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## Composite membranes of sulfonated polyether ether ketone and montmorillonite as electrolyte for direct methanol fuel cell

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### ABSTRACT

Composite polymer electrolyte membranes made of sulfonated polyether ether ketone (SPEEK) polymer host and montmorillonite (MMT) ceramic fillers (2–10 wt.%), was prepared by a solution casting method. The characteristic properties of the SPEEK/MMT composite polymer membranes were investigated using thermo gravimetric analysis (TGA), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), and the AC impedance method. The SPEEK/MMT composite membrane showed good thermal and mechanical properties and appreciable ionic conductivity in the order of  $10^{-3}$  S/cm. Due to the incorporation of the inorganic filler, there is a decrease in the ion exchange capacity (IEC) when compared to the pristine SPEEK which was 2.20 mequiv/g. Though the ionic conductivity decreased with increasing content of MMT, there is an improvement in the mechanical properties with the introduction of MMT. The tensile strength of virgin SPEEK was 24.6 MPa, whereas the composite with 10% MMT showed 40.1 MPa. The incorporation of MMT into the SPEEK matrix enhanced the resistance to the permeation of methanol. The selectivity ratio of the composite membranes were well ahead of pristine SPEEK indicating its suitability for DMFC. It was revealed that the addition of MMT fillers into the SPEEK matrix could markedly improve the electrochemical properties of the composite membranes; which can be accomplished by a simple blend method. As a result, the SPEEK/MMT composite polymer appears to be a good candidate for the DMFC applications.

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### KEYWORDS

SPEEK;  
MMT;  
DMFC;  
Composites;  
Polymer Electrolyte.

### INTRODUCTION

In the last one to one and half decade, fuel cells are extensively studied as one of the new energy conversion devices<sup>[1,2]</sup> for applications such as transportation, small portable devices like mobile phone, laptop etc.

Among the diverse fuel cells, the proton exchange membrane fuel cells (PEMFCs) offer advantages of high power density, low operating temperature (60-100°C) with consequent rapid start up and dynamic response. However, the major barriers of PEM fuel cells using hydrogen as a fuel includes production, distribution, stor-

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age, humidification etc. Also the very low flash point of hydrogen (-423 F) causes increasing concerns about the safety issues of hydrogen. All these limitations enabled researchers to think of other fuels that can be easily oxidized. Direct oxidation fuel cells using liquid methanol as a fuel has already attracted intensive research<sup>[3-6]</sup>. There are many types of fuel cells like Proton Exchange Membrane Fuel Cell (PEMFC), Alkaline Fuel Cell (AFC), Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC), Phosphoric Acid Fuel Cell (PAFC). Among the different types of fuel cells, direct methanol fuel cells (DMFCs) are one of the most promising candidate to provide the strong impetus for technological expansion due to their low temperature operation, fast startup, and high specific power density which makes it suitable for portable devices, mobile phones, and automobiles.

One of the key component that determines the efficiency of the fuel cell is the proton exchange membrane (PEM) which not only acts as a medium for the transportation of protons but also as a barrier that prevents mixing of the fuel gases (hydrogen and oxygen). The currently developed fuel cell technology is based on perfluoro sulfonic acid membranes as electrolytes, such as Nafion<sup>®</sup><sup>[7-9]</sup> which exhibits many attractive properties like excellent proton conductivity, high thermal and mechanical stability. The commercialization of the Nafion<sup>®</sup> membrane was severely affected due to the drawbacks like (i) high cost, (ii) non eco-friendly nature, (iii) high cross-over of methanol especially in the case of Direct Methanol Fuel Cell (DMFC), (iv) dependence on relative humidity in maintaining proton conductivity, (v) loss of proton conductivity at elevated temperatures, etc. To overcome these shortcomings associated with the Nafion<sup>®</sup> and other similar perfluorinated membranes, several hydrocarbon based aromatic polymers were considered for the synthesis of PEM. It includes sulfonated polyether ether ketone (SPEEK)<sup>[10-12]</sup>, sulfonated polyphenylene oxide (SPPO)<sup>[13-14]</sup> and sulfonated polybenzimidazole<sup>[15-17]</sup>. In all the above cases, the ionic conductivity at higher temperatures (> 100°C) must be improved which implies that better water retention at higher temperatures is an absolute requirement. In this context, in order to enhance the water retention property of the polymer electrolyte membranes and also to improve the stability of such

membranes, various inorganic fillers such as silica, titania, zeolites, montmorillonite (MMT) have been added into the polymer systems<sup>[18-27]</sup>. Among the various aromatic hydrocarbon based polymers, sulfonated polyether ether ketone (SPEEK) has been demonstrated to exhibit stable performance that is comparable to Nafion<sup>®</sup> in a fuel cell at 50°C for more than 4300 hours<sup>[28]</sup>. In order to enhance the proton conductivity of SPEEK, the incorporation of several inorganic heteropolyacids were considered<sup>[29-31]</sup>. J.H.Chang et al<sup>[32]</sup> reported SPEEK fuel cell membranes incorporated with MMT with a special effort to reduce the methanol permeability.

