Makara Journal of Science

Volume 25
Issue 3 *September*

Article 4

9-30-2021

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Silvy Djayanti
Center of Industrial Pollution Prevention Technology, Ministry of Industry of the Republic of Indonesia (BBTPPI Kementrian Perindustrian Republik Indonesia), Semarang 50136, Indonesia

Syarifa Arum Kusumastuti
Center of Industrial Pollution Prevention Technology, Ministry of Industry of the Republic of Indonesia (BBTPPI Kementrian Perindustrian Republik Indonesia), Semarang 50136, Indonesia

Januar Fatkhurrahman
Center of Industrial Pollution Prevention Technology, Ministry of Industry of the Republic of Indonesia (BBTPPI Kementrian Perindustrian Republik Indonesia), Semarang 50136, Indonesia

Agus Purwanto
Center of Industrial Pollution Prevention Technology, Ministry of Industry of the Republic of Indonesia (BBTPPI Kementrian Perindustrian Republik Indonesia), Semarang 50136, Indonesia

Agung Budiarto
Center of Industrial Pollution Prevention Technology, Ministry of Industry of the Republic of Indonesia (BBTPPI Kementrian Perindustrian Republik Indonesia), Semarang 50136, Indonesia

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Makara Journal of Science, 25/3 (2021), 155−161
doi: 10.7454/mss.v25i3.1219

Synthesis and Characterization of Cellulose Acetate Membrane from Cotton Spinning Waste

Silvy Djayanti[1], Syarifa Arum Kusumastuti[1], Januar Fatkhurrahman[1], Agus Purwanto[1], Agung Budiarto[1], and Alex Lukmanto Suherman[2]*

1. Center of Industrial Pollution Prevention Technology, Ministry of Industry of the Republic of Indonesia (BBTPPI Kementrian Perindustrian Republik Indonesia), Semarang 50136, Indonesia
2. Department of Computer Engineering, School of Electrical Engineering, Telkom University, Bandung 40257, Indonesia

*E-mail: alexsuherman@telkomuniversity.ac.id

Received June 23, 2021 | Accepted April 20, 2021

Abstract

Cellulose acetate membrane (CAM) was successfully synthesized and characterized from the cotton spinning waste of the textile industry. The membrane was produced through the isolation, acetylation, and phase inversion stages. The highest yields of cellulose fiber and α-cellulose contents were obtained using 3.0% and 6.0% v/v NaClO, respectively. The C–O acetyl bond detected by Fourier Transform Infrared (FTIR) analysis indicates the formation of the CAM. The resulting membrane can be potentially applied as an ultrafiltration membrane for water desalination purposes in water and wastewater treatment facilities. Furthermore, the utilization of cotton spinning waste as raw material aims to produce inexpensive products and recycle solid waste from the textile industry.

Keywords: cellulose acetate membrane, FTIR, sodium hypochlorite, cotton spinning waste, textile

Introduction

The textile industry produces yarn fibers, fabrics, clothing, and products made of fiber. Generally, the textile manufacturing process consists of several steps, namely, fiber production, fiber processing, spinning, yarn preparation, fabric production, bleaching, dyeing, printing, and finishing. The raw materials used to produce them can be sourced from plant fibers (such as cotton, flax, bamboo, and jute), animal fibers (such as wool and silk), and synthetic materials (such as nylon, polyester, and acrylic) [1, 2]. These raw materials are abundantly available both naturally and artificially but have not been utilized optimally for other applications.

Cotton fiber and polyester, the raw materials of thread, contain a relatively high amount of cellulose. This cellulose content can be utilized to synthesize the cellulose acetate membrane (CAM). A membrane is defined as a thin film, a barrier between two phases that are semipermeable [3]. Membrane technology has been widely used in various fields, including food, energy, waste and water treatment, and the health sector [4]. The advantage of using membrane technology is that its energy requirements are lower than those of other alternative separation methods. The application of membrane technology is simple and environmentally friendly [4, 5].

In this work, the cellulose content of cotton spinning waste from the textile industry will be used as a raw material to synthesize the CAM. Using the proposed method, the resulting cellulose acetate is expected to have similar characteristics as commercial membranes and a high potential to be used as a raw material for membrane production. To achieve this aim, four continuous stages, namely, (1) the isolation of cellulose fiber from cotton spinning waste from the textile industry, (2) the acetylation of cellulose to obtain cellulose acetate, (3) the synthesis of the CAM, and (4) the characterization of the CAM, are presented. Moreover, the best operating conditions to synthesize the CAM are discussed thoroughly.

