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Partially fluorinated proton exchange membranes based on PVDF–SEBS blends compatibilized with methylmethacrylate block copolymers

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Abstract

This paper reports on a new route to prepare functional polymer blends for fuel cell's proton exchange membrane applications. Polyvinylidene fluoride (PVDF) and styrene-ethylene/butylene-styrene (SEBS) thermoplastic elastomer were melt blended and extruded into films. Interface modification using poly(methylmethacrylate-butylacrylate-methylmethacrylate) block copolymer (MAM), and two grades of poly(styrene-butadiene-methylmethacrylate) block copolymer was used to optimize the blends performance. The films made out of these blends were grafted with sulfonic acid moieties to obtain ionic conductivity leading to semi-fluorinated proton exchange membranes. The effect of varying the nature and concentration of the compatibilizer on the morphology and properties of a 50/50 wt.% PVDF/SEBS blends was investigated. SEM analysis showed that the addition of the block copolymers to the blends affected the morphology significantly and in the best case, that as low as 1 wt.% block copolymer was sufficient to dramatically reduces the segregation scale and improves mechanical properties. The samples were characterized in terms of morphology, microstructure and thermo-mechanical properties and in terms of conductivity, ion exchange capacity (IEC) and water uptake to establish the blends morphology–property relationships. Compatibilized blend membranes showed conductivities up to 3×10^{-2} S cm^{-1} at 100% relative humidity, and an IEC = 1.69 meq g^{-1}. Water swelling decreased for compatibilized blend membranes.

Keywords: Proton exchange membrane; Melt extrusion; PVDF; SEBS; SBM block copolymer; Compatibilization

1. Introduction

Much attention is currently being paid to the study of proton exchange membrane (PEM) due to their application in polymer electrolyte membrane fuel cells (PEMFC). The major requirements for a PEM are high ionic conductivity, good mechanical strength and chemical resistance, and low fuel permeability. Membrane materials are typically phase-segregated materials where a percolated network of a hydrophilic phase can conduct protons while the hydrophobic phase confers the mechanical strength and dimensional stability in the hydrated environment. To date, the most investigated proton exchange membranes are based on perfluorosulfonic acid polymers, often referred to under Dupont tradename Nafion®. These membranes have a PTFE-like backbone and are considered the standard for PEMFC. However, the cost of this material remains very high and its lack of selectivity for methanol reduces drastically its performance in direct methanol cells. In view of this, research efforts are focused on developing more economical alternatives based on partially fluorinated or non-perfluorinated polymer.

Partially fluorinated PEM can be made from synthesis of block copolymers where one of the blocks is a fluoropolymer. Recent publications have shown that it is possible to synthesize poly(arylene ethersulfone-*co*-vinylidene fluoride) block copolymer by polycondensation of α,ω-dihydroxy poly(arylene ether sulfone) precursors and α,ω-dibromo polyvinylidene fluoride [1,2]. Proton exchange membranes are produced by sulfonation of resulting block copolymer and casting from solution. Radiation grafting of reactive groups on perfluorinated base polymer is extensively used to produce partially fluorinated proton exchange membranes. Recently, γ-ray or electron beam irradiation was used to graft styrene onto poly(vinylidene fluoride) (PVDF) and poly(ethylene-tetrafluoroethylene), and subsequently sulfonating styrene resulting in proton conducting materials [3–7]. Buchi et al. [3] have reported that partially fluorinated PEMs based on grafted polystyrene systems have

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physical and electrochemical properties superior than Nafion® but an inferior performance in a H_2/O_2 fuel cells. They attributed this loss of performance to the excessive gas permeability of membranes that allow radical attack on the polystyrene grafts. Other research works, have demonstrated that sulfonated partially fluorinated PEMs based on styrene-grafted membranes have similar or higher performance in direct methanol fuel cells (DMFC) [4,8].

The approach presented in this paper is based on melt blending of thermoplastic polymers. Polymer blending allows combining the intrinsic properties of each component and is potentially a cost-effective route to achieve partially fluorinated PEMs. It could present a few key advantages over current solvent-cast or radiation-grafted membranes such as a lower-cost as well as a solvent free approach to large-scale membrane fabrication. Furthermore, the degree of crystallinity reached for extruded fluoropolymers is greater than in the solvent-cast form leading to improved mechanical strength and durability of polymer membranes.

Most polymer blends are immiscible due to thermodynamic considerations. The properties of these blends are to a large extent determined by the blend morphology, which in turn depends on the processing history and on the interfacial properties. Interfacial modification is a key step to get finely dispersed and homogeneous blends and to insure the solid-state adhesion between the blend components. Compatibilization usually involves a third component that reduces the interfacial tension in the melt-state. This third component is ideally a block copolymer in which each of the blocks is entirely miscible in one of the blend components as this improves the solid-state adhesion between the blend components. In this paper, melt blending of polyvinylidene fluoride (PVDF) and styrene-(ethylene-butylene)-styrene block copolymer (SEBS) is examined as a potential route toward phase-segregated materials suitable for proton exchange membrane applications. PVDF, a semi-crystalline and chemically resistant polymer, is well suited to the fuel cells environment [9,10]. SEBS is a phase-segregated thermoplastic elastomer (TPE) in which the styrene blocks can be selectively functionalized offering high ionic conductivity [11–17]. In a previous study [18], partially fluorinated membranes based on SEBS and PVDF blends have been produced by extrusion in the melt state and films produced by calendaring technology. The phase-segregated materials exhibited relatively good mechanical properties. Proton conductivity was obtained by successfully grafting sulfonic acid groups on the styrene blocks of SEBS. The reported conductivities were in an acceptable range for proton exchange membranes applications, and were varied through changes in blend composition and sulfonation conditions. Compatibilization of a SEBS/PVDF blend was reported with the use of a triblock copolymer of methylmethacrylate-butylacrylate-methylmethacrylate (MAM) [18]. It was shown that the incorporation of concentration as low as 1 wt.% decreases the segregation scale leading to higher mechanical properties; and improved electrochemical properties. The compatibilization effect was provided by the well-known miscibility of acrylic blocks into PVDF [19–21], and the low interfacial tension between the butylacrylate blocks and the ethylene-butylene block of the SEBS.

