

CHAPTER IV

POLYMER ELECTROLYTE MEMBRANE BASED ON SULFONATED POLY(ETHER KETONE ETHER SULFONE) (S-PEKES) WITH LOW METHANOL PERMEABILITY FOR DIRECT METHANOL FUEL CELL APPLICATION

4.1 Abstract

Poly(ether ketone ether sulfone), (PEKES), was synthesized by the nucleophilic aromatic substitution polycondensation between bisphenol S and 4,4'-difluorobenzophenone (system A), and between bisphenol S and 4,4'-dichlorobenzophenone (system B). The oxidative stability was characterized by using a Fenton's reagent. S-PEKES membranes show a higher thermal stability than that of Nafion 117 and comparable to that of S-PEEK 150XF. The proton conductivity values of S-PEKES of the highest DS are comparable to those of Nafion 117 and S-PEEK. The methanol permeability of the synthesized and fabricated S-PEKES membrane is lower than that of Nafion 117 by at least an order of magnitude.

Keywords: Sulfonated poly(ether ketone ether sulfone); Proton Exchange Membrane (PEM); Degree of Sulfonation (DS); Proton conductivity

4.2 Introduction

A proton exchange membrane (PEM) is an electrolyte used in both polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFCs), which transfers protons from anode to cathode and acts as a barrier to avoid the crossover of fuel. Currently, PEMs are mainly the commercially Nafion (DuPont) membranes, which is a perfluorinated polymer with sulfonic acid groups as pendant groups. It has excellent ionic properties, and the most important advantage of Nafion is its excellent proton conductivity in the fully hydrated condition. Furthermore, it has good physical, chemical, and mechanical stability. Even though Nafion

membranes have demonstrated good performance in hydrogen fuel cells, the high cost and the high methanol permeability have limited their applications in direct methanol fuel cells (DMFCs) (Carette *et al.*, 2001).

An ultimate aim in the PEM development is to find novel materials as alternatives to Nafion that are of low cost and can operate at a higher temperature. Presently, existing PEM materials are, for example, Nafion 117 (proton conductivity 90–120 mS.cm⁻¹ at 80 °C and 34–100% RH), Nafion 115 (41 mS.cm⁻¹ at 25 °C), sulfonated poly(ether ether ketone) (SPEEK) (0.9 mS.cm⁻¹ at 20 °C), sulfonated poly(benzimidazole) (SPBI) (10–40 mS.cm⁻¹ at 130–180 °C), sulfonated poly(phosphazene) (40 mS.cm⁻¹ at 25 °C), AMPS asymmetric-based acrylic (42 mS.cm⁻¹ at 90 °C), poly(vinylidene fluoride) (PVDF)+styrene membrane (resistance 0.454 Ω.cm²), PVDF +SiO₂ or SiO₂ gel (70 mS.cm⁻¹ (SiO₂) and 200 mS.cm⁻¹ (gel) at 25 °C), etc (Neburchilov *et al.*, 2000).

The poly(arylene ether ketone) family is of particular interest because it is an engineering thermoplastic with excellent thermal and chemical stability, high mechanical strength, good insulating properties, and a relatively low cost compared to Nafion. The sulfonated poly(ether ether ketone) (S-PEEK) has good thermal stability and appropriate proton conductivity at a high degree of sulfonation (DS). Several articles have investigated and reported the sulfonation of PEEKs and their properties (Li *et al.*, 2003). Synthesized derivatives of poly(ether ketone ether sulfone) have been reported using various starting monomers (Rao *et al.*, 1998). Sulfonated poly(arylene ether ketone) can dissolve in some organic solvents that allow it to be cast as a membrane. This solubility property offers a more convenient and less expensive process when compared with fabricating perfluorosulfonic acid membrane.

In this work, two synthesized S-PEKESs were investigated (System A and System B). System A and System B contain 4,4'-difluorobenzophenone and 4,4'-dichlorobenzophenone as the starting monomers, respectively. The synthesis and properties of System B have not been fully investigated and reported so far. In addition, the introduction of sulfone group (-SO₂-) in to the polymer backbone leads to better solubility of PEKES in H₂SO₄ relative to that of PEEK 150XF, which

results in higher sulfonation degrees. Furthermore, the S-PEKESs backbones contain the aromatic rings, the carbonyl groups (-C=O), and the sulfone groups (-SO₂-), which promote the chain stiffness and thermal stability. The degree of sulfonation was varied by the reaction time. The synthesized polymers were characterized by TGA to identify the thermal properties, the methanol permeabilities (*P*) were measured by Gas Chromatography (GC). The storage modulus (*G'*) of these membranes were investigated and measured by a melt rheometer (Rheometric Scientific, ARES). The oxidative stability was characterized by using a Fenton's reagent.

4.3 Experimental

4.3.1 Materials

Bisphenol S or 4,4'-sulfonyldiphenol, 4,4'-dichlorobenzophenone, and 4,4'-difluorobenzophenone (98–99%, Aldrich) were used as the monomers. Concentrated sulfuric acid (Merck, 98 wt%), sodium chloride (Univar, 99.9%), and sodium hydroxide (Univar, 97%) were used as received. Potassium carbonate (Riedel-de-Haen, 98–100%) and dimethyl sulfoxide (Riedel-de-Haen, 99.5%), and toluene (Fisher-Scientific 99.99%) were used as received. PEEK 150XF was purchased from Victrex. Nafion117 was purchased from Electrochem, Inc.

4.3.2 Synthesis of Poly (ether ketone ether sulfone) (PEKES) and Sulfonated Poly(ether ketone ether sulfone) (S-PEKES)

Both PEKES and S-PEKES of various degrees of sulfonation (DS) were synthesized according to the previous work reported elsewhere (Changkhamchom *et al.*, 2010). The poly (ether ketone ether sulfone)s were synthesized via the nucleophilic aromatic substitution reaction by using these monomers: 4,4'-difluorobenzophenone (System A), 4,4'-dichlorobezophenone (System B), and bisphenol S. The monomers were mixed with potassium carbonate in DMSO toluene, in a 250-ml three necked round bottom flask equipped with a Dean-Stark trap, a reflux condenser, a nitrogen inlet, and a thermostat. The mixture

was refluxed for 3 h at 150 °C, and then the excess toluene was distilled off. Toluene was used to eliminate the water which was a product in the reaction, and the solution was heated at 175 °C for 20 h. The reaction mixture was then cooled to room temperature and poured into a mixture of methanol and distilled water (ratio 1:1). The crude product was then washed with water to remove any inorganic salt. The polymer was filtered and dried in a vacuum oven at 80 °C for 48 h.

The synthesized PEKES and the commercial PEEK 150XF powder were dried in a vacuum oven at 100 °C overnight. Then, 5.0 g of the polymer was dissolved in 50 ml concentrated sulfuric acid (98%), which was kept under a molecular sieve 4 A for 24 h, and vigorously stirred at 25 ± 2 °C for durations of 12, 24, 36, 48, 60, 72, and 84 h. Then, the solution was gradually precipitated into ice-cold water under mechanical stirring. The polymer suspension was left overnight. Then, the precipitate was filtered, washed several times with distilled water until neutral a pH was obtained, and dried under vacuum at 60 °C for 24 h. The chemical structures of S-PEKES-A, B, and S-PEEK 150XF are shown in Figure 4.1.

