

CHAPTER V

COMPOSITE PROTON EXCHANGE MEMBRANES OF SULFONATED POLY(ETHER KETONE ETHER SULFONE) (S-PEKES) AND MOLECULAR SIEVE WITH HIGH MECHANICAL STRENGTH FOR DIRECT METHANOL FUEL

5.1 Abstract

Composite proton exchange membranes are prepared by solvent casting via the incorporation of molecular sieves 3A, 4A, and 5A into the sulfonated poly(ether ketone ether sulfone) (S-PEKES) at the sulfonation degree of 0.66, with varying the ratio at of 3, 6, 9, and 12% v/v. The influences of type and amount of the molecular sieves on the proton conductivity, methanol permeability, structural, thermal, and mechanical stabilities of the membranes are investigated. The composite membranes are characterized by FTIR, TGA, LCR meter, and GC techniques. All properties of the composite membrane are compared with the pristine S-PEKES and Nafion 117 membranes.

Keywords: Sulfonated poly(ether ketone ether sulfone); Molecular Sieve; Proton Exchange Membrane (PEM); Proton conductivity

5.2 Introduction

Direct methanol fuel cell (DMFC) has attracted substantial interest as an alternative energy source for applications in various portable devices such as mobile phone, laptop, and etc. A proton exchange membrane (PEM) is a solid polymer electrolyte membrane used in both polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). It allows protons to pass through from the anode to the cathode and acts as a barrier to prevent the methanol crossover.

Currently, Nafion membrane is mainly used as PEM due to its excellent proton conductivity in the fully hydrated condition. However, Nafion still has high methanol permeability and cannot be used at high temperature. Furthermore, its cost is very high. The challenge of PEM development with high proton conductivity and thermal stability, low cost and methanol permeability is of interest (Carette *et al.*, 2001).

In recent years, there are many types PEM developed: perfluorinated, partially fluorinated, nonfluorinated, acid-base blends, and other supported composite membrane (Smitha *et al.*, 2005). Non-fluorinated polymer membranes are based on the aromatic main chain such as the modified sulfonated poly(arylene ether ketone) series, considered as a novel and excellent proton exchange membrane material. They are composed thermoplastics with excellent chemical and thermal stabilities, good insulator, high mechanical strength, and a relatively low cost compared to Nafion membrane. These sulfonated polymer membranes have good thermal stability and high proton conductivity at a high sulfonation degree. Several articles have reported the sulfonation of these membranes and their properties (Zhang *et al.*, 2005; Wang *et al.*, 2012).

In order to improve the functioning of PEM, it is possible to modify the membrane composition by adding other materials to form different type of membrane: adding plasticizers and/or crosslinking agent to the polymer matrix, polymer blended membrane, and inorganic/polymer composite membrane. The latter is of interest towards the increase in proton conductivity, the maintenance of water at high temperatures, and the increased mechanical support (Ramirez-Salgado *et al.*, 2007). In this context, the incorporation of inorganic additives such as molecular sieves, into the polymer matrix, has been developed to form composite membranes. The incorporation of a molecular sieve, within an appropriate polymer matrix, can offer several advantages: proper mixing of inorganic and polymer at a molecular level provides good mechanical stability compared with a pure polymer membrane; since proton conductivity is the effect of proton transporting on the surface of the proton conductor particles, an increase in surface area is expected to increase the proton conductivity obtained for a composite membrane (Smitha *et al.*, 2005). In the previous work, the proton conductivity of the composite membrane of zeolite beta filled SPEEK increased to 0.13 S.cm^{-1} from the 0.06 S.cm^{-1} of the pristine SPEEK

(Sengul *et al.*, 2009). Tetrapropylammonium (TPA) and tetrabutylammonium (TBA) were incorporated to a Nafion membrane, thus lowering its methanol permeability and higher selectivity compared to Nafion (Krivobokov *et al.*, 2010). The proton conducting composite membranes comprising of sulfoated poly(1,4-phenylene sulfide) and zeolite molecular sieve 3A were prepared (Choi *et al.*, 2010), they possessed higher thermal stability than the pristine polymer membrane by reason of the strong specific interaction between the molecular sieve 3A particles and the sulfonic acid group of polymer matrix. The Nafion-Faujasite composite membranes were fabricated by Zhang *et al.*, 2005, the Faujasite zeolite addition increased the water uptake and mobility due to the hydrogen bonding between the Si-OH and SO₃H groups, leading to the increase in proton conductivity (Zhang *et al.*, 2011). The HZSM-5 zeolite with a higher aluminum content, exhibits a higher proton conductivity due to its high water retention, and improve the thermomechanical properties (Han *et al.*, 2012). The composite polymer membranes comprising of P(VDF-*co*-CTFE)-*g*-PSSA graft polymer and a zeolite showed high thermal stability up to 300 °C suitable for the DMFC application (Patel *et al.*, 2009).

In this work, the effect of a molecular sieve zeolite was investigated. The synthesized S-PEKES were used as the polymer matrix, where 4,4'-difluorobenzophenone and 4,4'-dichlorobenzophenone are the starting monomers (Changkhamchom *et al.*, 2010). The S-PEKES with a sulfonation degree of 0.66 was chosen to prepare the composite membranes. The molecular sieve 3A, 4A, and 5A were used as the inorganic fillers at various volume percentages. The composite membranes were fabricated by solvent casting. The influence of the molecular sieves on the structural, thermal and mechanical properties, proton conductivity, and methanol permeability of the membranes were characterized and compared with those of the pristine S-PEKES and Nafion 117 membranes. The addition of the molecular sieve zeolite into the S-PEKES improves drastically the mechanical and thermal stabilities, and the proton conductivity relative to the pristine S-PEKES membrane. In particular, the proton conductivity of the highest ratio of molecular sieve/S-PEKES composite membrane is close to that of the commercial Nafion 117 membrane.

