

Highly selective sulfonated poly(vinylidene fluoride-co-hexafluoropropylene)/poly(ether sulfone) blend proton exchange membranes for direct methanol fuel cells

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ABSTRACT: Proton exchange membranes (PEMs) based on blends of poly(ether sulfone) (PES) and sulfonated poly(vinylidene fluoride-co-hexafluoropropylene) (sPVdF-co-HFP) were prepared successfully. Fabricated blend membranes showed favorable PEM characteristics such as reduced methanol permeability, high selectivity, and improved mechanical integrity. Additionally, these membranes afford comparable proton conductivity, good oxidative stability, moderate ion exchange capacity, and reasonable water uptake. To appraise PEM performance, blend membranes were characterized using techniques such as Fourier transform infrared spectroscopy, AC impedance spectroscopy; atomic force microscopy, and thermogravimetry. Addition of hydrophobic PES confines the swelling of the PEM and increases the ultimate tensile strength of the membrane. Proton conductivities of the blend membranes are about 10^{-3} S cm⁻¹. Methanol permeability of 1.22×10^{-7} cm² s⁻¹ exhibited by the sPVdF-co-HFP/PES10 blend membrane is much lower than that of Nafion-117. AFM studies divulged that the sPVdF-co-HFP/PES blend membranes have nodule like structure, which confirms the presence of hydrophilic domain. The observed results demonstrated that the sPVdF-co-HFP/PES blend membranes have promise for possible usage as a PEM in direct methanol fuel cells. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43907.

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INTRODUCTION

Fuel cells are commonly regarded as effective and alternate energy resource to fossil fuels. Among the various types of fuel cells, direct methanol fuel cells (DMFCs) are environmentally friendly and have high energy efficiency.¹ Owing to these reasons, DMFCs are widely projected as the important power sources for the devices such as computers, laptops, cell phones, and other electronic appliances.^{2–5} In DMFC, Nafion is an eminent polymer used as PEM, which has hydrophobic domains and hydrophilic sulfonic acid at regular intervals that helps the moving of ions. Moreover, Nafion boons excellent thermal stability, high proton conductivity, and good chemical, mechanical stability at room temperature.^{6–9} The main disadvantages of Nafion proton exchange membrane (PEM) is high methanol crossover due to the solvated hydrogen ions through fully hydrated state ion-cluster channels.¹⁰ At high temperature, Nafion in a fully hydrated state, possesses low mechanical strength, a low glass transition temperature and significant dimensional change. The

methanol crossover not only drops the methanol consumption but also produces cathode depolarization, which results in decreasing in fuel efficiency and performance of DMFCs.^{11–14} Hence, this research focusing on manufacturing PEM with reduced methanol cross over for DMFC applications.

In fuel cells, fluoropolymers such as PVdF are used for membrane preparation because of their good mechanical strength and its stability and excellent promising results are revealed by its copolymer and their composites. Among the fluoropolymers, PVdF-co-HFP is observed as a gifted material for the membranes of fuel cells. The reason is the liquid electrolyte are trapped by the hexafluoropropylene group (amorphous phase) and the mechanical strength of the PEM can be maintained by vinylidene fluoride group (crystalline regions). Owing to the presence of distinctive strong carbon–fluorine bond,¹⁵ the hydrophobic nature of PVdF-co-HFP makes the polymer electrolyte with low ion exchange capacity, water uptake and the conductivity of protons. This hydrophobic nature is reduced by

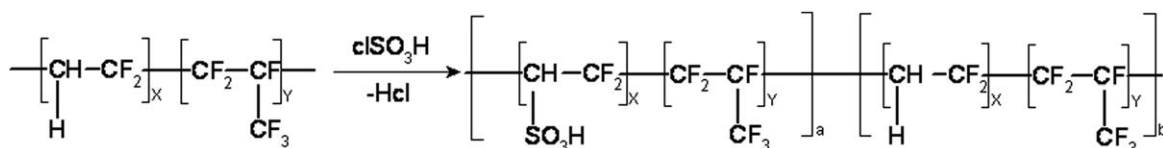


Figure 1. Sulfonation of PVdF-co-HFP.

sulfonating the PVdF-co-HFP and then it can be used as a PEM material in the fuel cells. Besides sulfonated poly(vinylidene fluoride-co-hexafluoropropylene) (sPVdF-co-HFP) have both hydrophilic sulfonated group and vinylidene fluoride blocks. Thus, the presence of sulfonic acid group increases the proton conductivity, water uptake, ion exchange property.¹⁶

