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Nira Potential as Membrane Preparation Materials

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Abstract. The cellulose acetate membrane based on nira (coconut flower water) was successfully synthesized by phase inversion method. This research was conducted through some steps which were microbial cellulose synthesis, cellulose acetate synthesis, synthesis of cellulose acetate membrane with PEG additive and characterization of membranes. The characterizations were flux, rejection, tensile strength, and pore sizes. The result showed that cellulose acetate membrane flux were 27.52 L/m^2.h and rejection of dextran T-500 were 63.30 %. The tensile strength was 1,6 N/m^2 and the pore sizes was 0.25 – 0.5 µm which were ultrafiltration membranes.

1. Introduction

Coconut nira is a water which is contained in coconut flower. Nira is obtained by tapping the coconut flower. Coconut nira contains high levels of sugar which are about 15.40% [1]. This fluid is the best medium for microorganisms growth, so the coconut nira has a potential to be used as a microbial cellulose. Microbial cellulose is cellulose obtained from the fermentation process that is composed of single fibers produced by a strain of Acetobacter aceti subspecies xylinum. Microbial cellulose has the same chemical structure as cellulose derived from plants. According to [2], microbial cellulose has several advantages including high purity, high degree of crystallinity, having a density between 300-900 kg/m3, high tensile strength, elastic and biodegradable. Its potential can be used as the base material synthesis of cellulose acetate by acetylation method.

The cellulose acetate is a polymer which is widely used in fibers, plastics, and membrane industry [3]. Membrane technology has been developed over the past decades. Some applications of a membrane such as wastewater treatment, desalination, demineralization, even hemodialysis using cellulose acetate as materials for the membrane. However, cellulose acetate that is used are synthesized from wood that is expensive. Moreover, the use of wood for membrane must compete with other industries that use wood as raw material. In order to find alternative raw materials other than wood, the research was conducted.

2. Experimental

2.1 Materials

The materials used were coconut nira, Acetobater xylinum, sugar, ammonium sulfate, glacial acetic acid, sodium hydroxide, concentrated sulfuric acid, acetic anhydride, polyethylene glycol 600 were obtained from Merck while dextran T-500 from Sigma.

2.2 Preparation of acetylated nira microbial cellulose

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 must have acidity in pH 4. The solution was poured into plastic trays each containing 400 ml, closed with sterile newspapers, and allowed 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. Then 20 mL of glacial acetic acid and 0.09 mL of concentrated sulfuric acid as catalyst were added and stirred again for 45 min. The mixture was cooled until its temperature reached 16^{o}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. This is the acetylation stage. Then the hydrolysis stage was carried out by adding 30 mL of acetic acid 67% drop by drop within 2 h at 38^{o}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^{o}C.

2.3 Characterization of acetylated nira microbial cellulose

The acetyl content of the synthesized cellulose acetate was determined by volumetric method. 0.15 g of dried cellulose acetate was mixed with 5 mL of ethanol and 20 mL of 0.5 M sodium hydroxide. The mixture was heated and stirred at 60 ^{o}C for 2 h. It was cooled at room temperature then titrated with 0.5 M hydrochloric acid and phenolphthalein until the pink color disappears. 4 mL of hydrochloric acid was added and stirred for 5 min then was added 2 -3 drops of phenolphthalein and titrated with 0.5 M sodium hydroxide until the solution was pink. The same treatment without cellulose acetate was done as a blank. The acetyl content was determined with equation:

Acetyl content (%) =$[(D-C)M_a+(A-B)M_b]x\ 4{,}305/W]$

where A : volume of NaOH for sample titration
B : volume of NaOH for blank titration
M_b : molaritas of NaOH
C : volume of HCl for sample titration
D : volume of HCl for blank titration
M_a : molaritas of HCl
W : sample mass

The viscosity – average molecular weight (Mv) of cellulose acetate was determined in acetone as solvent by viscometry method using the Mark-Houwink-Sakurada equation: $[\eta] = KMv^{a}$ with K = 1.33 x 10^{-3} and a = 0.616. while the functional groups of the cellulose acetate were analyzed by FTIR spectroscopy.

