

Polymer Nanocomposite Membranes Based on Sulfonated Poly(ether ether ketone) and Trisilanol Phenyl POSS for Fuel Cell Applications

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Received 8 January 2010; accepted 26 April 2010

DOI 10.1002/app.32707

Published online 1 July 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polymer nanocomposite membranes based on sulfonated poly(ether ether ketone) (SPEEK) (degree of sulfonation 60%) containing varying amounts of open cage trisilanol phenyl polyhedral oligomeric silsesquioxane (POSS) ranging from 0.5 to 5 phr (parts per hundred parts of the polymer resin) were prepared and characterized. The composite membranes were characterized by water uptake, proton conductivity, methanol permeability, X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The presence of nanofillers in the composite films was confirmed by XRD and SEM-EDX. The domain size of POSS (for 0.5 phr sample) as determined by SEM was in the range of 50–100 nm. Thermal stability of SPEEK remained unaffected by the addition

of varying amounts of POSS. Equilibrium water uptake of all the composite membranes (maximum 42%) was higher than that of pure SPEEK membrane (23%) at 80°C. Proton conductivity of SPEEK as measured by two probe method increased upon incorporation of POSS and maximum value was obtained when the POSS content was 2 phr (w/w), that is, 4.5 mS/cm, which was higher when compared with SPEEK (1.5 mS/cm) and Nafion (3.4 mS/cm) at 90°C. Methanol permeability of composite membranes was lower than that of SPEEK/Nafion membrane. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3013–3023, 2010

Key words: fuel cell; membrane; SPEEK; POSS; proton conductivity

INTRODUCTION

Polymer electrolyte membranes (PEM's) have received attention over the last few years due to their use in PEM fuel cell and in direct methanol fuel cell (DMFC). Till date perfluoro sulfonic acid ionomers, such as Nafion[®] (DuPont), Aciplex[®] (Asahi Glass), Flemion are the state of the art materials being used in fuel cell applications,^{1–3} however, they suffer from certain disadvantages, such as high cost, high methanol cross over and reduced proton conductivity at higher temperature.^{4,5} Therefore, there is a need to develop new PEM materials, which can overcome some of these shortcomings. Several aromatic polymer ionomer membranes based on sulfonated polysulfone, sulfonated poly(ether ether ketone) (SPEEK), sulfonated polyimides, and so forth, are being explored for their potential application as fuel cell membranes.^{6–8} Another approach to obtain membranes with good proton conductivity and low cost is to prepare organic-inorganic composite membranes using these aromatic polymers with inorganic fillers and has been adopted by many groups.^{7,9–16}

Sulfonated SPEEK (SPEEK) has a very good thermal, chemical and mechanical stability which makes it a promising candidate for PEM's.^{17–22} SPEEK membranes have low methanol permeability when compared with Nafion but their proton conductivities are also lower when compared with Nafion. To improve the desired properties (increase in proton conductivity, mechanical strength, decrease in methanol permeability etc.) of SPEEK, researchers have incorporated different inorganic fillers, such as different heteropolyacids, nanoclays, inorganic proton conducting materials, and so forth in the SPEEK matrix.^{7,10–16,23–35}

Bridged polysilsesquioxanes (POSS), a class of hybrid organic-inorganic materials, find applications in the form of surface modifiers, coatings, catalysts, membrane materials, and so forth.³⁶ They are also being explored in the field of polyelectrolyte research.³⁷ These are prepared from different organo-bridged trialkoxysilane monomers by sol-gel polymerization. By using different monomers these materials can be tailored to give desired properties, such as porosity, permeability, chemical functionality [sulfonic acid groups (S-POSS), a mixture of sulfonic acid and octadecyl groups (SAPOSS) and phosphonic acid half-ester groups (PPOSS)], mechanical and thermal stability.^{38–43} When compared with Nafion, S-POSS/S-PPSU composite membranes (prepared by mixing

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POSS nanoadditive [10–20%] to sulfonated poly (phenyl sulfones) [S-PPSU containing 20.7–23.5 wt % SO_3H prepared by aromatic electrophilic sulfonation reactions using chlorosulfonic acid/acetic anhydride]) had superior dimensional stability, mechanical strength, and proton conductivity almost comparable with Nafion. As compared to control S-PPSU membranes, the composite membranes had higher proton conductivity, comparable dimensional stability and slightly decreased mechanical strength. The proton conductivity increased linearly with increasing sulfonic acid content. The presence of POSS nanoadditives increased water uptake without affecting the dimensional stability. Leaching experiments on membranes resulted in small mass losses caused by the dissolution of a small fraction of highly sulfonated water-soluble S-PPSU (30 wt % SO_3H) rather than the loss of any POSS additive. The high proton conductivity and excellent dimensional stability and mechanical properties of S-PPSU-POSS composite membranes in combination with their known resistance to acidity, oxidizing environments and leaching, make them very promising alternatives to Nafion as fuel cell proton exchange membrane materials.⁴²

A significant increase in conductivity, decrease in methanol permeability and improvement in water stability has been reported dependent upon the nature of filler, its shape and content. However, no reports are available on the use of POSS in SPEEK. It was therefore considered of interest to investigate the effect of POSS, which has hydroxyl groups at the surface on the performance properties of SPEEK.

In this work, composite membranes were prepared using SPEEK and trisilanol phenyl POSS. SPEEK was used as the polymer matrix because of its low cost and good stability when compared with perfluoro sulfonated ionomers. SPEEK with degree of sulfonation less than 50% is insoluble in most of the polar solvents and that with degree of sulfonation higher than 70% swells in water,^{44,45} therefore, SPEEK with degree of sulfonation $\sim 60\%$ was chosen for the preparation of composite membranes.

