Hydroquinone based sulfonated poly (arylene ether sulfone) copolymer as proton exchange membrane for fuel cell applications

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Received 16 April 2015; accepted in revised form 8 July 2015

Abstract. Synthesis of sulfonated poly (arylene ether sulfone) copolymer by direct copolymerization of 4,4'-bis(4-hydroxyphenyl)valeric acid, benzene 1,4-diol and synthesized sulfonated 4,4'-difluorodiphenylsulfone and its characterization by using FTIR (Fourier Transform Infrared) and NMR (Nuclear Magnetic Resonance) spectroscopic techniques have been performed. The copolymer was subsequently cross-linked with 4, 4'-(hexafluoroisopropylidene)diphenol epoxy resin by thermal curing reaction to synthesize crosslinked membranes. The evaluation of properties showed reduction in water and methanol uptake, ion exchange capacity, proton conductivity with simultaneous enhancement in oxidative stability of the crosslinked membranes as compared to pristine membrane. The performance of the membranes has also been evaluated in terms of thermal stability, morphology, mechanical strength and methanol permeability by using Thermo gravimetric analyzer, Differential scanning calorimetry, Atomic force microscopy, XPERT-PRO diffractometer, universal testing machine and diffusion cell, respectively. The results demonstrated that the crosslinked membranes exhibited high thermal stability with phase separation, restrained crystallinity, acceptable mechanical properties and methanol permeability. Therefore, these can serve as promising proton exchange membranes for fuel cell applications.

Keywords: polymer membranes, copolymer, crosslinking, proton exchange membrane

1. Introduction

There is an ever-growing demand for the alternative energy resources that can generate energy and could be environmental friendly. The petrol crisis and the emission problems resulting from it have impelled the mankind to develop new energy conversion technologies. Fuel cells achieved an important place in the application of alternative energy due to low greenhouse gas emission and high energy conversion efficiency. In the past decade, the polymer electrolyte membrane fuel cells (PEMFCs) have attracted considerable attention as one of the most promising clean energy sources for transportation, stationary and portable power applications. The proton exchange membranes (PEMs) are the cardinal components of

PEMFCs, as these membranes play dual duty of transferring protons from anode to cathode as well as act as barrier to the fuel gas cross leaks between two electrodes. The perfluorinated membrane such as Nafion is the well-known commercially used PEM due to high proton conductivity. But some specific limitations associated with these perfluorinated ionomers including high cost, high fuel cross over and loss of preferable properties at elevated temperature ($>80^{\circ}\text{C}$) demand a search for alternative PEMs [1–5]. In the recent years a varied class of aromatic hydrocarbon polymers have been synthesized and evaluated as backbone, in terms of their applicability as proton exchange membranes. These include poly(arylene ether ketone)s, poly(arylene

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ether sulfone)s [6–12], poly(arylene ether nitrile)s [13, 14], polyimides [15, 16], poly(phthalalazinone ether)s [17]. Extensive work has also been carried out by the researchers on polybenzimidazole based membranes which represents the class of PEMs having acid-base interactions and are suitable for high temperature operating fuel cell applications. Therefore, these membranes can enhance the CO tolerance of the catalyst. Polybenzimidazole (PBI) based PEMs have been extensively studied, in the form of their complexes with phosphoric acid [18, 19]. But the leaching out of the phosphoric acid from the membranes is one of the major problems of phosphoric acid doped PBI membranes which consequently reduce their proton conductivity. Several modified PBI based membranes are reported in the literature. Pyridine based PBI membranes with improved proton conductivity and oxidative stability; membranes of PBI segmented block copolymers and random block copolymers of PBI by using tetra-amine and dicarboxylic acid combinations have also been synthesized and examined as their applicability in PEMFCs [20–22].

However, among the promising candidates, sulfonated poly (arylene ether sulfone)s (SPAES)s are well-known engineering thermoplastics and these are reasonably good choice for high temperature operating PEMFCs. Apart from possessing adequate mechanical properties with high thermal and chemical resistance these are also more economical as compared to Nafion.

The hydroquinone based copolymers can provide many advantages over the biphenyl systems such as low cost, high IEC and better nanophase separation between hydrophilic and hydrophobic domains [17, 23, 24]. To the best of our knowledge the sulfonated poly arylene ether sulfone (SPAES) membranes using hydroquinone along with 4,4'-bis (4-hydroxyphenyl)valeric acid (DPA) as co-monomers have not yet been reported.

In the present work we have endeavoured to synthesize the SPAES crosslinked membranes based on benzene 1,4-diol (HQ) and DPA as PEMs for fuel cell applications. With the purpose to enhance proton conductivity of the membranes, a monomer DPA containing carboxylic acid group on the flexible aliphatic side chain of aromatic backbone has been taken. It is assumed that it can provide protons and help in

nanophase separation of hydrophilic and hydrophobic domains. Further keeping in view mechanical integrity, the crosslinking of the synthesized (sulfonated poly arylene ether sulfone) copolymer (SPAES-H-0) with the synthesized 4,4'-(hexafluoroisopropylidene)diphenol epoxy resin (EFN) has been done, where carboxylic acid groups of DPA react with oxirane rings of EFN and form crosslinked membranes. The crosslinked membranes have been characterized to evaluate their properties such as ion exchange capacity, water/methanol uptake, proton conductivity, oxidative stability, morphology, mechanical strength and thermal stability as PEMs for fuel cell applications.

