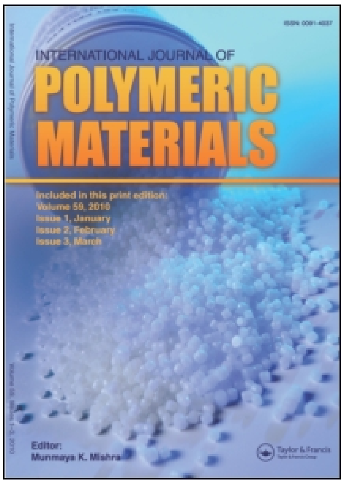

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Evaluation of Sulfonated Poly(Ether Ether Ketone) Silicotungstic Acid Composite Membranes for Fuel Cell Applications

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Fuel cells have received much attention for clean power generation for transportation, portable power systems, etc. Composite membranes are better than the homopolymeric membranes, as their properties can be altered by varying the composition.

In our present study, five samples of sulfonated poly(ether ether ketone) (SPEEK)/silicotungstic acid (SWA) composite membranes were prepared. The molecular interactions of the composite membranes were characterized by FTIR and XRD techniques. The ion exchange capacity (IEC) was studied. The thermal suitability was found to be excellent as confirmed by TGA. SEM analysis revealed uniform distribution of the hetero poly acid (HPA) in the composite membranes. The protonic conductivity determined by impedance spectroscopy was found to be in the order of 10^{-3} S/cm. The change in the mechanical properties of the composite membranes was observed by Universal Testing Machine (UTM).

Overall, the composite membranes proved to be an excellent candidate for fuel cell applications.

Keywords: composites, ion exchange capacity, PEMFC, proton conductivity

INTRODUCTION

In the last decade, the government and industry have paid much attention to the production of energy through nonpolluting devices, especially for automotive purposes. One of the most interesting and

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promising devices for the production of electric energy is the fuel cell, which is the best possible answer for a sustainable growth and for nonpolluting devices. Fuel cells are excellent electrochemical energy conversion devices that directly convert the chemical energy of the fuel into electric energy without the intermediate mechanical energy. Among the different types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) has attracted much interest both for automotive as well as stationery power applications [1–3]. The successful performance of a PEMFC essentially depends on the role played by the membranes. The currently used solid polymer electrolyte materials are either perfluorinated polymers, designated as Nafion® or Nafion-like polymers supplied by Dow, Asahi and other companies. In the past years, two classes of materials were investigated for use in PEMFC [4]. One is the homopolymeric materials, which includes polyimides [5–7], polyketones [8–10], poly(phthalizinones) [11–14] and polysulfones [15–17] with higher efficiency, lower cost, long-term stability, and, appreciable mechanical and electrical properties. The second is the composite materials [18–23] of organic-inorganic composition with nanosize interface between organic and inorganic domains. These types of materials with their unique properties offer exceptional ways to synthesize new materials [4]. A comprehensive review of the extensive literature on the emerging relevant materials was published by Savadogo [24].

The heteropoly acids (HPAs) are not only strong Bronsted acids but also excellent solid electrolytes [25]. The hydrated form of silicotungstic acid (SWA) has an ionic conductivity of $2 \times 10^{-2}\,\mathrm{Scm}^{-1}$ at room temperature [26]. The major disadvantage with HPAs is their solubility in water. Consequently, the major research objective is to fix the HPAs in a stable structure by forming composites [27]. In the dehydrated phase or in polar solvents, HPAs exhibit a primary structure called a Keggin unit as illustrated in Figure 1. It consists of a central atom in a tetrahedral arrangement of oxygen atoms surrounded by twelve oxygens octahedrally connected with tungsten or molybdenum. There are four types of oxygen atoms found in the Keggin unit: the central oxygen atoms, two types of bridging oxygen atoms and the terminal oxygen atoms [4].

The primary objective of this article is to prepare a series of sulfonated poly(ether ether ketone) (SPEEK)/SWA composite membranes of flexible, homogeneous and large-sized hybrid macromolecules with different SWA concentrations, and to evaluate their properties for a successful application in PEMFC.

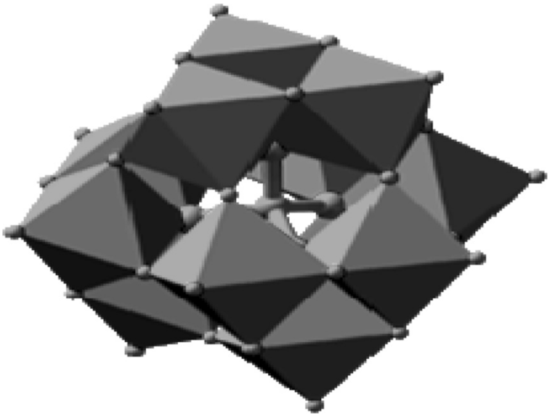


FIGURE 1 Keggin structure of $(SiW_{12}O_{40})^{3-}$ anion.