Montmorillonite is a very soft phyllosilicate group of minerals that typically form in microscopic crystals, forming a clay. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped. MMT has large surface areas (220–270 m<sup>2</sup>g<sup>-1</sup>) and a negative layer charge. Its proton form possesses a proton conductivity of 10<sup>-4</sup> S/cm at room temperature<sup>[33]</sup>. Recently MMT has been used to improve the performances of Nafion<sup>[24, 34-37]</sup> and SPEEK polymer electrolyte membranes<sup>[32]</sup> with a special effort to reduce the methanol permeability.

In concise, the PEM has to serve three purposes in a DMFC, (i) it has to be stable under the operating conditions employed, (ii) it has to provide high proton conductivity and (iii) it needs to have a low permeability for methanol<sup>[6]</sup>. But one of the serious problems that limit the commercialization of DMFCs is the cross-over of methanol from the anode (where it is fed) to the cathode through the polymer electrolyte membrane. The cross-over of methanol seriously affects the overall cell performance.

In our current investigation, we made an attempt to characterize of SPEEK membranes incorporated with various amounts of unmodified MMT. Various properties like IEC, Water and methanol absorption, durability, mechanical properties, methanol permeability and proton conductivity were determined. The selectivity ratio of the composite with 10% MMT was 8.60 x 10<sup>5</sup> Sscm<sup>-3</sup> which is very well better than pristine SPEEK with 1.93 x 10<sup>5</sup> Sscm<sup>-3</sup>. All the composite membranes were stable upto 200°C for a successful application as PEM in DMFC. The T<sub>g</sub> values of various composite

membranes were obtained from the DMA studies.

## EXPERIMENTAL

### Materials and chemicals

PEEK was procured from Victrex, England and was dried overnight at 100°C before use. The organic clay montmorillonite (MMT) was kindly supplied by Sigma-Aldrich, USA. Sulfuric acid was procured from Merck, N-Methyl pyrrolidone (NMP) and methanol was obtained from SRL Chemicals, India.

### Sulfonation of PEEK

In a typical process, about 10g of dry PEEK was taken in a three-necked RB flask. Then calculated quantity of sulfuric acid was added and the contents of the flask were vigorously stirred at room temperature. After six hours, the contents of the flask were poured into a large excess of crushed ice. The innumerable number of fibres that was formed was recovered by filtration. It was then washed plenty of times with deionised water until the pH of the wash water falls between 6.5 and 7.0. It was then dried in an oven at 90°C for 10 hours. The resulting product is the sulfonated form of polyether ether ketone (SPEEK).

### Preparation of composite membrane

The procedure given by Y. F. Lin et al<sup>[38]</sup> was followed. To prepare the composite membrane, a desired amount of unmodified MMT was added to a 4 wt% SPEEK solution (SPEEK dissolved in NMP). It is then allowed for stirring and degassed by ultrasonication. The solution was poured onto a clean petri dish. The solution was kept in a hot air oven at 90°C for 12 hours. The composite membrane was obtained in the form of a clear, pale brown, transparent membrane. It was peeled off from the petri dish and was stored for further

**TABLE 1 : Membrane code and composition of composite membranes**

Membrane Code	% Composition SPEEK:MMT
SM 0	100:00
SM 2	98:02
SM 4	96:04
SM 6	94:06
SM 8	92:08
SM 10	90:10

investigation. The thickness of the membranes was maintained at 60 μ. The variations in the composition of the different composites are given in TABLE 1.

In the coding given for the composite membranes, SMX, S stands for SPEEK, M stands for MMT and X denotes the dosage of MMT in the composite membrane.

### Characterization

Proton NMR spectra were obtained with Bruker H<sup>1</sup>-NMR spectrometer. In order to avoid the peaks due to the solvent, deuterated dimethylsulfoxide was used as the solvent.

