The Effect of Cellulose Acetate Concentration from Coconut Nira on Ultrafiltration Membrane Characters

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Abstract. Cellulose acetate is one of material in produce ultrafiltration membrane. Many efforts have been done to produce cellulose acetate from natural product to replace commercial one. In this research, ultrafiltration membrane has been produced from coconut flower water (nira). Ultrafiltration membrane is widely used in separation processes. This research aims to determine the characteristics of ultrafiltration membrane at a various concentration of cellulose acetate. The ultrafiltration membrane is conducted by phase inversion method at various concentration of cellulose acetate. The cellulose acetate concentration was 20%, 23% and 25% (w/w) with formamide as additives. The results showed that the greater the concentration of cellulose acetate, the smaller the flux value. The highest flux was a membrane with 20% cellulose acetate concentration with water flux value 55.34 L/(m². h). But the greater the concentration of cellulose acetate the greater the rejection. The highest rejection value was on a membrane with 25% cellulose acetate concentration of 82.82%. While from the tensile strength test and the pore size analysis, the greater the cellulose acetate concentration the greater the tensile strength and the smaller the pore size

1. Introduction

Membrane technology is widely used in the separation process. Membrane technology is chosen because the process is very simple, low energy consumption, does not damage the material, not use additional chemicals and not produce new waste hence it is classified as clean technology [1]. In the previous research [2], a membrane was made from nira, but the resulting membrane performance was low. The performance of the separation process depends on the characteristics of the membrane structure. Several factors which influencing membrane structure characteristics are the polymer type and polymer concentration, solvent type, membrane-making method, and the addition of additive [3].

In order to produce membrane with good characteristic, this research was used various polymer concentration. The polymer was cellulose acetate (CA). CA was obtained as a result of cellulose acetylation from a variety of sources, including bacterial cellulose [4]. Bacterial cellulose is a cellulose that is produced by microorganisms, especially the genus Acetobacter. Bacterial cellulose has superior purity properties compared to wood cellulose, including highly hydrophilic, high mechanically physical properties in wet and dry, uniquely smooth and distinct wicker form and can be produced from a variety of relatively inexpensive substrates [5]. A wide variety of substrates that have high glucose levels can be used for the manufacture of bacterial cellulose. One of them is nira. Nira is a water from coconut flowers that has a high enough glucose level. The content of glucose in nira was around 15.40% [6]. Nira is also a fertile medium for microorganisms to growth so that the process of glucose conversion into cellulose by *Acetobacter xylinum* bacteria is higher. This research used coconut nira as a source of
bacterial cellulose. Acetylation of bacterial cellulose produce cellulose acetate which was used as the basic material of ultrafiltration membranes. Membrane characterization included the measurement of flux, rejection, tensile strength, and pore size. This study is expected providing information on the effect of cellulose acetate concentration made from coconut palm to the membrane characteristics produced.

2. Experimental

2.1 Materials
The materials used were coconut nira, *Acetobacter xylinum*, sugar, ammonium sulfate, glacial acetic acid, sodium hydroxide, concentrated sulfuric acid, acetic anhydride, formamide where obtained from Merck while dextran T-500 from Sigma.

2.2 Preparation of cellulose acetate
Nira microbial cellulose was carried out by boiling 5 L of nira. Then 500 g of sugar and 25 g of ammonium sulfate were added until dissolved. The solution had an acidity in pH of 4. The solution was poured into plastic trays each containing 400 mL, closed with sterile newspapers, and aged 24 hours at room temperature. Then 10% of starter bacteria *Acetobacter xylinum* was added and incubated at room temperature for 7 days to obtain microbial cellulose.

The microbial cellulose was purified by boiling for 20 minutes, then soaked in a solution 1% of NaOH for 24 hours at room temperature. It was soaked again with 1% of acetic acid for 24 hours at room temperature and washed with running water. Then the microbial cellulose was pressed and dried.

