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The influence of polyvinyl alcohol concentration toward conductivity and permeability of chitosan–montmorillonite composite membrane

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Abstract: The composite membrane is synthesized using chitosan as a matrix membrane with montmorillonite (MMT) as a filler and modified using polyvinyl alcohol (PVA). The main aim of this study is to find out the influence of PVA concentration and the working temperature toward the permeability of chitosan–MMT/PVA composite membrane. Fourier transform infrared spectroscopy (FTIR) characterization is performed in order to identify the interaction between the chitosan matrix and the modified MMT with PVA. The presence of new absorption at 1116.82 and 619.17 cm^{-1} indicated the interaction between MMT and PVA. Further, the widening of OH absorption indicated the hydrogen bond which is formed between chitosan matrix and PVA. This interaction is also demonstrated by the evenly distributed surface on scanning electron microscope (SEM) topography analysis. The thermal stability of composite membrane is determined by thermal gravimetry analysis (TGA). In addition, the composite membrane containing PVA has four patterns decomposed. When the TVA is absent from the composite membrane, it has three decomposition patterns, which are shown by TGA analysis. Based on its tensile strength, the composite membrane has good mechanical properties. The proton conductivity of the composite membranes are directly proportional to the PVA concentration. On the other hand, the methanol permeability of composite membranes is inversely proportional with the PVA concentration. The highest proton conductivity was obtained with the addition of 2 % PVA of 2.94×10^{-4} S cm^{-1}. Further, it also has the lowest methanol permeability with the value of 5.05×10^{-6} cm^2 s^{-1}. As a result, the crosslinked composite membrane chitosan–MMT prepared by PVA-crosslinking technique has the potential to be exploited for the direct methanol fuel cell application.

Keywords: proton conductivity; methanol permeability; direct methanol fuel cell.

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INTRODUCTION

Currently, the expansion of the renewable energy sources has gained attention. Among the most prospective sources of the environmentally friendly, cheap and safe energy is hydrogen. The fuel cell is among many alternative devices that can tap and use the hydrogen energy. The fuel cell is capable of producing electrical energy by reacting hydrogen and oxygen with water as the product. Fuel cell is composed of two electrodes, namely the anode and the cathode, that are separated by polymer membrane. This membrane is known as polymer electrolyte membrane (PEM). It become the medium which transports the hydrogen ions produced by the reaction of the anode towards the cathode. Hence the cathode can generate electrical energy.[1]

The membranes 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 achieved. The permeability membrane that is applied to the direct methanol fuel cell (DMFC) is one of the key components of DMFC performance, which results in the environmentally friendly and power efficient energy for a wide range of different applications.[2]

An alternative membrane material that can be used for PEM is chitosan. Chitosan is a well-known biopolymer waste, consisting of monomer *N*-acetyl glucosamine (GlcNAc) and also D-glucosamine (GlcN). Chitosan is a well-organized chemical structure material, inert and good ion conductive properties. Furthermore, the level of chitosan toxicity is relatively low. Therefore, the chitosan polymeric materials provide good properties for fuel cells. However, the low solubility of chitosan in water is a deficiency for PEM because chitosan can become waterless. Hence, cross-linking chitosan with other materials is necessary to improve the PEM properties.[3]

In this study, chitosan act as matrix membrane which was cross-linked with the inorganic filler montmorillonite (MMT) which is a hydrophobic material. MMT offers several advantages for being economical, environmentally friendly and high rate of SiO_2. Further, the SiO_2 plays an important role in the process of the cross-linking. Another reason for choosing MMT as inorganic filler are the hydrophobic properties of MMT curb methanol crossover, when it is in contact with methanol. However, MMT cannot interact with chitosan directly due to the weak interfacial interaction between the two surfaces.[4] 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. The additional 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.[5] PVA also presents the water-resistant bond between the inorganic filler and polymer matrix. Next, PVA can form a strong bond which can provide high mechanical strength is also more resistant to the presence of methanol that can destruct the composite membrane's structure. Therefore, the modifications using PVA could decrease the permeability properties of the PEM.