The proposed method can be used as an alternative solution to overcome and utilize the cotton spinning waste from the textile industry. The novelty of this work was the synthesis of CAM using a simple and reproducible method. The yields of cellulose fiber and α-cellulose contents were markedly affected by the use of sodium hypochlorite (NaClO). Furthermore, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) analyzes were performed to obtain more in-depth insights into the resulting CAM.

Materials and Methods

Chemicals. Cotton spinning wastes containing a mixture of natural cotton and polyester were obtained from the local textile industry in Semarang, Central Java, Indonesia. Sodium hypochlorite (NaClO), sodium hydroxide (NaOH), acetic anhydride ($C_4H_6O_3$), and sulfuric acid (H_2SO_4) were sourced commercially from Merck KGaA, Darmstadt, Germany. Polyethylene glycol (i.e., PEG 600) was sourced commercially from Sigma Aldrich and used as received.

Synthesis of the cellulose acetate membrane. Synthesis of the CAM involves several stages. First, cellulose isolation or extraction was performed in four steps, namely, bleaching, hemicellulose removal, delignification, and purification. The bleaching process was done by soaking the cotton spinning waste in NaClO solution in a water bath at 80 °C for 4 h. Afterward, the cotton spinning waste was immersed again in NaOH solution in a water bath at 60 °C for 24 h to remove hemicellulose. In this step, the cotton spinning waste from the textile industry was bleached and heated with different solutions, namely, sodium chlorite ($NaClO_2$), hydrogen peroxide (H_2O_2), and HCl, each 3% v/v at acidic pH. The acidic state is obtained by dropping an acetic acid solution into the sample solution until the desired pH is reached and left alone for 3 h at 80 °C in a water bath. This process is repeated twice, and the sample solution is washed with distilled water until it is free from acid. Then, delignification was done by mixing the cotton spinning waste with NaOH solution in a water bath at 80 °C for 4 h. Finally, the product was immersed in NaOH solution, heated at 60 °C for 4 h to obtain pure cellulose fibers, and dried under ambient temperature.

In the second stage, the resulting dried cellulose fibers underwent acetylation to form cellulose acetate. This process was done by mixing 10 g of cellulose fiber with 20 mL of $C_4H_6O_3$ and 5 mL of H_2SO_4 solutions at a specific concentration to form a paste. Afterward, the paste was mixed with a dope solution (containing 80% acetone and 5% PEG 600) using a magnetic stirrer for 8 h at ambient temperature. The mixture was left overnight to remove the bubbles. The final stage was phase inversion. The mixture of the cellulose fibers and dope solution was poured and printed onto a glass plate using manual casting to conduct this experiment. A thin layer was formed on the glass plate and left for approximately 5 min at ambient temperature to dry completely. The thin layer was inserted into a tube filled with pure water to remove the excess solvents. Subsequently, a CAM was formed. Finally, the resulting CAM was characterized using FTIR (Thermo Scientific Nicolet iS10) and SEM (with an accelerating voltage of 10 kV) to determine its chemical structure, components, and morphology.

Results and Discussion

This section outlines the results of the bleaching, hemicellulose removal, acetylation of the cellulose, delignification, and purification stages during the synthesis of the CAM. Afterward, the characterizations of the CAM were presented and discussed. The workflow is shown in Figure 1.

Cellulose isolation. In this stage, the cellulose fiber was obtained by isolating 50 g of cotton spinning waste using 250 mL of 4.0 M NaOH and 20 mL of acetic acid 96% v/v solutions as oxidizing agent and catalyst, respectively. Subsequently, the cotton spinning waste was filtered and individually mixed with 3.0%, 4.5%, and 6.0% v/v NaClO. NaClO was used to oxidize and hydrolyze the cells, in which osmosis can drain water out of the cells because of its hypertonic nature. The percent conversion of the cellulose fiber (i.e., the yield) is shown in Table 1.

