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Chapter

Characterization of Chitosan Membrane Modified with Silane-Coupled Nanosilica for Polymer Electrolyte

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Abstract

The electrolyte membrane currently being developed is limited to materials that are toxic and expensive. Chitosan as a natural organic polymer supports modification to produce the desired physical and chemical properties, one of which is as solid electrolyte. In the presence of functional groups on chitosan, it is possible to modify it with nanosilica as inorganic filler to improve its characteristics. Incorporation of chitosan matrix with of silane-coupled nanosilica in nanosilica:silane ratio (w/w) are 1:0; 1:0.25; 1:0.50; 1:1; 1:1.50; and 1:2. Evaluation on their properties are both quantitatively (water uptake, tensile strength, proton conductivity, methanol permeability, and selectivity) and qualitatively (functional groups, morphology, topography, and thermal properties). The results show that silane addition to the chitosan-nanosilica membrane in nanosilica:silane as 1:0.50 achieve the best characteristics for polymer electrolyte. The results of functional groups, morphology and topography analysis on selected membranes show that optimum silane addition provides the hydrogen interaction between chitosan matrix and silane-coupled nanosilica so there is an enhanced in membrane properties for electrolyte membrane.

Keywords: chitosan matrix modification, polymer electrolyte, silane-coupled nanosilica

1. Introduction

People's dependence on energy from fossil fuels is now getting higher, so energy resource supply is day by day decreasing. One of the alternative energy sources that is potential to overcome that problem is fuel cell [1]. A fuel cell is an electrochemical device that converts chemical energy into electrical energy continuously. The use of fuel cells is expected to reduce people's reliance on fossil fuels and reduce the damage to the atmosphere due to emissions [2]. Therefore, fuel cell is a promising alternative energy that is environmentally friendly.

The main component of the fuel cell is polymer electrolyte membrane (PEM) [2]. Since the role of polymer electrolyte membrane in fuel cell performance is very important, the study of technological development of polymer electrolyte

membrane is needed [3]. Currently, the electrolyte membrane that most widely used in industry is Nafion 117 membrane or Perfluoro sulfonic acid [1]. As a polymer electrolyte membrane in Direct Methanol Fuel Cell (DMFC), the Nafion 117 membrane has very good ability to deliver proton with good chemical stability, but it has a weakness of methanol cross over which is signed by the high methanol permeability and low operating temperature (60–120°C) [1]. Another drawback is its poisonous nature due to the elemental fluorine content and its high price. Therefore, several studies have been conducted to obtain membranes that environmentally friendly and have better capabilities than Nafion 117 membrane at an economical cost [4].

Chitosan is one alternative polymer matrix that is potential for replacing the Nafion 117 membrane. Chitosan is an environmentally friendly biopolymer, produced by utilizing marine waste such as shrimp, crabs, lobsters, and fish shells. Chitosan is easily generated through deacetylation process of chitin by strong alkali or prepared from fungal cell walls via fermentation technology [5]. Chitosan is inexpensive, hydrophilic, has a functional group in the backbone that can be modified according to the desired characteristics and has low methanol permeability [6]. Chitosan has a free amine group that can be protonated and has a hydroxy group, so it can be categorized as natural polycation. These two groups make it possible to modify chitosan to produce the desired physical and chemical properties [7]. However, according to [8], chitosan membrane still has low proton conductivity that is 1.74×10^{-2} S/cm, so this value is lower than the proton conductivity of Nafion 117 membrane that is 5.66×10^{-2} S/cm.

To improve the performance of chitosan-based membrane matrix, some efforts have been done to modify chitosan by combining with other such as silica based materials [8, 9]. Silica based materials are chosen for several reasons. They can reduce hydrophilicity degree of the chitosan main chain that is hydrophilic due to the presence of free amino acid groups and hydroxides on its carbon atom [9]. Silica materials can absorb methanol on the surface of chitosan membrane so that most of the methanol does not pass through the membrane. The addition of inorganic additives such as zeolites and montmorillonites which able to act as molecular filters will provide tetrahedral silica that can cover the pores in the membrane so that the transfer of methanol through the membrane is very small [8, 10]. It is reported that silica addition into the polymer matrix can reduce crystallinity of the polymer and increase mechanical strengths such as water resistance, stretch strength, and tensile strength [11]. The ability of silica to combine with chitosan is very limited because of the different hydrophilicity properties of the two materials. Therefore, silica in the form of nanoparticles was developed to create strong composites.

Tetraethylorthosilicate (TEOS) or $Si(OC_2H_5)_4$ is a source of silica materials which is widely used because it is easy to do purification, the reaction rate is slow and it can be controlled [12]. TEOS is even easily converted into nanosilica particles by reacting with water. The hydrolysis reaction occurs in the sol–gel process. TEOS is commonly used as a crosslinking agent in inorganic polymers synthesis because of its ability to form Si-O-Si chains. The sol–gel method has been extensively developed in the surface modification of silica particles because it will form a more reactive silica precursor with the formation of Si-OH groups [13]. The weakness is that silica is insoluble in chitosan solution, so the dope solution formed from nanosilica and chitosan is not homogeneous [14] because physical mixing causes nanosilica dispersion in the chitosan matrix to be less homogeneous and weak interface interactions of the two material surfaces.

To improve the compatibility of silica particles and chitosan, it is needed a coupling agent [15]. The addition of 10% of GPTMS (3-glycidyloxypropyl

trimethoxysilane) on chitosan/zeolite-β membrane produces methanol permeability of 2.20 × 10^{-7} cm^2/s and proton conductivity of 1.31 × 10^{-2} S/cm [8]. The electrolyte membrane investigation of SPAEK-C with 10% GPTMS addition produces proton conductivity of (1.5 ± 0.1) × 10^{-2} S/cm and methanol permeability of 2.99 × 10^{-7} cm^2/s [12, 16].

Therefore, in this study, the addition of silane (GPTMS) is done as a coupling agent on the chitosan-nanosilica membrane. This coupling agent is selected because it has epoxy groups that can react with a free amine group in chitosan, so nanosilica can also be bounded strongly with chitosan (12, 15). Nanosilica is chosen because of its small size and wide surface so that making it possible to penetrate the polymer matrix easily.

The use of GPTMS as a coupling agent and nanosilica particles (from TEOS) as fillers in the chitosan matrix for polymer electrolyte membrane makes this study different from previous studies. The use of GPTMS as a coupling agent on nanosilica particles was carried out by [17]. Silica precursors used were silica fume and the investigation carried out was nanosilica variations on chitosan and did not investigate silane variation effect on membranes. The membranes produced for biopolymer applications which have high thermal resistance. Chitosan modified with silica (TEOS) and GPTMS has been coated on a cotton fabrics in [18] results clear transparent thin layer on cotton surface. While [19] has combined chitosan with silica and GPTMS for tissue engineering application. For dehydration of ethanol application, chitosan-silica study has been performed by [20, 21]. For fuel cell application, chitosan have been combined with silica-based material [5, 8, 10, 22, 23]. The result of [5, 10] used GPTMS-montmorillonite as filler in chitosan membrane, while research [8] used GPTMS-modified zeolite, [22] used sulfonated polyaniline/ silica and [23] used silica/ sulfonated polyether-ether ketone as filler in chitosan.

