RESULTS AND DISCUSSIONS

Although there are many techniques used to characterize polymers. Spectroscopic and thermal characterizations are two important techniques used to gather information. Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (H NMR) were employed to provide structural and compositional characterizations of the sulfonated polymers. Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to explore the thermal behavior of the polymers synthesized in this investigation. The water uptake property was determined by measuring the dry weight of the films and the equilibrium wet weight of the polymer. The ion exchange capacity (IEC) was determined by using the titration technique. And the Instron mechanical testing machine was used to determine the tensile strength of the polymer membranes.

1. Fourier Transform Infrared (FTIR) Spectroscopy

Standardized FTIR spectra were allowed for the qualitative and quantitative determination of the functional groups of the post sulfonated polymers. Assignments of the main peaks shown in Table 1 are based on the literature values (Kim *et al*., 2002). Figure 10 shows the FTIR of 5 different samples, which are PPSU, SPPSU, pure PWA and two composite membranes, containing 13% inorganic at the ratio of PWA to ZSM-5 equal to 7.5 to 2.5 (denoted as SPPSU/(PWA/ZSM-7.5 2.5)-13%) and 30% PWA in the membrane (denoted as SPPSU/(PWA)-30%). The FTIR peak at 1006 cm^{-1} is characteristic of Ar-O-Ar linkage, which was selected for normalizing in the polymer backbone. Peak at 1030 cm^{-1} corresponded to symmetric stretching of sulfonic acid group ($-SO_3^-$). As seen, the new absorption peak at 1021cm^{-1} was found in both SPPSU and composite polymers, but was missing in PPSU. This results show the success of sulfonation to the polymers.

Table 1 Infrared assignments of pure PWA, SPPSU and SPPSU/PWA.

Sample		Wave number (cm^{-1})				
		SO_3	P-O	W=O_t	W-O_c-W	W-O_e-W
Kim *et al* ., 2002	PWA	-	1080	980	887	795
	SPPSU	1030	-	-	-	-
	SPPSU/(PWA)-30%	1026	1076	980	897	816
Present work	PWA	-	1080	980	887	802
	SPPSU	1021	-	-	-	-
	SPPSU/(PWA)-30%	1021	1080	980	897	817

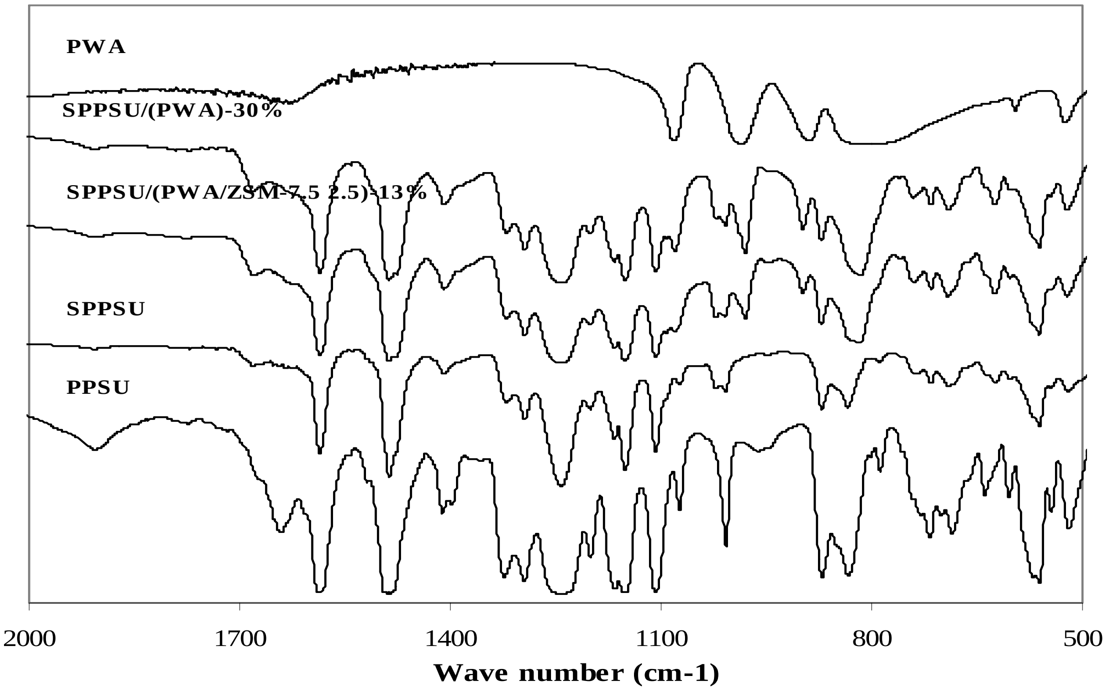


Figure 10 FTIR spectra of PPSU, SPPSU and composite membranes (SPPSU/(PWA/ZSM-7.5 2.5)-5% and SPPSU/PWA-30%).

While the spectra of pure PWA and composite membranes can be similarly observed at 980 and 1080 cm^{-1} for central tetrahedron W-O$_t$ band and terminal oxygen P-O band, respectively. In addition, the corner-sharing W-O$_c$-W peak at 887 cm^{-1} in pure PWA was shifted to value 897 cm^{-1} when PWA was incorporated into the polymer structure. Also there is a small shift of edge-sharing W-O$_e$-W peak from 802 cm^{-1} in pure PWA to 817 cm^{-1} in the composite membranes. As seen, the peaks present in this research are in good agreement with what were observed in Kim’s work (Kim, *et al.*, 2002), which they claimed that the frequency shifts indicated the PWA interacted with sulfonic acid groups of the SPPSU.

2. Nuclear Magnetic Resonance (NMR) Spectroscopy

Figure 11 shows the NMR spectrum for the SPPSU dissolved in DMSO-d6, which confirmed the presence of sulfonic acid groups in the polymer which was undergone the post-sulfonation reaction. Using the H-NMR technique, the degree of sulfonation (DS) of the polymer can be obtained by dividing the area under *h* peak by the sum of areas under *c* and *d* peaks divided by eight protons. In our case, it was found to be 8%.

