

Irradiation-Induced Grafting of Poly(vinylidene fluoride)-graft-Poly(styrene sulfonic acid) for the Preparation of Planar and Tube-Shaped Air-Drying Membranes

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ABSTRACT: A novel air-drying membrane was developed and investigated as an alternative for planar and tube-shaped drying membranes composed of Nafion[®]. The new membrane is based on poly(vinylidene fluoride) (PVDF) polymer types grafted with polystyrene sulfonic acid. Modification of the PVDF membrane by chemical grafting was initiated via γ -irradiation of pre-made film and tube-shaped samples. The grafting was conducted while the pre-irradiated PVDF samples were immersed in styrene monomer solution. Three unique characterization methods were introduced to evaluate the ion exchange and barrier functions of the membrane. This investigation focuses on optimizing the degree of grafting yield, and subsequently the

control of the membrane's overall functional performances, through (1) monitoring the PVDF's degree of crystallinity and (2) monitoring the styrene monomer solution temperature, respectively. Different levels of crystallinity were achieved by melt blending the PVDF-copolymer with PVDF-homopolymer, in various mixing ratios. Another variable examined in this investigation was the introduction of an ionic complex on the sulfonic acid end groups, and its effect on the membrane functional performance was studied. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: radiation graft; sulfonated PVDF; dehydration; pervaporation membrane

INTRODUCTION

Nafion[®], a DuPont registered trademark for perfluorosulfonic-acid/PTFE copolymer, belongs to the class of ion exchange polymers. The Nafion[®] is widely used as a polymer-electrolyte membrane for fuel cells applications. The Nafion[®] is also used as an air-drying membrane for medical systems, specifically, systems used to analyze and monitor patient respiratory. In those monitoring systems, known as capnograph, the Nafion[®] is used as micro-tube geometry to selectively remove moisture from the patient exhaled sample to protect the monitoring system sensor and provide low-moisture content carbon dioxide (CO₂) sample. The Nafion[®] microtube are connected to the patient-system piping lines and pervaporate the patient sample by selectively remove water molecules while keeping the same CO₂ content. Figure 1 illustrate the capnograph system layout and illustrate the roll of the Nafion[®] microtube as a pervaporation membrane. The ability of the Nafion[®] membrane to evaporate water molecules is due to the unique molecular structure of its constituent polymers.^{1–4} The terminal hydrophilic

sulfonic acid allow the polymer to absorb great amount of water molecules through hydration mechanism, then the polymer permits the pervaporation of water molecules by "solution-diffusion" mechanism.^{5,6} This is a basic permeability mechanism based on Fick's law, which indicates that the flux of the water through a membrane depends upon the pressure gradient of the water from both sides of the membrane, and the ability of the membrane to absorb the water molecules through it. As the membrane in question is a nonporous type, manifested by an ion-exchange mechanism, it is termed an "ion-porous" structure,^{3,4} and the instantaneous permeation of CO₂ molecules (or any air-containing molecules) throughout the dense polymer thin walls of the tube membrane, may be completely excluded. The existing commercial Nafion[®] microtube membranes are very expensive due to high material costs and processing complications. Therefore, the need to identify a replacement material is crucial, to create an alternative to the purely commercial Nafion[®] tube membrane. Polyvinylidene fluoride (PVDF)-based copolymers known as an alternative for the Nafion[®] in fuel cell application. This study will examine the feasibility of using the PVDF-based copolymer electrolyte as an alternative pervaporation microtube membrane. The most-studied PVDF electrolyte system is based on PVDF-grafted polystyrene sulfonic acid (PVDF-g-PSSA).^{7–21} This material is

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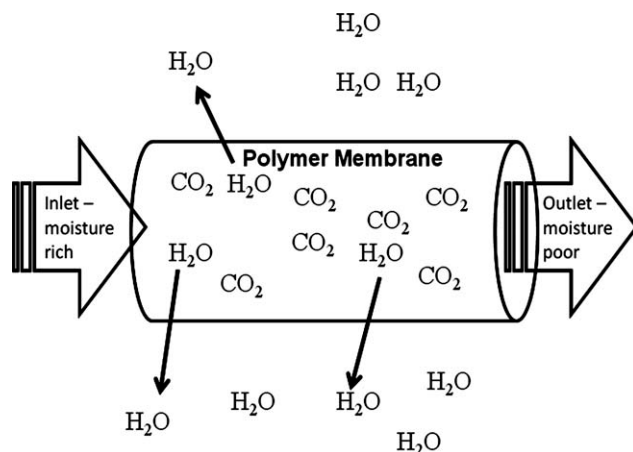


Figure 1 Capnograph system layout.

