

Synthesis and Properties of Sodium Vinylbenzene Sulfonate-Grafted Poly(vinylidene fluoride) Cation Exchange Membranes for Membrane Capacitive Deionization Process

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Abstract: In this study, a poly(vinylidene fluoride)-*graft*-sodium 4-vinylbenzene sulfonate copolymer (PVDF-*g*-PSVBS) was prepared by grafting sodium 4-vinylbenzene sulfonate (SVBS) onto dehydrofluorinated poly(vinylidene fluoride) (PVDF). The PVDF-*g*-PSVBS cation exchange membranes were prepared using a casting method. The structure of the membranes was investigated with Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Morphology using scanning electron microscope with energy-dispersive X-ray analysis (SEM-EDS) demonstrated as increasing the degree of grafting, the sulfur element is uniformly distributed and increased. The effects annealing temperature on the properties of the PVDF-*g*-PSVBS membranes were investigated. To prepare the consistent and homogeneous membranes, it was suggested that the annealing temperature of PVDF-*g*-PSVBS membranes is below 60 °C. The salt removal efficiency for application to the membrane capacitive deionization (MCDI) process was conducted.

Keywords: PVDF-*g*-PSVBS cation-exchange membrane, annealing temperature, membrane capacitive deionization (MCDI).

Introduction

The availability of clean water is increasing concern because of the increase in water demand caused by the rapid development of industries and population growth. As a result, there is a large interest in the development of economically attractive desalination technologies.¹ Membrane separation technologies, using ion exchange membranes in particular, are very effective in employing to remove ions from water to generate fresh water from sea water and brackish water.^{2,3}

In these applications, ion exchange membranes require high ion selectivity, ion conductivity, as well as, excellent mechanical, thermal, chemical, and dimensional stability. Of these features, ion selectivity is particularly important for pollution management.⁴ Radiation graft polymerization is a common technique used to increase ion selectivity by increasing the degree of sulfonation in membrane. Generally, the amount of water uptake increases with the increase in the degree of grafting in radiation-induced graft ion exchange membranes. This is due to the increase in the number of hydrophilic fixed acid groups. Highly water uptake causes a decrease in the membrane selectivity together with considerable loss in the mechanical strength.^{5,6}

PVDF has emerged as a possible alternative to Nafion in

membranes used in fuel cells and redox batteries due to its mechanical, thermal, and chemical stability, excellent membrane formability. However, PVDF lacks hydrophilicity due to the fluorine content and lack of reactive functional groups. If this drawback is resolved, PVDF could be a more suitable alternative to Nafion.⁷

Modifying the surface of PVDF by irradiation and subsequent graft polymerization of functional monomers is well known technique.^{5,6} It offers many advantages including the ease of preparation, the controllability over the composition and properties of the graft copolymers through optimization of the grafting conditions.⁶⁻⁸ Nasef⁹ have reported the preparation of radiation grafted pore-filled membranes. Also, Flint¹⁰ has represented the electron beam irradiation of PVDF films followed by styrene graft polymerization and sulfonation. However, in the radiation-induced copolymers, it has relatively wide range of the water uptake variation compared to the solution grafting method.

Dutta¹¹ and Farrokhzad¹² have reported sulfonated PVDF membranes that were produced by directly introducing sulfonic acid groups into the main chains using chlorosulfonic acid. The material was brittle due to low mechanical properties and changes in main chain structures. Also, their ion selectivity is lower than that of Nafion membranes because their ion exchange capacity is lower. In particular, the introduced sulfonic acid groups are cross-linked, it affected their material

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property.

The sulfonated monomers such as sodium vinylbenzene sulfonate could be realized by eliminating the sluggish sulfonation that adversely affects the crystalline structure and hence the mechanical strength of PVDF films.¹³⁻¹⁵

Luo,¹⁸ Shen,¹⁹ and Deniz²⁰ have prepared the membranes *via* graft copolymerization from alkaline-treated PVDF. The solution-grafting method is good dimensional stability due to the narrow range of water uptake variation according to the degree of grafting. Also, the grafting of ion conducting structures to fluoropolymer chains brings molecular design flexibility, chemical versatility, precise sulfonation levels and positions, and membrane fabrication convenience.^{16,17}

In this study, the graft copolymerization consisting of sodium vinylbenzene sulfonate (SVBS) and PVDF base matrix was prepared *via* using the radical polymerization method, *i.e.* solution grafting method, after dehydrofluorination of PVDF powder by alkaline treatment. FTIR and Raman spectroscopy were used to provide information about chemical structure of PVDF-*g*-PSVBS membranes. Morphology of the membranes was observed through scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis. We investigate the effects of annealing temperature on the properties of the membranes. The salt removal efficiency for application to the Membrane capacitive deionization (MCDI) process was conducted.