2. Experimental

2.1. Materials and synthesis

2.1.1. Materials

4,4'-(hexafluoroisopropylidene)diphenol (6F-bisphenol-A/6F-BPA, 97% Sigma Aldrich Chemie GmbH, Germany), formaldehyde (37–41%, Merck Specialities Private Limited, Mumbai India), Isopropanol (99.0%, Merck Specialities Private Limited, Mumbai India), para-toluene sulfonic acid (PTSA, 98%, Merck Specialities Pvt. Limited, Mumbai India), Methyl isobutyl ketone (MIBK, 99.5%, Merck Specialities Pvt. Limited, Mumbai India), epichlorohydrin (ECH, 98.0%, Loba Chemie Pvt. Ltd. Mumbai India), and sodium hydroxide (98%, Loba Chemie Pvt. Ltd. Mumbai, India) were used for the synthesis of novolac based epoxy resin (EFN). 4,4'-bis(4-hydroxyphenyl) valeric acid (DPA, 97%, Alfa Aesar chemicals, Johnson Matthey Company, Heysham, England), benzene 1,4-diol (hydroquinone/HQ, 99% Sigma Aldrich Chemie GmbH, Germany), 4,4'-difluorodiphenylsulfone (DFDPS, 99%, Sigma Aldrich Chemie GmbH, Germany), dimethyl sulfoxide (DMSO, 99.9%, Sigma Aldrich Chemie GmbH, Germany), potassium carbonate (K_2CO_3 , 99.9%, Loba Chemie, Pvt. Ltd. Mumbai, India), toluene (99%, Thermo Fisher Scientific India Pvt. Ltd. Mumbai, India) and hydrochloric acid (35–38%, Thermo Fisher Scientific India Pvt. Ltd. Mumbai, India) were used for synthesizing sulfonated poly arylene ether sulfone copolymer. Fuming sulfuric acid (20%, Alfa Aesar chemicals, Johnson Matthey Company, Heysham, England) was used for the sulfonation of DFDPS.

2.1.2. Synthesis of 4,4'-(hexafluoroisopropylidene) diphenol (6F-BPA) based novolac epoxy resin (EFN)

A 40 mL methyl isobutyl ketone (MIBK) solution containing 6F-BPA (0.05 mol) and PTSA (0.0014 mol) was added to a 250 mL three-necked round bottom flask equipped with a mechanical stirrer and dean and stark trap with a reflux condenser. Nitrogen gas was purged for 30 minutes and the reaction solution was heated to 100°C with stirring. 0.08 moles of formaldehyde solution (37–41%) was added to the reaction mixture drop wise. Then, the reaction mixture was heated to 120°C with constant stirring and maintained at this temperature for five hours. The condensation of novolac resin is a reversible process; therefore (0.13 mol) of water generated during the reaction was removed as an azeotropic mixture with MIBK. The reaction mixture was cooled to room temperature and washed with deionised water several times until it became neutral. The solution was then distilled at 120°C in order to remove the MIBK solvent. The product was washed with a mixture of water/methanol (7/3 v/v) several times to remove the unreacted 6F-BPA. A red brown solid product was obtained after vacuum drying at 60°C for 48 h.

To the above dried product of 6F-BPA novolac, 8 moles of epichlorohydrin for every phenolic group of novolac resin, isopropyl alcohol (0.83 mol) was added to 250 mL three necked round bottom flask equipped with a mechanical stirrer and a condenser. After increasing the reaction temperature to 70°C with constant stirring, 0.078 mol of 20 wt% aqueous solution of sodium hydroxide was added drop

wise into the reaction solution within one hour. The system was maintained at 70°C for another four hours with constant stirring. The reaction product in the flask was washed several times with deionized water to remove sodium chloride. The product was dissolved in toluene and filtered in order to remove the residual salt. Toluene and excess of ECH were distilled off under reduced pressure. Finally the product obtained was dried at 60–70°C under vacuum for 48 hours (Figure 1).

2.1.3. Synthesis of sulfonated 4,4'-difluorodiphenylsulfone (SDFDPS)

The DFDPS (0.01 mol) and 15 mL of 20% fuming sulfuric (15 mL) acid were added to a 100 mL three-necked round bottom flask equipped with overhead mechanical stirrer and a condenser. The mixture was heated to 110°C with constant stirring for six hours. After cooling the reaction mixture was poured into 200 mL ice water stirred with magnetic stirrer, and neutralized with 2M NaOH solution to a final pH 8. To this solution excess of NaCl was added and allowed to stand overnight. Finally the precipitates (ppts) were filtered and recrystallized from a mixture of methanol and water (9/1 v/v) (Figure 2).