This study is aimed to find out the effect of PVA concentration on the conductivity and permeability of chitosan–MMT/PVA composite membrane. The concentration percentages of PVA that we used in this study were 0, 1, 1.5 and 2 %.

EXPERIMENTAL

Materials

The composite membrane used in this study was synthesized from chitosan (Merck, Singapore), montmorillonite K-10 (97 % purity degree, Sigma Aldrich, Singapore), polyvinyl alcohol (98 % purity degree, Sigma Aldrich, Singapore). Other chemicals with pro analysis purity were CH_3COOH (97 % purity degree, Merck, Singapore), demineralized aqua, concentrated H_2SO_4 (98 % purity degree, Merck, Singapore), and methanol (96 % purity degree, Merck, Singapore).

Instrumentation

Several tools that used on this study such as scale, thermometer, electric heater, erlenmeyer, pH indicators, condenser, volume pipette, magnetic stirer, beaker glass, stirrer ultrasonic, an utensil of the permeability test, electrochemical impendance spectroscopy (EIS) of Autolab with FRA32M module, Fourier transform infra red (FTIR) 8400 Shimadzu, scaning electron microscopy (SEM) Hitachi TM3000, thermo gravimetry analysis (TGA) of Mettler Toledo and Stograph VG10-E.

The Fabrication of chitosan membrane

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

Montmorillonite modification using polyvinyl alcohol

In this phase, 0.08 g of MMT was dissolved in 25 ml of 2 vol. % acetic acid. Then 1 g of polyvinyl alcohol was dissolved in 100 mL of aqua DM at 80 °C and stirred for 2 h. Further, the PVA solution mixed with MMT, it then stirred for 3 h 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 Preparation of composite membrane chitosan–montmorillonite/polyvinyl alcohol

In this part, 1.5 g of chitosan were dissolved in 37.5 mL of 2 vol. % acetic acid. The solution was then stirred and heated at 80 °C for 2 h. Next the solution was homogenized with the ultrasonic bath for 30 min. Further, the modified MMT solution at the concentration level of PVA 0, 1, 1.5 and 2 % was mixed with chitosan solution. Then the mixture was stirred and heated at 80 °C for 30 min. After that, the mixture was handled with the ultrasonic bath for 30 min, left for 30 min and handled again with the ultrasonic bath for 30 min. After the process of degasification, the mixture was flattened on a glass plate and dried for 48 h at room temperature. In the end, the membrane was saturated in a solution of 2 M H_2SO_4 for 24 h and washed with aqua DM, and also dried at the room temperature for 24 h. The membranes were characterized with FTIR and SEM to find out the interaction between chitosan and MMT which is modified with PVA. The membrane conductivity measurement was carried out using EIS and permeability test was also conducted using the permeability tool test. TGA analysis was also conducted to find out the thermal stability of composite membrane.

Tensile strength

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

RESULTS AND DISCUSSIONS

Modification of montmorillonite using polyvinyl alcohol

The initial stage of montmorillonite modification using polyvinyl alcohol was done by dissolving a number of MMT in acetic acid. The presence of acetic acid in this process is significant because it can perfectly modify MMT. Next in a different container, a certain amount of PVA concentrations (0, 1, 1.5 and 2 %) was dissolved in aqua DM. Then it was heated and stirred to form a homogeneous solution. Further, the PVA solutions were mixed with MMT solution and stirred for 3 h at room temperature to form the 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 %. It was combined with the ratio of chitosan and MMT of 70:30. Monroy-Barreto *et al.* revealed that the filler reached the amount of the matrix at this ratio.[6] The pure chitosan membrane and the composite membrane were in the form of brownish yellow plastic sheets with varied concentration of PV, as shown in Fig. 1.

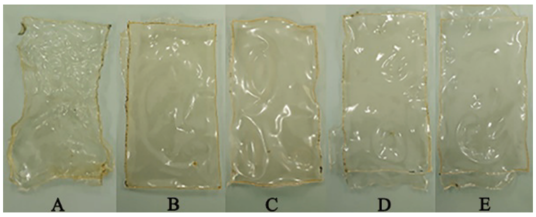

Fig. 1. A) Pure chitosan membrane; chitosan–MMT composite membrane with 0 (B), 1 (C), 1.5 (D) and 2 % (E) concentration.

