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SYNTHESIS AND CHARACTERIZATION OF PROTON-CONDUCTING MEMBRANES BASED ON BACTERIAL CELLULOSE AND HUMAN HAIR KERATIN

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ABSTRACT

Studies on composite proton-conducting membranes made of human hair keratin and bacterial cellulose have been done. Keratin from human hair is produced through hydrolysis using NaOH as a solvent. Composite membranes constructed of bacterial cellulose and human hair keratin had mass variations of 4.5/0.5, 4.7/0.3, and 4/1. At temperatures of 25 ºC, 40 ºC, 60 ºC, and 80 ºC, the proton-conducting composite membrane was evaluated for Fourier Transform InfraRed, X-Ray Diffraction, degree of swelling, and proton conductivity. The interaction of bacterial cellulose and human hair keratin appeared at the peak of 3000-3500 cm^{-1}, as evidenced by functional group analysis of bacterial cellulose and human hair keratin composite membranes from Fourier Transform InfraRed. The produced composite membrane was semicrystalline in each mass variation, according to the results of the X-Ray Diffraction examination. The variant of bacterial cellulose and human hair keratin 4/1 showed the highest degree of swelling (34.09%). The composite membrane keratin made of bacterial cellulose and human hair had the maximum proton conductivity, with a variation of 4/1 and a value of 3.673×10^{-5} S/cm at a temperature of 25 ºC.

Keywords: Proton Conducting, Membrane, Human Hair, Keratin, Bacterial Cellulose.
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INTRODUCTION

Bacterial cellulose is a type of cellulose produced by microorganisms through fermentation.[1] The advantage of using bacterial cellulose is to reduce deforestation, so that forest sustainability can be maintained. Chemically, the structure of cellulose can be expressed by the molecular formula proposed by Haworth, which is a polymer consisting of β-glucose in the pyranose form linked to each other by 1,4 β glycoside bonds. If the configuration of β -glucose is described in terms of chairs, the atoms of the pyranose ring will be in two planes. Bacterial cellulose is cellulose synthesized by microorganisms such as Acetobacter, Rhizobium, and Agrobacterium. Bacterial cellulose has a composition similar to that of plant cellulose, but differs in: three-dimensional tissue structure, degree of polymerization usually 2000-6000, and physicochemical properties. In static culture, cellulose accumulates on the surface of liquid nutrients in the form of gelatin, which is called a pellicle or gel. After purification and drying, the gel produces a parchment product with a thickness of 0.01-0.5 mm. The use of bacterial cellulose as proton-conducting membranes has been widely reported.[2,3,4] The other natural polymer that can be offered for membranes in fuel applications is keratin from human hair. Human hair is very difficult to destroy even if it has been buried in the ground for a long time. Human hair contains a protein substance in the form of keratin which is able to make hair strong. Keratin is the main constituent of human hair fiber which is able to withstand proteolytic enzymes. Keratin protein greatly affects the resistance of hair fibers to degradation under stress and can provide good mechanical strength and elasticity.[5] Many efforts have been made in the context of providing energy that must be able to replace fossil energy sources. Fuel cells are one very profitable solution. The energy produced is quite clean and very efficient, whereas the processes that occur in fuel cells are based on oxidation-reduction chemical reactions. The proton-conducting membrane requires hydrophilic properties in the main chain.[6] Polymers such as cellulose are thought to facilitate the movement of protons, on the other hand, it is possible that cellulose-based membranes can also absorb many water molecules due to a large number of hydrophilic groups in this material. This can cause swelling in the membrane which results in a decrease in proton conductivity. In light of what has been said thus far, it is conceivable to add more polymers to the membrane, in this case, keratin, to allow proton conduction. Due to the formation of a Bronsted acid-base pair between two macromolecules, the membrane will be able to serve as a fuel cell that can operate at high operating temperatures and low humidity levels.[7]

EXPERIMENTAL

Material and Methods

Coconut water is obtained from the sale of grated coconut in Bengkulu city, the haircut waste is obtained from a barbershop in Bengkulu city, sodium hydroxide, glacial acetic acid, ammonium sulphate, dimethyl formamide (DMF), acetone and *Acetobacter xylinum*.