There is a significant interaction between the required properties of proton-conducting membranes and the type of materials, method of fabrication, degree of sulfonation, phase separation into hydrophobic–hydrophilic domains, etc. For example, higher levels of sulfonation typically lead to higher conductivity, but also has the undesirable effect to increase the swelling of membrane in humid environment [22]. A number of considerations must therefore be taken into account to balance these conflicting requirements.

In this work, a new type of block copolymer made of styrene; butadiene and methyl methacrylate blocks will be investigated. The presence of the polystyrene block is expected to improve the blend compatibility through increased interaction with the SEBS material. The objective of the present work is therefore to study the effect of compatibilization of different block copolymers on the morphology and properties of semi-fluorinated blend films. Further attention has been dedicated to the investigation of the membranes properties after functionalization to prepare ion exchange membranes.

2. Experimental

2.1. Materials

Polymers used were polyvinylidene fluoride (PVDF) and styrene-(ethylene-butylene)-styrene triblock copolymer (SEBS). The PVDF grade was Solef 1010 supplied by Solvay with Mw = 77,000. The SEBS grade, G1652 supplied by Kraton Polymers contained 30 wt.% styrene and has an average molecular weight Mw = 125,000. The compatibilizers used are three experimental block copolymers supplied by Arkema Research, MAM a triblock copolymer of methylmethacrylate-butylacrylate-methylmethacrylate, and two grades of SBM, a triblock copolymer of styrene-butadiene-methylmethacrylate. The first one, SBM55 has a mass composition comprising 20% styrene, 25% butadiene and 55% methylmethacrylate (Mn PS = 11,000). The second one, SBM20, has higher styrene and butadiene contents with composition 35% styrene, 45% butadiene and 20% methylmethacrylate (Mn PS = 27,000). The content of copolymers used as compatibilizers in the blends was in the range of 1–5 wt.%. Chlorosulfonic acid, dichloroethane (DCE), dimethylacetamide (DMAc), methanol, sodium chloride, sodium hydroxide and phenolphthalein were purchased from Aldrich and used as received.

2.2. Membrane fabrication

Membranes were prepared in a three-step process. First, 50/50 wt.% PVDF/SEBS blends, were compounded on a 30 mm W&P co-rotating twin-screw extruder operated at a barrel temperature of 230 °C, a throughput of 5 kg/h and a screw speed of 150 rpm, using concentrations of block copolymers in the range of 0–5 wt.%. The studied compositions are listed in Table 1. The extruded strands were quenched in water, cut into granules and dried 24 h in an oven at 80 °C prior to film extrusion-calendaring. The films were extruded in a second step on a Randcastle laboratory cast film extrusion line at 230 °C and 100 rpm. The rolls'

Table 1
Samples composition

Sample	PVDF (wt.%)	SEBS (wt.%)	MAM (wt.%)	SBM20 (wt.%)	SBM55 (wt.%)
PVDF	100	–	–	–	–
M-01	50	50	–	–	–
M-11	49.5	49.5	1	–	–
M-12	47.5	47.5	5	–	–
M-21	49.5	49.5	–	1	–
M-22	48.5	48.5	–	3	–
M-23	47.5	47.5	–	5	–
M-31	49.5	49.5	–	–	1
M-32	48.5	48.5	–	–	3
M-34	47.5	47.5	–	–	5

temperature and speed were set to 70 °C and 0.5 cm min^{-1}, respectively, to achieve 150–200 μm thick films. The third step was the film functionalization using chlorosulfonic acid according to the procedure described previously in reference [18] to obtain proton exchange membranes. Sulfonation time was varied to obtain proton exchange membranes with different ionic exchange capacities.

2.3. Composite membranes characterization

SEM and AFM were used for morphology analysis. For SEM, strands extruded by the twin-screw extrusion process were microtomed perpendicular to the extrusion direction, and PVDF was extracted using DMAc as solvent. Scanning electron microscopy (SEM) was carried out on the platinum-sputtered surfaces at a 1 kV acceleration voltage. Dispersed-phase size and size distribution were determined using the image analysis program Sigma Scan Pro 5.0. From the droplet size distribution, the number-average diameter D_n, and the volume-average diameter D_v were calculated using the following equations:

$$D_n = \frac{\sum n_i D_i}{\sum n_1} \quad (1)$$

$$D_v = \frac{\sum n_i D_i^4}{\sum n_1 D_i^3} \quad (2)$$

where n_i is the number of droplets with diameter D_i. The polydispersity of the droplet diameter was calculated as the ratio D_v/D_n.

For AFM analysis, samples were microtomed at −100 °C and examined without further treatment. Tapping mode was used at 300 KHz frequency and good contrast was found between PVDF and SEBS as these materials exhibit very different surface properties. Differential scanning calorimetry (DSC) was used to determine the thermal transitions of the blends. Samples were first cooled to −90 °C, and scanned from −90 to 250 °C to determine glass transition and melting temperatures, and from 250 to −90 °C to determine the crystallization temperature. The heating/cooling rate used was 20 °C/min. The crystallinity of PVDF in the samples was determined from the area under the melting peak, assuming a heat of fusion of $\Delta H_m^\circ = 104.5$ J/g for PVDF [23]. The tensile mechanical properties of films were measured according to standard ASTM D882. The test specimens consisted of strips 19 mm wide and 150 mm long. The gage length used was 50 mm. The samples were drawn at 500 mm min^{-1}. Each reported value is the average of five measurements.