2.1.4. Synthesis of sulfonated poly (arylene ether sulfone) copolymer (SPAES) copolymer

Sulfonated poly (arylene ether sulfone) copolymer (SPAES-H) was synthesized in a 250 mL three necked round bottom flask equipped with a mechanical stirrer and dean and stark trap. DPA (0.012 mol), HQ (0.012 mol) and 35 mL of DMSO were charged into the reaction flask. To this reaction mixture potas-

Figure 1. Synthesis of EFN epoxy resin

Figure 2. Synthesis of SDFDPS

Figure 3. Synthesis of SPAES-H-0 copolymer

sium carbonate (0.06 mol) was added and stirred at 80°C for 8 hours for producing reactive phenolate ions. Then SDFDPS (0.025 mol), 17 mL of toluene and 15 mL of DMSO were then added and the temperature was increased to 150°C the reaction mixture was stirred for 4 hours in order to dehydrate the system. After this, the temperature was increased to 180°C with constant stirring; reaction was carried out at this temperature for another 26 hours until the reaction mixture became very viscous. After cooling, the solution was dissolved in DMSO and then filtered. Precipitation of the copolymer was carried out by adding isopropyl alcohol to the filtrate. The precipitates were filtered and dried at 70°C (Figure 3).

2.1.5. Preparation of membrane and its cross-linking

The crosslinking of the SPAES-H-0 copolymer was done by dissolving 1 g in 10 mL DMSO at 30°C in a 50 mL round bottom flask and further adding EFN resin to this. The weight ratio of EFN to SPAES-H-0 copolymer was varied in the range 50–70%. The crosslinking reaction between SPAES-H-0 and EFN was carried out at 70–80°C for 24 hours with constant

stirring. The solution was then filtered and cast onto the glass plates and dried at 70–80°C for 24 hours; the temperature was then subsequently raised to 150°C for another 5 hours. The membranes thus obtained were dipped in 1M HCl solution for 48 hours at room temperature for their proton exchange (Figure 4).

2.2. Characterization

2.2.1. Structural characterization

FTIR spectra of the samples were recorded by using Perkin Elmer 1600 FTIR spectrophotometer in the range of 4000–400 cm^{-1} on the KBR pellets. ^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE II 400 NMR spectrometer using deuterated dimethyl sulfoxide as solvent, and tetramethyl silane as the internal standard.

2.2.2. Ion exchange capacity (IEC)

IEC was determined by titration method, which was used quantitatively to determine sulfonic acid concentration in the membranes. 0.2 g of the membrane samples in acid form were immersed in 50 mL of 1M NaCl solution at room temperature for 48 hours to allow the exchange process between H^+ ions with

Figure 4. Crosslinking of SPAES-H-0 copolymer with EFN epoxy resin

Na⁺ ions. The liberated H⁺ ions were titrated against 0.01M NaOH solution using phenolphthalein as an indicator [25, 26]. The IEC was calculated by using Equation (1):

$$\text{IEC} = \frac{\text{Consumed NaOH [mL]} \cdot \text{molarity NaOH} \left[\frac{\text{meq}}{\text{g}} \right]}{\text{Weight of dry membrane}} \quad (1)$$

2.2.3. Swelling property

The water and methanol absorption of the membranes were determined by measuring the change in the weight of dry and swollen membranes. After measuring the weights and lengths of the dry membranes, the sample membranes were immersed in water and methanol for 24 h. The excess water and methanol from the sample films were removed by wiping with filter paper. The percentage of water and methanol absorption was calculated by using Equation (2):

$$\text{Water/Methanol uptake [\%]} = \frac{W_w - W_d}{W_d} \cdot 100 \quad (2)$$

where W_w and W_d were the weights of the wet and corresponding dry membranes, respectively.

Swelling ratio of the membranes in water was determined by using the Equation (3):

$$\text{Swelling ratio [\%]} = \frac{L_w - L_d}{L_d} \cdot 100 \quad (3)$$

where L_w and L_d were the lengths of the wet and corresponding dry membranes, respectively [27–29].

2.2.4. Gel fraction [%]

The gel fraction of the crosslinked membranes was determined according to ASTM D2765 method using Soxhlet extractor. The membrane samples were refluxed in DMAc for at least 48 h, until the sample attained a constant weight [17]. The gel fraction of the crosslinked membranes were calculated by using Equation (4):

$$\text{Gel fraction [\%]} = \frac{W_2}{W_1} \cdot 100 \quad (4)$$

where W_2 was the weight of the dried membranes after extraction and W_1 was the weight of the membranes before extraction, respectively.