EXPERIMENTAL

Materials

PEEK procured from Victrex, England was dried overnight at 105°C before use. N-methyl pyrollidone, sulphuric acid and SWA were purchased from SRL Industries and were used as received.

Sulfonation of PEEK

In a typical experiment, 10 g of dry PEEK powder were dissolved in a suitable quantity of sulphuric acid under nitrogen atmosphere. The reaction was allowed to proceed for a definite time with constant stirring. The resulting reaction mixture was then poured on crushed ice and the innumerable fibers that were formed were recovered by filtration. They were then washed several times with deionized water until the pH ranges between 6 and 7. They were then dried at 80°C for 15 h. The product obtained is the sulfonated form of polyether ether ketone with a sulfonation degree of 40–45%.

Preparation of SPEEK/SWA Composite Membrane

SPEEK/SWA composite membranes were prepared by casting a solution of the acid form of SPEEK and SWA. SPEEK was first dissolved in NMP at 70°C and then SWA was added slowly over time with constant stirring. The percentage of SWA in the mixture was varied from 5 to 25%. The stirring was continued for another 4 h at 60°C. The fluid mixture was then spread on a glass plate with the help

TABLE 1 Composition and Properties of Composite Membranes

Membrane code	Composition (wt %) (SPEEK:SWA)	IEC, milliequi/g	Absorption, wt %		Conductivity, $\times 10^{-3}$ S/cm
			Water	Methanol	
CMS 1	95:05	2.09	10.29	6.36	0.92
CMS 2	90:10	2.21	7.69	3.24	1.82
CMS 3	85:15	2.42	3.14	1.13	2.02
CMS 4	80:20	2.60	1.05	−1.39	2.03
CMS 5	75:25	2.90	−2.09	−2.42	2.04

of a doctor's knife. The film was dried at 80°C for 10 h and then at 100°C for 6 h. The resulting membranes were transparent and pale brown in color with a thickness of about 60 μ. The variation in the percentage composition of the composite membranes is given in Table 1.

MEASUREMENTS

Ion Exchange Capacity

The ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1 g of the dry polymer. It was determined by titration. The membrane in its acid form was weighed and then soaked in saturated KCl solution in order to extract all the protons from the membrane. The solution was then neutralized using a very dilute solution of sodium carbonate of known concentration. The EW (equivalent weight) values were calculated from the dry weight of the membrane divided by the volume and normality of the sodium carbonate solution. The IEC values were expressed as the number of milliequivalents of sulfonic groups per gram of the dry polymer.

Thermal Studies

TGA analysis was carried out to determine the thermal suitability of the membrane. The weight loss of the membrane with increasing temperature at a heating rate of 20°C/min over the temperature range of 30 to 800°C under nitrogen atmosphere was followed using a SDT Q600 US Analyzer.

Water and Methanol Uptake

The maximum water/methanol uptake of the composite membranes was determined by measuring the change in the weight before and after immersion in the corresponding solvent. The membrane was first immersed in distilled water/methanol overnight. It was then weighed quickly after removing the surface water/methanol to determine the wet membrane weight (W_{Wet}). The dry membrane weight (W_{Dry}) was determined after drying the membrane at 100°C for 2 h. The water/methanol uptake was calculated by using the following equation.

$$H_2O/MeOH\ \mathrm{Uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

FTIR Measurements

The IR spectra ($450–4000\,cm^{-1}$) for the dried membranes were recorded with a Perkin Elmer FTIR spectrometer at 25 ± 2°C. The samples were dried at 100°C for an hour before recording the spectrum. The interactions of SWA with the sulfonic groupings of SPEEK were studied.

XRD Measurements

XRD measurements were performed using the X' Pert Pro diffractometer. The dried membranes were mounted on an aluminum sample holder. The scanning angle was varied from 1° to 80° with a scanning rate of 2° per min. All the spectra were taken at ambient temperatures (25 ± 2°C).

Scanning Electron Microscopy

The surface morphology of the composite was investigated using scanning electron microscope (JEOL 6360 instrument). A piece of membrane was vacuum-sputtered with a thin layer of platinum prior to SEM examination. The nature of pores, the level of dispersion and the crystal formation of the SWA were examined.