based on irradiation grafting of styrene onto the PVDF matrix, followed by sulfonation of the styrene sites. In the field of radiation grafting, two major techniques are used: pre-irradiation grafting (PIG) and mutual grafting.^{7,8} The PIG protocol includes the following: (1) irradiation of PVDF raw material to create terminals of free radicals on the polymer chain backbone and (2) successive immersion of the pre-irradiated material in a monomer solution, accompanied by the grafting reaction under controlled temperature conditions. The mutual grafting rationale is practically an *in situ* irradiation grafting of a pre-impregnated system of the main polymer, which already contains the reactive monomer to be grafted. Earlier studies reported⁸ that for PVDF, the technique of PIG with styrene monomer yields better grafting efficiency than the mutual route. Many of the studies performed using PVDF-*g*-PSSA as an alternative for the Nafion[®] membrane were based on chemical grafting of a porous PVDF membrane.^{9–13} The porosity and large surface area of the based polymer enable high absorption of the styrene monomer and therefore ensure relatively high yield of the grafting reaction. This technique is found suitable for fuel cell-membrane polymer electrolyte but might fall short in the case of the air-dryer tube-shaped membrane. The reason for that is the fact that the pervaporation membrane required to maintain high barrier properties against CO₂ molecules. The concern is that porous-based PVDF will interrupt with the selective mechanism of the microtube membrane and affect the CO₂ content of the sample, in the case, the porous were not fully closed due to grafting and sulfonation. This study introduces the pre-irradiation technique that has been used to create PVDF-*g*-PSSA on dense (nonporous) PVDF films and microtubes. The method of grafting polystyrene onto a dense PVDF substrate is mentioned in several data in the published reports.^{13–21} Soresi et al.¹³ even compared grafting of dense PVDF with porous

PVDF. Using a dense polymer matrix preserves the high gas barrier properties, although it modifies the process to achieve a high-degree of grafting (DOG) that is highly complicated. The grafting yield is recognized to be directly concerned with the amorphous phase characteristics of the polymer,¹⁴ indicating that the grafting reaction mostly occurs in the amorphous regions of the matrix polymer to be modified. The higher the degree of crystallinity, the lower will be the yield of grafting. Other parameters that are involved and affect the DOG are the reaction conditions such as: irradiation dose, reaction temperature, and reaction time.^{7,8} Therefore, this study aims at elucidating the effect of crystallinity on the grafting yield of polystyrene on PVDF-dense substrates as films and tubes and measuring the resultant direct effect on the performances of manufactured PVDF-*g*-PSSA membranes, in terms of water pervaporation, CO₂ gas barrier, air leakage, and mechanical properties.

EXPERIMENTAL

Materials

The study was based on two types of PVDF polymers and blend mixtures of both: (1) PVDF-homopolymer, (2) hexafluoropropylene/PVDF-copolymer, and copolymer/homopolymer 50/50 by weight blend, to elucidate the effect of crystallinity on the grafting yield of polystyrene on PVDF dense films and tubes. The materials used were KynarFlex 2801 PVDF-copolymer, supplied by Arkema[®], Dyneon 6012 PVDF-homopolymer, supplied by Dyneon[®]. Styrene monomer 99%, Toluene, 1,2-dichloroethane, and chlorosulfonic acid were supplied from sigma-Aldrich Israel and used as is.

Sample preparation and processing procedures

Film samples, from both PVDF homopolymer and PVDF copolymer, were prepared in compression molding using hydraulic hot press carver. The temperature was set to 230°C and the process carried out under hydraulic pressing pressure of 30,000 psi. The molten film was then cooled down to solid phase in a free-air environment. The planar dimensions of the produced film samples were 75 by 75 mm with a thickness of 110 microns. The microtube-shaped samples were produced in continuous extrusion process, using a 1.75-inch Betol[®] extruder, operated at 230°C melt temperature 10 RPM screw speed and in 15:1 take-off draw down ratio. The cooling water temperature, in the water bath downstream, was 10°C. The dimensions of the produced microtubes were: outer diameter of 2 mm and wall thickness of 0.15 mm.

Grafting procedure

The grafting procedure for the dense PVDF films was performed following these successive stages: the films were first cleaned in ethanol and then sealed in a polyethylene plastic bag and purged with inert nitrogen gas to preserve the radical sites following γ -irradiation, a method mentioned in earlier articles.^{10–13} The films were then radiated at SORVAN RADIATION LTD CO, using ^{60}Co γ -ray irradiation source (ACEL type C-1882) with a total dose amount of 25 kGy. Immediately, after the irradiation process, the treated films (having functional terminals of free radicals) were placed in a low-temperature isolated vessel (at -20°C conditions) to keep the activated sites stable. The grafting process was performed using 1 L glass ball vessel half-filled with the styrene monomer liquid. The grafting was carried out in two different sets of temperatures: 55°C and room temperature (RT), using closed vessel with reflux and under inert nitrogen atmosphere, for 24 h. Following this, the filtrated samples were Soxhlet in toluene for 8 h and then soaked in toluene for another 16 h to clean any residual monomers. Finally, the grafted samples taken out and washed-dried repeatedly, with distilled water, until reach a steady constant weight.

Sulfonation procedure

Sulfonation of the PVDF-g-PS films was carried out by immersing the polymer film in a 0.5-M chlorosulfonic acid solution in 1,2-dichloroethane. Sulfonation occurred at RT for 24 h. The sulfonated samples were then washed with 1,2-dichloroethane, followed by washing with distilled water until constant pH was reached. The reaction procedure, from raw material through grafting and till sulfonation, is illustrated in Figure 2.

Neutralization procedure

Some of the grafted and sulfonated samples were subjected to chemical neutralization of the sulfonic acid groups to form an ionomer. This stage of treatment was performed with 0.5 M KOH water solution at RT for 24 h, after which the membranes were washed again with distilled water.

Table I lists all the different membrane samples (film or microtube) investigated in this study, with the various treatments and conditions applied. The control untreated PVDF copolymer and homopolymer films are identified as FC and FH, respectively. Grafted films that did not undergo sulfonation were also synthesized to characterize the chemical reaction and are identified as X-graft.

