carried out using the Bruker Alpha II Platinum-ATR FTIR instrumentation at the Engineering Laboratory of Politeknik Negeri Cilacap. Figure 2 shows the results of the analysis of functional groups and wave numbers formed in kepok banana peel cellulose from delignification with 1%, 1.5%, and 2% NaOH solvent variations.

Based on Figure 2, it was discovered that 1% NaOH solvent showed the absorption of functional groups typical for cellulose compounds. The absorption depth at wave number 3334.03 cm^{-1} indicated the presence of the O-H stretch functional group, and wave number 2850.11 cm^{-1} proved the presence of the C-H stretch functional group. Furthermore, the absorption depth of wave numbers 1462.26 cm^{-1} and 1159.88 cm^{-1}, showed the existence of the CH_2 bend and C-H bend functional group. The absorption depth of 1036.84 cm^{-1} wave numbers proved the existence of the C-O stretch functional group.

The functional group and wave number analysis of cellulose kepok banana peel with 1.5% NaOH variations also demonstrated the absorption of functional groups that are characteristic of cellulose compounds. The absorption depth at wave number 3328.88 cm^{-1} indicated the presence of the O-H stretch functional group and C-H at 2851.32 cm^{-1}. Furthermore, the absorption depth of wave numbers 1374.60 cm^{-1} and 1156.15 cm^{-1}, indicated the presence of the CH_2 bend and C-H bend functional groups. The absorption depth of 1032.23 cm^{-1} wave numbers showed the existence of the C-O stretch functional group.

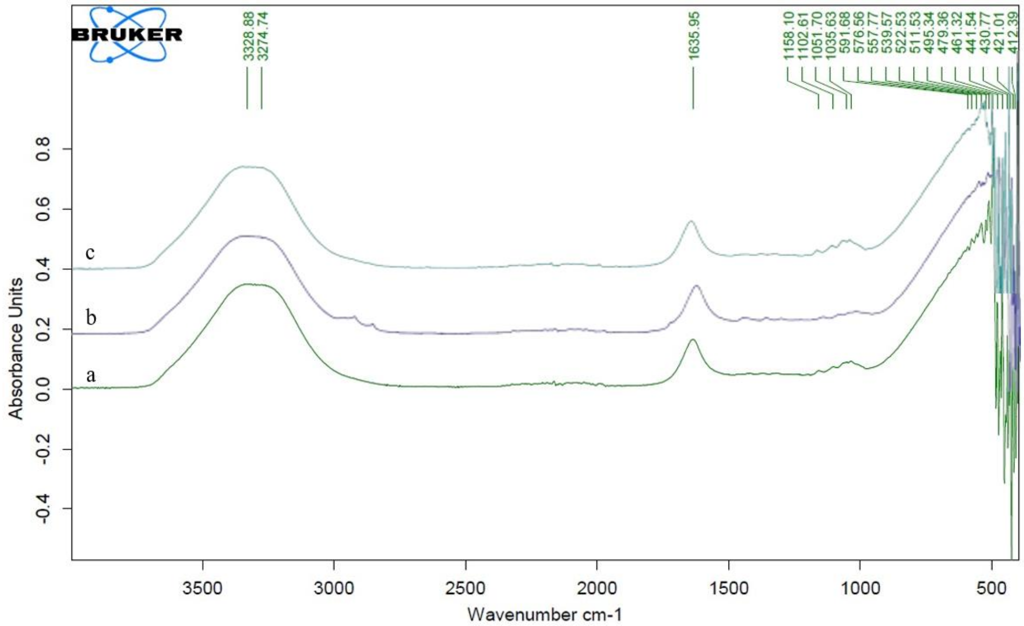
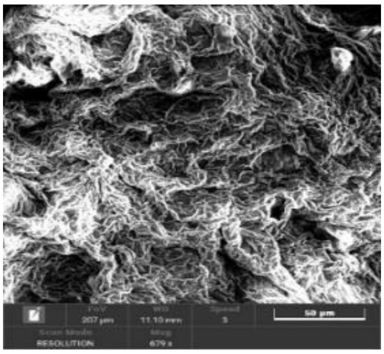
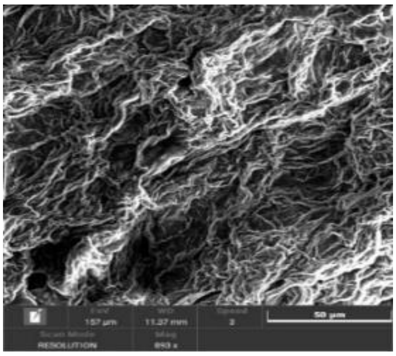