2. Experiments and characterization

2.1 Materials

The materials are tetraethyl orthosilicate (TEOS 99%, ρ = 0.94 L/kg Merck), absolute ethanol (C_2H_5OH 99–100%, ρ = 0.79 L/kg Merck), ammonia (NH_3 25%, ρ = 0.90 L/kg Merck), aqua demineralization, chitosan from CV Ocean Fresh Bandung (deacetylation degree = 82.7%, solubility in 1% acetic acid ≥99%, molecular weight = 8.78 kDa), acetic acid (CH_3COOH 100%, ρ = 1.05 L/kg Merck), methanol (CH_3OH 99.9%, ρ = 0.79 L/kg Merck), dimethyl formamide (DMF $HCON(CH_3)_2$ 99.80%, ρ = 0.94 L/kg Merck) and silane (3-glycidyloxypropyl trimethoxysilane) (GPTMS $C_9H_{20}O_5Si$ ≥ 98%, ρ = 1.07 L/kg Sigma-Aldrich).

2.2 Nanosilica preparation

Nanosilica synthesis from TEOS by sol–gel method was adopted from [8]. A total of 2.27 mL of TEOS was dissolved in 46 mL absolute ethanol at a speed of 600 rpm at room temperature for 15 minutes. Then ammonia was added dropwise until pH 10. After 1 hour, 1 mL distilled water was then added dropwise into the solution. The stirring process was continued for 6 hours. Then the solution was allowed to stand for 24 hours during the aging process. After the aging process, the obtained gel was then roasted at a temperature of 80°C for 24 hours. The crystals were crushed into powder in further calcined for 2 hours at the temperature of 600°C. The resulting crystals were sieved at 230 mesh.

2.3 Silane-coupled nanosilica preparation

The coupling process of nanosilica and silane was done by developing [12] method. A total of 0.03 grams of nanosilica and 0.0075 grams of 3-glycidoxypropyl trimethoxy silane (GPTMS) (nanosilica:silane = 1:0.25) were dissolved in 0.3 mL dimethylformamide (DMF) at room temperature, then stirred using magnetic stirrer for 6 hours. Then the homogeneous solution was put into a beaker and heated in an oven at 60° C for 24 hours. After that, it was heated at 100° C for 1 hour and at 120° C for 2 hours. Drying was carried out at 155° C for 2 hours. The obtained solids were soaked with 1 M HCl solution at 80° C for 24 hours until hydrolysis and condensation occur in the solution. The resulting solids were crushed and sieved with 230 mesh sieves. The final produced powder is nanosilica filler that had been modified with silane coupling agent. Furthermore, the coupling process was also carried out at the ratio of nanosilica: silane = 1:0; 1:0.50; 1:1.0; 1:1.5 and 1:2.0.

2.4 Membrane synthesis by modifying chitosan with silane-coupled nanosilica

The chitosan membrane synthesis with silane-coupled nanosilica addition by developing [8, 24] method. First, a total of silane-coupled nanosilica (w:w) with nanosilica:silane respectively 1:0; 1:0.25; 1:0.50; 1:1.0; 1:1.5 and 1:2.0 was dissolved in each 50 mL of 2% acetic acid and was stirred at a temperature of 60°C for 7 hours. Secondly, as many as 1 g of chitosan was dissolved in 50 mL of 2% acetic acid at room temperature for 4 hours. Then the first solution and second solution were mixed and stirred for 4 hours at the temperature of 60°C. The homogeneous solution formed is called dope solution that was then poured in the acrylic mold of 20 x 20 cm and was dried in an oven at the temperature of 60°C for 21 hours that produced dry membrane. The process of membrane formation used the phase inversion method.

2.5 Membrane characterization

The characterization of chitosan-nanosilica membrane with silane addition was performed by water uptake measurement, membrane tensile strength analysis (by tensile test equipment Strograph VG 10-E Toyoseiki), methanol permeability (by diffusion cell method), proton conductivity analysis (by EIS or Electrochemical Impedance Spectroscopy Autolab PG STAT 128 N Instrument) [2], membrane selectivity determination, functional group analysis (by FT-IR PRESTIGE-21 Shimadzu), membrane morphology analysis (by SEM FEI Inspect S50), membrane topography analysis (by AFM Bruker N8 Neos 5.5 IF367), and thermal degradation analysis (by TGA Mettler Star SW 10.00).

Water uptake is the ability of a membrane to absorb water for 24 hours, so it is performed by weighing the mass of absorbed water (w_2) and comparing it with the mass of membrane (w_1) in a percentage format as expressed in Eq. (1) adopted from [10, 25–27]. In determining the water uptake, demineralized water which is free of metal ions is used.

$$\text{Water uptake} = \frac{w_2 - w_1}{w_1} \times 100\% \quad (1)$$

The mechanical strength test is generally measured by tensile strength test, in which material sample of a certain size is exerted with force and pulled until it breaks. Eq. (2) until Eq. (4) express the equation for determining tensile strength, elongation break and modulus young adopted from [10, 28]. Tensile strength test performed according to ASTM D882 at room temperature at a

constant cross head speed of 10 mm min^{-1} and 100 N load cells. The samples were dumbbell-shaped with gauge dimensions of 15 mm × 3 mm × 0.22 mm. Eq. (2) until Eq. (4) describe that σ is tensile strength, ε is elongation break, E is modulus young, P is the force applied to the specimen, A is the specimen cross-sectional area (cm^2), ΔL is the length increase (cm) and L_0 is the initial length of the specimen (cm).

$$\sigma = \frac{P}{A} \tag{2}$$

$$\varepsilon = \frac{\Delta L}{L_0} \tag{3}$$

$$E = \frac{\sigma}{\varepsilon} \tag{4}$$

Proton conductivity measured by Electrochemical Impedance Spectroscopy as Eq. (5) adopted from [5, 25–27]. Where σ is the proton conductivity (S cm^{-1}), d is the membrane thickness (cm), Rb is the bulk resistance value (Ω) and A is the membrane area in the sample (cm^2) [2].

$$\sigma = \frac{d}{R_b \times A} \tag{5}$$

Methanol permeability of the membrane is measured by counting the methanol concentration passing the membrane for the diffusion of methanol in progress [16, 26]. The methanol permeability test is carried out using a permeation measurement cell that has two identical compartments. Compartment A is filled with methanol solution in deionized water, and compartment B is filled with deionized water. The principle used cell diffusion between the two compartments. The solution in both compartments is stirred until it is homogeneous so that the diffusion process runs well [14]. Methanol permeability was calculated from the methanol concentration versus permeation time curve. The methanol concentration in compartment B (C_B) is obtained from the Eq. (6) adopted from [25, 27].

$$C_B = \frac{A}{V}\frac{DK}{L}C_A\left(t - t_0\right) \tag{6}$$

Where C_A is the methanol concentration in compartment A, A and L are the polymer membrane area and thickness, D and K are the methanol diffusivity and the partition coefficient between the membrane and solution, V is solution volume in compartment B and t is permeation time. The result of DK or P is the methanol permeability of membrane (DK = P), and t_0 is also called the time lag associated with diffusivity, $t_0 = L^2 / 6D$ [29].

