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Synthesis and charachterization of sulphonated Poly (Ether ether ketone)-mont morillonite clay compositesfor polymer electrolyte membranes

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ABSTRACT

Polymer composites of Sulphonated Poly Ether Ether Ketone (SPEEK)-Mont Morrilonite clay (MMT) with varying concentrations of MMT, were considered as materials for synthesizing Polymer Electrolyte Membranes (PEM). The MMT was added to check for variations in the mechanical stability, solvent absorption and proton conductivity of the composites with virgin SPEEK. The membranes were cast from solution using N-Methyl-2-Pyrrolidone (NMP). FT-IR confirmed the presence of sulphonic acid groups in the membranes and X-Ray Diffraction (XRD) confirmed the amorphous nature of the composites. Scanning Electron Microscopy (SEM) showed good dispersion and distribution of the MMT particles without any agglomerations. Thermal analysis confirmed thermal stability of the composite membranes upto 200°C and tensile test measurements showed higher tensile strength for the composites than virgin SPEEK. Electrochemical Impedance (EIS) showed an increase in proton conductivity for the composites when compared to virgin SPEEK. After characterization, Membrane Electrode Assembly (MEA) was fabricated with Nafion, SPEEK, SPEEK-MMT for performance evaluation of the membranes. The composites showed higher current density when compared to virgin SPEEK and Nafion.

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KEYWORDS

Sulphonated poly ether ether ketone (SPEEK);
Mont morrilonite clay (MMT);
Polymer electrolyte membrane fuel cell (PEMFC);
Membrane electrode assembly (MEA);
Proton conductivity;
Virgin SPEEK.

INTRODUCTION

Nafion proves to be a reliable PEM for fuel cells as it has very good proton conductivity, water absorption, durability and dimensional stability[1]. However, Nafion, with its fluorine backbone can be a cause for concern in terms of high cost, environmental factors, and poor capability to perform at high operating temperatures[1,2]. Thus, an alternate energy system seems necessary in this era of sustainable development and green technology as the energy derived from the existing resources prove to be potential poisons and pollutants. Sulphonated Poly (Ether Ether Ketone) membranes have been investigated extensively[1-3] as alternatives for Nafion primarily due to the flexible ether-ether linkage, good water absorption, moderate proton conductivity and ability to perform at temperatures upto 180°C[3,4], most importantly, SPEEK membranes are less expensive. Ability to withstand the reductive environments in the fuel cell and good mechanical properties become important considerations for PEM. These can be achieved by preparing composites of SPEEK with inorganic materials, which can be uniformly dispersed in the SPEEK matrix. Many research works based on composites of SPEEK and inorganic materials such as $TiO_{2,}$ SPEEK-Boron Orthophosphate[5] composites have resulted in membranes with good chemical resistance, high thermo-oxidative stability, good mechanical strength and being less expensive. SPEEK-PANI composite membranes, which showed, reduced methanol uptake upto four times lower than Nafion 117 and reasonable electrochemical data and thermal properties[6].

The current research aims at developing alternative PEM using SPEEK-MMT composites and are synthesized and tested for the application as PEMs in PEMFC. MMTis selected due to the presence of hydrogen bonding, which is expected to provide excellent mechanical stability and flexibility to the membranes. Moreover, MMT is proven to have excellent water absorption capabilities, which can have a direct and positive effect on the proton conductivity of the polymer electrolyte membrane[7]. SPEEK-MMT composite is expected to show better properties than virgin SPEEK in terms of tensile strength, initial decomposition temperature, solvent absorption and Proton conductivity.

The objectives of the present work are

- Synthesis of virgin SPEEK and SPEEK-MMT composite membranes
- Testing of composites for IEC, solvent absorption and chemical stability
- Characterization of composites using FT-IR, XRD, TGA, SEM, EIS, UTM
- Fabrication of MEA and performance evaluation in PEMFC

EXPERIMENTAL

Materials and methods

(a) Sulphonation of PEEK

PEEK powder, 150XF, was purchased from Victrex (England) Sulphuric acid, Analytical reagent, was purchased from Nice Chemicals (India). A known quantity of PEEK powder was taken in a round bottom flask and reacted with 150 ml sulphuric acid for 3 hours[2,8] with continuous stirring using a magnetic stirrer. The reaction was terminated at the end of 3 hours in an ice bath and the resulting Sulphonated PEEK (SPEEK) fibres were washed in double distilled water to neutral pH. and dried at 60°C for 3 hours in a hot air oven[2,8].