One of the problems that foil the extensive commercialization of the DMFCs is high methanol permeability of PEM material. To overcome this problem in an easily hybrid membrane forming polymer like poly(ether sulfone) (PES) was selected to blend with the sPVdF-co-HFP matrix. PES is the most important promising polymeric membrane material widely used for the separation fields such as ultrafiltration, microfiltration, gas separation, and also in biomedical fields.^{17–21} In recent years, PES incorporated membrane is also used in DMFCs because of it is (i) high thermal and chemical stability, (ii) excellent hydrolytic stability owing to the strong dipole–dipole interactions with water, (iii) outstanding mechanical properties, (iv) good oxidative resistance, (v) high glass transition temperature, (vi) inertness, and (vii) hydrophobic character (which reduces the methanol cross over problem occurs in DMFCs).^{22–24}

This work focused on the preparation of sPVdF-co-HFP/PES blend PEM for DMFC applications. Prepared pure and blend membranes were characterized in terms of ion exchange capacity, water uptake, swelling ratio, Fourier transform infrared (FTIR) spectroscopy, thermal stability, and mechanical stability. Surface of pristine and blend membranes were examined by AFM technique. Performance of membranes was also studied by means of proton conductivity, methanol permeability, and selectivity.

EXPERIMENTAL

Materials

A PVdF-co-HFP pellet ($M_w = 400$ kDa) was purchased from Sigma Aldrich. The blend material PES (Gafone 3200P, $M_w = 123$ kDa) was provided by Ghardha chemicals limited India. Methanol was obtained from SRL, India. 1-Methyl-2-pyrrolidone (NMP), 1,2-dichloroethane (DCE), and sulfuric acid (98%) were purchased from Merck, India. Chlorosulfonic acid and sodium chloride was received from Loba Chemie, India. All the reagents and chemicals were used as received. For all the experimental work, de-ionized water was used.

Partial Sulfonation of PVdF-co-HFP

The partial sulfonation of PVdF-co-HFP was done on the basis of the procedure of Suparna *et al.*²⁵ PVdF-co-HFP pellets were dried in a vacuum at 60 °C for 12 h before sulfonation. In a round-bottom flask having chlorosulfonic acid and successively added PVdF-co-HFP, the sulfonation reaction was executed under a constant stirring circumstance, and maintaining the

temperature of 60 °C. After 7 h, the obtained black pellets were washed consequently with DCE, 100% methanol and water. Finally, the black pellets were dried in vacuum at 60 °C. Sulfonation of PVdF-co-HFP is shown in Figure 1 where the values of “a” and “b” are 0.0248 and 0.9752.²⁶ The degree of sulfonation was found to be 2.5%.

Preparation of Blend Membranes

Solution casting method was followed for the preparation of membranes. The composition of the casting dope is given in Table I together with the code of the membrane prepared from the dope. PES was dissolved in NMP under constant stirring at the temperature of 80 °C. Then sPVdF-co-HFP was added to this homogenous solution and the mixture was stirred for 12 h. Then the blend solution was cast on a petri dish and the solvent NMP was evaporated under vacuum at the temperature of 80 °C for 24 h. The obtained proton exchange blend membranes were immersed in 3% hydrogen peroxide for 1 h then in 1 M sulfuric acid for 1 h and finally with deionized water. This pretreatment was used to remove both organic and inorganic impurities from the blend membranes.^{16,27}

Water Uptake

For the determination of water uptake, membrane sample of 2×2 cm² size was dried in vacuum at 80 °C for 24 h. Then the dried membrane was weighed and immersed in deionized water for 24 h. The excess of surface water was removed by using filter paper and the wet sample membrane was weighed immediately. The water uptake was calculated by using the eq. (1).

$$WU = \frac{W_{\text{wet membrane}} - W_{\text{dry membrane}}}{W_{\text{dry membrane}}} \times 100\% \quad (1)$$

where $W_{\text{dry membrane}}$ and $W_{\text{wet membrane}}$ are the weight of the dry and wet membranes, respectively.²⁸

Swelling Ratio

To determine the swelling ratio, 2×2 cm² size of all the prepared membranes were first dried at 80 °C. Using a thickness gauge, thicknesses of the dry membranes were measured. Then, it is immersed in deionized water for 24 h to swell. The excess water was wiped away and the thickness again measured. To calculate the extent of swelling in percentage the following eq. (2) was used

$$\text{Swelling ratio} = \frac{T_{\text{wet membrane}} - T_{\text{dry membrane}}}{T_{\text{dry membrane}}} \times 100\% \quad (2)$$

where $T_{\text{dry membrane}}$ and $T_{\text{wet membrane}}$ are the thickness of the dry and wet membranes, respectively.²⁸

Ion Exchange Capacity

Usual titration method was used to determine ion exchange capacities (IECs) of the composite membranes.^{23,29} Square

Table I. Lamda Value, Oxidative Stability, Elongation at Yield and Young's Modulus Values of the Pure sPVdF-co-HFP and sPVdF-co-HFP/PES Blend Membranes