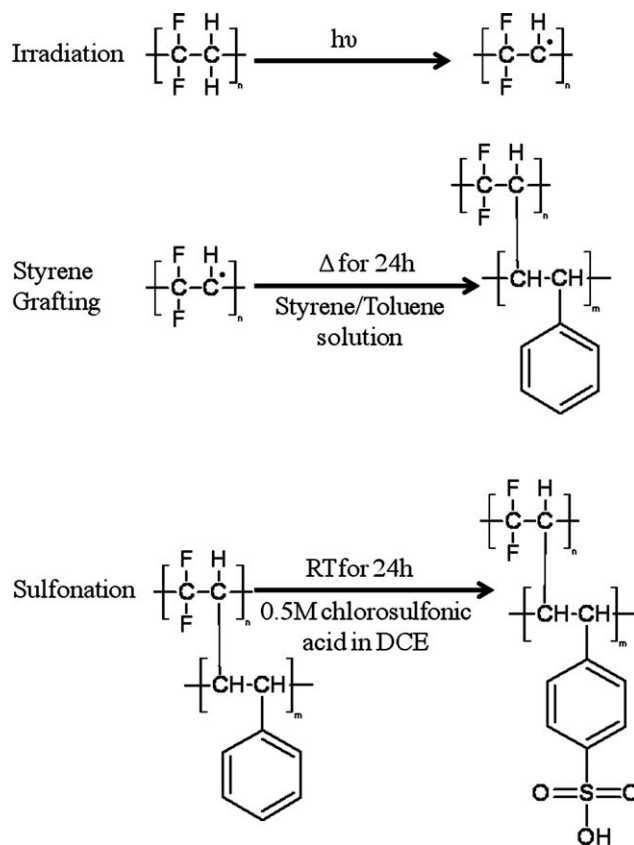


Figure 2 Reaction scheme for the sulfonation and grafting of PVDF-g-PSSA (the scheme is illustrated for PVDF homopolymer, although the same procedure is used for PVDF copolymer).

Chemical and morphological characterizations

All membranes were characterized with BRUKER[®] FTIR spectrometer to track grafting level and sulfonation. Specific peaks for the styrene grafting and the sulfonation substitution were recorded as proof of the chemical reaction. The membranes were also checked with differential scanning calorimeter (DSC) TA Q2000 to estimate the degree of crystallinity. Contact angle (CA) measurements were used to characterize the surface energy of the membrane. The measurements were carried out using a video based CA analyzer (OCA 20, Dataphysics Instruments). The DOG was determined by applying the following equation:

$$\text{DOG} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

Where W_0 indicates membrane weight prior to grafting and W_g refers to weight after grafting.

Light transmittance microscopy images were recorded on Zeiss Axioplan microscope at magnification of $\times 20$. The images were taken from a 50-microns pressed film samples.

TABLE I
Sample Types and Treatment Conditions

Name of specimen	Polymeric system	Membrane type	Grafting temperature (°C)	Neutralization stage
FC	PVDF copolymer	Film	Not grafted	
FH	PVDF homopolymer	Film	Not grafted	
FC-i	PVDF copolymer	Film	Not grafted (only irradiated)	
FC-graft	PVDF copolymer	Film	55	Not sulfonated
FH-graft	PVDF homopolymer	Film	55	Not sulfonated
FC55	PVDF copolymer	Film	55	No
FC55N	PVDF copolymer	Film	55	Yes
TC55N	PVDF copolymer	Microtube	55	Yes
TC55	PVDF copolymer	Microtube	55	No
TC25	PVDF copolymer	Microtube	25	No
TH55	PVDF homopolymer	Microtube	55	No
TCH55	PVDF 50/50 copolymer/ homopolymer	Microtube	55	No
TCH25	PVDF 50/50 copolymer/ homopolymer	Microtube	25	No

Water evaporation characterizations

The water-uptake test (which is the basic test to determine membrane performance) was conducted according to ASTM D-570 and the results were determined by applying the following equation:

$$WU = \frac{W_f - W_i}{W_i} \times 100 \quad (2)$$

Where W_i refers to membrane weight without water and W_f indicates membrane weight at the end of the test.

The evaporation performance of the film-shaped membranes was measured using ASTM E-96 (water vapor transmission test) at 37°C to simulate human breathing atmosphere.

The evaporation performances of the microtube-shaped membrane were measured by two different methods. The first method called the water evaporation test. In this test, the difference in weights is calculated within a period of time for a membrane system and a reservoir PVC tube, which are filled with distilled water. The results are given at microliter per hour and the test performed at RT for 30 min.

The second method, termed the water penetration test, involves a system that simulates a patient's breathing, and is based on air streaming through a 37°C humidifier, which then leads to a water trap via PVC pipes. The membrane is set up in front of the water trap and air flow occurs by pumps and measured by a flow meter. Three measuring lines are seen in this system – one is for a neat PVC pipe (reference), and the other two are for the membrane tubes. The humid air temperature was monitored using a thermocouple. The flow rate was set at a constant value and the test was conducted

for 3 h. The change in weight of the air trap was measured and the results given in microliter per hour.

Air leak test

One of the problems likely to occur in an air sample membrane is the penetration of outside air into the sample. In this study, the CO₂ concentration decreases due to the air penetrating from outside. The air leak test is used to check this phenomenon. The test involves connecting the membrane to a manometer, followed by vacuum application. The negative pressure is read in the manometer followed by noting the change (Δ) after 30 s. The test is conducted under ambient conditions and the results are expressed in microliter per minute.