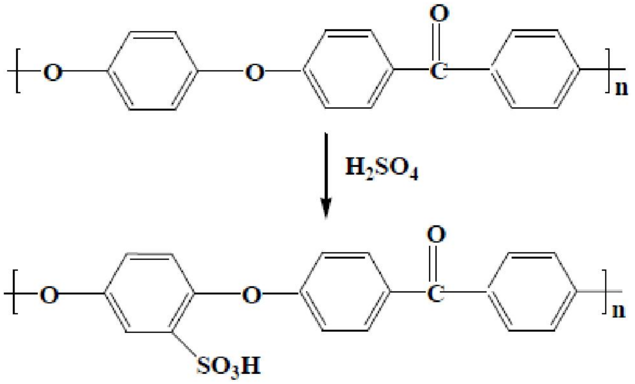

Figure 1 : Sulphonation of PEEK molecule.

(b) Synthesis of SPEEK and SPEEK-MMT composite membranes[7,8]

Surface modified MMT powder was purchased from Sigma Aldrich and NMP (AR Grade) from Nice Chemicals. For the preparation of the membrane, the following procedure was adopted. SPEEK was dissolved in NMP at room temperature and the resulting solution was stirred for few hours. The homogenous solution obtained was then filtered and cast onto a clean dry petri dish. The contents of the petri dish are heated to 60°C for a further 24 hours. The membranes thus obtained were pale brown in colour.

For the composites, measured quantity of MMT was dispersed in NMP and the solution was stirred for 2 hours. The MMT dispersion was then added drop by drop into the SPEEK in NMP solution and the resulting mixture was stirred for 4 hours till it turned homogeneous[7,8]. This homogeneous solution was cast onto a clean petri dish and the contents were dried in the oven at 60°C for slow evaporation of the solvent to avoid any fissures in the final membrane. After the solvent had evaporated, the membranes were peeled off from the container, treated with 0.5N H_2SO_4, and washed with deionized water. A set of four different composites with varying concentrations of 98%SPEEK-

2%MMT, 4%MMT, 6%MMT, 8%MMT were synthesized using the aforementioned technique. The synthesized membranes were of 80-100µ in thickness.

(c) Fabrication of membrane electrode assembly (MEA)[4,8]

The procedure for preparing a MEA adhered to standard protocols. Carbon Vulcan XC-72 was purchased from Precision Scientific, Coimbatore. Pt on Vulcan XC-72 was purchased from Precision Scientific, Coimbatore. 60% Teflon dispersion was purchased from Sigma Aldrich. Isopropyl Alcohol (IPA) was purchased from Rankem Chemicals.

A. Purification of the membrane
B. Teflonization of the porous carbon cloth
C. Carbonization of the teflonized carbon cloth
D. Catalyst layer first stage coating
E. Catalyst layer second stage coating
F. Hot pressing of the electrodes on the membrane

(A) Purification of the membrane

Purification of the membrane is very crucial and must be performed before the preparation of MEA. Initially, all membranes are allowed to boil in 3% H_2O_2 for 45 minutes which removes the impurities, if any, present on the surface of the membrane. It is then washed thoroughly with distilled water and boiled for 30 minutes in 10% H_2SO_4 to remove any inorganic impurities and to get the membrane in a complete protonated form. Finally, the membrane is washed with boiling water to remove any excess acid present on the surface of the membrane and and the membrane are dried.

(B) Teflonization of the porous carbon cloth

For the teflonization process, a 60% Teflon dispersion in water available commercially is procured and is further diluted with deionised water in the ratio of 1:5. The carbon cloth is highly porous in nature and is dipped in the above dispersion for 30 seconds. Then it is placed in a muffle furnace at 350°C for 3 hours. The process of teflonization improves the hydrophobicity of the carbon cloth.

(C) Carbonization of the teflonized carbon cloth

This is also called as the Gas Diffusion Layer (GDL). Initially Vulcan XC-72 (3mg/cm^2) is mixed with 3ml of deionised water and sonicated for 10 minutes. The sonication is done to obtain a fine dispersion of the carbon particles. Then 2-3 ml of isopropyl alcohol is added and sonicated again for 10 minutes. Finally, a drop of Teflon dispersion is added, mixed and immediately coated on the carbon cloth by means of a brush. The cloth is then kept in a muffle furnace at 350°C for 3 hours.