2.2.5. Proton conductivity

The conductivity of the membranes was checked at room temperature by four point probe technique. The four point probe arrangement was attached with Keithley 6221 sourcemeter and Keithley 2182A nanovoltmeter. The membranes were cut into 2×2 cm² and immersed in deionised water for 12 h before the measurement. The excess water from the membrane surface was wiped off with the help of filter paper. These membranes were further mounted onto the cell and an alternating current (I) ranging from 0.1–1.0 mA was applied to the cell, while the corresponding voltage (V) was obtained from the nanovoltmeter [30]. The resistance (V/I) was determined from the slope of the linear plot of V vs I , based on the Equations (5) and (6):

$$\text{Resistivity } (\rho) = \frac{V}{I} \cdot \text{thickness of the membrane} \cdot \frac{\pi}{\ln 2} \quad (5)$$

$$\text{Conductivity } (\sigma) = \frac{1}{\rho} \left[\frac{\text{S}}{\text{cm}^2} \right] \quad (6)$$

2.2.6. Methanol permeability

Methanol permeability was determined by using diffusion cell consisting of two compartments A and B which were partitioned by a membrane sample. 1M solution of methanol was placed in compartment A and water was placed in compartment B of the diffusion cell. The membrane sample was clamped in the middle of the two compartments. The solution in each compartment was continuously stirred with the help of magnetic beads to maintain uniform concentration. The concentration of the methanol in compartment B was measured using T80 UV-VIS spectrometer. The methanol concentration in compartment B as a function of time (t) is given by the Equation (7):

$$C_{B(t)} = \frac{A(D_K)C_A(t - t_0)}{V_B L} \quad (7)$$

where C_A is the concentration of the methanol in compartment A, V_B [cm³] is the volume of compartment B, A [cm²] and L [cm] are the area and thickness of the membranes. t and t_0 are the initial and final diffusion time, D_K is the methanol permeability of the membrane, respectively [26, 31].

2.2.7. Oxidative stability

Square pieces (0.2 g) of membrane samples were immersed in Fenton's reagent (4 ppm FeSO_4 in 6% H_2O_2) at 30°C. The oxidative stability was evaluated by recording the retained weights of the membranes after treatment in Fenton's reagent and observing the expended time when membranes started to break and the time when the membranes disappeared completely [9, 31].

2.2.8. Atomic force microscopy

The surface morphology of the membranes was observed with an AFM system (Agilent 5500 SPM) at room temperature and room humidity. It was operated in tapping mode using nanosensor silicon probe with spring constant of 10–130 N/m and a resonance frequency of 204–497 kHz. The membranes were soaked in distilled water for 12 hours and average three tests were taken for each sample.

2.2.9. X-ray diffraction study

The XRD diffraction patterns of the membranes before and after crosslinking were obtained with a rotating anode XPERT-PRO diffractometer using Cu-K α radiation source with a wavelength of 1.54060 Å.

2.2.10. Mechanical properties

The mechanical properties of the membranes were measured by using Hounsfield Universal Testing Machine at the deformation rate of 2 mm·min⁻¹. The films were cut into a size of 5×50 mm as reported by [17, 32]. Thicknesses of the membranes were 0.3 mm and for each testing at least three measurements were made and the average value was considered.

2.2.11. Thermal properties

Thermal degradation of the membranes was examined with EXSTAR TG/DTA 6300 thermal gravi-

metric analyzer under nitrogen atmosphere (200 mL·min⁻¹) at heating rate of 10°C·min⁻¹ with sample size of 10±1 mg from 25 to 900°C. The glass transition temperature of the prepared membranes was measured on Mettler Differential Scanning Calorimetry equipment. The samples were pre-heated under 200 mL·min⁻¹ nitrogen from room temperature to 150°C at a scanning rate of 10°C/min to remove moisture then cooled to 50°C and reheated from 50 to 350°C at a heating rate of 10°C/min.

3. Results and discussion

3.1. EFN resin

Figure 5a shows the FTIR spectrum of EFN novolac epoxy resin, characteristic absorptions at 3057 and 2929 cm⁻¹ were due to stretching vibrations of aromatic rings and bridging methylene groups, respectively. A characteristic absorption band at 1299 cm⁻¹ depicted the ring breathing frequency of epoxy ring, the appearance of the band at 916 cm⁻¹ proved the asymmetric ring deformation and the band at 762 cm⁻¹ showed the symmetric ring deformation of epoxy ring. The peaks in between 932–999 cm⁻¹ were due to the presence of C–F bonds.

Figure 5b shows the ¹H NMR spectrum of novolac epoxy resin EFN. The spectrum showed proton resonance signals at 3.6–3.8 and 6.7–7.3 ppm due to –CH₂ bridging and aromatic protons respectively. Characteristic proton resonance signals at 2.7–2.9, 3.3 and 3.9–4.2 ppm due to –O–CH₂, –CH and –CH₂ protons of the epoxy ring, respectively, were also observed.