The literature clearly show that the incorporation of inorganic filler into the organic matrix resulted in an improvement in the performance properties.^{7,10–35} The use of hetero-polyacids, nanoclay, nanosilica is well reported in the literature, however no reports are available on the use of POSS in SPEEK. It was therefore considered of interest to investigate the effect of trisilanol phenyl POSS (TSP), which has hydroxyl groups at the surface. POSS has a cage-like structure, which can entrap small water molecules, and thus, increasing the water uptake of the membranes. In this work trisilanol phenyl POSS was used as the additive as it has three $-\text{OH}$ groups on its surface, which may further increase the water uptake. Dodecaphenyl POSS was also tried but it

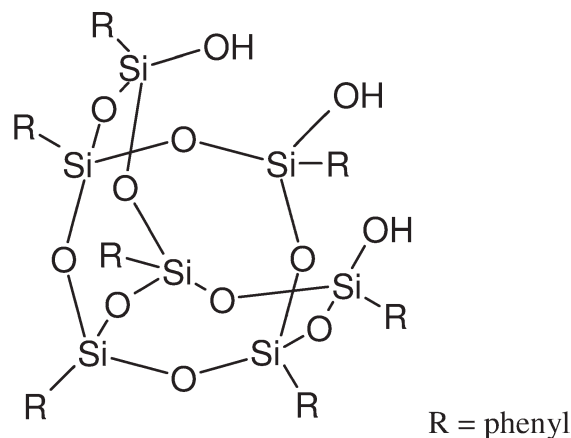
was not possible to disperse in the matrix as it did not dissolve in dimethyl sulfoxide (DMSO), therefore, TSP POSS was selected for this work.

The composite membranes thus prepared were then characterized for water uptake, proton conductivity, methanol permeability. For the morphological characterization XRD, SEM, EDX, and AFM were used. Thermal characterization of the composite films was done using thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Victrix PEEK (150 XF) was purchased from ICI (USA) and was sulfonated using sulphuric acid (Merck; 98%). Dimethyl sulfoxide (DMSO) was purchased from Merck and was used as such. Trisilanol phenyl polyhedral oligomeric silsesquioxane (POSS) was obtained from Hybrid Plastics (USA). The structure of POSS ($\text{C}_{42}\text{H}_{38}\text{O}_{12}\text{Si}_7$, Molecular Weight: ~ 931.34 FW, Specific Gravity: 1.05–1.1) used is given below:



Structure of trisilanol phenyl POSS

Preparation of SPEEK

Sulfonation of PEEK was done using concentrated sulphuric acid (98%) as the sulfonating agent. PEEK (5 g) was dissolved in 100 mL conc. H_2SO_4 at room temperature. After the complete dissolution of PEEK in H_2SO_4 , the reaction temperature was increased to 50°C and heating was done for another 2 h followed by quench cooling. The sulfonated PEEK (SPEEK) was then precipitated by drop-wise addition of reaction solution to ice cooled distilled water. SPEEK thus obtained was separated by filtration and washed repeatedly with distilled water till the filtrate was free of acid. It was then dried in a vacuum oven at 70°C for 12 h.

TABLE I
Details of Sample Preparation Along with Designation

Sample designation	SPEEK (g)	POSS (g)
SPEEK	1	–
SPEEK-0.5	1	0.005
SPEEK-1.0	1	0.010
SPEEK-2.0	1	0.020
SPEEK-5.0	1	0.050

Preparation of composite membranes

Membranes were prepared by solution casting method. The composite membranes were prepared in two steps. In the first step, POSS was dispersed in DMSO and SPEEK dissolved separately in DMSO (10% w/v). The solution of SPEEK (in DMSO) mixed with required amounts of POSS (dissolved separately in DMSO) was stirred for ~ 10 min followed by ultrasonication for 1 h. Composite films were prepared by pouring the solution mixture in petri dish followed by evaporation of solvent by heating at 80°C for 24 h. The dried films were stored in desiccator under ambient conditions. Membranes containing 0.5, 1, 2, and 5 phr of trisilanolphenyl POSS were prepared and the samples have been designated as SPEEK followed by numerals indicating the weight percent of POSS. For example, SPEEK having 0.5 and 2 phr of POSS have been designated as SPEEK-0.5 and SPEEK-2.0, respectively. Thickness of the films obtained was in the range of 80–210 μm. The details of sample preparation along with designation are given in Table I.

Characterization

Structural characterization

Structural characterization of the sulfonated PEEK (SPEEK) was done using ATR FTIR (Thermo Nicolet IR 200 spectrophotometer) and ¹H-NMR (Bruker 300MHz spectrophotometer) using DMSO-*d*₆ as solvent. For recording FTIR spectra, film samples were used.

X-ray diffraction

X-ray diffraction (XRD) analysis on SPEEK (film and powder), POSS and composite films was performed using a Panalytical X'pert PRO diffractometer (Philips X'pert PRO) with CuKα radiation source. The XRD patterns were obtained for 2θ varying between 2° and 60°.

Morphological characterization

The morphology of the composite membranes containing inorganic POSS was studied using ZEISS EVO-50 scanning electron microscope (SEM). The samples were coated with gold for observation using

the microscope. To determine the distribution of POSS, elemental profiles of the composite films was done by Bruker-AXS (model Quan Tan) energy dispersive X-ray system (EDX) and it was compared by comparing the peaks corresponding to Si.

Atomic force microscopy was performed using a Nanoscope IIIA Veeco Metrology group in tapping mode. For tapping mode silicon tip was used and samples were prepared by dip coating on silicon wafers. For the measurements, a force constant of ~ 50 N/m was used at a scan rate of 1 Hz.