(D) Catalyst layer first stage coating

(1) Anode

The catalyst used is Pt dispersed in carbon. For the first stage, the amount of Pt taken is 0.125 mg/cm^2. The required amount of the catalyst is weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of IPA is added and sonicated for another 10 minutes. Finally, one drop of Teflon dispersion is added, mixed with the help of a painting brush and coated immediately on the carbonized cloth. It is then heated in a muffle furnace at 350°C for 3 hours.

(2) Cathode

The first layer of catalyst was coated as done for anode.

(E) Catalyst layer second stage coating

(1) Anode

For the second stage, the amount of Pt taken is 0.125 mg/cm^2. The required amount of the catalyst is weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of S-PEEK solution is added and then coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It is then dried in a hot air oven at 80°C for 4 hours. The electrode obtained after drying can be used as the anode for the fabrication of the MEA.

(2) Cathode

For the second stage, the amount of Pt taken is 0.375 mg/cm^2. The required amount of the catalyst is weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of S-PEEK solution is added, mixed and coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It is dried in an oven at 80°C for 4 hours. The electrode obtained is the cathode that can be used for the fabrication of the MEA.

(F) Hot pressing of the electrodes on the membrane

On either side of the membrane, a solution of S-

PEEK in NMP is applied and the electrodes are placed on either side. It is hot pressed at 80°C for 45 seconds with a load of 0.5 tonnes. The two electrodes stuck onto the membrane after the hot pressing treatment. The resulting assembly is the Membrane Electrode Assembly.

The above MEA is used in the PEMFC for performance evaluation.

Characterization

(a) Fourier transform infrared spectroscopy (FTIR)

The IR spectra (450 – 4000 cm-1) for the dried membranes were recorded with a Perkin Elmer FT-IR spectrometer with an accuracy of ± 0.001 cm^{-1}at 25 ± 2°C. The samples were dried at 100ºC for an hour before recording the spectrum.

(b) X-ray diffraction (XRD)

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° at a scanning rate of 2° per min. All the spectra were taken at ambient temperatures (25 ± 2°C).

(c) Scanning electron microscopy (SEM)

The surface morphology of the electrolyte membranes was analysed using SEM (Hitachi S – 3400 N). The samples were cut into sufficient size and sputter coated with gold to make the samples electro conductive. The samples were then analyzed under vacuum condition at an accelerating voltage of 10 KV.

(d) Thermogravimetric analysis (TGA)

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 10°C/min in the range of the temperature between 30°C and 500°C is followed using a STA 449 F1/F3 Jupiteranalyzer. All the runs were carried out under nitrogen atmosphere.

(e) Universal testing machine (UTM)

The tensile testing is done according to ASTM D 638, (Type V) wherein the polymer composite samples are cut in dumbbell shape with specified dimensions. Hounsfield UTM was used for the purpose. The testing was done in standard laboratory atmosphere of 23°C ± 2°C and 50 ± 5 % relative humidity at a crosshead speed of 10 mm/min and 500 N force.

(f) Ion exchange capacity (IEC)[4,8]

The ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1g of the dry polymer. It was determined by titration method. The membrane in its protonated form was weighed and then soaked 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_2CO_3 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_2CO_3 solution. The IEC values were expressed as number of meq. of sulphonic groups per gram of dry polymer.

IEC is calculated using the formula,

$$\mathbf{IEC} = \frac{\textbf{Titer value (in ml) x Normality of the titrant (Na2CO3)}}{\textbf{Weight of the dry polymer membrane (in grams)}}$$

(g) Solvent absorption[4,8]

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 40 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,

$$\mathbf{SW} = \frac{\mathbf{M}_{\mathbf{wet}} - \mathbf{M}_{\mathbf{dry}}}{\mathbf{M}_{\mathbf{dry}}}$$

where,

M_{wet} = Weight of wet membrane,
M_{dry} = Weight of dry membrane.

(h) Durability of membranes[8]

For checking the durability of the electrolyte membranes, the following procedure was adopted. Initially a 4ppm ferrous ammonium sulfate in 3% H_2O_2 was freshly prepared and the temperature of the solution was maintained at 80°C. The electrolyte membrane with the dimension of 0.5cm^2 was cut and soaked in the solution. The time required for the physical disintegration of the membrane was noted down and reported. The reaction is expected to occur by free radical mechanism.

