CHAPTER 4

SPEEK/PES/MMT BLEND COMPOSITE MEMBRANES

4.1 DETERMINATION OF DEGREE OF SULFONATION

(\(^1\)H-NMR)

The presence of a sulfonic acid group causes a significant down field shift (7.5 ppm) of the hydrogen \(\text{H}_{13}\) compared with other hydroquinone ring. The intensity of this \(\text{H}_{13}\) signal is equivalent to the \(\text{SO}_3\text{H}\) group content (Woei-Jye Lau et al. 2009, Mohtar et al. 2011). Figure 4.1 shows the \(^1\)H-NMR spectrum of the synthesized SPEEK. The ratio between the peak area of the distinct \(\text{H}_{13}\) signal (\(\text{AH}_{13}\)) and the integrated peak area of the signals (\(\text{AH}_{\text{integrated signal}}\)) corresponding to all the other aromatic hydrogen confirms the degree of sulfonation. The estimated degree of sulfonation of the prepared SPEEK is 71.75%.

![Figure 4.1 \(^1\)H-NMR spectra of synthesized SPEEK](image)
4.2 FTIR ANALYSIS

The FTIR spectrum of PEEK, SPEEK, MMT, PES and SPEEK/PES/MMT composite membranes are shown in Figure 4.2. For the spectrum of SPEEK, the bands at around 1224 cm\(^{-1}\), 1082 cm\(^{-1}\) and 1024 cm\(^{-1}\) correspond to the stretching vibration of sulfonic acid groups, confirming the successful sulfonation of PEEK; and the broad band at around 3447 cm\(^{-1}\) is assigned to the O - H vibration from sulfonic acid groups interacting with water molecules (Aylin Rahnavard et al. 2015). In the spectrum of PEEK the peak observed at 1485 cm\(^{-1}\) is due to C-C aromatic ring corresponding to 1,2,4 substitution. The sulfonation process causes the intensity of aromatic C-C band to be decreased and the peak is seen to split to absorption band at 1479 cm\(^{-1}\) and 1407 cm\(^{-1}\).

In the FTIR spectra of MMT, broad band appears at 3625 cm\(^{-1}\), 3434 cm\(^{-1}\) and 1636 cm\(^{-1}\) corresponds to the stretching and bending vibrations for the hydroxyl groups present in nanoclay. Anti symmetric Si – O stretching vibration is observed at 1053 cm\(^{-1}\) and Si-O-Al vibrations at 797 cm\(^{-1}\) and 529 cm\(^{-1}\) (Hacer Doğan et al. 2011).

In PES 3635 cm\(^{-1}\) and 3400 cm\(^{-1}\) are the non-hydrogen and hydrogen bonded O-H vibrations. The peaks observed at 3070 cm\(^{-1}\) and 1592 cm\(^{-1}\) confirms the C-H stretching from aromatic rings. The vibrations at 2395 cm\(^{-1}\) and 1784 cm\(^{-1}\) confirms the O = S = O and S = O stretching vibrations respectively (Sa Liu et al. 2012, Woei-Jye Lau et al. 2009 and Kalambettu Aravind et al. 2014).

The presence of H-O-H stretching bands at 3461 cm\(^{-1}\) and H-O-H bending bands at 1650 cm\(^{-1}\) indicate the formation of composite membranes. The peak at 3066 cm\(^{-1}\), 2439 cm\(^{-1}\), 1474 cm\(^{-1}\) confirms the C-H stretch, O=S=O vibration and C–C aromatic ring respectively.
Figure 4.2 FTIR spectra of (a) PEEK, SPEEK, MMT, PES, SPM 2
(b) Composite Membranes
The emergence of small peak is due to the presence of O-S-O stretching vibration, which was reported to be appeared at around 1023 cm\(^{-1}\). The shifting of O=S=O peaks to the right (2356 cm\(^{-1}\)) when compared with that of PES (2395 cm\(^{-1}\)) and the observation of a new peak at 1629 cm\(^{-1}\) was indicative of an interaction between SO\(_3\)H group of SPEEK and O=S=O group of PES.