Membrane selectivity is comparison between proton conductivity and methanol permeability [8] expressed in Eq. (7). Where β is membrane selectivity, σ is proton conductivity, and P is methanol permeability.

$$\beta = \frac{\sigma}{P} \tag{7}$$

The chitosan membrane to be analyzed for its functional groups by FT-IR PRESTIGE-21 Shimadzu was taken as much as 0.1–0.2 g. In addition, KBr powder of 0.5–1.0 g was also prepared. The two solids were mixed and grinded until smooth, then the mixture powder was made into pellets with a hydraulic press and the measurement analysis was carried out with a wavelength between 4000 and 400 cm^{-1} [30, 31].

The membrane surface morphology was observed using SEM FEI Inspect S50. The membrane (1x1 cm^2) was firstly coated using gold so that it could be detected by the device.

Membrane topography was observed in three dimensions and two dimensions using AFM Bruker N8 Neos 5.5 IF367. The membrane was taken several parts then put on the tip and detected by the device at certain distance.

Thermal stability analysis using TGA Mettler Star SW 10.00 was carried out on the selected membrane specimens that had the best and worst properties therefore it represented all variations. Thermal stability analysis data was recorded in nitrogen atmosphere at every 10°C/minute heating rate at 30–500°C temperatures.

3. Results and discussions

3.1 Synthesis of silane-coupled Nanosilica and its incorporation into chitosan matrix

Figure 1 illustrates the interaction model between chitosan, nanosilica, and silane in membranes. At the final stage of silylation process that is epoxy groups deformation (ring-opening) on silane organofunctional group end chain, silane form two hydroxyl groups (–OH) which interacts with the amine group ($–NH_2$) and and hydroxyl groups (-OH) in chitosan to form hydrogen bonds that could form a good interface interaction of chitosan and silane-coupled nanosilica network. Thus forming groups Si–OH via hydrogen bonds [5, 10] and siloxane groups (Si–O–Si) via oxane bonds [32].

3.2 The results characterization of chitosan membrane modified with silane-coupled nanosilica

3.2.1 Water uptake of chitosan-nanosilica membrane with silane addition

The water uptake determines how much water is absorbed by the membrane, so the PEM membrane must be able to hold water because the proton will be transported along the water channel created in the membrane polymer matrix. Thus, the high water uptake is favorable for PEM high-performance to facilitate great numbers of protons hopping and diffusion through the membrane [5, 14]. **Figure 2** shows all chitosan-nanosilica membranes with silane addition in this research potentially can be used as a DMFC membrane because it has water uptake value <50% as mentioned by [33]. The water on the membrane serves as proton transport medium and needed as the mobile phase to facilitate proton conductivity but if is it too high it will damage the membrane easily and lower their mechanical properties [33]. In **Figure 2**, it appears that silane addition to nanosilica has an impact on water uptake, which is an increase in water uptake on nanosilica:silane variations of 1:0, 1:0.25 to 1:0.5, but decrease on nanosilica:silane variations of 1:1 to 1:2. The most optimum membrane is variation nanosilica:silane 1:0.50 with water uptake is 37.52%, while chitosan-nanosilica membrane without silane reaches 32.16% water uptake.

The addition of silane to nanosilica increases the active Si-OH groups as shown in **Figure 1** (silane-coupled nanosilica) which will cause increased water absorption of the membrane. The addition of more silane that is silane 1:1 to 1:2 addition causes excess silane to interact with silica. Silane itself is hydrophobic so that if it is added to hydrophobic nanosilica [23] it will increase water absorption to chitosan membrane. This fact is following the results of the [14] study that pure chitosan

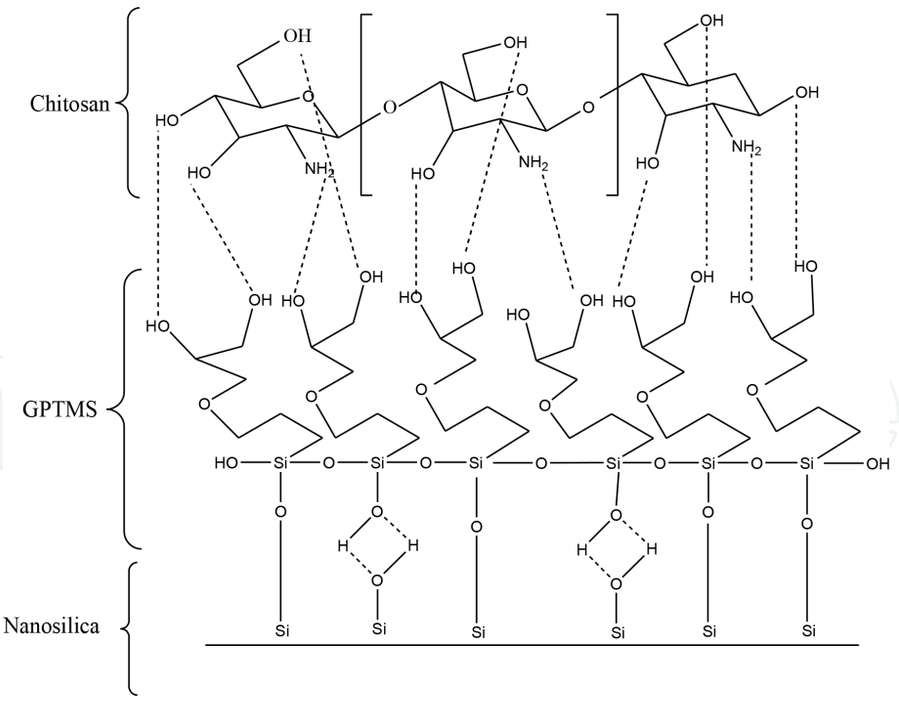


Figure 1.
Illustration of nanosilica-silane and chitosan interaction in membrane.

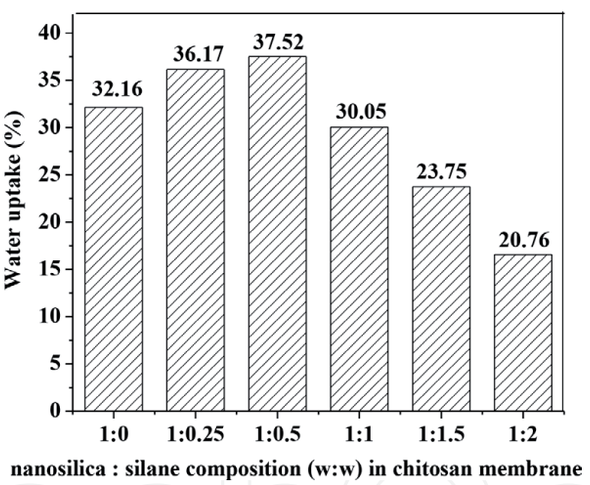


Figure 2.
The relationship between water swelling value (%) and nanosilica:silane composition (w:w).

membrane has 40.66% water uptake and increases along with nanosilica increase addition and water uptake increase along with silane addition in line with the results of [12] study. Nafion 117 has 18,3% in water uptake [12], so the water uptake membranes produced in this study have bigger than Nafion 117.