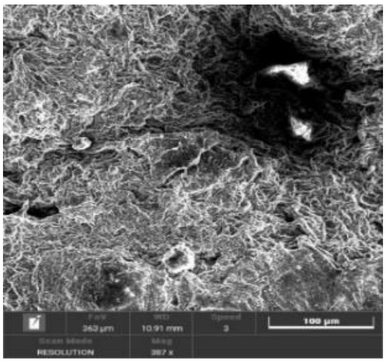
Figure 2. FTIR spectra of kepok banana peel cellulose with various concentration NaOH solvents a) 1%; b) 1.5% and c) 2%



(a)



(b)



(c)

Figure 3. Surface structure of kepok banana peel cellulose with NaOH solvent variations a) 1%; b) 1.5% and c) 2%

The analysis results of functional groups and wave numbers of cellulose kepok banana peel with variations in the 2% NaOH solvent showed the absorption of cellulose compounds. The absorption depth at wave number 3335.24 cm^{-1} indicated the presence of the O-H stretch functional group, while 2163.74 cm^{-1} showed C-H stretch. Furthermore, the absorption depth of wave numbers 1634.77 cm^{-1} and 1158.99 cm^{-1}, proved the existence of the CH_2 bend and C-H bend functional groups. The absorption depth of 1035.29 cm^{-1} wave numbers indicated the existence of the C-O stretch functional group.

Figure 3 shows the analysis of the surface structure of cellulose kepok banana peel resulting from delignification of 1%, 1.5%, and 2% NaOH solvent variations. The analyses were carried out using the SEM instrumentation of the Tescan brand located at the Environmental Physics Laboratory of Politeknik Negeri Cilacap.

Figure 3 (a) shows that the surface structure of 1% cellulose is smoother, with more fibers and a hollow structure, as observed at Mag 679x magnification. Furthermore, 1.5% concentration as presented in Figure 3 (b) shows a widened and fibrous pore surface structure observed with Mag 893x magnification. A 2% concentration, as illustrated in Figure 3 (c) showed a flat and dense fiber surface structure at magnification 387x. Based on the results, it was concluded that cellulose with 1% NaOH solvent produced the optimal surface structure.

3.2 Kepok Banana Peel Cellulose Acetate

In this study, an acetylation method with 2 and 2.5 hours variations was used to create the cellulose acetate of kepok banana peel. acetylation is a chemical reaction in which a different substance is substituted for the acetyl group.

During the acetylation process, a solution of acetic acid anhydride is used as a reagent, where the cellulose reacts with acetic anhydride to form cellulose acetate. Sulfuric acid is used as a catalyst to add a positive charge to the acid, accelerating the reaction and lowering the activation energy. Consequently, chemical reactions occur more easily and acetyl groups can be substituted by hydroxyl groups [9]. In cellulose acetate, the hydroxyl group is replaced by an acetyl group in the form of a white, tasteless, non-toxic, and odorless solid. In this research, the synthesis of cellulose acetate from kepok banana peel obtained a white and odorless product, as shown in Figure 4.

Figure 4. Kepok Banana Peel Cellulose Acetate

The analysis of cellulose acetate content and DS of kepok banana peel was carried out at 1% NaOH solvent and varying acetylation times of 2 hours and 2.5 hours. Moreover, the analysis was performed to determine the type of cellulose acetate produced in this research, including monoacetate, diacetate, or triacetate. At 1% NaOH solvent and an acetylation time of 2 hours, the results showed that the cellulose acetate content was 34% with a DS of 1.9%. Meanwhile, 1% NaOH solvent at 2.5 hours obtained a content of 38.23% and 2.3% DS. An increasing trend was also observed in acetylation time as the cellulose acetate and the DS of kepok banana peel increased. The maximum increase in cellulose acetate levels occurred at 2.5 hours of acetylation time. Moreover, longer acetylation reaction time resulted in reduced cellulose acetate content [10][14]. The content of cellulose acetate is directly proportional to DS, with a higher value causing an increase in its melting point. Previous studies have established that the melting point of cellulose acetate ranged from 170 to 240°C. In this research, it was discovered that concentration at 1% NaOH solvent and acetylation time of 2.5 hours served as a type of cellulose diacetate effective for the production of membrane from kepok banana peel [15].