(i) Electrochemical impedance spectroscopy (EIS)

The proton conductivity measurements was taken using an alternating current impedance spectroscopy device over a frequency range of $1\text{-}10^7$hz with 50-500mV oscillating voltage using a solatron gain phase analyzer. Films having 13mm diameter, sandwiched between two stainless steel block electrodes with ~3 kg/cm2 pressure, were placed in an open, temperature-controlled cell. The films were previously hydrated by immersion for 24 h at room temperature. The conductivity σ of samples in the transverse direction was calculated from the impedance data, using the relationship $\sigma = d/RS$, where d and S are the thickness and face area of the membrane sample, respectively, and derived from the low intersection of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis. The impedance data were corrected for the contribution from empty and short-circuited cell.

(j) Performance evaluation

All the samples were subjected to testing in real time PEMFC environment with hydrogen gas as fuel. Standard fuel cell grade graphite plates and copper current collectors were used for this purpose. The output voltage and the current were measured with a multimeter under different resistances as loads.

RESULTS AND DISCUSSIONS

FTIR

Shown below are the comparative FTIR spectra of SPEEK and the various compositions of SPEEK-MMT composites.

FTIR measurements

All the five spectra exhibit an absorption peak at approximately 1580 cm^{-1}**[9]** as a result of C=C stretching and an absorption peak at 1680 cm^{-1} owing to the C=O stretching. The characteristic stretch for O=S=O group is in the region of 1050 cm^{-1}**[9]**. The experimental values coincide with the data from literature**[9]** as the peaks for SPEEK at 1077cm^{-1} and 1021 cm^{-1} confirm the presence of O=S=O groups. Similarly, the blends of 2% MMT show stretching at 1075 cm^{-1} and 1018 cm^{-1}confirming sulphonation. The 4% MMT and 7% MMT blends showed similar stretching at 1080 cm^{-1} and 1022 cm^{-1}, all of which corroborated the sulphonation of the polymers.

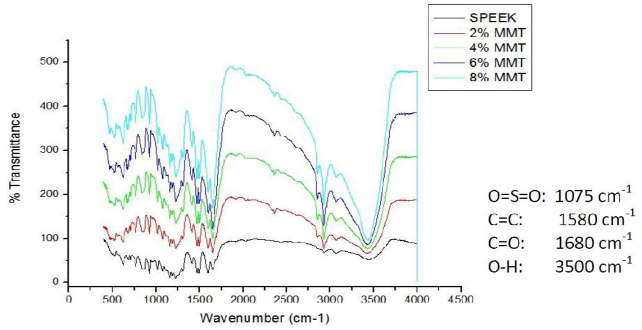

Figure 2 : FTIR of SPEEK and SPEEK-MMT composites.

XRD

From the above figure, we find that the intensity of the peak decreases from SPEEK to the blend. If the intensity of peak is greater, then the crystalline nature is greater in the sample. We can conclude that as the concentration of MMT increases, the amorphous nature of the membrane also increases along with it. Amorphous compounds have their atoms separated wide apart providing excellent mechanical strength and durability to the membranes. The SPEEK-MMT membranes thus potentially possess higher mechanical properties due to its increased amorphous character.

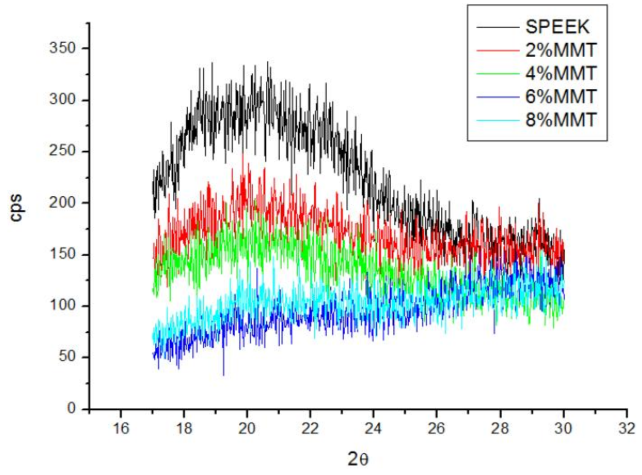

Figure 3 : XRD patterns of SPEEK and SPEEK-MMT composites.