2.4 Preparation of acetylated nira membrane

The membrane was carried out by phase inversion method. Casting solution composed of cellulose acetate, acetone, and polyethylene glycol (PEG) as additive. The composition were 20% of cellulose acetate, 66% of acetone, and 14% of PEG. The mixture was stirred for 24 h at room temperature until homogeneous. The dope was allowed for 24 h to get rid of air bubbles, then cast on a glass plate. After evaporation for 10 s, the glass plate was gently immersed into cold water at 4 ^{o}C. The membrane was formed and washed with deionized water for several hours until all the solvent and additive have been removed.

2.5 Characterization of acetylated nira membrane

The flux and rejection of the membrane were measured in dead-end test cell under a constant applied pressure 3 kgf/cm^2. Water and dextran T-500 were used as feed. The flux water and dextran was measured every 10 m until the volume of permeat was constant. For rejection measurement, the feed and permeat concentration of dextran T-500 were determined by mixing the dextran with 5% of phenol and concentrated sulfuric acid in rasio 1:1:5, then the absorbance was determined with spectrophotometric at 490 nm of wave length. The flux was determined using equation : $J_v = \frac{V}{A.t}$ with Jv = flux (L/(m^2.h)); V = permeat volume; A = surface dimension, and t = time. The rejection was determined using equation : % R = (1- C_p/C_f) x 100 % with R = rejection; Cp = permeat concentration; and Cf = feed concentration.

The membrane morphology was 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 Characterization of acetylated nira

The FTIR spectrum of cellulose acetate from nira in Figure 1 shows the existence of characteristic carbonyl peak (C=O) at 1737 cm^{-1} and acetyl peak (C-O ester) at 1230 cm^{-1}. The spectra of microbial cellulose (Figure 2) has no peaks at those regions. It shows that acetylation is succeeded. This result is

also confirmed by the acetyl content which is 39.97%. According to [4] this value refers to cellulose diacetate with acetyl contents ranging from 35 – 43.5%. It can be concluded that the kind of cellulose acetate is cellulose diacetate.

The determination of viscosity-average molecular weight of acetylated nira was 7.01 x 10^4 g/mol. It has the same value with the commercial cellulose acetate. [5] showed that viscosity-average molecular weight of commercial cellulose acetate was 7.50 x 10^4 g/mol. The molecular weight of the obtained cellulose acetate depends strongly on the acetylation condition. The acetylation and hydrolysis times influence the cellulose acetate molecular weight.