In this research, fine composite membranes are made in the presence of acetic acid. The acid dissolved chitosan and modified the MMT perfectly. The another advantage of acetic acid treatment is to render chitosan as a good proton conductor. When chitosan is solvable in acetic acid, both H^+ and CH_3COO^- of acetic acid are scattered in the chitosan and can be mobilized under an electric field. Further the mixed solution was heated at 80 °C and stirred. During this treatment the chitosan molecules were intercalated into the MMT to obtain a homogeneous solution mixture. The intercalation was caused by the hydrogen bond between the amine and the hydroxyl group of chitosan with the silica of MMT. Next, the ultrasonic treatment was conducted to make collision among the molecules and disperse the filler evenly on the membrane surface. Moreover, the repeated ultrasonic treatment is intended for the maximum interaction between the chitosan matrix and modified MMT. Hence, a perfect interaction can be formed between the two materials.[7,8] In addition, the interaction can also turn the solution into a gel form. Afterward, it was placed on flat glass for the membrane casting process. The cast membrane was dried at room temperature for 48 h to release the residue of acetic acid. Hence the bond, which was formed between chitosan matrix and modified MMT filler, became stronger. Further, the dry membrane was soaked in 2 M sulfuric acid solution. This treatment aimed to create the cross-linking process between chitosan and modified MMT. Thus, the interaction between them became optimal. The another objective of sulfuric acid handling was to make the chitosan polycationic. As a result, the chitosan matrix could donate its electron through the amine group.

As is shown in Fig. 1, the colour of the membrane is influenced by its composition. It is directly proportional to the concentration of PVA in the membrane. The pure chitosan membrane (see Fig. 1A) has the brightest colour among the others and it is wrinkled. The pure chitosan membrane is wrinkled due to its hydrophilic properties. The chitosan–MMT with 0 PVA (see Fig. 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 (see Fig. 1C), makes the colour of the membrane brighter and more plastic than the chitosan–MMT composite membrane with no PVA. When the concentration of PVA was 1.5 % in the composite membrane, the colour of the membrane was even brighter than the membrane with the concentration of PVA 0 and 1 %. It is also more plastic than hydrophobic, and consequently it is more resistant to breakage when soaked in water/methanol. Further, the membrane with the PVA concentration of 2 % had the brightest colour and the most plastic of all the others. Hence it is become more resistant to water/methanol.[9] Before the measurements and characterizations of the samples, the samples were dried at 60 °C by heated in vacuum oven.

Composite membrane characterization

Fourier transform infra red (FTIR). FTIR was conducted to find out the bond which had been formed in composite membrane. The result of the FTIR characterization can be seen at Fig. 2. While the various FTIR absorbances in the chitosan–MMT composite membrane can be seen in Table I.

