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Preparation and Permeability Test of Chitosan-Montmorillonite Modified Polyvinyl Alcohol Composite Membrane

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Abstract
In this research, we reported the preparation of composites membrane based on chitosan and montmorillonite (MMT). Chitosan act as matrix membrane while MMT as filler. This composite modified with polyvinyl alcohol (PVA) to strengthen the interaction between chitosan and MMT. The main aim of this study to find out the influence of PVA addition and operated temperature toward permeability of chitosan – MMT / PVA composite membrane. The color of the membrane is influenced by its composition. It is directly proportional to the concentration of PVA in the membrane. The mechanical properties of composite membrane has also been analyzed based on its tensile strength and showed that the composite membrane has good mechanical characteristic. The lowest methanol permeability are achieved with the addition of PVA of 2 % with the value of 5.05×10^{-6} cm^2 s^{-1} at room temperature, 4.32×10^{-5} cm^2 s^{-1} at 40 °C and 5.05×10^{-5} cm^2 s^{-1} at 60 °C. Further, the characteristic of water and methanol uptake is directly proportional to membrane permeability. Membrane with low water and methanol uptake indicates that it has low membrane permeability. In reverse, decomposition of all composite membranes is found at 80 °C. Hence, the composite membrane has limited operating of 60 °C.

Keywords: Membrane, Methanol Permeability, Polyvinyl Alcohol, Water and Methanol Uptake

Introduction

Fuel cell is an electrochemical device that works by reacting hydrogen and oxygen to produce electricity with water as side product. It consists of two electrodes separated by a polymer membrane that serves as an electrolyte. Membranes in fuel cell applications known as Polymer Electrolyte Membrane (PEM). Membrane PEM fuel cells become the medium which transports hydrogen ions produced by the reaction of the anode towards the cathode. Therefore, the cathode reaction can produce electrical energy [1].

The provisions of good membrane for fuel cells are made from cheap materials that are, resistant to high temperatures and high energy density. As a result, the permeability membrane and its ability to retain water or methanol can be retained. Permeability membrane in PEM that is applied to the Direct Methanol Fuel Cell (DMFC) is one of the key components of DMFC performance which results in environmentally friendly and power efficient energy for a wide range of different applications [2].

An alternative membrane material used for polymer fuel cell is chitosan. Chitosan is a well-known biopolymer waste consisting of monomer N-acetyl glucosamine (GlcNAc) and also D-glucosamine (GlcN). Chitosan is a hydrophilic material with well-organized chemical structure, inert condition, and good conductive properties. Furthermore, chitosan level of toxicity is relatively low. Therefore, chitosan polymeric materials provide good properties for fuel cells. However, low solubility of chitosan in water is a drawback for fuel cell membranes because chitosan becomes waterless. Hence, cross-linking chitosan with other materials is required in order to improve PEM properties [3, 4].

In this study, chitosan was cross-linked with inorganic filler montmorillonite (MMT) as a modification. MMT offers several advantages for being economical, environmentally friendly and high rate of SiO_2. In addition, the SiO_2 played an important role in the process of the cross-linking. Another reason for choosing MMT as inorganic filler is the hydrophobic properties of MMT can prevent methanol crossover when it is in contact with methanol. However, MMT cannot interact with chitosan directly due to weak interfacial interaction between the two surfaces [5]. Hence, it needs modifications with another material and Polyvinyl Alcohol (PVA) was used in this study. PVA was selected because of its hydrophilic properties and good chemical resistance. Among the other reasons of choosing PVA are that it can interact with chitosan through hydrogen bond between hydroxyl group of PVA and free amine group of chitosan and bind strongly with MMT [6]. PVA also present water-resistant bond between inorganic filler and polymer matrix. Therefore, modifications using PVA could decrease the permeability properties of the PEM. This study aimed to find out the effect of PVA concentration and operated temperature on the permeability of chitosan-MMT/PVA composite membrane.

Experimental

Chemicals and Materials

Composite membrane which has been used in this study were synthesized from chitosan (Merck, Singapore), Montmorillonite K-10 (Sigma Aldrich, Singapore), Polyvinyl alcohol (Sigma Aldrich, Singapore). Other chemicals with pro analysis purity were CH3COOH (97% purity degree, Merck, Singapore), demineralized aqua, concentrated H2SO4 (98% purity degree, Merck, Singapore), and methanol (96% purity degree, Merck, Singapore).