Once the polymer films were functionalized with chlorosulfonic acid, their electrochemical properties were measured. First, ionic exchange capacity (IEC) was determined by equilibrating the membranes for at least 24 h in NaCl (0.2 M) at room temperature with occasional agitation. Aliquots of exchanged solutions were then titrated with NaOH (0.005 M) to the phenolphthalein end point. The procedure was carried out in triplicate and the results averaged. For water uptake determination, the samples were equilibrated in water at room temperature. They were then removed from the water container, quickly dry-wiped and immediately weighed. Subsequently, they were dried to weight constancy under vacuum at room temperature and again weighed. The water uptake ϕ_w or swelling is defined as the mass of water absorbed by the membrane divided by the dry weight [24], according to the following equation:

$$\phi_w = \frac{m_{wet} - m_{dry}}{m_{dry}} 100 \quad (3)$$

where m_{wet} is the weight of the water swollen membrane. The dry weight m_{dry} is calculated from the weight of the vacuum dried membrane. Three repeat measurements were carried out for each membrane. The hydration number λ of the membrane is defined as the number of water molecules per sulfonic acid site. It is calculated from the ion exchange capacity IEC and the swelling ϕ_w according to the following equation, with $M(H_2O) = 18$ g/mol:

$$\lambda = \frac{n(H_2O)}{n(SO_3H)} = \frac{\phi_w}{IEC} \frac{1}{M(H_2O)} \quad (4)$$

Electrochemical impedance spectroscopy (EIS) was used to measure ionic-conductivity of the membrane at ambient temperature and 100% relative humidity (RH). The impedance spectra were measured with an HP4192A impedance analyzer. For transverse resistivity measurements, samples were sandwiched between blocking electrodes, and measured in deionized water (to simulate 100% RH). Scans were carried out in the 50 kHz–13 MHz frequency range with a 0.1 V applied AC signal. A Nafion112® sample was measured as a reference before each series of measurements. As commonly accepted, the resistivity of a membrane was evaluated from the high frequency part of the Nyquist plot that coincides with the bulk resistance of the polymer. Ionic conductivity of the samples can be calculated by the following equation:

$$\rho = \frac{1}{R_b} \frac{d}{S} \quad (5)$$

where ρ is the conductivity (Ω^{-1} cm^{-1}), d the distance between electrodes (cm), S the area electrodes contacting with the polymer film (cm^2), and R_b the bulk resistance calculated from Nyquist plots (Ω).

3. Results and discussion

The results of this work can be separated into three sections. The first two will be dedicated, respectively, to the blend structure and mechanical properties prior to the material functionalization through solid-state sulfonation. The third section will focus on the functional properties most relevant to membrane applications. The blend morphology and crystalline structure described in the first section are not expected to be modified by the solid-state sulfonation and can be put in direct relation with the membrane functional properties. This is not the case for the membrane mechanical properties, which will clearly be modified by the sulfonation and subsequent hydration of the membrane. However, the mechanical results prior to sulfonation give important indications on the material homogeneity and isotropy and can be used as a preliminary assessment for the membrane mechanical performance.

3.1. Morphological and thermal analysis

For the membrane application, a continuous network of a proton-conducting phase within the material is essential. In the current system, the SEBS material must therefore form the matrix while the PVDF must form the dispersed phase or in the limiting case could form a co-continuous network. The shape of dispersed PVDF phase is expected to play a critical role on the mechanical integrity and hydro-mechanical stability of the films, which in turn will have a significant impact on the functional properties of the membrane. Formation of elongated PVDF fibrils during the extrusion process for example could provide higher rigidity than a nodular dispersion and could lead to anisotropy due to a preferential stretching in the extrusion direction.

In the first part of this study, we examine the effect of different methylmethacrylate (MMA) based block copolymers on the PVDF/SEBS blend morphology. For all the samples studied, 50 wt.% PVDF content was used which corresponds on a volume basis to 34 vol.%. Since the viscosity of PVDF and SEBS are relatively well matched at the processing deformation rates, it is expected that PVDF will be the dispersed phase. Fig. 1 presents scanning electron micrographs (SEM) obtained after PVDF extraction using DMAc as solvent. For the unmodified blend (Fig. 1a), a very coarse morphology with irregular and large size domains is obtained. The phase size is reduced significantly with all block copolymers. By far, the most effective copolymer in terms of size reduction is the SBM55, which contains the highest MMA level. This clearly indicates that the studied block copolymers are decreasing the interfacial tension between PVDF and SEBS in the blend.

Fig. 2 presents the effect of SBM block copolymer concentration on the blends morphology. For SBM55, a dispersed phase size reduction was observed when concentration was increased from 1 to 3 wt.%, but the morphology remained unchanged for higher concentrations. For SBM20, the domain size continued to decrease when the concentration was increased up to 5 wt.%. (Fig. 3), indicating that higher concentration may be necessary for complete interfacial coverage. For the MAM copolymer (not presented in the figure), no significant changes in phase size were noticed when concentration was increased from 1 to 5 wt.%.