5.3 Experimental

5.3.1 Materials

Bisphenol S or 4,4'-sulfonyldiphenol and 4,4'-dichlorobenzophenone (98–99%, Aldrich) were used as the monomers. Sodium chloride (Univar, 99.9%), concentrated sulfuric acid (Merck, 98 wt%), and sodium hydroxide (Univar, 97%) were used as received. Toluene (Fisher-Scientific 99.99%), dimethyl sulfoxide (Riedel-de-Haen, 99.5%), and potassium carbonate (Riedel-de-Haen, 98–100%) were used as received. Dimethyl sulfoxide was purchased from RCI Labscan Limited. Molecular Sieve 3A, 4A, and 5A as the inorganic fillers were purchased from Aldrich. Nafion 117 was purchased from Electrochem, Inc.

5.3.2 Synthesis of poly (ether ketone ether sulfone) (PEKES) and sulfonated poly(ether ketone ether sulfone) (S-PEKES)

Both PEKES and S-PEKES at the 0.66 degree of sulfonation (DS) were synthesized according to the previous work reported elsewhere (Changkhamchom *et al.*, 2010). S-PEKES was synthesized by using these monomers: 4,4'-dichlorobezophenone and bisphenol S via the nucleophilic aromatic substitution reaction. The two monomers were mixed with DMSO and toluene, K_2CO_3 as catalyst, in a 250-ml three necked round bottom flask equipped with a Dean-Stark trap, a nitrogen inlet, a reflux condenser, and a thermostat. The mixture was refluxed for 3 h at 150 °C, excess toluene was distilled off during the reflux process. Toluene was used to remove the water byproduct, and the solution was heated at 175 °C for 20 h. The mixture was cooled to room temperature and poured into a solution of methanol and distilled water (50%v/v). The crude product was then washed with water to remove any inorganic salt, filtered, and dried in a vacuum oven at 80 °C for 48 h.

Then, 5.0 g of the PEKES powder was dissolved in 50 ml concentrated H_2SO_4 (98%), and vigorously stirred at 25 ± 2 °C for 84 h. The solution was precipitated on crushed ice. The suspension was left for 12 h at room temperature. Then, the precipitate was filtered, washed with de-ionized water several

times until neutral pH was obtained, and dried under vacuum to get the S-PEKES powder at 60 °C for 24 h. The chemical structure of S-PEKES is shown in Figure 5.1.

5.3.3 Membrane Preparation

One gram of mixture was dissolved in 30 mL dimethyl sulfoxide (DMSO) with vigorous stirring for 12–18 hours until the polymer solutions were homogeneous and the molecular sieve was dispersed evenly. Composite proton exchange membranes were prepared by solvent casting via the incorporation of 3, 6, 9, and 12% v/v of molecular sieves 3A, 4A, and 5A into the solution of the sulfonated poly(ether ketone ether sulfone) (S-PEKES) at the sulfonation degree of 0.66. Each solution was cast on a petri dish and kept at room temperature for 12 h, followed by drying at 80 °C for 2 days under a vacuum

5.3.4 Polymer Characterization

5.3.4.1 *Fourier Transform Infrared Spectroscopy (FTIR)*

The FTIR spectra of the molecular sieve 3A, 4A, and 5A/S-PEKES composite membranes with 12%v/v were taken, using a Thermo Nicolet/Nexus 670 FTIR spectrometer, and the background material was spectronic-grade KBr. The operation condition covered the wavenumber of 4000–400 cm^{-1} under the absorption mode with 32 scans at a resolution of $\pm 4 \text{ cm}^{-1}$.

5.3.4.2 *Thermal Behavior*

A thermogravimetric analyzer (TGA) (PerkinElmer/TGA7) was used to investigate the degradation temperature of all composite proton exchange membranes: the pristine S-PEKES; molecular sieve 3A, 4A, and 5A/S-PEKES; and Nafion 117 membranes. Between 5.0 and 10.0 mg samples were heated from 50–800 °C at a rate of 10 °C/min under N_2 atmosphere (Wang *et al.*, 2006).

5.3.4.3 Proton Conductivity

The proton conductivity values of the composite proton exchange membranes were measured by an Agilent E4980A LCR meter at a AC potential of 1 V and in the frequency range between 20 Hz to 2 MHz, at 27 ± 1 °C, and at 50%RH. The composite membranes were immersed in de-ionized water at various soaking times to obtain 10 and 50% water contents. The water uptake (%) of the membranes was calculated from the method previously reported (Unnikrishnan *et al.*, 2010). The conductivity values (σ) of all samples were calculated from the impedance data, using the relation $\sigma = d/RS$ where σ is the proton conductivity (S/cm), S is the membrane surface area (cm²), d is the membrane thickness (cm), and R is the resistance which can be derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) or Z' axis (Mikhailenko *et al.*, 2004). The impedance of each sample was measured for 3 times to ensure data reproducibility. The proton conductivity values of all composite membranes were compared with the pristine S-PEKES and Nafion 117 membrane.

5.3.4.3 Methanol Permeability

The methanol permeability of the membranes was determined by using the two compartments diffusion cell as previously reported (Changkhamchom *et al.*, 2013). The compartment A ($V_A = 250$ ml) was filled with a solution of methanol (2.5 mol/L). The compartment B ($V_B = 250$ ml) was filled with de-ionized water. The membrane was clamped between the two compartments. The solutions in the two compartments were mechanically stirred during the permeation periods. Methanol diffused across the membrane due to the methanol concentration difference between the compartment A and the compartment B (Mukoma *et al.*, 2004). The methanol permeation in the receiving compartment as a function of time was calculated by:

$$P \text{ (cm}^2\text{/s)} = \frac{k_B \times V_B \times L}{A \times (C_A - C_B)} \text{ ,} \quad (1)$$

where P is the methanol permeability, C_A and C_B are the methanol concentrations in the compartment A and B respectively, k_B is the slope of the methanol concentration gradient in the compartment B, V_B is the volume of the solution in the compartment B, A and L are the area and the thickness of a membrane respectively. The methanol concentrations were measured by using a gas chromatography (Pr2100) fitted with a thermal conductivity detector (TCD); ethanol was used as an internal standard.