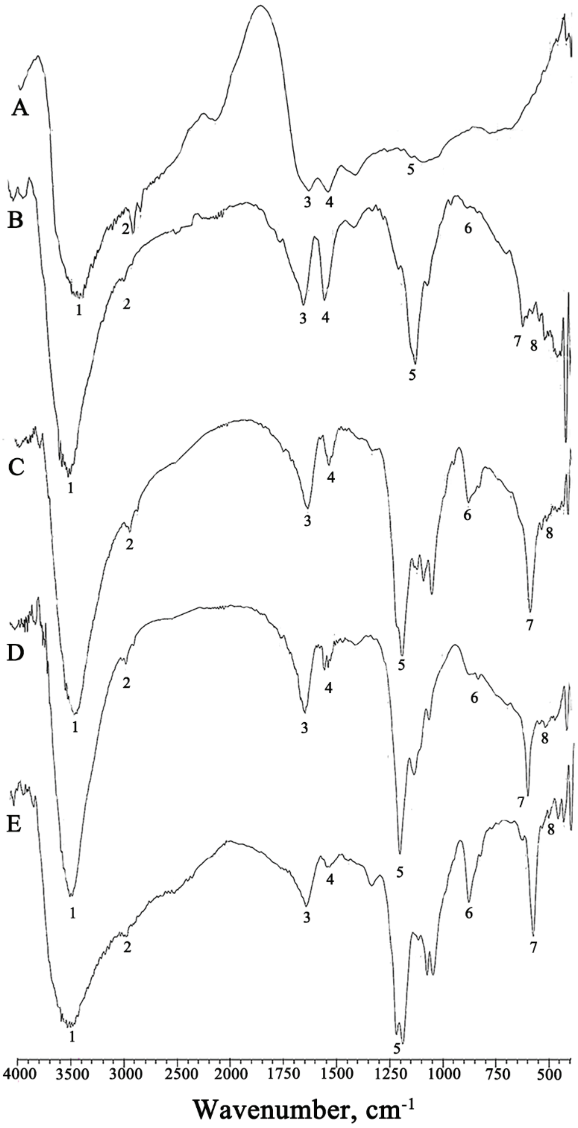

Fig. 2. FTIR spectra of chitosan membrane (A) and composite membranes with various PVA concentration: B) 0; C) 1; D) 1.5; E) 2 %.

TABLE I. Various wavenumber (cm^{-1}) of chitosan (CS)–montmorillonite (MMT) composite membrane FTIR absorption with various polyvinyl alcohol (PVA) concentration

No.	Vibration type	Membrane				
		CS	CS–MMT	CS–MMT/PVA 1 %	CS–MMT/PVA 1.5 %	CS–MMT/PVA 2 %
1	–OH	3435.34	3444.98	3435.34	3425.69	3433.41
2	–CH$_2$	2920.32	2931.90	2926.11	2928.04	2930.05
3	C–N	1635.69	1633.76	1633.76	1639.55	1635.69
4	–NH$_2$	1543.10	1537.32	1535.39	1543.10	1539.25
5	C–O	1263.42	1116.82	1193.98	1193.98	1220.98
6	Al–O	–	880.56	885.36	871.85	887.28
7	Si–O–Si	–	619.17	597.95	601.81	592.17
8	Si–O	–	542.02	543.94	549.73	551.66

The alteration of wave number of the absorption peaks and the emergence of the new absorption peaks, indicate the interaction between chitosan and MMT. Further, it also demonstrated that MMT had been successfully reacted with the chitosan matrix. Meanwhile, the wider and sharper of the –OH absorption indicate the interaction between chitosan and MMT (see Fig. 2B), and also between the chitosan matrix and PVA through the formed hydrogen bonds (see Fig. 2C, D and E).

The sharper of −CN vibration indicated the cross linking of chitosan and PVA.[10] Whereas, the interaction between MMT and PVA can be seen by the shifting wavenumber of Si−O–Si absorption from 619.17 to 592.17 cm^{-1}. This absorption shift occured because of the overlapping between Si−O vibration of MMT and C−O vibration of PVA. This condition is confirmed by the existence of strong enough the bend of Si−O which appeared in the wavenumbers 543.94, 549.73 and 551.66 cm^{-1} (Fig. 2B–E).[11]

Scanning electron microscopy (SEM). SEM characterization was carried out in order to determine the surface morphology of the membrane. The result of the SEM characterization can be seen at Fig. 3.

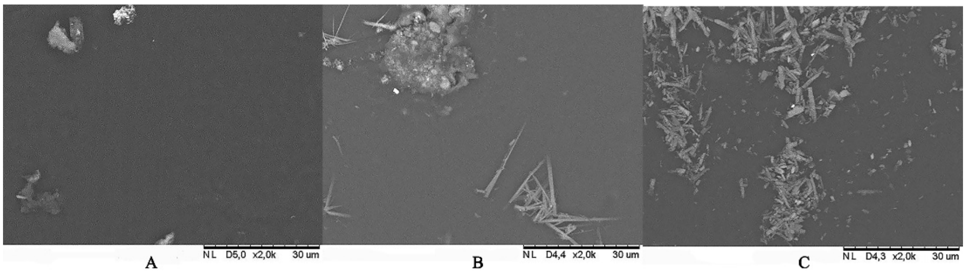

Fig. 3. SEM micrograph of surface membrane: A) pure chitosan; B) composite chitosan–MMT; C) chitosan–MMT / PVA 2 %.