Protonic Conductivity

The proton conductivity was measured by the impedance technique (Autolab) over the frequency range 10 Hz–40 kHz in the hydrated condition. The proton conductivity (σ) of the composite membranes was calculated from the resistance offered by the membrane using the relationship $\sigma = L/RA$, where L is the thickness of the membrane in cm, R is the resistance of the membrane in ohms and A is the area of the membrane under study in cm^2.

UTM Studies

The mechanical properties were obtained from a Hounsfield Universal Testing Machine. The samples were cut into a size of 5 mm × 50 mm as reported by F. C. Dung et al. [28]. The crosshead speed was set at a constant speed of 10 mm/min. For each testing at least three measurements were made and the average value was reported.

RESULTS AND DISCUSSION

Ion Exchange Capacity

The IEC values of the composite membranes are given in Table 1. A linear increase in the ion exchange capacity with increase in the percentage of the heteropoly acid is observed. The milliequivalents of protons per gram of the membranes for different amounts of SWA in the membranes are 0.07, 0.14, 0.21, 0.28, and 0.35 for CMS 1, CMS 2, CMS 3, CMS 4, and CMS 5, respectively.

But the actual amount of protons that was available for ion exchange was several times higher than the above values. Hence it is not the protons of SWA alone, but those of the SO_3H groupings of the sulfonated polymer, that are involved in the proton exchange. Again, the increase in the IEC values with increase in the SWA loading reveals that SWA is not completely blocked from exchanging ions by the host polymer. The higher IEC reveals that even the protons that are buried inside the bulk portion of the polymer may also be involved in ion exchange through the hopping mechanism.

Thermal Studies

The thermogravimetric analysis of the composite membranes was carried out between 30 and 800°C. The TGA curves of PEEK, CMS 1 and CMS 4 are shown in Figures 2a–c, respectively. The initial weight loss between 30 and 150°C is due, to the loss of adsorbed water on the surface of the membrane. It is followed by another weight loss in the composite membranes extending up to 325°C. This assigned to the loss of SO_3H groupings based on the thermogram of the parent sulfonated polymer. From 340 to 545°C, there is another weight loss which can be attributed to the decomposition of SWA. The decomposition above 545°C is due to the degradation of the polymer matrix. The percentage of the residue was found to be around 36% and is assigned to the inorganic oxides derived from the tungstic acid. A higher value of the residue therefore indicates inorganic as well as the char that remains after the final stage of decomposition.

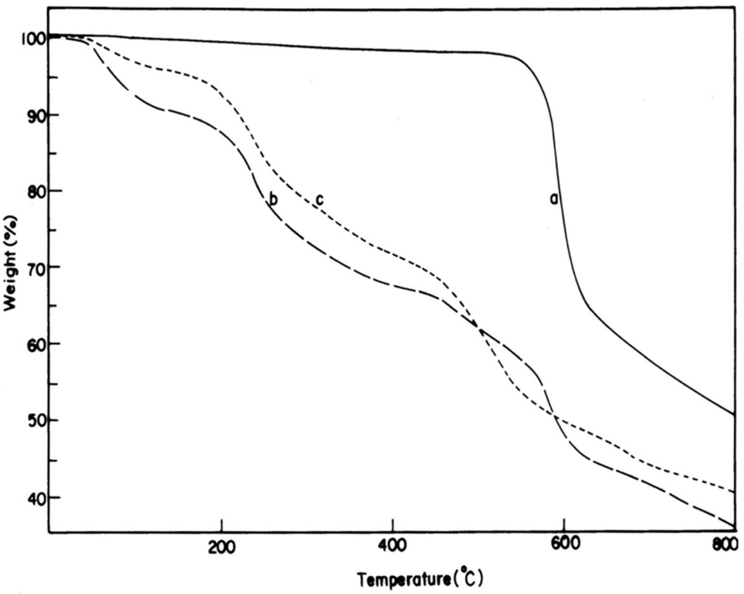
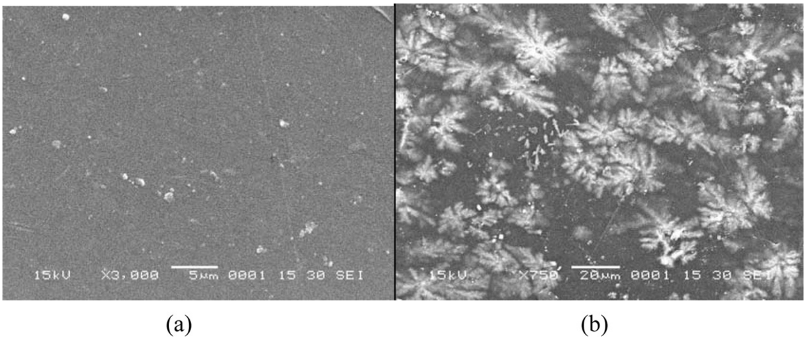


FIGURE 2 TGA curves of (a) PEEK, (b) CMS 1, and (c) CMS 4.