5.3.4.4 Mechanical Properties

Mechanical properties such as Young's modulus, tensile strength, and elongation at break were measured (Lloyd, UTM) for all proton exchange membranes: the pristine S-PEKES; molecular sieve 3A, 4A, and 5A/S-PEKES; and Nafion 117 membranes. They were previously equilibrated in water for 24 h and at 27 °C as strips (60 mm×10 mm×0.2 mm). A crosshead speed of 100 mm/min was used. And the gauge length was 30 mm. The measurements were run at 27 °C and at 50% RH. The samples for the dry state test were dried at 100 °C in vacuum for 12 h before each test. For each reported data point, five samples were tested, and the average value was calculated and reported.

5.4 Results and Discussion

5.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the composite proton exchange membrane, incorporated with 12 %v/v molecular sieves with the highest degree of sulfonation S-PEKES (DS 0.66), are shown in Figure 5.2. The absorbance peaks at around 1585 and 1655 cm^{-1} represent the stretching of the carbonyl group, and the peaks at 1242 and 1149 cm^{-1} represent the stretching of the sulfone group (Gil *et al.*, 2004). The absorption band at 1243 cm^{-1} represents the asymmetric stretching of the sulfone group, the bands at 1013, 1070, and 1030 cm^{-1} correspond to the symmetric stretching of the $-\text{SO}_2-$ of the sulfonic acid group (Xiao *et al.*, 2002). The broad band of all composite membranes appear in the wavenumber range 3700–3100 cm^{-1} , which can be assigned to the hydroxyl group. The FTIR spectra, in the wavenumber

range 1800-400 cm^{-1} , indicate various characteristic peaks of S-PEKES functional groups as in our previous work (Changkhamchom *et al.*, 2010).

The hydroxyl characteristic peak of the molecular sieve 4A/S-PEKES composite proton exchange membrane has higher intensity than those of the 3A and 5A composite membranes. The pore size of molecular sieve 4A is more suitable than those of the molecular sieves 3A and 5A for water molecules to penetrate and adsorb. This is because the 4A pore size is close to that of the water molecule, significantly affecting the amount of water trapped inside the composite membrane. Typically, the sulfonic acid group of S-PEKES is very hydrophilic and has high affinity towards water molecules. Water molecules are absorbed on the sulfonic group along the S-PEKES backbone and trapped inside the molecular sieve pore. The higher amount of water trapped inside the composite membrane can be related to the broad band of the hydroxyl group. The presence of water molecules in the membrane is indicated by the enlargement and increased intensity of the band. Thus, the addition of the molecular sieves facilitates and improves the hygroscopic property of the composite membrane (Wang *et al.*, 2006)

5.4.2 Thermogravimetric Analysis (TGA)

Thermograms of the molecular sieve 4A/S-PEKES composite proton exchange membranes (3, 9, and 12%v/v) are shown in Figure 5.3. The first step weight loss of the S-PEKES membrane starts above 300 °C, representing the splitting-off of the sulfonic acid group. The second step weight loss occurs at 420–450 °C, representing the degradation temperatures of S-PEKES backbone. Nafion 117 membrane, on the other hand, possesses the most inferior thermal stability, its first degradation step occurs around 250–280 °C and the second step weight loss is at 400 °C. The composite membrane thermograms are compared with those of the pristine S-PEKES and Nafion 117 membranes. The molecular sieve 4A/S-PEKES composite membranes (3, 9, and 12%v/v) possess the thermal degradation temperature in the same range as the pristine S-PEKES, although the composite membranes cannot degrade completely. The remaining weights or chars of the composite membranes are about 8, 50, and 50%, for the composite membranes at 3, 9, and 12 %v/v

molecular sieve, respectively (Gil *et al.*, 2004). Furthermore, the composite membranes show highly thermal stability than Nafion 117 membrane. The molecular sieve 4A itself has extremely high thermal stability and cannot be degraded in this temperature range (Osterholm *et al.*, 2012). In summary, all molecular sieve/S-PEKES composite membranes have high thermal stability within the temperature range 25–120 °C, and thus are suitable for use in DMFC application.

5.4.3 Water Uptake (%)

Water uptake (%) of the molecular Sieves 3A, 4A, and 5A/S-PEKES composite proton exchange membranes at room temperature (27 °C) with various amount of molecular sieve (%v/v) are shown in Figure 5.4. The water uptake (%) values of the pristine S-PEKES membranes at 0.66 DS is $20.44 \pm 1.90\%$. After adding the molecular sieve 3A to form the composite membranes at 3, 6, 9, and 12 % v/v, the water uptake (%) increases to $34.03 \pm 1.53\%$, $37.22 \pm 1.51\%$, $40.98 \pm 1.55\%$, and $44.60 \pm 0.87\%$, respectively. The water uptake (%) values of the molecular sieve S-PEKES membranes 4A/S-PEKES composite membranes are $37.00 \pm 1.57\%$, $40.62 \pm 1.20\%$, $43.00 \pm 1.79\%$, and $47.45 \pm 0.73\%$, corresponding to 3, 6, 9, and 12 %v/v of molecular sieve 4A. The molecular sieve 5A/S-PEKES composite membranes show the lowest water uptake (%) which are $27.05 \pm 1.44\%$, $30.62 \pm 1.37\%$, $34.51 \pm 1.31\%$, and $35.63 \pm 1.43\%$, corresponding to 3, 6, 9, and 12% v/v of molecular sieve 5A. The molecular sieve 4A/S-PEKES composite membrane has the highest water uptake (%) among three types of composite membranes, consistent with the TGA results which indicate its high ability to adsorb water molecules. The molecular sieve has the hydrophilic property which promotes the composite membrane to adsorb more water apart from the sulfonic acid group. The water cluster can be trapped in the molecular sieve pore, consistent with the work previous reported (Coma *et al.*, 1997).

5.4.4 Ion Exchange Capacity (IEC)

Figure 5.5 represents the ion exchange capacities (IECs) of the molecular sieves 3A, 4A, and 5A/S-PEKES composite proton exchange membranes

at room temperature (27 °C). The IEC values of the pristine S-PEKES membranes at 0.66 DS is $0.64 \pm 0.05 \text{ meq.g}^{-1}$. The highest IEC belongs to the molecular sieve 4A/S-PEKES composite membrane which shows the values of $1.16 \pm 0.10 - 1.36 \pm 0.04 \text{ meq.g}^{-1}$, corresponding to 3-12% v/v of the molecular sieve 4A. The molecular sieve 3A and 5A/S-PEKES composite membranes possess lower IEC values than that of 4A. The IEC values of all composite membrane systems increase with increasing amount of molecular sieve (%v/v). The IEC increase is in the same trend with the water uptake (%).