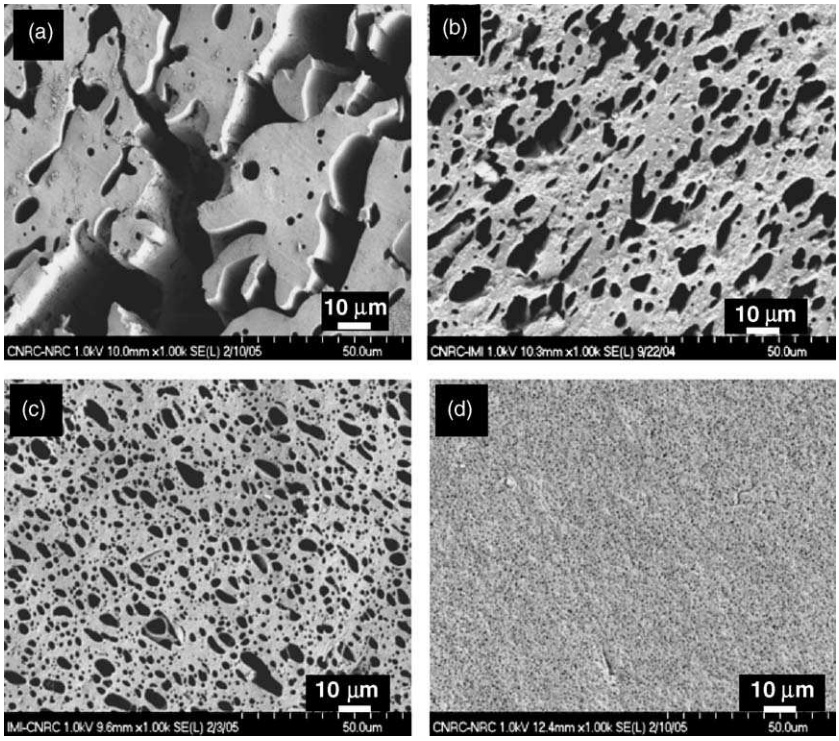

Fig. 1. SEM micrographs on microtomed strands of SEBS/PVDF (50:50 wt.%) blends, after PVDF extraction (a) without compatibilizer, (b) with 1 wt.% MAM, (c) 1 wt.% SBM20 and (d) 1 wt.% SBM55.

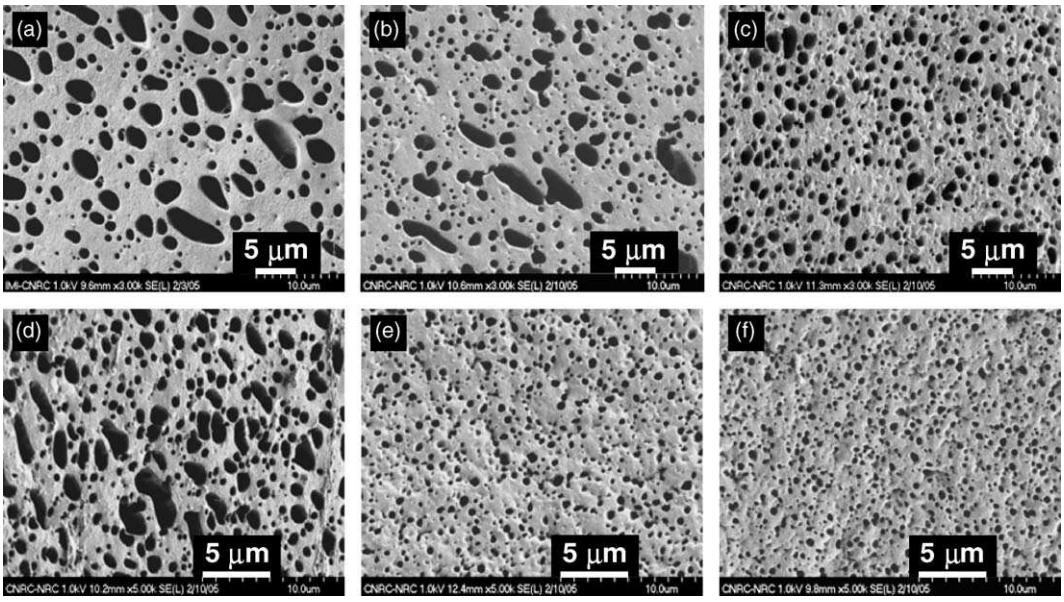

Fig. 2. SEM micrographs on microtomed strands of SEBS/PVDF (50:50 wt.%) blends, after PVDF extraction with (a) 1 wt.%, (b) 3 wt.% and (c) 5 wt.% SBM20 (magnification, 3000×), and (d) 1 wt.%, (e) 3 wt.% and (f) 5 wt.% SBM55 (magnification, 5000×).

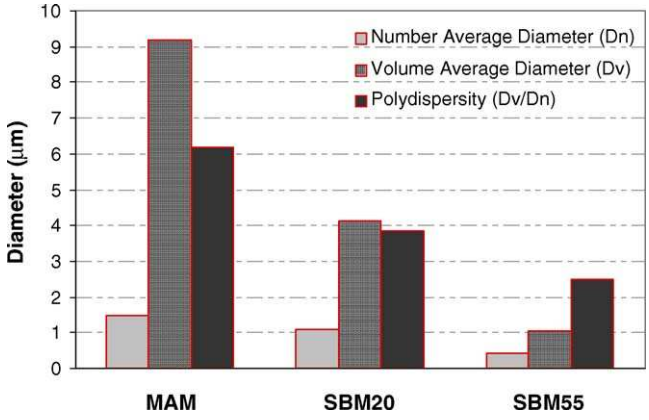

Fig. 3. Dependence of D_n, D_v and D_v/D_n on type of MMA block copolymer: 50 wt.% PVDF blends with 1 wt.% compatibilizer.

Fig. 3 illustrates the dependence of D_n, D_v, and D_v/D_n on the nature of the compatibilizer. It can be seen that as phase size decreases, the droplet size distribution becomes narrower and a smaller dispersity index is obtained. D_v/D_n was estimated to 6.2 when MAM compatibilizer was used, 3.8 for SBM20 and 2.5 for SBM55.