SEM

The SEM images look dense and clear. The inorganic content was well dispersed in the organic matrix and the membranes appeared to be pores-free even at higher magnification. Surface of the membranes was found to be smooth. The evaporation of NMP solvent (boiling point 202°C) was performed at 80°C indicating a very slow process of evaporation.

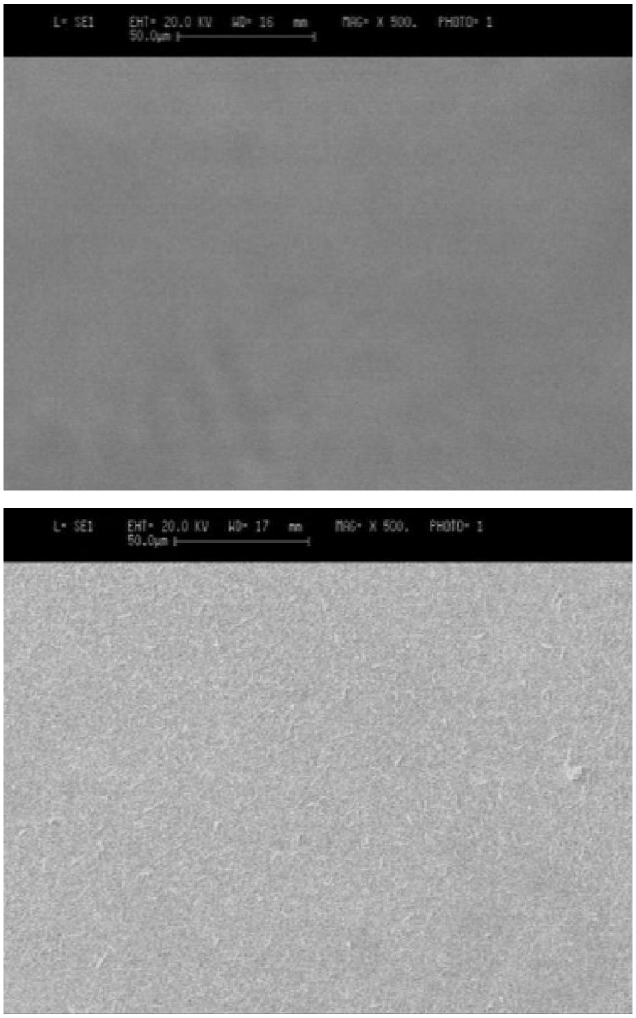

Figure 4 : SEM images of virgin SPEEK membrane (left), SPEEK-2%MMT composite (right).

TGA

Careful evaluation of the thermogram of the composite membrane reveals a trend similar to SPEEK. Three-stage decomposition was observed for the composite membranes. The first weight loss occured between 30°C and 150°C and is due to the evolution of physically and chemically bound water molecules along with trace amounts of solvent. MMT nanoclay is very well known to hold a large amount of water. Hence the loss is maximum for composite with 8% MMT and minimum for composite with 2% MMT. Second weight loss occured between 200°C and 250°C and this is due to the loss of sulphonic acid groups from the main chain. The third weight loss that occured after 400°C may be attributed to the initial degradation stage of the polymeric backbone. The membranes are sover 200°C which is sufficient for successful operation in the fuel cell environment. The final weight loss above 400ºC could be due to the decomposition of the polymeric backbone.

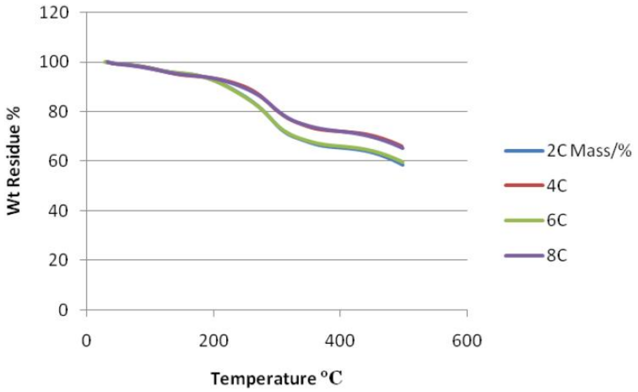

Figure 5 : Mass residue vs. temp plot of SPEEK-MMT composites.

