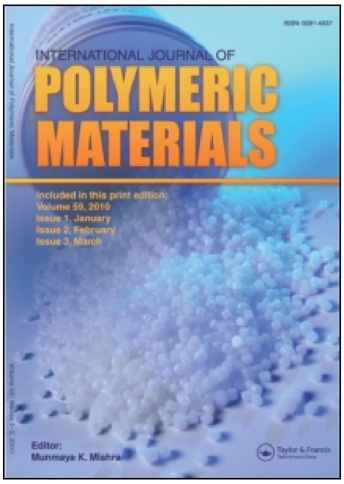

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Sangeetha, Dharmalingam(2007) 'Sulphonated Poly(ether ether ketone) Proton Exchange Membranes for Fuel Cell Applications', International Journal of Polymeric Materials, 56: 5, 535 — 548

To link to this Article: DOI: 10.1080/00914030600992228

URL: http://dx.doi.org/10.1080/00914030600992228

International Journal of Polymeric Materials, 56:535–548, 2007
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ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600992228

Sulphonated Poly(ether ether ketone) Proton Exchange Membranes for Fuel Cell Applications

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Polymer electrolyte membrane fuel cells (PEMFCs) are promising new power sources for automotive and portable devices. Nafion® is the currently used membrane in PEMFCs. Although these membranes show high proton conductivity and excellent chemical stability, their high cost makes them unpractical for commercial purposes. Sulphonated poly(ether ether ketone) (SPEEK) ionomers were synthesized using chlorosulphonic acid as the sulphonating agent in dichloromethane medium. Homogeneous proton-conducting membranes were developed from the obtained SPEEK by solvent casting method. Membranes were assessed for their suitability in fuel cell applications. The extent of sulphonation was controlled by varying the reaction time, concentration of polymer, and concentration of sulphonating agent. The SPEEK membranes exhibit degree of sulphonation from 10 to 66%, ion exchange capacity from 0.29 to 1.92 meq/g and maximum water and methanol uptake up to 54 and 22%, respectively, at 25°C. The membranes were characterized by FTIR to confirm sulphonation, and DSC and TGA to investigate the thermal stability. The proton conductivities of such membranes were found to be excellent in the order of 10^{-2} S/cm in the fully hydrated condition at room temperature as measured by impedance spectroscopy. The durability of the membranes was also tested. The study revealed the possibility of a cheaper alternative membrane for use in PEMFC.

Keywords: fuel cell, ion-exchangers, ionomers, membranes, proton conductivity, sulphonated poly(ether ether ketone)

INTRODUCTION

Fuel cells are electrochemical energy converters, which directly transform chemical energy into electricity. They are an attractive alternative to power generators, due to numerous benefits such as lower emissions, high efficiencies, and lower maintenance requirements.

Received 21 August 2006; in final form 4 September 2006.

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Proton Exchange Membrane Fuel Cells (PEMFCs), which are considered to be the power generators for the next generation of automation of zero-emission vehicles, employ polymer electrolyte membranes as an electrolyte. Nafion®, a perfluorosulfonic acid polymer membrane [1–4], is the most widely used proton conductor in PEMFCs. It has high ionic conductivity, good thermal stability, adequate mechanical strength, and excellent chemical stability. However, the high cost of the membrane and the environmental hazards associated with its disposal have led research in search of low-cost and more environmentally friendly hydrocarbon ionomer membranes. Some of the non-perfluorinated membranes under investigation include PEEK [5–7], polysuphone [8–10], poly(phenylene oxide) [11–12] and polybenzimidazole [13–14]. The ideal proton exchange membrane for fuel cell is expected to have high proton conductivity, good chemical stability, excellent mechanical stability along with low-cost. None of the membranes, till date, satisfy all the desired specifications.