Fig. 4 presents the atomic force microscopy analysis for the uncompatibilized blend and for the two blends compatibilized with the SBM compatibilizer. The AFM imaging offers higher magnification and since no selective solvent extraction is required, it is ideally suited for fine morphological features. As mentioned previously, the analysis is obtained in tapping mode and good contrast is found due to the significant difference in the elastic properties of PVDF and SEBS. The lighter color, corresponding to the higher phase angle, is the PVDF phase while the SEBS appears in the darker color. The significant phase size reduction observed by AFM corroborates the SEM information. We further note for the compatibilized blends, that some sub-included SEBS seems to be trapped within the PVDF droplets. This is clearly a sign of reduced interfacial tension as sub-inclusion creates additional interfacial area. The PVDF droplets for the SBM20 compatibilized blends are between 0.5 and 5 µm. For the most efficient SBM55, all PVDF particles are below 1.5 µm with particles down to the 100 nm range.

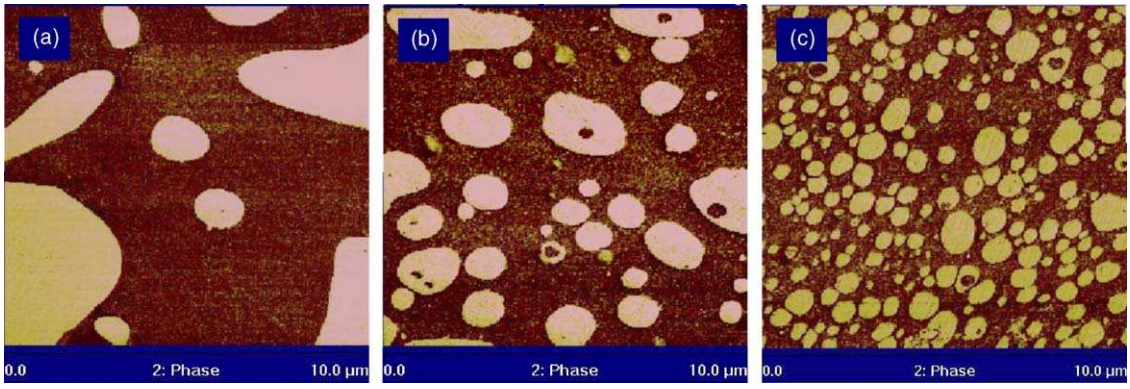

Fig. 4. AFM analysis on microtomed strands of PVDF/SEBS 50/50 wt.%: (a) no compatibilizer, (b) 1 wt.% SBM20 and (c) 1 wt.% SBM55.

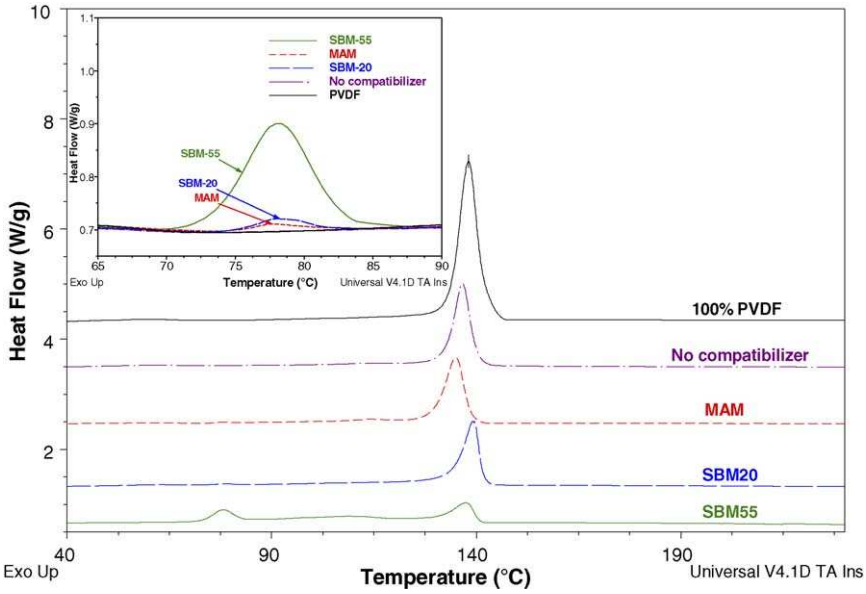

Fig. 5. DSC crystallization curves of pure PVDF and PVDF/SEBS 50:50 wt.% blends membranes with different compatibilizers.

Fig. 5 presents DSC crystallization curves for pure PVDF and for the PVDF/SEBS blends as well as a close-up view of the crystallization curve in the 65–90 °C range. While a single melting behavior is observed for PVDF in the blends independently of the presence of the block copolymer, two separate crystallization exotherms, around 78 and 137 °C, are observed in the crystallization thermograms. This behavior can be observed when a polymer exhibits two different types of crystal structure or when secondary crystallization occurs.

In a previous paper [18], it was shown from FT-IR study, that compatibilization occurs through attractive intermolecular interactions (hydrogen bond), between MMA carbonyl group and hydrogen atoms of PVDF CH_2 groups. Fig. 6 presents the crystalline content of the PVDF in the blends with 1 wt.% compatibilizer added, determined from the area under the melting peak obtained from DSC thermograms (Table 2). The crystallinity drop seems to be linked to the compatibilization efficiency of the block copolymer used. The most pronounced reduction, from 61 to 51% crystallinity, is observed when 1 wt.% SBM55 was incorporated (Fig. 6). This is due to the disruption of the PVDF crystalline network by the miscible but non-crystallizable MMA blocks of the copolymer. This is supported by similar observations for PVDF–PMMA blends [25].

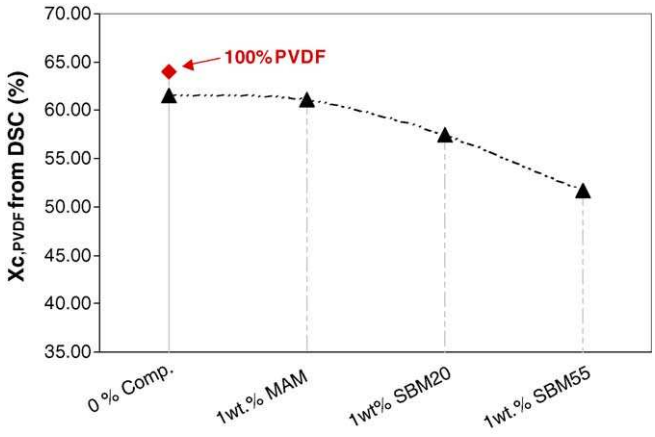

Fig. 6. Crystalline fraction of PVDF in pure PVDF and in the 50:50 wt.% blends determined from DSC melting thermograms when 1 wt.% of the different compatibilizers were added.