The functional group analysis was carried out to identify the presence of functional groups and wave numbers based on the bonds contained in the cellulose acetate of kepok banana peel, as shown in Figure 5.

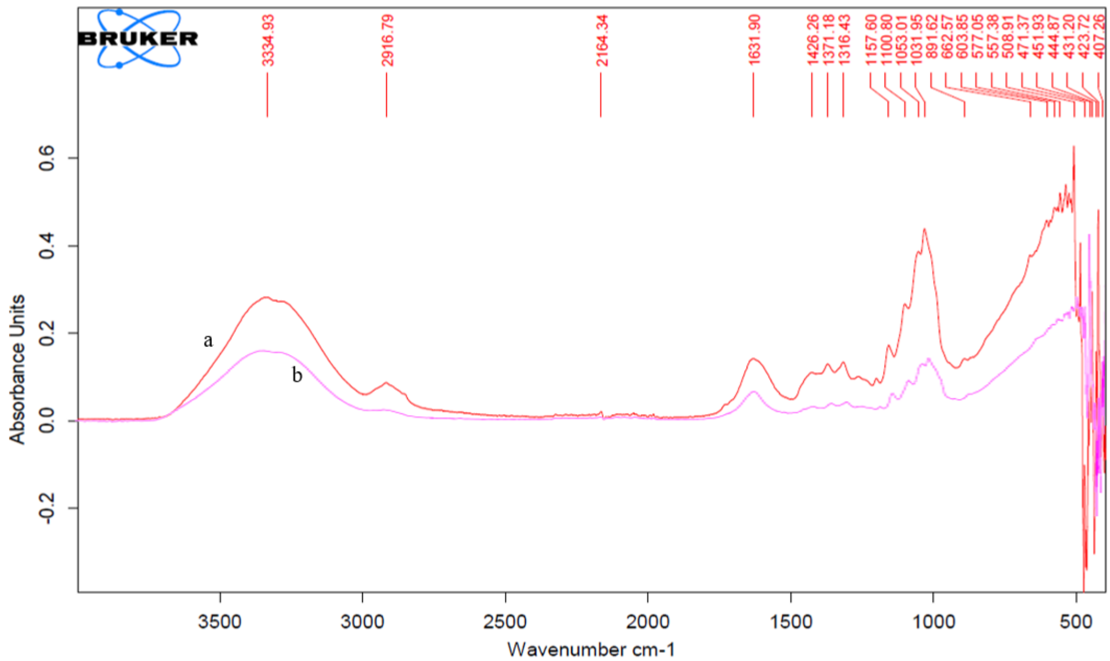


Figure 5. FTIR spectra of kepok banana peel cellulose acetate in 1% NaOH solvent with variations in acetylation time a) 2 hours and b) 2.5 hours

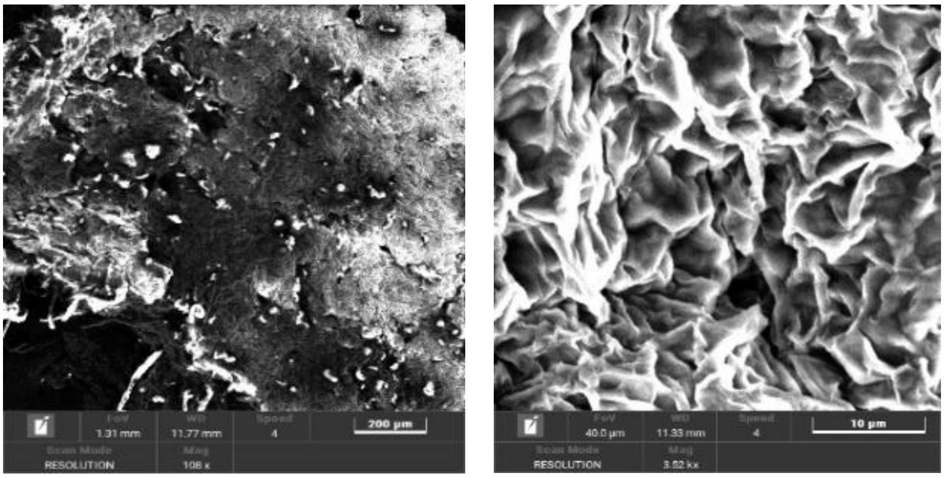
Table 1. Functional group of kepok banana peel cellulose acetate with 1% NaOH and acetylation time