CO₂ tests

This test designed on the capnography system, examines the ability of the membrane to prevent CO₂ penetration from the surrounding air into the patient's exhalation sample. First, 5% CO₂ gas is sent into the capnograph through a regular PVC pipe, and the capnograph read is recorded. Later, another reading is taken when the membrane is attached to the system. The test result is, in fact, the difference (Δ) between the two successive reads. The test is performed under ambient conditions.

Mechanical tests

Mechanical tests, using INSTRON tensile testing machine, were performed on the film samples. This test was conducted at room temperature, under a cross-head speed of 50 mm/min. All films were cut

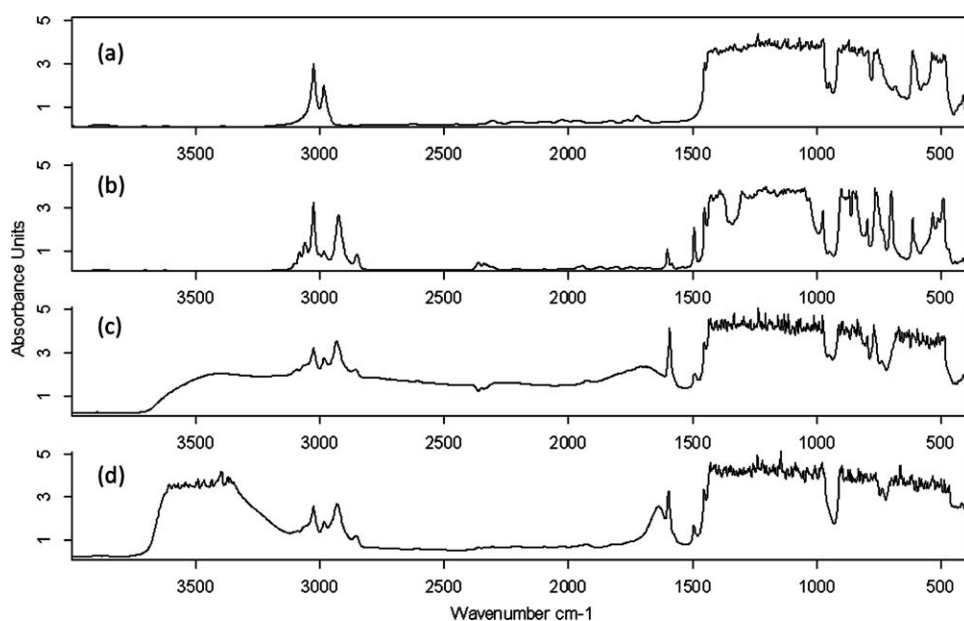


Figure 3 FTIR spectrum for (a) neat PVDF (FC); (b) PVDF-g-PS (FC-graft); (c) PVDF-g-PSSA (FC55); (d) neutralized PVDF-g-PSSA (FC55N).

into samples with planar dimensions of 50 mm length by 6 mm width. The thickness was measured separately for each specimen since the grafting procedure effect the film thickness.

RESULTS

The FTIR results, as seen in Figure 3, show the different chemical changes in the PVDF copolymer, from raw material (FC) through PVDF-g-PS (FC-graft) and finally to neutralized (FC55N) or non-neutralized (FC55) PVDF-g-PSSA. This spectrum is for copolymer-based material. As seen, the peak at 1700 cm^{-1} indicates the substitution of the benzene ring in the Para position, whereas the wide peak at 3500 cm^{-1} is related to the sulfonic acid group. The DOG for the FC55 sample measured to be 33.5% and the water evaporation performances, measured by E-96 apparatus were 858 g/cm^2 day (compared with 7.9 g/cm^2 for the pristine FC film and 15.1 for the FC-graft film).

Figure 4(a-c) shows optical micrographs of pristine PVDF, PS grafted PVDF, and PVDF-g-PSSA (FC, FC-graft, and FC55, respectively). The changes in morphology due to chemical modification are well observed.

The FTIR spectrum in Figure 5 shows no chemical changes in the homopolymer PVDF film (FH55) when compared with the pristine film (FH). Both the FTIR spectra are identical and the FH55 spectra do not exhibit the characteristic substitute benzene ring at 1700 cm^{-1} .

The results of the enthalpies of melting from the DSC thermograph are seen in Figure 6. The enthalpy of melting is regarded as an indication of the degree

of crystallinity. The copolymer of PVDF is lower in crystallinity than the homopolymer. A mixture of the two can be used to vary the degree of crystallinity as seen from the enthalpy of melting of the mixture. The extrusion of tube is also noted to produce material with lower crystallinity than films due to the faster cooling rate in the water.

Table II displays the variety of water evaporation tests for the different tube-shaped membranes including the water uptake test, E-96 test, water penetration, and water evaporation test. In addition, the Table shows the CO_2 barrier test and the air-leak test. The Table displays the dimensional stability of the membranes caused by chemical modification and the change in dimensions resulting from water absorption, phenomena observed in the water uptake, water evaporation, and water penetration tests.

The graphs in Figure 7 reveal the mechanical properties for the different copolymer membrane films: from pristine film (FC) to irradiated film (FC-i), to grafted (FC-graft), then sulfonated (FC55), and finally neutralized (FC55N) film. An analysis is made of the modulus and the yield stress as well as for the strain and energy at break point. As the chemical reaction (i.e., irradiation, grafting of styrene, sulfonation of the benzene ring, etc.) proceeds, the polymer can be observed to be more rigid and less tough. For all of the grafted films, the DOG was 33.5% as already mentioned.