Experimental

Materials. PVDF used in this study is sold under the name of KYNAR®761 (M.W.=400,000) from Arkema Co. The potassium hydroxide was an at least 85% pure first grade reagent manufactured by Samchun Co. and the tetra-*n*-butylammonium bromide (TBAB), which is a phase transition catalyst, was a 99% pure special grade reagent. The monomer sodium 4-vinylbenzene sulfonate (SVBS) was a Sigma-Aldrich product. The solvents *N,N*-dimethylacetamide (DMAc; 99%), dimethyl sulfoxide (DMSO; 99%), methanol, and ethanol were special grade reagents manufactured by Samchun Co. and were used as they were without purification. In addition, the initiator benzoyl peroxide (BPO) used was a product of Junsei Chemical Co.

PVDF Dehydrofluorination. First, 35 g of dried PVDF powder and 2.0 M KOH solution containing 0.05 wt% ethanol, 0.025 mol of TBAB were placed into a 1-L 3-neck flask reactor with an agitator, cooler, and a nitrogen inlet attached, and then the mixture was stirred. Dehydrofluorination reactions were induced at 80 °C with different reaction times at 10, 30,

and 50 min. After the reactions, the products were vacuum filtered, washed multiple times with distilled water, and dried for 24 h in a 60 °C vacuum oven to provide the dehydrofluorinated PVDF.

Synthesis of the PVDF-*g*-PSVBS ion Exchange Solution. As can be seen in Table I, to synthesize the PVDF-*g*-PSVBS copolymers by graft copolymerizing monomers containing sulfonic acid groups on dehydrofluorinated PVDF, 55 mL of a DMSO solvent was put into a 250 mL four-mouth flask, 6 g of dehydrofluorinated PVDF and 90 mg of BPO were put into the solvent, and the mixed solution was stirred at 80 °C after nitrogen substitution. Then, 45 mL of DMSO was added to the solution, SVBS was put into the reactor, and reactions were heated for 12 h at 80 °C. To remove homopolymer and unreacted monomers in the reaction products, the products were immersed in an excess amount of methanol, vacuum filtered, and washed multiple times with distilled water. The reaction products were dried for 24 h in a 60 °C vacuum oven. The synthetic yields and the degree of grafting (D.G) of the PVDF-*g*-PSVBS copolymers were calculated using eqs. (1) and (2).

$$\text{Yield (\%)} = \frac{\text{Wt. of PVDF-}g\text{-PSVBS}}{\text{Wt. of PVDF} + \text{Wt. of SVBS}} \times 100 \quad (1)$$

$$\text{D.G (\%)} = \frac{\text{Wt. of PVDF-}g\text{-PSVBS} - \text{Wt. of PVDF}}{\text{Wt. of PVDF}} \times 100 \quad (2)$$

The Wt. of PVDF-*g*-PSVBS is the weight of PVDF-*g*-PSVBS ion exchanger after being dried for 24 h in a 60 °C vacuum oven, the Wt. of PVDF is the weight of modified PVDF, and the Wt. of SVBS is the weight of the reacted monomer.

Preparation of the PVDF-*g*-PSVBS Membrane. To prepare cation exchange membranes, the synthesized PVDF-*g*-PSVBS was dissolved in DMAc at a 15 wt% concentration. The thickness of the prepared solution was adjusted (150 μm) using a Doctor blade and the solution was cast on an Over Head Projector film (V2000, Printec®) (OHP film) at a rate of 10 mm/s using an Auto film applicator P100 (Lab Q, Korea).

Annealing Condition: The prepared membrane was annealed in a vacuum oven while the annealing temperature was in the 45, 60, and 100 °C. It was annealed for 24 h in the 45 °C, 12 h in the 60 °C and 6 h in the 100 °C observing the membrane. The resultant membrane was immersed in distilled water for three hours and in 1 M sulfuric acid solution for 24 h thereafter to manufacture a protonated cation exchange membrane.

Membrane Characterization.

Structure Identification: To identify changes in the structure of PVDF through the dehydrofluorination reactions and

Table I. Synthesis Conditions of PVDF-*g*-PSVBS Cation Exchanger

Batch No.	MPVDF (g)	SVBS (g)	BPO (mg)	DMSO (mL)	Temp. (°C)	Time (h)
PVS-1	6.0	2.0	90.0	100.0	80	12
PVS-2	6.0	3.0	90.0	100.0	80	12
PVS-3	6.0	6.0	90.0	100.0	80	12

the synthesized PVDF-*g*-PSVBS ion exchanger, FTIR and Raman spectroscopy were used. FTIR spectra were collected on a FTIR spectrometer (IR Prestige-21, manufactured by Shimadzu Co.) with an attenuated total reflectance (ATR) attachment. Measurements made at wave number 4000-600 cm^{-1} , scan number 20, and resolution 4 cm^{-1} . Raman spectra were collected using a Lab RAM HR-800, Near Infrared spectrometer manufactured by Horiba jobin yvon Co. under analysis conditions as follows; 514 nm laser, 10% ND filter Acq. time(s) 5, Accumulation 5, in a range of 500-4000 cm^{-1} .