UTM-tensile test

The tensile strength showed a linear decrease with decrease in the composition of MMT, whereas, the percentage elongation showed a decrease with decrease in the content of MMT. As MMT chains can strongly associate through their –OH groupings by H-bonding, their contribution to tensile strength and percentage elongation, therefore, might be more significant than that of SPEEK. Hence, it is inferred that the content of MMT mainly decides the tensile strength as well as percentage elongation of the membrane.

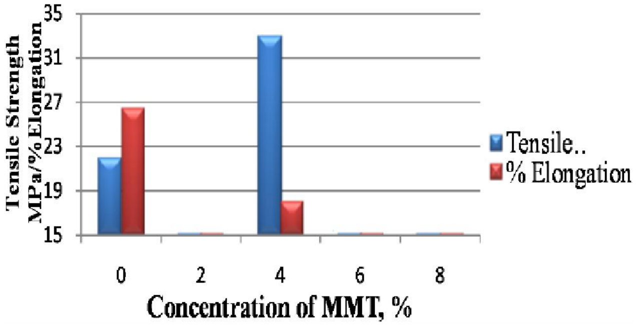

Figure 6 : %Elongation and tensile strength of SPEEK-MMT composites.

Ion exchange capacity (IEC)

The results from the measurements of IEC values for SPEEK and composite membranes are shown in the table below. In order to explain the trends seen in

TABLE 1, the presence and amount of available H^+ ions in sulphonic acid groups that directly influence the conductivity of the membranes is noted. As the composition of MMT in the composite increases respectively, there is a decrease in the number of effective replaceable protons. The effective amount of SPEEK decreases, with an increase in the content of MMT in the case of composite.

TABLE 1 : IEC values of SPEEK- MMT composites.

Membranes	IEC (meq/g)
S-PEEK	1.72
2% MMT	1.65
4% MMT	1.59
6% MMT	1.54
8% MMT	1.47

Solvent absorption

Water and Methanol, both polar in nature, were the two solvents used in this aspect of the product characterization. It is known from the prior work reported in the literature[9] that increased water uptake leads to increase in the conductivity of the membrane. However, beyond a threshold (> 30% to 40%), the benefit of increased conductivity is offset by the onset of mechanical degradation of the membrane. Keeping this in mind, the following observations may be noted from the below table.

In comparing the water uptake of Nafion®117, which is known to be 38%[10], for the composite membranes, up to a certain level of MMT, an increase in the percentage of MMT increases the water (and methanol) uptake. These results are consistent with the fact that MMT particles are capable of storing a huge quantity of water (and methanol). Increasing the % MMT any further seems to have no effect on water (or methanol) uptake. We infer the reason for this as the uptake having reached a saturation level.

Based on the above, the recommendation is that composites with %MMT between 6% and 8% be used for optimal water (and methanol) uptake.

Durability studies

Chemical and mechanical degradation expectedly have an adverse effect on the durability of the membrane. The stability studies of the membrane towards peroxide solutions give an idea about the lifetime (durability of membrane) of the membrane. The peroxide test is considered as an accelerated stability testing method.

TABLE 2 : Solvent absorption values for membranes.

Membrane	Water uptake (%)	Methanol uptake (%)
S-PEEK	9.52	14.40
2%-MMT	26.67	14.97
4%-MMT	28.57	15.52
6%-MMT	28.59	15.60
8%-MMT	28.57	15.58

In the present study, the durability decreases with an increase in the amount of MMT nanoclay content. In composites, it is recognized that the space between the polymer matrix is occupied by the MMT particles – as a result of this, there is loss of continuity in the polymer. It may be argued that though there is some interaction between MMT and the individual polymer chains, that interaction may not be sufficient to hold all the polymer chains together. There is a possibility for the chains to break at positions where MMT is present, which may be due to the loss in continuity of the polymer chain. As we are more concerned about the physical disintegration of the polymer matrix in the peroxide solution, it is expected that the durability of the membranes may decrease with increase in the concentration of MMT in the composite.

TABLE 3 : Durability of SPEEK membranes with PEES blends.

Membrane	Time for disintegration
S-PEEK	3 hours 15 minutes
2%-MMT	3 hours
4%-MMT	3 hours
6%-MMT	3 hours
8%-MMT	2 hours 55 minutes

Proton conductivity

The proton conductivity decreases with the increasing composition of MMT in the membrane. With increasing MMT, the exchangeable H^+ ions (SO_3H groups) decreases in the sample, but an important aspect to note here is the water absorption capability of MMT. Water plays an important role in the proton conducting property of the PEM. It itself possesses exchangeable H^+ ions and supports the effective transport of the ions across the membrane. Hence, even though the amount of SO_3H groups decreases with increasing MMT, the proton conductivity increases owing to the high hydrophilic character of MMT. The proton conductivity of the 6% composite and 8% composite is almost equal to that of the previously reported value of Nafion.