3.2. SDFDPS

Figure 6 represents ¹H NMR spectrum of the SDFDPS in which the proton (H₁) adjacent to the sodium sulfonate group gets deshielded and appear at 8.3 ppm due to electron withdrawing nature of sulfone group and H₂ and H₃ protons appeared at 7.7 and 7.3 ppm, respectively.

Figure 5. (a) FTIR and (b) ¹H NMR of EFN epoxy resin

Figure 6. ^1H NMR spectrum of SDFDPS

3.3. SPAES-H-0 copolymer

Figure 7 showed the FTIR spectra of SPAES-H-0 and its crosslinked membranes. A characteristic absorption band at 1254 cm^{-1} suggested the C–O stretching vibrations of carboxylic acid group. Appearance of a doublet at 1330 and 1300 cm^{-1} , band at 1178 cm^{-1} were due to O=S=O asymmetric, symmetric and peak at 621 cm^{-1} was due to S–O

stretching vibrations of pendant sodium sulfonate groups, respectively. A characteristic absorption band at 1040 cm^{-1} was due to C–O symmetric stretching vibrations of ether linkages.

In cross linked cr-SPAES-H-50, cr-SPAES-H-60 and cr-SPAES-H-70 membranes a characteristic new absorption band was observed at 1774 cm^{-1} due to C=O stretching vibrations of ester linkages formed after crosslinking of the SPAES-H-0 copolymer with EFN epoxy resin. The appearance of peaks at $948\text{--}969\text{ cm}^{-1}$ indicated the stretching vibrations of C–F bonds due to the presence of CF_3 groups in the EFN resin.

Figure 8a represents the ^1H NMR spectrum of the SPAES-H-0 copolymer. The protons (H_1 , H_2 and H_3) present at ortho positions to the electron withdrawing groups (sulfone and sodium sulfonate) get deshielded and show signals at 8.2, 7.9 and 7.8 ppm, respectively. The aromatic protons (H_4) of the hydroquinone aromatic ring appeared at 7.4 ppm. The

Figure 7. FTIR spectra of the SPAES-H-0 and its cr-SPAES-H membranes in the region (a) $4000\text{--}450\text{ cm}^{-1}$ and (b) $1900\text{--}450\text{ cm}^{-1}$

Figure 8. (a) ^1H NMR and (b) ^{13}C NMR spectra of SPAES-H-0 copolymer

methylene protons (H_7 , H_8) and methyl (H_9) protons of the pentanoic group of DPA showed resonating signals at 2.1, 1.6 and 1.4 ppm, respectively. Figure 8b shows the ^{13}C NMR spectrum of the SPAES-H-0 copolymer. A characteristic signal for the carboxylic acid group carbon (C_1) appeared at 177 ppm. The peaks for the aromatic carbons were observed in the range of 117–135 ppm. The 147–161 ppm region showed peaks for the C–O carbons. The peaks corresponding to other carbons have also been identified.

4. Ion exchange capacity, water uptake and Swelling ratio

The IEC is determined by titration method at room temperature and the values are summarized in Table 1. The water uptake of the membranes at room temperature is shown in Figure 9. IEC tells about the exchangeable ions in the polymer backbone and is

Figure 9. Water and methanol uptake of the SPAES-H-0 and its cr-SPAES-H membranes

Table 1. Properties IEC, proton conductivity and methanol permeability of the membranes at 30°C

Membranes	IEC [meq/g]	Proton conductivity [S/cm]	Methanol permeability [cm^2/s]
SPAES-H-0	$7.4 \cdot 10^{-1}$	$6.8 \cdot 10^{-3}$	–
cr-SPAES-H-50	$6.7 \cdot 10^{-1}$	$5.7 \cdot 10^{-3}$	$4.9 \cdot 10^{-6}$
cr-SPAES-H-60	$5.5 \cdot 10^{-1}$	$4.1 \cdot 10^{-3}$	$3.7 \cdot 10^{-6}$
cr-SPAES-H-70	$3.8 \cdot 10^{-1}$	$3.0 \cdot 10^{-3}$	$2.6 \cdot 10^{-6}$

Table 2. Properties water/ methanol uptake, and swelling ratio of the membranes

Membranes	WU [%]			Methanol uptake [%]			Swelling ratio [%]		
	30°C	60°C	80°C	30°C	60°C	80°C	30°C	60°C	80°C
SPAES-H-0	21.5	44	69	19	37	58	–	–	–
cr-SPAES-H-50	16.5	36	54	15	28	39	8	14	36
cr-SPAES-H-60	8.5	17	42	7	13.5	27	5.5	10	23
cr-SPAES-H-70	4.4	8	19	3.5	8	12	4	7.5	15