Water Uptake: To measure the water uptake of the PVDF-*g*-PSVBS membrane, the membrane was cut into 3 cm \times 3 cm pieces, immersed in distilled water for 24 h, and weighed after removing the moisture on the surface. The obtained weight was substituted into eq. (3) to calculate the water uptake of the membrane.

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (3)$$

The W_{dry} is the weight of the dried membrane and the W_{wet} is the weight of the swelled membrane.

Ion Exchange Capacity: To measure the ion exchange capacity (IEC) of the PVDF-*g*-PSVBS membrane, the membrane was immersed in a 1.0 M sulfuric acid solution to substitute functional groups with the protonated form and then immersed in a 1.0 M NaCl solution to substitute protons with Na^+ ions. Thereafter, 3 to 4 drops of phenolphthalein were added. The membrane was titrated with 0.01 M NaOH. Then, the consumed amount of NaOH was substituted into eq. (4) to obtain the ion exchange capacity.

$$\text{ICE (meq/g)} = \frac{V_{\text{NaOH}} - C_{\text{NaOH}}}{W_{\text{dry}}} \times 100 \quad (4)$$

The W_{dry} is the weight of the dried membrane, the V_{NaOH} is the volume of the consumed NaOH, and the C_{NaOH} is the concentration of the consumed NaOH.

Electrical Resistance: To measure the electrical resistance (E.R) of the PVDF-*g*-PSVBS membrane, the membrane was cut into 1.5 cm \times 1.5 cm pieces using an LCR meter (Model 3522-50 from HIOKI Co.). 1.5 cm \times 1.5 cm pieces were immersed in a 0.5 M NaCl solution for 24 h and fixed on a 2-compartment cell. Using a 0.5 M NaCl solution as an electrolyte, the electrical resistance values of the membrane before and after inserting the membrane into the cell were measured. The values were substituted into eq. (5) to obtain the resistance value of the pure membrane.

$$\text{E.R. } (\Omega \cdot \text{cm}^2) = (R_1 - R_2) \cdot A \quad (5)$$

The R_1 is the electrical resistance value of the membrane before being installed into the cell, the R_2 is the electrical resistance value of the membrane after being installed into the cell, and the A is the effective area of the membrane.

Electrical Conductivity: To identify the ion conductivity

of the PVDF-*g*-PSVBS cation exchange membrane, the measured electrical resistance value was substituted into eq. (6) to obtain the electric conductivity.

$$\sigma \text{ (S/cm)} = \frac{L}{\text{E.R} \times A} \quad (6)$$

The E.R represents the electrical resistance (Ω) of the membrane, the A represents the effective area (cm^2) of the membrane, and the L represents the thickness (cm) of the membrane.

SEM Morphology Analysis. To analyze the surface of the membrane, scanning electron microscope measurement was conducted using the PVDF-*g*-PSVBS membrane as a sample. The SEM used in the present study is a JSM-840A which is a product of JEOL Instrument Co. The surface of the membrane was Osmium coated in the ion sputtering method before being measured.

Desalination Experiment. The PVDF-*g*-PSVBS cation exchange membrane was applied to an MCDI cell and changes in the efficiency were checked. Desalination experiments were conducted by applying an electrochemical cell and it was composed of a Nylon spacer, silicon barriers, cation exchange membrane, an anion exchange membrane, a cathode, and an anode. Through a peristaltic pump, NaCl aqueous solution at a concentration of 250 mg/L was applied to the cell at a flow rate of 20 mL/min. A working electrode and a sensor electrode were connected to the anode and a counter electrode and a reference electrode were connected to the cathode. For measurement of the amounts of changes in the concentration while supplying a constant potential of +1.5 V and a constant potential of -1.5 V alternatingly to the electrodes using a Potentiostat (WEIS 500, WonA Tech Corp.), alternating lengths of time were set to 120 and 180 s, respectively. The concentration of NaCl was measured through the TDS (Total dissolved solids) sensor and the results were obtained at intervals of 1 s using a Midi Logger GL220 (Graph-Tech). The obtained salt removal rate (%) as NaCl was calculated using eq. (7).

$$\text{Salt removal rate (\%)} = \frac{C_f - C_p}{C_f} \times 100 \quad (7)$$

The C_f is the initial NaCl concentration of the feed water and the C_p is the NaCl concentration of the diluted feed water.

Results and Discussion

Structure Identification of the PVDF-*g*-PSVBS. As can be seen in Figure 1, after dehydrofluorination reaction, C=C double bonds were formed onto the PVDF backbone. By using the initiator BPO at 80 $^{\circ}\text{C}$, graft copolymerization takes place as a result of formation of free radicals onto the PVDF backbone and it can react with the sodium 4-vinylbenzene sulfonate as monomers.