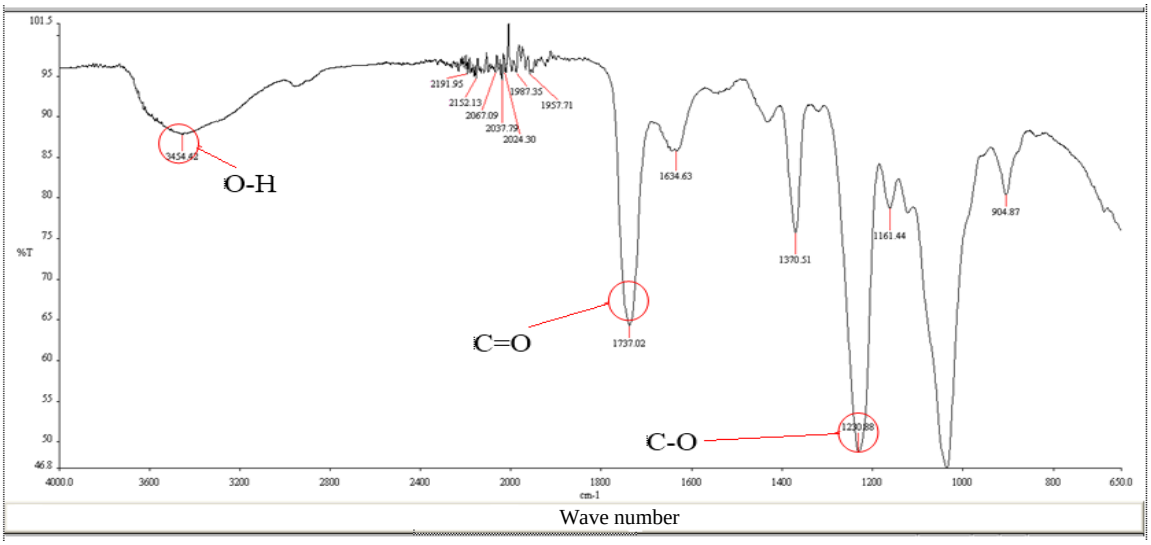

Figure 1. Cellulose acetate from nira

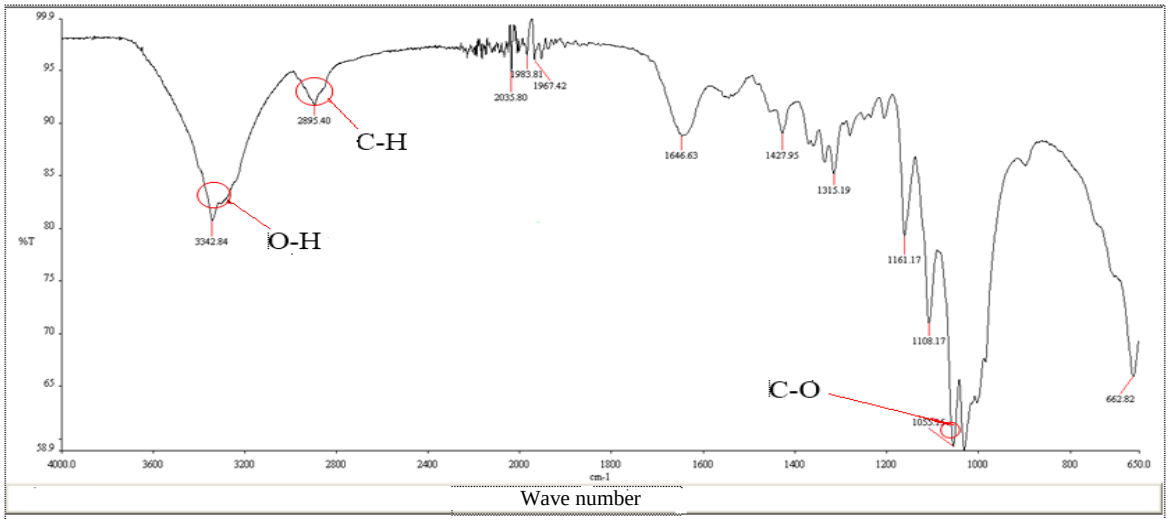

Figure 2. Microbial cellulose from nira

3.2 Effect of additive on water flux and rejection of acetylated nira membrane

Membrane was carried out by inversion phase method. Inversion phase method is a polymer transformasion process from liquid phase into solid in under control condition [6]. The method have four stages i.e polymer solution preparation, casting solution, solvent evaporation, and polymer precipitation [7]. Membrane was prepared with addition of PEG as additive. PEG can increase membrane pores distribution and keep the resistance from external influence. It is biocompatible, very hydrofil, and anti fouling that can increase membrane characteristic. As the control, another membrane was prepared without PEG addition.

Membrane characteristic in this research were flux and rejection. Flux can show how fast sample to pass the membrane. In Figure 3 shows that flux of membrane with PEG addition has a higher value

than without PEG. Flux value is determined by quantity and size of pores [2]. Adding PEG can make homogenous pores of the membrane. It increases flux value of membrane. In other hands, PEG can also increase the rejection of dextran T-500. The rejection was 63.20% for membrane with PEG while rejection for membrane without PEG was 48.20%.