Poly(ether ether ketone) (PEEK) is a polymer with high degree of crystallinity and has very high thermal stability as well as mechanical stability. The polymer is also highly resistant to chemical agents and has several technological and industrial applications. Chemically, it is an aromatic polymer with non-fluorinated backbone, in which −O− and −CO− linkages separates 1,4-disubstituted phenyl groups. Because PEEK is insoluble in almost all common organic solvents and is soluble only in sulphuric acid, its sulphonation is carried in a medium of sulphuric acid [15–19]. The chemical structures of PEEK and sulphonated PEEK are depicted in Figure 1. On sulphonation of the PEEK polymer, it simultaneously becomes proton conductive as well as hydrophilic in nature. At higher sulphonation levels, it has better conductivity, but at the same time, it becomes more water-soluble

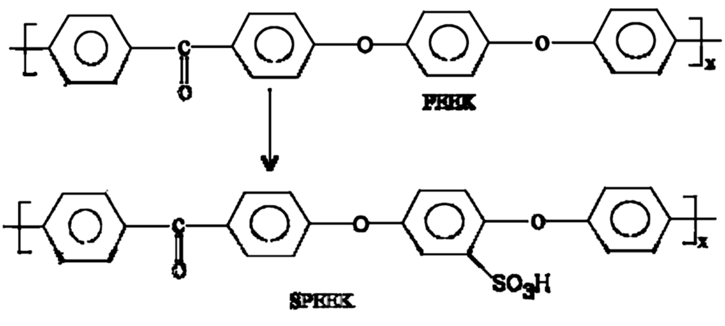

FIGURE 1 Structure of PEEK and SPEEK.

and hence results in insufficient mechanical strength. In order to possess an ideal membrane for fuel cell applications, the polymer should be highly homogeneous and uniform in proton conducting property. It should also not dissolve or swell too much in water, loosing its dimensional stability. Hence, it is required that the polymer is sulphonated homogeneously to a desired level, to best suit the fuel cell environment. The commercially available PEEK (Victrex and Gatone) has been extensively studied for sulphonation [5–7,15–23]. Recently, Xing and his coworkers [24] have compared the sulphonation of Victrex and Gatone PEEK using sulphuric acid for the proton exchange membranes. It has been reported that the sulphonation of PEEK using chlorosulphonic acid leads to chlorosulphonated polymers and subsequently degradation of polymer occurs at higher degree of chlorosulphonation [25]. However, no systematic studies have been conducted on the sulphonation of PEEK using chlorosulphonic acid as the sulphonating agent.

In the present study, sulphonation of PEEK is for the first time conducted in the medium of dichloromethane, using chlorosulphonic acid, to prepare a uniform and homogeneous SPEEK membrane. Various factors, which influence the percentage of sulphonation and ion exchange capacity of the membrane, are extensively studied. Durability of the membrane is also tested and compared with Nafion® membrane.

EXPERIMENTAL

Materials

The PEEK (polyoxy-1,4-phenylene oxy-1,4-phenylene-carbonyl-1,4-phenylene) in a powder form (very fine 150 XF) was obtained from Victrex. Chlorosulphonic acid was obtained from Spectrochem Pvt Ltd., India. Solvents, dichloromethane (DCM), and N-methyl 2-pyrrolidone (NMP) were purchased from Merck.

Sulphonation of PEEK

Sulphonation of PEEK was conducted in a nitrogen atmosphere, employing chlorosulphonic acid in a medium of dichloromethane (DCM). PEEK powder was dried overnight in a vacuum oven at 100°C to remove the moisture. Weighed amount of the PEEK polymer was transferred into a three-necked round-bottomed flask. Measured quantity of DCM was added to it with stirring. The reactor was allowed to cool to 0°C in an ice bath. Then the required amount of chlorosulphonic acid was added drop-wise over a period of time. Continuous stirring was maintained during the course of reaction. The reaction was allowed to proceed to the required time and was terminated by adding a lower aliphatic alcohol and the contents of the flask were poured into a tray containing large amount of cold water. The sulphonated PEEK in the form of numerous fibers was recovered by precipitation in water. The complete removal of residual acid from the product obtained after sulphonation is important because it can interfere with the properties of the final product. The product was washed several times with water until a neutral pH was obtained. The product was then dried at 100°C for one day. The finally obtained product was the suphonated PEEK (SPEEK). A number of experiments were performed to determine the optimum conditions of sulphonation of PEEK, by varying the concentrations of polymer and sulphonating agent and the reaction time.