The irradiation process appears to damage the PVDF mechanical properties, lowering its modulus and its elongation suggesting that the radiation is more likely to cause chain degradation rather than cross-linking in the PVDF matrix.⁸

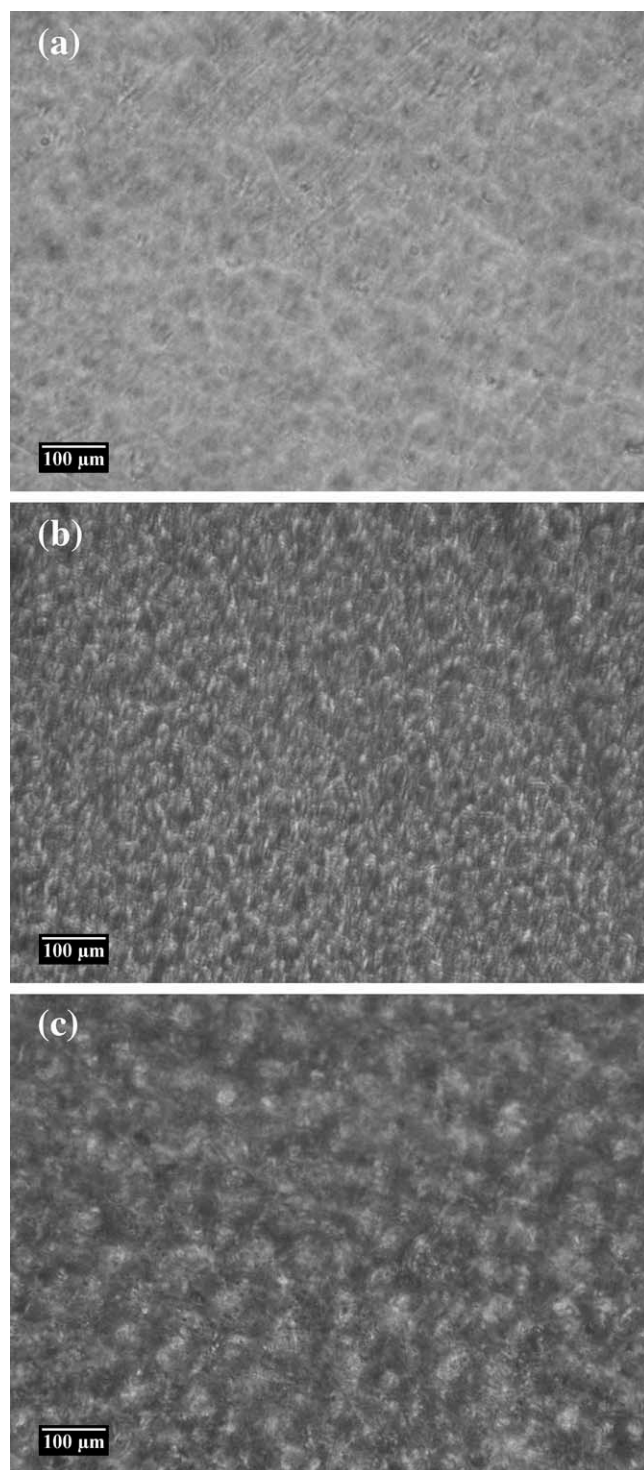


Figure 4 Optical micrographs of different modification stages: (a) pristine PVDF film; (b) PVDF grafted PS film (FCgraft); (c) PVDF-grafted-PSSA film (FC55).

DISCUSSION

Membrane water evaporation performances

The water evaporation properties of the PVDF-g-PSSA membrane can be structured to achieve better performances than that of Nafion[®]. The E-96 test for

the membrane films and the water-evaporation test series show that chemical modification enhances penetration inside the polymer bulk creating a “breakthrough point” that allows the flow of water molecules from outside the membrane to within. This was achieved without damaging the inherent properties of PVDF of blocking the penetration of CO₂ and air molecules. The high barrier and selectivity properties are mainly achieved due to the chemical reaction occurring on the “dense” film/tube, rather than by causing a chemical modification on a porous membrane. The “dense” modification concept also allows the membranes to retain their properties for a long period. The CO₂ barrier test and the air-leak test were also performed while the membranes were performing water evaporation. No changes in the barrier properties were observed although the membranes were soaked in water.

Table II indicates that as the grafting degree increases, more acidic groups can be attached to more benzene groups, thus creating a greater interaction with the water molecules, and therefore leading to better evaporation performances. An increase in the DOG does not damage the membrane’s barrier properties.

Mechanical behavior

As the chemical modification proceeded in which the addition of more chemical group grafts, the polymer becoming more and more brittle as the modulus increases and the elongation at break decreases. This can be explained by the interference of the polystyrene chains in the polymer-chain mobility. Sulfonated membranes are observed to show higher modulus and lower elongation than membranes, which were grafted by only styrene groups. A possible explanation for this is the creation of strong hydrogen bonds between the sulfonic acid groups in the modified polymer. The effect of the hydrogen bonds can be seen in Figure 8, where the DSC thermograph of the PVDF-g-PSSA shows a much wider crystalline region. Of course, no new crystals are created during the sulfonation reaction, which is the only explanation for this effect is the presence of the hydrogen bond complex.