Fig. 3 shows that pure chitosan membrane (see Fig. 3A) has more homogenous than that the surface of composite membrane chitosan–MMT modified PVA. This condition occurred because no fillers were added. Whereas, Fig. 3B illustrates that the surface of the membrane has uneven spots, which means that the filler particles are not evenly distributed on the chitosan matrix. The addition of MMT filler without PVA modification causes the uneven distribution of filler in the chitosan matrix. As a result, the membrane solution is not thoroughly mixed. Further, the intercalation between the chitosan matrix and the filler still occured, despite of the low efficiency. Meanwhile, the presence of PVA on the Fig. 3C caused the membrane surface to have even and uniform spots, which means that the filler particles were evenly distributed. A protective layer is formed over the chitosan surface, which could improve the chitosan polymer stability. This indicates that there was strong interaction not only between chitosan and PVA, but also between MMT and PVA. Further, the crosslinking among chitosan, MMT and PVA provides no phase separation. It also increases the compability and mechanical strength of the composite membrane. Nevertheless, it also provided the stable interface and inter-linking network of the composite membrane.[12]

A similar study reported on chitosan–polyvinyl alcohol composite membrane for the fuel cell applications.[13] The results of SEM analysis showed that the pure chitosan membrane has more even surface than the composite membrane. Further, the composite membrane was the uniform and free of any surface pores and cracks. The distributed particles could be oriented perpendicular to each other by the polymer chain, thanks to the electrostatic repulsion, thus, forming an inter-linking network.

Thermo gravimetry analysis. Thermo gravimetry analysis (TGA) characterization was conducted to determine the thermal stability of chitosan–MMT composite membrane. The result of TGA analysis of the composite membrane is shown in Fig. 4. Fig. 4 also illustrates that the presence of PVA on the composite membrane affected the decomposition pattern which can be seen at the thermogram spectra. It shows four decomposition patterns of the composite membrane with PVA while the composite membrane with the absence of PVA has three decomposition patterns. The first decomposition started at 60 °C and it was attributed to the evaporation of water molecules in the membrane for the composite membrane without PVA (Fig. 4A).[14] The first decomposition of the composite membrane with PVA (Fig. 4B) is also associated with the water evaporation, which is followed by the broken linkage between chitosan and PVA. The second decomposition of the composite membrane with PVA was related to the decomposition of polymer chain in chitosan, caused by dehydration, which triggered the formation of various different molecules with low molar mass that evaporates and it leads to the broken of hydrogen bonds between the amine groups of chitosan and the silica groups of MMT that occured at about 185 °C. The PVA caused the strong interaction between MMT and the chitosan matrix through hydrogen and covalent bonds. This condition is confirmed with Zawadzki and Kaczmarek, who conducted thermal analysis of chitosan at various temperatures. They state that the chitosan decomposition, which occurred above 180 °C, was related to the decomposition of pyranose rings through dehydration and deamination, further ring-opening reaction.[15]