### 4.3 XRD ANALYSIS

The XRD Spectra of pure, Figure 4.3(a) and composite membranes, Figure 4.3(b) are displayed. From the XRD pattern of PEEK it is known that the pure polymer has crystalline nature. The four sharp crystalline peaks of pure PEEK are found at 20 equal to 18.5°, 20.2°, 23° and 28.7° which corresponds to the diffractions of (110), (111), (200) and (211) crystalline planes respectively (Aylin Rahnavard et al. 2015). The crystalline peak for pure PES polymer was found at 18.04° with a d spacing of 4.80Å. SPEEK is amorphous due to the introduction of the sulfonic acid groups that could induce disorderliness to the polymer structure. Based on the intensity of the peaks (2θ) between 10 and 25°, the material was evidenced to be more amorphous than crystalline. In the XRD pattern of MMT Zhang Gaowen et al., observed one crystalline peak at 2θ = 5.82° with silicate layer spacing of 1.51 nm (Mehrab Fallahi Samberan et al. 2013 and Zhang Gaowen et al. 2005) in the d\(_{001}\) crystalline plane. No peaks are observed in the case of blend nanocomposite membrane, which implies the good miscibility of PES with SPEEK and formation of exfoliated structures due to loss of the structural patterns of the silicate layers (MMT), which is completely dispersed in the blend composite matrix.
Figure 4.3 XRD Spectra of (a) PEEK, SPEEK, PES, MMT, SPM 2 (b) Composite Membranes
4.4 SEM ANALYSIS

Figure 4.4 SEM image of (a) Blend Membrane (b) Composite Membrane
Figure 4.4 shows the morphology of the blend and composite membrane which are helpful to examine the formation of blend composite membrane. The observation of high surface roughness of the composites is easily interpreted from the images. The composite membrane appears to be pores – free even at high magnification. The composites with low filler content were wet well by the polymer matrix. The darker region represents the presence of hydrophilic ionic clusters while the lighter part represents the hydrophobic part of the membrane.

4.5 THERMAL STRENGTH OF THE MEMBRANES

Good thermal properties are required for PEMs in DMFCs to guarantee a long lifetime of fuel cells. The TGA thermo gram of pure PEEK and SPEEK are displayed in Figure 4.5(a). It is observed that PEEK starts losing weight after 550°C under moisture free condition. The degradation temperature for SPEEK is lower than that for PEEK because of the catalytic degradation of the polymer chain caused by SO$_3$H. Thermogravimetry profiles of the blend composite membranes are shown in Figure 4.5(b). All the membranes exhibit three steps of degradations due to the processes of thermal dehydration, degradation and decomposition of the polymer backbone (Hacer Doğan et al. 2011). The first weight loss between 50°C and 220°C is due to the evaporation of physically weakly and chemically strongly bound water molecules by SO$_3$H groups of the blend composite membranes. The second weight loss between 220°C and 450°C is attributed to the cleavage of sulfonic acid groups. The third weight loss starts at 490°C reflects the decomposition of polymer backbone of both SPEEK and blend composite membranes. Comparison of the TGA curves of SPEEK and blend composite membranes reveals that the addition of PES improves the thermal stability of the membranes. The weight loss observed beyond 620°C is for the decomposition of SPEEK/PES main chain.
Table 4.1 Glass transition and decomposition temperature of the membrane

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>$T_d$ (5% mass loss)</th>
<th>$T_d$ (10% mass loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEEEK</td>
<td>185</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES</td>
<td>227</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPM 1</td>
<td>172</td>
<td>222</td>
<td>268</td>
</tr>
<tr>
<td>SPM 2</td>
<td>198</td>
<td>227</td>
<td>270</td>
</tr>
<tr>
<td>SPM 3</td>
<td>255</td>
<td>232</td>
<td>288</td>
</tr>
<tr>
<td>SPM 4</td>
<td>265</td>
<td>233</td>
<td>289</td>
</tr>
</tbody>
</table>

The determination of the glass transition temperature provides information on the miscibility of blends. It is observed from the Table 4.1 that the blend membranes exhibit only one glass transition temperature ($T_g$) indicates good miscibility of two polymers. As PES content in the blend membrane increases a shift in $T_g$ to higher temperatures compared with the pure SPEEK membrane is observed (Han-Lang Wu et al. 2006 and Woei-Jye Lau et al. 2009). MMT shows a typical weight loss transitions around 630°C, which is attributed to dehydroxylation of the aluminosilicate structure (Hacer Doğan et al. 2011). The higher decomposition temperature attributes to the barrier characteristics of clay nanolayers, which implied a delayed dehydration process due to slowing down of out diffusion of water from the SPEEK matrix (Priscila Anadãoa et al. 2013). It was observed that the thermal decomposition of blend composite membrane was well above the normal operating temperature of DMFCs.