Effect of neutralization

As the Nafion[®] membrane is mostly used in its neutralized form, the initial efforts at creating the membrane involved neutralization of the membrane. However, as the research proceeded further, there was no crucial need to neutralize the grafted polymer into an ionomeric form, because the water permeation mechanism does not necessarily depend on the ion exchange mechanism but rather on the

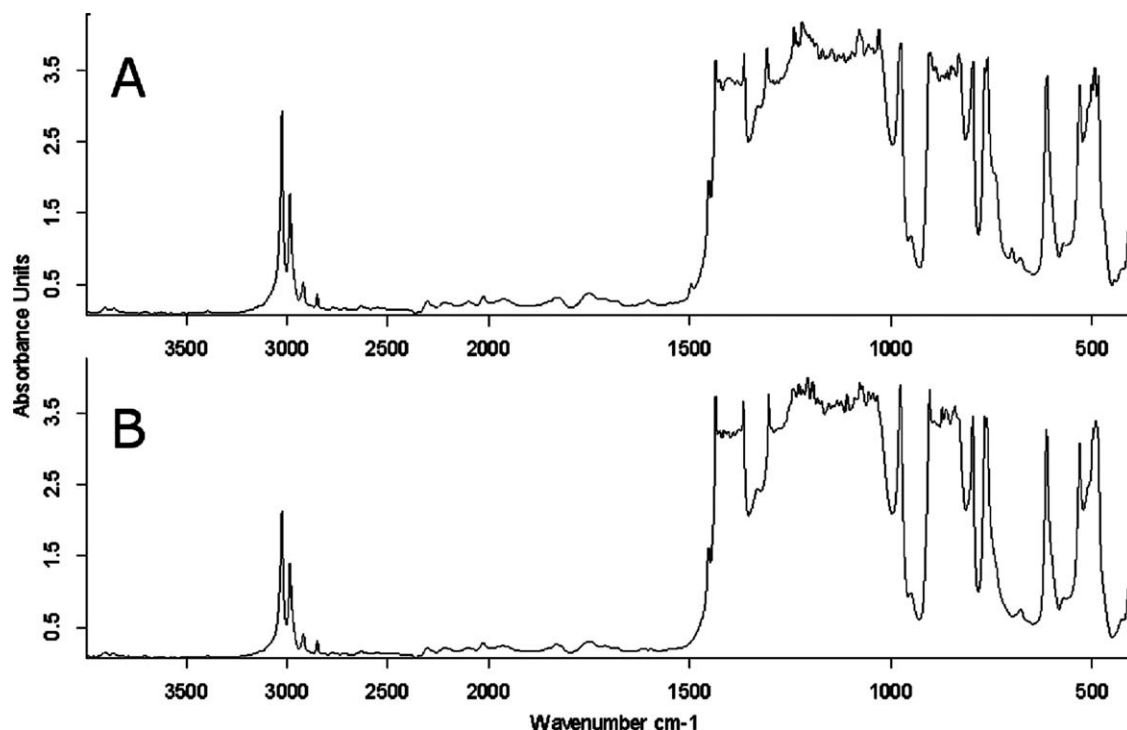


Figure 5 FTIR spectrum for (a) PVDF homopolymer (FH) and (b) PVDF homopolymer that sustained a polystyrene grafting procedure (FH-graft). No change occurs in the spectrum due to the grafting modification.

classic absorption–diffusion mechanism. Although a neutralized membrane has been prepared from both films and microtubes, from Table II, it is evident that the neutralization enhances the higher water evaporation properties (e.g., comparing the results of TC55 with the TC55N membrane), and at the same time, turn the mechanical behavior of the polymer into a brittle one.

This effect can be explained by the polar nature of the ion complex. To study the differences in polarity of the different membrane, a contact angle measurement was used. Pristine PVDF film exhibit contact

angle of 96° , PVDF-g-PSSA (unneutralized) exhibit angle of 80° and sodium neutralized PVDF-g-PSSA membrane has a contact angle of 70° . The neutralized membranes smaller contact angle indicating that the surface energy is higher. This can explain that the interaction of the ion complex with the water molecules is much stronger than the interaction of the sulfonic acid group itself. The higher energy surface of the ion complex probably also increases the energy of the inter-molecular bonds between the polymer chains, making them stiffer, and increases the polymer modulus while decreasing its elongation.

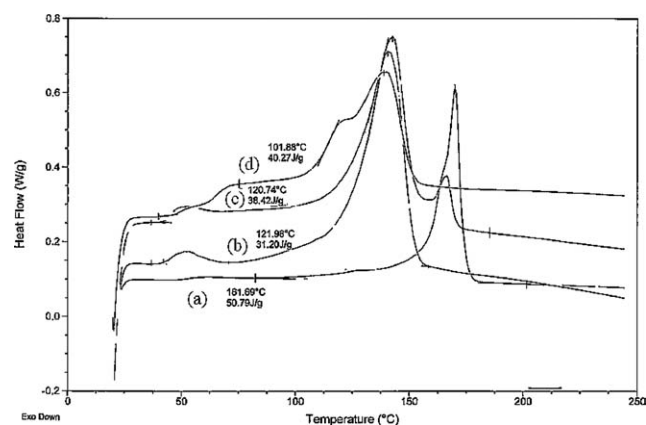


Figure 6 DSC results, including the melt enthalpy, for (a) homopolymer film; (b) copolymer tube; (c) copolymer film and (d) tube from a 50/50 blend of homopolymer and copolymers.