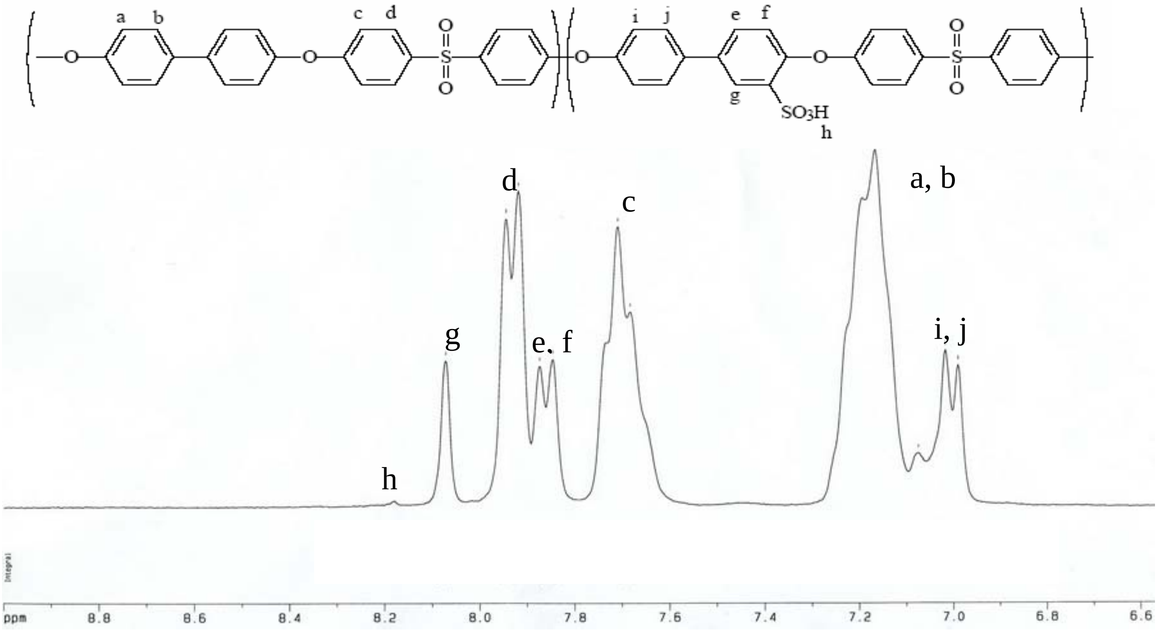


Figure 11 H-NMR spectrum of SPPSU.

3. Thermo Gravimetric Analysis (TGA)

The thermal stability of the polymer membranes under nitrogen and air atmospheres was studied by heating samples in DSC-TGA. The heating procedure is as follows, the sample and the reference were first heated to 120°C and kept at this temperature in the DSC-TGA furnace for 30 min., then were cooled down to 80 °C at a rate of 10°C/min. As soon as the temperature reached 80°C, both sample and reference were immediately heated to 1000°C at a heating rate of 10°C/min. Figure 12 shows the weight loss of the PPSU, SPPSU and composite membranes (SPPSU/(PWA/ZSM-37)-25% and SPPSU/(PWA)-30%) in nitrogen atmosphere. The figure showed the change in weight loss during the second heating only. As seen, the first large weight loss of each graph represents the loss of water remained in the polymer membranes. Also, the residual solvent was removed at 200°C, corresponding to the second big drop of the weight loss. The PPSU membrane was found to be stable until 500°C, the indicative of the potential in being operated at high temperature in a fuel cell. In addition, the SPPSU and composite polymer membranes displayed two steps degradation. The first degradative weight loss was obtained around 300°C, which was assigned to the loss of sulfonic acid groups, consistent with other previous reports (Kim *et al*., 2002). The second weight loss was occurred in the range of 380–500°C due to the degradation of the polymer backbone. As mentioned, our sulfonated membranes were thermally stable above 200°C, satisfying the requirement of the proton-exchange membrane fuel cell using hydrogen and oxygen as fuels.

The stability of all the membranes in the nitrogen atmosphere was greater than that in the air atmosphere, as shown in Figure 13, which is similar to what Kim found (Kim *et al*., 2002).