In the acetylation experiment, there were three stages i.e. activation, acetylation, and hydrolysis. The activation stage was carried out by mixing and stirring 5 g of microbial cellulose and 12 mL of glacial acetic acid for 60 min. The acetylation stage was conducted by adding 20 mL of glacial acetic acid and 0.09 mL of concentrated sulfuric acid as catalyst and stirred again for 45 min. The mixture was cooled until its temperature reached 16°C and 13.5 mL of acetic anhydride 98% was added. Another mixture containing 20 mL of glacial acetic acid and 0.6 mL of concentrated sulfuric acid was added into the first mixture and stirred for 20h. Then the hydrolysis stage was carried out by adding 30 mL of acetic acid 67% drop by drop within 2 h at 38°C. The hydrolysis reaction was allowed to continue for 20 h. The product was poured into water with strong agitation and the precipitated was washed with water until the pH became neutral and finally dried at 50°C.

2.3 Preparation of ultrafiltration membranes
The membrane was carried out by phase inversion method. Casting solution composed of cellulose acetate, acetone, and formamide as additive. The composition of cellulose acetate was made in 3 variations i.e. 20, 23, and 25%. The mixture was stirred for 24 h at room temperature until homogeneous. The dope was aged for 24 h to get rid of air bubbles, then casted on a glass plate. After evaporation for 10 s, the glass plate was gently immersed into cold water at 4°C. The membrane was formed and then washed with deionized water for several hours until all the solvent and additive have been removed.

2.4 Characterization of ultrafiltration membrane
The flux and rejection of the membrane were measured in dead-end test cell under a constant applied pressure 3 kgf/cm². Water and dextran T-500 were used as feed. The flux water and dextran was measured every 10 m until the volume of permeate was constant. For rejection measurement, the feed and permeate concentration of dextran T-500 were determined by mixing the dextran with 5% of phenol and concentrated sulfuric acid in ratio of 1:1:5, then the absorbance was determined by spectrophotometric at the wave length of 490 nm. The flux was determined using equation: \( J_v = \frac{V}{A \cdot t} \) with \( J_v \) = flux (L/(m².h)); \( V \) = permeate volume; \( A \) = surface dimension, and \( t \) = time. The rejection was determined using equation: % \( R = (1 - \frac{C_p}{C_f}) \times 100 \% \) with \( R \) = rejection; \( C_p \) = permeate concentration; and \( C_f \) = feed concentration.
The membrane morphology were observed by scanning electron microscope JSM-6510 and the mechanical properties were measured by using Autograph Shimadzu AGS-500D.

3. Results and Discussion

3.1 Characteristics of cellulose acetate
Microbial cellulose was produced from coconut nira through the fermentation process by Acetobacter xylinum [7]. The fermentation process produced yellowish-white coloured nata with an average thickness of 1 cm. Nata that had been dried had 4% water content. According to Syamsu & Kuryani (2014) the water content required for the acetylation process is 3-7%. Acetylation of cellulose was carried out to replace part or all of the hydroxyl (OH) groups in the cellulose molecule with the acetyl group (CH-CO) of the acetic anhydride to form cellulose acetate [8].

The cellulose acetate is a white solid with a 38% acetyl content and a relative molecular weight of $9.29 \times 10^4$ g/mol. Measurement of acetyl content was performed to determine the type of cellulose acetate and the corresponding solvent on membrane preparation. The acetyl content of 38% was cellulose diacetate which dissolves in acetone [1].

3.2 Characteristics of Ultrafiltration Membranes
Flux is one of the important parameters used in the performance of membrane filtration. The flux value is expressed as the volume of the feed solution which can pass through the membrane per unit area of membrane (L/m$^2$.hours). Flux is directly related to the amount of pore and pore size of the membrane surface. The increase in cellulose acetate concentration the increase the viscosity of the mixture, and as a consequence is the decrease the diffusivity between the components in the system during the solidification process of the dope solution, then the precipitation became slower resulting in smaller pore membranes. At lower cellulose acetate concentrations, more voids formed inside the membrane and the increase of the speed of molecules passing through the membrane leaded to higher flux. Figures 1 and 2 show the relationship between the flux values and various concentrations of cellulose acetate.