Water uptake

Water uptake (WU) of the films was determined by immersing the weighed amount of samples in water at 80°C. After a given interval of time, the films were taken out, pat dried, and weighed using an analytical balance. The change in weight as a function of immersion time was noted and the percent water uptake at equilibrium was calculated using the following equation:

$$W_U = (W_s - W_d)/W_d \times 100$$

where

$$W_d = \text{Weight of dry film}$$

$$W_s = \text{Weight of film after immersion in water}$$

Proton conductivity

The proton conductivity measurements were carried out using Autolab PGSTAT-20 frequency response (Metrohm) AC impedance analyzer. A sample of the membrane with diameter 20 mm having thickness in the range of 80–210 μm was placed between the spring loaded steel block electrodes. The cell was placed in a thermo jacket connected to a thermostat. The impedance was measured in the frequency range between 100 Hz and 1 MHz. FRA software was used to fit the impedance spectra. The membrane conductivity was calculated using the formula

$$\sigma = L/RA$$

where *L* is the membrane thickness in cm and *A* is the surface of the electrode in cm² and *R* is derived from the lower intercept of the high frequency that produced the minimum imaginary response (i.e., due to the diffusion characteristics of the film) on a complex plane with the Re (*Z*) axis. All the proton conductivity measurements were carried out at 100% RH in the temperature range of 30–90°C. Average of three films was taken for reporting the proton conductivity values.

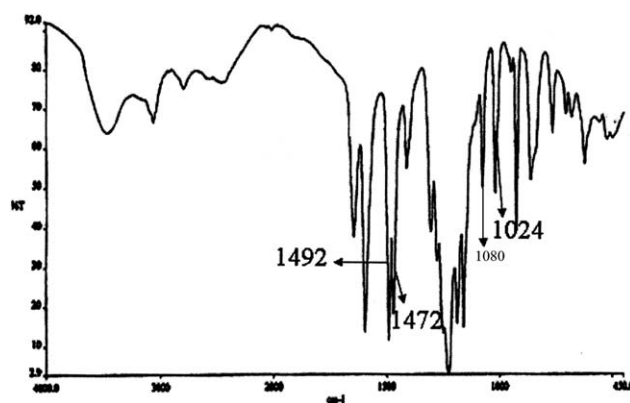


Figure 1 FTIR spectrum of SPEEK.

Methanol permeability

The measurement of methanol diffusion coefficient through the membrane was performed using an in-house built diffusion cell having two double wall compartments, which were separated by a membrane situated horizontally. One compartment contains distilled water and the other a solution of 20% (w/v) methanol. The solution was stirred using magnetic stirrer. A thermostat provided a constant temperature in the outer environment. Before measurement, the membranes were dipped in distilled water for 24 h. The measurements were done at 50°C for a time period of 5 h and the methanol content in permeate was measured using gas chromatography with capillary column of dimethyl polysiloxane at a temperature of 60°C. For each sample average of three readings was taken.

The methanol diffusion coefficient for the membrane was then measured by first Fick's law, using the following equation:

$$D = \frac{L * V_{\text{perm}}}{A * T_{\text{exp}}} \ln \left(\frac{C_{\text{startperm}} - C_{\text{feed}}}{C_{\text{endperm}} - C_{\text{feed}}} \right)$$

Where, L = membrane thickness (cm)

A = surface area of the membrane (cm²)

V_{perm} = volume of the permeate (cm³)

t_{exp} = time (s)

$C_{\text{startperm}}$ = permeate concentration at $t = 0$

C_{endperm} = permeate concentration at $t = t_{\text{exp}}$

C_{feed} = feed concentration (constant)

Thermal characterization

Thermal stability of the polymers was evaluated by recording thermogravimetric (TG) and derivative thermogravimetric (DTG) traces in nitrogen atmosphere (Pyris 6 TGA, Perkin Elmer) in the temperature range of 50°C–800°C. A heating rate of 20°C/min and the sample size of 10 ± 2 mg in the film form were used in each experiment.

RESULTS AND DISCUSSION

Characterization of SPEEK

Structural characterization of SPEEK was done using FTIR and ¹H-NMR. A typical FTIR of SPEEK is shown in Figure 1. Presence of sulfonic acid groups was confirmed by FTIR by the appearance of peaks at ~ 1080 (asymmetric) and 1030 cm⁻¹ (symmetric), which are characteristic peaks of SO₂. C–C absorption band of aromatic ring at 1492 cm⁻¹ splits upon sulphonation (1472 cm⁻¹) thereby confirming the structure of SPEEK.

Figure 2 shows ¹H-NMR spectrum of SPEEK. Because of the presence of sulfonic acid group, the H_E proton (structure of SPEEK), which is ortho to the sulfonic acid group shows a downfield shift when compared with H_C and H_D and is observed at ~ 7.6 ppm. The intensity of H_E is equivalent to SO₃H content, therefore degree of sulfonation can be calculated by taking the ratios between the peak area of H_E to the peak areas of the rest of the aromatic hydrogens, that is, H_{A,A',B,B',C,D}.

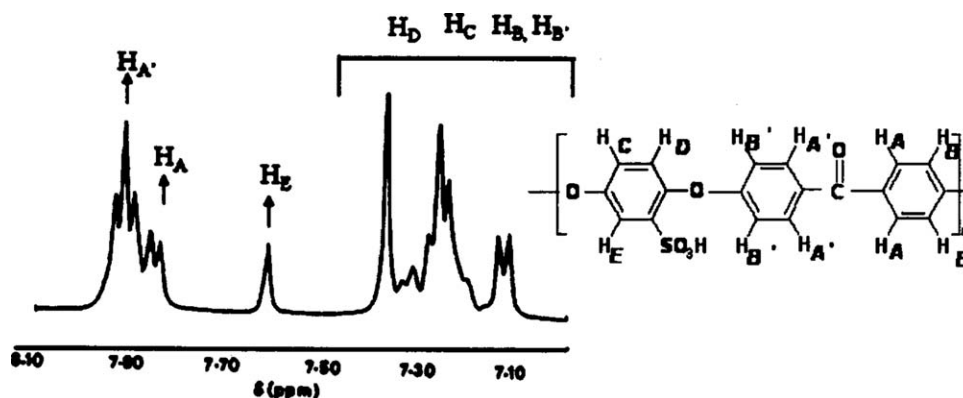


Figure 2 ¹H-NMR spectrum of SPEEK.