Membrane code	Polymer blend composition (10 wt %)		Solvent NMP (wt %)	Lambda value	Oxidative stability (wt %)	Elongation at yield (%)	Young's modulus (MPa)
	sPVdF-co-HFP (wt %)	PES (wt %)					
sPVdF-co-HFP	100	0	90	26.53	95.6	28.20	381.67
sPVdF-co-HFP/PES2	98	2	90	25.58	96.5	33.32	395.23
sPVdF-co-HFP/PES4	96	4	90	25.19	97.3	38.67	405.35
sPVdF-co-HFP/PES6	94	6	90	24.66	98.0	44.24	416.14
sPVdF-co-HFP/PES8	92	8	90	24.23	98.7	48.80	426.87
sPVdF-co-HFP/PES10	90	10	90	24.03	99.2	53.81	437.35

pieces of composite membrane were first immersed in 1 M H₂SO₄ solution for 24 h. The excess of acid was removed by washing the membrane with deionized water, and then the pieces are kept separately in 50 mL of 1 M sodium chloride overnight. During this time, all the protons are replaced by sodium ions. Using phenolphthalein indicator the solution was titrated with 0.01 N NaOH solution. By knowing the volume of NaOH consumed, IEC values (meq. g⁻¹) of the membranes can be calculated from the following eq. (3).

$$\text{IEC} = \frac{\text{Volume of NaOH consumed} \times \text{Strength of NaOH}}{\text{Weight of the dried membrane sample}} \quad (3)$$

The lambda value (λ) of the prepared membranes was calculated from the following eq. (4).

$$\lambda = \frac{\text{Water uptake}}{\text{Ion exchange capacity} \times M_{\text{H}_2\text{O}}} \quad (4)$$

where the molecular weight of water,³⁰ $M_{\text{H}_2\text{O}} = 18.01 \text{ g mol}^{-1}$.

Fourier Transform Infrared

The pure and blend membranes were subjected to FTIR using RX1 spectrophotometer (Perkin Elmer) at wave number range of 500–4000 cm⁻¹.

Proton Conductivity

The ionic conductivities of the pure and blend membranes were measured at room temperature by using ac impedance spectroscopy. The potential and frequency range applied were 10 mV and 1 MHz to 100 Hz, respectively. Before the measurement of proton conductivity, the membranes were soaked in 1 M sulfuric acid solution for 24 h and then the membranes were washed completely with deionized water. These hydrated membranes were retained between the two electrodes. From the impedance data, the proton conductivity of the membranes (σ) was calculated by using the eq. (5).

$$\sigma = \frac{T_{\text{mem}}}{RA_{\text{mem}}} \quad (5)$$

where T_{mem} is the thickness of the membrane sample, R is the resistance of the membrane sample obtained from the low intersect of the high frequency semi-circle on a complex impedance plane with the real (Z) axis, and A_{mem} is the cross-sectional area of the membrane sample.³¹

Methanol Permeability

Methanol permeability of all the prepared membranes was determined by using diffusion cell.²⁶ The diffusion cell consists of two compartments A and B separated vertically by the prepared membrane of area 12.5 cm². First, the compartment A contains with 2 M methanol and the compartment B contains deionized water. Before performing the experiment, the test membranes are kept in deionized water for 24 h. The methanol from compartment A diffuses into compartment B because of continuous stirring. The rise in concentration of methanol in compartment B was noted by computing the refractive index by means of refractometer (ABBE NAR3T). The methanol permeability of the prepared blend membranes is calculated using the following eq. (6).

$$\tau = m \times \frac{V_B}{A_{\text{mem}}} \times \frac{T_{\text{mem}}}{C_A} \quad (6)$$

where τ (cm² s⁻¹) is the methanol permeability of the membrane, m (mol L⁻¹ s⁻¹) is the slope obtained from a plot between the concentrations of the methanol and time, V_B (cm³) is volume in the compartment B, A_{mem} (cm²) is effective area of the membrane, T_{mem} (cm) is the thickness of the membrane, C_A (mol L⁻¹) is the concentration of the methanol in the compartment A.

Thermal Stability

TG/DTA-6300 was used for the analysis of thermal stability of the pure and blend membranes at the temperature range of 30–1000 °C and the heating rate is 20 °C/min under nitrogen as carrier gas.

Oxidative Stability

Oxidative stability of the PEMs was established by dipping the pure and blended membranes into 50 mL of Fenton's reagent (3 wt % H₂O₂ containing 4 ppm FeSO₄) at room temperature for 5 h. After the desired period, the membrane samples were taken out from Fenton's reagent the solution and weighed again. Oxidative stability of the membrane samples were calculated from the weight loss percentage.