Preparation

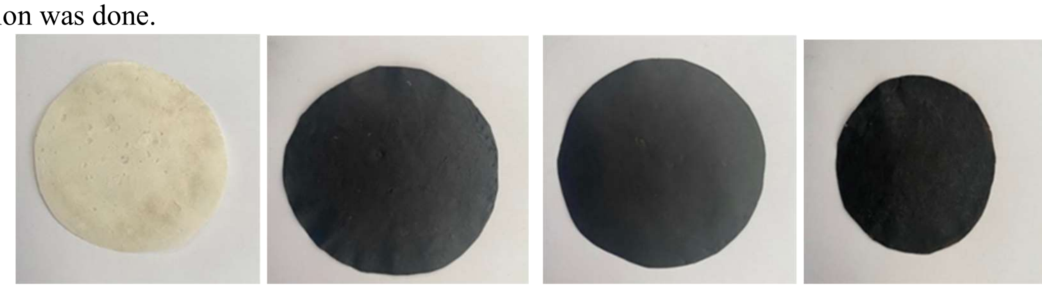
Bacterial cellulose was obtained through fermentation as in the previous research procedure1. The haircut waste was washed with water and detergent several times and then dried in an open space. Dry hair is soaked and washed with acetone for 30 minutes and then dried again in an open space. Haircut waste that has dried is then cut by scissors, and 50 grams of human hair is dissolved in 250 mL of 1 M NaOH solution at 70 ºC for 3 hours and stirred. After that, add glacial acetic acid to neutralize the solution then the solution is heated at 70 ºC in a water bath until a gel is formed. The resulting gel was reheated at 70 ºC until dry and mashed using a blender until it becomes powder 8. Preparation composite membrane, bacterial cellulose was blended until smooth until it became a slurry and filtered, then a bacterial cellulose membrane with a mass of 5 grams was printed. After that, 0.5 grams, 0.7 grams, and 1 gram of human hair keratin were weighed and then dissolved in DMF solvent. Furthermore, human hair powder was added with bacterial cellulose with the mass ratio of bacterial cellulose and hair powder was 4.5/0.5; 4.3/0.7; 4/1 then stirred until well mixed and printed using a petri dish and heated on a hotplate at a heating temperature of 30 ºC.

Characterization

On a Bruker Alpha-P (Wismar, Germany), Fourier Transform InfraRed (FTIR) spectra were captured in the attenuated total reflectance (ATR) band of 4000-400 cm^{-1}. Utilizing an X-ray diffractometer (Rigaku D-MAX2200, Japan) and Cu Ka (λ = 1.5406 Å) radiation spanning the range 2 between 0° and 100°, the X-ray powder diffraction (XRD) investigation was carried out. IM 3590 Chemical Impedance Analyzer HIOKI was used to evaluate the membrane's conductivity at 1 kHz, 0.05 Volt, and temperatures between 25 °C and 80 °C.

RESULTS AND DISCUSSION

The composite membrane and the bacterial cellulose membrane were depicted in Fig.-1. The composite preparation was done by combining keratin from human hair with bacterial cellulose. The bacterial cellulose-human hair keratin mass ratios used to create the membranes were 4.5/0.5, 4.3/0.7, and 4/1. To determine how mass affected the properties of the resultant proton-conducting composite membrane, mass variation was done.



(a) (b) (c) (d)

Fig.-1: (a) The Bacterial Cellulose Membrane and the Composite Membrane; (b) 4.5/0.5, (c) 4.3/0.7, (d) 4/1.

According to Fig.-2, bacterial cellulose has unique peaks that may be detected at wave numbers of 3341 cm^{-1} for O-H groups and 1050 cm^{-1} to 1157 cm^{-1} for C-O groups, COC and COH, stretch taking in from a cluster. This suggests that the cellulose ring contains glycosidic linkages. It reveals the presence of a C-H group of alkanes at a wave number of 2898 cm^{-1}. Methylene and methyl exhibit C-H bending vibrations at wave numbers 1379-1431 cm^{-1}, while the aromatic C-H bond 2 exhibits buckling vibrations at wave number 665 cm^{-1}.

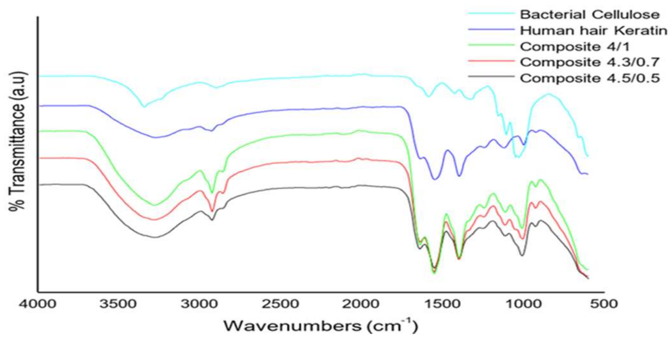


Fig.-2: FTIR Spectra of the Bacterial Cellulose Membrane, Human Hair Keratin and the Composite Membrane; 4.5/0.5, 4.3/0.7, 4/1.