The increment in both water uptake (%) and IEC, of the molecular sieve/S-PEKES membrane when compared with the pristine S-PEKES membrane, can be related to the proton conductivity enhancement, as reported in a previous work (Changkhamchom *et al.*, 2013).

5.4.5 Proton Conductivity (σ)

The proton conductivity (σ) is the most important property of the proton exchange membrane, indicating the performance of the PEMFC or DMFC. The effects of molecular sieve amount (v/v%) and water uptake (%) within the composite proton exchange membranes on the proton conductivity are investigated next. The calculated proton conductivities of all membranes with 10 and 50% water uptakes at a room temperature (27 °C) and 50% RH are shown in Table 5.1. The pristine S-PEKES membranes (DS 0.66) attain the proton conductivity enhancement from $4.41 \times 10^{-6} \pm 4.84 \times 10^{-7}$ to $8.45 \times 10^{-3} \pm 5.74 \times 10^{-7} \text{ S.cm}^{-1}$, as water uptake is varied from 10 to 50%. The molecular sieve 3A/S-PEKES composite membranes (6%v/v) with various water uptake (%) from 10 to 50% possess the proton conductivity varying from $6.89 \times 10^{-08} \pm 1.08 \times 10^{-08}$ to $5.65 \times 10^{-03} = 1.69 \times 10^{-03} \text{ S.cm}^{-1}$.

At 50% water uptake, the molecular sieve 3A/S-PEKES composite membranes possess proton conductivities of $5.65 \times 10^{-3} \pm 1.69 \times 10^{-3}$, $7.81 \times 10^{-3} \pm 7.97 \times 10^{-4}$, and $1.06 \times 10^{-2} \pm 1.13 \times 10^{-3} \text{ S.cm}^{-1}$, corresponding to 6, 9, and 12% v/v of molecular sieve 3A, respectively. Furthermore, at 50% water uptake, the

molecular sieve 4A/S-PEKES composite membranes possess proton conductivities of $7.59 \times 10^{-3} \pm 6.82 \times 10^{-4}$, $8.26 \times 10^{-3} \pm 3.13 \times 10^{-4}$, and $1.06 \times 10^{-2} \pm 7.19 \times 10^{-4}$ S/cm, corresponding to 6, 9, and 12% v/v of molecular sieve 4A, respectively. The molecular sieve 5A/S-PEKES composite membranes show the proton conductivities in the range of $1.06 \times 10^{-3} \pm 1.10 \times 10^{-4}$ to $8.36 \times 10^{-3} \pm 3.07 \times 10^{-4}$ S.cm⁻¹, corresponding to 6 to 12 %v/v molecular sieve 5A.

The highest proton conductivity of molecular sieve 4A/S-PEKES composite membrane (12%v/v) at 50% water uptake is nearly the same as that of Nafion 117 membrane which has the value of $1.09 \times 10^{-2} \pm 1.39 \times 10^{-3}$ S.cm⁻¹ at the same condition. From these results, the proton conductivities of all proton exchange membranes increase with increasing water uptake (%). The type of molecular sieve can affect the proton conductivity; the molecular sieve 4A/S-PEKES composite membrane has the highest proton conductivity, followed by the 3A and 5A composite membranes, respectively. Auimviriyavat *et al.*, 2011, prepared the Ferrierite zeolite/sulfonatedpoly(ether ether ketone) composite membranes with various %v/v of Ferrierite zeolite (5, 10, 15, 17, 20%v/v). They confirmed that the inorganic filler enhanced the proton motion by the sieve water retention characteristics (Sengulet *et al.*, 2009). Thus, the addition of molecular sieve into the S-PEKES matrix promotes the increase in the proton conductivity of the membrane.

The mechanism of proton transport within the composite membrane can occur via two pathways: first, the transport mechanism by water, where there is the formation of water channels. The combination of protons and water molecules generates a set of hydronium ions (H₃O⁺) which can transport the protons of water through the channels (Jiang *et al.*, 2008; Cui *et al.*, 2008). In this case, the molecular sieve provides additional water channels within the composite membrane. The second mechanism, called Grotthuss mechanism, occurs in the electrostatic interactions. For this mechanism, protons are transferred along the chain via ionic interactions and the hydrogen bonding "jumping" from a functional group to another. In this case, the sulfonic acid group (-SO₂-) reduces the energy barrier for the proton transport (Ramirez-Salgado *et al.*, 2007; Wang *et al.*, 2008).

5.4.6 Methanol Permeability

Methanol crossover is always a problem to the DMFC; methanol permeates easily through the electrolyte membrane from the anode to the cathode side of the DMFC. As a consequence, excessive methanol crossover of any PEM not only wastes the methanol fuel but also decrease the efficiency in fuel cell performance (Carette *et al.*, 2001). It is known that 40% of the methanol can be wasted in DMFCs via methanol crossover through the membranes (Beatie *et al.*, 2001). Table 5.2 represents the methanol permeability (P) of all proton exchange membranes investigated here at the temperatures of 27 °C, 50 °C, and 70 °C, respectively. The methanol permeability values of Nafion 117 at 27, 50, and 70 °C are 1.42×10^{-6} , 1.07×10^{-5} , and $1.17 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively (Han *et al.*, 2012). Between 6 and 12 %v/v, the methanol permeability of the molecular sieve 3A/S-PEKES composite membranes increases from 1.12×10^{-7} to $7.47 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ at 27 °C. The same results occur for the molecular sieve 4A and 5A composite membranes. The molecular sieve 5A/S-PEKES composite membranes have the highest methanol permeability over the molecular sieve 4A and 3A composite membrane, respectively. At 27 °C and 6%v/v composite membrane, the methanol permeabilities are 1.1213×10^{-7} , 2.6219×10^{-7} , and $4.1295 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ for molecular sieve 3A, 4A, and 5A/S-PEKES composite membranes, respectively.