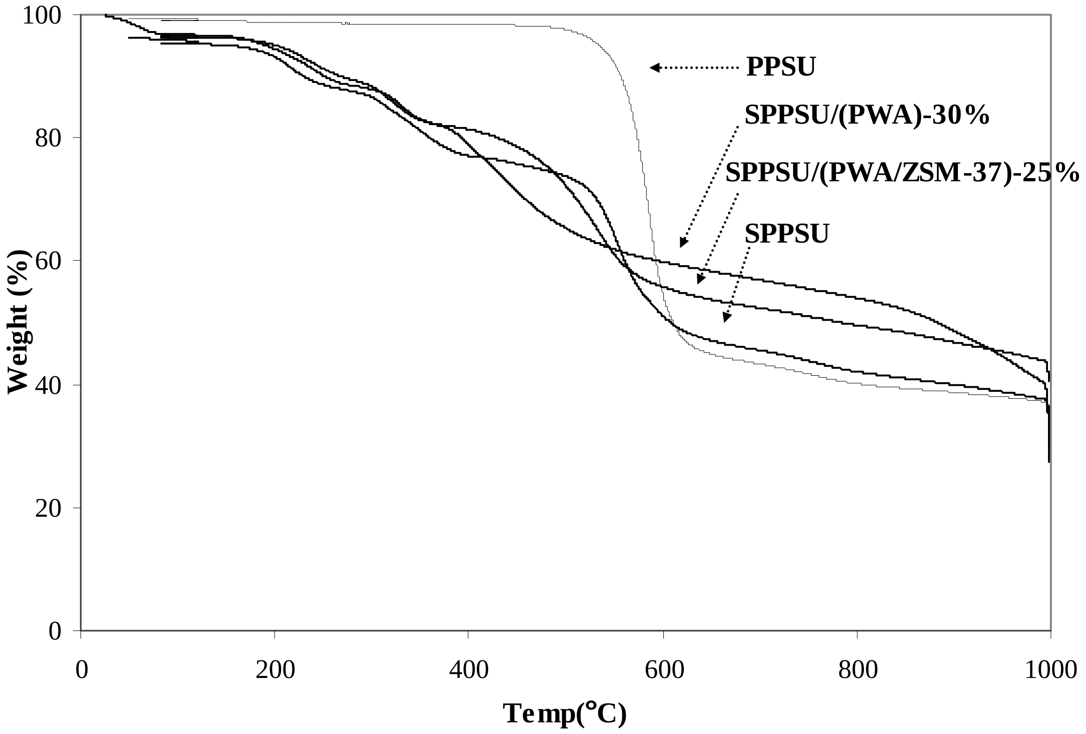


Figure 12 TGA curves for a PPSU, SPPSU and composite membranes measured in nitrogen at heating rate 10°C/min.

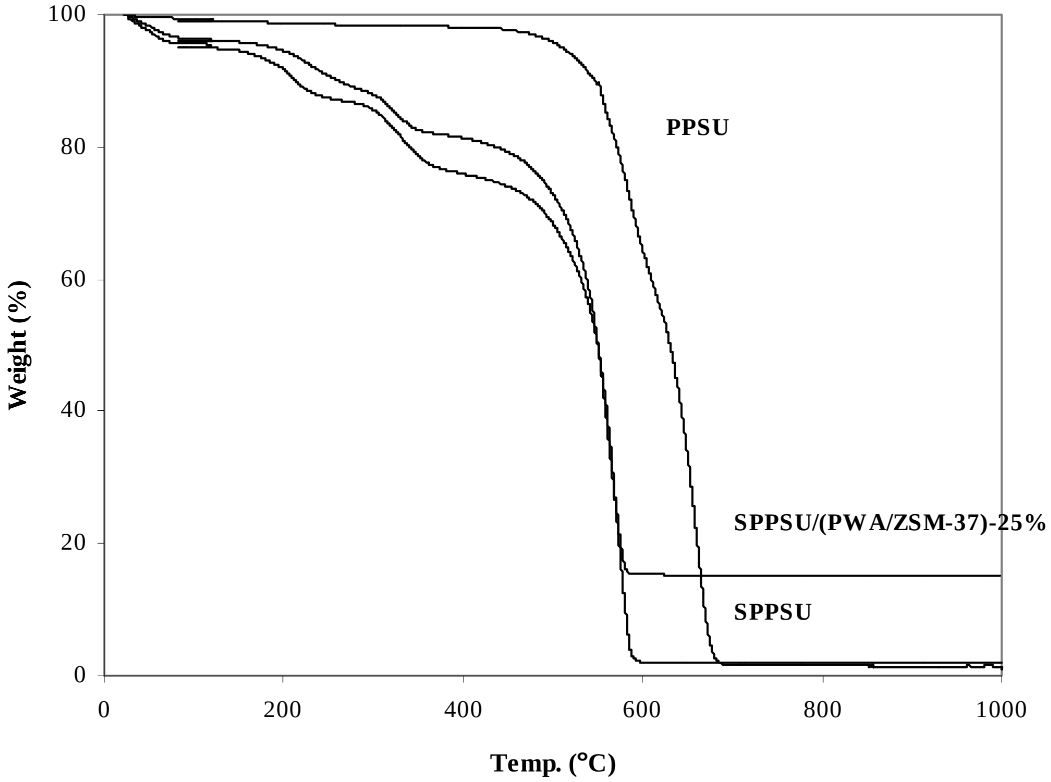


Figure 13 TGA curves for a PPSU, SPPSU and composite membranes measured in air at heating rate 10°C/min.

4. Differential Scanning Calorimetry (DSC)

DSC analysis was used to characterize the thermal transition of the membranes using the same heating procedure described earlier. Unfortunately using DSC, the T_g's of all membranes were indistint from the heat flow versus temperature plots. The similar observations have been reported for sulfonated polymer (Kim *et al.*, 2002). However, they can be discerned clearly from the Figure 14, showing the first derivative of heat flow of the membranes as a function of temperature. As seen, the T_g of the SPPSU (315°C) is higher than that of PPSU (225°C) which may be due to the strong interactions between sulfonic acid groups and polymers per se. In case of the composite membranes, the T_g's were 300 and 330°C for SPPSU/(PWA/ZSM-37)-25% and SPPSU/(PWA)-30% membranes, respectively.