The PVDF was treated with KOH for different dehydrofluorination reaction time. FTIR and Raman spectroscopy were used to identify the structures. As can be seen in Figure 2,

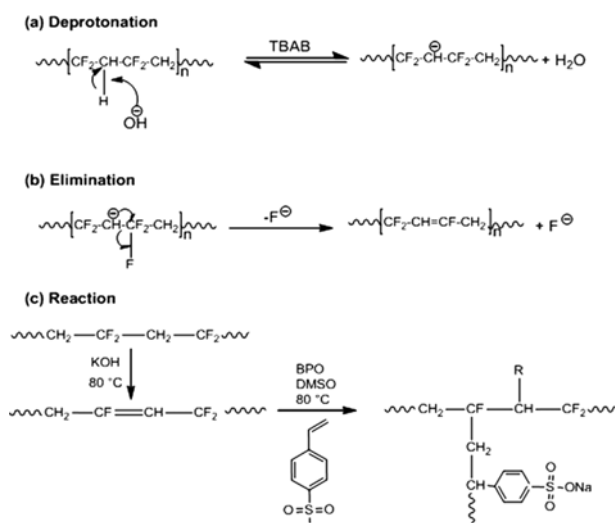


Figure 1. Synthesis scheme of the PVDF-g-PSVBS cation exchanger.

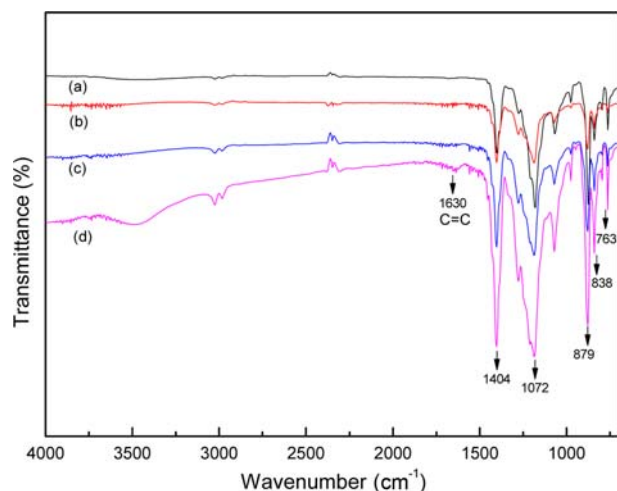


Figure 2. FTIR spectra of PVDF before and after treated with KOH reaction time; (a) PVDF; (b) 10 min; (c) 30 min; and (d) 50 min.

FTIR spectra of the PVDF looked almost identical before and after reaction when the time was not longer than 30 min, indicating that dehydrofluorination reactions did not occur. After 50 min, a new peaks appeared near 1630 cm^{-1} (Figure 2(d)), indicative of the dehydrofluorination reactions have occurred.^{21,22}

In addition, in the raman spectra of PVDF, as dehydrofluorination reactions progressed, when reaction time was longer than 10, 30 min, C=C double bond peaks appeared at 1520 cm^{-1} and C-C peaks was at 1130 cm^{-1} as can be seen in Figure 3. The intensity of the peaks showed a tendency to increase along with reaction time. According to the results conducted by Ross *et al.*, when PVDF was treated with KOH, C-C and C=C stretching vibration peaks appeared at 1125 cm^{-1} and 1520 cm^{-1} , respectively. Given the formation of double bonds in PVDF after KOH treatment, the progression of dehydrofluorination reactions could be confirmed once more.^{7,23}

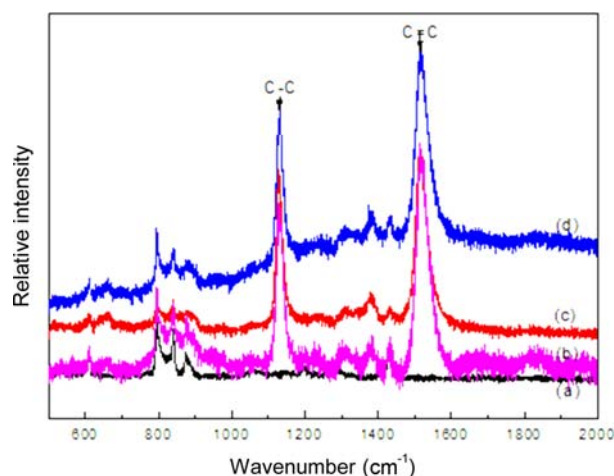


Figure 3. Raman spectra of PVDF before and after treated with KOH reaction time; (a) PVDF; (b) 10 min; (c) 30 min; and (d) 50 min.