The methanol permeability values of Nafion 117 are the highest among all proton exchange membranes by two orders of magnitude at a given temperature. For the effect of temperature, the methanol permeabilities of all membranes increase with increasing temperature, as methanol molecules are more active to penetrate through the membrane (Xue *et al.*, 2006). The type of the molecular sieves seems to have an influence on the methanol permeability. The molecular sieve 5A/S-PEKES composite membrane has the highest methanol permeability over the molecular sieve 4A and 3A composite membrane, respectively, due to the largest pore size of the molecular sieve 5A in which the water molecule can pass trough more easily. However, the methanol permeabilities of all composite membranes are significantly lower than that of Nafion 117 membrane.

Sulfonated poly(ether sulfone ether ketone ketone)/sulfonated poly(ether sulfone) blend membranes were prepared by Zeng *et al.*, 2012, the methanol permeability of all the blend membranes are in range of $0.58\text{--}2.18 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ which are higher than our composite membranes by an order of magnitude.

5.4.7 Mechanical properties

Mechanical properties of all proton exchange membranes at room temperature (27 °C) and 50% RH are shown in Table 5.3. The mechanical properties of all membranes were evaluated by means of the standard tensile test in the same method with the previous work (Changkhamchom *et al.*, 2013). The tensile strength, elongation at break, and Young's modulus were measured and are reported here. The tensile strengths, of the composite membranes at 12%v/v, for 3A, 4A, and 5A/S-PEKES composite membranes, are higher than the value of the pristine S-PEKES membrane by factors of 5, 4, and 3 times, respectively. In the previous work, the sulfonated poly(ether sulfone ether ketone ketone)/sulfonated poly(ether sulfone) blend membranes showed a lower tensile strength than our present work; their membranes exhibited the tensile strength only in the range of 47.8–71.9 MPa (Zeng *et al.*, 2012). All molecular sieve/S-PEKES composite membranes show much higher tensile strengths and the lower elongations at break than those of the pristine S-PEKES and Nafion 117 membrane, especially in the dry state. In the hydrous state, water acts as an external plasticizer between polymer chains, leading to the ease in the chain movement and a decrease in the tensile strength. The mechanical strength in the hydrous state is thus lower than that in the anhydrous state (Changkhamchom *et al.*, 2013). The composite membranes in all system are thus strong and flexible enough to be used as polymer electrolytes in a fuel cell. Thus, the addition of the molecular sieve significantly improves the mechanical strength of the PEM.

5.5 Conclusions

The composite membranes show high thermal stability, because the degradation temperature start at above 250 °C indicate that the composite membranes can be safely operated for DMFC at normal condition (Sangeetha *et al.*, 2007) and

can be used in PEMFC as well (Guhan *et al.*, 2009). The water uptake (%), IEC, proton conductivity of the molecular sieve composites membranes are found to be higher than that of the pure S-PEKES membrane and they increase with increasing content of molecular sieve. Especially, the mechanical strength of composite membrane is the property which shows the most significant improvement. Although, the methanol permeability of composite membrane increases from the pristine one, the value is still much lower than that of Nafion 117 membrane. From the overall results, the molecular sieve 3A/S-PEKES composite membrane at 12% v/v is selected to be the PEM candidate for DMFC, due to its higher proton conductivity, lower methanol permeability, and much higher tensile strength, when compared with the two other composite membranes.

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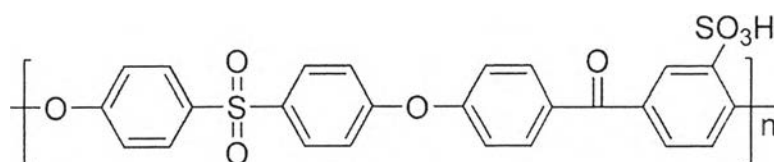


Figure 5.1 Sulfonated poly(ether ketone ether sulfone) (S-PEKES).

