CHAPTER 5

SPEEK/PES/PWA COMPOSITE MEMBRANES

5.1 DEGREE OF SULFONATION

The $^1$H-NMR spectra of SPEEK have a distinct signal of protons $H_{13}$ at 7.5 ppm indicating the presence of the $-\text{SO}_3\text{H}$ group. The intensity of the $H_{13}$ signal was used to determine the sulfonic group content that is equivalent to the DS of SPEEK per repeat unit. The measured NMR spectrum for prepared SPEEK is shown in Figure 5.1. The ratio between peak area of distinct signal ($AH_{13}$) and the integrated peak area ($\sum AH_{1,2,3,4,5,6,7,8,9,10,12,14,15,16}$) of the signals corresponding to all other aromatic hydrogens (Song Xue et al. 2007) gives the degree of sulfonation. It is estimated that the degree of sulfonation for the prepared SPEEK is 67.25%.

Figure 5.1 $^1$H-NMR spectra of SPEEK polymer
5.2 FUNCTIONAL GROUP ANALYSIS

The FTIR spectrum of PEEK, PES, PWA, SPEEK, SPEEK/PES and SPEEK/PES/PWA composite membranes are given in Figure 5.2(a). In the spectrum of PEEK, the characteristic peaks are appeared at 1644 cm$^{-1}$(C=O) and 1487 cm$^{-1}$(C-C). After sulfonation the obtained SPEEK shows C=O peak at 1639 cm$^{-1}$. The sulfonation process causes the intensity of aromatic C-C band to be decreased and the peak is seen to split to two absorption bands at 1482 cm$^{-1}$ and 1409 cm$^{-1}$. The bands at 1081, 1025 cm$^{-1}$ and 714 cm$^{-1}$ correspond to the stretching vibration of sulfonic acid groups, confirming the successful sulfonation of PEEK (Gosalawit et al. 2010).

The characteristic peak of PES at wave number 1598 cm$^{-1}$(C–H) is visualized. In SPEEK/PES spectrum the observation of a new peak at 1651 cm$^{-1}$ and 1593 cm$^{-1}$ suggests the good blend formation between the two polymers (Kalambettu Aravind et al. 2014).

The spectrum of PWA exhibits absorption bands at 1088 cm$^{-1}$ (P-O), 989 cm$^{-1}$ (W=O$_t$) (O$_t$ is the terminal oxygen), 888 cm$^{-1}$ (W-Oc-W), (corner- shared octahedral) and 797 cm$^{-1}$(W-O$_e$-W) (edge-shared octahedral) are attributed to the stretching vibrations of Keggin unit respectively. After incorporation of PWA, frequency shifts at 1081 cm$^{-1}$, 982 cm$^{-1}$, 871 cm$^{-1}$, and 769 cm$^{-1}$ are observed in the composite membranes (Sheng Wen et al. 2012 and Lishuang Xu et al. 2015). These frequency shifts clearly demonstrate that there is a specific interaction between Keggin structure of PWA molecules and SPEEK polymer, which is probably by both the terminal and bridging oxygen interaction with sulfonic acid groups of polymer in connection with protonated water molecules. These results indicate that the composite membranes of SPEEK/PES/PWA were prepared successfully.
Figure 5.2 FTIR spectra of (a) PEEK, PES, PWA, SPEEK, SPEEK/PES and SPW 4 (b) Composite membranes
5.3 XRD ANALYSIS

Figure 5.3 XRD spectra of (a) PEEK, SPEEK, PES, SPEEK/PES, SPW4 Membrane (b) Composite membranes
The XRD pattern of pure as well as composite membrane is given in Figure 5.3. PEEK is a semi-crystalline polymer, showing sharp crystalline peaks in the 2θ range of 20-30°.

The introduction of -SO₃H groups into the PEEK alters the chain conformation and could induce disorderliness to the polymer structure and SPEEK is reported to be totally amorphous (Aylin Rahnavard et al. 2014). In the case of the polymer blends, there is a broad peak developed between 2θ = 10° and 30° due to the introduction of PES with SPEEK polymer. The lower crystallinity indicates that the blends are more amorphous and hence exhibit a better flexibility (SrinivasanGuhan et al. 2012).

Pure PWA powder is crystalline in nature shows two characteristic peaks at 2θ of 6.8° and 8.5°. The XRD peaks of PWA in the composite membranes became weaker and broader than those of pure PWA. The increase in the concentration of PWA shows gradual increase in the disperse level and the value of intensity decreases with increasing PWA content (Guhan et al. 2009). The hydrogen bonding between the PWA particles and the -SO₃H groups immobilized the PWA particles from the micro pores of PES. Thus, both SPEEK and PES prevented the PWA particles from leaching away in water (Lishuang Xu 2015 and Song Xue et al. 2007). No characteristic peaks of the PWA were observed in the pattern of composite membranes. These results suggest that the PWA was finely dispersed in the composite membranes with amorphous structure.