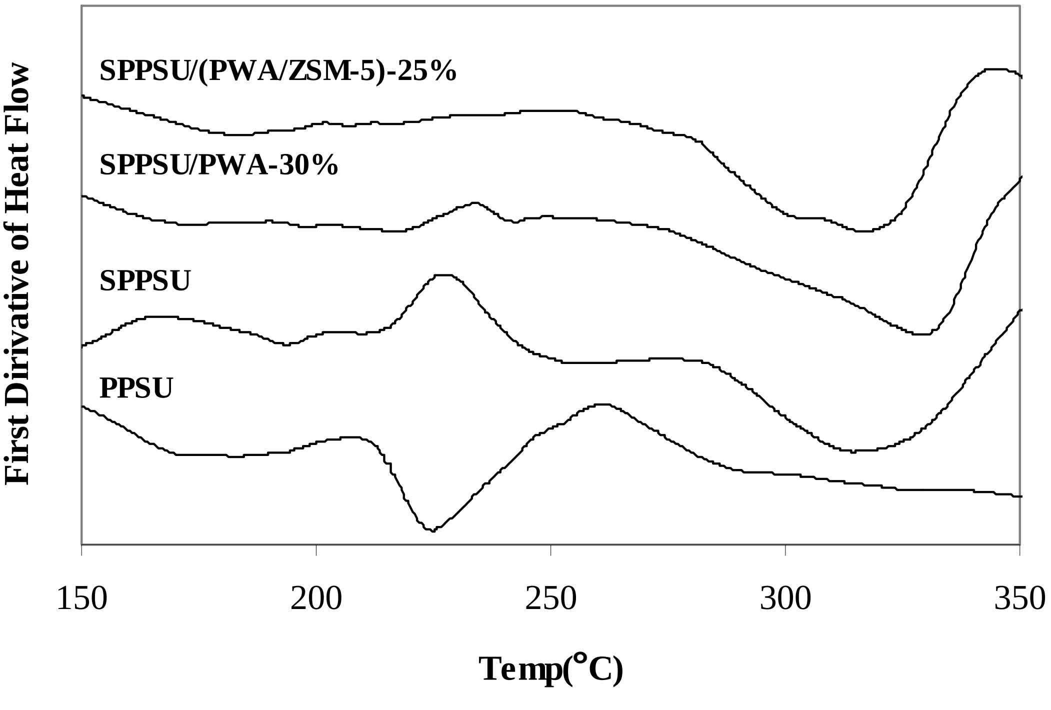


Figure 14 DSC curves for a PPSU, SPPSU and composite membranes measured in nitrogen atmosphere at a heating rate of 10°C/min.

That is, the T_g's of composite membranes were higher than that of unfilled SPPSU membrane. The results suggest that adding inorganic into the SPPSU can enhance the thermal stability of the membranes.

5. Scanning Electron Microscopy (SEM)

The distribution of inorganic can be identified by SEM. As shown in Figure 15, the ZSM-5 powder was composed of agglomerates, and the mean agglomerate size ranged approximately from 3 to 10 µm. In order to determine the presence and distribution of inorganic in the composite membranes, SEM was carried out on the surface and cross section of the SPPSU and SPPSU/(PWA/ZSM-37) membranes with 5, 15 and 25% inorganic, respectively, which are shown in Figures 16 and 18, respectively. For better view of cross-section of membranes (Figure 18), the thickness of all membranes prepared for this particular work was approximately 90 µm. The membrane in Figures 16a and 18a did not contain inorganic, and thus the surface looked smooth. The 5% composite membrane had shown a little bit of inorganic agglomerate distribution along the cross section and the surface of the membrane. In case of membranes with 15% and 25% inorganic, there were conglomerates of inorganic particles. They were clearly seen in Figures 17 and 19, which were made by using Energy Dispersive Spectrometer (EDS). Dots were represented silicon atoms. As seen, the number of dots was increased with the amount of inorganic present, clearly showing aggregates of inorganic.

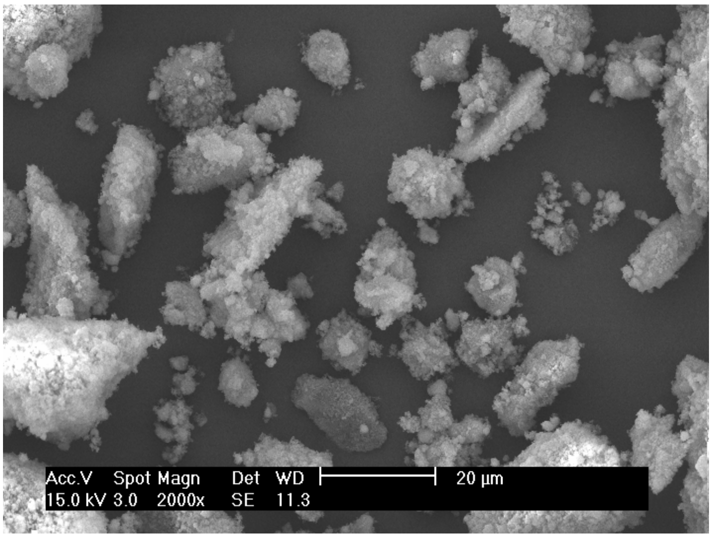


Figure 15 SEM photographs of the ZSM-5 particles.