As shown in Table 1, the yield percentage of cellulose fiber was decreased by increasing the NaClO concentration. The results indicate that above 3.0% v/v NaClO, the physical structure of cellulose fiber in the cotton spinning waste is most likely decomposed into CO_2, water, and carboxylic acid. Notably, the removal of lignin (i.e., delignification), a component in the fiber, is indicated by the blackish brown color of the solution phase [6].

The amount of lignin removed after the initial treatment ranges from 50% to 70% v/v, depending on the biomass type (i.e., source of natural cotton) [7]. To assess the delignification stage, the cotton spinning waste was immersed in a solution containing 4.0% v/v NaOH and three different NaClO concentrations (i.e., 3.0%, 4.5%, and 6.0% v/v) as oxidizing and bleaching agents, respectively. In this work, 4.0% v/v NaOH was used to eliminate lignocellulose (delignification) because it causes the degradation of the esters and glycoside side chains of the cotton spinning waste. This delignification stage results in lignin structural changes, cellulose swelling, and partial cellulose and hemicellulose dissolution [8]. Moreover, the amount of lignin is reduced at a long immersion time of cellulose acetate in NaOH, as indicated by the mass [9]. The decrease in mass and increase in the length of immersion time make the cellulose fiber more soluble and softer, thus facilitating the acetylation process. The cellulose content that has been isolated from the cotton spinning waste is shown in Table 2.