5.4 SEM ANALYSIS

The SEM was used to visually investigate the morphology of the pure SPEEK and blend composite membranes. The level of dispersion of inorganic filler depends on the degree of compatibility and dispersibility between the polymer and inorganic components. The morphology of the pure
SPEEK membrane is shown in Figure 5.4(a) reveals the uniform and smooth surface. Furthermore, the microstructures of blend membrane became more compact as the density of PES increases. Strong hydrogen-bonding interactions exist between sulfonic acid groups and PES backbones. The interaction between sulfonic groups of SPEEK and PES changed the morphology of the composite membranes as shown in Figure 5.4(b). The connectivity and the size of hydrophilic regions strongly affect the transport properties and methanol diffusion of the membranes (Yao-Chi Shu et al. 2008). Figure 5.4(c) shows a uniform distribution of fillers throughout the sulfonated polymer matrix, although there was a little aggregated phenomenon in the composites.
The Keggin structure of heteropolyacids is the main reason for occasional occurrence of discordant sites present in the micrographs (Zaidi et al. 2006). This can be explained by the strong hydrogen-bonding interactions between -SO$_3$H and PWA, as confirmed by the FT-IR spectra (Lishuang Xu et al. 2015). The light domains surrounded by dark domains are regarded as hydrophilic segments, which represent the hydrophilic sulfonated groups. The dark regions were assigned to the hydrophobic polymer matrix (Yilser 2014). The -SO$_3$H groups had not only played a role in immobilizing the PWA particles, but also dispersed them evenly in the films. This homogeneous distribution will be favourable for proton transport as it minimizes the distance between particles (Lei Li et al. 2006).

5.5 THERMAL STABILITY

![TGA Profile of PEEK, SPEEK, SPEEK/PES and SPEEK/PES/PWA membranes](image_url)

Figure 5.5 TGA Profile of PEEK, SPEEK, SPEEK/PES and SPEEK/PES/PWA membranes
The thermal stability of membranes was evaluated by TGA. The TGA curves of PEEK, SPEEK and SPEEK / PES blend membranes are shown in Figure 5.5. Three degradation stages are observed in this figure. The initial weight loss below 150°C could be ascribed to dehydration and loss of entrapped solvent. A major weight loss, which occurs in the temperature range between 220°C and 380°C, is due to the desulfonation of sulfonic acid groups in SPEEK. The third degradation at temperature range between 420°C and 580°C, is due to the decomposition of polymer chains (Song-Yul Oha et al. 2010). However, the residue that remains at 800°C in the case of blend membranes was slightly higher than that of SPEEK membrane. This increase in the amount of residue at 800°C is due to the decrease in the effective concentration of the sulfonic acid groupings with the increase of PES content (Srinivasan Guhan et al. 2012 and Yongli Li et al. 2013). The TGA curve of PWA shows a slight weight loss at about 150°C, probably because of dehydration of the water of crystallization, and no further significant weight loss is observed until 700°C (Sheng Wen et al. 2012 and Lishuang Xu et al. 2015). An increase in the PWA content increased the interaction between PWA and -SO₃H, thus increasing the thermal stability of the membrane. The char yield of the SPEEK/PES/PWA (SPW 4) composite membrane was higher than that of pristine SPEEK membrane. The above analysis indicates that the composite membranes possess excellent thermal stability, sufficient to meet the requirements of fuel cells.