Morphological Study

Tapping mode atomic force microscopy (TM-AFM) is a powerful technique used to characterize the surface roughness of the membranes. Surface morphology of the membranes was

characterized using semicontact TM-AFM (NTMDT, Ireland) equipment having a silicon nitride, single crystal, N-type tip of radius 6 nm, with a resonance frequency of 140–390 kHz and a force constant of 3.1–37.6 N/m. The membrane samples were cut into small square pieces ($\sim 1 \times 1 \text{ cm}^2$) and glued on the glass substrate. The surface of the membranes was imaged in a scan size of $1 \times 1 \text{ mm}^2$. Before testing, all the pure and blend membranes samples were dried at 100°C for 24 h under vacuum.³²

Mechanical Stability

To analyze the dynamic mechanical property of the prepared sPVdF-co-HFP/PES blend membranes, Universal Testing Machine (Instron 3382) of maximum capacity 100 kN was used²⁶ Rectangular shape membrane strip of length 60 mm and width 10 mm was taken for testing. For all membrane samples, the average values of three measurements were reported.

RESULTS AND DISCUSSION

Water Uptake

The water uptake value for the sPVdF-co-HFP/PES blend membranes are shown in the Figure 2. The pure sPVdF-co-HFP membrane has higher water uptake value of 21.5%.²⁵ This may be due to the partially sulfonated PVdF-co-HFP consists of sulfonic acid group that promotes water uptake, also enabling the sPVdF-co-HFP membrane to be a good conductor of protons. In an aqueous atmosphere, these protons are movable because of the dissociation of sulfonic acid groups. There is a decrease in the water uptake values by increasing the content of hydrophobic PES. This result confirms that small amount of hydrophobic PES polymer is dispersed well in hydrophilic sPVdF-co-HFP matrix. The blend membrane containing high amount of PES also possess water uptake value of 17.1%, which is comparable value for PEM used in DMFCs.

Swelling Ratio

The swelling ratio of sPVdF-co-HFP/PES blend membranes is shown in the Figure 2. While increasing the content of PES, the swelling ratio values decreases from 18.2 to 13.2%. Similar trend was obtained for the water uptake analysis as well.³¹ This reduction in swelling ratio is due to the decrease in the sulfonic acid group by the addition of PES content which is hydrophobic in nature.

IEC and Lambda Value

Electrochemical property of the membranes is mainly based on the IEC as well as water uptake values. The IEC defined as the number of milliequivalents of ions present in 1 g. of the dry polymer (meq. g^{-1}). IEC value depends on the concentration of sulfonic acid group present in the membrane structure. The variation of IEC values of the sPVdF-co-HFP/PES blend membranes are represented in Figure 3. A regular decrease in the IEC value of all blend membranes with increasing PES content is due to the hydrophobic nature of PES, which reduces the $-\text{SO}_3\text{H}$ group in the blend membranes. This trend is similar to the earlier reports in the literature.^{33,34}

Lambda values for the sPVdF-co-HFP/PES blend membranes can be calculated and are shown in Table I. The number of water molecules absorbed per ion exchange capacity (lambda

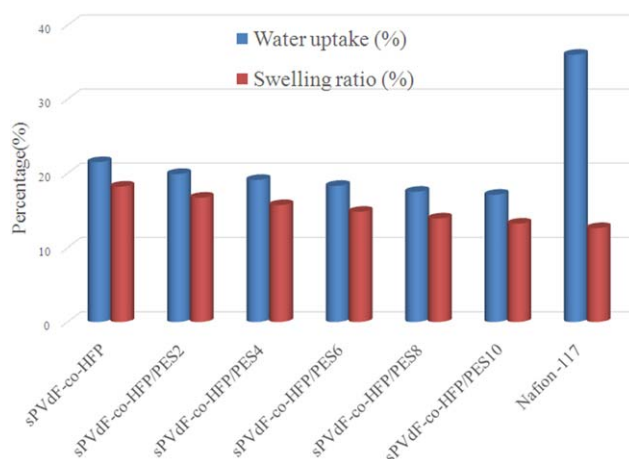


Figure 2. Water uptake and swelling ratio of sPVdF-co-HFP/PES blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

value) decreases when PES content increases.³⁰ Since lambda value depends on both water uptake and IEC values, there is a regular decrease in lambda value, which shows that the presence of PES decreases the density of hydrophilic sulfonic acid group in the blend membranes.