The ion exchange capacity (IEC) indicates the number of milli equivalents of ions in 1g of the dry polymer. It was determined by titration method. The membrane in its acid form was weighed and then soaked at room temperature in an aqueous solution containing a large excess of KCl in order to extract all the protons from the membrane. The electrolyte solution was then neutralized using a very dilute Na<sub>2</sub>CO<sub>3</sub> solution of known concentration (0.01N). The EW (equivalent weight) values were calculated from the dry weight of the membrane divided by the volume and the normality of the Na<sub>2</sub>CO<sub>3</sub> solution. The IEC values were expressed as number of meq. of sulfonic groups per gram of dry polymer.

The amount of solvent intake by the membranes was studied. The dried membranes were weighed and soaked in water and methanol separately and allowed to get equilibrated at room temperature for 24 hours, above which the weight was constant. The swollen membranes were then quickly weighed after blotting the surface water and the values noted. The swelling degree was determined using the formula,

$$SW = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100$$

Where,

$M_{\text{wet}}$  = Weight of wet membrane,

$M_{\text{dry}}$  = Weight of dry membrane.

The number of water molecules per sulfonic site ( $\lambda$ ) can be determined by the following equation,

$$\lambda = \frac{(M_{\text{wet}} - M_{\text{dry}}) / M_{\text{water}}}{M_{\text{dry}} \text{ IEC}}$$

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Evaluation of methanol permeability was carried out using an in-house glass diffusion cell, which consisted of two compartments. Initially one compartment (Cell A = 50 ml) was filled with a solution of methanol in deionized water (20% methanol). The other cell (Cell B = 50 ml) was filled with deionized water. The membrane was clamped between the two compartments. The solution in each compartment was continuously stirred by means of magnetic stirrers to ensure uniform concentration. The methanol concentration was determined by refractometer. The concentration of methanol in cell B as a function of time is given by

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C_A (t - t_0)$$

Where  $C_A$  and  $C_B$  are the concentrations of methanol in cell A and cell B respectively. A, L and  $V_B$  are the area of the membrane, thickness of the membrane and volume of methanol in cell B respectively. D and K are the methanol diffusivity and partition coefficient between the membrane and adjacent solution respectively. The product DK is the methanol permeability, which was calculated from the slope of the straight-line plot of methanol concentration vs permeation time.

The measurements of proton conductivity,  $\sigma$  (S/cm) of the membranes were carried out using Autolab Potentiostat Galvanostat impedance analyser at ambient temperature and 100% RH. Membranes with required dimensions were cut and pre-treated with 0.01N sulphuric acid and kept in water for 100% hydration. Then it was placed between two silver electrodes with an area of 1.33cm<sup>2</sup> with a uniform pressure applied to hold the system. The cell set-up is Ag/MMT + SPEEK/Ag.

The resistance offered by the membrane was calculated and then converted to conductivity values using the formula;

$$\sigma = L / (R \times A)$$

Where,  $\sigma$  is the conductivity in S/cm, R is the resistance offered by the membrane in ohms, L is the thickness of the membrane in cm and A is the area of the membrane in cm<sup>2</sup>.

XRD measurements were performed using an X'Pert Pro diffractometer. The dried samples were mounted on an aluminium sample holder. The scanning angle ranged from 1° to 80° with a scanning rate of 2°

per min. All the spectra were taken at ambient temperatures ( $25 \pm 2^\circ \text{C}$ ).

The surface morphology of the composite membranes was investigated using Scanning Electron Microscope (JEOL 6360 instrument). A piece of membrane was vacuum sputtered with a thin layer of Gold prior to SEM examination.

The dynamic mechanical measurements were made using the Dynamic Mechanical Analyzer 242C instrument supplied by NETZSCH, Germany. The temperature ranged from RT to 240°C with the heating rate of 5°C/min.

TGA analysis is mainly carried out to determine the thermal stability of the composite membranes. The change in weight of the membrane with increase in temperature at a heating rate of 20°C/min in the range of the temperature between 30°C and 800°C is followed using a SDT Q600 US analyser.

The mechanical properties were obtained from Hounsfield Universal Testing Machine. The samples were cut into a size of 5 mm x 50 mm as reported by D.