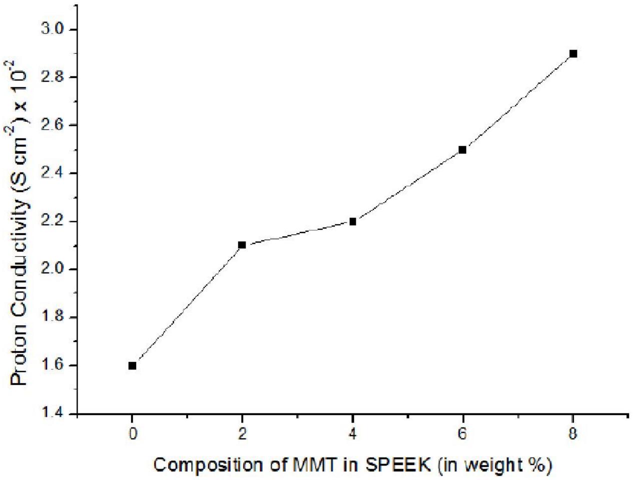

Figure 7 : Proton conductivity SPEEK-MMT composites.

TABLE 4 : Load vs Current values for SPEEK-MMT composites.

Load (Ω)	Current Measured (A)				
	Nafion	SPEEK	Composites		
			2%	6%	8%
0.0	0.38	0.45	0.68	0.70	0.72
0.5	0.30	0.27	0.44	0.42	0.38
1.0	0.24	0.19	0.32	0.31	0.25
1.5	0.21	0.14	0.26	0.25	0.20
2.0	0.17	0.11	0.22	0.21	0.16
2.5	0.16	0.09	0.19	0.18	0.14
3.0	0.14	0.08	0.17	0.16	0.12
3.5	0.13	0.07	0.15	0.14	0.10

Performance evaluation

From the above tabulations, it is clear that, SPEEK-MMT composites possess the potential of performing better than Nafion in a PEMFC environment. Moreover, the voltage measured for the 2%MMT and 6%MMT composite membranes (values) are close to that of Nafion. From the TABLE 4, the current vs. load data, we see that the current obtained for different loads in the case of 2% and 6% composites are higher than that of Nafion and virgin SPEEK membranes. This can be attributed to the water absorption capability of the composite membranes. However, beyond 6%MMT, the voltage decreases and current data are almost equal to Nafion. This concludes that an optimized level of MMT in SPEEK enhances the performance of the polymer membrane owing to the good water absorption. From the above results, it is valid to say that, SPEEK-2%MMT and SPEEK-6%MMT is a viable alternative Nafion for PEMs.

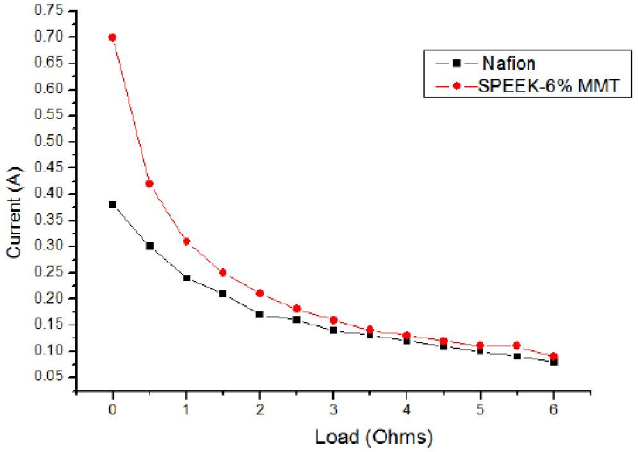

Figure 8 : Comparative plot of current vs. load for nafion and SPEEK-6%MMTcomposites.

CONCLUSIONS

From the results documented, it can be can concluded that 6wt % SPEEK-MMT composites are good candidates for Polymer Electrolyte Membrane Fuel Cells (PEMFC's) owing to their good water uptake, excellent proton conductivity and good thermal stability.

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