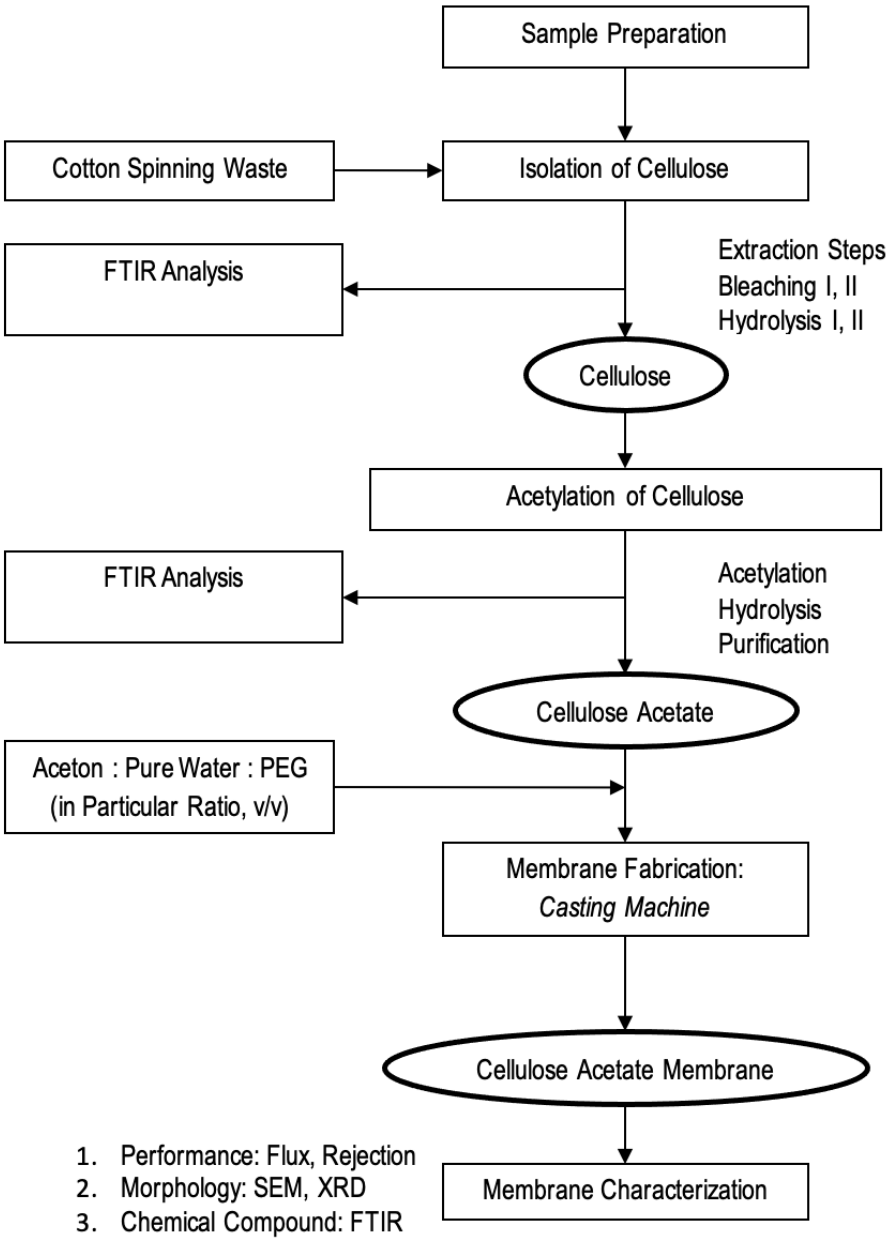

Figure 1. Workflow of the Synthesis and Characterization of the Cellulose Acetate Membrane

Table 1. Cellulose Isolation from the Cotton Spinning Waste with Different Sodium Hypochlorite (NaClO) Concentrations

Batch	Sample	NaClO (% v/v)	Resulting Cellulose (g)	Yield (%)
	1	3.0	39.12	78.24
I	2	4.5	33.94	67.88
	3	6.0	34.80	69.60
	1	3.0	32.56	65.12
II	2	4.5	19.13	38.27
	3	6.0	14.14	28.29
	1	3.0	31.52	63.04
III	2	4.5	43.39	43.39
	3	6.0	34.44	34.33

Table 2. Cellulose Content from the Isolation Stage with Different NaClO Concentrations

Batch	NaClO (% v/v)	α-cellulose (% v/v)	Viscosity (Cp)	Yield (mL g^{-1})	Degree of Polymerization
1	3.0	37.9	2.7	89	220
2	4.5	38.0	2.2	67	157
3	6.0	40.1	2.4	26	52

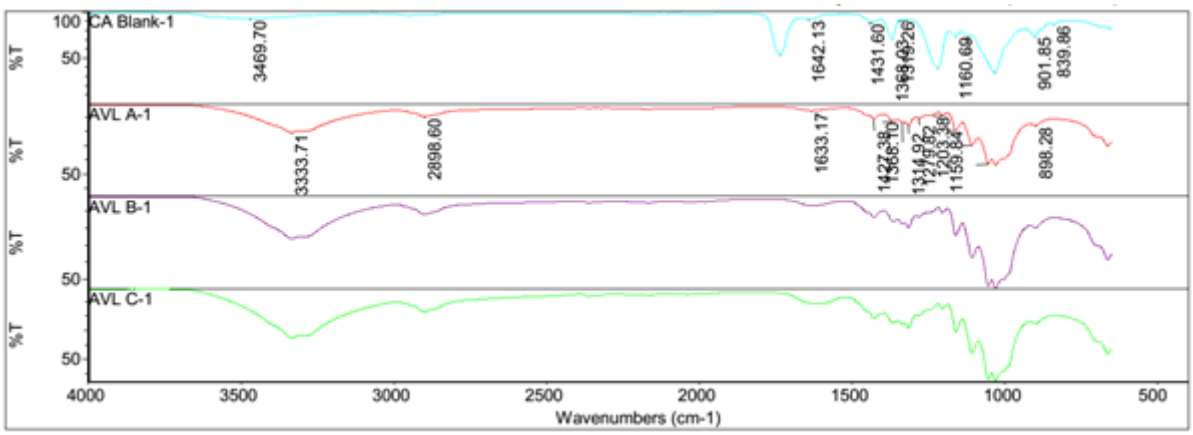

Figure 2. Fourier Transform Infrared (FTIR) Spectra of each Cellulose Fiber using Different Sodium Hypochlorite (NaClO) Concentrations (i.e., 3.0%, 4.5%, and 6.0% v/v for AVL A-1, AVL B-1, and AVL C-1, Respectively).