The FTIR spectrum of human hair keratin shown in Fig.-2 shows that the characteristic absorption peak of human hair powder is the N-H group at a wave number of 3275 cm^{-1} which indicates an overlap between the hydroxyl group (O-H) and the amine group (N-H). The amine functional group (N-H) indicates the presence of peptide bonds in each protein, while keratin is included as a fiber protein consisting of amino acids. Wave number 2930 cm-1 shows the functional group of alkanes (C-H). At wave numbers, 1642 cm^{-1} and 1551 cm^{-1} are amide I bonded to (C-O) and amide II bonded to carbon C-N. At wave number 1395 cm^{-1}, there is a methyl group ($-CH_3$) and methylene groups ($-CH_2$) and at wave number 640 cm^{-1}, there are sulfide functional groups (S-S).[8] After being composited, the results of the FTIR analysis are shown in Fig.-2. The spectrum produced in composites comparisons is almost the same as the spectrum of human hair keratin, only that there is a slight change in widening due to the functional groups present in cellulose. This shows that there is a physical interaction between hair powder and bacterial cellulose so that the resulting spectrum does not differ much from the spectrum of bacterial cellulose and human hair keratin before being composited.

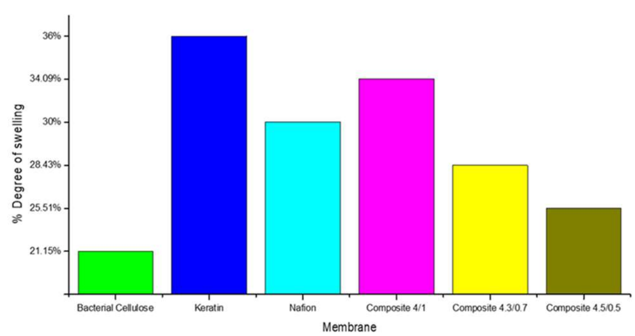


Fig.-3: Degree of Swelling Bacterial Cellulose, Keratin, Nafion, and the Composite Membrane; 4.5/0.5, 4.3/0.7, 4/1

Figure-3 showed the degree of swelling of cellulose without the addition of keratin of 21.15%. The degree of swelling of bacterial cellulose ranged from 17%-36%. The degree of swelling of keratin without the addition of cellulose is 36%.[9] The degree of swelling of the Nafion is 30%.[10] Figure has shown that the absorption of keratin is greater than that of Nafion. This shows that keratin can be used as a substitute for Nafion in fuel cell applications. The degree of swelling after being composited was bacterial cellulose/human hair keratin 4.5/0.5 of 25.51%, 4.3/0.7 of 28.43%, and 4/1 of 34.09%. The more the amount of hair powder increases, the value of the degree of swelling also increases.

In the previous study, the XRD results of bacterial cellulose were in the form of crystals with peaks at an angle of 2θ between 15º and 22.5º.[11] Meanwhile the XRD diffractogram for bacterial cellulose in this study showed the formation of a crystalline phase at an angle of 2θ between 14.2111º and 22.7042º which has shown in Fig.-4. The XRD diffractogram results from bacterial cellulose show the fiber structure. Where the diffraction pattern obtained is crystalline causing the fiber in bacterial cellulose to have high purity.

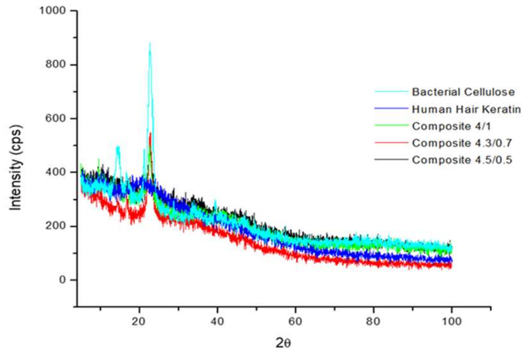


Fig.-4: XRD Diffractogram (a) The Bacterial Cellulose Membrane, Human Hair Keratin and the Composite Membrane; (b) 4.5/0.5, (c) 4.3/0.7, (d) 4/1.