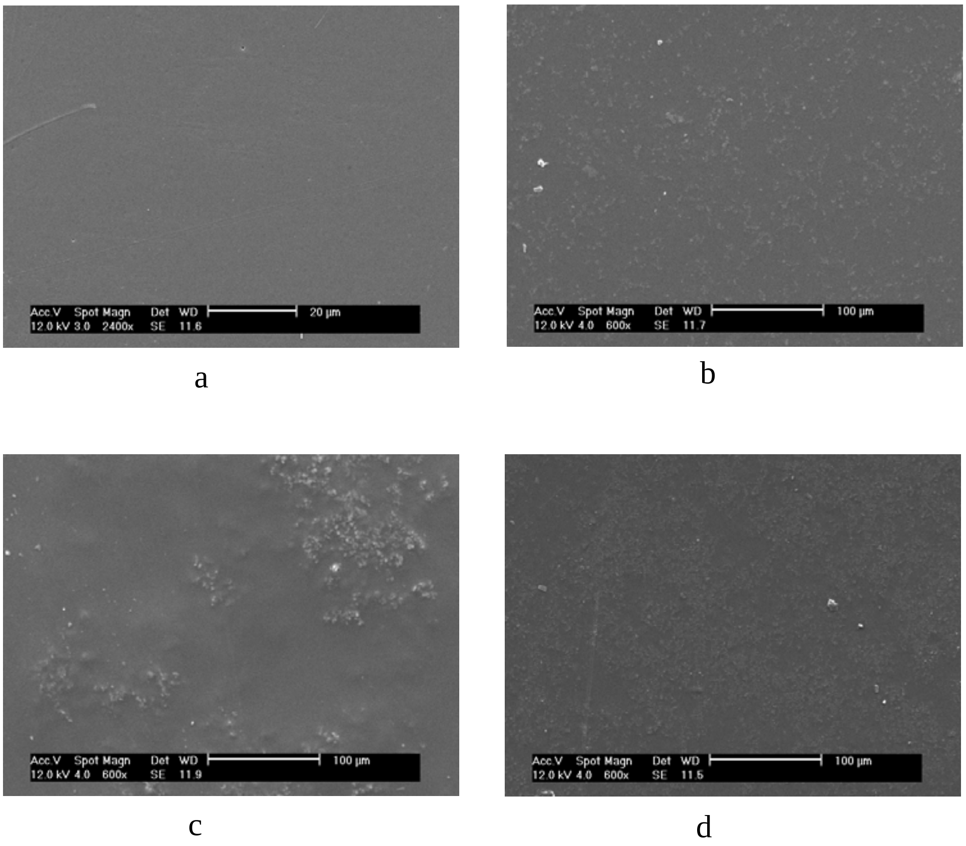


Figure 16 SEM photographs for surface of composite membranes with various inorganic, PWA and ZSM-5, contents: (a) pure SPPSU (b) 5 wt.% (c) 15 wt.% (d) 25wt.%

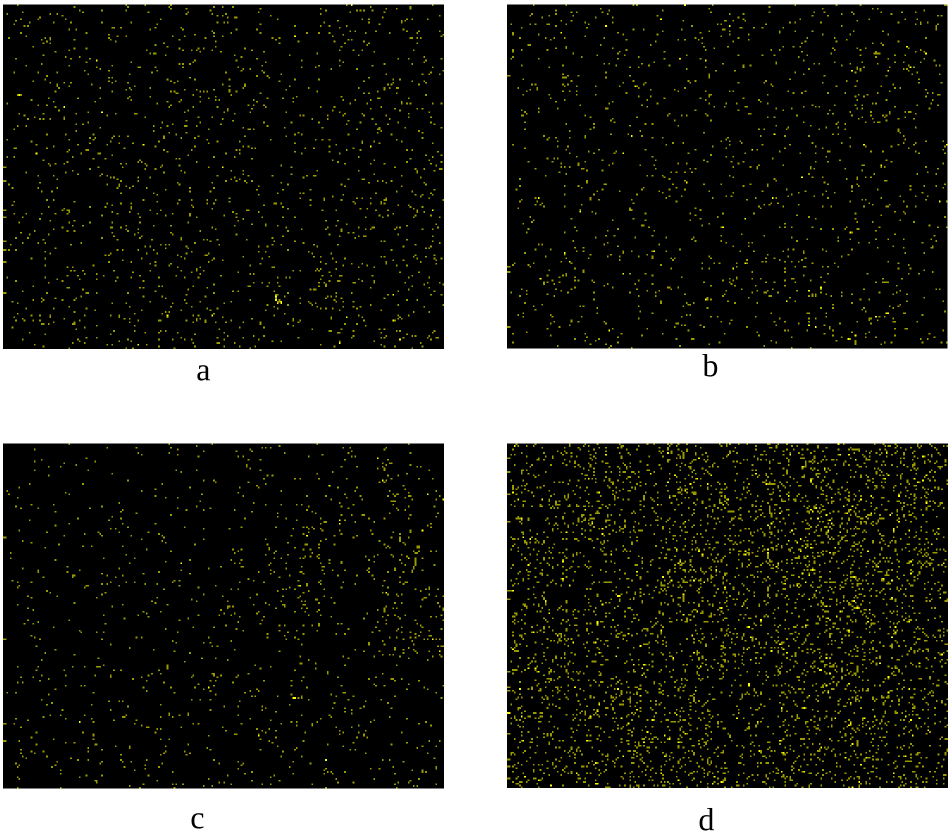
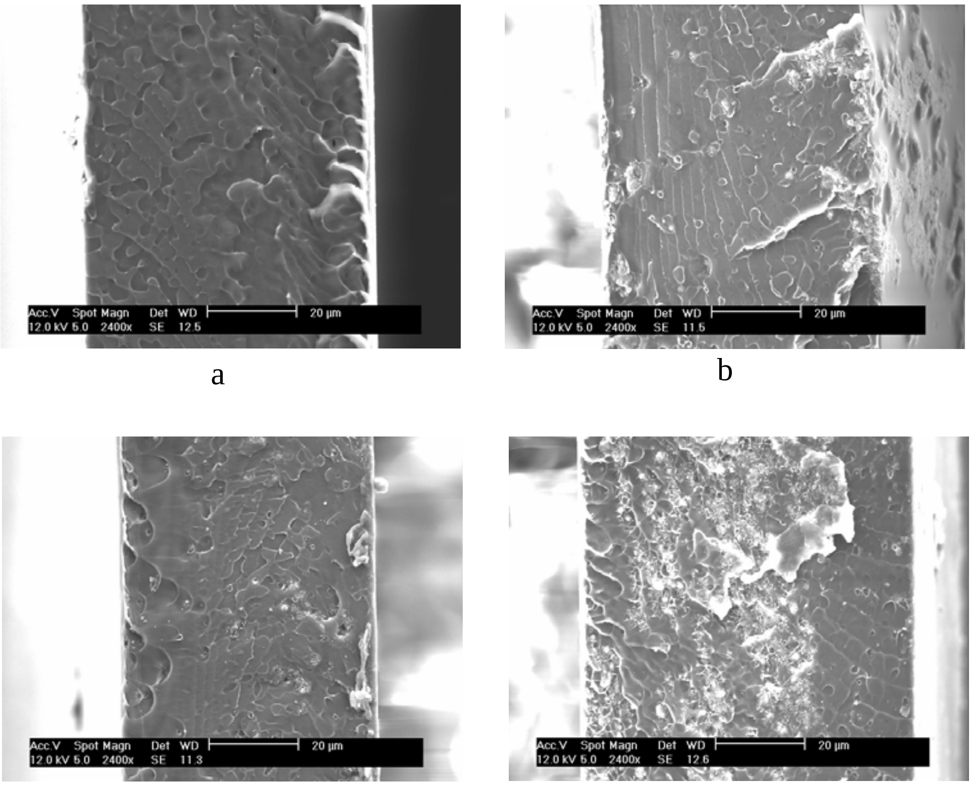