Figures 1 and 2 show that the value of flux decreases as the cellulose acetate concentration increases. Water fluxes of cellulose acetate concentration of 20%, 23% and 25% are 55.03; 45.86; and 30.57 L/m$^2$.h respectively whereas the dextran fluxes for the same cellulose acetate concentration are 33.02; 32.10 and 20.79 L/m$^2$. hour. The water fluxes are higher than the dextran flux as dextran has higher molecular weight hence it took longer time to pass through the membrane pores. The highest flux value was obtained by a membrane with a concentration of 20% cellulose acetate. The greater the concentration of cellulose acetate added, the smaller the flux.

The rejection was determined by passing dextran on the three variations of the ultrafiltration membrane. Feed and permeate were measured by spectrophotometer at wavelength of 490 nm. The value of rejection for each cellulose acetate concentration is displayed at Table 1.
Increasing concentrations of cellulose acetate increased the percent of rejection. The highest rejection value was obtained on the membrane with 25% of cellulose acetate. Membrane rejection was closely tied to the cellulose acetate concentration.
related to membrane selectivity [9]. Selectivity can be used to determine the ability of the membrane to retain or pass a particle. The selectivity depended on the interaction of the membrane with the dissolved particles, the pore size of the membrane, and the size of the particles passed through the membrane pores [10]. The more concentrated cellulose acetate, the smaller the pore size and the more particles were retained on the membrane hence the percentage of rejection increases.

3.3 Mechanical properties of ultrafiltration membranes

The tensile test results supported the flux and rejection measurements. The membrane with a 25% cellulose acetate concentration provided the best tensile strength value. The value of the tensile strength of the membranes for the compositions 20, 23, and 25% were 0.672, 0.973, and 1.233 MPa, respectively. The membrane morphology determined with SEM shown at Figure 3, 4, and 5. It showed that increasing concentration of cellulose acetate produce membrane with smaller pores. The membranes pore sizes are in range 0.05 until 0.1μm. Ultrafiltration membrane has size pores ranging from 0.01 until 2 μm [11].

Figure 3. SEM photo of membrane with 20% of cellulose acetate surface
Figure 4. SEM photo of membrane with 23% of cellulose acetate surface

Figure 5. SEM photo of membrane with 23% of cellulose acetate surface

The authors should give deep analysis regarding the SEM images and correlate these images with the membrane performance

4. Conclusion

The higher the concentration of cellulose acetate in the preparation of ultrafiltration membranes, the higher the value of rejection and tensile strength, but the lower the flux value and pore size.
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References
[1] Lindu M, PuspitasariT, and Ismi E, 2010, Jurnal Sains Materi Indonesia 12 (1) : 17-23.
[2] WidyaningsihS, Chasani M, dan Zusfahair, 2016, Unsoed Purwokerto
[3] Ciptaraharja I and Praptowidodo V S, 2006, Jurnal Teknik Kimia Indonesia 5(3): 478-489.
[4] Widyaningsih S, Rastuti U, dan Arifah N I, 2012, Prosiding Seminar Nasional Kimia dan Pendidikan Kimia Tahun 2012 Purwokerto
[5] GustianI, Sutanto T D, and Adfa M, 2006, Jurnal Gradien 2 (1): 126-129
[6] RukmanaRand Yuniarshih Y, 2001, Membuat Kecap: Tempe Busuk, Nira, dan Air Kelapa (Yogyakarta: Kanisius)
[7] Piluharto B, 2003 Jurnal Ilmu Dasar 4 (5): 52-57
[8] Radiman C L, 2004, Kimia Polimer (Bandung: Penerbit ITB) p 5-20
[9] Radiman C L, Widyaningsih S, and Sugesty S 2008 Journal ofMembrane Science 315: 141-146
[10] SilviaV, Pinem J A, and Irianty R A 2016 Jom FTEKNIK 3 (1): 1-9
[11] Meijuan Z, Nemade P R, Lu X, Zeng X, Hatakeyama E S, Noble R D, and Gin D L 2007 Journal of The American Chemical Society 129: 9574-9575.