Sulfonated Poly (Ether Ether Ketone) and its Blended Nanocomposite for Proton Conducting Membranes

ABDUL KALAM AZAD[1], ARVIND GUPTA[3], LAKSHMI UNNIKRISHNAN[2,3*],
SMITA MOHANTY[3] AND SANJAY KUMAR NAYAK[2,3]

[1]*Department of Chemical and Process Engineering Technology, Jubail Industrial College, Jubail Industrial City 31961, Saudi Arabia.*

[2]*CIPET, School for Advanced Research in Polymers (SARP)-APDDRL, Hi Tech Defence and Aerospace Park, Bengaluru 562149, India.*

[3]*CIPET, School for Advanced Research in Polymers (SARP) - LARPM, B/25, CNI Complex, Patia, Bhubaneswar 751 024, India.*

ABSTRACT

Proton conducting hydrophilic channels were created successfully in poly (ether ether ketone) (PEEK) by means of step by step modification followed by the optimization of sulfonation process (SPEEK70, DS=68.57%). Although highly sulfonated PEEK has excellent proton conductivity, it lacks in mechanical stability due to low swelling degree. Therefore, a potential method has been proposed in this work by integrating poly (sulfone) and nanosilica (SiO_2) into SPEEK matrix. SPEEK 70 (S) was utilized to prepare blended nanocomposite membranes for further enhancement of hydrophilic channels. The blended nanocomposite membranes are, SPEEK/SiO_2 as SNS, SPEEK blended with poly (sulfone) as SP, SPEEK blended with sulfonated poly (sulfone) as SSP and SPEEK blended with sulfonated poly (sulfone)/ (SiO_2) as SSPNS. All the prepared membranes were characterized and its performance was discussed in detail to identify the appropriate membrane for the better replacement of Nafion. Expected intermolecular interaction and its obstruction of free hydrophilic channels were confirmed with the gradual increase in proton conductivity from 0.0165 to 0.2557mS/cm.

KEYWORDS: *Sulfonated PEEK, Blended nanocomposite, Water uptake, Proton conductivity.*

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Correspondence author e-mail: lakshmipvallath@gmail.com
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1. INTRODUCTION

The science and technology which are used to protect the nature and its environment is commonly called as green technology, (also called clean technology or environmental technology) because of its outspread tremendous benefits in all the areas which include recycling and waste management, water purification, elimination of industrial emissions, waste to energy, solar energy and fuel cells.[1] Among the several applications of green technology, fuel cell is one of the promising areas to reduce pollution. It is an electrochemical device which converts the chemical energy into electrical energy with the elimination of water and heat as by products in the case of reactants as air and hydrogen. Whereas, hydrocarbons and carbon dioxide are the additional by products when there is a usage of fossil fuel in particular fuel cells.[2]

Grubb in 1959 is the one who introduced the concept of using proton exchange membrane as a medium to transfer the protons in fuel cells.[3] For portable applications, direct methanol fuel cells are more preferable over proton exchange membrane fuel cell which is also referred as solid polymer fuel cell.[7] Nafion®, which is a sulfonated Poly (tetra fluoro ethylene) (PTFE) a commercial membrane for fuel cell applications. Though its major drawbacks are high cost, lower ionic conductivity, methanol permeability and lower operation temperature has inspired the researchers to find an alternative membrane for this Nafion®.[4-6]

Sulfonated PEEK (SPEEK) is one of the potential membranes for fuel cell applications and it's a semi crystalline polymer which belongs to poly ether ketones family, introduced by Imperial Chemical Industries in 1978 which exhibits excellent mechanical, chemical stability, fire and hydrolysis resistance at elevated temperature.[16] However, when the degree of sulfonation is >70% and the operation at higher temperature results in swelling of SPEEK membrane in water, which allows the researchers to blend with other polymers[11-15] and inorganic filler[9,10] to overcome the drawbacks of SPEEK membrane. Polymer blending is an appreciable method to enhance the various properties and the performance with affordable cost when compared to the individual polymer. Nevertheless polymer blends are immiscible due to its nature of the backbone, chemical structure and higher degree of polymerization. To enhance the miscibility of polymer blends, it is mandatory to confirm the specified intermolecular interactions such as acid/base types, π–π, ion-dipole, charge transfer and hydrogen bonding interactions exist between the two core materials of the blend.[17] S.W. Kuo recommended the presence of hydrogen bonding interactions to develop the miscible polymer blend with outstanding properties.[18] When Nafion® is compared with blended SPEEK membrane, the latter exhibited reduction in swelling, superior mechanical and thermal stability with no loss of proton conductivity.[9-15]

The main objective of the current study is to prepare the proton conducting membrane for fuel cell application. In this work, Poly (ether ether ketone) (PEEK) as a core material was used which was further modified by the addition of nano silica and further blended with Poly sulfone (PSF). The incorporation of nanosilica introduces strong inter molecular forces which lead to enhanced properties. We have utilized this technique as it has been recognized as the suitable method to produce nano-fillers for the use as engineering polymers.[19] On the other hand, blending with PSF makes the polymer to possess superior qualities such as resistance to high temperature, hydrolysis and oxidation. In addition, the resultant polymer releases less smoke when burnt.[20] The corresponding nano-composite membranes from the above mentioned materials were prepared because of its inherent properties and relative compatibility with each other. Moreover, various properties and comparative analysis among the modified form of different membranes were investigated and reported.

