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Study of Azoles As Bifunctional Additives for Proton Exchange Membranes Melt-Processing from LSC and SSC Perfluorosulfonic Acid Ionomers

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Azoles are investigated as potential bifunctional additives for proton exchange membranes (PEM) manufacturing through direct melt-processing of acidic ionomers. The additives selected are highly polar additives with relatively high boiling points that are expected to interact with the ion-rich aggregates that compose the nanophase separation in ionomers and act as plasticizers improving the viscoelastic behavior during melt processing. Long Side Chain (LSC) and Short Side Chain (SSC) Perfluorosulfonic acid (PFSA) based ionomers membranes have been prepared using a series of heterocyclic azoles, the study describes the properties of the obtained materials.

Introduction

The development of high-volume manufacturing processes to prototype PEM fuel cell components with a reduced number of steps is vital to reduce system cost and complexity, and to meet the demands of high volume production and durability requirements especially for automotive applications. Melt processes represent one of the greatest technologies to mass production of homogeneous thin polymer films at low cost. Besides eluding the serious safety and environmental concerns related to the mass production of membranes by solution-casting, melt processes provide a mechanical reinforcement through chain orientations following extrusion-stretching. This structural reinforcement at a molecular level provides extruded PEM with the mechanical durability required for building robust and long-lasting PEM fuel cells, particularly for automotive applications.

The strong ionic associations in ionomers act generally as physical cross-links, increasing by several orders of magnitude both melt-viscosities and relaxation times, resulting in ionomeric materials that are very difficult to melt-process with high shear rate processes such as melt-casting or melt-blowing. The strength of the ionic interactions in ionomers, and hence their physical and mechanical properties, depends on the acidity of the pendent anion. Polymers modified with the stronger acid, such as sulfonic acid ($pK_a \sim 1$), exhibit more dramatic changes in thermal, viscoelastic, and rheological properties than those modified with the weaker carboxylic acid ($pK_a \sim 4-5$). However, most ionomers may be melt-processed in very low shear rate operations such as compression-molding, which reveals that these ionic associations are not permanent cross-links and can be reversibly disrupted under suitable conditions.

Heterocycles such as imidazole and triazole, have been extensively studied as a replacement of water to assist proton conduction by Grotthus hopping mechanism under

anhydrous/high temperature conditions (1,2), which in turn minimize humidity dependence and enhance temperature tolerance of the PEMFC. The approach investigated is based on the use of selected bi-functional additives from heterocyclic azoles molecules, that act as a sulfonic acid groups (-SO₃H) protection and a melt-processing aid. The additives selected are highly polar additives with relatively high boiling points that are expected to interact with the ion-rich aggregates that compose the nanophase separation in ionomers and act as plasticizers which expectantly improve the viscoelastic behavior during melt processing. Additives from the azole family, imidazole, 1,2,4-triazole and benzimidazole have been investigated as potential bifunctional additives. SSC-PFSA possess higher and more stable performance at elevated temperature up to 130 °C compared to conventional long-side-chain LSC-PFSA membranes. Moreover, the shorter side-pendent chains and the absence of the ether group and of the tertiary carbon also provide SSC-PFSAs with better durability, making them more suitable for working at harsh conditions in fuel cell systems (3). Three commercial PFSA ionomers have been considered for this study; Nafion® DE-2020 with long side chain (LSC), and Aquivion® D83-24B and D79-20BS with short side chain (SSC).

Experimental

Materials

Polymers: Nafion® Long Side Chain (LSC) perfluorosulfonic acid (PFSA) polymers NR-40, R-1000 and D-2020 were purchased from Ion Power, Aquivion® short side chain (SSC) PFSA dispersion D83-24B and D79-20BS were kindly provided by Solvay Specialty Polymers. The structure of selected ionomers is shown in Figure 2.1.

Figure 1. Structures of selected perfluorinated acid ionomers.

Table 2.1 lists the properties of the ionomers used for this first study. Ionomers in the dispersion form were dried in an oven at 60°C before use, until all solvents were removed and solid weight constant.

TABLE I. Properties of selected ionomers.