4.3.3 Membrane Preparation

Membranes were prepared by dissolving 1.0 g of polymer in 30 mL dimethyl sulfoxide (DMSO) with vigorous stirring for 12–18 hours until the polymer solutions were homogeneous. 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.

4.3.4 Polymer Characterization

4.3.4.1 *Thermal Behavior*

A thermogravimetric analyzer (TGA) (PerkinElmer/TGA7) was used to investigate the thermal stability of the post-sulfonated membranes. Between 5.0 and 10.0 mg samples were heated from 50–800 °C at a rate of 10 °C/min under N₂ atmosphere (Wang *et al.*, 2006).

4.3.4.2 Proton Conductivity

The water uptake (%) of the membranes could be calculated from the method reported elsewhere (Unnikrishnan *et al.*, 2010). The proton conductivity values of the polymer membranes were measured by using an Agilent E4980A LCR meter at a AC potential of 1 V and in the frequency range of 20 Hz to 2 MHz, at 27 ± 1 °C, 50%RH. The membranes were immersed in de-ionized water at various soaking times to obtain 10, 20, 30, 40, and 50% water content. 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), d is the membrane thickness (cm), S is the membrane surface area (cm²), 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) axis (Mikhailenko *et al.*, 2004). The impedance of each sample was measured for 3 times to ensure data reproducibility.

4.3.4.3 Methanol Permeability

The methanol permeabilities of the membranes were determined by using the two compartments diffusion cell in Figure 4.2. One compartment (compartment A, $V_A = 250$ ml) was filled with a solution of methanol (2.5 mol/L). The other compartment (compartment B, $V_B = 250$ ml) was filled with deionized water. The membrane was clamped between the two compartments. The solutions in the two compartments were magnetically stirred during the permeation experiments. Methanol flux was 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 is given by:

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

where P is methanol permeability, C_A and C_B are the methanol concentrations in the compartment A and B respectively, A and L are the area and the thickness of a

membrane respectively, V_B is the volume of the solution in the compartment B, k_B is the slope of the methanol concentration profile in the compartment B. The methanol concentrations were measured by using a gas chromatography (Pr2100) fitted with athermal conductivity detector (TCD); ethanol was used as the internal standard.

4.3.4.4 Storage Modulus

The dynamic mechanical properties of S-PEKES-A, S-PEKES-B, S-PEEK 150XF, and Nafion 117 were measured with a melt rheometer (Rheometric Scientific, ARES). The measurements were performed in the shear oscillatory mode using a parallel plate fixture (diameter of 25 mm). The range of angular frequency was from 0.04 to 100 rad/s at four different temperatures from 303, 323, 343, and 363 K. The strain amplitude of 0.1 % was selected to be the suitable strain to measure dynamic moduli (G' and G'') in the linear viscoelastic regime. The oscillatory shear strain was applied and the G' and G'' were measured as functions of frequency and temperature.

4.3.4.5 Oxidative Stability

The oxidative stability was investigated by immersing the small pieces S-PEEK ($5 \times 5 \text{ mm}^2$) into a Fenton's reagent (3% H_2O_2 containing 2 ppm FeSO_4) at 80 °C and recording the time in which the membranes began to break into pieces (Shang *et al.*, 2007).

4.3.4.6 Mechanical Properties

Tensile properties of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF membranes, equilibrated in water for 24 h at 27 °C as strips (60 mm \times 10 mm \times 0.2 mm), were measured using a Lloyd UTM. Crosshead speed of 100 mm/min was maintained for all the samples. The gauge length is 30 mm. The measurements were run at an ambient condition (at 30 °C and 50% RH), The samples for the dry state test were dried at 100 °C in vacuum for 12 h before test. For each data point five samples were tested, and the average was recorded.

4.4 Results and Discussion

4.4.1 Degree of Sulfonation (DS)

The synthesized PEKES-A, PEKES-B, and the commercial PEEK 150XF were sulfonated with 12–84 h reaction times. The DS of S-PEKES-A are 0.30, 0.50, and 0.67, of S-PEKES-B are 0.33, 0.51, and 0.67, and of S-PEEK 150XF are 0.25, 0.38, and 0.52, corresponding to the sulfonation times of 36, 60, and 84 h, respectively (Changkhamchom *et al.*, 2010).

4.4.2 Thermogravimetric Analysis (TGA)

The S-PEKES-A, S-PEKES-B, and S-PEEK 150XF membranes with DS of 0.50, 0.51, and 0.52, respectively are shown in Figure 4.3. The thermograms of all membranes were compared with that of Nafion 117. The first step weight loss of the synthesized S-PEKES-A membrane starts at around 230–250 °C, representing the splitting-off of the sulfonic acid group. The second step weight loss occurs at 430–450 °C, representing the degradation temperatures of SPEKES-A main chain. For the synthesized S-PEKES-B membrane, its thermogram shows the first weight loss starting at 200–230 °C and the second step weight loss occurs at 430–450 °C. The degradation of both S-PEKES-A and S-PEKES-B membranes are not complete because the char occurs and the remaining weights of the polymers are about 40%. The S-PEEK 150XF membrane shows the highest thermal stability since its first slight weight loss occurs at around 400–450 °C and the second step weight loss is at 580 °C corresponding to the main PEEK chain decomposition; it is completely degraded and no char remains (Gil *et al.*, 2004). The poorest thermal stability belongs to Nafion 117 membrane, it shows the first degradation step at 250–280 °C and the second step weight loss occurs at 400 °C. In summary, all sulfonated polymers are thermally stable within the temperature range 25–120 °C and are suitable for use in DMFC application.

4.4.3 Proton Conductivity (σ)

Table 4.1 shows the proton conductivities of all membranes of various water uptakes (%); 10, 20, 30, 40, 50%, at a room temperature (27 °C) and 50% RH. The proton conductivity increase with increasing DS, which can be related to the number of acid sites increment that can enhance the proton transfer through the membrane (Sengul *et al.*, 2009). The enhancement of the water uptake (%) within the hydrated membrane can also increase the DS. Figure 4.4 shows the effects of the degree of sulfonation and the water uptake (%) on the proton conductivities of S-PEKES-B membranes with the sulfonation degrees (DS) of 0.33, 0.51, and 0.66, respectively, and of Nafion 117 at a room temperature (27 °C) and 50% RH. For the S-PEKES-B membrane when the water uptake is varied between 10–50%, the proton conductivity increases from 6.22×10^{-8} to 6.07×10^{-3} S/cm at DS = 0.33, the proton conductivity increases from 2.08×10^{-7} to 6.61×10^{-3} S/cm at DS = 0.51, and the proton conductivity increases from 4.41×10^{-6} to 8.45×10^{-3} S/cm at DS = 0.66. These results confirm that the increments in DS and the water uptake (%) both enhance the proton conductivity. Figure 4.5 shows the effect of PEM type on the proton conductivity. The proton conductivities of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF membranes, at comparable degrees of sulfonation (DS) of 0.50, 0.51, and 0.52, respectively, are compared with that of Nafion 117 at a room temperature (27 °C) and 50% RH. For the S-PEKES-A membrane at DS = 0.50, the proton conductivity increases from 2.01×10^{-7} to 6.25×10^{-3} S/cm; for the S-PEKES-B membrane at DS = 0.51, the proton conductivity increases from 2.08×10^{-7} to 6.61×10^{-3} S/cm; for the S-PEEK 150XF membrane at DS = 0.52, the proton conductivity increases from 3.36×10^{-7} to 6.67×10^{-3} S/cm; when the water uptake value falls between 10–50%. The proton conductivities of the three PEM systems are comparable due to their comparable degrees of sulfonation. The proton conductivity of Nafion 117 increases from 8.56×10^{-7} to 1.09×10^{-2} S/cm, as the water uptake is varied between 10–50%.