Instrumentals

This study used several tools to do the experiments for instance scale, thermometer, electric heater, erlenmeyer, pH indicators, condenser, volume pipette, magnetic stirer, beaker glass, stirrer ultrasonic, a utensil of permeability test, pycnometer, Stograph VG10-E.

The Preparation of Chitosan Membrane

In this phase, 2 g of chitosan were dissolved in 2% of acetic acid and heated at 80ºC and stirred for 30 minutes. Then, the solution was treated with ultrasonic for 30 minutes, left for 30 minutes, and treated again with ultrasonic for 30 minutes. After the process, the solution was flattened on a glass plate and dried for 48 hours. Further, the membrane was washed with aqua DM and dried at room temperature for 24 hours.

Montmorillonite Modification using Polyvinyl Alcohol

In this phase, 0.08 g of MMT was dissolved in 25 ml of 2% acetic acid. Then 1 g of polyvinyl alcohol was dissolved in 100 mL of aqua DM at 80ºC and stirred for 2 hours. Further, PVA solution mixed with MMT, it then stirred for 3 hours at room temperature. The homogenized solution was modified MMT solution with PVA 1%, and referred to PVA concentration 0; 1.5 and 2%. They were also modified using the same procedure.

The Fabrication of Composite Membrane Chitosan-Montmorillonite/Polyvinyl Alcohol

In this part, 1.5 g of chitosan were dissolved in 37.5 mL of 2% acetic acid. The solution then stirred and heated at 80ºC for 2 hours. Next the solution was homogenized with ultrasonic for 30 minutes. Further, modified MMT solution at the concentration level of PVA 0; 1; 1.5 and 2% were mixed with chitosan solution. Then the mixture was stirred and heated at 80ºC for 30 minutes. After that, the mixture was handled with ultrasonic for 30 minutes, left for 30 minutes and handled again with ultrasonic for 30 minutes. After the process of degasification, the mixture was flattened on glass plate and dried for 48 hours at room temperature.

In the end, the membrane was saturated in a solution of 2 M H_2SO_4 for 24 hours and washed with aqua DM, and also dried at room temperature for 24 hours. The membrane permeability test was also carried out using permeability test instruments.

Variation of Temperature Operating System

Composite membrane chitosan - MMT with PVA concentration of 0; 1; 1.5 and 2% (w/v), was respectively performed at varied temperatures of 40, 60 and 80ºC. The permeability measurement using permeability tool test.

Water and Methanol Uptake Tests

Dry membrane was weighed to obtain dry weight of membrane (W_{dry}). Next, the membrane was soaked in methanol with variable concentration of 0M (aquadest) and 5M for 24 hours to check the water and methanol uptakes. After being soaked, the membrane then was weighed to obtain wet weight of membrane (W_{wet}). Moreover, water and methanol uptakes were calculated with following formula.

$$\textit{Water and methanol uptake } (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\ \%$$

Note:

W_{wet}: Wet weight of membrane (g)

W_{dry}: Dry weight of membrane (g)

Tensile Strength

Tensile strength test of the composite membranes was conducted by making the membrane that measured 140mm x 25mm in dry state. Next, the pull velocity of 10 mm/minute and pull strength of 100 N were applied to the membrane at room temperature.

Results and Discussion

The Preparation and Modification of Montmorillonite using Polyvinyl Alcohol

The initial stage of montmorillonite modification utilizing polyvinyl alcohol was done by dissolving a number of MMT in acetic acid. The existence of acetic acid on this process becomes significant because it can modify MMT perfectly. Next in a different container, a certain amount of PVA concentrations (0; 1; 1.5; and 2 % (w/v)) was dissolved in aqua DM. Then it was heated and stirred to form homogeneous solution. Further, the PVA solutions were mixed with MMT solution and stirred for 3 hours at room temperature to form homogenous solution. This treatment is intended in order that PVA could coordinate with MMT through polysiloxane network between them.

Preparation of Composite Membrane Chitosan-Montmorillonite

Composite membranes were made from chitosan with montmorillonite integration. Chitosan acted as matrix membrane, while montmorillonite acted as a filler. MMT was modified with various PVA concentrations of 0; 1; 1.5; and 2% (w/v). It was combined with the ratio of chitosan and MMT of 70:30% (w/v). Monroy-Barreto *et al*. revealed that filler reached the amount of the matrix at this ratio [7]. The pure chitosan membrane and composite membrane were in the form of brownish yellow plastic sheets with varied concentration of PVA as shown in Fig 1.