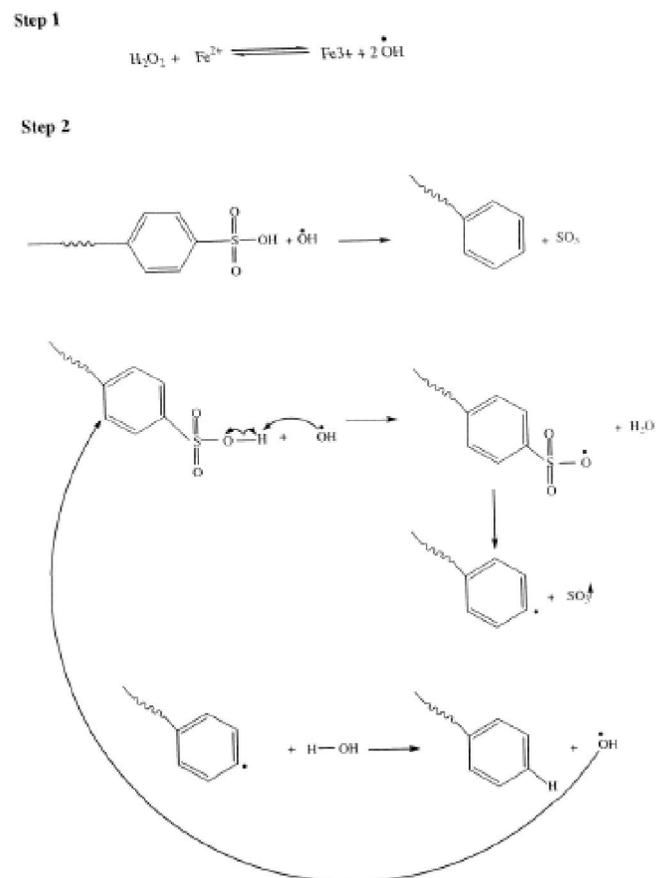


Figure 1 : Mechanism of durability testing

H. Jung et al<sup>[39]</sup>. The cross head speed was set at a constant speed of 10 mm/min. For each testing reported, at least three measurements were taken and the average value was reported.

For testing the durability of the composite membranes, the following procedure was adopted. Initially, a 4 ppm ferrous ammonium sulfate in 3% H<sub>2</sub>O<sub>2</sub> was freshly prepared and the temperature of the solution was maintained at 80°C. The composite membrane with the dimension of 0.5cm<sup>2</sup> was cut and soaked in the solution. The time required for the physical disintegration of the composite membrane is carefully noted down and reported. The reaction is expected to occur by free radical mechanism and the probable mechanism is shown in Figure 1.

## RESULTS AND DISCUSSION

The process of sulfonation is considered to be the most important stage during the synthesis of the polymer electrolyte. It not only provides the exchangeable protons to make the polymer capable of exchanging ions, especially protons but also increases the hydrophilicity of the polymer electrolyte. An increase in the hydrophilic character is highly appreciable as it increases the water uptake capacity which in turn increases the proton conduction, the most characteristic property for the polymer electrolyte to be used in fuel cells. Though on one hand an increase in the hydrophilic character is desired, on the other hand too much of sulfonation could lead to dissolution of the electrolyte itself in water.

The <sup>1</sup>H-NMR spectra of SPEEK sample is shown in Figure 2 and the numbering of various protons is shown in Figure 3. As expected, the aromatic proton resonance signals are observed in the range of 7 - 7.75 ppm. The H<sub>B</sub> protons appear as a doublet at 7 ppm. H<sub>C</sub> and H<sub>D</sub> appear as a doublet at 7.15 ppm. The multiplet at 7.8 corresponds to H<sub>A</sub> protons. In the spectra, the H<sub>C</sub> of the unsubstituted hydroquinone ring of PEEK repeat unit appears as a characteristic singlet at 7.26<sup>[40]</sup>. The presence of a sulfonic acid group causes a new peak at 7.51 which can be assigned to H<sub>E</sub>.

The ion exchange capacity (IEC) values of the various composite membranes were given in Figure 4.

Though the IEC values were found to be decreasing with the content of MMT in the composite, all the