3.2.2 Mechanical properties of chitosan-nanosilica membrane with silane addition

Figure 3 explains the relations between silane addition in chitosan-nanosilica membrane and their mechanical properties, that is tensile strength, break and elasticity (modulus young) elongation. The tensile strength value of nanosilica:silane variations of 1:0 to 1:0.5 increases with the increasing silane composition that is 4.7, 5.1, 11.8 MPa respectively. It shows that the coupling agent presence causes strong interaction through hydrogen bonding between chitosan and nanosilica so that the tensile strength of the resulting membrane also increases. However, there

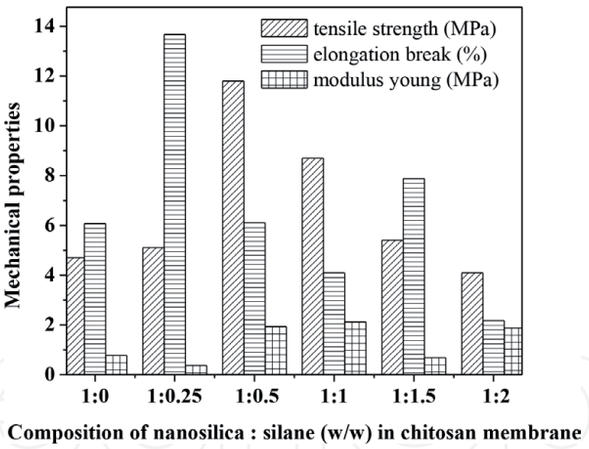


Figure 3.
The relationship of silane addition in chitosan-nanosilica membrane to their mechanical properties.

is a decrease in the silane variation of 1:1 to 1:2 (excess) that is 8.7, 5.4, and 4.1 MPa respectively. This happens because excess silane causes an imbalance in the interaction between silane and nanosilica. The effect of silane addition to nanosilica gives various levels of elongation at break on the membrane that are 6.07, 13.67, 6.1, 4.1, 7.88, and 2.18% respectively. Membrane elasticity is determined by the magnitude of modulus young. The fact is that silane addition can increase modulus young value of nanosilica:silane variation membrane 1:0.25 to 1:1, and decrease significantly in 1:1.5, then increase again in silane addition variation 1:2.

A membrane is said to be good and has the best mechanical performance seen from the high tensile strength values and low elongation at break values [22, 34], so modulus young values which expected is high. In this research chitosan-nanosilica membrane with nanosilica:silane is 1:0.5 reach optimum mechanical properties. Silane addition to nanosilica increases physical interaction between nanosilica and chitosan. Hydrogen bonds formed between hydroxyl groups in polysiloxane with amine and ether groups in chitosan as described in **Figure 1**. Strong interaction between nanosilica and chitosan causes high physical and mechanical strength including tensile strength, elongation and modulus young.

3.2.3 Proton conductivity, methanol permeability, and selectivity of chitosan-nanosilica membrane with silane addition

Proton conductivity of chitosan-nanosilica silane addition membrane can be seen in **Figure 4(a)**. The membrane proton conductivity is measured by using EIS to determine impedance of the membrane. **Figure 4(a)** explains that the proton conductivity increases in line with silane addition to a certain point then decreases. Chitosan-nanosilica with the addition of silane membrane nanosilica:silane variation 1:0.50 has the highest proton conductivity value than another variation of silane addition. It shows that silane composition addition is optimal for interacting with amine group on the chitosan matrix and form a polysiloxane network on nanosilica addition of silane. Excess silane addition (>50%) on the variation nanosilica:silane 1:1, 1:1.50 and 1:2 can cause proton conductivity value become low. This is because the hydrogen bonding that occurs between the silane with chitosan matrix and polysiloxane network is already saturated, so the ability to transport proton facilitate is less than optimal. **Figure 4(a)** shows the highest proton conductivity values obtained at chitosan-nanosilica addition of silane membrane variations nanosilica:silane 1:0.50 is 7.89 x 10^{-4} S/cm. This fact is consistent with the previous fact obtained in the water uptake test. The membrane with the highest

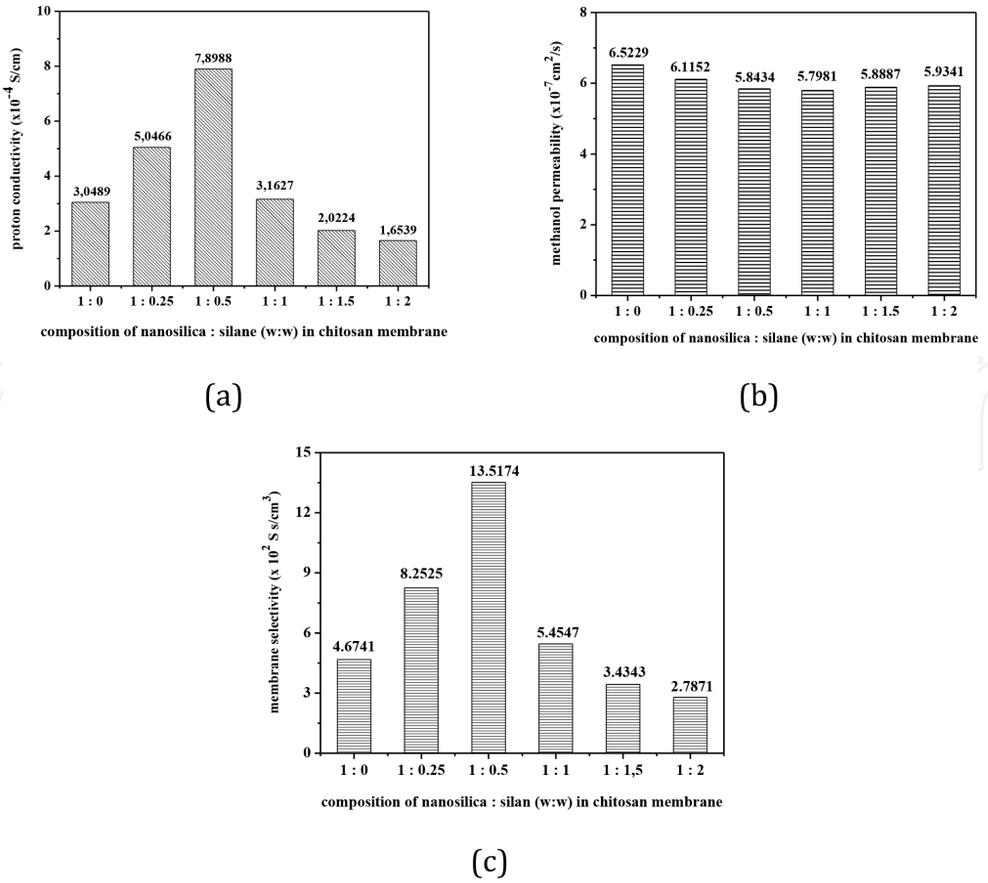


Figure 4.
The relationship of silane addition in chitosan-nanosilica membrane to their (a) proton conductivity, (b) methanol permeability, (c) membrane selectivity.

water uptake has the highest proton conductivity as well. This is true as water in a proton exchange medium, so the higher the water uptake the higher the proton conductivity.

The proton conductivity value obtained by chitosan-nanosilica membrane by silane addition of nanosilica:silane 1:0.5 is 7.89 x 10^{-4} S/cm. This value is smaller than the Nafion 117 proton conductivity membrane which is 5.66 x 10^{-2} S/cm [8]. According to [35], this is related to the Nafion 117 structure. There are many Fluor atoms (F) which have large electronegativity value so that Nafion 117 can be more easily forming hydrogen bonds with water, so it is more easily to absorb water that is needed as a proton transport medium, so the conductivity of the Nafion 117 proton is greater. Although the proton conductivity value of chitosan-nanosilica membrane of nanosilica:silane = 1:0.5 in the study is smaller than Nafion 117, but this membrane can still be used as PEM for applications in DMFC. The membrane can still deliver protons even though they are slow. The proton conductivity value obtained is above the minimum requirement, which is must be bigger than 1 × 10^{-5} S/cm [35].