Figure 17 EDS photographs for surface of composite membranes with various inorganic, PWA and ZSM-5, contents: (a) pure SPPSU (b) 5 wt.% (c) 15 wt.% (d) 25wt.%



a b

c d

Figure 18 SEM photographs for cross section of composite membranes with various inorganic, PWA and ZSM-5, contents: (a) pure SPPSU (b) 5 wt.% (c) 15 wt.% (d) 25wt.%

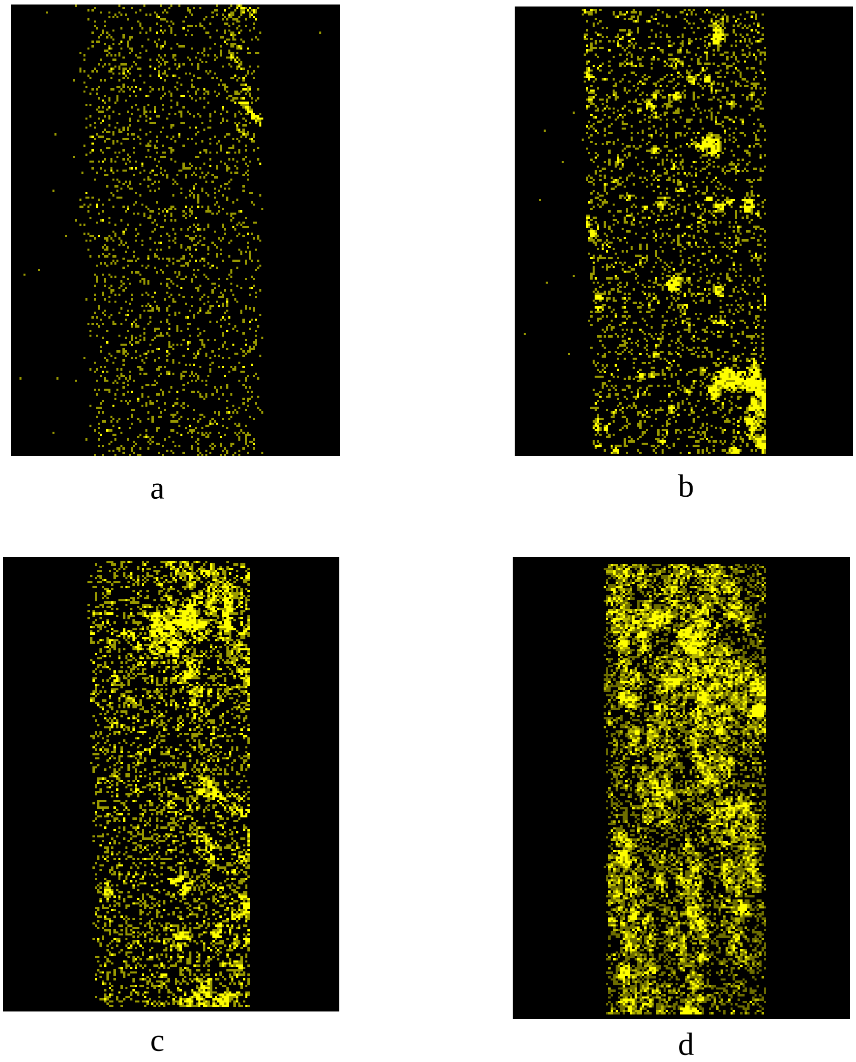


Figure 19 EDS photographs for cross section of composite membranes with various Inorganic, PWA and ZSM-5, contents: (a) pure SPPSU (b) 5 wt.% (c) 15 wt.% (d) 25wt.%

6. Ion exchange capacity (IEC) and Water uptake

The IEC describes the amount of ion exchange groups per unit weight of dry polymer and is determined via titration. Figure 20 shows the IEC of the SPPSU/(PWA/ZSM-cd)-15% composite membranes with different ratios of PWA to ZSM-5. c and d represents the weight ratio of PWA and ZSM-5, respectively. Note that the sum of them was equal to 10. As seen, the IEC of the composite membrane containing 30%w/w of PWA in the inorganic mixture was higher than those of the other composite membranes. Therefore, this research only employed the 30%wt. of PWA in the inorganic mixture for all experiments. Figure 21 shows the IEC and water uptake of the SPPSU/(PWA/ZSM-37)-a% membrane containing different amounts of inorganic mixture (a = 0, 5, 15 and 25%w/w inorganic mixture) by fixing the weight ratio of PWA to ZSM-5 at 3 to 7. As shown, increasing amount of inorganic could be insignificant to the IEC. That is, inorganic particles were aggregated, and thus obstructing the proton paths across the membrane. The IEC and water uptake values were also summarized in Table 2. In Figure 21, one may observe that increasing the amount of inorganic can enhance the water uptake more or less, which might be caused by water being captured inside inorganic or in gaps between inorgaic and polymer. For instance, immersing polymers in water for 24 hr, the SPPSU/(PWA/ZSM-37)-5% membrane could uptake water almost 15% while the SPPSU/(PWA/ZSM-37)-15% membrane about 22.14%. Nevertheless, the water uptake at 5% inorganic was lower than that of pure SPPSU. This might be an error.

Table 2 The ion exchange capacity and water uptake of the SPPSU and composite membranes.