closely related to the water uptake of the membranes. Water acts as a medium for the transportation of the protons according to Ionic cluster network model and Grothuss and Vehicle mechanism [33–36], where protons are believed to be transported along with hydrogen bonded ionic channels and cationic mixtures such as H_3O^+ , H_5O_2^+ , H_9O_4^+ in water medium. Therefore, level of hydration of the membranes is dependent on the presence of hydrophilic groups such as carboxylic and sulfonic acid groups. It was observed that IEC capacity and water uptake of the pristine SPAES-H-0 membrane was found to be higher than its counterpart crosslinked membranes. This was because of the more propensities of the pristine membrane to absorb water and form ionic channels by pendant sulfonic acid and carboxylic acid groups for the transport of the protons. The cross-linked membranes showed reduction in water uptake, which might be due to the unavailability of the protons of carboxylic acid groups. These carboxylic groups might have participated in proton transportation in the pristine SPAES-H-0 membrane. Swelling ratio is also very important property in PEMFC applications because it is related to the dimensional stability, which determines the mechanical stability of the membranes. It can be seen from the Table 2 that for the higher crosslinked membranes swelling ratio was found to decrease due to the formation of tight molecular structure. The presence of hydrophobic CF_3 groups of unreacted epoxy resin also play role in reducing the water uptake and swelling ratio of the crosslinked membranes with the increase in the amount of epoxy resin.

5. Proton conductivity

Adequate proton conductivity is the prime requirement for PEMs for their applicability in PEMFCs. The water uptake and IEC is directly related to the proton conductivity of the membranes. For the high proton conductivity the polar groups such as sulfonic and carboxylic acid groups play important role. In fully hydrated state the sulfonated polymers

may slack immobile polar sulfonic acid groups and mobile protons into the solution and form ionic channels for the transport of the protons. The protons get transported from one acid group to another in the form of hydronium ions. From the results tabulated in Table 1 it was observed that proton conductivity of the pristine SPAES-H-0 membrane was $6.8 \cdot 10^3$ S/cm and found to be higher than that of its corresponding crosslinked membranes i.e. 5.7, 4.1 and $3.0 \cdot 10^3$ S/cm for cr-SPAES-H-50, cr-SPAES-H-60 and cr-SPAES-H-70, respectively. This was owing to either reduction or disconnectivity of ionic channels due to bonding of the carboxylic acid groups of the SPAES-H-0 membrane with oxirane rings of the EFN epoxy resin, which leads to decrease in water uptake, IEC and hence proton conductivity of the crosslinked membranes.

5.1. Methanol permeability and selectivity ratio

It was observed that methanol permeability of the pristine membrane could not be found, because the membrane of SPAES-H-0 copolymer was difficult to cast into a definite shape and size due to brittleness of the copolymer. However, it was interesting to note that on crosslinking the copolymer with EFN resin in 50–70% weight ratio of EFN to SPAES-H-0 using a set procedure; well defined cr-SPAES-H membranes were obtained. From the results summarized in Table 1 it was observed that the methanol permeability of the crosslinked membranes decreased as the content of epoxy resin has increased. This was owing to the close packing in case of cr-SPAES-H membranes, which may have contributed towards a decrease in the methanol crossover (Table 3).

In general for the better performance of the PEMs in PEMFCs it should possess high proton conductivity and low methanol permeability. Selectivity ratio is the ratio of the proton conductivity (σ) to methanol permeability (D_K). Higher the value of σ/D_K better will be the performance of the membrane. Figure 10 shows the selectivity ratio of crosslinked membranes cr-SPAES-H-50, cr-SPAES-H-60, cr-SPAES-H-70, respectively. Results revealed that selectivity ratio decreases with the increase in the content of epoxy resin in case of crosslinked membranes. This was due to fall in their proton conductivity, which was due to the absence or reduction in the number of carboxylic acid groups in the cross-

Figure 10. Selectivity ratio of the crosslinked cr-SPAES-H membranes

linked membranes, which might have participated in proton transportation.

6. Oxidative stability

Figure 11 shows the weight residue of the membranes as a function of time in Fenton's reagent at 30°C. This method has been used to stimulate the oxidation reaction of the membranes by the attack of free radical species ($\text{HO}\cdot$ and $\text{HOO}\cdot$) of Fenton's reagent. The presence of highly electron withdrawing sulfone groups and pendant sulfonic acid groups in the backbone of the polymeric chain might be responsible for the reduction of electron density of the nearby aromatic rings and thus enabling the membranes to exhibit better tolerance for electrophilic attack by these hydroxyl radicals. From the results it was also observed that crosslinked membranes were found to be more stable against the oxidative attack as compared to pristine SPAES-H-0 membrane. This was due to the formation of three dimensional infusible network structure via the reaction between pendant carboxylic acid groups of the main polymeric chain and oxirane ring of EFN epoxy resin.