Figure 4(b) shows that membrane methanol permeability is affected by silane addition. Methanol permeability occurs due to methanol transport in aggregate pores that is further dependent on the pores volume in the membrane. There are two types of pore in the polymer membrane: network pores or ionic clusters and aggregate pores. Proton transport occurs through two types of pore, while the mass transport (methanol, water, and gas) occurs only through the porous aggregate [36]. Network pores is a small cavity between the polymer chains that is responsible for proton conduction. Aggregate pores are large cavities that cover polymer aggregates which cause mass transport (methanol) [37].

The decrease in methanol membrane permeability as shown in **Figure 4(b)** from the composition of nanosilica:silane 1:0 to 1:1 is caused by properties adhesion and interface interaction (hydrogen bonds) of chitosan-nanosilica with the silane addition is stronger [15] than chitosan-nanosilica membranes without silane addition (1:0). According to [29], the decrease in hydrophilicity in this case is due to the silane nature which is able to balance the hydrophilic and hydrophobic nature of an organic or inorganic material. The addition of nanosilica which has been carried out by silane can close pores on the chitosan membrane through strong interactions between amines in chitosan with polysiloxane in nanosilica so that most of the methanol does not pass through the membrane.

Chitosan-nanosilica membrane with silane addition in nanosilica:silane variation 1:1.5 and 1:2 there is an increase in methanol permeability value that is 5.8887×10^{-7} cm^2/s and 5.9341×10^{-7} cm^2/s respectively. This is due to the composition of silane addition cannot interact perfectly with chitosan matrix so the adhesion force decreases and the chitosan matrix interaction with silane nanosilica addition is weak. The highest methanol permeability value was obtained on the chitosan-nanosilica membrane without silane is equal to 6.5229×10^{-7} cm^2/s. The addition of silane chitosan nanosilica membrane that has good performance in methanol permeability value followed by high proton conductivity value is the chitosan-nanosilica membrane addition of nanosilica:silane 1:0.5 variation which is 5.8434×10^{-7} cm^2/s. This is also supported by the proton conductivity value obtained by 7.8988×10^{-4} S/cm. Chitosan-nanosilica membrane with silane addition nanosilica variation: silane 1:0.5 has the lowest methanol permeability value when compared to Nafion 117 membrane that is 1.01×10^{-6} S/cm [16]. For DMFC applications, it is expected that membranes with small methanol permeability. Small permeability prevents leaks and avoids methanol cross over.

Figure 4(c) explains that the highest membrane selectivity is obtained on the chitosan-nanosilica membrane with silane addition in nanosilica:silane variation 1:0.5. Membrane selectivity is a parameter that connects proton conductivity with methanol permeability. For DMFC applications, the desired membrane is a membrane with high conductivity and low methanol permeability, so the determination of membrane selectivity uses Eq. (7) [8]. Through this membrane selectivity determination, the facts show that the chitosan-nanosilica membrane with 1:0.5 silane addition is the membrane with the best performance as PEM for DMFC applications. Membrane selectivity aims to evaluate membrane performance capability based on high proton conductivity values and low methanol permeability values. The membrane selectivity is influenced by modulus young value as mechanical properties of the membrane. It can be explained that the higher membrane selectivity, the higher modulus young so that the membrane physical properties are in harmony with the membrane chemical properties as polymer electrolyte membrane (PEM). The results of membrane synthesis in this study are supported by high modulus young values, high proton conductivity values and low methanol permeability.

When compared to Nafion 117, chitosan-nanosilica membrane with silane addition in nanosilica:silane variation 1:0.5 has lower membrane selectivity value. It shows that chitosan-nanosilica membrane with silane nanosilica variation: silane 1:0.5 addition has the ability under Nafion 117, but this membrane can still be used as PEM for DMFC applications, it means that the membrane can deliver protons even though it runs slowly but it can reduce the entry of methanol fuel through the membrane supported by methanol permeability obtained that is smaller than Nafion 117 membrane.

3.2.4 Functional groups analysis of chitosan-nanosilica membrane with silane addition

Figure 5 shows FT-IR spectra of nanosilica and chitosan-nanosilica membrane with silane addition. The FT-IR spectrum of chitosan on the membrane is characterized by the presence of —CN groups (amide groups) in all variations of the chitosan-nanosilica membrane with the addition of silane at the wavenumbers 1627.92 cm^{-1} and 1635.64 cm^{-1} [38]. The wavenumbers shift in the FTIR spectrum of chitosan indicates an interaction between the amide group in the chitosan matrix and the polysiloxane network in the nanosilica addition of silane through hydrogen bonds. The absorption around the wave number 1060–1084 cm^{-1} indicates the —CO group (ketone group) [38]. The —CO group (ketone group) which is a characteristic of the polysaccharide appears at the wave number 1080.14 cm^{-1}. The -CH bonds in $-NHCOCH_3$ appear at wave numbers 2854.65 cm^{-1} and 1404.18 cm^{-1} [39, 40]. This absorption in assigned to the $-^{+}N-H$ bonds, indicating that the chitosan could be interacting with another groups by coulombic forces [40].

In FT-IR spectrum of nanoslilca in **Figure 5**, the main functional group analysis results is the emergence of Si–O–Si groups on nanosilica and chitosan-nanosilica membrane with silane addition. Absorption around wave numbers 1100–1200 cm^{-1} and 460–480 cm^{-1} indicates the presence of the Si–O–Si group (siloxane group) [39]. This absorption band (Si-O-Si groups) did not appear in the chitosan membrane spectra but appear in chitosan-nanosilica membrane. This sharp increase in absorption band intensity indicates the presence of stretching vibrations of Si–O–Si (siloxane group) which is getting stronger. According to [24], it indicates that some of the siloxane groups (Si–O–Si) of polysiloxane network in silane addition and nanosilica have interacted strongly with chitosan matrix. Absorption band at wave number 894.97 cm^{-1} indicates the presence of the Si–OH groups (silanol groups) [38]. The Si–OH groups (silanol groups) show hydrogen bonds existence between silanol groups in nanosilica-silane with amide groups in the chitosan matrix. It is also seen in **Figure 5** that there are absorption bands around wave number 3400–3500 cm^{-1} which indicate the –OH (hydroxyl)