5.6 WATER UPTAKE, METHANOL UPTAKE, SWELLING RATIO AND IEC OF THE COMPOSITE MEMBRANES

The water uptake of membranes is known to have a profound effect on the proton transfer and increases the conductivity of solid electrolytes. On increasing the content of PES in the blend, there is a reduction in the water
absorption as evidenced by the results reported in Table 5.1. The decreasing trend may be attributed to the hydrophobicity of PES and similar trend was observed with methanol also. The introduction of hydrophilic solid PWA resulted in the increase of water uptake and swelling ratio of membranes. The increase of the water uptake by the solid proton conductors may be due to the presence of Keggin structure owned by heteropoly acids which itself contains large amount of water and still can take more water due to the specific Keggin properties. Clustered ionomers absorb more water, therefore a large increase in water uptake results in the presence of ion rich regions where proton transfer is particularly fast (Zaidi et al. 2006). Water transportation and methanol permeation take place through the same pathways in the membrane, i.e., through the hydrophilic cluster channels. The swelling ratio is a reflection of the dimensional stability of a membrane, which directly affects the stability of the membrane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (wt%) SPEEK/PES/PWA</th>
<th>Water uptake (%)</th>
<th>Methanol uptake (%)</th>
<th>Swelling ratio (%)</th>
<th>IEC (meqv/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPW1</td>
<td>100/0/0</td>
<td>32.0</td>
<td>29.0</td>
<td>21.3</td>
<td>1.95</td>
</tr>
<tr>
<td>SPW2</td>
<td>90/10/0</td>
<td>18.4</td>
<td>5.2</td>
<td>4.2</td>
<td>1.70</td>
</tr>
<tr>
<td>SPW3</td>
<td>90/10/5</td>
<td>20.5</td>
<td>6.8</td>
<td>7.6</td>
<td>1.63</td>
</tr>
<tr>
<td>SPW4</td>
<td>90/10/10</td>
<td>24.3</td>
<td>7.3</td>
<td>8.9</td>
<td>1.58</td>
</tr>
<tr>
<td>SPW5</td>
<td>80/20/0</td>
<td>15.4</td>
<td>4.7</td>
<td>3.1</td>
<td>1.64</td>
</tr>
<tr>
<td>SPW6</td>
<td>80/20/5</td>
<td>18.7</td>
<td>5.4</td>
<td>6.4</td>
<td>1.57</td>
</tr>
<tr>
<td>SPW7</td>
<td>80/20/10</td>
<td>21.2</td>
<td>6.2</td>
<td>7.8</td>
<td>1.43</td>
</tr>
</tbody>
</table>
Low Methanol uptake indicates low methanol permeability coefficient. On one side, the channels were considerably narrowed by the hydrophobic backbone of PES, so a decrease in the methanol permeation upon loading it with SPEEK (SrinivasanGuhan et al. 2012) is observed. The methanol absorbed by the membranes was very little at low methanol concentration, hence decreases the methanol permeability coefficient of the composite membranes. On the other side, the PWA acted as a “barrier” and stopped the permeation of methanol because of no affinity for methanol (Lishuang Xu et al. 2015).

The ion-exchange capacity plays a vital role in deciding the water uptake and proton conducting ability of the blend membranes. IEC values gradually decreased with increase in the content of PES. Actually, the H⁺ ions available in the sulfonic acid groupings of SPEEK are responsible for the ion-exchange property. When the content of PES is increased in the blend, the effective concentration of SPEEK and hence the SO₃H grouping of SPEEK in the blend decreases. This results in decreasing trend in the IEC values with increasing concentration of PES. Addition of PWA increases the IEC values of the composite membrane than the blend membrane but higher content of PWA decreases the IEC values due to reduction in sulfonic group.

5.7 CONTACT ANGLE OF THE MEMBRANES

The static water contact angles for all of the samples had been evaluated and shown in Figure 5.6. The contact angle of SPEEK/PES blend membranes was higher than that of pristine SPEEK due to hydrophobicity of PES polymer (Shiwen Li et al. 2016). A decrease in contact angle of the composite membrane implies that the surface becomes more hydrophilic by the addition of PWA. All the membranes show contact angle value below 90°, indicating that all membranes were hydrophilic in nature due to the
presence of the sulfonic group in the SPEEK polymer chain and PWA content. The increased hydrophilicity of the membranes could decrease the water contact angle and increase the water flux. The water uptake increases with the increase of PWA content and this is consistent with the decreasing trend (Weifeng Zhao et al. 2013) of contact angle of the membranes.

![Figure 5.6 Contact angle of composite membranes](image)

5.8 PROTON CONDUCTIVITY OF THE MEMBRANES

Proton conductivity depends on various factors, such as the IEC, water uptake and microstructure of the membrane. The proton conductivity of the PEM is expected to be a strong function of the water content of the membrane, with the highest conductivity corresponding to a fully hydrated membrane (Zaidi et al. 2006).
Figure 5.7 Proton conductivity of (a) Blend membrane (b) Composite membrane
As shown in Figure 5.7(a) the conductivity of the blend membrane decreases as PES content increases. The size of the clusters and the connected channels may increase upon the introduction of PWA. The PWA particles in the pores of the composite membrane surface provided more active sites for proton transfer. In addition, the PWA is a kind of strong solid acid, and may donate protons under fully hydrated condition (Song Xue et al. 2007, Hong Wu et al. 2014 and Lishuang Xu et al. 2015). Moreover, the PWA particles dispersed evenly in the membrane matrix formed bridges among the -SO$_3$H groups for proton hopping according to Grotthuss mechanism. The proton conductivities of the membrane at 100% RH are increased with increasing temperatures and PWA contents as shown in Figure 5.7(b). By looking at the water uptake and the conductivity results, it can be seen that water uptake results correlate with the conductivity of the composite membranes. The membrane having higher conductivity has lower value of contact angle, these results suggest that the composite membranes may meet the requirements of fuel cells for portable applications.