2. EXPERIMENTAL

2.1.1. Materials

PEEK pellets (450 G) were purchased from Victrex, England. Sulfonated poly (sulfone) (SPSF, 33.07% DS) was used from our earlier research work.[21] Nanosilica (SiO_2, particle size <25nm, 99% purity) was purchased from Gyeonggi-do, Korea. Concentrated sulfuric acid (H_2SO_4, 98% pure) was obtained from Merck, Germany. PSF pellets, Chlorosulfonic acid ($ClSO_3H$, 99%), N,N – Dimethylacetamide(DMAc), 1,2-Dichloroethane (EDC), Methanol (CH_3OH) sodium hydroxide (NaOH), and Phenolphthalein (phph) were used as received from Sigma Aldrich, USA.

2.1.2. Sulfonation of PEEK

The modification of sulfonation is to increase the hydrophilic nature by introducing SO_3H group into the backbone of PEEK material. In this work, post-sulfonation process was used because of its affordable cost for production together with uncomplicatedness as it is one of the main targets for all the researchers to produce the cost effective membrane for the replacement of currently used NAFION® membrane.[22] However, pre-sulfonation process will be more effective which is avoided due to the complexity of the process.[23] Sulfonation of PEEK was carried out at room temperature by adding 15 g of dried PEEK into the conical flask containing 175 mL of 98% concentrated Sulfuric acid. The process was continued with the help of mechanical stirrer by varying the reaction time to a maximum of 120 hours in order to achieve the different degree of sulfonation. Where the hydrogen atom in the aromatic group will be replaced by the sulfonic acid group which facilitates the conductivity of protons. After sulfonation, the acidic polymer solution was poured slowly into the magnetically stirred beaker containing cold water to precipitate the polymer. Thereafter, the precipitated polymer was washed thoroughly with the deionized water until the rinsed water attain the pH value of 7. Then the washed out samples were separated with the help of vacuum filtration process.[8] Lastly, the sulfonation process was optimized by carrying out the water uptake test at an elevated temperature and methanol uptake test.

2.1.3. Membrane preparation (SPEEK and its modified form)

Optimized sulfonated PEEK (68.57% DS) was considered for its modified form of membrane as a base polymeric material. In the beginning, dried SPEEK powder was dissolved in DMAc solvent @ 80°C to obtain a 5 wt% of homogeneous solution for the preparation of membrane and its nano-composite membrane. Among the unmodified and sulfonated nanosilica, unmodified silica (10wt%) was chosen for SNS and SSPNS membrane because of its higher water uptake, low methanol permeability, better thermal and mechanical stability as reported.[9], [32]SNS membrane was prepared by dissolving nanosilica in a solvent separately to achieve 10wt% of homogenous solution and then added slowly into the beaker containing SPEEK solution which was stirred for 24 hours. Then the resultant solution was kept under ultra-sonication process for the desired time to attain the uniform dispersion of nano particles. Similar procedure was utilized to prepare SP membrane (10wt% of PSF in SPEEK solution), SSP membrane (10wt% of sulfonated poly sulfone in SPEEK solution) and SSPNS membrane (10wt% of sulfonated poly sulfone and nanosilica in

SPEEK solution). Then the prepared solutions were labelled separately and casted on a scratch free Petridish for the purpose of drying in vacuum oven at 80°C for 12 hours. At the end, the designated membranes were removed with the help of distilled water and spatula. The thickness of all the membranes were measured with the help of micrometer and found to be ~300μm.

2.2. Characterization.

2.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

Comparative FTIR spectra of virgin polymer and sulfonated polymer samples were recorded and analyzed with the structural changes by using Nicolet Continuum 6700 model FTIR spectroscope (Thermoscientific, USA) in the range of 500–1700cm^{-1}.

2.2.2. Degree of sulfonation (DS) and Ion exchange capacity (IEC)

DS and IEC for all the sulfonated PEEK were obtained by varying the reaction time was identified by dissolving 1.0 g of powdered sulfonated sample in 20 mL of DMAc solvent and titrated with 0.1 molar NaOH solution. The values are obtained by using the formula reported in the earlier work.[8]

2.2.3. Water and methanol uptake

Firstly, SPEEK and its blended nanocomposite membranes were dried in a vacuum oven at 80°C until the constant weight appears and then weighed. Secondly, the dried membrane samples were neatly cut into a size of 2cm x 2cm, soaked in distilled water at room temperature for 24 hours and then at higher temperature of 600°C, 800°C and 1000°C for 2 hours. Membrane samples of similar size were soaked in methanol solution at room temperature for 24 hours to determine the % of methanol uptake. Finally, the membranes were removed after the desired time, wiped with the help of tissue paper on both sides of membranes and weighed again. Similar kind of process was repeated for three times to record the average value in order to attain the accuracy. The % of water and methanol uptake value was calculated using the following formula (1).

$$\text{Water/Methanol uptake (\%)} = \frac{\text{soaked membrane} - \text{dried membrane}}{\text{dried membrane}} \text{X } 100 \ldots (\mathbf{1})$$

2.2.4. Differential scanning calorimetry (DSC)

Glass transition temperature (T_g) of Virgin PEEK, SPEEK and its modified nanocomposite membranes were analyzed by Differential Scanning Calorimetry (DSC Q20, TA Instruments, USA). Empty aluminium pan was used to calibrate the baseline prior to carry out the test for each sample respectively. Thereafter, samples with a mass of ~20mg were heated at 10°C/min from 25 to 350°C under the nitrogen atmosphere.

2.2.5. Thermogravimetric Analysis (TGA)

Thermal stability of the PEEK and its nano composite membranes were carried out by using Thermogravimetric analysis (TGA50, TA Instruments, USA). Solvent and moisture free samples were obtained by vacuum dried at 150°C for one hour exactly before going to start the test. Each sample of approximately 10 mg was heated under nitrogen atmosphere from 25 to 750°C with a heating rate of 20°C/min.