PVDF exhibits diverse crystalline forms α, β, γ and δ. It is known that crystallization of PVDF from the melt takes place mainly in the α-phase, at temperatures between 110 and 150 °C. β-phase with a crystallization temperature around 70–80 °C, can be obtained from solution crystallization or from melt by addition of small concentrations of PMMA [20,21]. The small exotherm observed at 78 °C is therefore an independent indication that the PMMA block of the SBM block copolymer is interacting with the PVDF phase and explains the observed double crystallization exotherms. The β peak is most important for the most efficient compatibilizer, the SBM55, indicating that a high MMA content (55% in the SBM55) is preferable for compatibilization efficiency. The β peak for the SBM20 and MAM copolymers are much smaller and near the detection limits for DSC analysis.

Table 2
Melting temperature (T_m), crystallization temperature (T_c), and crystallinity (X_c) determined from DSC for blend membranes with different compatibilizers and pure PVDF

Sample	T_m (°C)	X_c (%)	T_c (°C)
M-01	172.07	61.53	136.65
M-11	171.19	61.10	134.99
M-21	171.74	57.51	139.12
M-31	171.45	51.69	137.49
PVDF	170.79	63.96	138.11

3.2. Mechanical properties

When blending a low modulus elastomer with a stiffer PVDF material, the resulting properties will be very sensitive to the blend composition, morphology and interfacial properties. Fig. 7a and b present the strain at break and toughness of blend films without and with 1 wt.% of different block copolymers studied. The addition of concentrations as little as 1 wt.% of block copolymer causes a drastic increase in both MD and TD properties. The strain at break in the transverse direction increases from 10% for non-compatibilized blend to 240–370% for compatibilized samples, and from 220% to 490–590% in the machine direction. We can also observe that as compatibilization effect improves, the toughness increases, as expected from the improved adhesion between the blend components. The highest mechanical properties are obtained with SBM55.

It is noteworthy as well that the compatibilization reduces the film anisotropy. The film extrusion and calendaring process induces more stretching in machine direction (MD) than in transverse direction (TD). This clearly translates into higher MD than TD strain at break and toughness. This MD/TD property ratio is much more pronounced in the case of the uncompatibilized blend. In this case, the very large PVDF phases can more easily be deformed and elongated into fibrils in the extrusion and film-stretching step. This generates a highly anisotropic morphology, which translates into high MD/TD property ratios. For the compatibilized blends, the micron-range droplets cannot be deformed as severely and properties remain more isotropic.

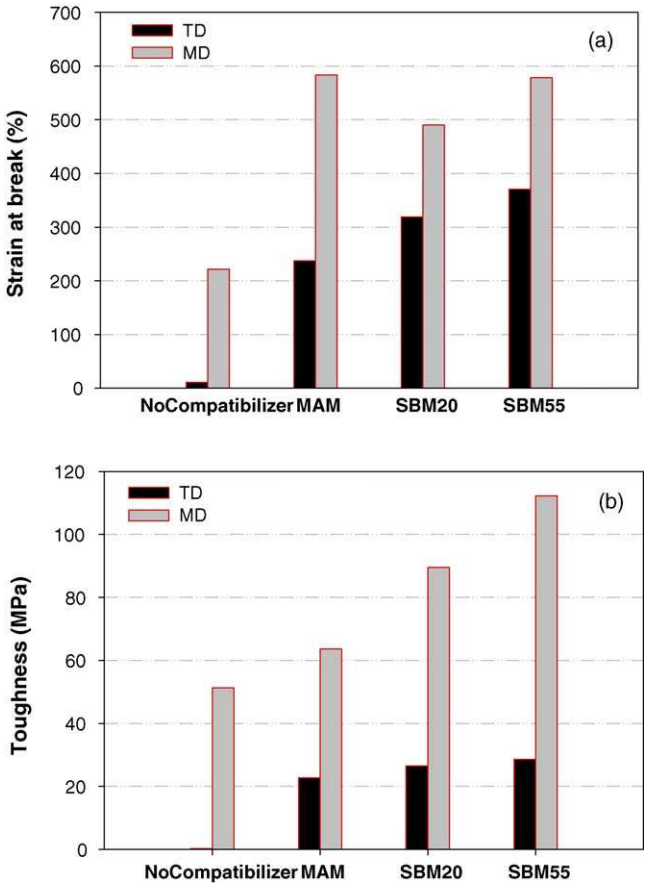

Fig. 7. Mechanical properties in transverse (TD) and machine direction (MD) for SEBS/PVDF blend membranes with different compatibilizers: (a) strain at break and (b) toughness.

3.3. Characterization of functionalized membranes

In this part of the study, we will evaluate how properties of sulfonated membranes vary with sulfonation time for the blends with and without the block copolymer compatibilizers. In sulfonic acid based membranes, the proton conductivity depends on the number of available acid groups and their dissociation capability in water. When the membrane is in the hydrated form, water molecules dissociate acid functionality and facilitate proton transport. Therefore, the conductivity and ionic exchange capacity (IEC) are important parameters in studying PEMs. Swelling is also a key factor for the mechanical integrity of the membranes. Excessively high levels of water can result in dimensional changes leading to failures in mechanical properties. In this case, considering that PVDF is inert to sulfonation and all conduction occurs through sulfonic acid groups grafted in styrene blocks of SEBS, morphology will play an important role to ensure equilibrium between hydrophilicity and hydrophobicity requirements.