Effect of degree of crystallinity

Grafting modification is shown, beyond doubt to endow the membrane with water evaporation properties. The problem is that the grafting produces side effects that alter other membrane properties. As evident from the results, the higher the DOG, the greater are the changes in dimension. In addition, the dimensional stability of the polymer, under humid conditions, is reduced, causing great changes in the membrane diameter and thickness. The second side effect is that the polymer transforms its behavior from a ductile one (relatively high elongation and low modulus) to a brittle behavior. Both the side effects become more and more extreme with an increase in the DOG. One way to control the DOG is by controlling the degree of crystallinity. As

TABLE II
Sample Performances

Test	PVC	Nafion [®]	TC55	TC55N	TC25	TH55	TCH55	TCH25
Degree of grafting (%)	–	–	132	132	60	30	35	28
Water uptake (%)	–	22	260	395	60	–	–	22
Leak ($\mu\text{L}/\text{min}$)	0	0–10	0–10	0–10	0–10	0–10	0–10	0–10
ΔCO_2	–	1	1	1	1	1	1	1
Water evaporation ($\mu\text{L}/\text{h}$)	–	155	260	352	230	–	155	97
Vapor penetration ($\mu\text{L}/\text{h}$) (the Δ from PVC)	433 (0)	151 (282)	No evidence of water in the trap	No evidence of water in the trap	145 (288)	–	–	194 (239)
Change in thickness due to chemical reaction (%)	–	–	146	146	60	–	45	12.5
Change in diameter due to chemical reaction (%)	–	–	97	97	60	–	37	15
Change in thickness due to evaporation action (%)	–	–	42	42	36	–	25	11
Change in diameter due to evaporation action (%)	–	–	15	15	14	–	13	10

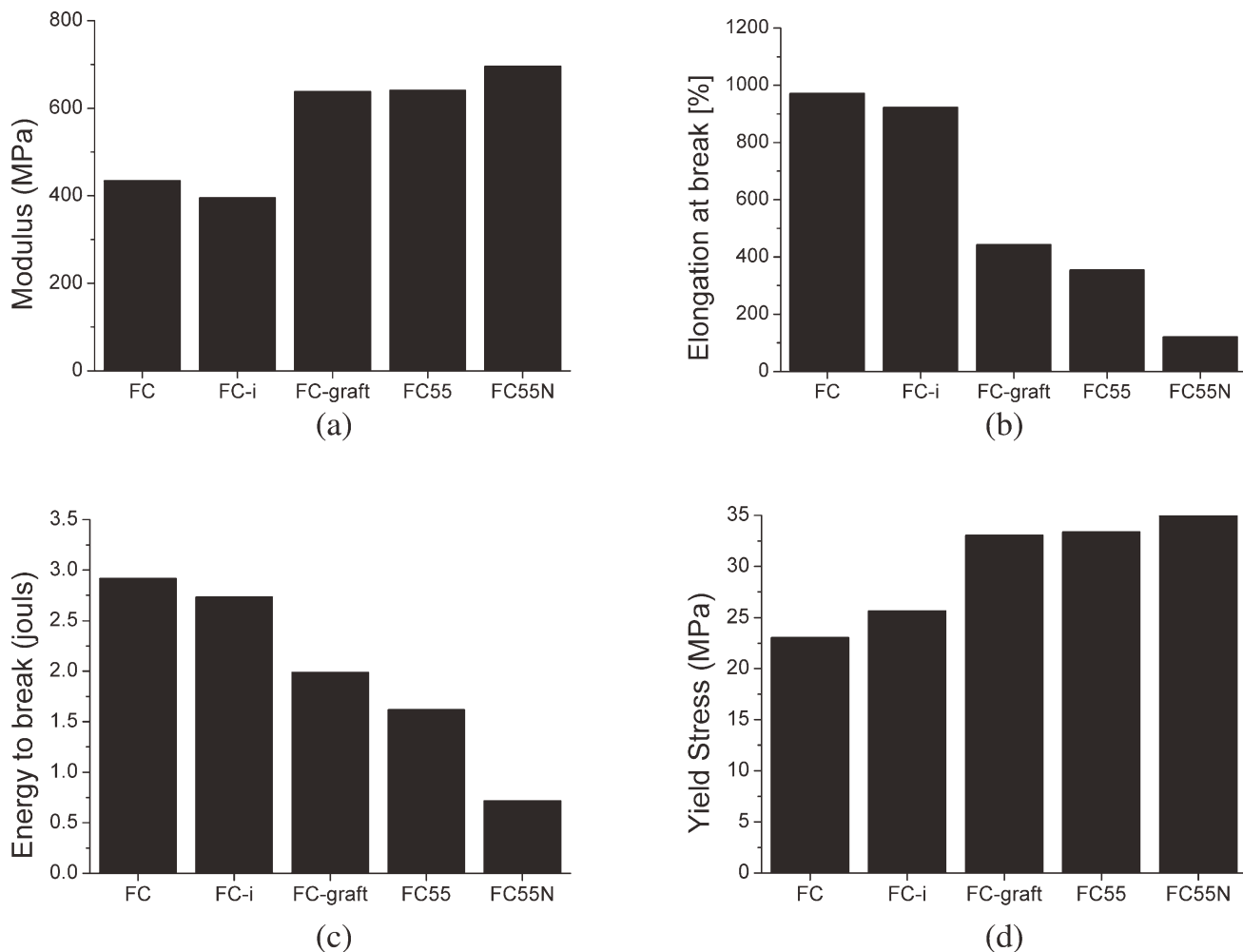


Figure 7 Mechanical performances divided into (A) modulus, (B) break energy, (C) strain at break and (D) yield stress. The results are for neat PVDF copolymer film (FC), irradiated PVDF (FC-i), PVDF-g-PS (FC-graft), PVDF-g-PSSA (FC55) and sodium neutralized PVDF-g-PSSA (FC55N).

seen, tailoring the DOG can be achieved by controlling the cooling rate using a cooling medium (standing air for press samples and water stream for the tubes samples) or by changing the temperature of the medium. The degree of crystalline can also be controlled by material selection, homopolymer for a high degree of crystallization, copolymer for a low degree of crystallization, and a mixture of both homo and copolymers for a medium degree of crystallization. Figure 9 relates the different sample degrees of crystallinity (all modifications are made at same temperature) with the sample DOG as taken from Table II. Evidently, as the degree of crystallinity decreased, the DOG increased because more free volume is available for the chemical reaction to occur.