The results of the hydrolysis of human hair keratin diffractogram showed does not appear to indicate a peak at an angle of 2θ which has shown in Fig.-4. It was shown that human hair keratin had a wide peak which indicated that the structure of human hair keratin was amorphous. Bacterial cellulose composite membrane/human hair keratin 4.5/0.5 has a peak with an intensity of 406.95 and 501.8457 at an angle of 9.401º and 22.7588º. In the ratio of bacterial cellulose/human hair, keratin 4.3/0.7 has a peak with an intensity of 298.340 and 501.789 at an angle of 16.8522º and 22.7912º while the bacterial cellulose composite membrane/human hair keratin 4/1 has a peak with an intensity of 498.3235 at an angle of 22.7953º. The results of the XRD analysis, it has shown that the more human hair keratin added, the lower the intensity diffractogram of the composite membrane. The composite membrane that has the widest amorphous peak is the ratio of bacterial cellulose/human hair keratin 4/1, with an explainable reason that the amorphous phase of human hair keratin is more dominant than the crystallinity phase of bacterial cellulose. From Table-1, it is known that the bacterial cellulose membrane has the highest proton conductivity, which is at a temperature of 25 ºC 2.213 x 10^{-5} S/cm. Nafion membrane has proton conductivity of 10^{-1} S/cm at temperatures below 100 ºC.[10] From these results, the proton conductivity of the Nafion membrane is greater than that of bacterial cellulose, but bacterial cellulose can still be used as a membrane to be applied to fuel cells because the proton conductivity of bacterial cellulose meets the standards for fuel cells.

Table-1: Proton Conductivity

Temperature (ºC)	Bacterial cellulose (S/cm)	Membranes composite (S/cm)		
		4.5/0.5	4.3/0.7	4/1
25	2.213 x 10^{-5}	1.357 x 10^{-5}	1.684 x 10^{-5}	3.673 x 10^{-5}
40	1.613 x 10^{-5}	7.482 x 10^{-6}	1.203 x 10^{-5}	7.798 x 10^{-6}
60	1.096 x 10^{-6}	1.603 x 10^{-6}	1.385 x 10^{-6}	2.456 x 10^{-5}
80	7.21 x 10^{-7}	4.472 x 10^{-6}	4.265 x 10^{-6}	6.490 x 10^{-6}

The highest proton conductivity in composite membranes in each comparison was bacterial cellulose/human hair keratin 4.5/0.5 at 25 °C is 1.357 x 10^{-5} S/cm, bacterial cellulose/human hair keratin 4.3/0.7 at 25°C is 1.684 x 10^{-5} S/cm and bacterial cellulose/human hair keratin 4/1 at a temperature of 25 ºC 3.673 x 10^{-5} S/cm. This shows that the lower the temperature produced the higher the proton conductivity. Meanwhile, the highest proton conductivity of the composite membrane was in the mass variation of bacterial cellulose/human hair keratin 4/1 of 3.673 x 10^{-5} S/cm at 25 ºC, the more human hair keratin added will be the higher the proton conductivity. This proton conductivity is one order better than previous studies based on bacterial cellulose[12], and when compared to proton-conducting membranes based on synthetic polymers such as sulfonated polysulfone which operates at 70 ºC as in previous studies[13], proton-conducting membranes based on bacterial cellulose/human hair keratin are one order lower than sulfonated polysulfone. The phenomenon of these study's findings shows that the actual mechanism of proton delivery is not the Grotthus mechanism, which involves moving protons from one site on the membrane to another where they are transferred to another molecule, but rather the diffusion of protons as a component of protonated molecules along with the diffusion of uncharged molecules (vehicles).[14]

CONCLUSION

Studies on proton-conducting composite membranes based on bacterial cellulose and human hair keratin have been carried out. Human hair keratin is obtained from hydrolysis using NaOH solvent. Bacterial cellulose and human hair keratin composite membranes were made with mass variations of 4.5/0.5; 4.7/0.3; 4/1. Where it is obtained that the degree of swelling for bacterial cellulose is 21.15% while on the composite membrane, the degree of swelling for variations in the mass of bacterial cellulose and human hair keratin is 4.5/0.5 and 4.3/0.7, namely 25.51% and 28.43% respectively. The highest proton conductivity of bacterial cellulose was 2.213 x 10^{-5} S/cm at 25ºC and the highest composite membrane was in the variation of bacterial cellulose/human hair keratin 4/1 at 3.673 x 10^{-5} S/cm at 25ºC. The XRD results of bacterial cellulose showed the formation of a crystalline phase at an angle of 2θ between 14.21 and 22.70, on human hair keratin the results of hydrolysis showed that the human hair keratin was amorphous and the composite membrane was semicrystalline in each mass ratio.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The profile A. Melanda doesn't exist yet, due to her first publication. The research profile of the authors can be verified from their ORCID ids, given below:

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