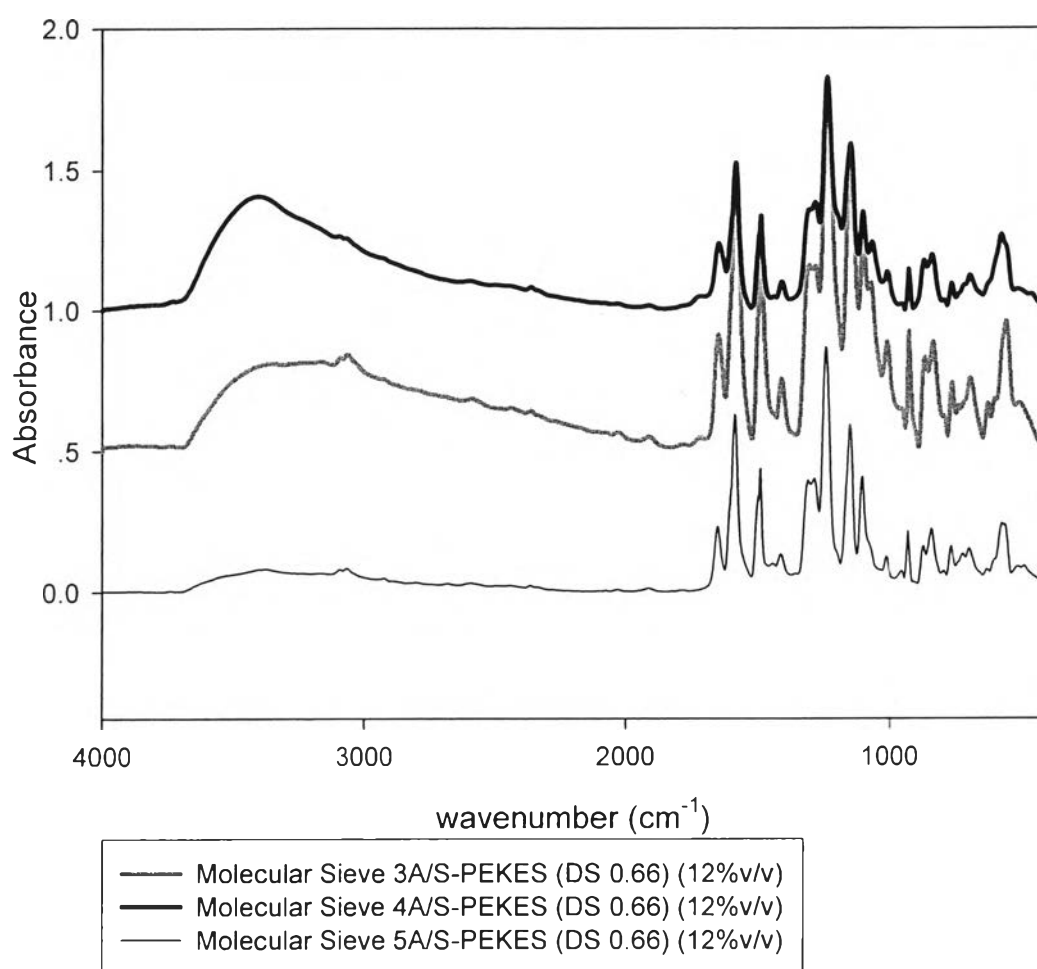


Figure 5.2 FTIR spectra of composite proton exchange membrane incorporated with 12%v/v molecular sieves with the highest degree of sulfonation S-PEKES (DS 0.66).

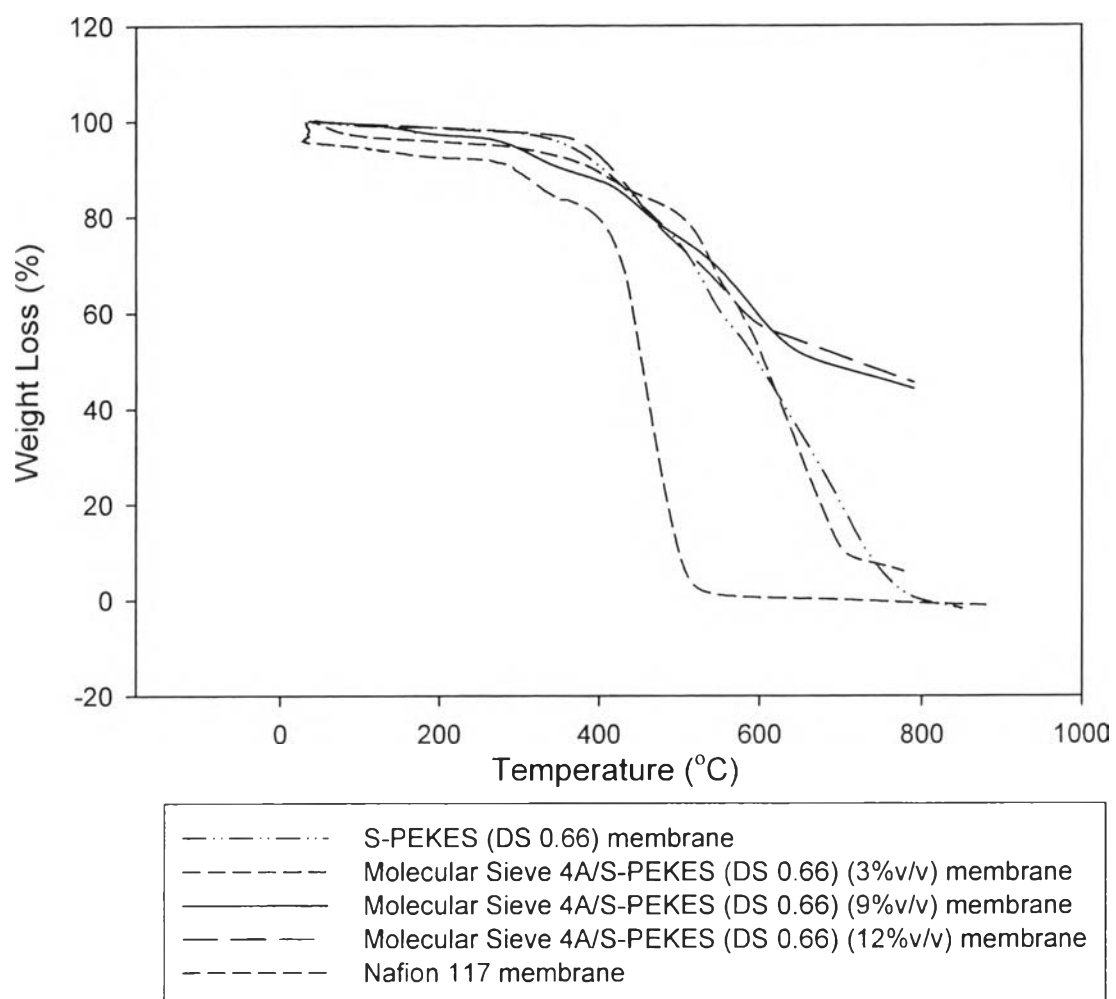


Figure 5.3 Thermograms of the pristine S-PEKES membrane, Molecular Sieve 4A/S-PEKES composite membranes (3, 9, and 12 %v/v, respectively), and Nafion 117 membrane.