2.2.6. X-ray Diffraction (XRD)

The effect of incorporated nano-silica and its blended materials on SPEEK matrix in a membrane form were studied by using XRD (XRD-7000L, Shimadzu, Japan) with monochromatized Cu Kα radiation (λ=1.541°A) radiation in the range of 2°≤2θ≤10° at 40 kV.

2.2.7. Proton conductivity

The proton conductivity of SPEEK and its modified form of membranes were determined by electrochemical impedance analyzer (N4L PSM -1735, UK) with a frequency range of 100 kHz-1Hz at 10mV amplitude. Damage free samples of hydrated membranes were prepared by immersion in distilled water for 24 hours. Resistance of the hydrated membrane samples (2cm x

2cm) were calculated by placing the samples between the electrodes in conductivity cell using two probe method as it is convenient for the sample measurement with resistance greater than 1000Ω.[35] The conductivity value was calculated by using the following formula (2).

$$\sigma\ (\text{mS/cm}) = \frac{\text{Thickness of the membrane sample (cm)}}{\text{Area resistance of the membrane sample (mS/cm}^2)} \quad \text{.... (2)}$$

3. RESULTS AND DISCUSSION

3.1. Sulfonation reaction, DS and IEC

Sulfonated PEEK (Figure 1) was prepared through an electrophilic substitution reaction wherein one of H+ ion on the aromatic ring is substituted by -SO_3H group. Conc. H_2SO_4 (98%) provides an easy and simple reaction for the production of degradation-free polymers. The remaining few percent of water in H_2SO_4 prevents the cross-linking by decomposing aryl pyrosulfonate intermediate, required for the sulfone formation which in turn causes cross-linking.[24] While increasing the reaction time, DS and IEC value increases which is directly proportional to each other as displayed in Figure 2. Increase in DS is also believed to increase in hydrophilicity of the polymer matrix with the introduction of –SO_3H groups. Higher level of sulfonation would increase the proton conductivity. However, membrane brittleness along with the deterioration of mechanical and thermal stability was observed in highly sulfonated polymers (SPEEK 90 and SPEEK 120) which is agreed and proved with the earlier studies.[8,9,14,21,26] Hence, the process was

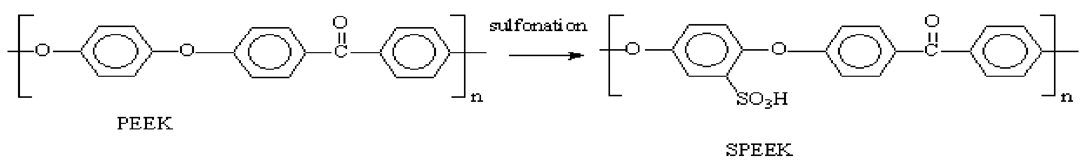


Fig. 1. Sulfonation of PEEK

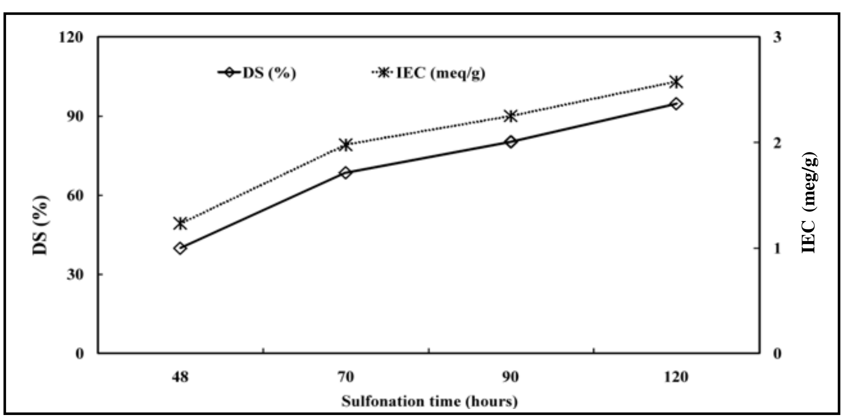


Fig. 2. Effect of reaction time on DS and IEC of SPEEK

optimized and controlled by varying the reaction time at room temperature associated with the data's obtained from water uptake test at higher temperature, methanol uptake test and TGA.

3.2. SPEEK and its Blended Nanocomposite Membranes

SPEEK and its blended nanocomposite membranes were casted using (DMAc) solvent. Earlier studies stated that the blended membranes exhibit the various intermolecular interactions such as van-der-waals, dipole-dipole, acid-base (electrostatic), hydrogen bonding and covalent crosslinking interactions. The hydrogen bonding interactions which enable the proton transfer from one spot to another through the formation and breaking of hydrogen bonds. This could be observed in all the prepared membranes which leads to the cost reduction and swelling tendency of sulfonated membranes. Sulfonated PEEK was blended with 10% of non-sulfonated polymer (PSF) in order to reinforce the membrane and expected to have dipole-dipole interactions. However, these dipole-dipole interactions are weak when compared to other type of interactions.[27] Covalent crosslinking interactions are considered to be stronger but in this research we did not use any crosslinking agent to attain this interaction. Similarly, acid-base interactions can be found in the acidic and basic polymer blends which stimulate the proton conductivity through grotthuss mechanism together with the improved mechanical and thermal stability.[28, 29] The sulfonic acid group attached to the polymer backbone would make SPEEK based membranes to be highly hydrophilic by increasing the acid moieties in the polymer matrix which may further aid in proton transport. All the SPEEK based membranes are bendable with slight variations within each other which directs the membrane to find easier applications in fuel cell without any difficulties.