Performances balance

By calculating the number of sulfonic group chemically bonded onto the grafted benzene rings (by weights data) it can be noticed that the sulfonation yields is relatively high (around 95% of benzene ring present in the each sample were substituted with sulfonic acid). Therefore, the authors can conclude that the critical step in chemical modification of the membrane is obviously the styrene grafting. The polystyrene group has no notable effect of the evaporation performances. They are only used as a platform for the sulfonic acid group to attach onto. However, the polystyrene groups have a negative effect such as increasing the polymer brittleness. The higher the grafting yield, the higher are the water evaporation uptake and evaporation performances. In some grafting percentages, the evaporation properties exceed the Nafion[®] membrane's performances. Unfortunately, the higher the grafting yield, the

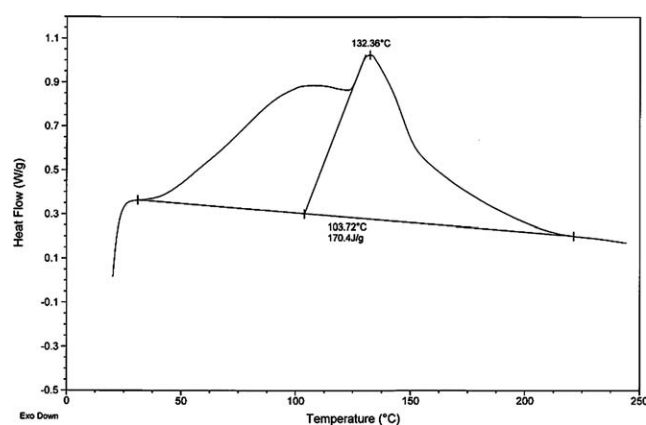


Figure 8 DSC results for PVDF-g-PSSA. The creation of hydrogen bonds due to the acidic group causes an artificial solidification effect which can explain the increase in the modulus.

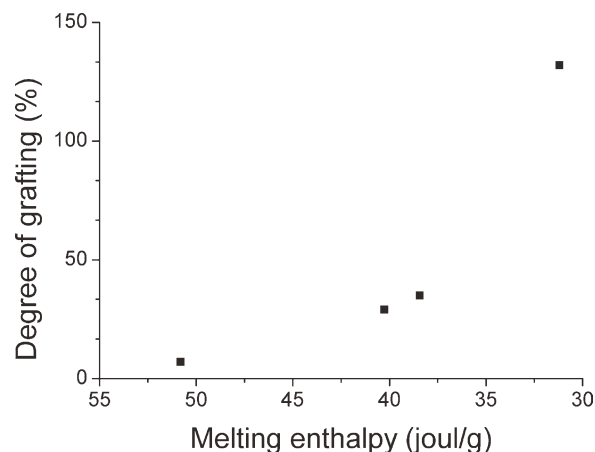


Figure 9 Observed change in the degree of grafting as a function of the degree of crystallinity. The data is based on Tables 1, 2 and Figure 6.

more brittle the membrane becomes and reveals dimensional instability. So in the final product design, a balance had to be struck between the evaporation performances and the mechanical behavior and dimensional stability.

Basically, three major techniques are present to achieve the desired DOG and striking a balance between the performances. The first one is controlling the degree of crystallinity. As the chemical grafting of styrene most often occurs in the amorphous segment of the polymer, then the higher the degree of crystallinity, the lower the DOG. In this article, the authors suggested the necessity to control the degree of crystallinity using a compound of highly crystallized PVDF (homopolymer) with low crystalline PVDF (copolymer) to achieve a different degree of crystallinity. Certainly, this is not the only possible method of doing so. Changing the crystalline kinetic by changing the cooling medium and temperature could be another approach. A second way to alter the graft yield is by changing the reaction temperature. The higher the reaction temperature, the higher the grafting yield is. The third strategy suggested to balance the membrane performances is by neutralizing the acidic groups. Thus, an artificial increase in the DOG can be induced. The ionic complex creates stronger bonds with the water molecules, thus increasing the evaporation properties and decreasing the dimensional stability. It also increases the inter-relationship between each ion complex and the other, thus increasing the polymer brittleness.

CONCLUSION

The authors can conclude this study by stating that a new air-dryer membrane can be created using irradiation grafting by attaching a hydrophilic sulfonic

acid group onto PVDF. The chemical modification conducted on microtube geometry and several test protocols reveals that such tubes can be used as membranes to reduce the humidity of a patient's exhalation. The research also suggests a strategic plan to manufacture tubes and a chemical modification to strike a balance between compete properties such as water evaporation and mechanical toughness. The new membrane was found to be valuable as a replacement for the existing Nafion[®] membrane used in diagnostic of breathing air application.

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