Fourier Transform Infrared

The FTIR spectra of pure sPVdF-co-HFP, sPVdF-co-HFP/PES2, and sPVdF-co-HFP/PES8 blend membranes are shown in Figure 4, which confirms the presence of the sulfonic acid group in sPVdF-co-HFP/PES blend membranes. While comparing these spectra, the peak appearing at 1076 cm^{-1} was due to the symmetric stretching of the $\text{O}=\text{S}=\text{O}$ bond of the sulfonic acid group and the peak appearing at 1419 cm^{-1} was due to the asymmetric stretching of the $\text{O}=\text{S}=\text{O}$ bond of the sulfonic acid group and the absorption peak at 3800 cm^{-1} was due to the $\text{O}-\text{H}$ stretching present in the $-\text{SO}_3\text{H}$ group.²⁸ All these peaks are absent in PVdF-co-HFP. Apart from this, three new peaks appearing at 1224 cm^{-1} assigned to the presence of aryl oxide of PES, $\text{C}-\text{O}-\text{C}$

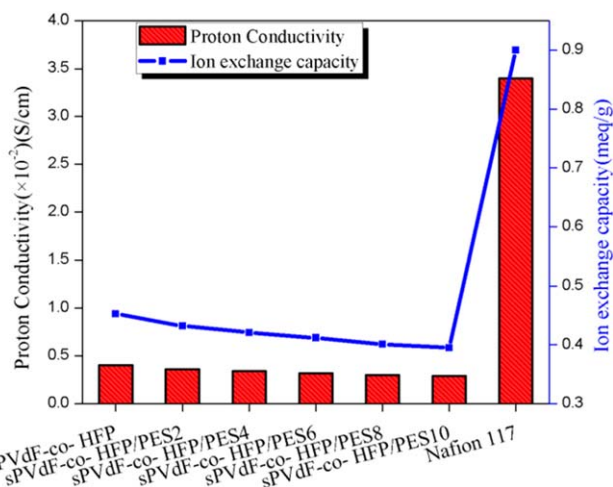


Figure 3. Ion exchange capacity and proton conductivity of sPVdF-co-HFP/PES blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

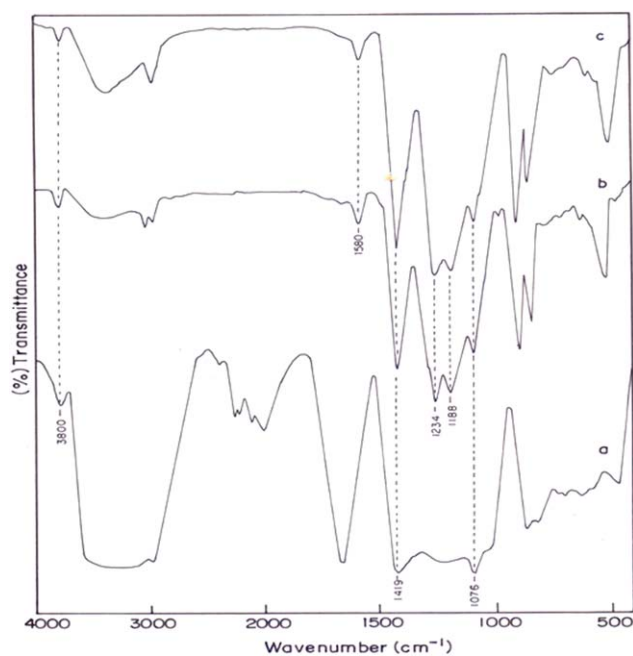


Figure 4. FTIR spectra of sPVdF-co-HFP (a), sPVdF-co-HFP/PES2 (b), and sPVdF-co-HFP/PES8 (c) blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of PES appears around 1188 cm^{-1} and the aromatic carbons of PES can be observed around 1580 cm^{-1} .^{32,35} Thus, the spectra of sPVdF-co-HFP/PES2, sPVdF-co-HFP/PES8 blend membranes are quite similar whereas these three peaks are absent in sPVdF-co-HFP. From the FTIR analysis, successful incorporation of PES within the partially sulfonated PVdF-co-HFP has been undoubtedly proved. Moreover the result shows that the $-\text{SO}_3\text{H}$ groups were indeed quantitatively introduced to the composite polymers as expected.

Proton Conductivity

Impedance spectroscopic technique was used to determine the proton conductivity of the prepared blend membranes.²⁶ The proton conduction is mainly due to free sulfonic acid groups. When PES is blended with sPVdF-co-HFP the proton conductivity decreases steadily as shown in Figure 3. This is mainly due to the addition of hydrophobic PES polymer decreases the density of the hydrophilic sulfonic acid group in sPVdF-co-HFP membrane so that the sulfonic acid groups produce isolated ionic clusters in the hydrophobic phase.³⁴ This result has good agreement with WU and IEC studies.