3.3. FTIR Analysis

The incorporation of sulfonic acid groups on the backbone of PEEK was confirmed through FTIR and the spectra of virgin PEEK and Sulfonated PEEK which are shown in Figure 3. When compared to the spectra of virgin PEEK, significant differences could be observed in the SPEEK. The stretching vibrations of O=S=O group were noticed at 1082 cm^{-1} (symmetric) and 1250 cm^{-1} (asymmetric), which were absent in the case of virgin PEEK. Also, as observed by SMJ Zaidi et al.,[25] the S=O stretching was visible at 1027 cm^{-1} and 1143 cm^{-1}. Absorption band at 1480 cm^{-1} shows the C–H bending (deformation) and it is believed to be slightly shifted to 1465 cm^{-1} upon sulfonation. The carbonyl bond (C=O) remains unaffected after sulfonation, thus revealing its absorption band at 1648 cm^{-1} in both virgin and sulfonated PEEK.

3.4. Water Uptake

Hydrophobic polymer becomes hydrophilic when it is sulfonated and attracts water, based on the available acidic group in the polymer which further enables the route for conduction of proton as broadly reported in the earlier studies. Hence, the water absorption capacity of sulfonated membranes is estimated in the temperature range from 30 to 100°C. Figure 4 (a) and (b) enumerates the water uptake and hydration number as a function of temperature. All the SPEEK membranes with different DS was in the range of 4-19% water uptake at room temperature, whereas it increased quickly at

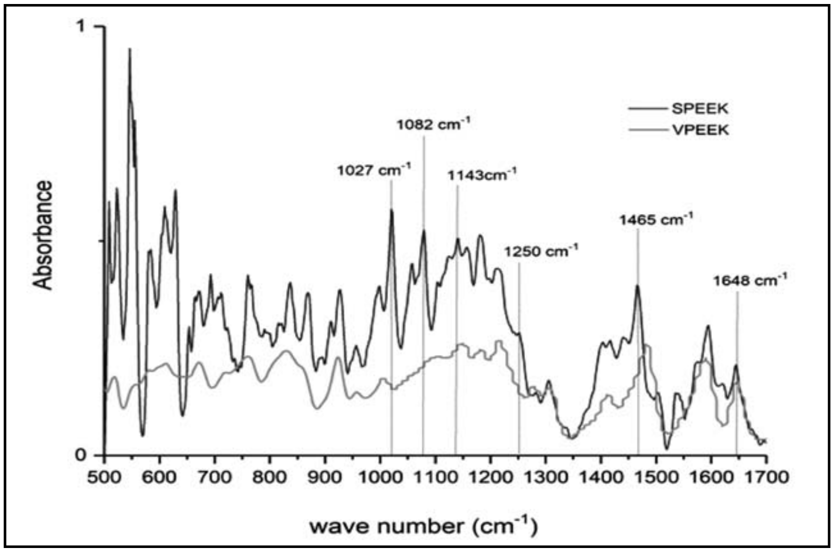
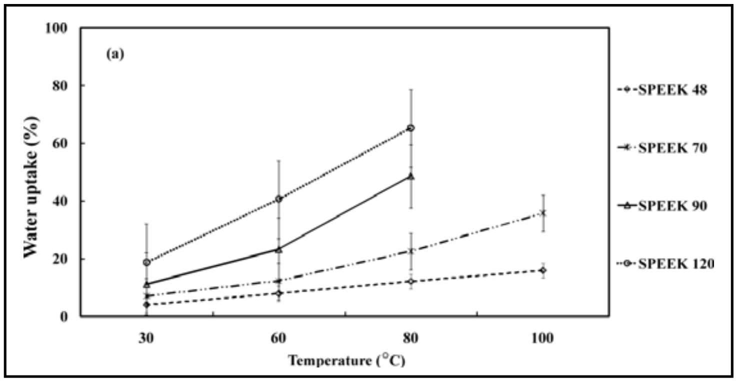


Figure 3. FTIR Spectrum of virgin and sulfonated PEEK

higher temperature which clearly reveals the key role of temperature in sulfonic group to absorb water molecules. Highly sulfonated polymers of SPEEK 90 (DS 80.23%) and SPEEK 120 (DS 94.68%) were dissolved and broken into fragments at 100°C which confirmed the study carried out by Xing et al.[26] Hydration number also shows a similar trend like water uptake test in the temperature range of 30-100°C, which denotes how much number of water molecules attracted by each sulfonic acid group as it directly relies on DS. Higher the DS, higher will be the water uptake & hence higher will be the hydration number. Sulfonated PEEK and its modified form of blended membrane was also observed for water uptake characteristics as displayed in Figure 5. When compared to SPEEK 70, SNS nanocomposite membrane shows the maximum water uptake of 52.48% at 100°C. This phenomenon could be due to the hydrophilic nature of nanosilica and its higher content (10wt %) which reflects the studies carried out by the earlier researchers.[30, 31, 32]

In the instance of SPEEK/PSF (SP) blend, SPEEK is highly hydrophilic whereas PSF is hydrophobic. Therefore, when the SPEEK is blended with virgin Polysulphone (PSF), the polyelectrolyte chain is caused to extend, resulting in a strong electrostatic repulsion of charges on it. Thus, pore size increases and so does the water uptake.[36, 37]

On the other hand, in the case of SPEEK/SPSF (SSP) blended membrane, both SPEEK and SPSF are highly hydrophilic and the density of bulky SO_3H group is more, which might lead to more water absorbance. The higher water affinity might be because of the more open structures of the sulfonated blend membranes as compared to that of virgin membrane.[36] Nevertheless it was observed that at elevated