As shown in Table 2, the highest α-cellulose content was obtained using the 6.0% v/v NaClO. Putera *et al.* [10]. reported that NaClO would induce cellulose oxidation, which contains a high percentage of hydroxyl groups in neutral or alkaline conditions, indicating each variable's degree of polymerization degree (DP). The DP is the number of monomeric units in a macromolecule or polymer or oligomer molecule. The DP does not reflect the variation in molecule size of the polymer that typically occurs; it only represents the mean number of monomeric units. This molecular weight has an effect on the polymer's chemical properties, where the higher molecular weight of the polymer indicates its stronger form [11]. In this study, the DP can be calculated as the ratio of the molecular weight of the polymer to the molecular weight of the monomers, as shown in Equation (1):

$$\text{DP} = \frac{M_n}{M_o} = \frac{Molecular\ Weight\ Polymer}{Molecular\ Weight\ monomer} \quad (1)$$

where M_n is the number average molecular weight and M_0 is the molecular weight of the monomer unit. The DP values of cellulose content resulting from the isolation stage with different NaClO concentrations are shown in Table 2.

Characterization of the cellulose fiber. The resulting cellulose fiber was characterized using FTIR and SEM to assess its structural and morphological changes. FTIR was performed (Thermo Scientific Nicolet iS10) to analyze the cellulose fiber at different NaClO concentrations. The results are shown in Figure 2.

The resulting infrared spectra of cellulose fibers showed identical spectra, indicating similar wavenumber positions for each chemical bonding, for all three samples. The spectra show the OH strain vibration in the area of 3,000–3,700 cm^{-1}, as reported by Fan *et al.* [12]. Moreover, the presence of O–H and C–O bonds indicate the presence of cellulose compounds. In 3.0% v/v NaClO, the C–H and O–H bonds were detected at the peak positions of 2,896.6 and 3,333.71 cm^{-1}, respectively. Water absorption was observed in the peak position of 1,633.17 cm^{-1}. The resulting OH group spectrum indicates hydroxyl groups from cellulose, of which the acetyl group does not substitute [13]. Hydrogen bonds are formed between hydrogen atoms from one hydroxyl group of a glucose monomer and an oxygen atom from another hydroxyl group of glucose monomers in a cellulose polymer chain. This hydrogen bond results in cellulose fibers that are insoluble in water [10].

Figure 3 shows the surface morphologies of cellulose fiber obtained by SEM analysis using magnifications of ×500 and ×5,000 at an accelerating voltage of 10 kV. Generally, the morphology of the cellulose fiber has

large pore sizes, ranging from 8.3 µm to 84.4 µm, with an average diameter of 50.0 µm. The results indicate that the isolated cellulose fiber is unsuitable for microfiltration purposes because of its large diameter. Therefore, the cellulose fiber needs further treatment to reach the desired diameters of 0.1 to 10 µm for microfiltration purposes. To achieve this desired size, the acetylation stage was conducted and discussed in the following section.

Acetylation of the cellulose fiber. After the cellulose fiber was successfully isolated from the raw material and characterized, the next step is acetylation to form cellulose acetate. In the acetylation stage, the acetyl group combines with the cellulose group, with the acetylating agents $C_4H_6O_3$ and H_2SO_4 as the catalysts of this reaction. First, the protonation of $C_4H_6O_3$ by the catalyst and the hydroxyl group from cellulose with nucleophile will charge $C_4H_6O_3$ to produce an intermediate product and continuously degrade the physical state of the cellulose fiber into cellulose acetate, followed by proton release.

In isolated cellulose fiber with 3.0% v/v NaClO, the clumped cellulose fiber structure is visually large, rough, and thick. This result indicates that 3.0% v/v NaClO is insufficient to induce the acetylation process. Therefore, acetylation was done using 4.5% and 6.0% v/v NaClO