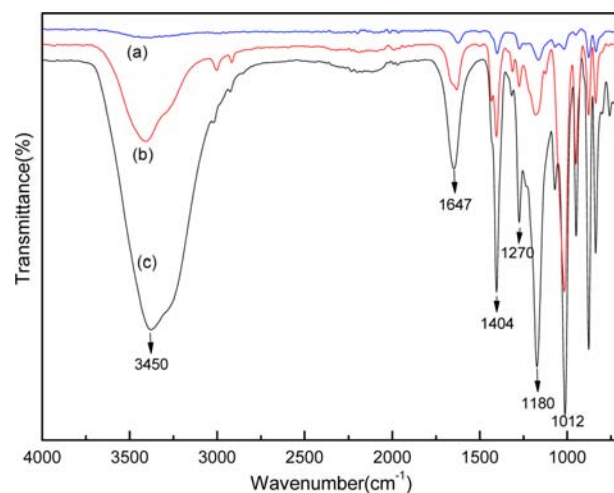


Figure 4. FTIR spectra of the PVDF-g-PSVBS cation membranes; (a) PVS-1; (b) PVS-2; and (c) PVS-3.

Meanwhile, FTIR spectrum analysis was conducted to identify the structure of the synthesized PVDF-g-PSVBS copolymer and the results are shown in Figure 4. Figure 4 is an FTIR spectrum of the PVDF-g-PSVBS ion exchange membrane. Given that OH characteristic peaks appear near 3450 cm^{-1} and O=S=O characteristic peaks of the sulfonic acid group (SO_3H) appear at 1647 cm^{-1} and 1012 cm^{-1} as can be seen in Figure 4, PVDF-g-PSVBS ion exchange membranes were synthesized and these characteristic peaks showed a tendency to increase along with the amount of SVBS monomers.^{10,21}

SEM-EDS Morphology Analysis. The SEM analysis was conducted to identify changes in the morphology of the PVDF-g-PSVBS cation exchange membrane. In order to evaluate sulfur distribution, the energy-dispersive X-ray analysis was conducted at the cross-section of the membrane. As can be seen in Figure 5, the morphology of the surface of the membrane was nearly equivalent implying that the content of SVBS