Preparation of SPEEK Membranes

Required amount of SPEEK (approximately 8–10% w/v) was weighed and dissolved in NMP solvent. The membrane was cast on a clean glass plate from this solution using solution-casting and solvent evaporation technique. The cast films were dried in an air oven at a temperature of 150°C for 6 h. Membranes of varying thickness (60 to 150 microns) were obtained by varying the amount of solution used.

Characterization Studies

To confirm the sulphonation of the polymer, FTIR spectra of thin polymer films were obtained on a Bruker Vector 22 Spectrophotometer for both un-sulphonated and sulphonated polymer samples. Calorimetric measurements were performed with a NETZCH DSC 200 PC operating in nitrogen atmosphere at a heating rate of 20°C/min. The mid point of the slope change of the heat capacity plot was taken as the T_g. A NETZCH TG 209 C thermogravimetric analyzer was used to analyze the thermal stability of polymers at a heating rate of 20°C/min under nitrogen. Both PEEK and SPEEK membranes were subjected to DSC and TGA studies.

Solvent Absorption Studies

Water and methanol uptake studies were measured gravimetrically. Membranes were oven dried at 100°C for 6 h, then weighed for their dry weight and then immersed in the respective solvents at room temperature for 24 h to reach equilibrium. The fully hydrated membranes were then blotted dry to remove the excess solvents present on the surface and weighed. The degree of swelling was calculated as follows:

$$\text{Swelling } (\%) = \left[\frac{(W_w - W_d)}{W_d}\right] \times 100$$

where, W_d and W_w are the weights of the membrane under dry and wet conditions, respectively. Also, the membranes being soaked were taken out at different soaking periods and weighed to determine the amount of absorption at various times.

Degree of Sulphonation

The ion exchange capacity (IEC) indicates the number of milli-equivalents of ions in 1 g of the dry polymer. The degree of sulphonation (DS) indicates the average number of sulphonic groups present in the sulfonated polymer. They were determined by titration method. The membrane in its acid form was weighed and then soaked in an aqueous solution containing a large excess of KCl salt in order to extract all protons from the membrane. The electrolyte solution was then neutralized using a very dilute Na_2CO_3 solution of known concentration. 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 meq. of sulphonic groups per gram of dry polymer. The DS values were also reported. It is the number of sulphonated units per 100 monomer units and is expressed as percentage.

Leaching Test

All the prepared membranes were subjected to the treatment of boiling water. Membranes were immersed in a 250 ml beaker containing large amount of deionized water. The water was brought to boiling and the condition of the membranes was continuously monitored for every 1°C raise in temperature till boiling temperature.

Proton Conductivity

Conductivity measurements of the membranes were made using a reported method [26–27] by complex impedance spectra obtained using Voltalab Dynamic-EIS Voltammetry Model PGZ 301. Studies were carried out using a 2-compartment electrochemical cell with the membrane introduced into the O-ring joint between the compartments, using platinum foil electrodes and 1 M sulphuric acid as the electrolyte. From the difference between the resistance of blank cell and the one with membrane separating the working and the counter electrode compartments, the resistance of the membrane was calculated and converted to conductivity values using the formula

$$C = \frac{t}{R \times A}$$

where C is the ionic conductivity in S/cm, R is the sample resistance in ohm, t is the wet sample thickness in cm and A is the sample area in cm^2. The proton conductivity of the samples was compared with that of the commercially available Nafion® 117.

Durability of SPEEK Membranes

Ageing test helps to know about the life cycle of the membrane, which undergoes degradation normally under fuel cell operating condition. The test involves accelerating of the degradation process, thereby indicating the mechanical and chemical stability of the membrane over a period of time. The membranes were subjected to a solution of 3% hydrogen peroxide accelerated by 4 ppm of ammonium iron (II) sulphate hexahydrate for 8 h at 68°C. The membranes after the peroxide test were tested for the loss in IEC.