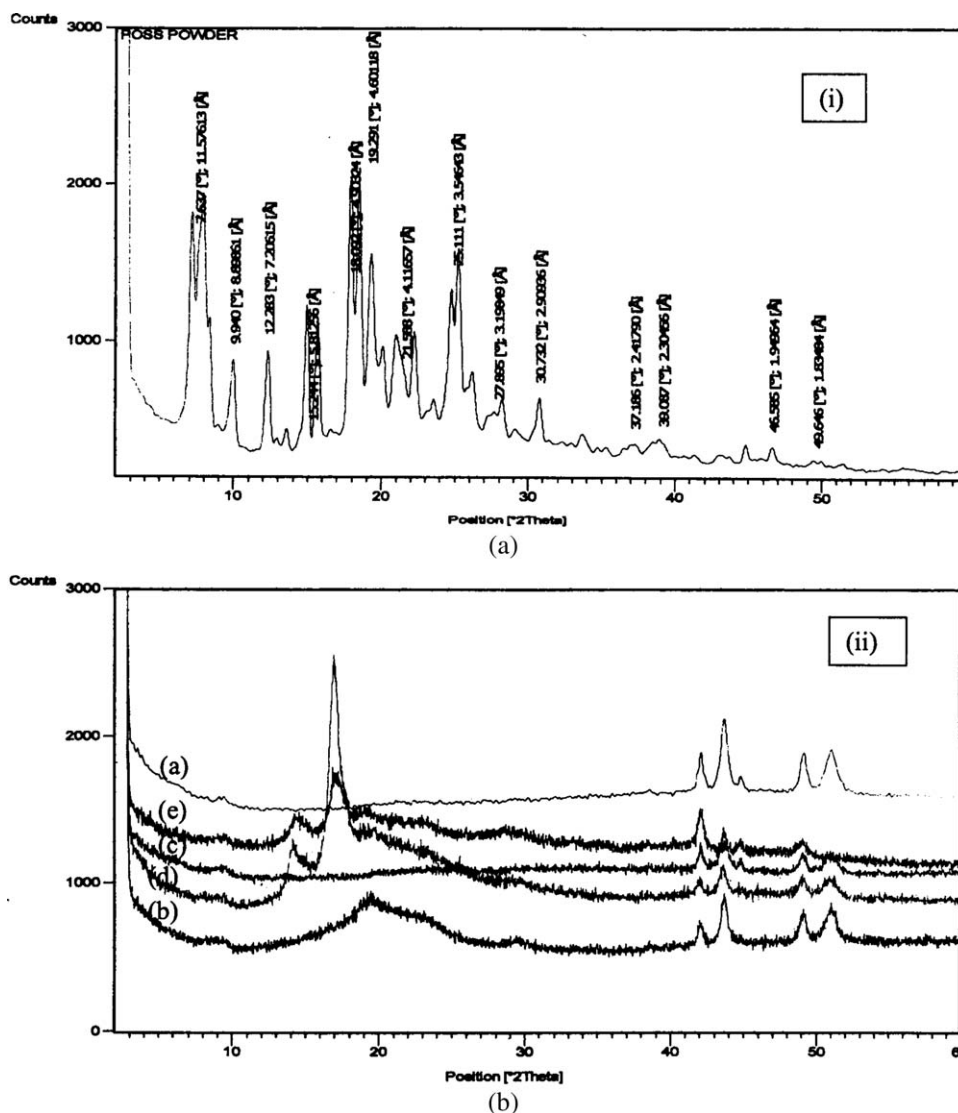
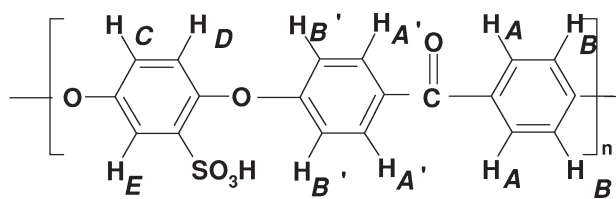


Figure 3 XRD diffractogram of (a) SPEEK, (b) SPEEK-0.5, (c) SPEEK-2.0, and (d) POSS.



Structure of SPEEK

Degree of sulfonation was calculated from ¹H-NMR using the following formula⁷

$$DS (\%) = n * 100$$

$$n = \frac{H_E}{\sum H_{A,A',B,B',C,D}}$$

Where 'n' is the number of H_E per repeat unit.

For the preparation of composite membranes in this study SPEEK with 60% DS was used.

Characterization of composite films

Morphological characterization

XRD. Figure 3 show the XRD patterns of SPEEK, triislanophenyl POSS, and the composite films. From the figure, it is evident that SPEEK is a semicrystalline, whereas triislanophenyl POSS is highly crystalline in nature. XRD pattern of SPEEK powder was also recorded and it did not show any crystalline peaks, but when it was dissolved and casted into a film it showed a semicrystalline nature, the same has been reported in the literature.³³ In the XRD of the composite films, it was observed that the crystallinity of POSS was disturbed and the crystalline peaks of TSP POSS were not observed in the