Figure 11. Oxidative stability of the SPAES-H-0 and its cr-SPAES-H membranes

Table 3. Solubility of the membranes in various organic solvents at 30 and 80°C

Membranes	Methanol		CH ₂ Cl ₂		THF		DMAc		NMP		DMSO		Gel fraction ^a [%]
	30°C	80°C	30°C	80°C	30°C	80°C	30°C	80°C	30°C	80°C	30°C	80°C	
SPAES-H-0	–	–	–	–	–	–	+	+	+	+	+	+	–
cr-SPAES-H-50	–	–	–	–	–	–	–	±	–	±	–	±	90
cr-SPAES-H-60	–	–	–	–	–	–	–	±	–	±	–	±	94
cr-SPAES-H-70	–	–	–	–	–	–	–	±	–	±	–	±	97

–: insoluble, +: soluble, ±: swollen

^a[17]

Moreover the enhancement in the oxidative stability of the crosslinked membranes may have led to less water absorption, and since lower the water content, lower will be the attack via the oxidizing species present in water. The carboxylic acid groups present in the pristine membrane a site prone towards oxidation get consumed due to the crosslinking with the epoxy and thus enhance its oxidative stability.

It was observed that cr-SPAES-H-60 membrane was found to possess better oxidative stability as compared to cr-SPAES-H-70 membrane. This was probably due to the presence of excess of epoxy resin in case of cr-SPAES-H-70. Since off-stoichiometric mixture contain latent sites [37], which could remain on the macromolecular structure and can become susceptible for the free radical attack.

7. Morphology of the membranes

Microscopic observation of the surface of the prepared membranes was investigated via tapping mode atomic force microscopy (AFM) and the images of the SPAES-H-0 and its corresponding cr-SPAES-H membranes are shown in Figure 12 and 13, respectively. Examination of the AFM images revealed the

presence of light and dark colored domains. The light colored region depicted the hydrophilic domains containing polar groups and dark areas represent the hydrophobic backbone. It can be seen that the light colored domains appeared wide and more distinct in the pristine SPAES-H-0 membrane Figures 12a, 12b. This was due to the fact that polar pendant sulfonic acid and carboxylic acid groups contain small amounts of water which aggregate to form ionic clusters or channels for the transport of the protons. Therefore, the uncrosslinked SPAES-H-0 membranes showed higher proton conductivity. After crosslinking it has been observed the size of these clusters, intensity of the peaks and connectivity among them decreased in case of the crosslinked membranes and can be clearly seen in case of cr-SPAES-50 membrane Figure 13a, 13b. This might be due to the bonding between carboxylic acid groups of the pristine membrane with the oxirane ring of the EFN epoxy resin that cause in the reduction of the ionic channels. In case of cr-SPAES-60 and cr-SPAES-H-70 Figure 13c, 13d membranes the distinction between hydrophilic and hydrophobic domains become difficult due to the formation of highly crosslinked

Figure 12. Tapping mode images of membrane (a) SPAES-H-0 in 2D mode and (b) SPAES-H-0 in 3D mode

Figure 13. Tapping mode images (a, b) of SPAES-H-50 and (c, d) of cr-SPAES-H-60, cr-SPAES-H-70 membranes, respectively

network structures and decrease in hydrophilic carboxylic acid groups. The increment in hydrophobic CF_3 groups of EFN resin was also another dilemma for no clear distinction between hydrophilic and hydrophobic domains in case of cr-SPAES-60 and cr-SPAES-H-70 membranes. These results concurred well with the water uptake, swelling ratio, ion exchange capacity and proton conductivity values which were found to be lesser in case of the cross-linked membranes.

8. X-ray diffraction study

Figure 14 shows the X-Ray diffractograms of the uncrosslinked SPAES-H-0 and its crosslinked cr-SPAES-H-50, cr-SPAES-H-60 and cr-SPAES-H-70 membranes, respectively. It can be seen from the Figure 14 that after crosslinking the width of the

peaks at $2\theta = 28, 31, 32, 44^\circ$, respectively was found to increase in case of cr-SPAES-H-50 membrane as compared to pure SPAES-H-0 membrane. It can also be seen from the figure that the peaks at $2\theta = 18, 19, 27^\circ$ and in the region of $31\text{--}33, 35\text{--}39, 41\text{--}49, 51\text{--}57^\circ$, respectively have disappeared in the case of cr-SPAES-H-60 membrane. The intensity of peak at $2\theta = 34^\circ$, has been reduced in case of cr-SPAES-H-60 and cr-SPAES-H-70 membranes. The increase in the width of the peaks, decrease in the intensity and disappearance of the peaks indicated the reduction of crystalline nature of the crosslinked membranes. Hence, it can be concluded that crosslinking of the SPAES-H-0 membrane with EFN epoxy resin reduced the crystalline behaviour of the crosslinked membranes.