Materials	Supplier	Form	Aspect	Side chain	EW
Nafion® DE-2020	Ion Power	SO ₃ H	Dispersion	Long	1000
Aquivion® D83-24B	Solvay Solexis	SO ₃ H	Dispersion	Short	830
Aquivion® D79-20BS	Solvay Solexis	SO ₃ H	Dispersion	Short	790

Additives

A series of additives from azoles family were selected for this study, namely imidazole, 1,2,4-Triazole and Benzimidazole. Their properties are listed in table 2. Azole additives have been selected for this study because of their common use as additives in polymer electrolytes to improve performance at high temperature and/or low humidity conditions, and more importantly because of their relatively high boiling point and thermal stability.

TABLE 2. Properties of selected additives.

Name	Structure	MW (g/mol)	Tm (°C)	Tb (°C)	Density (g/cc)
Imidazole		68.08	98-91	256	1.23
1,2,4-Triazole		69.07	120-121	260	1.19
Benzimidazole		118.14	170-172	360	1.23

Melt-processing

A 5-cc twin screw micro-extruder DSM-Explore was used (Figure 2.). The extruder is equipped with screws configured in a co-rotation or counter-rotation modes, and a film line equipped with several dies, 30 and 60 mm wide with various slot gaps; 0.1, 0.2 and 0.4 mm for each width.

Figure 2. Picture of the bench-top 5-cc micro-extruder equipped with a film line.

Melt-extrusion temperature was set to 230 °C. Other extrusion parameters such as RPM of the screws and calendar rolls speed were varied to achieve the required thickness, and minimize residence time of the materials in the extruder.

Characterization

Activation. Membranes obtained were activated with a solution 1:5 H₂SO₄:H₂O at 80 °C for 1 h and rinsed again with DI water at 80 °C for 1 h.

Ion Exchange Capacity (IEC): The membranes were vacuum-dried at 80 °C overnight, and then weighed. The membranes were placed in 0.2 M NaCl solutions for at least 48 hours to exchange all the H⁺ with Na⁺. The proton content in the salt solution was determined by titration with 0.008 M NaOH solution using Mettler Toledo A50 automatic titrator.

Water uptake (WU): The water uptake was determined by equilibrating the membranes in DI water at room temperature after the activation treatment. They were then removed from the water container, quickly dry wiped and immediately weighed. Subsequently, they were dried overnight under vacuum at 80 °C temperature and weighed again. The water content was calculated from the weight difference of the membrane (in H⁺ form) in its hydrated (m_{wet}) and dry (m_{dry}) state according to equation [1]:

$$WU (\%) = ((m_{wet} - m_{dry}) / m_{dry}) \times 100 \quad [1]$$

Volume change (VC): Thickness, width and length of wet and dried membranes (in H⁺ form) were determined. Dimensions of dried membranes were determined by drying them in a vacuum oven at 80°C overnight. The volume change is determined from the volume difference of the membrane (in H⁺ form) in its hydrated (V_{wet}) and dry (V_{dry}) state according to formula [2]:

$$VC (\%) = ((V_{wet} - V_{dry}) / V_{dry}) \times 100 \quad [2]$$

Conductivity: A Bekktech sample punch was used to cut a piece from the membranes for testing. The dimensions of the samples to be tested were approximately 5 mm x 25 mm. In-plane proton conductivities were measured using a Solartron Impedance Analyser 1260 and a Bekktech in-plane conductivity cell with platinum electrodes. A strip of membrane was set between 2 Pt electrodes and an alternating current was passed through the plane of the sample. Nyquist plots between 5 MHz to 10 Hz were collected and membrane resistances were extrapolated by fitting the semi-circle part of the data to Randles equivalent circuit. Proton conductivities were calculated from the equation [3], where σ is proton conductivity, L is the distance between the Pt electrodes, R is membrane resistance and A is the cross-sectional area of the strip.

$$\sigma = L / (R * A) \quad [3]$$

Thermo-Gravimetric Analysis (TGA): Thermal stability of the materials was investigated using a Setaram TG96 thermogravimetric analyzer. The temperature range used was from 30 to 700 °C at a heating rate of 5 °C/min under a flow rate of 50 ml/min of nitrogen gas.

Transmission Electron Microscopy (TEM): The samples were prepared by placing the films in a saturated lead acetate solution in water for 2 hours at room temperature (RT) to stain the ionic domains, cleaning with water and drying under vacuum RT. The

samples were then microtomed at RT into thin slices of 50nm using a diamond knife. TEM of ultrathin sections of the extruded ionomers before and after activation were obtained with a Philips CM 200 instrument with an acceleration voltage of 200 kV.