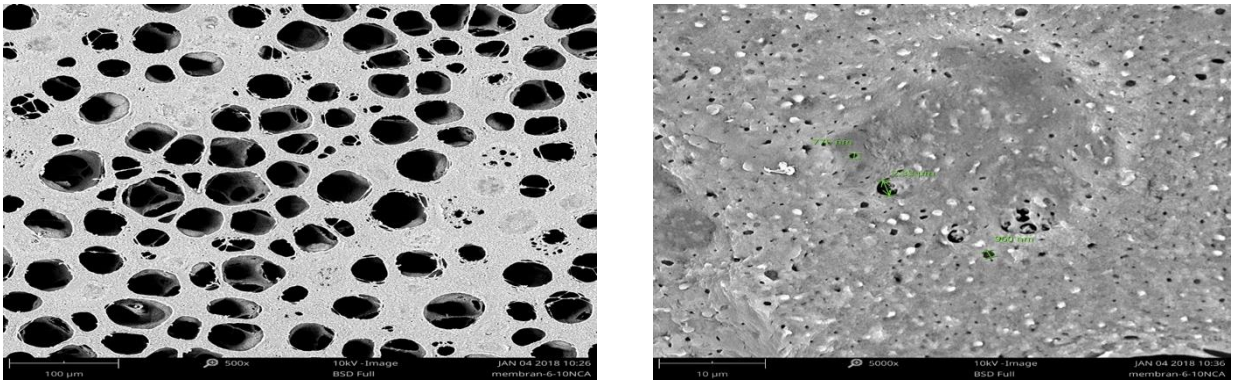

Figure 3. SEM Images of the Resulting Cellulose Fiber with ×500 and ×5,000 Image Magnifications

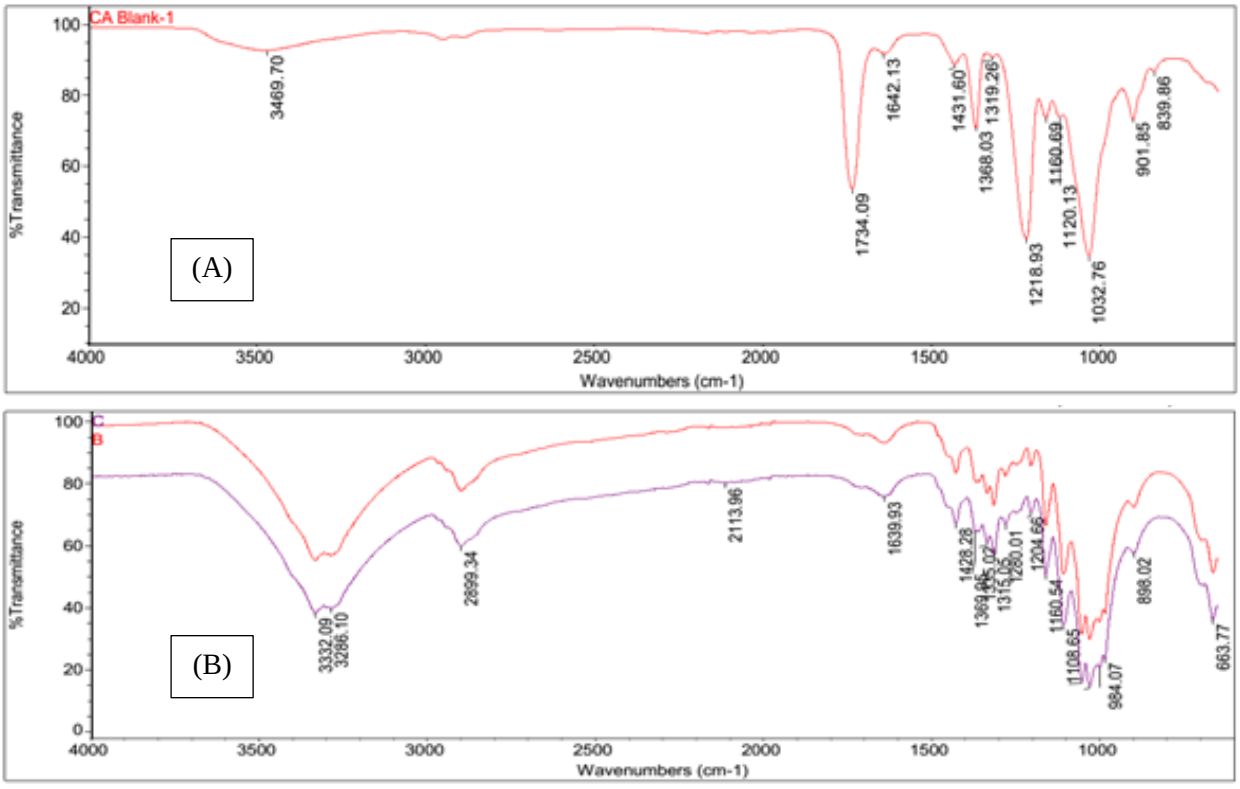

Figure 4. Comparison of the FTIR Analysis Results: (A) Untreated Cellulose Fiber, (B) Cellulose Acetate Fiber after Acetylation using 4.5% v/v (red line) and 6.0% v/v (purple line) NaClO Solutions

concentrations. Using these concentrations, the cellulose acetate fiber became finer, and the acetylation process became smoother. Apart from the shape and size of the cellulose acetate fiber, the stirring process during acetylation is relatively difficult because of the hydrophilic nature of the fiber; thus, the high water content of the fiber hampers the expected substitution reaction [13].