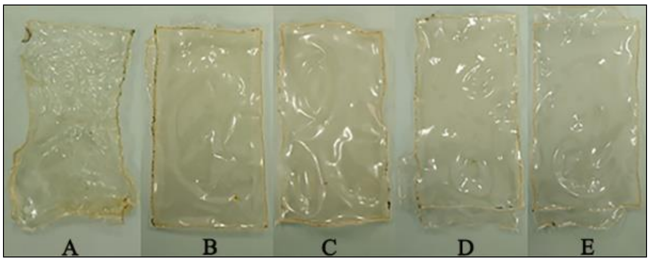

Fig 1: (A) Pure chitosan membrane; Chitosan-MMT composite membrane with (B)-0%; (C)-1%; (D)-1.5%; (E)-2% PVA concentration

As is shown in Fig 1, the color of the membrane is influenced by its composition. It is directly proportional to the concentration of PVA in the membrane. Pure chitosan membrane (Figure 1A) has the brightest color among the others and wrinkled. The wrinkled pure chitosan membrane was due to its hydrophilic properties. The chitosan-MMT with 0% PVA (Figure 1B) has darker brownish yellow membrane surface among the other composite membranes. The MMT reacted successfully with chitosan and made the colour of the composite membrane mixed from chitosan and MMT. 1% PVA which was found at MMT filler (Figure 1C) makes the color of the membrane brighter and more plastic than chitosan-MMT composite membrane with no PVA. When the concentration of PVA was 1.5% in composite membrane, the colour of the membrane was even brighter than the membrane with concentration of PVA 0% and 1%. It is also more plastic thus it was more resistant to breakage when it is soaked in water/methanol. Further, the membrane with PVA concentration of 2% had the brightest colour and the most plastic among the others [8].

Tensile Strength

Table 2: Tensile strength analysis of pure chitosan membrane and chitosan – MMT composite membrane with various concentrations of PVA in dry state

Membrane	Tensile Strength (MPa)
Pure chitosan	72.48
Chitosan – MMT/PVA 0%	853.69
Chitosan – MMT/PVA 1%	157.48
Chitosan – MMT/PVA 1.5%	205.04
Chitosan – MMT/PVA 2%	375.69

Table 2 illustrates that in dry state, composite membrane with PVA concentration of 2% has the highest value of tensile strength. The table also shows that tensile strength value is directly proportional to the addition of PVA on the membrane. This is related with PVA characteristic which is has good mechanical properties and high flexibility. This shows that the composite membrane chitosan – MMT modified with PVA is good material based on its mechanical properties [9].

Water Uptake dan Methanol Uptake

The result of analysing composite membrane chitosan–MMT characteristic in water and methanol can be seen in Fig 2. Fig 2 shows that pure chitosan membrane has the highest value of water and methanol uptake, namely 150.38% and 136.22% respectively. This condition was caused by the hydrophilic characteristic of chitosan. This characteristic enables the chitosan to interact with water or methanol well. Further it leads to water and methanol cross-over on the membrane. Fig 2 also informs that chitosan-MMT/PVA 2% composite membrane has the lowest value of water and methanol uptake, namely 48.65% and 30.41% respectively. This is because the hydrophobic characteristic of MMT increased the rigidity of chitosan polymer chain. Thus it can decrease the absorbing ability of chitosan[5]. In addition, the intercalation of PVA, which has high adhesion force, provided better mechanical properties for the composite membrane than without it [10]. The characteristic of water and methanol uptake is directly proportional to membrane permeability. Membrane with low water and methanol uptake indicates that it has low membrane permeability. It means that the membrane could restrain the water or methanol that passed through it. As shown in the Fig 2, the value of methanol uptake was lower than water uptake.