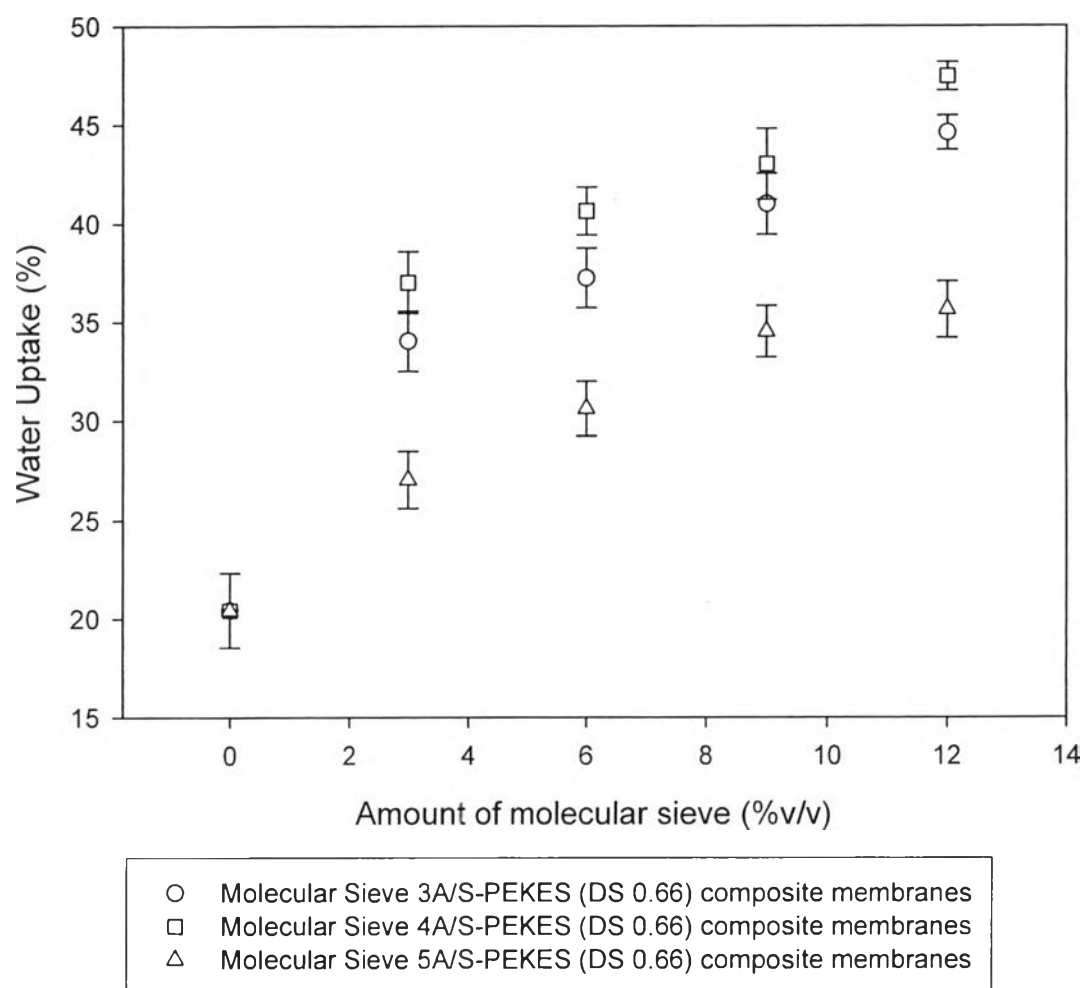


Figure 5.4 The water uptake (%) of the Molecular Sieve 3A, 4A, and 5A/S-PEKES composite proton exchange membranes at room temperature (27 °C).

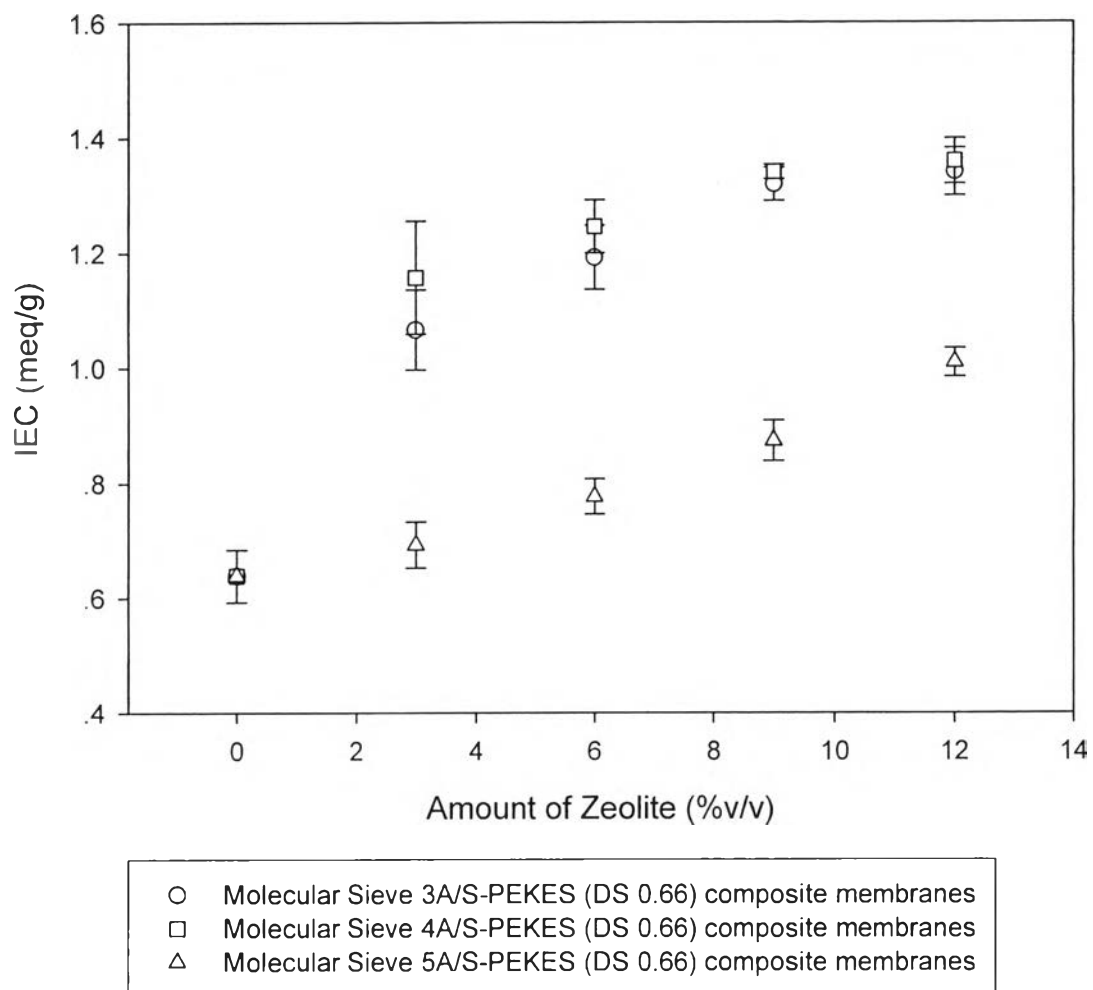


Figure 5.5 The ion exchange capacities (IECs) of the Molecular Sieve 3A, 4A, and 5A/S-PEKES composite proton exchange membranes at room temperature (27 °C).