Methanol Permeability

In DMFCs, the most important requirement of PEMs is low methanol permeability. Methanol permeability value corresponds to the capacity of the PEM to arrest methanol fuel; methanol permeability of the sPVdF-co-HFP/PES blend membranes was determined at room temperature and their values were represented in Figure 5. Methanol permeability of the sPVdF-co-HFP/PES blend membranes decreased steadily with increasing the composition of PES in the blend membrane. It may be due to the hydrophobic nature of PES. The presence of hydrophilic sulfonic acid group in pure sPVdF-co-HFP

membrane forms broad channels with hydrophobic PVdF-co-HFP, which increases not only proton conduction but also the methanol permeability. The addition of hydrophobic PES makes the channel narrow and blocks the fuel conduction. Among all the blend membranes, sPVdF-co-HFP/PES10 shows the methanol permeability of $1.22 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$, which is 2.8 times lower than Nafion 117 ($3.41 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$) under similar conditions.³⁰

Thermal Stability

The thermal stability of sPVdF-co-HFP and sPVdF-co-HFP/PES blend membranes was measured by thermogravimetric analysis. From the Figure 6, there are three main stages of weight loss namely dehydration, desulfonation, and decomposition of the polymer backbone. The first weight loss up to 100°C is due to the evaporation of free water molecules. The second weight loss from 200 to 450°C is due to the thermal decomposition of sulfonic acid group. The third stage of weight loss begins around 450°C is due to the decomposition of the polymer backbone.³⁶ That is both pure and blend membranes are stable up to 400°C , which is sufficiently high for common fuel cell application. During the investigation of the thermal stability of the pure and blend PEMs, membranes were kept in an oven under a nitrogen atmosphere at different temperatures. The ion exchange capacity was consequently measured and plotted as a function of the oven temperature. Under these conditions, the IEC value remains constant up to 200°C , but falls intensely thereafter, which confirms desulfonation. Thus results from the thermogravimetric analysis showed that all the fabricated PEMs are stable up to 200°C satisfying the operating temperature ($90\text{--}120^\circ\text{C}$) of direct methanol fuel cells.

Oxidative Stability

The oxidative stability of PEMs is an important factor affecting directly on the operation and durability of DMFCs. Herein, the oxidative stability of the sPVdF-co-HFP and sPVdF-co-HFP/PES blend membranes was investigated using Fenton's reagent and is given in the Table I. Peroxide radicals obtained from the Fenton's reagent split the sulfonic acid group and reduce the

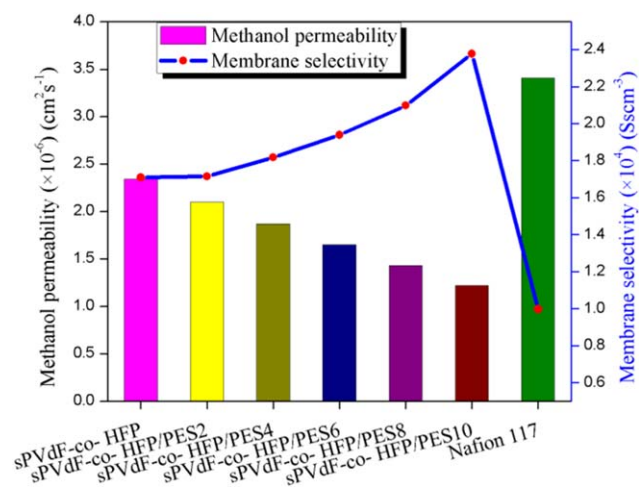


Figure 5. Methanol permeability and membrane selectivity of sPVdF-co-HFP/PES blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

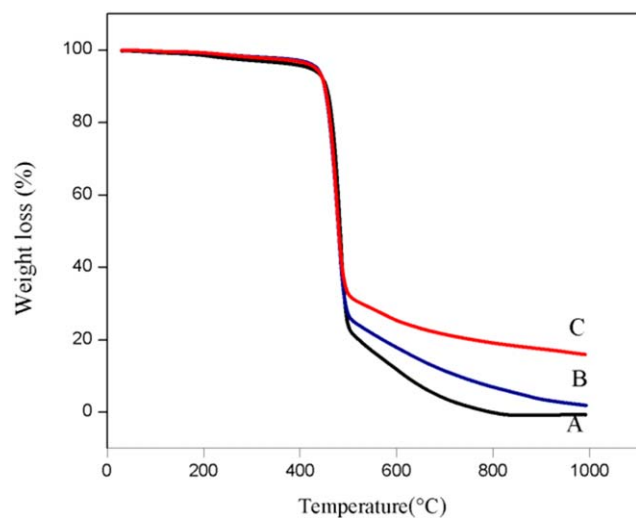


Figure 6. TGA curves of sPVdF-co-HFP (a), sPVdF-co-HFP/PES2 (b), and sPVdF-co-HFP/PES8 blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weight of the polymer chains in the PEM. After the Fenton's test, it was observed from Table I that the increase of PES to sPVdF-co-HFP system increases its weight residue from 95.6 to 99.2%, which showed that the oxidative stability of the blend membrane also raised steadily. The weight loss of sPVdF-co-HFP membrane in 5 h at room temperature was 4.4 wt %, whereas for sPVdF-co-HFP/PES10 was found to be 0.8 wt %.