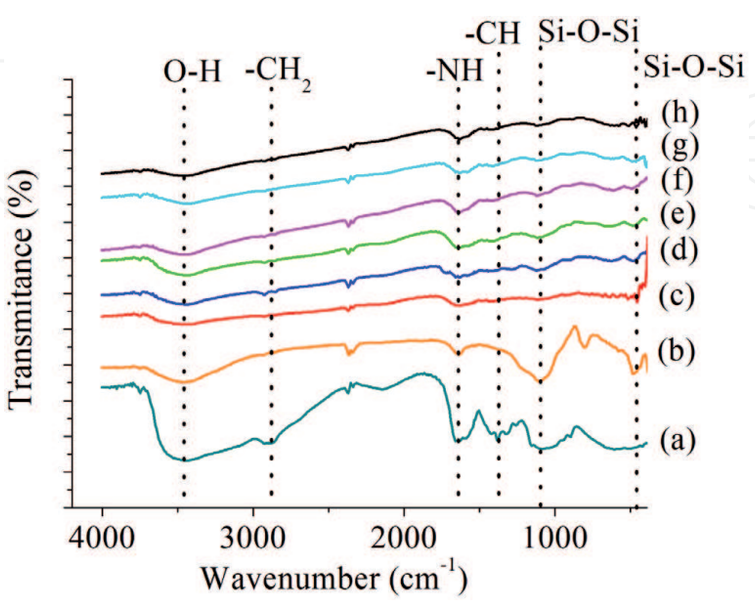


Figure 5.
FT-IR spectra of chitosan-nanosilica membranes with variation of silane addition. (a) Chitosan; (b)Nanosilica; (c) chitosan membrane with nanosilica:silane = 1:0; (d) 1:0,25; (e) 1:0,05; (f) 1:1; (g) 1:1,5; (h) 1:2.

groups presence. A sharp intensity increase occurs in the vibration stretching –OH (hydroxyl group). According to [39], it indicates that some hydroxyl groups (–OH) on the chitosan matrix have interacted strongly with the polysiloxane network in nanosilica-silane through hydrogen bonds. Another important absorption band is at 1644–1637 cm^{-1} which indicates the bending vibration H-O-H indicates the vibration of water molecules bound to the inorganic framework.

Variation of nanosilica:silane membrane at 1:0.50 is the best membrane that has the highest value of membrane selectivity and has the best mechanical properties. FT-IR spectra of the chitosan-nanosilica membrane with silane addition in nanosilica:silane membrane at 1:0.50 as in **Figure 5** shows that absorption band at wavenumber 3448.72 cm^{-1} is stretching vibration absorption –OH groups more sharply when compared with other variation. It shows that the hydrogen bonds between the chitosan matrixes with this silane addition on nanosilica more easily formed than the nanosilica without silane addition. The amine group on the chitosan is easier to form hydrogen bonds with epoxy groups on the silane. Besides, there are new absorption wavenumbers around 900–912 cm^{-1} which indicate the presence of epoxy groups (-C_2H_3O) in silane [15, 21], and from 2900 to 2960 cm^{-1} indicating –CH_2 groups of silane compound [4] in. It can be seen in **Figure 8** that absorption at wavenumber 902.69 cm^{-1} indicates epoxy groups presence of organofunctional group silane compound and absorption at wavenumber 2924.09 cm^{-1} that indicates the stretching vibration –CH_2 groups. Absorption at wavenumber 2924.09 cm^{-1} is absorption of the bridge group –CH_2 alkyl silane compound and it is not from chitosan.

3.2.5 Morphology analysis of chitosan-nanosilica membrane with silane addition

Figure 6 shows membrane morphology of chitosan, chitosan-nanosilica without silane addition (variation 1:0) and chitosan-nanosilica with silane addition. **Figure 6(a)** shows a homogenous surface of chitosan membrane, while in **Figure 6(b-d)** show heterogeneous surface of chitosan matrix containing nanosilica particles. Besides, there is fairly large agglomeration in **Figure 6(b)** as chitosan-nanosilica without silane. It suggests that the interaction between the chitosan matrix with nanosilica is poor without silane as coupling agent. Good interaction will produce homogeneous surface morphology [21].

Figure 6(c) shows membrane morphology of chitosan-nanosilica membrane with silane addition variation 1:0.50 (the best membrane) that shows good interaction between chitosan and nanosilica with silane addition. This is due to the occurrence of attachment between nanosilica and silane as coupling agents with relatively small amounts so that they can spread evenly with chitosan matrix, eventually being able to cover the pores of membrane well. Excessive agglomeration occurs in chitosan-nanosilica membranes with nanosilica:silane 1:2.0 composition (**Figure 6(d)**) due to excessive amounts of silane that interfere effective attachment process, so that the morphology resulting membrane appears to be lumps and not homogenous. But, other techniques are necessary to support this facts. A good alternative is X-ray photoelectron spectroscopy (XPS), specifically high-resolution XPS of C, O, N, and Si.

3.2.6 Membrane topographic analysis using AFM

Membrane topographic analysis using AFM quantitatively is shown in **Table 1**. Topographic analysis with backward amplitude results in surface morphology of surface roughness (S_a) and root mean square (RMS) roughness or S_q, as well as the highest surface height (H_{max}) and lowest surface (H_{min}) as in [41–45] studies. In

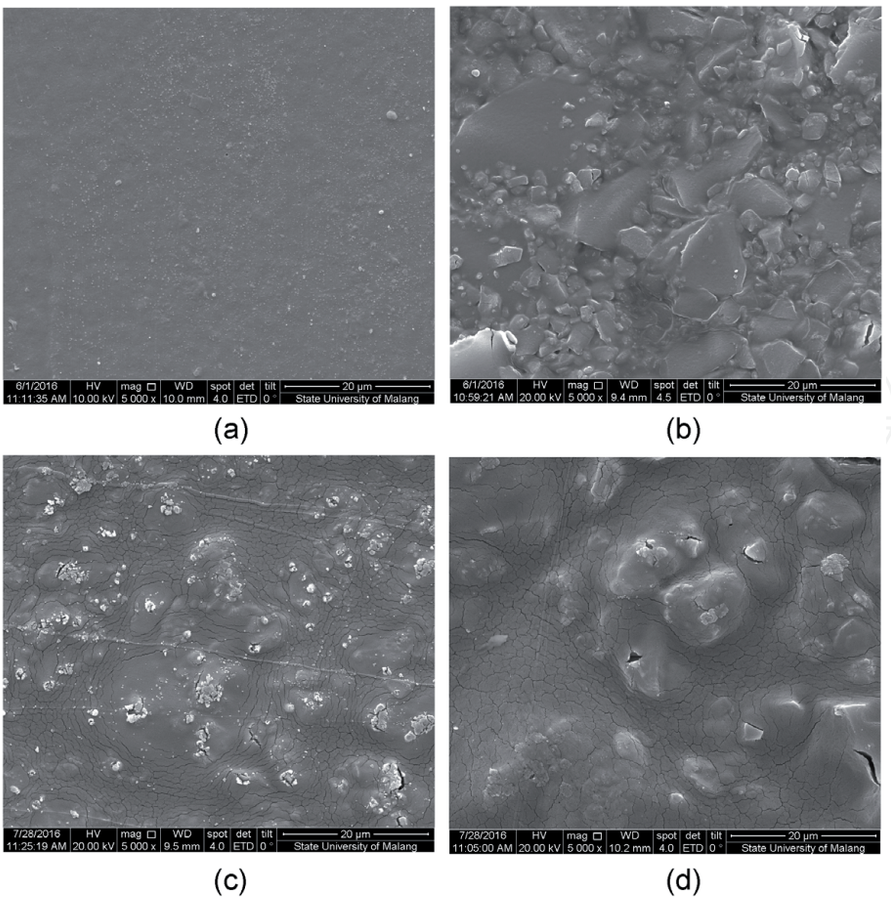


Figure 6.
Morphology surface (5000 magnification) by SEM of (a) chitosan; (b) chitosan-nanosilica membrane with nanosilica:silane = 1:0, (c) 1:0.5, and (d) 1:2.0.