Water and Methanol Absorption

The results of water and methanol absorption were given in Table 1. In both cases, negative absorption is observed. This may be due to leaching out of SWA from the membrane. The SEM picture (Figure 3b) clearly reveals the crystal formation of SWA above 10% dosage. These crystals occupy the space in between the polymer



(a) (b)

FIGURE 3 SEM images of (a) CMS 1 and (b) CMS 3.

chains and because of the crystal formation they do not have much interaction with the polymer chain and hence when immersed in the solvent, they undergo leaching. Also the crystals at the interlayer regions hinder the interaction between the SO_3H groups of one layer with the other layer. Therefore, a reduction in the mechanical properties is expected with increase in the concentration of SWA.

FTIR Measurements

The FTIR spectrum of CMS 3 is shown in Figure 4a. There is a broad envelope in the high-energy region lying between 2100 and 3900 cm^{-1}. It includes the OH stretch of SWA and SO_3H group of SPEEK and C-H vibrations of the aromatic ring. The fine structure bands at 2609 and 2428 cm^{-1} are due to hydrogen bonding of different OH groupings in the bulk material. This hydrogen bonding is responsible for the interaction between the SWA molecules and the polymer matrix. The C=O

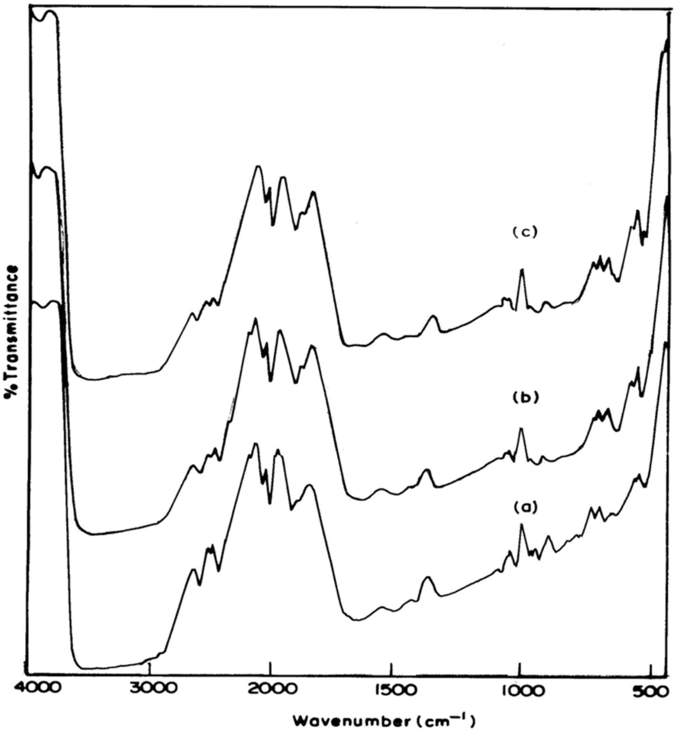


FIGURE 4 FTIR spectra of (a) CMS 3, (b) CMS 4, and (c) CMS 5.

vibration gives its peak at 1657 cm^{-1}. Generally this vibration occurs close to 1750 cm^{-1}. But because of the conjugation with the adjacent aromatic ring and phenolic oxygen, it is shifted to a very low value. The S=O vibration of the sulfonic acid occurs close to 1294 cm^{-1}. The peaks between 800 and 1000 cm^{-1} are due to W=O vibrations of SWA.

The FTIR spectra of CMS 4 and CMS 5 are shown in Figures 4b and 4c, respectively. The spectra appear very much closer to Figure 3a. But there are distinct shifts in the peak positions of C=O and S=O groupings. With an increase in the content of SWA, the S=O vibration gradually shifts to higher values. This observation suggests less electron flow from the aromatic ring to S=O grouping due to the hydrogen bonding interaction of phenolic oxygen with the protons of SWA. Again, the hydrogen bonding interaction of O-H oxygen of SO_3H with SWA also strengthens the S=O, thus shifting the vibration to higher values. The C=O vibration shifts toward the higher values with increased concentration of SWA due to the suppression of delocalization of phenolic oxygen over the carbonyl grouping. This suppression occurs due to the hydrogen bonding of phenolic oxygen with SWA protons.