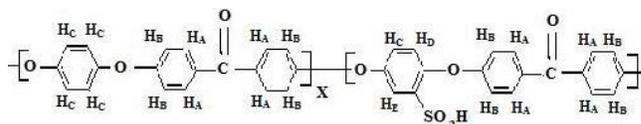


Figure 2 : Proton assignment in <sup>1</sup>H-NMR

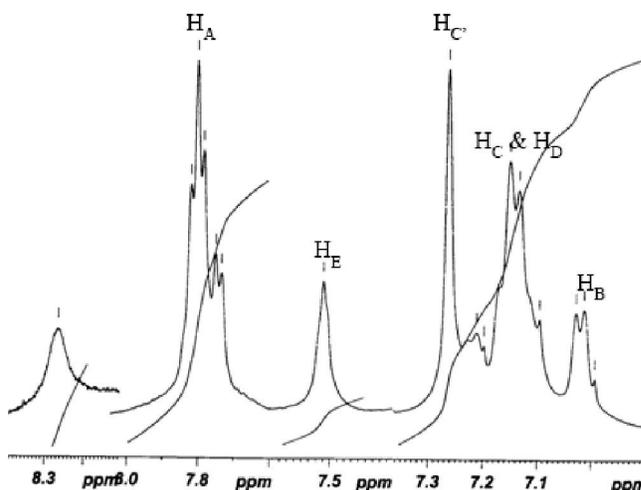


Figure 3 : <sup>1</sup>H-NMR Spectra of SPEEK

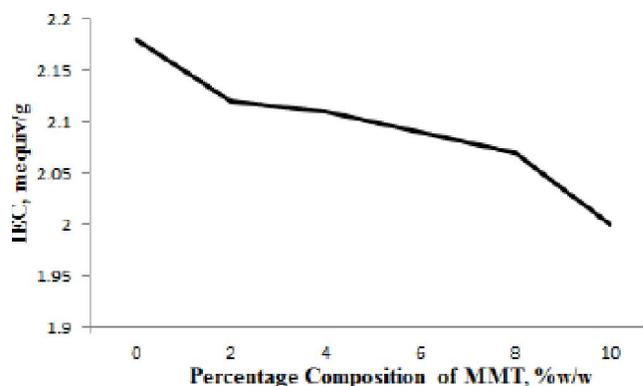


Figure 4 : IEC of composite membranes

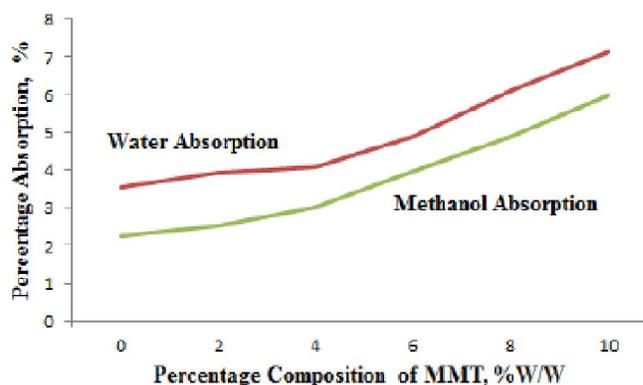


Figure 5 : Water and Methanol Absorption

composite membranes exhibit an IEC value better than Nafion<sup>®</sup> 117 which was reported to be 0.91 mequiv/g<sup>[37]</sup>. Actually, the protons that are available in the sulfonic acid groupings of SPEEK were responsible for the exchange of ions. When the concentration of MMT

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is increased in the composite, the concentration of SPEEK decreases and in other words, the effective concentration of the sulfonic acid groupings decreases. This obviously account for the lowering of IEC values.

The water/ alcohol absorption results were given in Figure 5.

The water content has great effects on the properties of electrolyte membrane. A high water content can facilitate the transport of protons, but too much water absorption results in mechanically less stable membrane. The water uptake of Nafion® 117 was reported to be 28.51%<sup>[41]</sup> and in the case of the composite membranes, the water absorption was found to be increasing with increasing content of MMT. It is well-known that the inorganic filler is capable of storing a lot of water with it. The water uptake is very crucial as it is closely related to the proton conducting ability<sup>[33]</sup>. The methanol absorption was also found to follow a similar trend like water absorption. The number of water molecules per sulfonic site ( $\lambda$ ) in the case of pristine SPEEK was found to be 7.

The methanol permeability is a serious factor which reduces the efficiency of the fuel cell particularly in the case of Direct Methanol Fuel Cell (DMFC). The permeation not only allows the methanol fuel to the cathodic compartment but also mixing of the fuel with the incoming gas at the cathode. This drastically reduces the performance of the fuel cell. With an increase in the MMT loading, the methanol permeability decreases and the results are shown in TABLE 2.

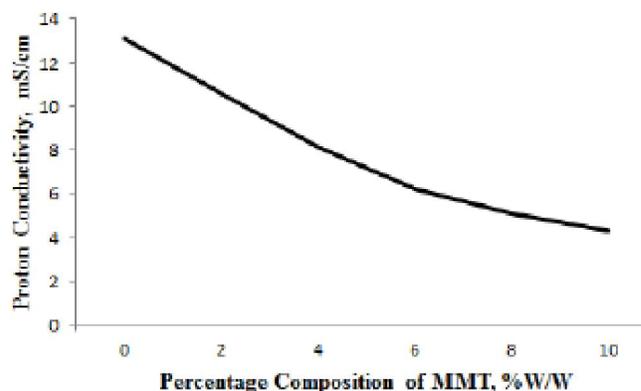
**TABLE 2 : Methanol Permeability and Selectivity Ratio of the composite membranes**