The room-temperature proton conductivity of the fully hydrated homogeneously S-PEEK membrane with a 68% degree of sulfonation was measured and compared with Nafion 117 (0.11 S/cm) (Do *et al.*, 2008). The S-PEEK (DS =

0.68) has the IEC equal to 1.99 and the proton conductivity is 0.13 S/cm, which higher than that of Nafion 117 under the same experimental conditions. In the present study, the S-PEKES-A membrane (DS = 0.67, IEC = 1.34) has a proton conductivity equal to 0.00848 S/cm, the S-PEKES-B membrane (DS = 0.66, IEC = 1.36) has a proton conductivity equal to 0.00845 S/cm, and the S-PEEK 150XF (DS = 0.52, IEC = 1.01) has a proton conductivity equals to 0.00667 S/cm (Changkhamchom *et al.*, 2010); thus these membranes have lower proton conductivity than that of Do's membrane due to the lower IEC and water uptake values. In 2010, the sulfonated derivative of amorphous polyetheretherketone, known as the SPEEK-WC membrane was studied (Fontananowa *et al.*, 2010). The proton conductivity of the SPEEK-WC membrane with DS equal to 0.8 is 0.0007 S/cm, for S-PEEK-WC/PW12 with the same DS is 0.001 S/cm, for S-PEEK-WC/SiW12 with the same DS is 0.0015 S/cm, and for S-PEEK-WC/PMo12 with the same DS is 0.00125 S/cm. The proton conductivity measurements were carried out at 20 ± 1 °C and with 100% relative humidity; all Do's membranes have lower proton conductivities than those in the present work.

4.4.4 Methanol Permeability

The methanol permeability causes conversion losses in terms of lost fuel and depolarization losses at the cathode, resulting in overall poor fuel cell performance (Carette *et al.*, 2001). Nafion has been found out that over 40% of the methanol can be wasted in DMFCs through leaks across such membranes (Beatie *et al.*, 2001). Table 4.2 represents the methanol permeability (P) of all membranes with various degree of sulfonation (DS) at 27 °C, 50 °C, and 70 °C, respectively. Their methanol permeabilities increase with both the degree of sulfonation (DS) and temperature. The methanol permeability (P) was calculated from the slope (k_B) of the straight-line plot of methanol concentration in the compartment B (C_B) vs. permeation time by using equation 1. The methanol permeability values of Nafion 117 are higher than those our synthesized S-PEKES-A and S-PEKES-B membranes by two orders of magnitude at a given temperature. 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} (cm²/s), respectively. Figure 4.6 shows the effects of the degree of sulfonation and the membrane type on the methanol permeability. The methanol concentrations (C_B) of all membranes increase linearly with permeation time. The slope (k_B) of these concentration profiles were used to calculate the methanol permeability (P). The S-PEKES-A membranes possess the methanol permeability values of 2.4970×10^{-8} , 6.6964×10^{-8} , and 1.1968×10^{-7} cm²/s, at the DS values of 0.30, 0.50, and 0.67, respectively; the S-PEKES-B membranes possess the methanol permeability values of 3.9329×10^{-8} , 6.8702×10^{-8} , and 1.0347×10^{-7} cm²/s, corresponding to the DS values of 0.33, 0.51, and 0.66, respectively; and the methanol permeability values of S-PEEK 150XF membranes are 1.0679×10^{-8} , 4.6316×10^{-8} , and 7.11470×10^{-8} cm²/s, with the corresponding DS values of 0.25, 0.38, and 0.52, respectively. These results indicate clearly that the methanol permeability of all membranes increases with increasing DS; the permeability values of S-PEKES-B membranes are higher than those of S-PEKES-A and S-PEEK 150XF, respectively. However, these values are in the same order of magnitude of 10^{-8} – 10^{-9} cm²/s and are lower than those of Nafion 117. Figure 4.7 shows the effect of temperature on methanol permeability, the methanol permeability of S-PEKES-B membrane increases with increasing temperature as the methanol molecules are more active to penetrate through the membrane (Xue *et al.*, 2006). For the highest DS (0.66) of S-PEKES-B, the methanol permeability values are 1.0347×10^{-7} , 7.9574×10^{-7} , and 3.1358×10^{-8} cm²/s, corresponding to the temperatures of 27, 50, and 70 °C, respectively. In the work of Do *et al.*, 2008, S-PEEK membrane methanol permeabilities were measured at a room temperature. The methanol permeabilities of the S-PEEK membranes are in the range of 0.10 – 0.35×10^{-6} cm²/s corresponding to the IEC values between 1.40–2.2, respectively, which are considerable higher than those in the present work. Li *et al.*, 2010, studied the methanol permeability of S-PEEK membrane, the pristine S-PEEK membrane has the methanol permeability in the range of 3.10 – 9.87×10^{-7} cm²/s, which is one order of magnitude lower than that of the commercial Nafion 117. However, Li's membranes show higher methanol permeabilities than those of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF in the present work.

4.4.5 Oxidative Stability

The hydrogen peroxide could be originated from the oxygen diffusion through the membrane and the incomplete reduction at the fuel cell anode, leading to a severe damage of PEM. The currently used membranes fail in the Fenton's tests, leading to low performances in actual fuel cell operations (Zhong *et al.*, 2006), their short life time, due to the occurring oxidative degradation. The accelerating oxidation measurement was taken by soaking the sulfonated membranes in Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C (Pascual *et al.*, 2009). In order to maintain the fuel cell performance during the operation, the oxidative stability of PEM should be sufficiently high. As shown in Table 4.3, the oxidative stability decreases with increasing sulfonation degree. In our experiment, the oxidative degradation of our synthesized membranes; S-PEKES-A and S-PEKES-B, and commercial S-PEEK 150XF, were evaluated and are compared with that of Nafion 117. The time interval in which the membrane is broken into pieces is referred as t_1 . Whereas t_2 refers to the time in which the total membrane disappears or becomes fully dissolved in a Fenton's reagent. The Nafion 117 possesses the lowest oxidative stability when compared with those of other membranes; it takes 24 min before the membrane starts to break into small pieces and 56 min before it dissolves in the solution. Whereas, the S-PEKES-A, S-PEKES-B, and S-PEEK 150XF membranes with the DS values of 0.66, 0.67, and 0.52, start to break at t_1 equal to 38 , 35, and 43 min, respectively. They are totally dissolved in the Fenton's solution at t_2 equal to 76, 73, and 94 min, respectively. Therefore, the S-PEEK 150XF membrane shows the best oxidative stability, following with the S-PEKES-A, S-PEKES-B, and Nafion 117 membranes, respectively. All sulfonated membrane systems with DS range of 0.50–0.52, show comparable oxidative stability with the crosslinked sulfonated polysulfone membranes of Furtado Filho *et al.*, 2010, which can stay in the Fenton's reagent until 94 minutes before they are completely decomposed.