RESULTS AND DISCUSSION

Sulphonation of PEEK

PEEK was sulphonated using chlorosulphonic acid in a physically supported medium, to avoid degradation [28], and crosslinking reactions [25,28–29] that occur if chlorosulphonic acid is employed directly. PEEK was sulphonated to various degrees by varying the following parameters:

1. Concentration of PEEK polymer, taken for sulphonation reaction.
2. Concentration of sulphonating agent added.
3. Reaction time.

Tables 1–3 show the effect of the aforementioned parameters on the various properties of the SPEEK. PEEK polymer was sulphonated at its different concentrations varying from 1 g in 150 ml (23 mol/L) to 1 g in 25 ml (135 mol/L) of dichloromethane (DCM), keeping the reaction time and concentration of sulphonating agent as constants at 2 h and

TABLE 1 Effect of Concentration of PEEK on Various Properties of SPEEK

[PEEK] (mol/L)	IEC (meq/g)	DS (%)	Water absorption (%) (after 24 h)	Boiling water treatment
23	0.70	26	45	Did not dissolve
28	0.80	29	47	Did not dissolve
35	0.98	36	54	Did not dissolve
46	1.15	42	60	Did not dissolve
70	1.39	51	#	#
138	1.58	58	#	#

#, Uniform membrane was not obtained.
$[C1SO_3H] = 0.129$ mol/L.
Reaction time = 2 h.

TABLE 2 Effect of Concentration of CSA on Various Properties of SPEEK

[CSA] (mol/L)	IEC (meq/g)	DS (%)	Water absorption (%) (after 24 h)	Boiling water treatment
0.086	0.32	11	33	Did not dissolve
0.107	0.76	26	43	Did not dissolve
0.129	0.98	36	54	Did not dissolve
0.150	1.55	53	Dissolves at 20 h	Dissolves at 50°C
0.172	1.92	66	Dissolves at 18 h	Dissolves at 44°C

[PEEK] = 35 mol/L.
Reaction Time = 2 h.

TABLE 3 Effect of Reaction Time on Various Properties of SPEEK

Time (h)	IEC (meq/g)	DS (%)	Water absorption (%) (after 24 h)	Boiling water treatment
1/2	0.29	10	30	Did not dissolve
1	0.46	16	40	Did not dissolve
1 1/2	0.88	31	48	Did not dissolve
2	0.98	36	54	Did not dissolve
2 1/2	1.49	55	220	Dissolves at 55°C
3	1.65	60	Dissolves at 18 h	Dissolves at 59°C

$[ClSO_3H] = 0.129$ mol/L.
[PEEK] = 35 mol/L.

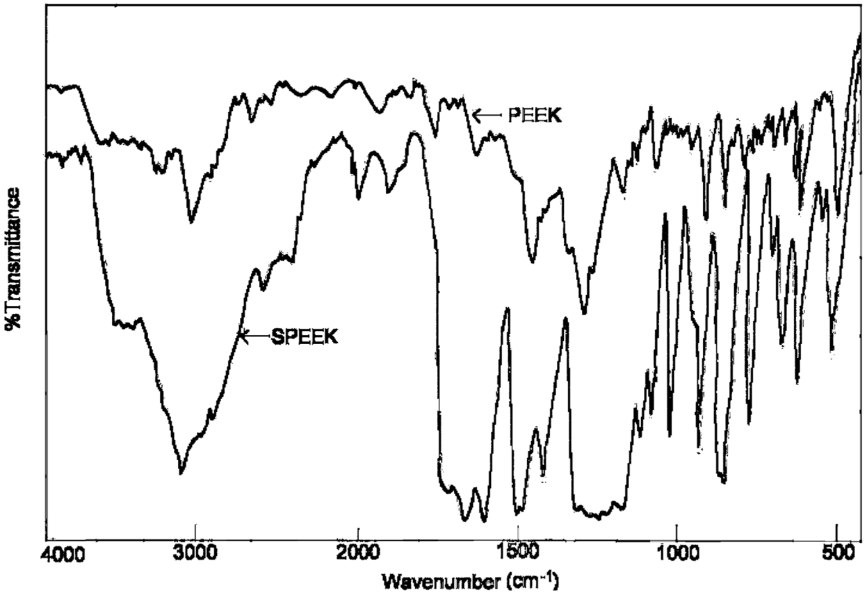

FIGURE 2 FTIR spectra of PEEK and SPEEK.