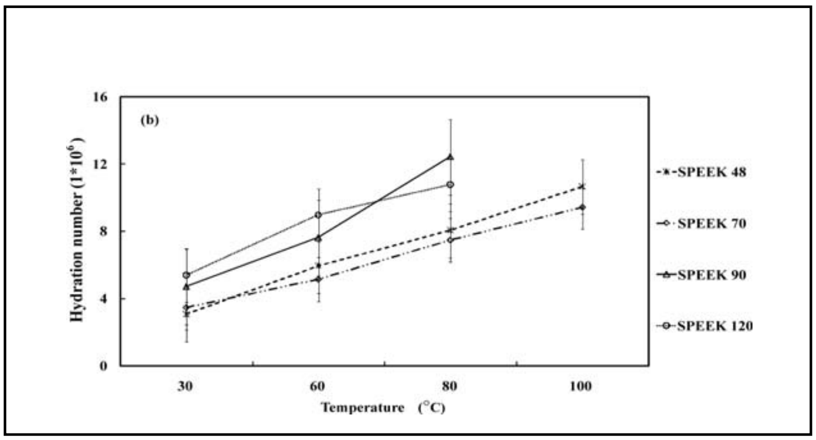


Figure 4. SPEEK membranes at varied temperature (a) Water uptake (b) Hydration number

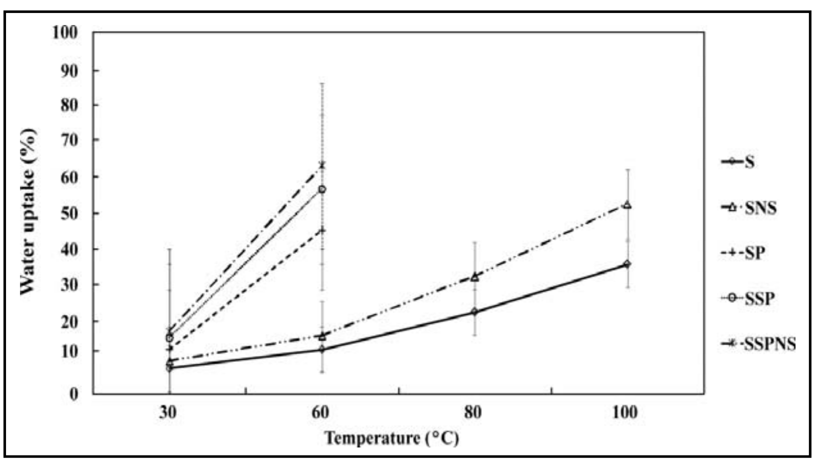


Figure 5. Water uptake test of blended SPEEK membranes at different temperatures

temperatures above 60°C, the blended membranes of SP, SSP, & SSPNS partially dissolved in water indicating instability at elevated temperatures.

3.5. Methanol Uptake

Figure 6(a) shows the methanol uptake characteristics of the SPEEK membranes which clearly indicates the impact of DS as it was increased with the increase in degree of sulfonation. At a higher degree of sulfonation (SPEEK 90 and SPEEK 120), the membranes were dissolved in methanol after 24 hours.

Modified form of SPEEK nanocomposite membranes were employed to methanol absorption test to study the effect of nanosilica and PSF. Methanol uptake was reduced after incorporation of nanosilica as clearly shown in Figure 6 (b). Moreover, small hydrophilic-hydrophobic separation along the main chain combined with uniformly dispersed nanosilica particles might have contributed to narrow proton channels thus restricting methanol transfer and the similar reduction was observed in G. Wu et al. study.[32] However incorporation of PSF to SPEEK increased the methanol uptake and addition of SPSF & SPSF/

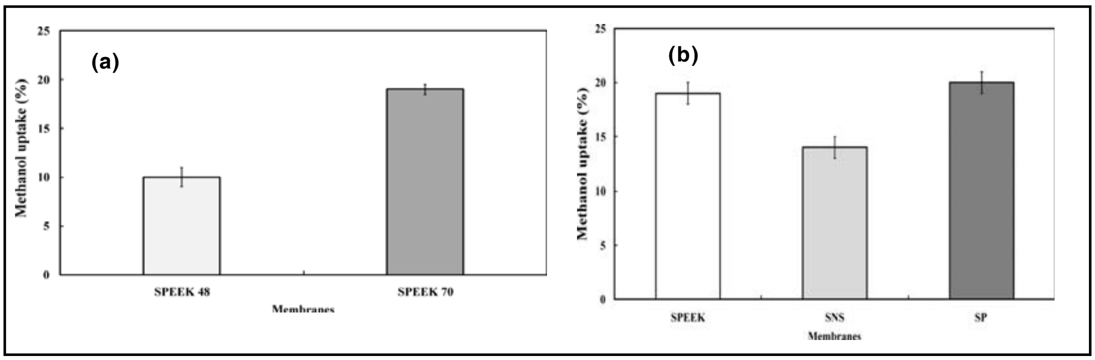


Figure 6. Methanol uptake test (a) SPEEK membranes (b) blended SPEEK membranes

nanosilica to SPEEK leads to dissolution of membranes in methanol after 24 hours at ambient temperature.