4.4.6 Storage Modulus

The storage moduli (G') of membranes with various sulfonation degrees (DS) at a room temperature (27 °C) are shown in Figure 4.8.

The storage moduli (G') of the membranes are rather constant with respect to frequency at 27 °C. The storage moduli (G') of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF decrease with increasing DS, due to the reduction in the level of crystallinity. Generally, the structures of the non-sulfonated polymer; PEKES-A, PEKES-B, and PEEK 150XF are of linear chains which are able to pack tightly leading to high crystallinity. When the sulfonic acid groups are attached to the polymer backbones, they can act as the bulky groups and obstruct the packing between the adjacent chains. Thus, the steric effect increases with the degree of sulfonation. Figure 4.9 shows the effect of temperature on the storage modulus (G') of the S-PEKES-B membrane with DS of 0.66. The storage modulus (G') of the membrane slightly decreases with increasing temperature, due to the increase of the free volume which allows the easier chain movement at a high temperature (Pascual *et al.*, 2009).

4.4.7 Mechanical Properties

Good mechanical properties of the sulfonated polymer membranes, in the anhydrous or the hydrous state, are desirable for functional proton exchange membrane. The mechanical properties of the S-PEKES-A, S-PEKES-B, and S-PEEK 150XF membranes are summarized in Table 4.4. The dry sulfonated membranes possess the tensile strength in the range of 17.8–53.3 MPa, Young's modulus of 459.9–34,382.74 MPa, and the elongation at break of 7.14–119.87%. The sulfonated membranes in the wet state possess good mechanical properties with the tensile strength of 7.75–31.55 MPa, the Young's modulus of 193.79–1,234.5 MPa, and the elongation at break of 137.88–538.44%.

In the hydrous or wet state, the tensile strength and the Young's modulus decrease with DS, while the elongation at break increases. The reason is that the sulfonic acid groups cause the steric hindrance and obstruct the polymer chains into a tight packing in which the crystallinity is reduced.

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. The sulfonated polymers which have DS value of around 0.3, are stronger than Nafion 117 (Liu *et al.*, 2007; Kim *et al.*, 2009).

In the work of Guhan *et al.*, 2009, the sulfonated poly(ether ether ketone) (SPEEK)/silicotungstic acid (SWA) composite membranes were prepared for use in fuel cell applications. The dry state tensile strength of all composite membrane systems are in the range of 7.5–15 MPa, which extremely lower than the sulfonated membranes prepared in our present work.

4.5 Conclusions

The sulfonated poly(ether ketone ether sulfone)s show a high glass transition temperature and a higher heat resistance in the solid state. The S-PEKES membranes with the highest DS and water uptake (%) values possess comparable proton conductivity values but with lower methanol permeability than those of the Nafion 117 membrane. In particular, its methanol permeability, $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, is much lower than that of the Nafion 117 membrane, $1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, at a room temperature. In addition, the oxidative stabilities and the storage moduli (G') of all the S-PEKES and S-PEEK 150XF membranes are better than those of Nafion 117. These results show that the S-PEKES and S-PEEK 150XF membranes are potential candidates for the application in direct methanol fuel cells operating at medium temperatures. The S-PEKES-B membrane shows superior properties than those of the S-PEKES-A and S-PEEK 150XF membranes.

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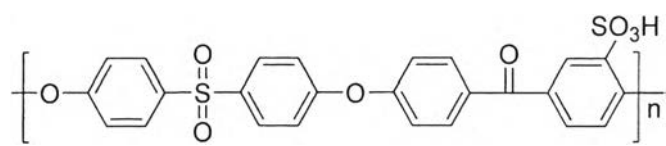
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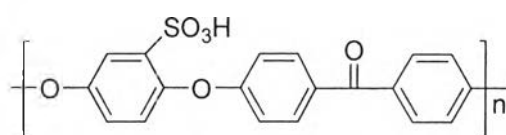
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S-PEKES-A and S-PEKES-B



S-PEEK 150XF

Figure 4.1 S-PEKES-A, S-PEKES-B, and S-PEEK 150XF.

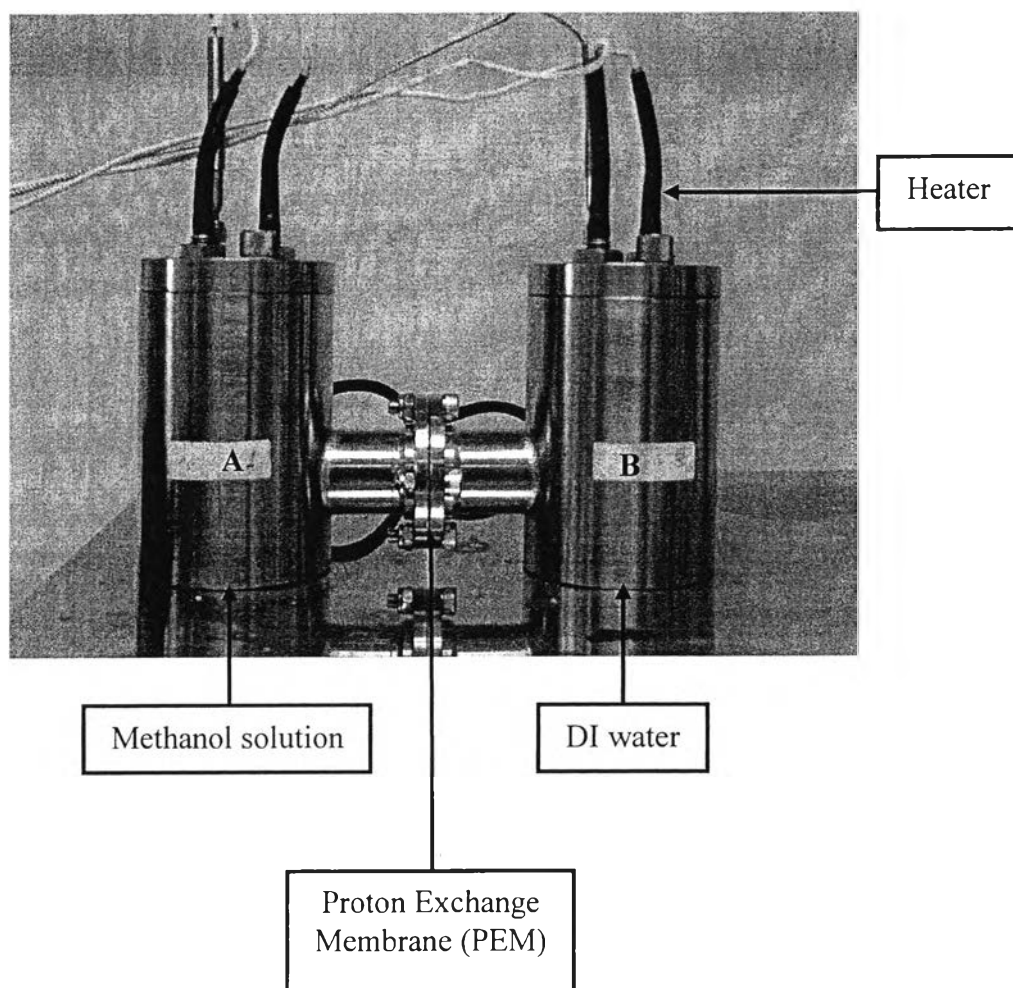


Figure 4.2 Methanol diffusion cell.