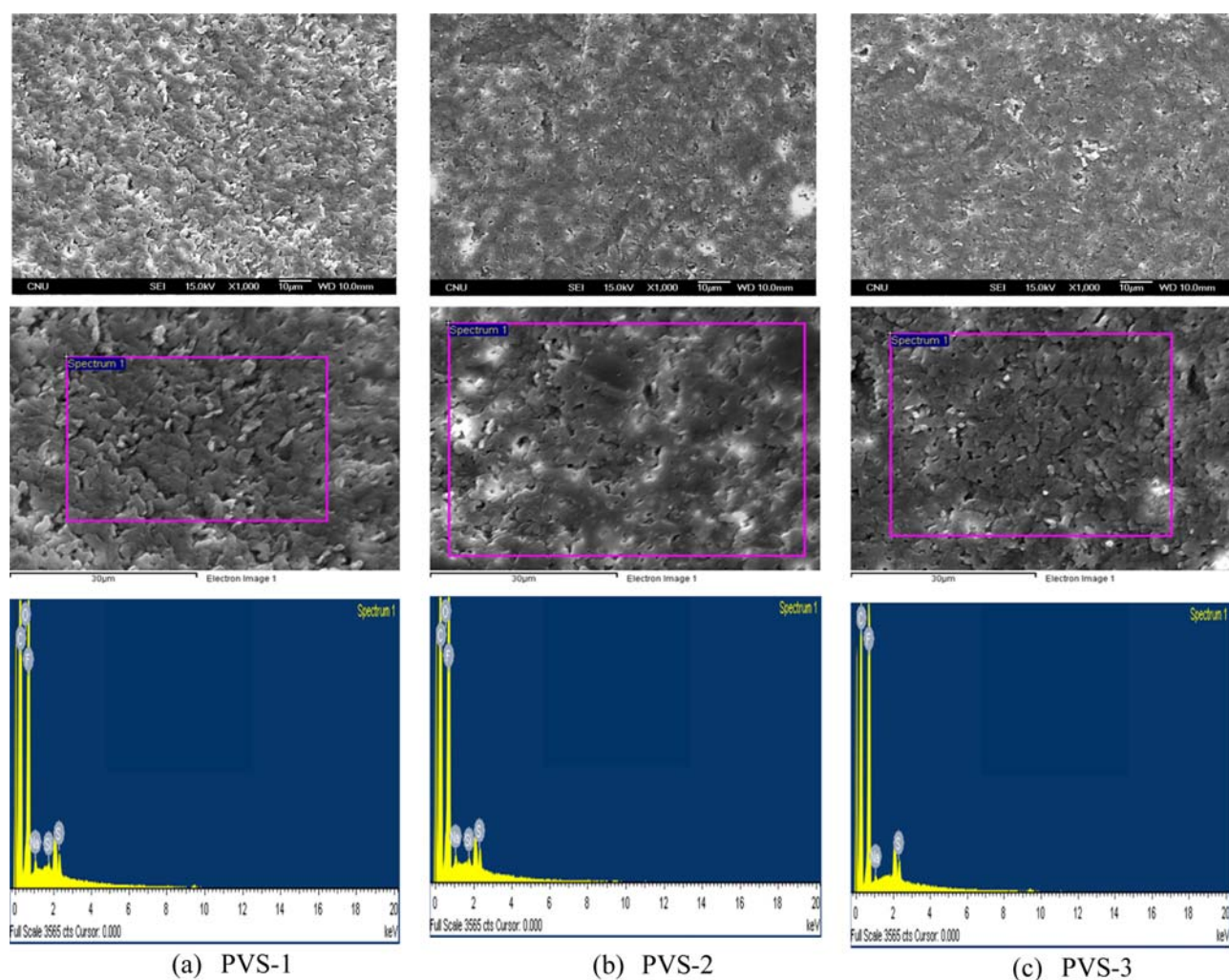


Figure 5. SEM images and EDS spectra of the PVDF-*g*-PSVBS cation exchange membranes; (a) PVS-1; (b) PVS-2; and (c) PVS-3.

Table II. Elemental Analysis of PVDF-*g*-PSVBS Membranes by SEM EDS

Batch No.	Elements (at%)					S/C
	C	F	O	S	Na	
PVS-1	63.3	34.9	1.22	0.37	0.22	0.006
PVS-2	57.3	39.7	1.28	1.46	0.24	0.025
PVS-3	57.7	39.3	1.30	1.70	0.22	0.030

monomers did not affect the physical structure of the membranes. But the surface shape showed a tendency to become smoother as the concentration of SVBS increased. As shown in Table II, the sulfur element is uniformly distributed and increased from 0.37% to 1.70% as increasing the degree of grafting. The increase in the S/C ratio (0.006, 0.025, and 0.030) indicates the increase in the sulfur concentration as a result of sulfonation.

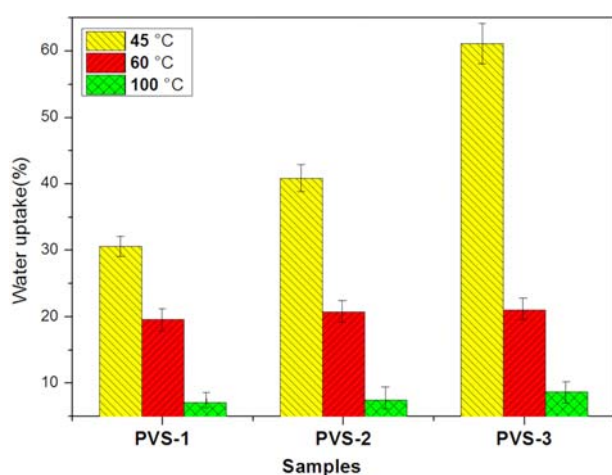
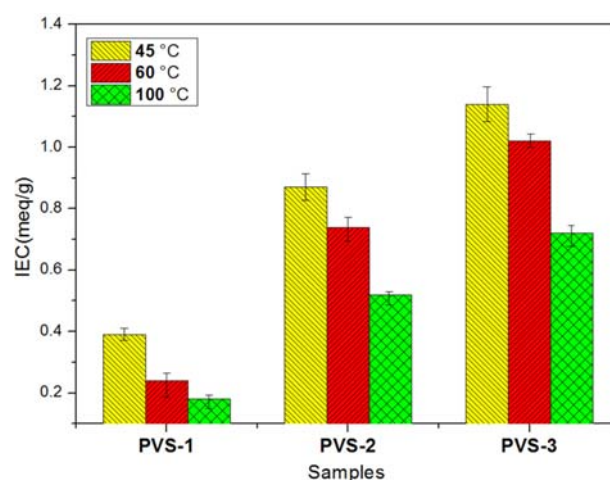
Influence of the Annealing Temperature on the Membrane Properties.

Water Uptake: According to different degree of grafting

and annealing temperatures, changes in the water uptake were measured and the results are in Table III and Figure 6. The water uptake was in the range of 7.14 to 30.6%, 7.52 to 40.9%, and 8.72 to 61.1% with respective to the PVS-1, PVS-2, and PVS-3 and showed a tendency to decrease as annealing temperature increased. It was increased as the degree of grafting increased. The water uptake of the membranes dried higher than at 60 °C was around 20% or lower. This was attributable to the cross-linking of some of the sulfonic acid groups as the annealing temperature increased, leading to a decrease in the number of sulfonic acid groups.²⁴ When DMAc is used