The DS of SPEEK can also be calculated from TGA curve by taking into account the weight loss corresponding to de sulfonation step and this agrees well with the $^1$H-NMR result (Soma Banerjeea et al. 2016).
Figure 4.5 TGA Profile of (a) PEEK and SPEEK (b) SPEEK and composite membranes
4.6 LIQUID UPTAKE, IEC AND HYDRATION NUMBER OF THE COMPOSITE MEMBRANES

The ion-exchange capacity plays a vital role in deciding the water uptake and proton conducting ability of the blend membranes. The liquid uptake, swelling ratio, IEC and hydration number of all the prepared membranes at room temperature are summarized in Table 4.2. When the content of PES is increased in the blend, the effective concentration of SPEEK and hence the SO$_3$H grouping of SPEEK in the blend membrane decreases. Actually, the H$^+$ ions available in the sulfonic acid groupings of SPEEK are responsible for the ion-exchange property. As the monovalent ions located between the silicates layers of MMT tend to attract polar solvent such as water, hence the water uptake and hydration number of blend composite membrane is higher than that of pristine SPEEK membrane (Mohtar et al. 2011 and Zhang Gaowen et al. 2005). However, the amount of hydrogen bonding generated between PES and sulfonic acid groups increases with the PES content, and this reduces the excessive swelling of the polymer under wet conditions and thereby improves the dimensional stability of the blend membranes (Yao-Chi Shu et al. 2008, Han-Lang Wu et al. 2006 and Kalambettu Aravind et al 2014). In the case of nanocomposite membrane the dispersion of silicate nanosheets restricts the migration of methanol molecules. At low MMT loading of 1.5wt% both the adequate water uptake and low methanol crossover have been fulfilled.

<table>
<thead>
<tr>
<th>Membrane Code</th>
<th>Water uptake(%)</th>
<th>Methanol uptake(%)</th>
<th>IEC</th>
<th>Hydration number(λ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPM 1</td>
<td>29.0</td>
<td>12.85</td>
<td>2.24</td>
<td>7</td>
</tr>
<tr>
<td>SPM 2</td>
<td>30.3</td>
<td>12.50</td>
<td>2.31</td>
<td>8</td>
</tr>
<tr>
<td>SPM 3</td>
<td>28.6</td>
<td>13.38</td>
<td>2.2</td>
<td>6</td>
</tr>
<tr>
<td>SPM 4</td>
<td>26.4</td>
<td>15.28</td>
<td>2.19</td>
<td>5</td>
</tr>
</tbody>
</table>
4.7 CONTACT ANGLE

Contact angle measurement was applied to investigate the relative hydrophilicity or hydrophobicity of the membrane surface. The static water contact angles for the prepared samples are shown in Figure 4.6. The contact angle of the SPM 2 membrane decreases due to addition of optimum content of MMT with blend polymer membrane. In addition, the water contact angles distinctly dependent on the contacting time between the membrane and water, and the angles decreased with the time. The hydrophilic groups on the membrane surface affected the water contact angle at the beginning; then the water was probably soaking into the membranes pores resulted in the decrease of the contact angle. As the content of hydrophobic PES increases the contact angle increases. The observed increase in contact angle reveals that additives enhanced the hydrophobicity of the membranes. This result is correlated with water uptake and conductivity data.

Figure 4.6 Water Contact angle of membranes
4.8 PROTON CONDUCTIVITY OF THE COMPOSITE MEMBRANES

The proton conductivity depends directly on the water uptake and the IEC of the sulfonated polymer. The water uptake decreases as the PES content increases. This is because the formation of hydrogen bonds with the sulfonated groups reduces the number of free SO$_3$H groups and water absorption. The objective of introducing optimum wt% of MMT particles into the polymer matrix was to enhance the proton transfer through the membrane by retaining water within the membrane and to create water mediated pathways while contributing their own proton conductivity. A good dispersion of MMT into SPEEK retains water within the membrane to yield the high ionic conductivity since more cations are mobile and available for conduction (SrinivasanGuhanet al. 2012 and Han-Lang Wu et al. 2006).

The dependence of conductivity with composition is shown in Figure 4.7 (a) and the temperature dependence of conductivity of the membrane is shown in Figure 4.7(b). When SPEEK is blended with a low concentration of PES the blend membrane possess a better conducting property than the pure SPEEK membrane. When the density of sulfonic groups is low, the hydrophilic sulfonic groups form isolated ionic clusters in the continuous hydrophobic phase, and the diameter of the channels formed by ionic clusters may be reduced upon the introduction of hydrophobic materials (SrinivasanGuhanet al. 2012 and Mohammad Mahdi Hasani-Sadrabadiaet al. 2010b). The proton conductivity of all the membranes increases as the temperature increases and conductivity of SPM 2 composite membrane approaches the value of $1.18 \times 10^{-1}$ Scm$^{-1}$ at 70°C.
Figure 4.7 Proton conductivity of Membranes as a function of (a) PES content (b) Temperature