Membrane Code	Methanol Permeability, $10^{-8}$ cm <sup>2</sup> /s	Selectivity Ratio, $10^5$ Sscm <sup>-3</sup>
SM 0	6.8	1.93
SM 2	1.5	7.07
SM 4	1.1	7.36
SM 6	0.8	7.75
SM 8	0.6	8.50
SM 10	0.5	8.60

This may be due to the dispersion of the inorganic filler in the composite membrane that prevents methanol from transferring through the membrane. The decrease in the methanol permeability makes these composite as a possible low cost alternative to Nafion® 117 for applications as an electrolyte membrane in DMFC.

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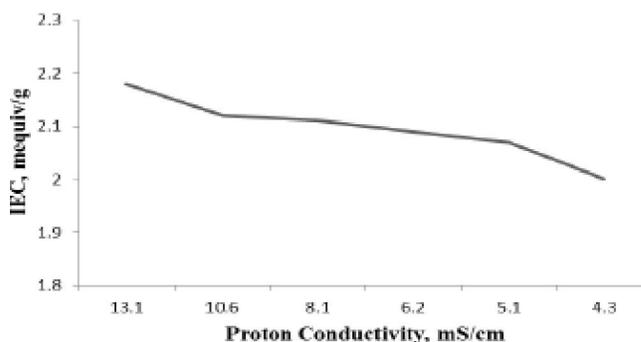
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**Figure 6 : Proton conductivity of the membranes**

The results of the proton conductivity are given in Figure 6.

The proton conductivity of Nafion® 117 was reported to be  $2.95 \times 10^{-2}$  S/cm. The proton conductivity of the composite membranes tends to decrease with the addition of MMT as reported elsewhere<sup>[38]</sup>. The water uptake plays an essential role in ionomer membrane properties. The swelling behavior is closely related to the proton conductivity<sup>[42]</sup>. Though the water uptake is more for the composite with higher MMT content, the proton conductivity was found to be decreasing with the dosage of MMT. A possible reason that could be attributed to the reduction in the proton conductivity is that, as the content of MMT is increased in the composite, the effective concentration of SPEEK and hence the SO<sub>3</sub>H groupings decreases. The protons of the sulfonic acid groupings are mainly responsible for the proton conductivity. This could be more clearly understood through Figure 7. As the IEC decreases there is a gradual reduction in the proton conductivity also.



**Figure 7 : IEC vs Proton Conductivity**

An electrolyte membrane in a DMFC should have two important properties; the proton conductivity should be as high as possible and the methanol diffusion should

be as low as possible. That is to say, the higher the ratio of proton conductivity to methanol permeability (referred to as the selectivity ratio), the better the membrane is. The selectivity ratios of pristine SPEEK as well as the composite membranes are given in TABLE 2. The pristine SPEEK electrolyte membrane exhibited a selectivity ratio of  $1.93 \times 10^5 \text{ Sscm}^{-3}$  while the composite membranes exhibited a higher ratio. The higher selectivity ratio of the composite membranes indicate that they are better suitable as electrolyte membranes for DMFC.

Figure 8 shows the XRD patterns of SPEEK, MMT and two representative composite membranes with various compositions. It was reported earlier that PEEK is semi-crystalline<sup>[43]</sup>. However, SPEEK is amorphous perhaps due to the introduction of the sulfonic acid groups, which may induce disorderliness to the polymer structure. It is well-known that MMT is crystalline in nature.