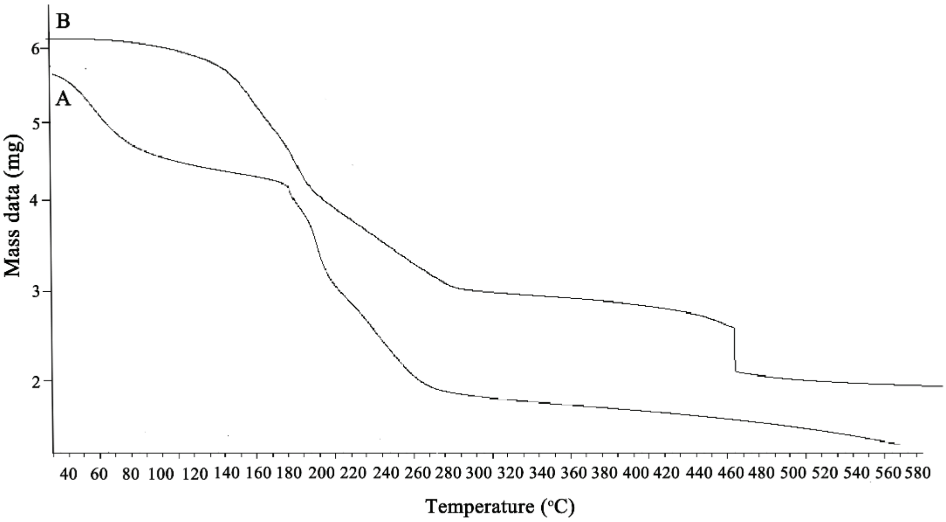

Fig. 4. Thermogram of composite membrane chitosan–MMT modified with PVA 0 % (A) and 2 % (B).

The third decomposition of the composite membrane with PVA and the second decomposition on membrane without PVA, occur at about 200 °C. For the composite membrane with PVA (Fig. 4B), the decomposition represented the broken chitosan and PVA bond on the membrane and also the disconnection of crosslinking between chitosan and MMT. The above fact was supported by Chen *et al*, who state that decomposition at the temperature of about 20–400 °C is related to the broken bond between chitosan polymer and PVA. Meanwhile, the composite membrane without PVA at the temperature for about 240–280 °C correspond to the disconnection bond between amine groups of chitosan and silica groups of MMT.[16]

The third decomposition of the composite membrane without PVA occurs around 310–340 °C. It is associated with the degradation and the decomposition polymer unit of chitosan and the decomposition of siloxane group from MMT. Next, the fourth thermal decomposition of the composite membrane with PVA related to chitosan polymer chain breakdown because of the dehydration at high temperatures. This phenomenon occurred at the temperature of about 290 °C. In addition, this thermal decomposition is also represented by the decomposition of the residual organic substrate of PVA. Moreover, at 280–460 °C, this is also related to the elimination of the polysiloxane network between MMT and PVA, and disconnection of the crosslinking between chitosan and PVA. This is also endorsed by Lin *et al.*, who worked on the thermal analysis of hybrid membrane. Their study revealed that at the temperature above 250 °C, the decomposition was associated to the elimination of the siloxane group.[11] Meanwhile, the chitosan–MMT the decomposition in this temperature range was associated to the destruction of crosslinking between chitosan matrix and MMT. This fact is confirmed by Palani *et al*. They state that the temperature range of 350–500 °C is responsible for to the destruction of bond between chitosan and the filler of chitosan matrix.[17] To conclude, from Fig. 4 it can be seen that the composite membrane with PVA has better thermal stability than without one. It has a complex decomposition pattern and at the end of the process, the remaining mass of composite membrane with PVA is more than the mass of composite membrane without PV.

Tensile strength. Table II illustrates that in dry state, the composite membrane with PVA concentration of 2 % has the highest value of break elongation, and it also shows that break elongation 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. Thus, the addition of PVA on the composite membrane makes it more elastic with the significant increment of break elongation properties. On the other hand, the composite membrane without PVA addition has the lowest break elongation. This is because the hydrophobic characteristics of MMT increased the rigidity of the membrane. Further, the addition of PVA increases the tensile strength of composite membrane. This condition shows that the composite membrane chitosan–MMT modified with PVA is a quality material based on its mechanical properties. Consequently, these composite membranes had reasonable strength and could potentially be used for DMFC application.[18]

TABLE II. Tensile strength analysis of pure chitosan membrane and chitosan–MMT composite membrane with various concentrations of PVA in dry state

Membrane	Break elongation, %	Tensile strength, MPa
Pure chitosan	173.43	157.48
Chitosan–MMT	72.48	129.40
Chitosan–MMT/PVA 1 %	654	205.04
Chitosan–MMT/PVA 1.5 %	867.86	250.47
Chitosan–MMT/PVA 2 %	963	375.69

Proton conductivity. Proton conductivity is one of the main benchmark for the membrane, which can influence the fuel cell's performance directly. In this study, it was measured by using EIS at room temperature which is shown in Table III.