Table 3 presents proton conductivity, IEC and water content determined for different functionalization times. PVDF and compatibilizer content were fixed to 50 and 1 wt.%, respectively, while sulfonation time was varied from 60 to 120 min. The PVDF/SEBS membranes were functionalized according to the procedure described in Section 2. It was verified by EDX that the sulfonation was uniform through the membrane thickness. All functional properties exhibit a dependence on the sulfonation time and on the compatibilization capability of interface modifier used.

In order to extract meaningful relations between results within a series of samples and between series, IEC, conductivity and water content were considered. Fig. 8a and b present the effect of sulfonation time on ionic exchange capacity (IEC) and conductivity, respectively. In general, the blends exhibited higher ionic exchange capacity than Nafion112®. IEC values determined by titration ranges from 0.8 to 0.97 meq g^{-1} for non-compatibilized samples and from 1.28 to 1.69 meq g^{-1} for compatibilized membranes, versus 0.74 meq g^{-1} for Nafion112® as measured with our experimental procedure and 0.9 meq g^{-1} for Nafion117®, with a thickness closer to our membranes, as reported in reference [26]. Within a series, the overall increase in IEC with increasing sulfonation time is consistent with a highest sulfonic acid content and highest degree of sulfonation. If we compare series, there is an increase in IEC related to the incorporation of the block copolymers, but it seems to have a minor effect, even if slightly higher IEC were measured for samples with 1 wt.% SBM55. Proton conductivity (Fig. 8b) appears to be much more affected by the nature of compatibilizer. The conductivity varies between 2.1×10^{-3} and 1.9×10^{-2} S cm^{-1} for uncompatibilized samples, and around $2.5–3.5 \times 10^{-2}$ S cm^{-1} when 1 wt.% SBM55 copolymer was added. These values are higher than the conductivity measured

Table 3
Properties of sulfonated SEBS/PVDF blend membranes with 1 wt.% compatibilizers

Sample	t_s[a] (min)	IEC[b] (meq g^{-1})	Water content (%)	λ[c]	Conductivity[d] (S cm^{-1})
Nafion112®	–	0.74	22.54	16.95	2.04E−02
Nafion117®	–	0.9	–	22	1.0E−02[e]
	60	0.80	56.53	39.04	2.06E−03
0 wt.% compat.	90	0.97	56.68	32.52	6.03E−03
	120	0.97	60.75	34.93	1.87E−02
	60	1.37	58.47	23.65	5.76E−03
1 wt.% MAM	90	1.54	59.44	21.47	6.30E−03
	120	1.59	57.52	20.05	6.75E−03
	60	1.42	45.06	17.92	5.21E−03
1 wt.% SBM20	90	1.67	44.96	16.15	1.39E−02
	120	1.69	45.11	16.41	2.07E−02
	60	1.28	41.21	17.67	2.61E−02
1 wt.% SBM55	90	1.61	46.92	17.97	3.28E−02
	120	1.62	47.77	14.79	3.27E−02

[a] Sulfonation time.
[b] Determined by titration.
[c] Hydration number = mol (H_2O)/mol (SO_3^-).
[d] Through the membranes, measured with two blocking electrodes at room temperature and 100% RH.
[e] From reference [28].

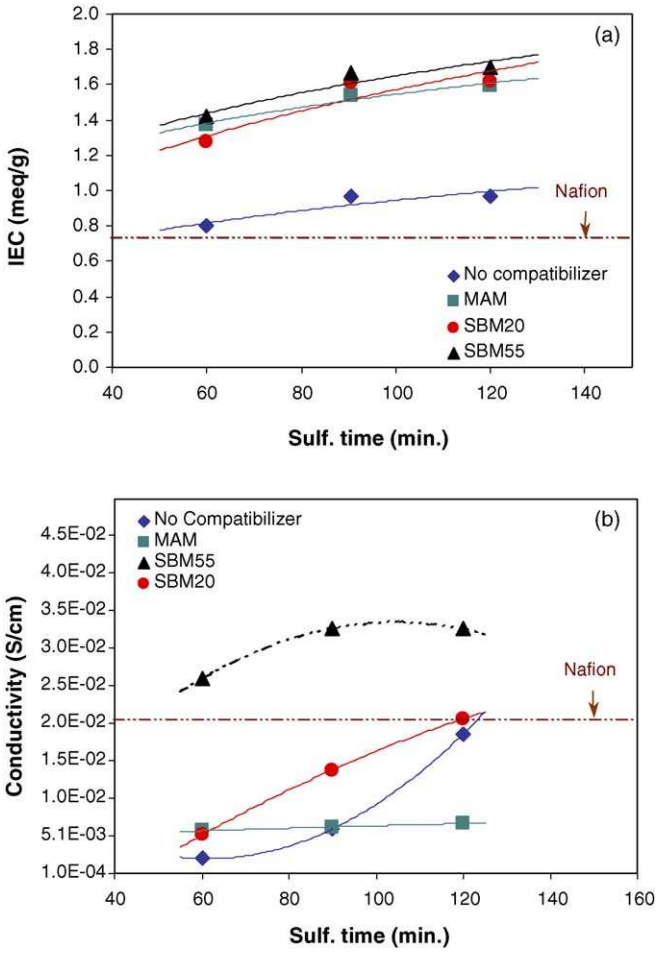

Fig. 8. Ionic exchange capacity (IEC) (a) and transverse conductivity (b) as a function of sulfonation time for s-SEBS–PVDF blend membranes with the different compatibilizers compared with Nafion112®.

for Nafion112® in our apparatus. Conduction mechanism are clearly influenced by compatibilizer's nature, and consequently by morphological changes induced by addition of the block copolymers. As discussed above, large and irregular shaped PVDF phase observed for the non-compatibilized blend break up into a finely dispersed morphology. This important phase size reduction in PVDF domains favors functionalization reaction and improves mobility of protons in the hydrated form, even if the numbers of proton carriers remains almost constant as determined from IEC.