The high oxidative stability of the sPVdF-co-HFP/PES10 may be due to the hydrophobic nature of PES, which resists the movement of the free radical within the blend membrane during the fuel cell performance.

Morphological Study

Figure 7 shows the three dimensional AFM images of membrane surface for pure sPVdF-co-HFP, low and high composition of PES with sPVdF-co-HFP in the casting solution at a scan size of $1 \times 1 \text{ mm}^2$. The line profile image has pores and nodules, which explains the roughness of the membrane. The roughness parameters were estimated from TM-AFM images on various parts of the same membrane sample and it is reported in Table II. Generally, the roughness parameter of the membranes became smaller with decrease in pore size and nodule size. In truth, when the surface contains pores (deep depressions) and nodules (high peaks), high roughness parameters are expected.³⁷ From Figure 7, sPVdF-co-HFP has cluster like structure with aggregation of nodules and the roughness of the blend membrane decreases on increasing the composition of PES. This is mainly due to the presence of hydrophilic sulfonic acid group increases the roughness parameters and nodule size in sPVdF-co-HFP membrane whereas in the blend membranes the roughness parameter values are decreased due to the hydrophobic nature of PES. Seemingly, the order of roughness variation is as follows:

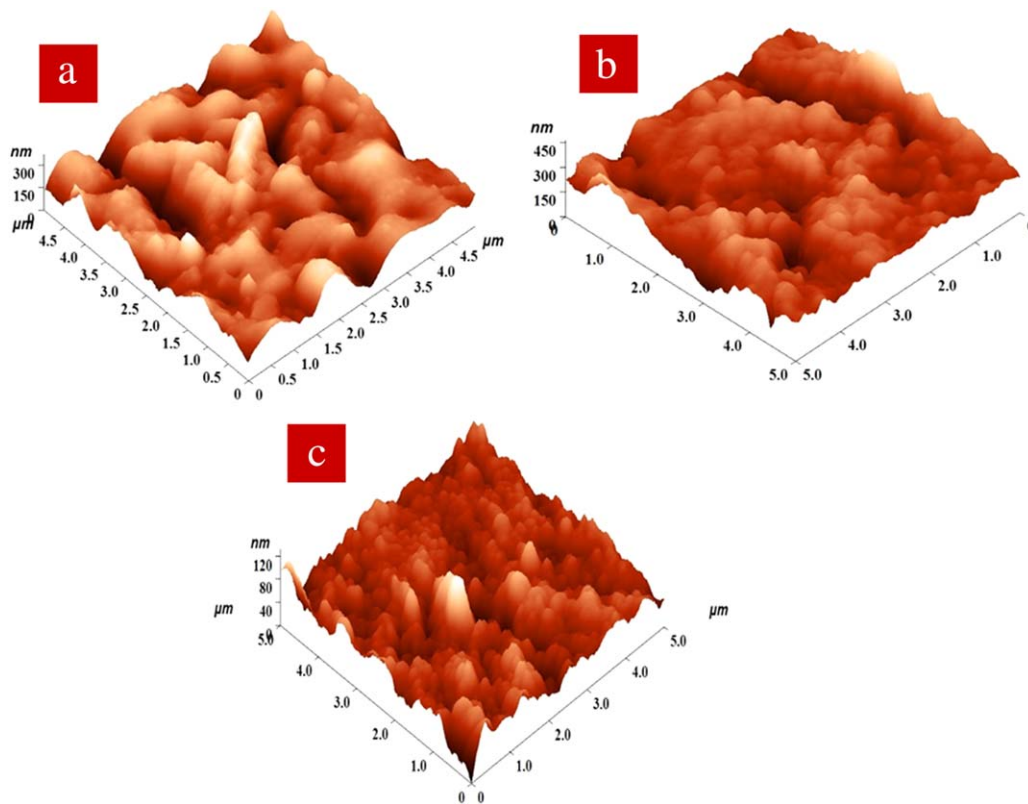


Figure 7. AFM images of sPVdF-co-HFP (a), sPVdF-co-HFP/PES2 (b), and sPVdF-co-HFP/PES8 blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Membrane Roughness Parameter

Membrane code	Roughness parameter		
	S_a (nm)	S_q (nm)	S_z (nm)
sPVdF-co-HFP	42.0	53.7	235.8
sPVdF-co-HFP/PES2	36.0	47.1	186.9
sPVdF-co-HFP/PES8	9.9	13.2	68.7

S_a , the mean roughness; S_q , the root mean square of Z data; S_z , mean height of roughness profile.

$$\begin{aligned} \text{sPVdF-co-HFP} &> \text{sPVdF-co-HFP/PES2} \\ &> \text{sPVdF-co-HFP/PES10} \end{aligned}$$

This trend has good agreement with water uptake study.