System	PWA:ZSM-5	IEC (meq/g)	Water Uptake (%)
SPPSU	-	1.40	21.79
SPPSU/(PWA/ZSM-5)-5%	30:70	1.27	15.18
SPPSU/(PWA/ZSM-5)-15%	30:70	1.46	22.14
SPPSU/(PWA/ZSM-5)-25%	30:70	1.32	25.06
SPPSU/(PWA/ZSM-5)-15%	50:50	1.16	24.03
SPPSU/(PWA/ZSM-5)-15%	70:30	1.10	21.65

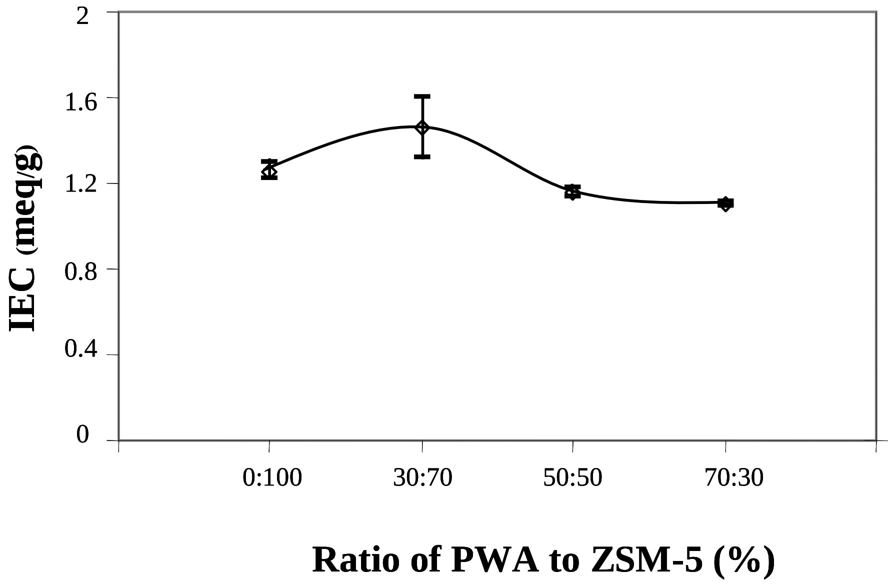


Figure 20 The effect of ratio of PWA to ZSM-5 on the ion exchange capacity.

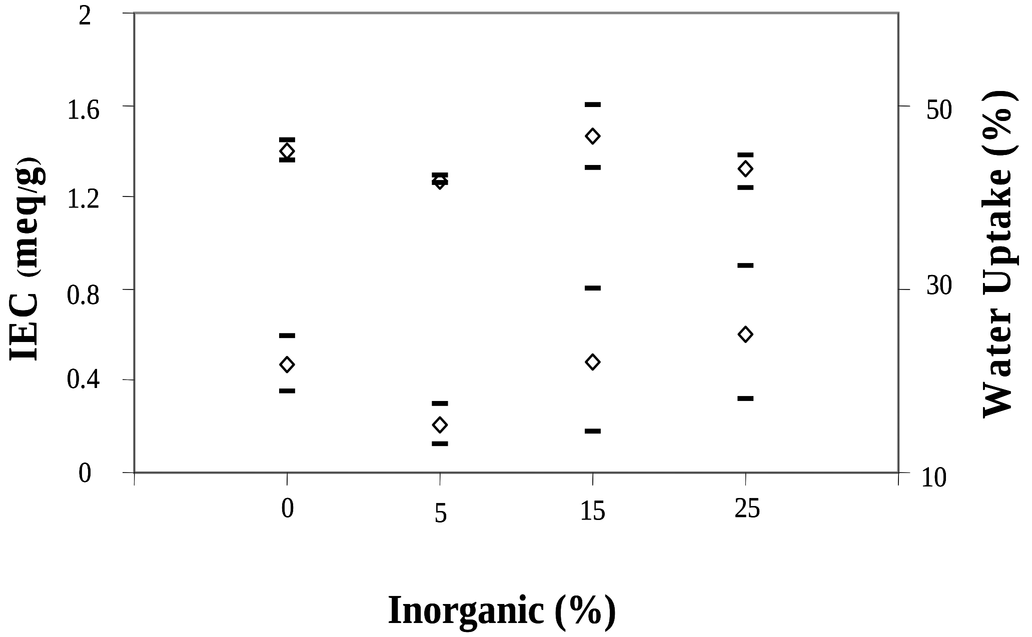


Figure 21 The effect of inorganic content in the polymer membranes with ion exchange capacity and water uptake

7. Tensile strength

According to our procedure of measuring proton conductivity, a membrane must be saturated with water first by soaking in water for 24 h. Therefore, to observe the tensile strength properties of membranes after aging at various temperatures and a constant relative humidity of 100%, we saturated a membrane with water using the same instruction above, then stored it in a closed-chamber for 3 h at various temperatures and 100% relative humidity, and due to the need to set-up a sample on the Instron machine the sample was left unattended in a sealed plastic bag for about 5 min. on the bench before starting to measure stress-strain properties in ambient conditions. In most work related to proton-exchange membrane fuel cell, only tensile strength and young’s modulus are reported. So in this work only tensile strength and young’s modulus were shown (Figures 22 and 23, respectively). After aging at different temperatures and a fix relative humidity, it was found that the tensile strength was roughly constant over the range of aging temperatures, indicative of no significant influence of the aging temperature on the strength. At 100°C, the distinct increase or decrease of both values were observed. However, at the moment there was no clear explanation as what could cause the phenomena.

In Figure 22, it can be seen that adding inorganic lowers the strength of membranes, which could be caused by the space between the polymers and inorganic in a membrane. In contrast, the effect of inorganic on Young's modulus over the range of aging temperature from room temperature to 120°C was not seen clearly.