0.129 mol/L, respectively. At higher concentrations, homogeneous and uniform membranes were not obtained. In general, the IEC and DS of SPEEK increase continuously with the increase in the concentration of PEEK. Maximum water uptake (% Swelling) of the membranes was determined for the membranes that did not dissolve in boiling water. The condition of the membranes was also tested for dimensional stability during boiling water test. Separately, the concentration of chlorosulphonic acid (CSA) was varied at 2 h reaction time, keeping the concentration of polymer a constant. Finally, the effect of reaction time was also studied. PEEK was sulphonated for different reaction times ranging from 30 min to 3 h, to produce SPEEK of various DS.

IR Characterization

Figure 2 shows the FTIR spectra of both PEEK and SPEEK membranes. Appearance of bands around $1241\,\mathrm{cm}^{-1}$, $1112\,\mathrm{cm}^{-1}$, and $1020\,\mathrm{cm}^{-1}$ in SPEEK indicates sulphonation of phenyl rings. They are attributed to the O=S=O symmetric and asymmetric stretching vibrations. These peaks were absent in the unsulphonated PEEK. The disappearance of peaks at the frequency of $700\,\mathrm{cm}^{-1}$ and $760\,\mathrm{cm}^{-1}$ on sulphonation indicated the substitution in the aromatic ring when compared to the un-sulphonated sample. The appearance of a broad peak around 3000 cm^{-1} indicates the water absorbed by the sample because of the sulphonic acid groups introduced into the polymer.

Thermal Characterization

DSC curves of the samples are shown in Figure 3. The inflection point of the slope change of the heat capacity plot was taken as the T_g and it was found to be around 115°C for SPEEK membranes. The peaks that appear around 200°C correspond to the melting of polymers. The TGA curves of the polymer samples are shown in Figure 4. The thermal decomposition temperature of the membrane is a function of sulphonation. The major weight loss of un-sulphonated PEEK was observed

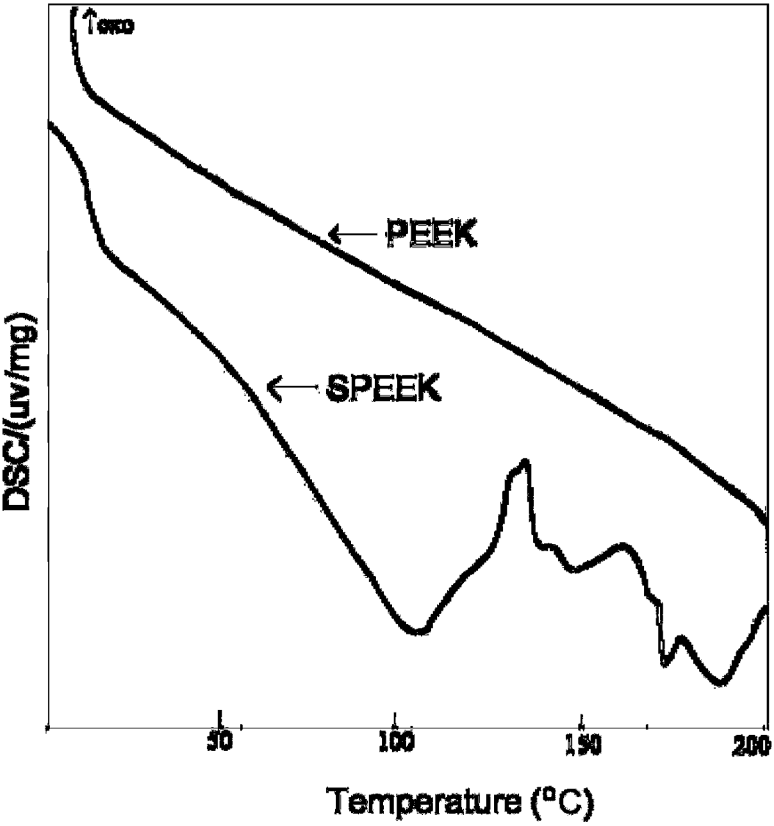

FIGURE 3 DSC curves of PEEK and SPEEK.