3.6. XRD Studies

The typical X-ray diffraction peaks for nanosilica were observed at a 2θ of 22.64° and 31.48° and displayed in Figure 7 along with the modified form of SPEEK membranes. PEEK is a semi crystalline polymer and shows distinct sharp peaks in the range 20°-30°as reported by Zaidi et al.[25] However, as observed in our study, sulfonated PEEK shows two weak and broad peaks, which occur at 2θ=19° and 21° are the reflections from 110 and 111 planes. This clearly implies that the sulfonation process greatly reduces the crystallinity of virgin PEEK, thus forming an amorphous structure in SPEEK which agrees well with the previously reported studies. The SPEEK / silica (SNS) nanocomposite membranes also showed amorphous structure due to the presence of silica in SPEEK matrix which results in more associated network.[31] Amorphous structure in membrane is believed to provide a conductive environment for the ionic transport. The incorporation of an amorphous polymer, PSF and SPSF, further decreased the crystallinity, as evident from the broader XRD spectra of SPEEK/PSF (SP) and SPEEK/SPSF (SSP) blend membranes. The hydrophilic SPSF altered the chain conformation and packing of SPEEK molecules, thus leading to loss of crystallinity. The SSPNS spectra was further

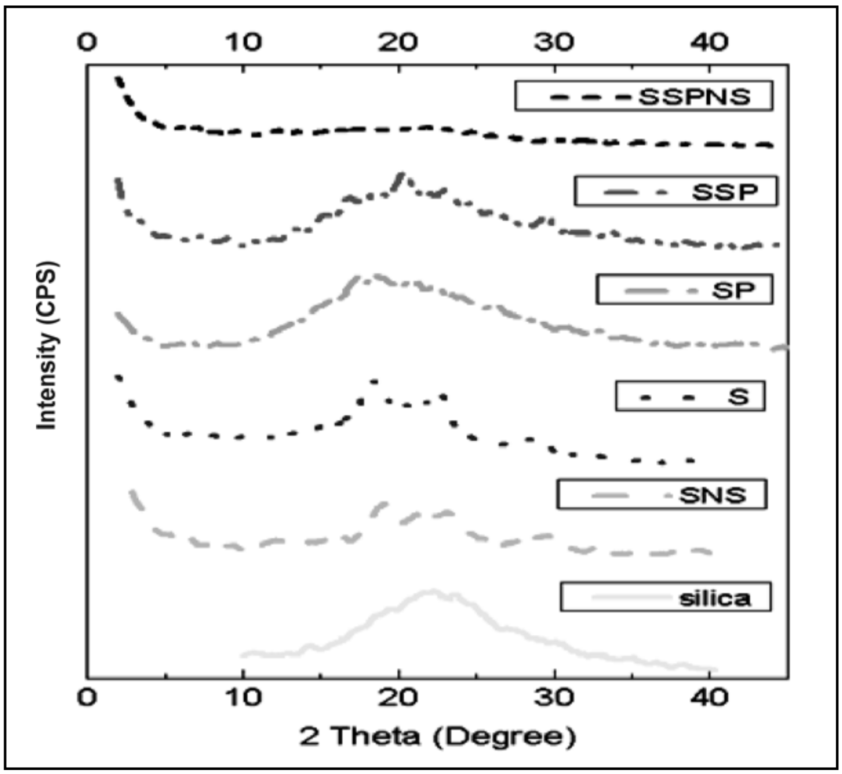


Figure 7. XRD Spectra of SPEEK nanocomposite membranes

broadened which clearly signifies the decrease in crystallinity due to the existence of amorphous nature of SPSF and nanosilica.

3.7. TGA Analysis

Figure 8 displays TGA thermogram of virgin PEEK, S, SNS, SP, SSP and SSPNS membranes. Initial degradation at 550°C evidentially shows the thermal stability of virgin PEEK as an appropriate base material for this study. After Sulfonation, SPEEK revealed a two-stage degradation process in which the weight reduction at 330°C corresponds to the thermal decomposition of SO_3H groups, and the main polymer degradation is observed at 530°C. In contrary to virgin PEEK, drastic difference in temperature breakdown was observed in SPEEK. This difference shows the existence of sulfonic acid group and its impact on the PEEK backbone, which could further increase with the increase in DS. Related effect was clearly noted in the TGA analysis reported by Xue and Yin.[38] The incorporation of nanosilica showed an increase of 6% residue due to the presence of inorganic silica as observed in Figure 8. All membranes except SPEEK displayed a 3-step weight loss with the initial weight loss at 50-100°C indicating removal of moisture. All the modified form of SPEEK membranes (SPEEK/PSF, SPEEK/SPSF, and SPEEK/SPSF/nanosilica) showed almost similar degradation statistics. Apart from the marginal increase in the maximum degradation temperature of nanosilica reinforced SPEEK/SPSF (SSPNS) blend membranes. This behavior might be due to the inherent thermal stability of nanosilica and the expected interactions (acid-base, Hydrogen bonding and dipole-dipole) between the SPEEK