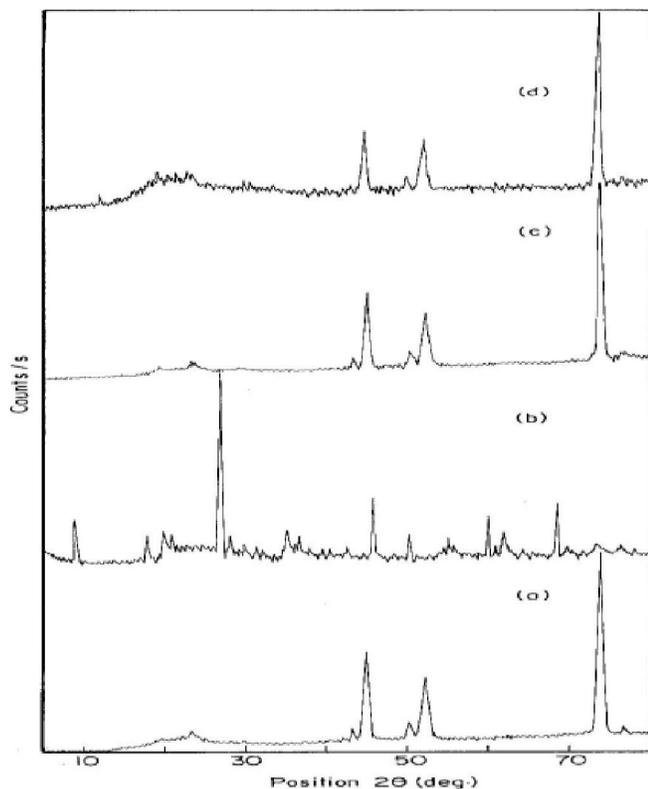
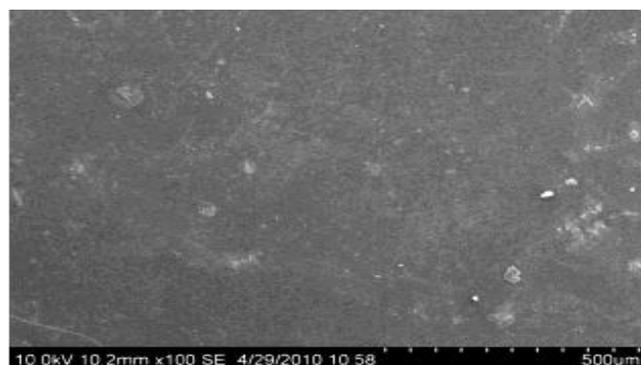


Figure 8 : XRD pattern of a) SPEEK, b) MMT, c) SM 4 and d) SM 8

From the diffraction patterns, it was observed that the sharp crystalline peaks at  $2\theta < 40^\circ$  in pure MMT became less prominent in the composite membrane. The



(a)



(b)



(c)



(d)

Figure 9 : SEM image of a) SPEEK b) SM 4 c) SM 8 and d) MMT

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MMT nanosized particles obtained from the crystalline parts of the original material diffuse inside SPEEK polymer chains and produce particulate nanocomposite membranes.

The SEM images of SPEEK and two representative composite membranes are given in Figure 9.

The SEM image looks dense, clear and homogeneous indicating homogeneity in the dispersion of the MMT particles seen as solid spots in the SEM images into the polymer matrix. Even at higher magnifications, the composite membranes showed no fissures which may be due to the high boiling solvent used for the casting purpose. The evaporation of NMP solvent (boiling point 203°C) was performed at 90°C indicating a very slow process of evaporation. On the other hand, if the evaporation was done at a faster rate or if a low boiling solvent is used, fissures could be observed<sup>[44]</sup>. The composite membranes appear to be pores-free even at higher magnification.

The DMA spectra of SPEEK and two composite membranes are given in Figure 10.

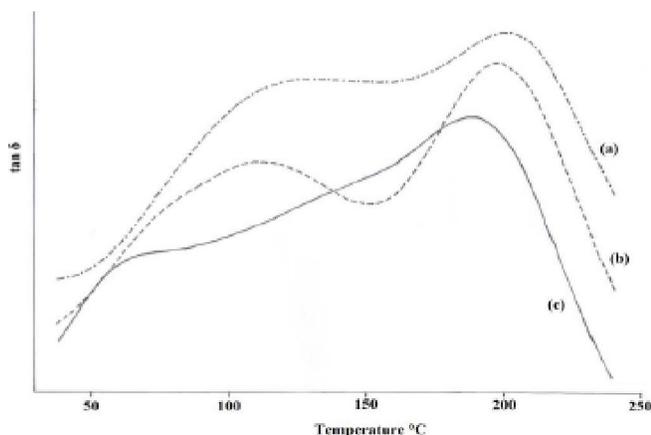


Figure 10 : DMA pattern of a) SPEEK, b) SM 4 and c) SM 8

The tangent delta ( $\tan \delta$ ) is the dissipation factor which is defined as the loss modulus over storage modulus. This parameter provides an indication of the strength of the material's ability to store and dissipate energy. A high tangent delta value indicates that the material is dissipating most of the energy supplied to it and hence the materials possess a high damping properties and viscous behaviour. On the other hand, a low tangent delta indicates that the material is storing most of the energy supplied to it and hence show low damping properties and elastic behaviour. The peak of the tangent delta plot as a function of temperature provides a less

ambiguous value of glass transition temperature when compared to DSC.