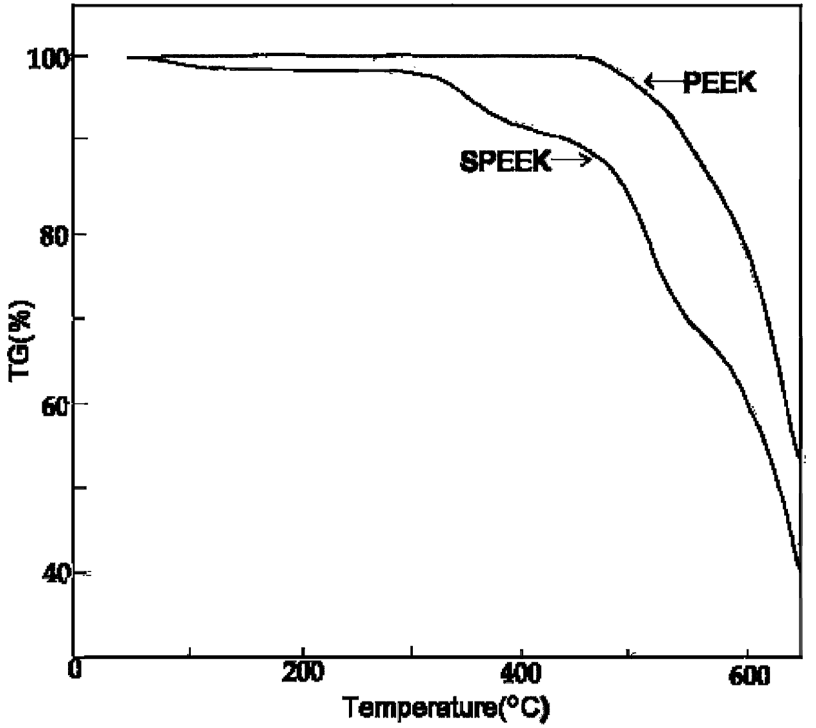

FIGURE 4 TGA curves of PEEK and SPEEK.

beyond 450°C, which is the result of decomposition of the polymer chain. Whereas, a three step loss of weight was observed in the thermogravimetric traces of sulphonated PEEK. The first step around 100°C is due to the loss of moisture. The weight loss between 250 and 450°C corresponds to the loss of sulphonic acid groups and the major thermal degradation that occurs above 450°C, is attributed to the polymer main chain scission. Thus, sulphonation decreases the thermal stability of the polymer due to the degradation of the sulphonic acid groups at lower temperatures. However, the sulphonated hydrocarbon polymer membrane has adequate thermal properties for application in fuel cells because their thermal decomposition is detected only beyond 230°C.

Maximum Uptake of Solvents

Investigations on the maximum uptake of water determined by gravimetric measurements resulted in a plateau after 4 h, representing the

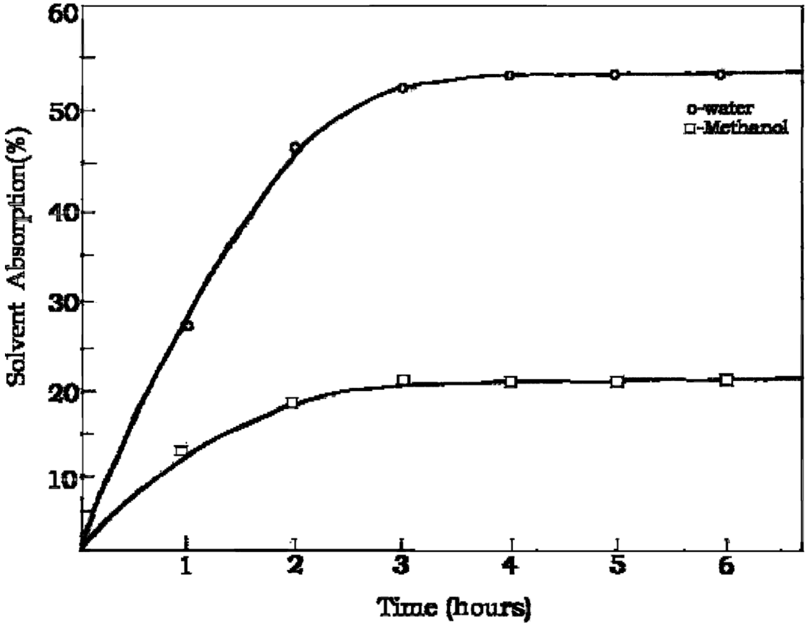

FIGURE 5 Water and methanol uptake of SPEEK.