Functional Groups	Wave Number (cm^{-1})*	Commercial Cellulose Acetate (cm^{-1})*	Acetylation Time	
			2 Hours (cm^{-1})	2.5 Hours (cm^{-1})
O – H Strectch	3750 – 3000	3486.97	3334.93	3328.12
C – H Strectch	3000 – 2700	2960.38	2916.79	2916.22
CH_2 Bend	1475 – 1300	-	1426.26	1429.75
C – H Bend	1300 – 1000	1383.89	1157.60	1263.64
C – O Strectch	1050 – 1000	-	1031.95	1033.03

**Source:* [8]

Figure 5 shows the analysis of functional groups and wave numbers of cellulose acetate from kepok banana peel in 1% NaOH solvent with acetylation time of 2 hours. Based on the results, a typical absorption of functional groups in the cellulose acetate compound was observed. The absorption depth at wave number 3334.93 cm^{-1} showed the presence of the O-H stretch functional group, while 2916.79 cm^{-1} indicated C-H stretch. Furthermore, the absorption depth of wave numbers 1426.26 cm^{-1} and 1157.60 cm^{-1} showed CH_2 and C-H bend functional groups, respectively. The absorption depth of 1031.95 cm^{-1} wave numbers indicated the existence of the C-O stretch functional group. The results of the FTIR spectrum analysis of cellulose acetate from kepok banana peel in 1% NaOH solvent with variations in the acetylation time of 2.5 hours above also showed the presence of functional group absorption in the cellulose acetate compound. At wave number 3328.12 cm^{-1}, the presence of O-H stretch was indicated, while 2916.22 cm^{-1} showed C-H stretch functional group. The absorption depth of wave numbers 1429.75 cm^{-1} and 1263.64 cm^{-1} indicated the existence of the CH_2 bend and C-H bend functional groups. Meanwhile, the absorption depth of 1033.03 cm^{-1} wave numbers indicated the presence of the C-O stretch functional group [16]. Table 1 further illustrates the functional groups of kepok banana peel cellulose acetate in 1% NaOH solvent at acetylation times of 2 hours and 2.5 hours.

The analysis of the surface structure of kepok banana peel cellulose acetate at varying acetylation times of 2 hours and 2.5 hours is shown in Figure 6. Cellulose acetate with 1% NaOH solvent and acetylation time of 2 hours showed a flat top surface, characterized by several spots resembling raisins when viewed with Mag 108 x magnification. Furthermore, cellulose acetate with 1% NaOH solvent and acetylation time of 2.5 hours showed a regular structure and hollow fibers with a magnification of 3.52 kx. In this research, the optimal results of surface structure analysis were obtained at a concentration of 1% NaOH solvent and an acetylation time of 2.5 hours.



(a) (b)

Figure 6. Surface structure of cellulose acetate kepok banana peel variation acetylation time a) 2 hours and b) 2.5 hours

4. Conclusion

In conclusion, this research showed that the optimal cellulose content of kepok banana peel was obtained at 56.07% in 1% NaOH solvent, with a smoother surface structure, more fiber, and hollowness as observed with Mag 679 x magnification. At 2.5 hours of acetylation, the optimal yield was 38.23% cellulose acetate levels and a 2.3% degree of substitution. Based on these results, cellulose acetate with 1% NaOH solvent and acetylation time of 2.5 hours, served as a cellulose diacetate, which is suitable for membrane production from kepok banana peel.

5. Acknowledgments

The author is grateful for the assistance received from various parties, including Mrs. Theresia Evila Purwanti Sri Rahayu, S.T., M.Eng. as the Coordinator of the Applied Undergraduate Study Program in Environmental Pollution Control Engineering Politeknik Negeri Cilacap. Furthermore, the author is grateful to Mrs. Ayu Pramita, S.T., M.M., M.Eng. and Mr. Dodi Satriawan, S.T., M.Eng. who served as the supervising lecturers. This research was facilitated by the facilities and infrastructure of the Politeknik Negeri Cilacap Study Program of Environmental Pollution Control Engineering.

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