As shown in Figure 4, the infrared spectra show identical peaks for two variables. The typical absorption peak for cellulose acetate is the C=O carbonyl group's absorption peak and the acetyl group's C–O ester group. The functional group of C=O from the carbonyl group and C–O from the acetyl group were detected at the absorption peaks of 1,690–1,760 and 1,210–1,320 cm^{-1}, respectively.[14] The remaining lignin was still detected in this structure, as indicated by the characteristics of the C=C group in the absorption peak of 1,500–1,700 cm^{-1} [15].

In 6.0% v/v NaClO, the absorption peak of 663.77 cm^{-1} shows an OH bond other than the bending phase, which indicates the moisture content of the sample. The strain of the C–O–C bond and–OH deformation was detected at 1,204.66 cm^{-1}. The presence of CH_2 vibrations in the C6 bonds and the C=C group shows the characteristics of lignin detected at the peak positions of 1,315.05 and 1,639.93 cm^{-1}, respectively. The C–O acetyl group is detected at 1,280.01 and 1,315.05 cm^{-1}. Meanwhile, the characteristics of cellulose acetate are indicated by the presence of –OH at the peak positions of 3,286.10 and 3,332.09 cm^{-1}.

Meanwhile, in 4.5% v/v NaClO, the absorption peak detected at 662.56 cm^{-1} indicates the water content. The C–O acetyl groups were detected at the peak positions of 1,247.61, 1,279.98, and 1,314.81 cm^{-1}. The absorption peak detected at 1,636.75 cm^{-1} indicates that lignin remains in the sample. Cellulose remains in the regions of 3,286.94 and 3,332.58 cm^{-1}. Notably, the carbonyl functional group C=O in 1,690–1,760 cm^{-1} was not observed in the 6.0% and 4.5% v/v NaClO concentrations. The presence of cellulose acetate can be identified from the functional group of C–O esters from the acetyl group.

The synthesis of the CAM was initiated by preparing a casting solution consisting of synthesized cellulose acetate fiber, acetone, and PEG 600. Then, a thin layer of the membrane was formed on the glass plate and left at ambient temperature to dry completely. The thin layer was inserted into a glass tube filled with pure water to remove the excess solvents. The results show that the CAM was not dissolved entirely and formed a cloudy mixture in the water [13]. Indeed, in this study, we have successfully synthesized the CAM from scratch, which is the cotton spinning waste. However, we cannot conduct further steps (i.e., reproducibility test, rejection test, and application in real-world samples) because the resulting membrane was prone to degradation when diluted in water or any aqueous sample. Therefore, the other retention characteristics of this membrane need to be evaluated in future thermodynamic and kinetic studies.

Conclusion

The highest yields of cellulose fiber and α-cellulose contents from the raw cotton spinning waste were determined using 3.0% v/v NaClO. The FTIR analysis showed the presence of–OH functional groups, which indicates the formation of cellulose acetate. The infrared spectra of the cellulose acetate samples indicated the presence of a C–O acetyl ester functional group. In 4.5% v/v NaClO, the C–O group was detected at the absorption peaks of 1,247.61, 1,279.98, and 1,314.81 cm^{-1}. Meanwhile, in 6.0% v/v NaClO, the acetyl group was observed in the regions of 1,280.01 and 1,315.05 cm^{-1}. Meanwhile, the morphology of the cellulose fiber has large pore sizes ranging from 8.3 µm to 84.4 µm, with an average diameter of 50.0 µm. In this study, the synthesis of the CAM can be done by thoroughly mixing acetone, PEG 600, and cellulose acetate fiber using a specific concentration, as described previously. The other retention characteristics of this membrane need to be evaluated in future thermodynamic and kinetic studies. Finally, this initial study indicates a potential production scheme of CAM from the solid waste of the textile spinning industry.

Acknowledgements

This work was partially supported by the Membrane Research Center of the Diponegoro University. The authors declare no conflicting financial interest.

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