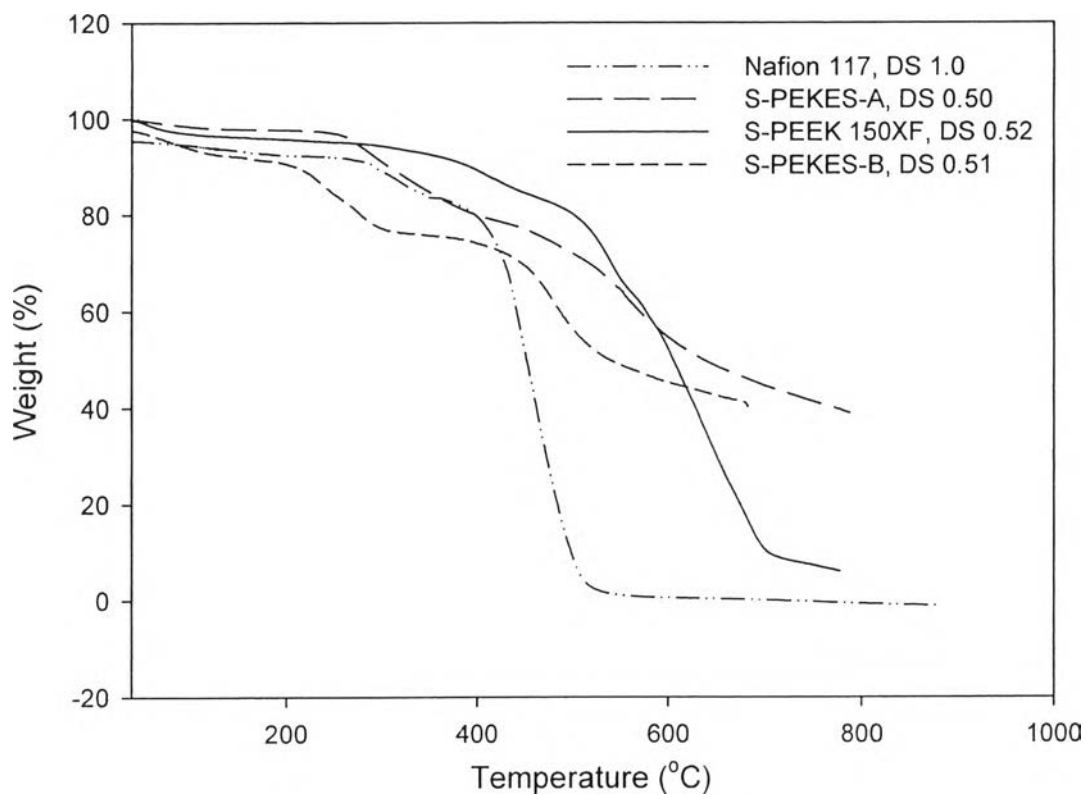


Figure 4.3 Thermograms of Nafion 117, S-PEKES-A, S-PEKES-B, and S-PEEK 150XF, with the sulfonation degrees of 1.0, 0.50, 0.51, and 0.52, respectively.

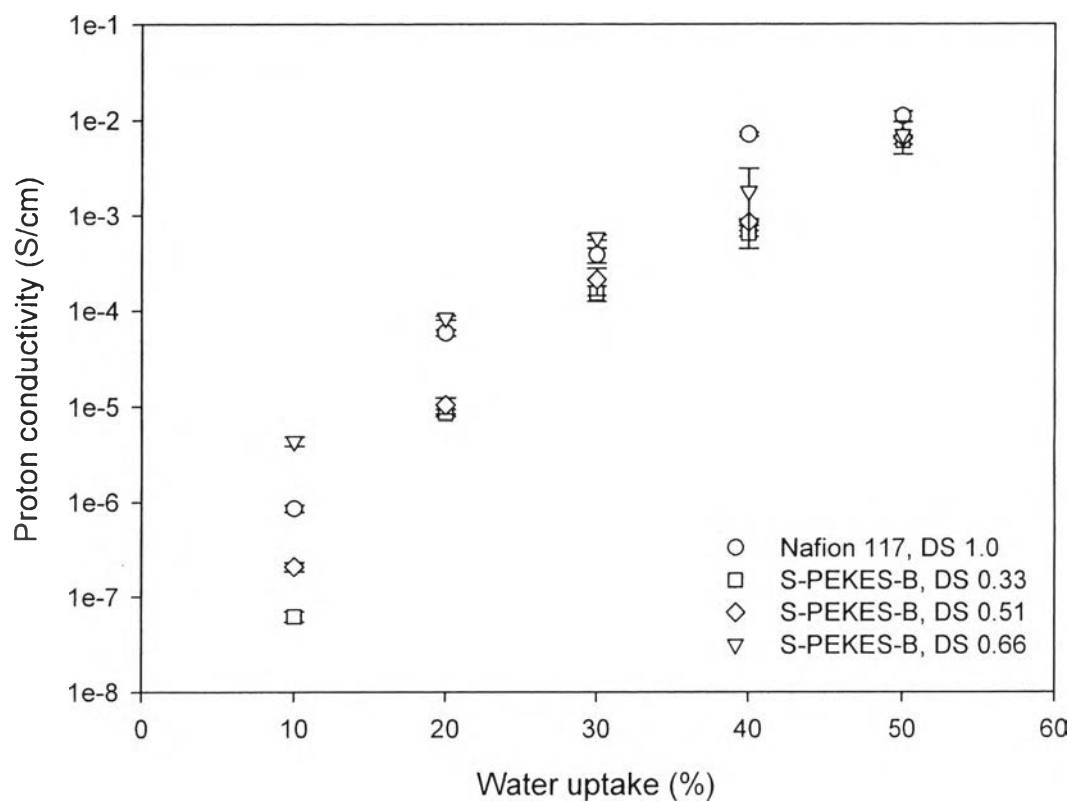


Figure 4.4 The proton conductivities of S-PEKES-B membranes with the sulfonation degrees (DS) of 0.33, 0.51, and 0.66, respectively, and of the Nafion 117, at a room temperature (27 °C) and 50% RH.