Fig. 9a plots water uptake ϕ_w for all the membranes as a function of their IEC. The two series with no compatibilizer and 1 wt.% MAM show water uptakes around 55–60%, but with much higher IEC for compatibilized samples. The series of samples with 1 wt.% SBM20 and SBM55, show lower swelling about 41–47%, with higher IEC for samples with SBM55. Evidently, we have different wetting properties of the membranes; this may be related to differences in microstructure and morphology that translate in differences in connectivity and geometry of the hydrophilic/hydrophobic domains.

Fig. 9b plots the hydration number λ of the membranes as a function of IEC. The $(H_2O)/(SO_3^-)$ ratio for a water-swollen membrane describes the number of water molecules per fixed ion sites and is equivalent to the ratio of water molecules to protons. Comparison of this ratio for different membranes allows for a qualitative comparison of the fraction of free water present within the membranes. As expected, the general tendency is a decrease of hydration number when increasing sulfonation time within each series, considering that water uptake remains approximately constant while concentration of proton carriers increases with sulfonation time.

The hydration number values obtained for the series of membranes with no compatibilizer is between 32 and 40. These high values may be related to debonding at the interface in the

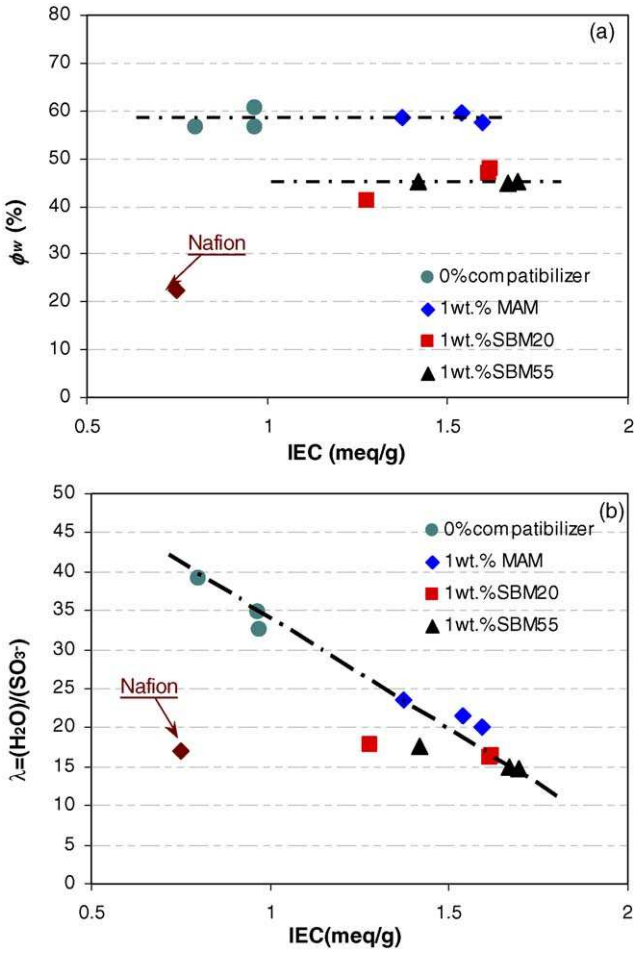

Fig. 9. Water uptake ϕ_w vs. IEC (a) and hydration number λ vs. IEC (b) for s-SEBS–PVDF 50:50 wt.% blend membranes with different MMA based compatibilizers.

non-compatibilized blends. This would create an additional free volume in which unbound water could be trapped. A decrease of the $(H_2O)/(SO_3^-)$ ratio is observed for series where the MMA block copolymers are incorporated to the blends (Fig. 9b). The hydration number for the series of compatibilized membranes, was typically between 14 and 25 which is roughly comparable to the hydration level of Nafion and other perfluorinated membranes in water swollen state [27]. Therefore, the SBM55, besides the improvement in morphology and mechanical properties due to its high compatibilization efficiency, induces stronger ionic network with highest IEC and the lower water uptake and hydration numbers for functionalized membranes.

Performance of these membranes in hydrogen or direct methanol fuel cell is under study. The optimization of the catalytic layer and MEA testing procedures adapted to the specific requirements of the alternative membrane materials will be investigated.

4. Conclusions

This work advances our knowledge on engineering of proton exchange membranes and clearly demonstrates that melt-processing of thermoplastic polymer blends can be used to produce semi-fluorinated proton exchange membranes, with a solvent-free process, using commercially available and inexpensive base polymers. Good proton conductivity can be obtained by grafting sulfonic acid groups on the styrene blocks of SEBS in films made of PVDF/SEBS blend. Compatibilization was identified as a key issue for mechanical and electrochemical properties, and the nature of the compatibilizer results to play an important role on the morphology of the membranes, which translates in an important influence on the mechanical properties as well as on the conduction properties and swelling behavior. Compatibilization of the blend can be best achieved using a styrene-butadiene-methylmethacrylate block copolymers, the use of as little as 1 wt.% of SBM in the PVDF/SEBS blend was found to decrease the dispersed phase size from more than 100 μm to a volume averaged diameter, D_v, around 1 μm. This change in dispersion state and the increased interfacial adhesion improved the membrane strain at break and toughness by factors up to three in machine direction and 10-fold in transverse direction. In the sulfonated state, the SBM compatibilized blends exhibited enhanced protonic conductivity and a reduced water uptake compared to uncompatibilized ones. Room temperature conductivity achieved in the hydrated state was about 3×10^{-2} S/cm with IEC = 1.6 meq/g and a hydration number around 15 mol (H_2O)/mol (SO_3^-).

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