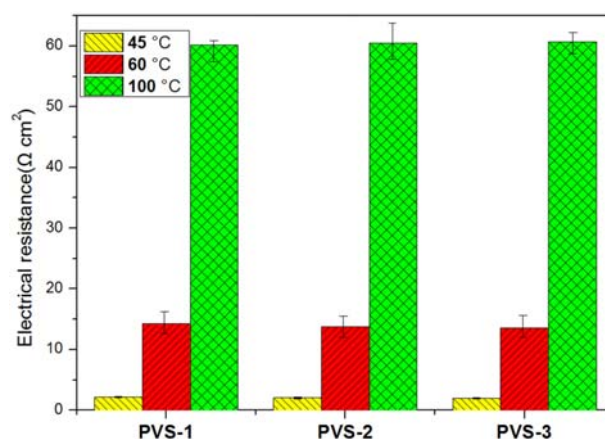
Table III. Characteristics of PVDF-g-PSVBS Cation Exchange Membranes

Batch No.	Annealing Temp.	Yield (%)	Grafting Degree (%)	Water Uptake (%)	IEC (meq/g)	E.R. ($\Omega \cdot \text{cm}^2$)	I.C. ($\text{S} \cdot \text{cm}^{-1}$)
PVS-1	45	85.0	13.3	30.6	0.39	2.13	0.058
	60			19.6	0.24	14.2	0.011
	100			7.14	0.18	60.2	0.006
PVS-2	45	83.3	25.0	40.9	0.87	2.02	0.074
	60			20.7	0.74	13.7	0.015
	100			7.52	0.52	60.5	0.007
PVS-3	45	70.8	34.2	61.1	1.14	1.98	0.076
	60			21.0	1.02	13.6	0.016
	100			8.72	0.72	60.7	0.009

**Figure 6.** Effect of annealing temperature on the water uptake of the PVDF-g-PSVBS membranes.**Figure 7.** Effect of annealing temperature on the ion exchange capacity of the PVDF-g-PSVBS membranes.

as solvent, the sulfonic acid groups of the membrane may react with the solvent, leading to form a hydrogen-bonding complex with sulfonic acid group in above 100 °C. When the membranes are annealed to improve their mechanical properties, the number of sulfonic acid groups decrease due to cross-linking reaction.^{25,26} Therefore, the annealing temperature is the parameter for affecting the sulfonic acid groups and membrane properties.

Ion Exchange Capacity: The IEC at different annealing temperatures were measured and the results are shown in Table III and Figure 7. The IEC was in the range of 0.39 to 0.18 meq/g, 0.87 to 0.52 meq/g, and 1.14 to 0.72 meq/g with respective to the PVS-1, PVS-2, and PVS-3 and showed a tendency to increase as the degree of grafting increased. From SEM-EDS, it was observed that there was an increased the sulfur element. As can be seen in Figure 7, as the annealing temperatures increased the IEC of the PVDF-g-PSVBS decreased. As explained in the results of analysis of water uptake, this was considered the fact that sulfonic acid groups were cross-linked with each other. This is also attributable to the hydro-

**Figure 8.** Effect of annealing temperature on the electrical resistance of the PVDF-g-PSVBS membranes.

gen bonding cross-linking reactions occurring between the solvent DMAc and sulfonic acid groups in above 100 °C leading to decreases in the sulfonic acid groups. And the reaction velocity increased as heat treatment temperatures increased

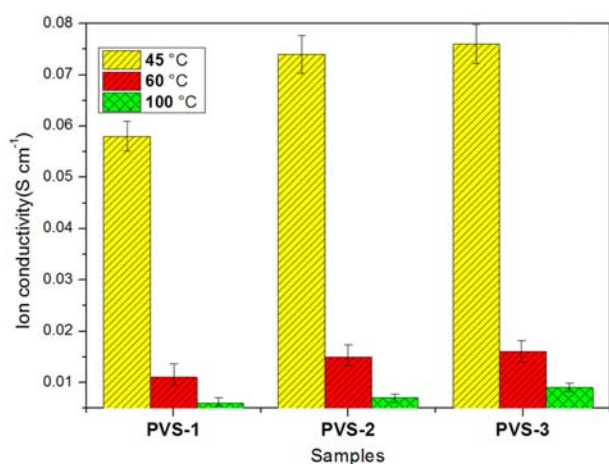


Figure 9. Effect of annealing temperature on the ion conductivity of the PVDF-g-PSVBS membranes.

leading to further decreases in the IEC.^{24,25} Therefore, it was identified that, to maintain the mechanical properties and IEC of the PVDF-g-PSVBS synthesized in this study, it is suggested that the below 60 °C of annealing temperature are appropriate.