Mechanical Stability

Normally, fluoro polymers have greater mechanical stability and outstanding chemical strength. The mechanical integrity of membranes is enhanced owing to the particular interactions, dipole–dipole, ion–dipole, and transfer of protons. Earlier it was reported that in DMFCs, these interactions significantly reduces the methanol cross over.³⁸ The presence of sulfonic acid group imparts the hydrophilic channel, which increases the proton transportation. Moreover, hydrophilic channel increases the swelling nature of the polymer, which causes reduction of mechanical strength.³⁹

To overcome this problem hydrophobic PES polymer was mixed with hydrophilic sPVdF-co-HFP to improve the mechanical stability of the membranes. All the blend membranes revealed outstanding tensile strength ranging from 20.01 to 22.78 MPa. This result confirmed that the PES was blended with sPVdF-co-HFP properly. Moreover, the tensile strength values of pure and blend membranes are higher than that of Nafion-117 (12.79 MPa).⁴⁰ The regular increase in the tensile strength as well as elongation is clearly displayed in the Figure 8. The ratio of ten-

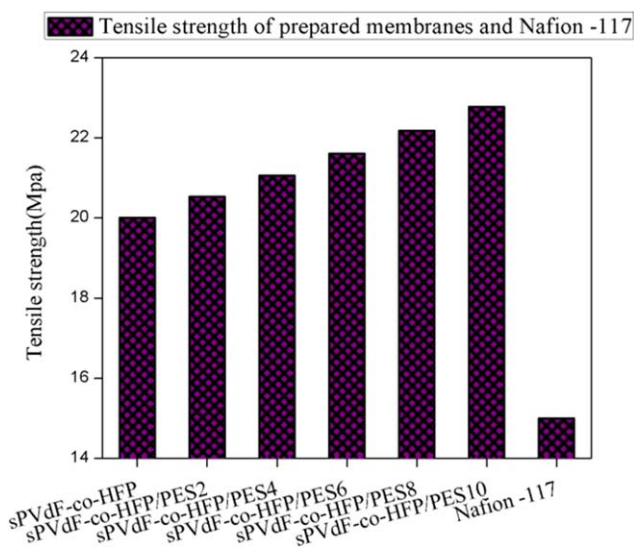


Figure 8. Tensile strength of sPVdF-co-HFP/PES blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sile stress (or compressive stress) to the corresponding strain within the elastic limit is called Young's modulus and its value for all the blend membranes are fairly increasing compared with pristine sPVdF-co-HFP membrane.

Membrane Selectivity

Membrane selectivity (δ) plays a vital role in the performance of membranes. It is defined as the ratio between the proton conductivity (σ) and methanol permeability (τ); as shown in Figure 5, the regular increase in the selectivity value implies that the addition of PES increases the membrane performance and makes the blend membranes as more suitable for PEM in DMFCs. Moreover the δ value of sPVdF-co-HFP/PES10 are $2.377 \times 10^4 \text{ S s cm}^{-3}$, which is 2.4 times greater than Nafion-117 ($0.997 \times 10^4 \text{ S s cm}^{-3}$).³⁰

CONCLUSIONS

Solvent casting method is effectively used to prepare sPVdF-co-HFP/PES blend membranes for DMFCs. Addition of PES to sPVdF-co-HFP increases the hydrophobic nature of the membranes. Thermogravimetric analysis indicates that the blend membranes have greater thermal stability. Determination of ultimate tensile strength, elongation value, and Young's modulus indicates that the composite membranes have improved mechanical property. Surface morphological study of the pure and blend membranes reveals that the surface roughness decreases by increasing the content of PES. FTIR spectral studies show that sPVdF-co-HFP/PES blend membranes consist of both $-\text{SO}_3\text{H}$ group and aryl oxide group. Thus, FTIR and AFM studies confirm that the hydrophobic PES polymer is uniformly blended with hydrophilic sPVdF-co-HFP. Although the water uptake and ion exchange capacity of the blend membranes decreases slightly, the blend membrane having high composition of PES possesses low methanol permeability value of $1.22 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is 2.8 times lower than that of Nafion 117. The overall performance of the blend membrane in terms of selectivity ratio also gradually increases by increasing the content of PES. Low methanol permeability value and moderate proton conductivity, high selectivity ratio implies that the developed sPVdF-co-HFP/PES blend membranes can be considered to be a suitable candidate as PEM especially for DMFC applications.

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