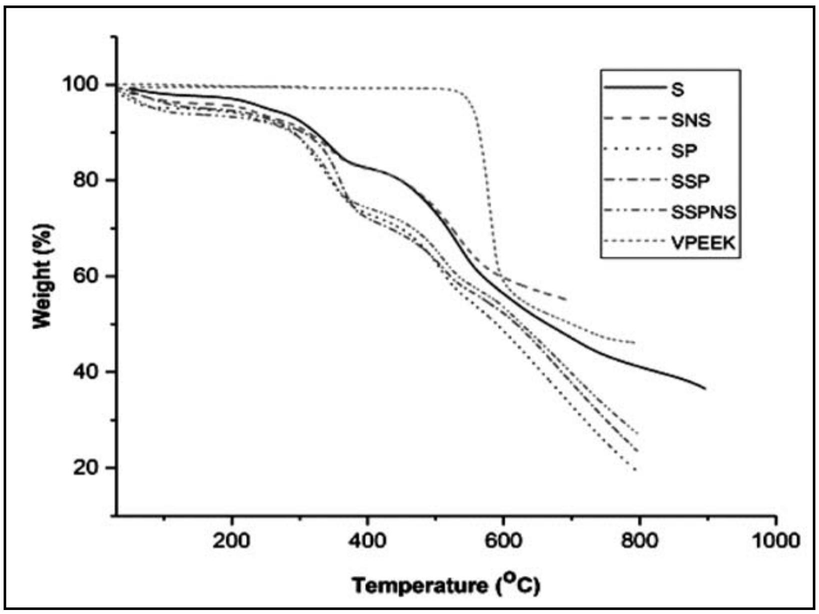


Figure 8. TGA curves of Virgin PEEK, Sulfonated PEEK and its modified membranes

and the SPSF. These ionic interactions between the polymeric blends can increase the thermal stability of blended nanocomposite membrane as indicated by Abu-Thabit et al.[14]

3.8. DSC Analysis

Proton conductivity of the polymer membrane is closely associated with the glass transition temperature (T_g) owing to the fact that higher the T_g, higher will be the tendency for conducting the proton because the membrane would lose its overall performance when it reaches above the T_g. Table 1, Figure 10 shows the data and curve for the DSC analysis. Lower T_g value was observed in virgin PEEK (169°C) when compared to SPEEK (195°C) which clearly

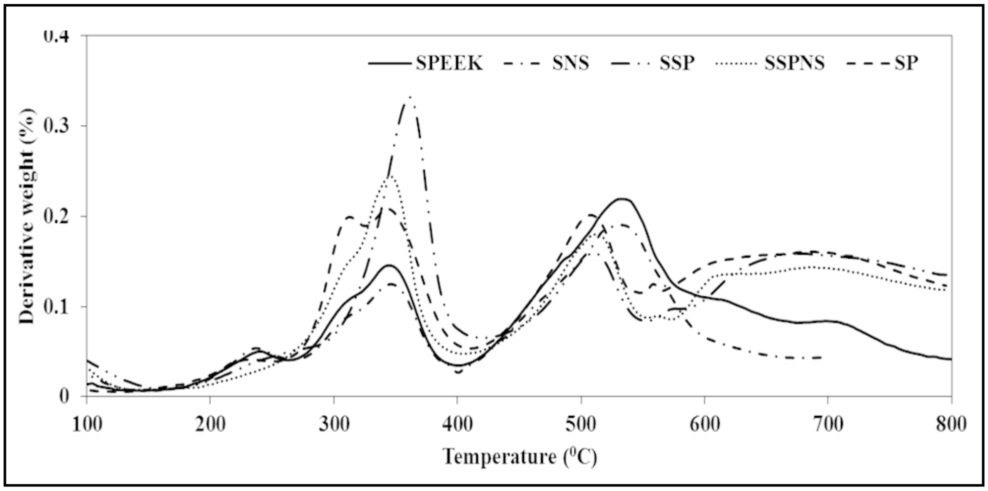


Figure 9. DTG curves for the prepared membranes

exposed that the T_g value increases with the increase in DS as it is directly proportional to each other and this attained value is agreed with the reference.[25] SPEEK and its modified form of blended membranes exhibited considerable increase in T_g which strongly confirm the existence of uniform dispersion along with the interaction of Hydrogen bonding, acid-base and dipole-dipole within the nanocomposite membranes. The incorporation of nanosilica might have restricted the chain mobility in SNS membrane thus increasing the T_g of polymer chain which confirmed the earlier studies.[9, 31, 32] SP and SSP blend membranes also displayed an increase in T_g to 225°C and 240°C respectively. The presence of bulkier groups (PSF and SPSF) has further enhanced the bulkiness of total system which causes the increase in T_g. SSPNS showed the maximum T_g value of 243°C when compared to other membranes. These attributes could be due to the presence of SP and nanosilica

TABLE 1: Thermal Properties and Proton Conductivity for the Prepared Membranes

Membrane	Glass transition temperature (°C)	Initial degradation temperature (°C)	Maximum degradation temperature (°C)	% of residue content at 750°C	Proton conductivity σ, mS/cm
SPEEK(S)	195.0	240.41	533.63	42.0	0.0165
SNS	210.0	236.08	531.08	48.0	0.2139
SP	225.0	229.63	507.96	21.0	0.2230
SSP	240.0	244.00	511.55	24.25	0.2439
SSPNS	243.0	258.00	520.24	32.84	0.2557

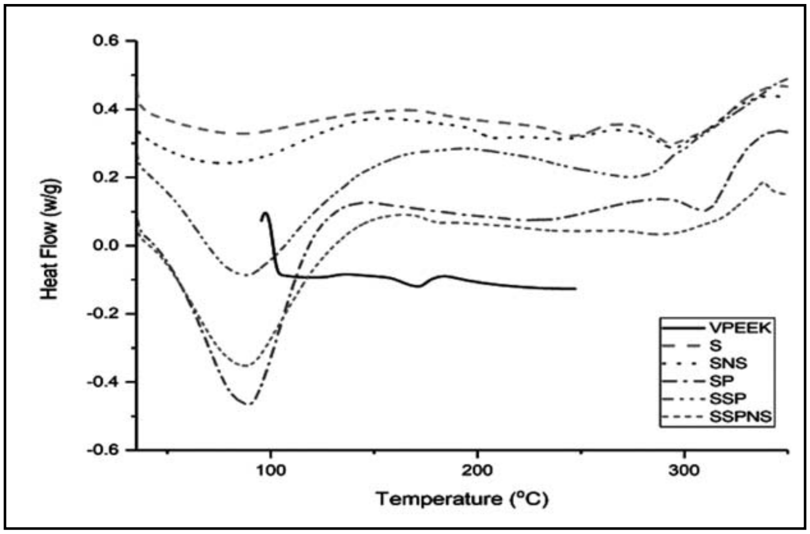


Figure 10. DSC curves of SPEEK and its modified membranes

(10wt %) which restricts the molecular mobility. The DSC results firmly reveals the existence of added bulky groups and all the possible expected intermolecular interactions.