Table 5.1 The proton conductivities of all membranes with 10 and 50% water uptakes at a room temperature (27 °C) and 50% RH

PEM	DS	Amount of molecular sieve (v/v)	Thickness (cm)	Water uptake (%)	Proton conductivity (S/cm)
Nafion 117	1.0	0	0.0200	10	$8.56 \times 10^{-07} \pm 7.39 \times 10^{-08}$
				50	$1.09 \times 10^{-02} \pm 1.39 \times 10^{-03}$
S-PEKES	0.66	0	0.0278	10	$4.41 \times 10^{-06} \pm 4.84 \times 10^{-07}$
				50	$8.45 \times 10^{-03} \pm 5.75 \times 10^{-04}$
Molecular sieve 3A/S-PEKES	0.66	6	0.0220	10	$6.89 \times 10^{-08} \pm 1.08 \times 10^{-08}$
				50	$5.65 \times 10^{-03} \pm 1.69 \times 10^{-03}$
		9	0.235	10	$2.51 \times 10^{-07} \pm 5.22 \times 10^{-08}$
				50	$7.81 \times 10^{-03} \pm 7.97 \times 10^{-04}$
		12	0.0208	10	$5.91 \times 10^{-06} \pm 6.01 \times 10^{-07}$
				50	$1.06 \times 10^{-02} \pm 1.13 \times 10^{-03}$
Molecular sieve 4A/S-PEKES	0.66	6	0.0214	10	$7.78 \times 10^{-08} \pm 9.74 \times 10^{-09}$
				50	$7.59 \times 10^{-03} \pm 6.82 \times 10^{-04}$
		9	0.0205	10	$2.60 \times 10^{-07} \pm 2.83 \times 10^{-08}$
				50	$8.26 \times 10^{-03} \pm 3.13 \times 10^{-04}$
		12	0.0255	10	$5.51 \times 10^{-06} \pm 6.06 \times 10^{-07}$
				50	$1.06 \times 10^{-02} \pm 7.19 \times 10^{-04}$
Molecular sieve 5A/S-PEKES	0.66	6	0.0248	10	$2.27 \times 10^{-08} \pm 5.77 \times 10^{-09}$
				50	$1.06 \times 10^{-03} \pm 1.11 \times 10^{-04}$
		9	0.0239	10	$1.06 \times 10^{-07} \pm 9.12 \times 10^{-09}$
				50	$8.88 \times 10^{-04} \pm 7.88 \times 10^{-05}$
		12	0.0210	10	$4.20 \times 10^{-07} \pm 6.84 \times 10^{-08}$
				50	$8.34 \times 10^{-03} \pm 3.07 \times 10^{-04}$

Table 5.2 Methanol permeability (P) of all proton exchange membranes at the temperatures of 27 °C, 50 °C, and 70 °C, respectively

PEM	DS	Amount of Zeolite (%v/v)	Thickness (cm)	Methanol Permeability, P (cm ² /s)		
				27 °C	50°C	70 °C
Nafion 117(Han <i>et al.</i> , 2013)	1	0	0.0200	1.4147E-06	1.0725E-05	1.1689E-05
S-PEKES-B	0.66	0	0.0278	1.0347E-07	7.9574E-07	2.1358E-06
S-PEKES-B/Molecular Sieve 3A	0.66	6	0.0220	1.1213E-07	6.9259E-07	4.7988E-06
	0.66	9	0.0235	4.8632E-07	1.0765E-06	7.7128E-06
	0.66	12	0.0208	7.4697E-07	1.3493E-06	1.1112E-05
S-PEKES-B/Molecular Sieve 4A	0.66	6	0.0214	2.6219E-07	8.7369E-07	5.9762E-06
	0.66	9	0.0205	7.0312E-07	1.2081E-06	9.2980E-06
	0.66	12	0.0255	1.2566E-06	8.6642E-06	2.4299E-05
S-PEKES-B/Molecular Sieve 5A	0.66	6	0.0248	4.1295E-07	1.0284E-06	7.0640E-06
	0.66	9	0.0239	7.2137E-07	1.2751E-06	9.5043E-06
	0.66	12	0.0210	1.0864E-06	8.3553E-06	2.2426E-05

Table 5.3 Mechanical properties of all proton exchange membranes at room temperature (27 °C) and 50% RH

PEM	DS (%)	Amount of zeolite % (v/v)	Tensile strength (MPa)		Young's modulus (MPa)		Elongation at break (%)	
			Dry	Wet	Dry	Wet	Dry	Wet
S-PEKES-B/Molecular Sieve 3A	0.66	6	212.73 ± 14.95	33.99 ± 3.85	2296.18 ± 63.91	498.09 ± 49.20	60.04 ± 11.03	6.86 ± 1.60
	0.66	12	159.78 ± 5.69	79.90 ± 3.22	2143.18 ± 61.24	973.47 ± 31.00	28.18 ± 1.73	190.52 ± 11.06
S-PEKES-B/Molecular Sieve 4A	0.66	6	71.17 ± 6.09	19.24 ± 0.45	861.22 ± 68.36	24289.65 ± 162.95	101.65 ± 0.72	6.36 ± 0.75
	0.66	12	122.44 ± 5.57	21.42 ± 0.67	360.46 ± 13.63	25991.62 ± 120.70	456.60 ± 18.20	6.69 ± 0.45
S-PEKES-B/Molecular Sieve 5A	0.66	6	96.45 ± 7.15	56.90 ± 1.52	984.75 ± 41.25	50542.63 ± 151.12	116.92 ± 9.86	164.47 ± 3.97
	0.66	12	101.42 ± 5.04	78.31 ± 3.54	844.40 ± 14.72	679.09 ± 10.09	121.94 ± 9.39	131.96 ± 11.44
S-PEKES-B	0.66	0	28.24 ± 1.28	7.94 ± 0.25	178.29 ± 6.74	16266.87 ± 75.54	495.37 ± 19.75	6.91 ± 0.46
Nafion117	1.00	0	38.0	28.4	180	100	301.5	329.2