Chitosan-nanosilica Membranes	S_a mean (nm)	S_q mean (nm)	H_{max} (nm)	H_{min} (nm)
Nanosilica:silane = 1:0	0.956	1.327	43.000	−28.000
Nanosilica:silane 1 = 1:0.5	2.308	3.713	121.667	−83.333
Nanosilica:silane 1 = 1:2.0	1.473	1.857	82.667	−66.333

Table 1.
Results of quantitative AFM analysis on chitosan-nanosilica membranes with Silane addition.

Table 1 the surface roughness parameter values on chitosan-nanosilica membrane without silane showing the value of S_a, S_q, H_{max}, and H_{min} have the lowest value. The addition of 50% GPTMS silane or in composition 1:0.5 as the coupling agent raises the value of the surface roughness parameter even at this point reaching the highest value. These peaks indicate the optimum interaction with the 50% silane addition to chitosan-nanosilica. It proves that silane addition as the coupling agent between chitosan and nanosilica at the optimum amount raises the value of average roughness or S_a and root mean square roughness S_q, as well as the highest surface height (H_{max}) and lowest surface (H_{min}) and then decreases at next addition. The next point is the addition of 100% silane or in composition of 1:2.0 the surface roughness parameter shows a decrease that is, the excess silane causes reduced interaction between chitosan and nanosilica.

The qualitative results of membrane topography are shown in **Figure 7**. The AFM analysis provides topographic information of chitosan-nanosilica composite membranes with GPTMS (silane) addition as coupling agent in two-dimensional

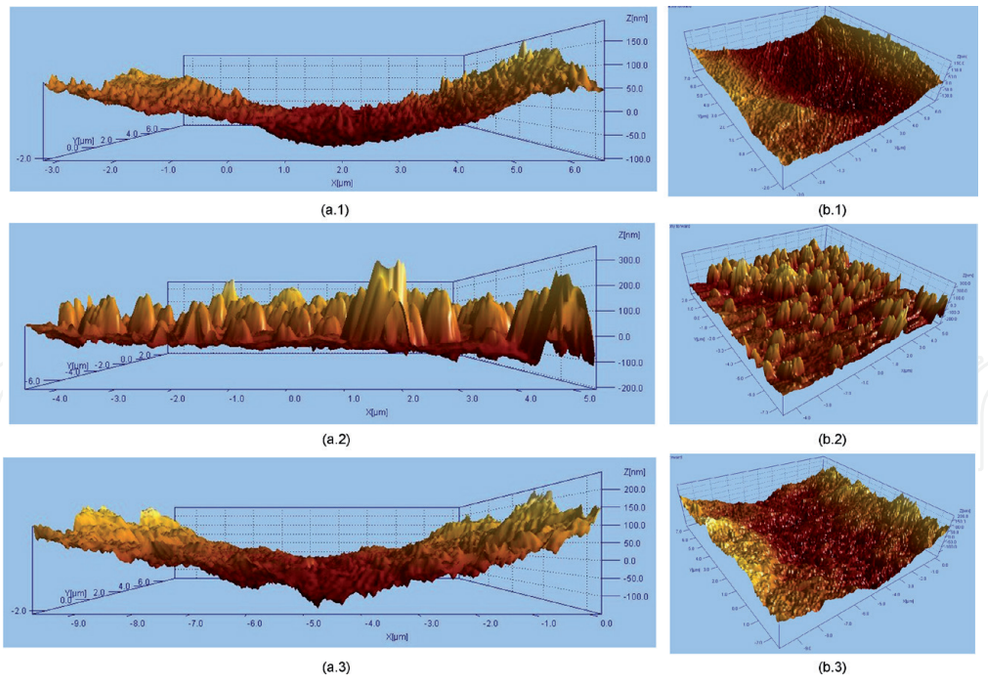


Figure 7.
The AFM analysis of chitosan-nanosilica composite membranes with GPTMS silane coupling agent addition in (a) two-dimensional (2D) and (b) three-dimensional (3D), variation nanosilica:silane (1) 1:0, (2) 1:0.5 and (3) 1:2.0.

(2D) (**Figure 7a(1–3)**) and three-dimensional (3D) (**Figure 7b(1–3)**) appearance. The analysis results using AFM shows that chitosan-nanosilica membrane without silane (chitosan-nanosilica:silane ratio = 1:0) shows that membrane topography tends to be regular and evenly distributed. It shows that the membrane still carries typical state of chitosan and nanosilica whose topography is not yet affected by other materials. It means between the two materials, chitosan and nanosilica, maximum interaction has not yet occurred. This result is in accordance with morphological analysis result with SEM which shows rough surface. In chitosan-nanosilica membranes with 50% silane addition to nanosilica, or the composition of chitosan-nanosilica = 1:0.5 indicates significant change in topography surface. The membrane surface forms irregular bumps (hills and valleys) caused by the certain amount of nanosilica composition that interacts well with chitosan on the membrane. On 100% silane addition or chitosan-nanosilica: of 1:2.0, bumps on membrane topography are no longer occurred, but the surface tends to be evenly distributed and more homogeneous, indicating prominent characteristics of each chitosan and nanosilica. The presence of nanosilica fillers interact with chitosan through hydrogen bonds as proven by FTIR analysis. The interaction will be maximized when the coupling agent is added in the form of silane at an optimum amount. In the presence of some silanes, the chitosan matrix will begin to be affected by the presence of silane-coupled nanosilica fillers to produce the formation of a certain number of hills and valleys at AFM analysis in line with capabilities of the existing filler and coupling agent. **Figure 7** shows a rough topography with fairly wide distribution of hills and valleys. The number of irregular areas is due to the presence of nanosilica hydrophobic fillers that interact with chitosan by the addition of an optimum amount silane as coupling agent. Rugged topography with many hills and valleys spread evenly over almost all surfaces that are found on the membrane with 50% silane addition. In this membrane, the chitosan and nanosilica matrices are no longer dominant, because the added nanosilica filler has interacted well with chitosan due to the GPTMS as coupling agent.

The interaction that occurs between the chitosan matrixes with nanosilica fillers in the presence of silane as coupling agent forms a unified and strong membrane. As a result, membrane topography is fused between two components, shown in more uniform color in **Figure 7**. The 3D images on the composition of chitosan-nanosilica:silane = 1:0.5 resulting from AFM analysis does not show any differences in the regions or parts of chitosan and nanosilica. The surfaces of both valleys and hills are joined in such a way that they show that the two materials interact very well. This phenomenon is supported by research [46] who makes a composite membrane from an organic matrix in the form of chitosan and alumina as an inorganic filler. The results of AFM analysis in [46] study shows that the chitosan/alumina composite membrane shows rough topography with membrane surface covered with granules show that chitosan has interacted strongly with alumina. Identical with [46] study, chitosan subtle areas are covered by nanosilica material so that the membrane topography in 3D shows the presence of hills and valleys that are evenly distributed to all surfaces. AFM analysis in [20] study also supports the facts and results of the AFM analysis in this study. As [20] research on chitosan-nanosilica supports mixed matrix membranes and the results of AFM analysis show that the incorporation of nanosilica and silane increases the membranes surface rippling which, as FTIR results shows, are attributed to strong bonds formed between nanosilica particles and chitosan matrix.