The DMA results showed that the glass transition temperature ( $T_g$ ) of SPEEK membrane was around 200°C, which was consistent with the results previously reported<sup>[45, 46]</sup>. On introducing MMT particles into the SPEEK matrix, the  $T_g$  of the resulting composite decreases to a lower temperature. This may be due to the weakening of the polymer chains because of the incorporation of the MMT particles into the polymer matrix.

The TGA spectra of SPEEK and two representative composite membranes (SM 4 and SM 8) were given in Figure 11. In the case of SPEEK, a three stage degradation was observed. The initial loss upto 175°C may be attributed to the loss of physically and chemically bound water along with trace amount of residual solvent. The weight loss that occurs between 200°C and 375°C may be due to the loss of sulfonic acid groupings. The penultimate weight loss from 450°C to 600°C may be correlated to the main chain degradation of the polymer backbone. The inorganic filler in the case of composite membrane are stable upto a very high temperature. Because of this high thermal stability, the composite membranes also follow a similar trend like SPEEK. However, the residue that remains after 800°C in the case of composite membranes are higher than that of SPEEK membrane which is a clear evidence for the existence of an inorganic material in the membrane under investigation.

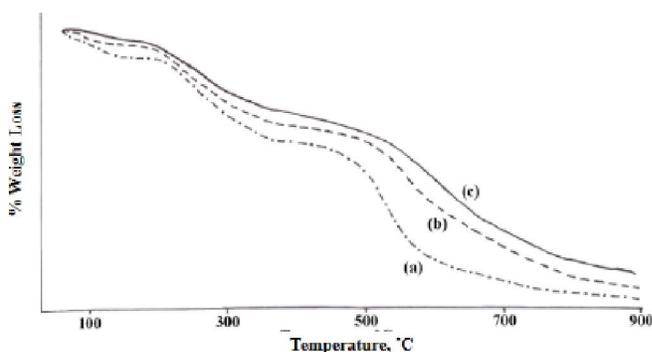


Figure 11 : TGA spectra of a) SPEEK, b) SM 4 and c) SM 8

The tensile strength and percentage elongation at break of the various composite membranes are given in TABLE 2. There is an increase in the tensile strength with increase in the content of MMT. One possible reason for this kind of behaviour in the mechanical properties may be due to the very good compatibility among

the constituents of the composite thus making the membrane stiffer. As a result, an increase in the tensile property was observed.

In the durability study, the time taken for the physical disintegration of the various composite membranes was studied and the results are shown in Figure 12.

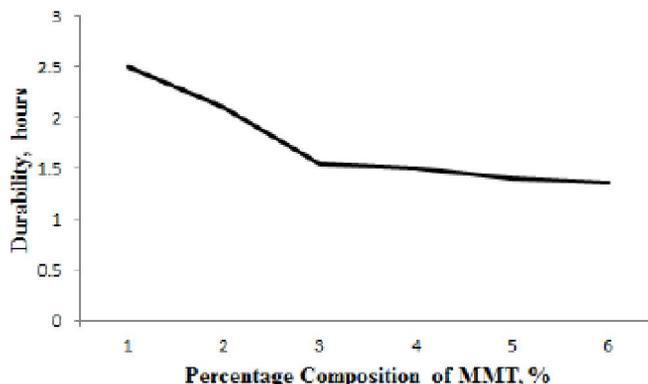


Figure 12 : Durability of composite membranes

The probable mechanism of this accelerated stability study involves two steps as shown in Figure 1. In the first step,  $\text{Fe}^{2+}$  attacks peroxide to generate the free radical  $\text{OH}\cdot$ . The second step is the attack of the generated free radical on the  $\text{SO}_3\text{H}$  group. It is evident from the Figure that there is a gradual decrease in the withstanding ability of the composites with increase in the MMT content. The possible reason could be that the continuity in the polymer matrix is lost due to the introduction of MMT particles between the polymer chains.

## CONCLUSION

In the present study, composite membranes with SPEEK as the host polymer matrix and MMT as the inorganic filler were synthesized. The composite membranes were found to be mechanically stable. The XRD patterns and the SEM images revealed good compatibility between the constituents of the composite. The prepared membranes were found to be thermally stable upto  $225^\circ\text{C}$ , which is highly suitable for DMFC applications. Although the water retention capacity of the composite membranes were increased due to the introduction of MMT inorganic particles, the proton conductivity was found to be decreasing due to the fact that there is an effective decrease in the number of exchangeable protons ( $\text{SO}_3\text{H}$  protons). However, the proton conductivity was in the order of  $10^{-3}$  S/cm and

the selectivity ratios of the composite membranes were higher when compared to pristine SPEEK. The presence of MMT has also influenced the methanol absorption and the composite membranes were better candidates for DMFC.

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