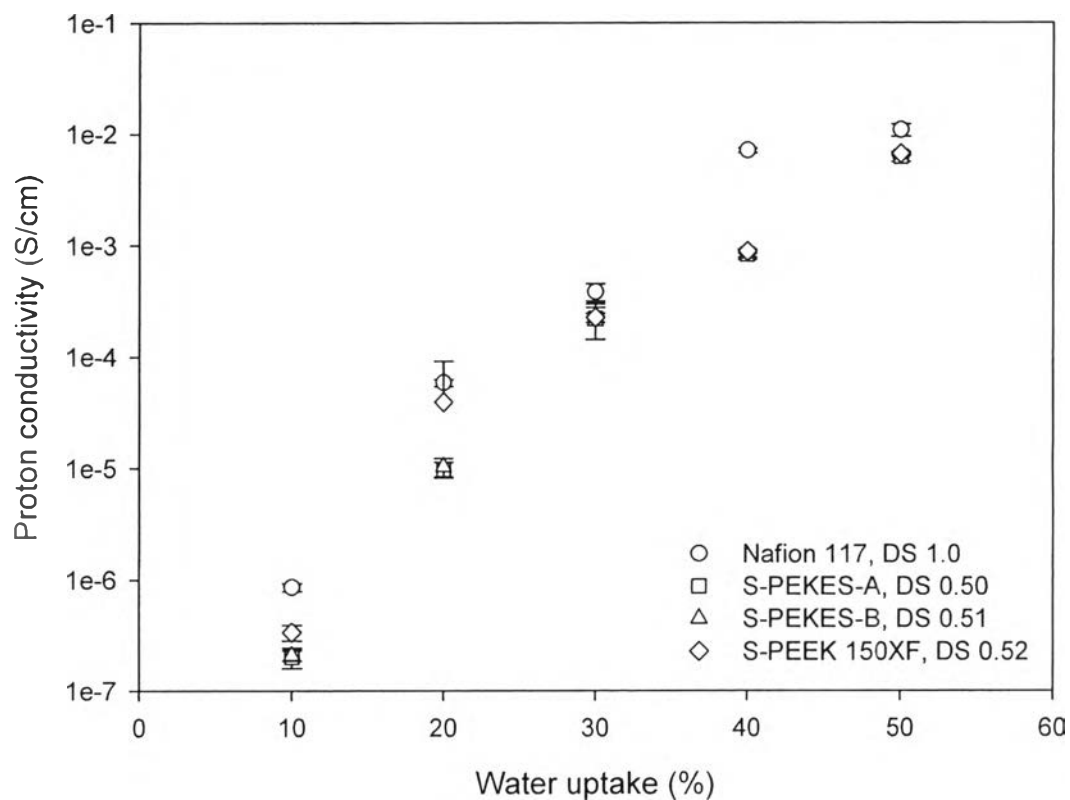


Figure 4.5 The proton conductivities of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF membranes with the sulfonation degrees (DS) of 0.50, 0.51, and 0.52, respectively, and of Nafion 117 at a room temperature (27 °C) and 50% RH.

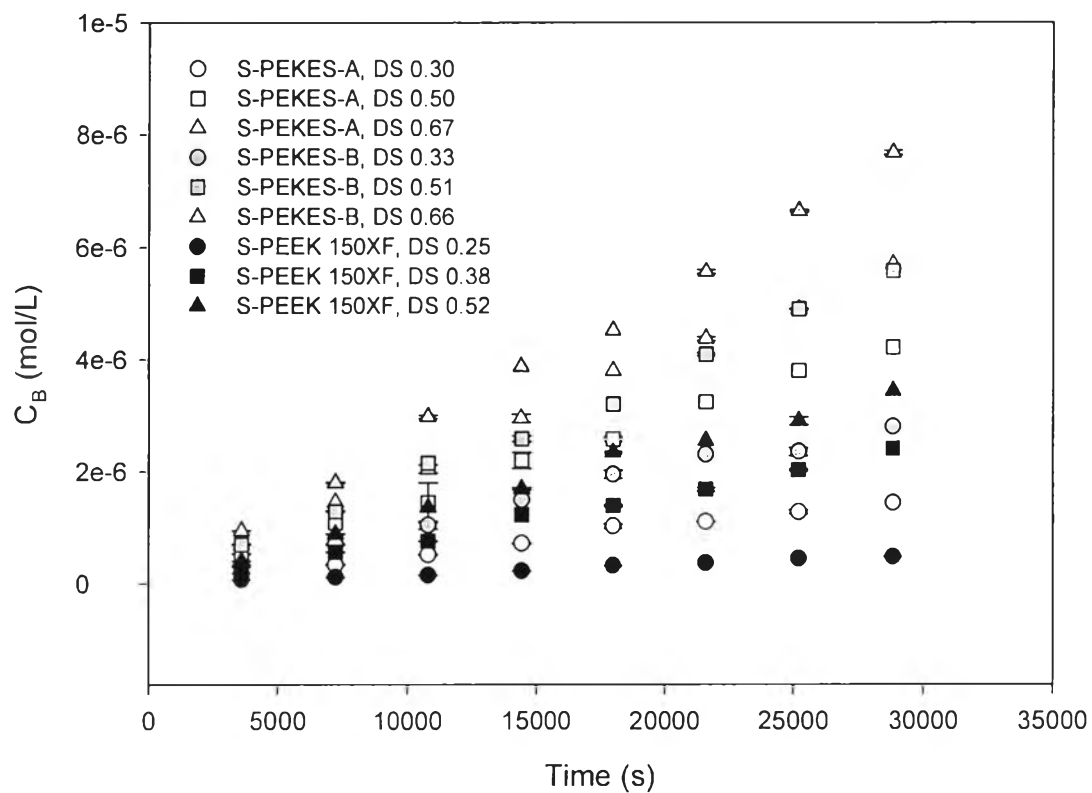


Figure 4.6 Methanol concentration in compartment B (mol/L) vs. time (s) of membranes, with 2.5 mol/L initial feed composition and at a room temperature (27 °C).