full hydration level at 54% by weight. Similarly, the maximum uptake of methanol of 22% by weight was reached at 3 h. Figure 5 shows the water and methanol uptake of SPEEK membrane over a period of time. Because the uptake of water is higher than that of methanol, these membranes are less permeable to methanol than water and are expected to perform better in direct methanol fuel cells (DMFC) than the Nafion® membranes, which shows higher permeability to methanol (Table 4). This behavior may be better explained if the microstructure of the ionomer is investigated.

TABLE 4 Solvent Absorptions of SPEEK and Nafion®

		Maximum absorption (wt%)	
Membrane	Dry thickness (microns)	Water	Methanol
Nafion® 117	170	36	85
Nafion® 115	120	36	87
SPEEK	90	54	22

TABLE 5 Proton Conductivities of SPEEK and Nafion®

Membrane	Dry thickness (microns)	IEC (meq/g)	DS (%)	Proton conductivity (S/cm)
Nafion® 117	170	0.91	—	0.030
Nafion® 115	120	0.91	—	0.077
SPEEK	90	0.98	36	0.045

TABLE 6 Percentage of Loss in IEC by Peroxide Test

	Nafion® 117		SPEEK	
Temperature ± 2 (°C)	After 4 h (%)	After 8 h (%)	After 4 h (%)	After 8 h (%)
Room temperature	3.6	7.7	9.0	16.0
40	4.0	13.0	18.0	33.0
50	7.0	21.0	23.0	50.0*
60	12.0	22.0	28.0	Disintegrates
68	15.0	27.0	30.0	Disintegrates

*Starts disintegrating.

Proton Conductivity

The proton conductivity of the SPEEK membranes with various thicknesses was found to be excellent in the order of 10^{-2} S/cm. The values of protonic conductivities for the membranes prepared, along with the values for Dupont's Nafion® are quoted in Table 5.

The percentage loss in IEC of both Nafion® 117 and SPEEK membranes at various temperatures under peroxide test is listed out in Table 6. It is observed that the loss in IEC of SPEEK membranes (90–100 µ) is always higher than the Nafion® 117 membrane (170 µ) and also the SPEEK membrane starts disintegrating beyond 50°C for more than 8 h in the peroxide accelerated medium. Hence, it is clear that the dimensional stability of these SPEEK membranes should be improved, especially at temperatures above 50°C, for an efficient performance in the fuel cell environment. Suitable blending or reinforcements may achieve this.

CONCLUSIONS

PEEK polymer was sulphonated using chlorosulphonic acid as the sulphonating agent in a medium of dichloromethane. Membranes of various thicknesses were prepared from the sulphonated product, whose proton conductivity was found to be excellent in the order of 10^{-2} S/cm. FTIR spectra confirmed the sulphonation of the polymer. DSC and TGA analyses showed that the thermal stability of the polymer decreases on sulphonation. Because the degradation of the polymer occurs only after 250°C, these membranes can be safely used for PEMFC and DMFC applications at normal operating conditions, up to 100°C. Solvent absorption properties were also studied. The uptake of water is higher than the uptake of methanol in the ionomer chain, when compared to the Nafion® membrane. These membranes, hence, are expected to perform better in direct methanol fuel cells (DMFC). In DMFC, the high methanol permeability of Nafion® leads to lower cell efficiencies. Hence, an attempt was made to develop a hydrocarbon-based membrane with high proton conductivities in general, by a new method and to increase the DMFC efficiencies. These results suggest the suitability of the membrane as a PEM in fuel cell applications. However, the long-term stability of these membranes still needs to be assessed.

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