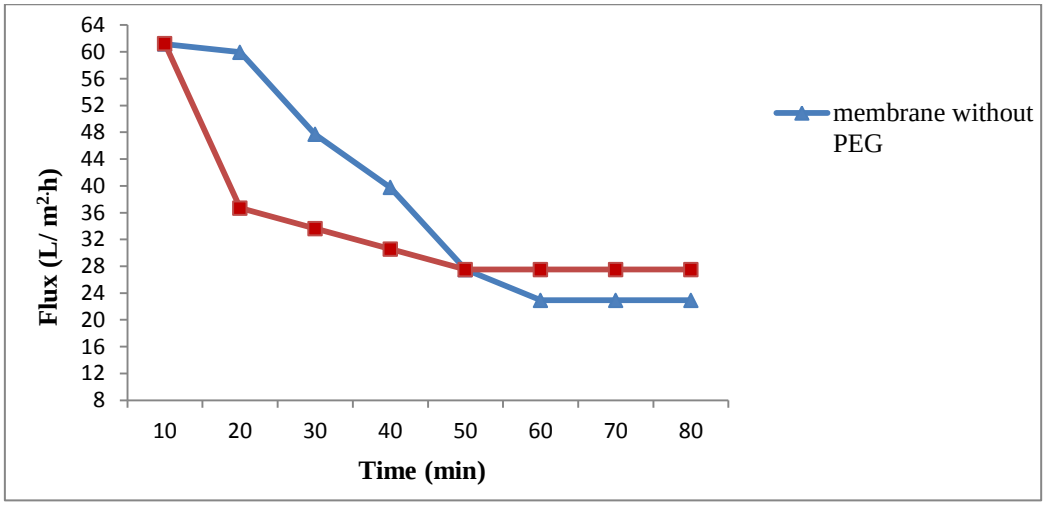

Figure 3. Effect of PEG addition on water flux

3.3 Morphology and mechanical property of acetylated nira membrane

Morphology membrane that was determined with SEM could be seen in Figure 4. It showed that the acetylated nira membrane was ultrafiltration because it had 0.25– 0.5 µm of size pores. Ultrafiltration membrane has size pores ranging from 0.01 until 2 µm [8].

Acetylated nira membrane has a good mechanical property. However, PEG addition decrease the tensile strength of membrane. Membrane without PEG had 6.9 N/m^2 of tensile strength while membrane with PEG had 1.6 N/m^2. According to PEG property which is used as the plasticiser, membrane with PEG was more elastic and it decreases the tensile strength.

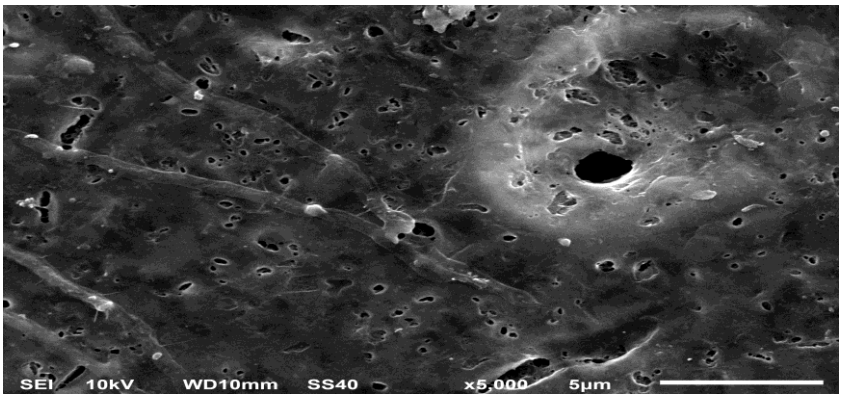

Figure 4. SEM photo of acetylated nira membrane surface

4. Conclusions

Nira can be modified into microbial cellulose that is a cellulose source in cellulose acetate synthesis. In order to prepare cellulose acetate membrane, adding additive increase flux and rejection of membrane but decrease the tensile strength.

Acknowledgements

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