TABLE III. Proton conductivity value of pure chitosan membrane and composite membrane chitosan–MMT with various PVA concentrations at room temperature; $A = 1.0$ cm^2

Membrane	Resistance, Ω	L / cm	σ / 10^{-4} S cm^{-1}
Pure chitosan	124.230	0.019	1.53
Chitosan–MMT	118.170	0.022	1.83
Chitosan–MMT/PVA 1 %	115.480	0.025	2.16
Chitosan–MMT/PVA 1.5 %	105.745	0.026	2.46
Chitosan–MMT/PVA 2 %	95.335	0.028	2.94

Table III illustrates the addition of PVA concentration effect on the membrane conductivity. The proton conductivity of the composite membranes rose from 1.83×10^{-4} to 2.94×10^{-4} S cm^{-1} as the PVA concentration, increased from 0 to 2 %. The composite membrane – 2 % PVA, has the highest conductivity among the others, because of the suitable amount of PVA to binding strongly the amine group of chitosan and it forms a polysiloxane network with MMT. Meanwhile, the pure chitosan membrane has the lowest value of conductivity among the others. This condition due to the hydrophility of chitosan, which makes the membrane soluble. As a consequence, the proton conductivity decreases significantly. Meanwhile, the composite membrane – 0 % PVA, has low conductivity because the absence of PVA makes the chitosan and MMT cannot bind strongly. Hence, proton conduction can't be conducted optimally. The composite membranes – 1 and 1.5 % PVA, have lower conductivity than the composite membrane – 2 % PVA. The addition of PVA concentration was not appropriate to the chitosan and MMT concentrations. Consequently, it cannot facilitate the conduction well and resulting poor proton conductivity value. On the system, chitosan–MMT composite membrane which is modified by PVA, have two factors that influence proton conductivity. These two factors are: *i*) the presence of polysiloxane network which can form a water-bound membrane layer to facilitate proton hopping. The proton hopping mechanism is the mechanism of transferring the proton across the membrane which determines the conductivity of membrane; *ii*) A strong hydrogen bond formed between the amine groups in chitosan and the epoxy on the silane ensures a high proton conduction.[2,8,19]

Those aforementioned is reinforced by Palani and co-workers, who also modified the chitosan membrane with polyvinyl alcohol for direct methanol fuel cell. They stated that the addition of PVA increase the proton conductivity of membrane. It is related with the amount of charge carrier (free functional groups) which is belongs to heterophasic morphology of PVA and influenced in protonic conduction. Moreover, PVA could make more flexible networks for the ionic transport.[17]

Methanol permeability. The methanol permeability is the parameter to find out the amount of methanol that passed through the membrane. The membrane of direct methanol fuel cell (DMFC) has too low methanol permeability to maintain optimum performance. Next, the methanol permeability is inversely proportional to the performance of membrane. The higher methanol permeability, the lower will be the performance.[2] The measurements of methanol permeability at room temperature is shown in Table IV. They indicate that the addition of PVA concentration influence on the methanol permeability. Table IV illustrates that the 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 is 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.[20,21] The addition of modified MMT filler to chitosan matrix affected the derivation of membrane permeability. Further, on the system chitosan–MMT composite membrane which is modified with PVA, has two factors that affect the membrane permeability. These two factors are: *i*) the dispersion of the anorganic particle on the composite membrane prolonged the path length and the tortuosity of methanol permeation. As a result, this made it difficult for the methanol molecule to pass through the membrane; *ii*) the presence of polysiloxane network on the composite membrane intensified the membrane ability to retain the structure when the methanol passed through. Next, the hydrophobicity of modified MMT on the composite membrane makes the rigidity of chitosan matrix and reduce the swelling ability of membrane.[2,19,22]

TABLE IV. Methanol permeability of pure chitosan membrane and composite membrane chitosan–MMT with various PVA concentrations at room temperature; A = 3.14 cm^2; V = 50 mL; C = 5 M

Membrane	Slope, M s^2	L / cm	Methanol permeability×10^6 cm^2 s^{-1}
Pure chitosan	0.0028	0.001	8.92
Chitosan–MMT	0.0019	0.0011	6.66
Chitosan–MMT/PVA 1 %	0.0008	0.0022	5.61
Chitosan–MMT/PVA 1.5 %	0.0007	0.0023	5.13
Chitosan–MMT/PVA 2 %	0.0006	0.0023	5.05

Table IV also shows that the existence of PVA on the composite membrane caused the lower membrane permeability. This is occurred because the hydroxyl group of PVA was dispersed well on the composite membrane and provided a strong crosslinking bond between the chitosan matrix and MMT modified with PVA.[5] Further, it enhanced the compatibility of MMT toward the chitosan matrix and increased the ability of composite membrane to resist the methanol. Hence the membrane permeability against the methanol stayed low, which is good for the performance of the membrane.