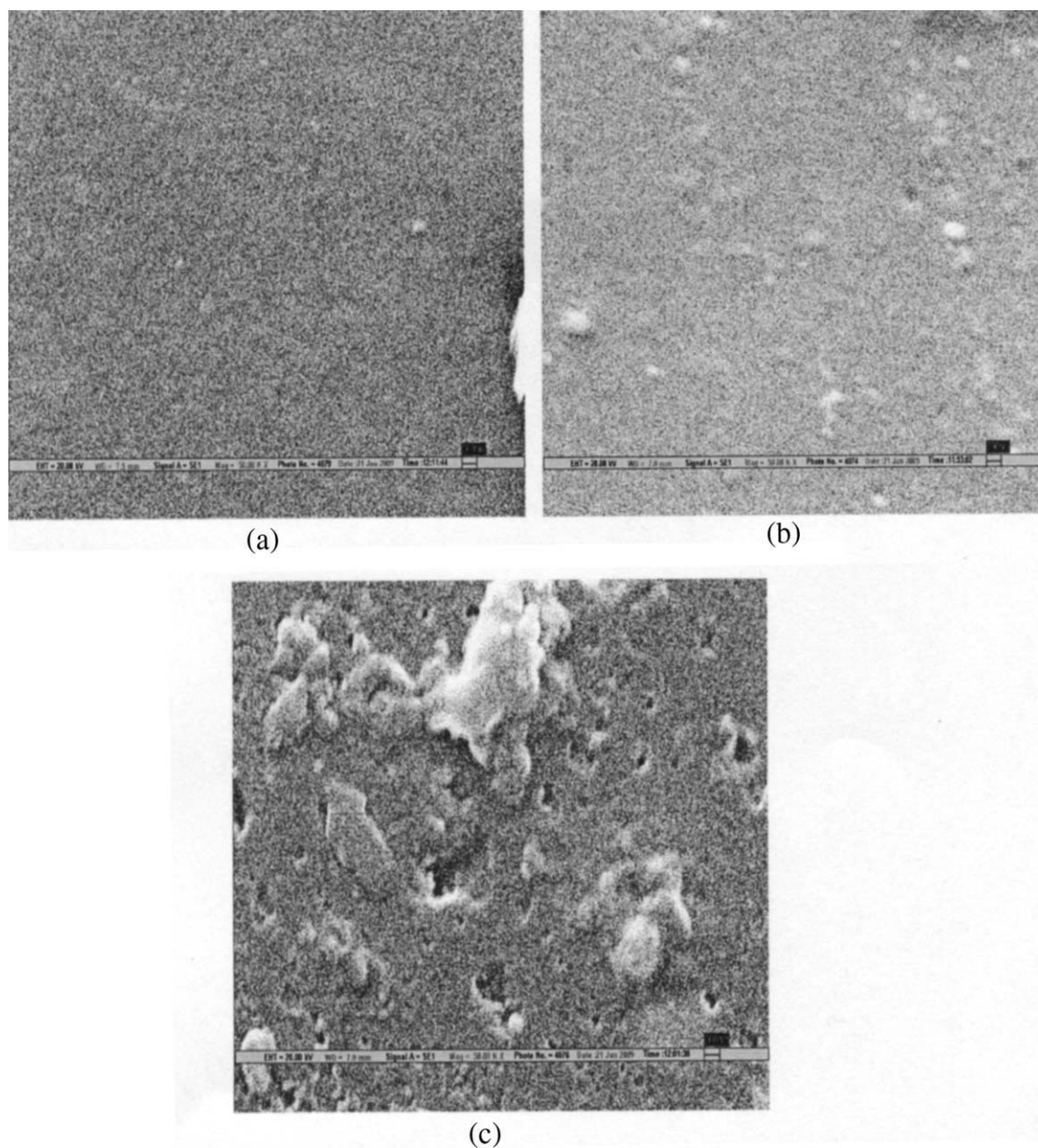


Figure 4 SEM micrographs (a) SPEEK, (b) SPEEK-0.5, and (c) SPEEK-2.0.

composite membrane of TSP POSS and SPEEK in all the samples except SPEEK-2.0. Similar observation was also made by Morgan et al. in the POSS/polystyrene composites.⁴⁶ They prepared composite membranes using polystyrene and octaisobutyl (OIB) POSS/ trisilanol phenyl (TSP) POSS. As such OIB-POSS and TSP-POSS are crystalline in nature. In the WAXD of octaisobutyl POSS/PS composites, they observed peaks corresponding to crystalline POSS as well as the amorphous nature of PS but in the case of TSP POSS/ PS composites, the nanodispersed TSP POSS showed no crystalline peaks.

Scanning electron microscopy. The dispersion of POSS in the SPEEK matrix was studied by SEM. The SEM images of composite membrane (sample SPEEK-0.5)

[Fig. 4 (b)] show a uniform distribution of the nanoparticles and the domain size of the POSS particles was in the range of 50–100 nm, whereas for the sample SPEEK-2.0 [Fig. 4 (c)], some agglomeration was observed in the SEM micrograph.

SEM-EDX. Figure 5 show the SEM-EDX images of composite membranes. To have a good interface between the additive and the polymer matrix it is desirable that the inorganic additive is uniformly distributed so that the two components behave in a synergistic manner. SEM-EDX clearly show the presence of silica and its content increases with increasing amount of POSS in composite membranes (Fig. 6).

Atomic force microscopy. AFM was used to study the topography of the pristine as well as composite

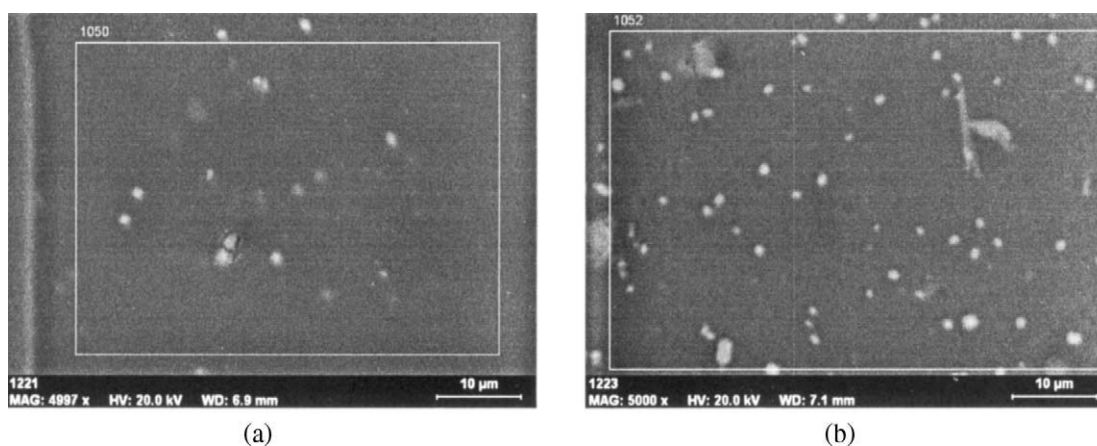


Figure 5 SEM-EDX of composite membranes (a) SPEEK-0.5 and (b) SPEEK-2.0.