Electrical Properties: The E.R. of the PVDF-g-PSVBS was measured and shown in the Table III and Figure 8. The E.R. was in the range of 2.13 to 60.2 $\Omega \cdot \text{cm}^2$, 2.02 to 60.5 $\Omega \cdot \text{cm}^2$, and 1.98 to 60.7 $\Omega \cdot \text{cm}^2$ with respect to the PVS-1, PVS-2, and PVS-3. They showed a tendency to rapidly increase as annealing temperatures increased and the E.R. of the membrane annealed at 100 °C was shown to be very high reaching 60.7 $\Omega \cdot \text{cm}^2$ at the maximum. This was attributable to the fact that, as explained in Figure 6 and Figure 7, E.R. is inversely proportional to the IEC and water uptake. Due to the annealing for improvement of the mechanical properties of the PVDF-g-PSVBS membrane, the introduced sulfonic acid groups were cross-linked with each other as temperatures resulting in rapid increases in the resistance.²⁶⁻²⁸

Table III and Figure 9 show the results of measurement of the ion conductivity of the PVDF-g-PSVBS membranes. The ion conductivity increased as the concentration of SVBS, that is, the concentration of sulfonic acid groups increased. The cross-linked sulfonic acid groups affect the protogenic functions of PVDF-g-PSVBS, reducing the number and/or mobility cations transport. These results show that ion conductivity was dramatically reduced. The electric conductivity of the membranes increased as the concentration of SVBS, that is, the concentration of sulfonic acid groups increased and showed a tendency to be a little lower than that of Nafion 117 membranes.

MCDI Process Application Test for the Membrane. Figure 10 shows the desalination efficiency of the MCDI unit cells was examined with the PVDF-g-PSVBS membranes of the different weight ratio dried at 60 °C. In the initial absorption-desorption cycle experiment, when the voltage of +1.5 V was applied in the PVS-3, the maximum TDS value showed a

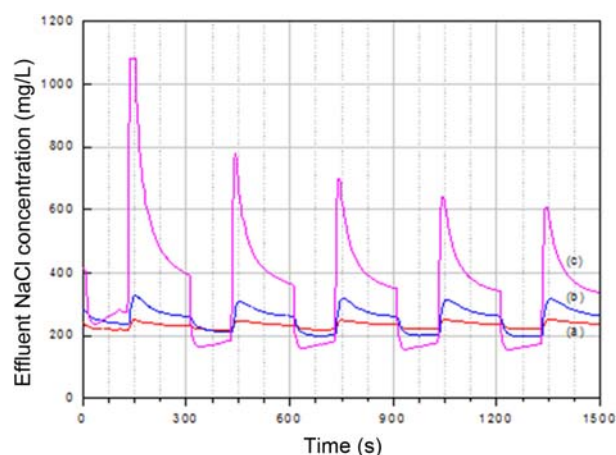


Figure 10. The NaCl concentration transient of effluent measured at a cell potential (a) PVS-1; (b) PVS-2; and (c) PVS-3.

tendency to decrease from 1,083 mg/L to 395 mg/L. In addition, when the voltage of -1.5 V was applied, the TDS value decreased to 145.5 mg/L. The salt removal rate calculated through eq. (7) was shown to be 41.6%. In the PVS-3, the salt removal rate was higher than the other different weight ratio of PVDF-g-PSVBS membranes. It can be seen that the PVS-3 membrane's IEC which closely related to water sorption was the highest. Geise²⁹ have reported that increasing the membrane's IEC (and thus water uptake) cause the water permeability of the membranes to increase. In order to draw the effect of annealing temperature, a more extensive study is needed where PVDF-g-PSVBS membranes with different annealing temperature or properties of membrane are prepared and investigated.

Conclusions

In this study, we synthesized a partially fluorinated PVDF cation exchange membrane. The approach consists of three steps: solution graft copolymerization of SVBS on dehydrofluorinated PVDF powder followed by dissolving, film casting and annealing. It was applied to the MCDI desalination. The conclusions are as follows:

(1) The PVDF dehydrofluorination reaction was confirmed by Raman spectroscopy. In the FTIR spectra, the appearance of absorption bands of PVDF-g-PSVBS copolymers demonstrated the graft polymer structure.

(2) The morphology of the membrane surface in the SEM-EDS suggests that the degree of grafting is from 13.3% to 34.2% and the sulfur element is increased from 0.37% to 1.70%. Because of the increase in the sulfonic acid groups, there was an increase in the IEC and the water uptake. It was observed that there was no substantial change on the structure of the membranes surface.

(3) The annealing temperature is an important parameter for the ion exchange membranes. It is proposed that the annealing temperature of less than 60 °C was appropriate to tune

the water uptake, IEC, electrical and mechanical properties.

(4) The desalination efficiency of the MCDI unit cells was applied to the PVDF-g-PSVBS membranes in the different weight ratio. It can be seen that the increase in the membrane's IEC and water uptake causes the water permeability of the membranes to increase the SVBS. The TDS removal rate of PVDF-g-PSVBS cation exchange membranes in the MCDI process was shown to be 41.6%.

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