This fact is reassured by Ayyubi and co-workers, who modified chitosan containing PVA using MMT. They revealed that the presence of PVA on the composite membrane makes methanol more difficult to pass through the membrane. Further, they also confirmed that the interaction between PVA and MMT narrowing the methanol pathway through the membrane.[23]

CONCLUSIONS

In this study, the composite membranes of chitosan–MMT modified PVA were prepared using varying PVA concentration and varying operating temperature to be used for DMFC application. Those composite membranes were made by the cross-linking technique. The interactions between chitosan–MMT with PVA was confirmed by the FTIR spectra through the widening and the sharpening of the OH absorption band and the existence of the new absorption at wave number 1116.82, 1193.98 and 1220.98 cm^{-1}. In the analysis using SEM, the interaction can be recognized by the surface, which has more even and uniforms spot. The thermal stability analysis via TGA illustrates that the composite membrane with PVA has good thermal stability. The tensile strength analysis shows that the composite membrane with various PVA concentrations have reasonable mechanical strength. Generally, the membrane conductivity value is directly proportional with the PVA concentration. When the PVA concentration increases, then it will escalate the membrane conductivity. On the contrary, the membrane permeability value is inversely proportional to the concentration of PVA. When the PVA concentration increases, it will decrease the membrane permeability. The composite membrane with the addition of 2 % PVA has the highest conductivity and the lowest permeability of all. Since the composite membrane chitosan–MMT prepared by PVA-crosslinking technique has good properties for the conductivity and the permeability, it is intended that this membrane will provide a particular performance for DMFC system.

ИЗВОД

УТИЦАЈ КОНЦЕНТРАЦИЈЕ ПОЛИ(ВИНИЛ-АЛКОХОЛА) НА ПРОВОДЉИВОСТ И ПЕРМЕАБИЛНОСТ ХИТОЗАН–МОНТМОРИЛОНИТ КОМПОЗИТНИХ МЕМБРАНА

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Композитна мембрана је синтетисана користећи хитосан као матрицу мембране са монтморилонитом (MMT) као пуниоцем и модификована коришћењем поливинил-алкохола (PVA). Главни циљ ове студије је да се сазна утицај PVA концентрације и температура на пермеабилност хитозана–MMT/PVA композитне мембране. Карактеризацијом FTIR се идентификује интеракција између хито-

санске матрице и ММТ модификованог са PVA. Присуство нове апсорпције на 1116,82 и 619,17 cm^{-1} указује на интеракцију између ММТ и PVA. Поред тога, ширење апсорпције OH указало је на водоничну везу која се формира између матрице хитосана и PVA. Ова интеракција је такође потврђена равномерно распоређеном површином у SEM. Термичка стабилност композитне мембране одређена је термогравиметријском анализом (TGA). Поред тога, у термограмима се виде четири ступња декомпозицију у присуству PVA. Без PVA постоје само три ступња декомпозиције. На основу јачине на кидање, композитна мембрана има добра механичка својства. Протонска проводљивост композитних мембрана је директно пропорционална PVA концентрацији. С друге стране, пермеабилност композитних мембрана метанолом је инверзно пропорционална PVA концентрацији. Највећа протонска проводљивост добијена је са додатком 2 % PVA од $2,94\times10^{-4}$ S cm^{-1}. Даље, мембрана тог састава такође има најнижу пермеабилност метанола са вредношћу од $5,05\times10^{-6}$ cm^2 s^{-1}. Као резултат тога, умрежена композитна хитозан–ММТ мембрана добијена умрежавањем са PVA има потенцијал да буде искоришћена у директним горивним ћелијама са метанолом.

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