SPEEK membranes. The tapping mode images of the samples are shown in Figure 7. The dark regions in the images were assigned to soft regions corresponding to hydrophilic regions containing water and the light regions were assigned to hydrophobic polymer backbone.⁴⁷ The phase separated structures have benefit to form proton transport channels, which lead to improvement of proton conductivity. Composite membranes showed better microphase separation than pure SPEEK membrane, which might help protons to transport.

Water uptake

The water uptake for all the membranes after 24 h of immersion was calculated at 80°C and the results are tabulated in Table II.

The water uptake of composite membranes was higher than that of pure SPEEK membrane. This may be due to the cage structure of POSS, which also has hydroxyl groups on the surface. Higher water uptake in composite membranes could be because of the entrapment of water molecules in the cage structure of POSS. Increase was much higher in case of SPEEK 0.5, which has lowest amount of POSS followed by a decrease with increase of POSS content from 0.5 to 5 phr. All the samples had water uptake much higher than SPEEK. The decrease in water uptake at higher concentration of POSS could be because of the agglomeration of POSS particles, which was also observed by SEM and thus all the hydroxyl groups may not be available.

Proton conductivity

Proton conductivity of SPEEK films in the absence or presence of varying amounts of POSS was measured in the temperature range of 30–90°C. Results of proton conductivity for all the composite membranes prepared using varying amounts of POSS are given

in Table III. Addition of POSS to SPEEK membrane increased the proton conductivity. Proton conductivity of the composite membranes was higher than that of pristine SPEEK membrane (1.5 mS/cm). The value of proton conductivity was highest over the whole temperature range for the composite membrane having 2 phr of trisilanol phenyl POSS followed by a decrease as the concentration of POSS increased beyond 2 phr. The decrease in proton conductivity at higher concentrations of POSS could be because of the hindrance in the exchange of protons, which is necessary for attaining higher proton conductivity. Similar reduction in proton conductivity was also observed by Karthikayen et al.⁴³ on addition of silica containing hybrid materials to SPEEK. They added these inorganic fillers in higher percentages, that is, up to 10 wt %. In this study, TSP POSS was added in very small quantity (from 0.5 to 5 phr) and increase in proton conductivity was observed up to 2 phr beyond which it showed a decrease but it was always higher when compared with pristine SPEEK. The increase in proton

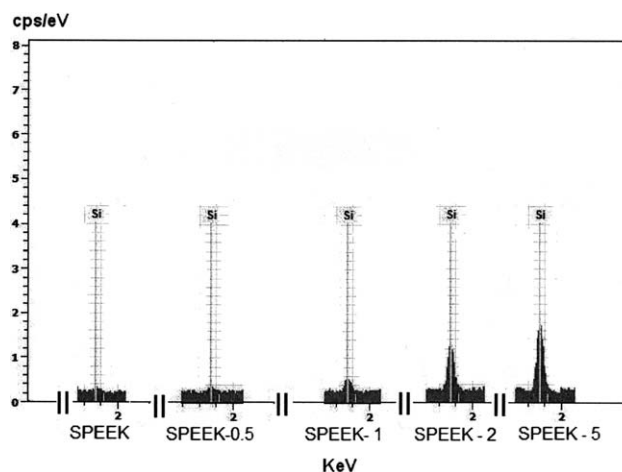


Figure 6 Comparison of Si content in different films as obtained from SEM-EDX.