Figure 14. XRD graphs of SPAES-H-0 and its corresponding crosslinked membranes

9. Mechanical properties

The mechanical stability of the membranes is one of the decisive parameters in determining the performance of the membranes because toughness and elasticity are also important factors of the membranes in addition to high proton conductivity for fuel cell applications. The stress strain behaviour of the membranes has been depicted in Figure 15 and results are summarized in Table 4. From the results it can be observed that cr-SPAES-H-60 membrane exhibit superior tensile strength, young's modulus and elongation at break as compared to its corresponding cr-SPAES-H-50 and cr-SPAES-H-70 mem-

Figure 15. Stress vs strain behavior of the SPAES-H-0 and its cr-SPAES-H membranes

Table 4. Mechanical properties of the membranes

Membranes	Tensile strength [MPa]	Young's Modulus [MPa]	Elongation at break [%]
SPAES-H-0	—	—	—
cr-SPAES-H-50	8.9	49.93	24.63
cr-SPAES-H-60	12.03	55.65	36.31
cr-SPAES-H-70	9.79	41.31	32.13

branes. The increase in the elongation at break values with the crosslinking could be related to the decrease in crystallinity of the polymeric chains, which is found in good agreement with the obtained X- ray analysis results.

10. Thermal properties

Thermal stability of the PEMs is significant for their durability during fuel cell operation at elevated temperature, it was evaluated using TGA technique and the results are presented in the Figure 16 and Table 5. The weight loss observed below 200°C was due to evaporation of absorbed water. Above 200°C the two step degradation profile was observed for all the membranes. The weight loss from 200–500°C region was attributed to the loss of sulfonic acid groups, whereas the weight loss above 700°C was assigned to the decomposition of the main chain

Table 5. Thermal behaviour description by differential scanning calorimetry and thermo gravimetric analysis

Membranes	T _g [°C]	T _g [°C]	Char residue at 700°C [%]	LOI
SPAES-H-0	161	230	73.62	46.94
cr-SPAES-H-50	188	245	30.09	29.53
cr-SPAES-H-60	—	258	50.57	37.72
cr-SPAES-H-70	148	262	55.36	39.64

Figure 16. TGA thermograms for the SPAES-H-0 and its corresponding crosslinked membranes

of the polymer. It has been observed that the decomposition temperature for the loss of sulfonic acid groups (T_s) in case of pristine SPAES-H-0 membrane was at 370°C and for crosslinked membranes was at 500°C. The higher T_s for the crosslinked membranes was due to the increased interactions between carboxylic acid groups of the polymeric membranes and the epoxy groups of the EFN resin. Thus the results of thermogravimetric analysis confirmed that crosslinking enhances the thermal stability of the membranes and makes the membranes more suitable for high temperature operating fuel cell applications.

The limiting oxygen index (LOI) value has been calculated by using Krevelen's equation [38] in order to confirm the flame retardancy of the synthesized membranes. All the membranes have LOI values greater than 27 which indicate the better flame resistance behaviour of the synthesized membranes.

10.1. Differential Scanning Calorimetry

Differential Scanning Calorimetry measurement of the membranes was carried out by using heating-cooling- heating procedure. The purpose of the first heating cycle was to remove any thermal history of the synthesized copolymer. Figure 17 shows the DSC scans for the pristine SPAES-H-0 and its crosslinked membranes, the results are summarized in Table 5. The glass transition temperature (T_g) of a polymer is the temperature at which polymeric chain segments in the amorphous regions of the polymer attain sufficient heat energy to move in a coordinated manner. From the results it was observed that the T_g for

the crosslinked membranes is higher than their corresponding pristine SPAES-H-0 membrane. This might be due to the increased intermolecular interactions between polymer chain segments and crosslinker (EFN). It can be seen that the SPAES-H membranes showed two glass transition temperatures. The lower and upper T_g 's for the SPAES-H-0 and cr-SPAES-50 membranes were attributed to the hydrophobic backbone and hydrophilic ionic clusters, respectively. The appearance of single T_g in case of cr-SPAES-60 indicated that all the carboxylic acid groups of the polymer backbone have been consumed during the crosslinking reaction with the oxirane rings of the epoxy resin. This resulted into the formation of a three dimensional infusible network structure. However, cr-SPAES-H-70 which has an off stoichiometric mixture shows two glass transition temperatures, since it contains unreacted epoxy resin. Therefore, it can be concluded that crosslinked membranes synthesized in the present work showed improved thermal properties which are good enough to use them as PEMs in fuel cell applications.

11. Conclusions

The sulfonated poly (arylene ether sulfone) copolymer (SPAES-H-0) has been synthesized and subsequently crosslinked with EFN epoxy resin. The properties and performance of the membranes before and after crosslinking were characterized by various ways. It has been observed that the crosslinked membranes showed reduction in the IEC, water and methanol uptake, proton conductivity and selectivity ratio with improvement in the oxidative stability and mechanical properties. Crosslinking also reduces the crystalline character of the membranes. As the ratio of the EFN resin has been increased the intensity of the peaks, size of the ionic channels and connectivity among them decreased as confirmed by AFM microscopy. The crosslinked membranes also showed high thermal stability in the temperature range of the PEMFC applications. Hence crosslinking of the SPAES-H-0 copolymer with EFN resin is found to be a suitable method for balancing high proton conductivity due to excessive water uptake and mechanical strength of the membranes for their usage in fuel cell applications.

Figure 17. DSC scans for the SPAES-H-0 and its corresponding crosslinked membranes

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