3.9. Proton Conductivity Measurements

Transferring proton is the main criteria of membranes to be utilized for fuel cell applications and this property is mainly based on the hydrophilic groups in the membrane, which has been attained from the modification of hydrophobic PEEK material via sulfonation, addition of nano-silica and sulfonated PSF. The incorporated hydrophilic groups are responsible for transferring the protons by two methods namely grotthuss and vehicle mechanism. Figure 11 shows the proton conductivity measurements at room temperature and the values are displayed in Table 1. It is recognized that the incorporation of 10 wt% nanosilica into the SPEEK material shows a rapid increase of conductivity from 0.016549 mS/cm (S) to 0.213917 mS/cm (SNS). This increment could be due to the addition of nanosilica which can absorb more water in their network to facilitate the proton conductivity.[9] Similar increment was reported by Sri and Eniya.[31] Further increase in ionic conductivity value of 0.2230 mS/cm was noted in SP membrane. This characteristics might be due to the proton conducting behavior of virgin PSF membrane[33] together with the combination of SPEEK blended with 10wt % PSF which agreed with the earlier studies carried out by Xianfeng et al.[36] Subsequent increment (0.24396 mS/cm) was found in SSP membrane which shows the influence of more sulfonic groups available in SPEEK (S) and SPSF (SP) matrix. Higher conductivity value (0.2557 mS/cm) was observed in SSPNS blended membrane upon addition of 10 wt% nanosilica. The results attained from this proton conductivity measurements reveals subsequent increase in value, when the SPEEK matrix is modified into blended nanocomposite membranes and this effect could be due to the interactions between the bonding which enables the hydrophilic channel for transferring the proton. However, the proton conductivities obtained from the examined membranes are in the range of 0.01 to 0.25 mS/cm which is ten times lower than that of the standard NAFION membrane.[39, 40] In addition, creating more hydrophilic channels are not recommended as it would compromise the mechanical stability, which can be realized in the case of SSP and SSPNS membranes under the hydration test at prescribed conditions.

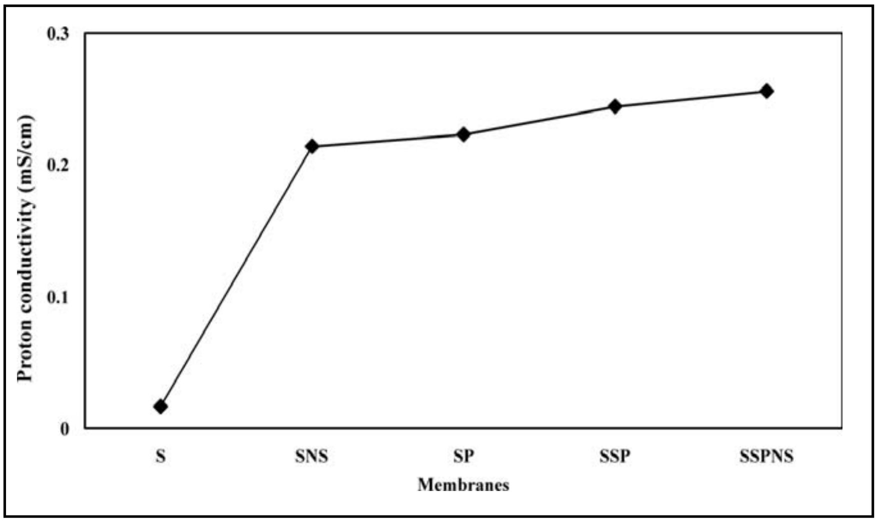


Figure 11. Proton conductivity of SPEEK and its modified membranes

4. CONCLUSION

SPEEK70 (68.57% DS) was concluded as the optimized sulfonated membrane with the maximum hydration number of 9.433×10^6 and 35.78% water uptake at 100°C without disintegration. Also, methanol uptake test exhibited the dimensional stability of SPEEK70 membrane which can be used for direct methanol fuel cell applications. Even though sulfonation process played a vital role in conducting proton which further carries the major drawback of membrane swelling, lower thermal stability and poor performance at higher operating temperature. This jeopardize had been overcome to some extend with the blended nanocomposite membrane. TGA shows little effect, whereas all the remaining tests reveal the similar steady improvement in favor of nanocomposite membranes. However, SSP and SSPNS membranes disclosed poor dimensional stability in methanol uptake test and water uptake at elevated temperature. Conversion of semi crystalline nature into amorphous was confirmed together with the results of DSC and XRD which evidence the proton conducting behavior of SPEEK and its nanocomposite membranes. When compared to pure sulfonated (S) membrane, this promising technique of SPEEK blended with nano silica, high performance polymer (PSF), and its sulfonated form exhibits more than ten times enhanced proton conductivity. However, S and SNS membranes are more stable in terms of heat and methanol uptake characteristics. The results attained from this study, strongly recommends that the SP, SSP and SSPNS membrane can be utilized for room temperature H_2-O_2 fuel cells. In addition, S and SNS membrane can be employed for direct methanol fuel cell and H_2-O_2 fuel cell at high temperature applications.

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Conflict of interest

There is no conflict of financial interest in this work.

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