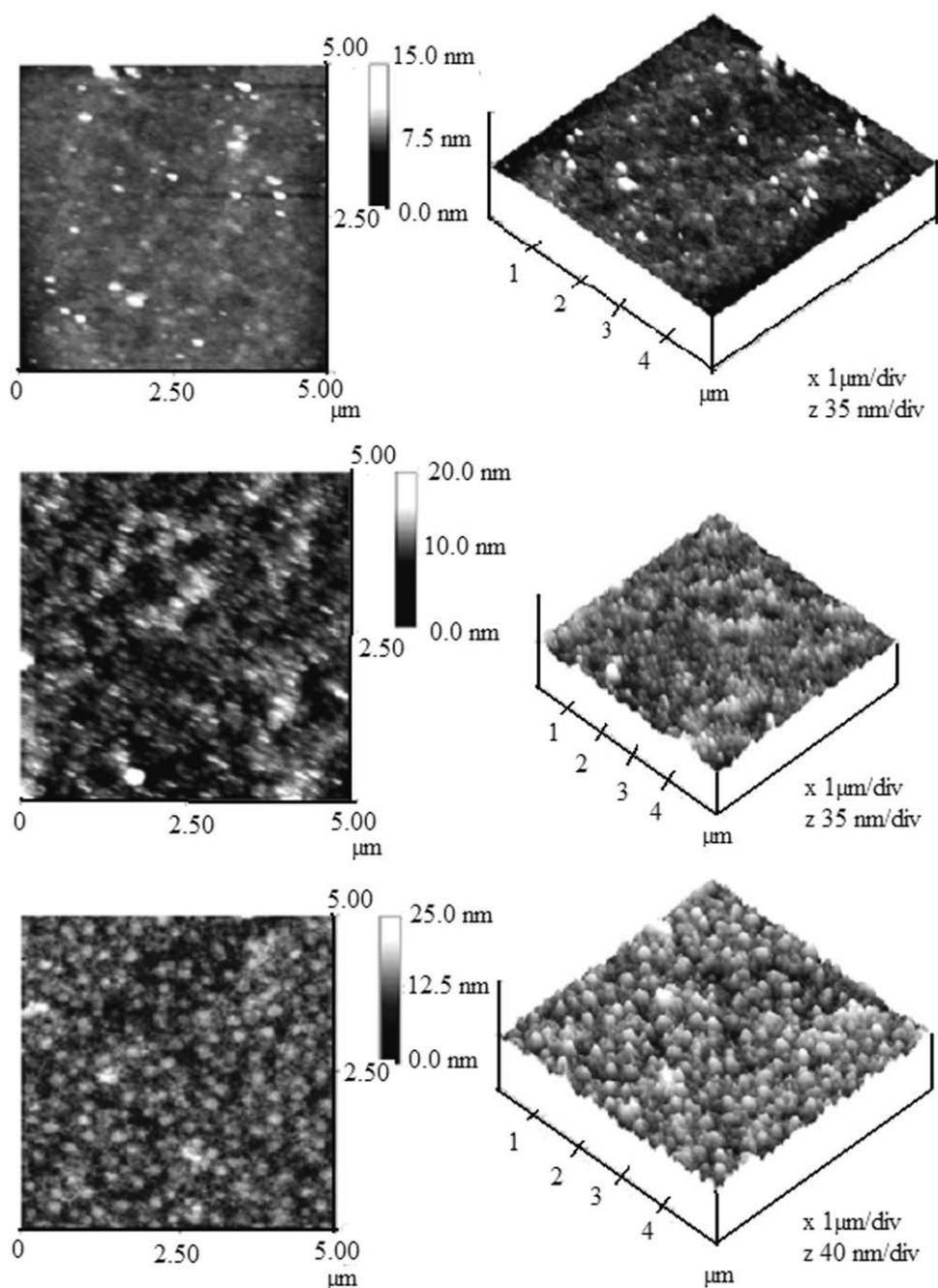


Figure 7 Topography of membranes from AFM (a) SPEEK, (b) SPEEK-0.5, and (c) SPEEK-2.0.

conductivity by the addition of crystalline POSS could be because of the formation of water channels, which were not observed in SPEEK membrane (Fig. 7) that helps in the exchange of proton, and thus, resulted in an increase in conductivity.

Inorganic fillers have been used extensively with sulfonated polymers to improve their proton conductivity, chemical, or mechanical stability. For example, Bello et al.²⁸ have reported that the proton conductivity of SPEEK increases on addition of inorganic fillers, such as tungsto-phosphoric acid and MCM-41(Mobil Composition of Matter No. 41)^{26,12} and they could achieve a maximum gain with an

inorganic filler loading of 30%. Similarly Zaidi²⁵ and Othman et al.³¹ have reported that by incorporating 20% boron phosphate to SPEEK/PBI blend and

TABLE II
Results of Water Uptake for SPEEK and Composite Membranes

Sample designation	Water uptake (%)
SPEEK	25
SPEEK-0.5	42
SPEEK-1.0	38
SPEEK-2.0	35
SPEEK-5.0	36

TABLE III
Proton Conductivity of Pristine and Composite SPEEK Films at Different Temperatures

Sample designation	Thickness (μm)	Proton conductivity (mS/cm)				
		30°C	40°C	50°C	70°C	90°C
SPEEK	84	0.86	1.01	1.1	1.3	1.5
SPEEK-0.5	199	1.01	1.22	1.37	1.8	2.1
SPEEK-1.0	185	1.7	2.3	2.5	3.4	3.5
SPEEK-2.0	207	3.4	3.5	3.9	4.3	4.5
SPEEK-5.0	203	0.5	0.56	0.61	0.87	1.2
Nafion-117	90	2.56	2.84	2.92	3.04	3.24

SPEEK, proton conductivity increased but it was lower when compared with Nafion. Composite membranes of SPEEK with laponite and MCM-41 as inorganic fillers have been reported by Karthikeyan et al.²⁶ The fillers were modified using imidazole glycidoxypopyl triethoxysilane (IGPTES) and 3-2-imidazolin-1-propyltrimethoxysilane (IPTMS). They added these fillers up to 30% and observed that till 10% of the filler the proton conductivity increased and on further increasing the amount of inorganic filler it started to decrease. Composite membranes of SPEEK with treated zirconium phosphate (ZrP) and tetraethoxysilane (for in situ generation of silica) have also been prepared²⁷ and these membranes showed an increase in the proton conductivity values with increasing amount of ZrP but still these membranes had a very low proton conductivity when compared with that of Nafion as measured under the similar conditions.

The amount of inorganic fillers required to attain the higher conductivity was very high, that is, in the range of 20–30 wt %. Second, they have the problem of leaching out and the conductivity values in most of the composite membranes was lower when compared with Nafion. It has been reported that S-PPSU-POSS composite membranes had high proton conductivity and excellent dimensional stability and mechanical properties in combination with resistance to acidity, oxidizing environments, and leaching.⁴² In this work also, a considerable increase in proton conductivity (approximately three-fold) of SPEEK was observed by adding 2 phr of POSS, which is nonleachable. To check non-leachability of POSS, the films were first dried and then kept in water and after that they were again dried and weighed. No change in the weight was observed. Also proton conductivity was measured again after keeping the samples in water and the two values were identical.

Methanol permeability

Methanol permeability of the composite membranes was calculated at 50°C and the results are tabulated in Table IV. All the composite membranes showed

lower methanol permeability as compared to SPEEK. The decrease in methanol permeability in the presence of POSS could be because of the hindrance of permeation of methanol by the caged structure of POSS nanoparticles. A similar decrease in methanol permeability has been observed by addition of different clays, such as laponite (modified and unmodified) and MCM-41 (Mobil Composition of Matter No. 41),^{26,12} MMT (Montmorillonite),¹⁶ ZrP and SiO₂,^{27,35} hydrated tin oxide,^{14,35} BPO₄,³¹ hetero-polyacids^{24,33} and so forth.

Selectivity, which is defined as the ratio of proton conductivity to methanol permeability is also given in Table IV. The selectivity values were calculated at 50°C. For a fuel cell membrane, it is desirable to have a higher value of selectivity. All the composite membrane had selectivity values higher than the pure SPEEK membrane, whereas samples SPEEK-1.0 and SPEEK-2.0 showed higher selectivity when compared with Nafion.

Thermal characterization

TG/DTG traces were recorded for the SPEEK as well as for all the composite membranes and are shown in Figure 8.