3.2.7 Thermal analysis using TGA

The thermal stability of the chitosan-nanosilica hybrid membrane is evaluated by thermo gravimetric analysis with TGA. The thermograms are shown in **Figure 8** and the change in mass percentage on each thermogram stage is presented in **Tables 2** and **3**. In TGA analysis, sample changes are marked by deviations from the horizontal line. As shown in **Figure 8** and **Table 2**, all membranes show three stages of weight-loss as area of change in mass percentage on TGA thermogram of membrane samples.

The first weight loss at around 35–150°C (**Table 2**) is attributed to the loss of water molecules present in hybrid membrane [10, 47] with mass reduction 12–14%. The difference in temperature range and the percentage of sample weight-loss is

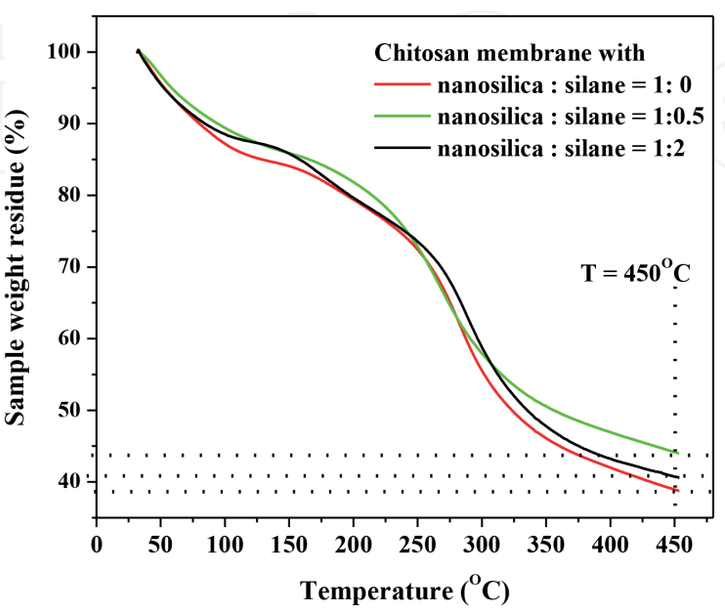


Figure 8.
TGA thermograms of chitosan-nanosilica membrane with silane addition.

Chitosan-nanosilica Membranes	Temperature range on an oblique curve (°C)			Mass reduction on an oblique curve (%)			Mass residue (%) at III
	I	II	III	I	II	III	
Nanosilica:silane = 1:0	35–120	120–220	220–430	12.72	9.96	36.02	41.58
Nanosilica:silane 1 = 1:0.5	40–150	150–330	330–450	13.72	34.06	7.79	44.09
Nanosilica:silane 1 = 1:2.0	35–140	140–335	335–450	14.35	36.16	8.78	37.93

Table 2.
The area of change (stages) in mass percentage reduction on TGA thermogram of membrane samples.

Chitosan-nanosilica Membranes	Mass residue (%) at 450°C	Temperature (°C) when sample is degraded and remaining 44%
Nanosilica:silane = 1:0	38.92	371.98
Nanosilica:silane 1 = 1:0.5	44.15	452.94
Nanosilica:silane 1 = 1:2.0	40.74	387.96

Table 3.
Chitosan-nanosilica:silane membrane thermal degradation.

not significant indicates that the water content in samples are not significantly different. Mass reduction in chitosan-nanosilica membrane samples with silane coupling agent is higher when compared to sample without silane. This shows that chitosan-nanosilica with silane is more hygroscopic.

The second weight-loss in **Table 2** appearing at around 150–335°C indicates the decomposition of chitosan polymer chain in hybrid membrane [10]. This chain decomposition is related to the loss of side groups as acetyl groups (as shown in **Figure 1**) in chitosan because the acetyl groups has a weak phi bond so it breaks easily first. The temperature range and the percentage of sample weight-loss is significantly different. The temperature range and the percentage of mass reduction in two samples with silane as coupling agent shows a large range. The second stage temperature range in the sample with silane shows a widened temperature region. This is due to the presence of the silane as coupling agent interact with the acetyl groups thus preventing the release of the acetyl groups. As a result, a large number of these groups release at higher temperatures.

The third weight-loss stage is observed near 335–450°C is due to unstable parts of the polymeric matrix whereas it is occurring due to complete decomposition of the backbone of polymeric matrix [48] and residual organic groups [8]. The temperature range and the percentage of sample weight-loss in this stage is significantly different. The temperature range in third stage in two samples with silane as coupling agent shows a large range while the percentage of mass reduction is a small range. The incorporation of silane has improved the interaction of nanosilica and chitosan by introducing more functional groups with hydrogen bond formation as **Figure 1** and FTIR results. Hydrogen bond between hydroxyl groups (–OH) in silane-coupled nanosilica interacts with the amine group ($–NH_2$) ether group (C–O–C) of chitosan that could form a good interface interaction [32]. This all makes it difficult for chitosan chain to degrade so that the degradation temperature range is greater and the remaining mass is less. In addition, chitosan membrane samples with silane-coupled nanosilica have higher component heterogeneity than chitosan-nanosilica without silane. High heterogeneity of polymer components causing a longer range of degradation and decomposition temperature. Therefore, it can be understood that **Table 3** shows that nanosilica:silane 1 = 1:0.5 have the

highest thermal degradation. This result is in line with the results of FTIR and AFM analysis which finds that the composition nanosilica:silane 1 = 1:0.5 provides the best hydrogen bond interaction. This result is in accordance with [17] which state that the proper addition of modified nanosilica with silane enhanced the thermal performance by acting as superior insulator and mass transport barrier to the volatile products generated during decomposition.

4. Conclusions

The influence of silane as coupling agent on the chitosan-nanosilica membrane causes homogeneity and prevents agglomeration between nanosilica and chitosan. The higher silane compositions added, it decrease the water uptake, increases proton conductivity, decreases methanol permeability, and increases selectivity of the membrane. The best membrane performance is on the variation of nanosilica: silane 1:0.50 which has water uptake of 37.52%, tensile strength of 11.8 MPa, proton conductivity of 7.8988 x 10^{-4} S/cm at 25°C, methanol permeability of 5.8434 x 10^{-7} cm^2/s, and membrane selectivity of 13.5174 x 10^2 S s/cm^3. This membrane has high thermal stability of 452.94°C with mass residue 44%. Based on the results of membrane selectivity analysis, the best and most suitable chitosan membrane for electrolyte polymer applications is the chitosan membrane with the addition of nanosilica:silane = 1:0.5; 1:0.25; 1:1; 1:0; 1:1.5 and 1:2.0 (w/w). This is based on the order of membrane selectivity values from the highest to the lowest. The results of FT-IR, SEM and AFM analysis on membranes show that optimum silane addition provides the best interaction between chitosan matrix and silane-coupled nanosilica so that they have higher thermal resistance. When compared to Nafion 117 membrane, this membrane has lower proton conductivity value, but the advantages are it more environmentally friendly, has lower methanol permeability, higher temperatures stability and of course more economical in terms of cost. Further efforts are needed to increase the proton conductivity of this chitosan membrane for DMFC applications.

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