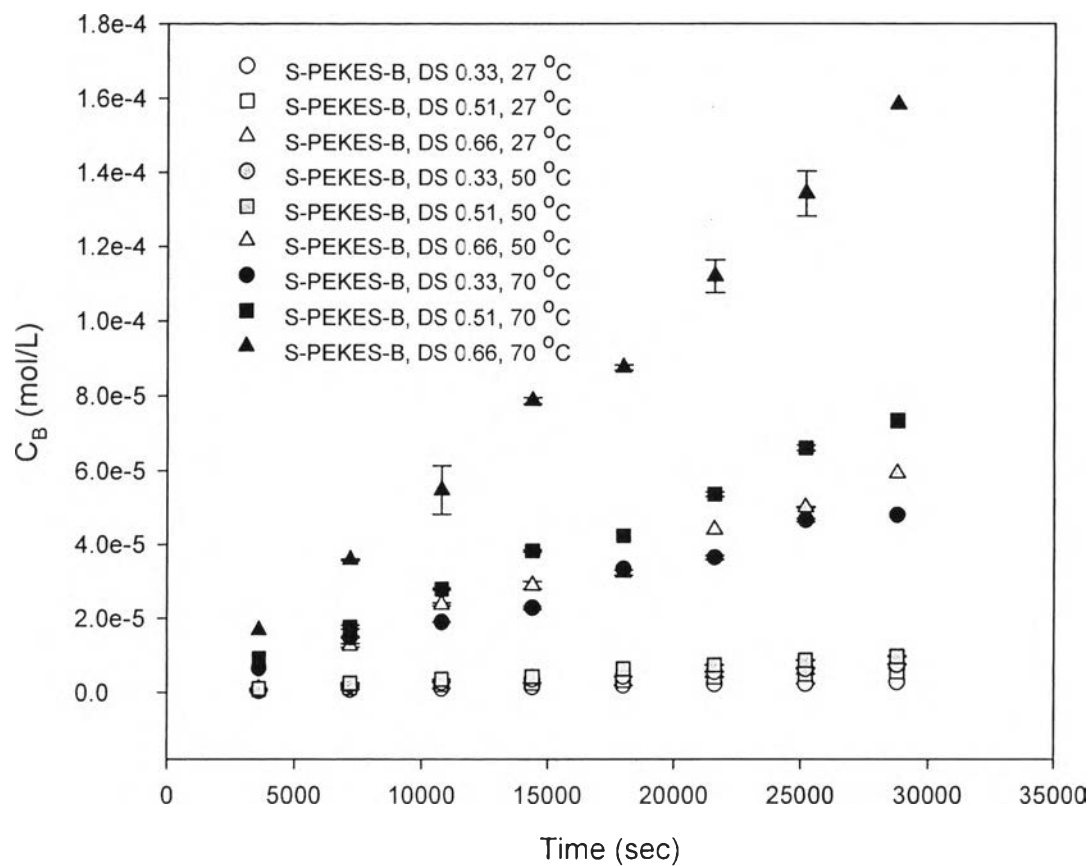


Figure 4.7 Methanol concentration in compartment B vs. time of S-PEKES-B membranes, with 2.5 mol/L initial feed composition, at the temperatures of 27 °C, 50 °C, and 70 °C.

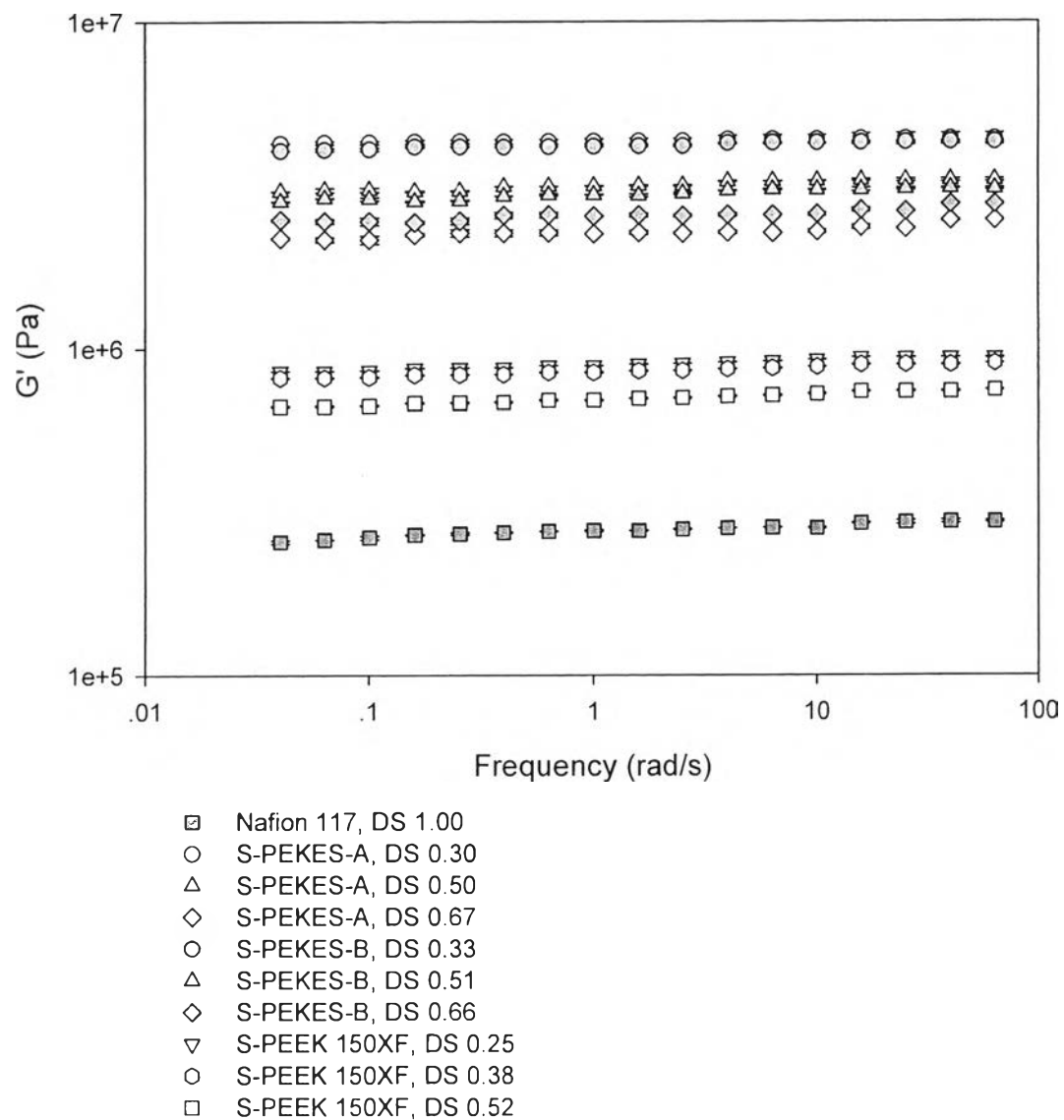


Figure 4.8 The storage modulus (G') of membranes of various sulfonation degrees (DS) at a room temperature (27 °C).