SPEEK and composite films showed three step decomposition. The first mass loss occurred in the temperature range of 50–200°C, (loss of physically and chemically bound water), of 200–450°C (decomposition of sulfonic acid groups) and 450–800°C (due

TABLE IV
Results of Methanol Permeability and Selectivity of Different Composite Membranes

Sample designation	Methanol permeability ($10^{-7} \text{cm}^2/\text{s}$)	Selectivity ($10^7 \text{ms}/\text{cm}^3$)
SPEEK	7.7	0.143
SPEEK- 0.5	5.4	0.254
SPEEK- 1.0	4.8	0.521
SPEEK- 2.0	4.0	0.975
SPEEK- 5.0	2.3	0.265
Nafion-117	11.0	0.265

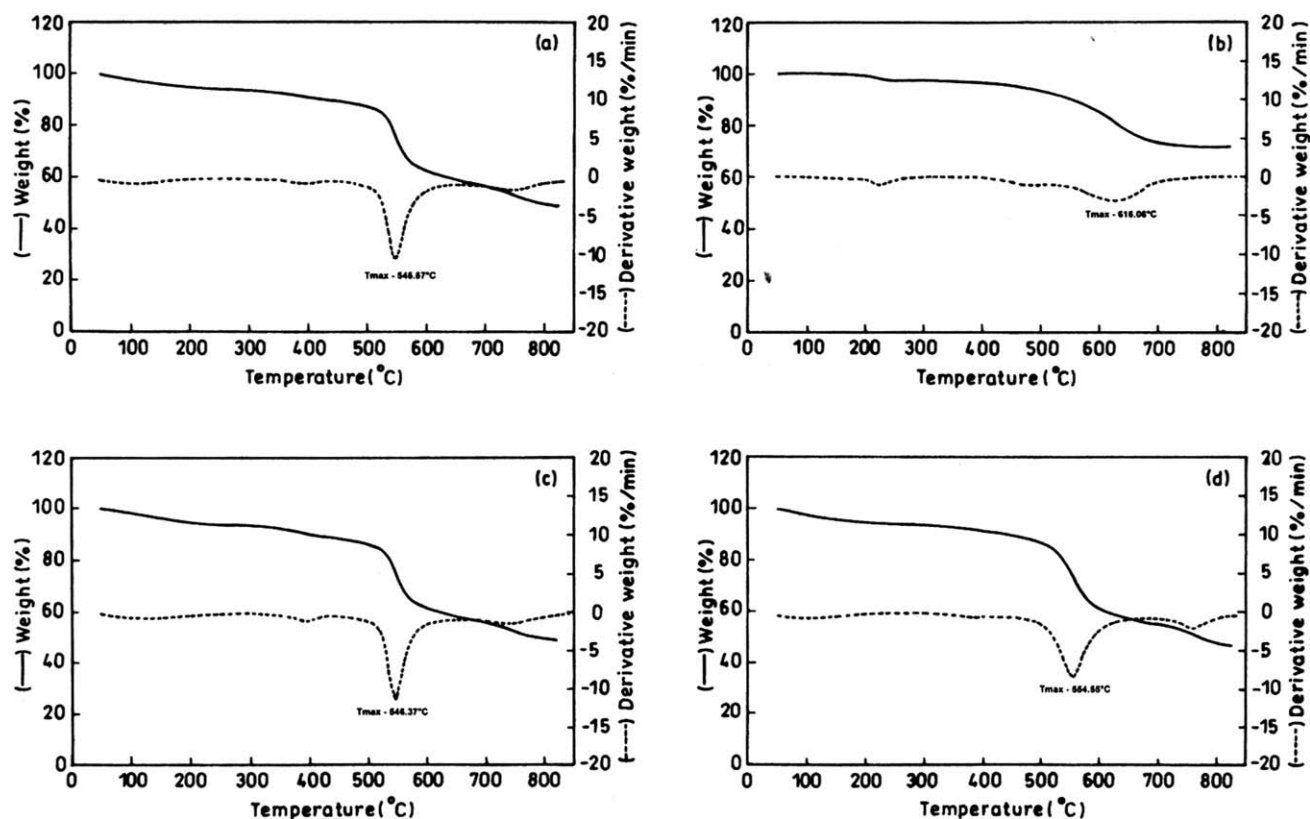


Figure 8 TG/DTG curves of (a) SPEEK, (b) POSS, (c) SPEEK-P 0.5, and (d) SPEEK-P 2.0.

to the main chain degradation of polymers) was used to compare the relative thermal stability of polymers. The results are summarized in Table V.

Percent mass loss decreased in the first step (below 200°C) upon incorporation of POSS up to 2 phr, whereas it showed an increase in the temperature range of 450–800°C. POSS also showed a mass loss of 22.7% in the temperature range of 450–800°C and the mass loss below 200°C and in the temperature range of 200–450°C was much less when compared with SPEEK. These results clearly show that the incorporation of varying amounts of POSS did not affect the thermal stability of SPEEK.

TABLE V
Results of TG/DTG Traces for SPEEK and SPEEK-POSS Composites in Nitrogen Atmosphere (Heating Rate 20 °C/min)

Sample designation	% Mass loss			Char yield at 800°C (%)
	Below 200°C	200–450°C	450–800°C	
SPEEK	5.4	5.4	39.2	50.0
SPEEK-0.5	4.6	6.9	39.2	49.2
SPEEK-1.0	3.8	6.2	41.1	48.8
SPEEK-2.0	4.6	6.2	41.5	47.7
SPEEK-5.0	6.1	6.4	38.5	49.0
POSS	1.2	3.8	22.7	72.3

CONCLUSIONS

From these results, it can be concluded that POSS can be used as a promising filler in SPEEK. The composite membranes prepared using 2 phr of POSS as filler and SPEEK as matrix showed a three-fold increase in proton conductivity with a significant decrease in methanol permeability. These composite membranes had much higher selectivity (approximately seven times) when compared with SPEEK. On the basis of these results, it can be concluded that such membranes can find applications in fuel cells.

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