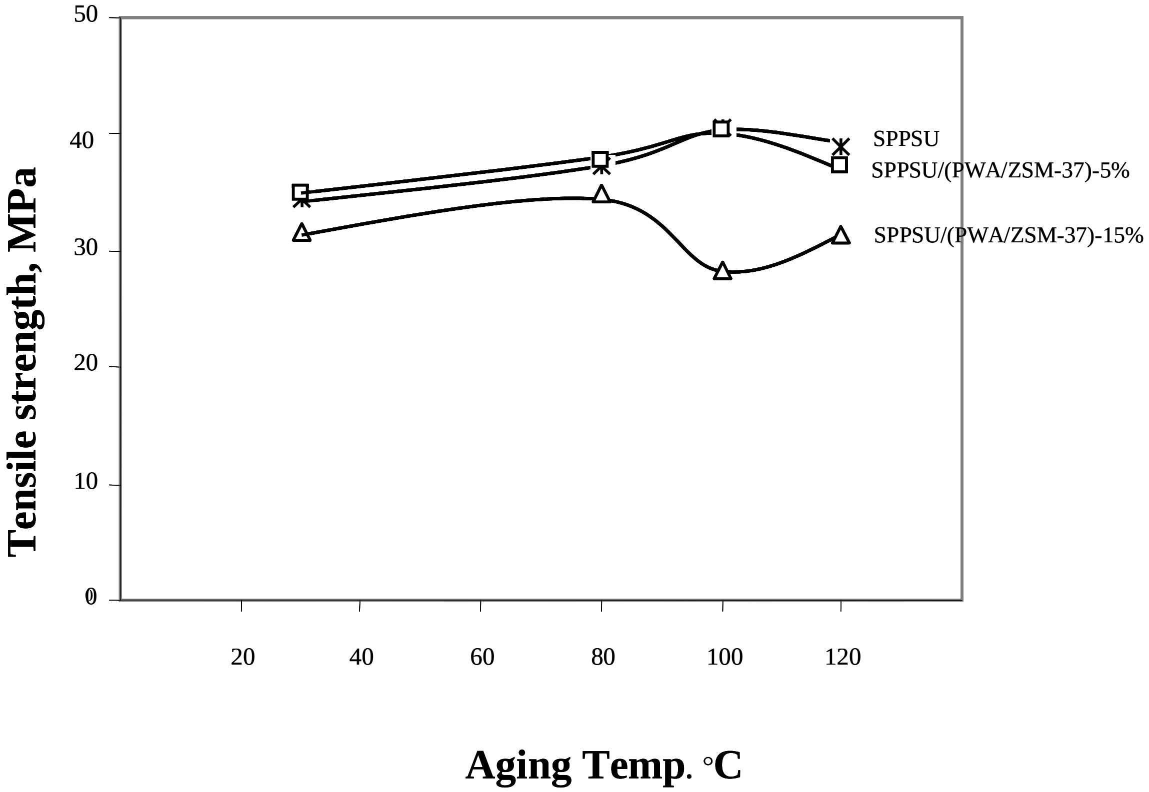


Figure 22 The tensile strength of the composite membranes at different amounts of the inorganic (0, 5 and 15%inorganic).

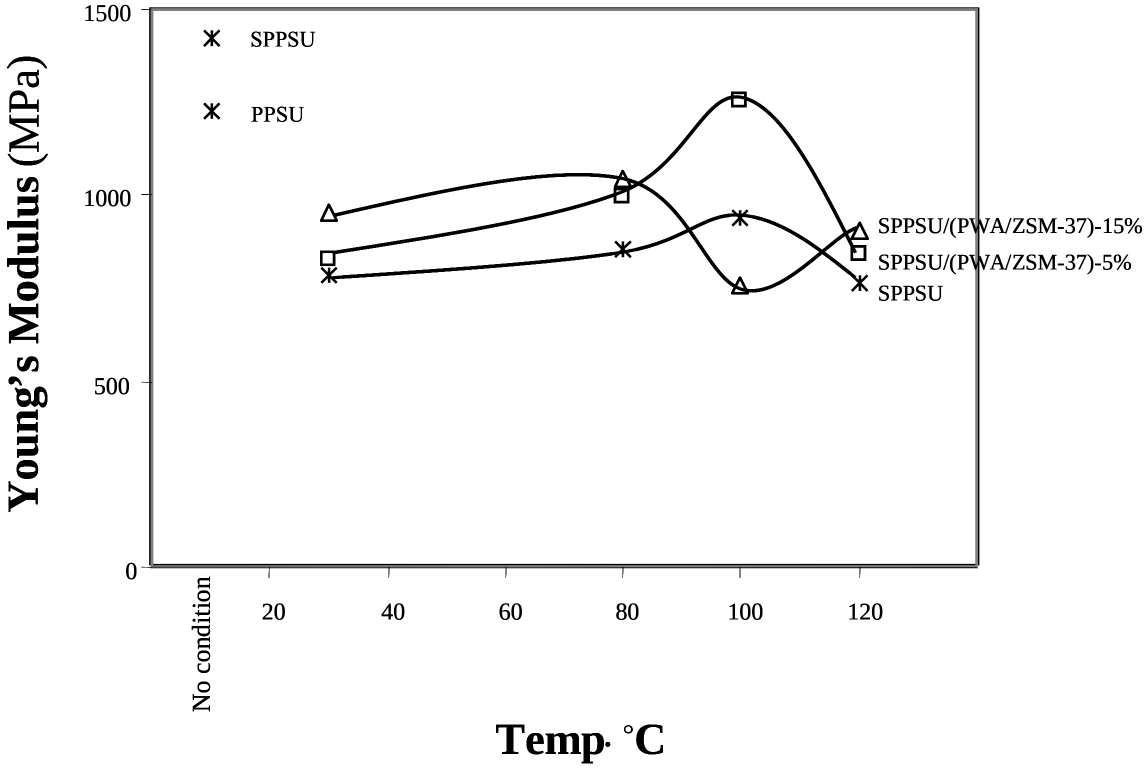


Figure 23 Young's moduli of composite membranes at different amounts of the inorganic (0, 5 and 15%inorganic).