XRD Measurement

The XRD spectra of SPEEK, SWA and one representative composite membrane (CMS 1) are shown in Figures 5a–c respectively. Many sharp intense peaks for SWA show its high crystallinity. The sharp intense peak at $2\theta = 73^\circ$ in the composite membrane is due to the host polymer. The absence of sharp peaks at lower 2θ values in the composite membrane indicates a good interaction of SWA with the polymer matrix. The peaks at $2\theta = 42$, 44, 50 and 52° are common in all the composite membranes.

Scanning Electron Microscopy

The SEM images of CMS 1 and CMS 3 are given in Figures 3a and 3b, respectively. The distribution of SWA was found to be uniform in CMS 1. When the dosage was increased to 15%, crystal formation of SWA was observed as seen in Figure 5b.

Conductivity Measurement

The conductivity values of the composite membranes are given in Table 1. They were found to be in the order of 10^{-3} S/cm. The conductivity value takes a deep rise, when the SWA concentration was

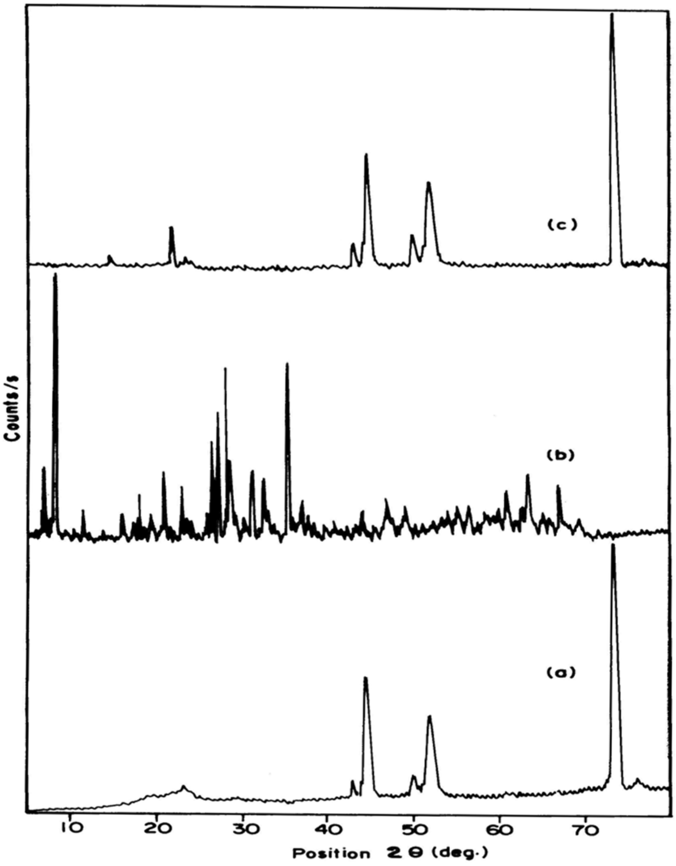


FIGURE 5 XRD spectra of (a) SPEEK, (b) SWA, and (c) CMS 1.

increased from 5 to 10%. After 10%, the increment is not steep. After 15% the conductivity remains constant irrespective of the addition of the inorganic component in the composite membrane. This could be due to the agglomeration and contacts between crystals of SWA in the composite membranes as evidenced by the SEM image.

Mechanical Properties

The tensile strength and the percentage elongation at break of the composite membranes are given in Table 2. When the content of the inorganic heteropoly acid is increased, there is a gradual decrease in the tensile strength as well as percentage elongation properties. Once

TABLE 2 Tensile Strength and Percentage Elongation

Name of Membrane	Tensile Strength, MPa	Percentage Elongation, %
CMS 1	15	4.1
CMS 2	10	3.5
CMS 3	9	3.25
CMS 4	8.5	3.1
CMS 5	7.5	2.5

again, this type of reduction can be attributed to the crystal formation of SWA in the composite membranes. The crystals behave as filler particles with poor adhesion to the polymeric matrix. The lowered mechanical properties as function of SWA concentration is obvious and expected.

CONCLUSIONS

In the present work, a series of SPEEK/SWA composite membranes were prepared. The IEC values were found to be appreciable for application in PEM fuel cells. The FTIR and XRD analysis revealed an interaction of the inorganic heteropoly acid with the polymer matrix up to 15% loading of SWA. The thermal studies showed that the membranes were thermally stable up to 250°C which is excellent for operation in the PEMFC. The SEM pictures revealed a good distribution of the SWA in the polymer matrix. But above 15% of SWA, crystal growths were observed. The conductivity values were also found to be promising for application in PEMFC. Further work is required to analyze the composite membranes with 1 to 10% SWA content and also to fix the SWA firmly in the polymer matrix to avoid leaching.

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