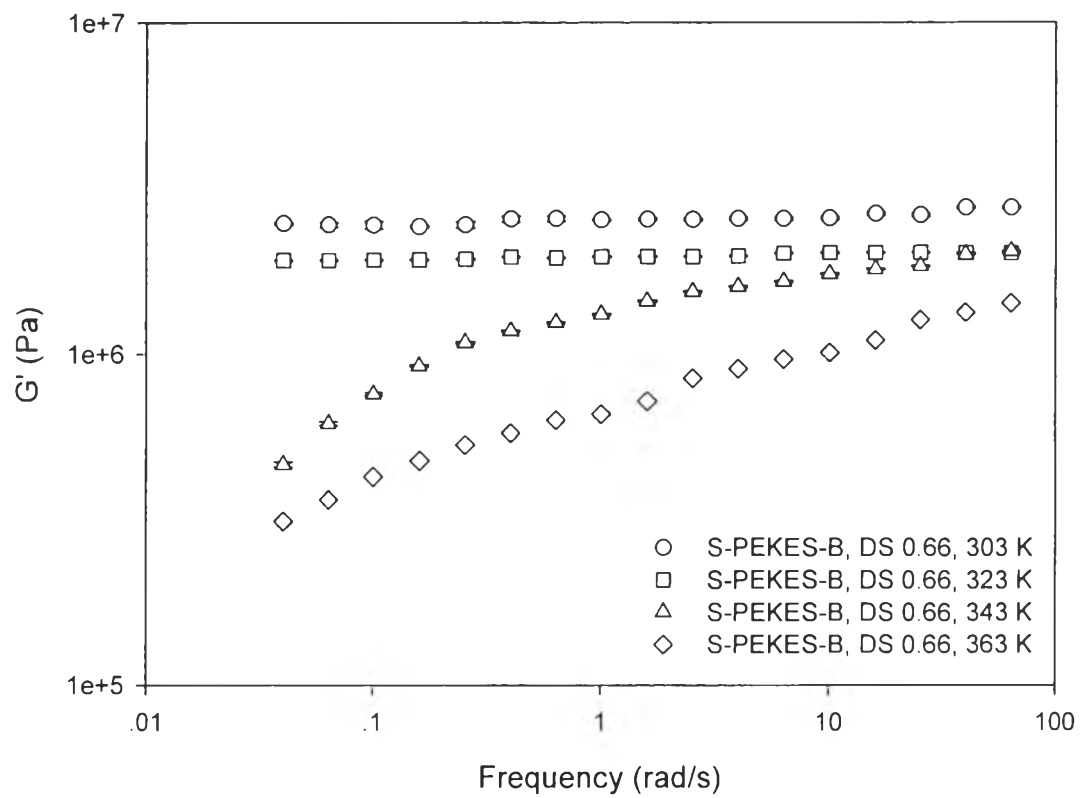


Figure 4.9 Storage modulus (G') vs. frequency of S-PEKES-B membranes with the DS of 0.66, at various temperatures.

Tables

Table 4.1 The proton conductivities of all membranes of various water uptakes (%) at a room temperature (27 °C) and 50% RH

PEM	DS	Thickness (cm)	Water uptakes (%)	Proton conductivity (S/cm)	STD
Nafion 117	1	0.02	10	8.56E-07	7.39E-08
			50	1.09E-02	1.39E-03
S-PEKES-A	0.3	0.0353	10	5.51E-08	8.67E-09
			50	4.52E-03	1.35E-03
	0.5	0.0322	10	2.01E-07	4.17E-08
			50	6.25E-03	6.38E-04
	0.67	0.0423	10	4.73E-06	4.81E-07
			50	8.48E-03	9.00E-04
S-PEKES-B	0.33	0.0278	10	6.22E-08	7.79E-09
			50	6.07E-03	5.45E-04
	0.51	0.0252	10	2.08E-07	2.26E-08
			50	6.61E-03	2.50E-04
	0.66	0.0278	10	4.41E-06	4.84E-07
			50	8.45E-03	5.75E-04
S-PEEK 150XF	0.25	0.0446	10	1.81E-08	4.62E-09
			50	8.51E-04	8.83E-05
	0.38	0.0404	10	8.45E-08	7.30E-09
			50	7.10E-04	6.30E-05
	0.52	0.0423	10	3.36E-07	5.47E-08
			50	6.67E-03	2.45E-04

Table 4.2 Methanol permeability (P) of all membranes at the temperatures of 27 °C, 50 °C, and 70 °C, respectively

PEM	DS	Thickness (cm)	Methanol Permeability, P (cm ² /s)		
			27 °C	50 °C	70 °C
Nafion 117	1.00	0.0200	1.4147E-06	1.0725E-05	1.1689E-05
S-PEKES-A	0.30	0.0353	2.4970E-08	8.3209E-08	5.6916E-07
	0.50	0.0322	6.6964E-08	1.1506E-07	8.8552E-07
	0.67	0.0423	1.1968E-07	8.2516E-07	2.3142E-06
S-PEKES-B	0.33	0.0278	3.9329E-08	9.7941E-08	6.7276E-07
	0.51	0.0252	6.8702E-08	1.2144E-07	9.0517E-07
	0.66	0.0278	1.0347E-07	7.9574E-07	2.1358E-06
S-PEEK 150XF	0.25	0.0446	1.0679E-08	6.5961E-08	4.5703E-07
	0.38	0.0404	4.6316E-08	1.0252E-07	7.3455E-07
	0.52	0.0423	7.1140E-08	1.2850E-07	1.0583E-06

Table 4.3 Oxidative stabilities of the membranes immersed in Fenton's reagent at room temperature (27 °C)

PEM	DS	Thickness (cm)	t ₁ (min)	SD	t ₂ (min)	SD
Nafion 117	1.00	0.0200	24.33	1.53	56.67	1.53
S-PEKES-A	0.30	0.0353	66.67	1.53	121.00	3.61
	0.50	0.0322	47.00	1.00	94.33	2.08
	0.67	0.0423	38.00	1.00	76.67	1.53
S-PEKES-B	0.33	0.0278	60.00	1.00	114.33	2.08
	0.51	0.0252	49.00	1.00	94.67	1.53
	0.66	0.0278	35.33	1.53	73.67	1.53
S-PEEK 150XF	0.25	0.0446	80.67	1.53	146.00	1.00
	0.38	0.0404	55.00	1.00	109.67	1.53
	0.52	0.0423	43.33	1.53	94.67	1.53

t₁ time of membrane breaking into pieces;

t₂ time of membrane disappearing

Table 4.4 Mechanical properties of sulfonated polymer at room temperature (27 °C) and 50% RH

PEM	DS (%)	Tensile strength (MPa)		Young's modulus (MPa)		Elongation at break (%)	
		Dry	Wet	Dry	Wet	Dry	Wet
S-PEKES-A	0.30	53.33 ± 3.75	31.55 ± 1.43	34,382.74 ± 102.80	1,234.50 ± 34.36	7.14 ± 0.84	137.88 ± 11.63
	0.50	24.18 ± 1.79	13.69 ± 1.55	529.44 ± 22.18	453.98 ± 7.91	33.23 ± 2.04	184.80 ± 4.47
S-PEKES-B	0.33	40.05 ± 1.43	30.70 ± 1.40	17,681.38 ± 82.11	1,152.25 ± 32.92	7.52 ± 0.50	143.8 ± 11.08
	0.51	22.93 ± 0.61	8.63 ± 0.27	463.02 ± 36.75	338.84 ± 33.47	70.80 ± 13.01	214.07 ± 12.43
S-PEEK 150XF	0.38	32.19 ± 1.30	25.42 ± 1.26	16,523.57 ± 110.85	662.23 ± 21.09	7.71 ± 1.80	148.27 ± 12.85
	0.52	17.84 ± 1.53	7.75 ± 0.18	459.93 ± 6.86	193.79 ± 7.33	119.87 ± 0.85	538.44 ± 21.47
Nafion117*	1.00	38.0	28.4	180	100	301.5	329.2

* The mechanical properties of Nafion 117 are report in Xue *et al.*, 2006, Li *et al.*, 2010.