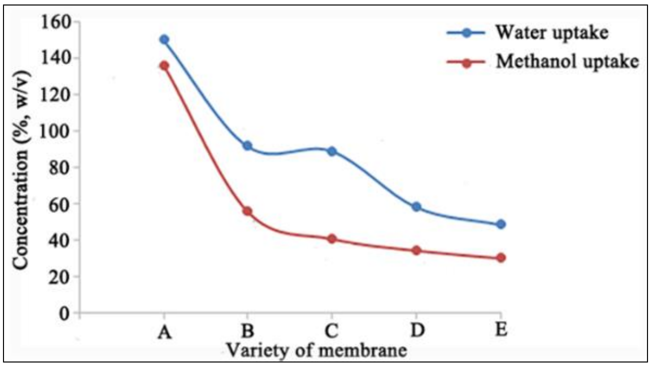

Fig 2: Water and methanol uptake of (A) pure chitosan membrane; composite membrane chitosan–MMT with various PVA concentration; (B) – 0%; (C) – 1%; (D) – 1.5%; (E) – 2%

Methanol Permeability

The measurements of methanol permeability at room temperature is shown in Fig 3. They indicate that the addition of PVA concentration influence on the methanol permeability. Table 3 illustrates that pure chitosan membrane has the highest value of methanol permeability. On the other hand, the composite membrane – 2% PVA has the lowest methanol permeability in comparison to the others, because the added amount of PVA was attributable to the strong hydrogen binding amine group of chitosan and formed a polysiloxane network with MMT. Moreover, the selectivity of PVA toward water-alcohol also affected the decrement of methanol permeability [11].

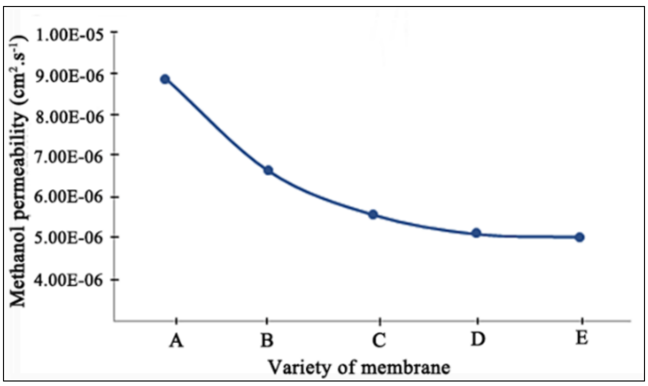

Fig 3: Membrane permeability toward methanol of (A) pure chitosan membrane; (B) composite membrane chitosan – MMT with various PVA concentration; (B) – 0%; (C) – 1%; (D) – 1.5%; (E) – 2%

Variation of Temperature Operating System

The methanol permeability measurement of composite membranes at various temperatures is shown in Fig 4. It illustrates that the operating temperatures affected the membrane permeability of the composite membrane.

Fig 4 shows, the methanol permeability of composite membrane is directly proportional to the operating temperature system. In general, at the same temperature with different PVA concentrations, the methanol permeability value of the composite membrane is higher than it is at room temperature. Fig 4 also shows that the composite membrane with – 2% PVA had the lowest methanol permeability value among the others. This is related to strong interaction which was formed between chitosan matrix and PVA as well as intense MMT and PVA cross-linking.

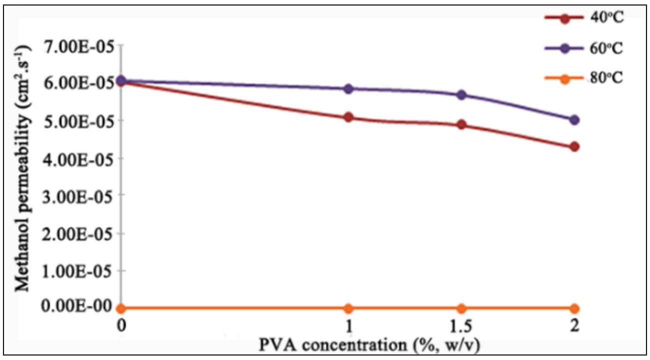

Fig 4: Methanol permeability value of composite membrane chitosan-MMT with various PVA concentrations at various temperatures

Conclusion

In this study, the composite membranes of chitosan – MMT modified PVA were prepared using varying PVA concentration and varying operating temperature. Those composite membranes were fabricated via cross-linking technique. Tensile strength analysis shows that generally the composite membrane with various PVA concentrations have reasonable mechanical strength. Further, water and methanol uptake analysis found that composite membrane with – 2% PVA concentrations has the lowest value, namely 48.65% and 30.41% respectively. In general, the methanol permeability value is inversely proportional with the concentration of PVA. When the concentration of PVA in membrane increases, the methanol permeability decreases. The operating temperature which affects directly proportional with the methanol permeability. When the operating temperature increases, it will also increase the methanol permeability.

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