Results and Discussion

Ionomer-additive blends characterization

Ionomer-additive blends series based on Nafion® and Aquivion® ionomers and three azoles additives selected (additives concentrations ranging from 1 to 4 moles of additive per mole of SO₃H), have been prepared and characterized. Thermal stability of starting ionomers as well as ionomers-additive blends was evaluated through the TGA experiments according to the protocol described in the experimental section. Results obtained for starting ionomers in the acid form recovered from dispersions are shown in Figure 3. Three consecutive mass loss steps are observed for all ionomers. Each weight loss step is responsible for i) water loss (30 to 250°C), ii) thermal desulfonation (250 to 370°C), and iii) thermal oxidation of the sulfonated polymer (370 to 700°C), respectively. Weight loss measured for starting ionomers for each temperature range are shown in Table 3. Mass loss corresponding to water loss and thermal oxidation of the polymer are approximately in the same range, while mass loss due to the loss of sulfonic acid groups is increases as ionomers IEC is higher.

TABLE 3. TGA data collected for Nafion® and Aquivion® ionomers in the acid form.

Sample	Weight loss at temperature range (%)		
	30 – 250°C	250 – 370°C	370 – 700°C
Nafion® DE-2020	5.28	7.81	84.91
Aquivion® D83-24B	5.30	9.30	85.40
Aquivion® D79-20BS	5.60	11.06	83.25

Thermograms obtained for ionomer-additive blends with 15 wt% additive are presented in Figure 4. Three consecutive mass loss steps were also observed for all the samples analyzed in general, starting at higher temperature for ionomer-additives (weight loss starts at 65°C for neat ionomers, and approximately at 130°C with additives). A first weight loss in the range 30–250 °C attributed to the elimination of adsorbed water, most of which is adsorbed in the ionic clusters of the PFSA ionomer matrix. The second mass loss step, in range of 250–370 °C, corresponds to the loss of sulfonic acid groups and CO₂ (and additive loss in case of ionomer-additive blends). The third mass loss step, ranging from 370 to 700 °C, consists of the complete oxidative degradation of the fluorocarbon backbone in Nafion®, side chains and of any remaining sulfonic acid moieties (some of the degradation products are, HF, CO, COF₂, COS, etc.

All the ionomers studied show a complete thermal degradation at 700°C. However, when additives are incorporated, the samples do not degrade completely, sign of a higher thermal stability. Residual mass measured for all the samples are shown in Table 3; thermal stability increases in the following order: 1,2,4-triazole < imidazole < benzimidazole. These results can be in part explained by a stronger interaction of the PFSA ionomers with benzimidazole additive; with the lowest pK_a = 5.3. After activation and removal of the additive, membranes show similar TG profiles as neat ionomers.

Figure 3. Thermogravimetric percent weight loss TG and it derivative DTG as a function of temperature of Nafion® and Aquivion® ionomers

TABLE 4. Composition and TGA data collected on Nafion® and Aquivion® ionomers with different azoles additives

Ionomer	EW _{th} (g/mmol)	additive		Weight loss at 250 °C (%)	Residual mass at 700°C (%)
		Type	wt. %		
Nafion® DE-2020	1000	-	0	5.28	0.00
Nafion® DE-2020	1000	Tz	15	8.29	1.37
Nafion® DE-2020	1000	Im	15	8.95	7.82
Nafion® DE-2020	1000	Bz	15	6.64	14.66
Aquivion® D83-24B	830	-	0	5.3	0.00
Aquivion® D83-24B	830	Tz	15	8.03	1.49
Aquivion® D83-24B	830	Im	15	12.81	9.87
Aquivion® D83-24B	830	Bz	15	7.93	18.22
Aquivion® D79-20BS	790	-	0	5.6	0.00
Aquivion® D79-20BS	790	Tz	15	5.22	2.16
Aquivion® D79-20BS	790	Im	15	12.54	10.86
Aquivion® D79-20BS	790	Bz	15	8.87	18.93

Figure 4. Thermogravimetric weight loss TG as a function of temperature for (a) Aquivion® D79-20BS (b) Aquivion® D83-24B and (c) Nafion® D-2020 ionomers with different azoles additives

Figure 5 shows a picture of samples obtained on compression-molded ionomers in the acid form with no additive. Samples show in general advanced signs of degradation; Aquivion® D79-20BS did not show the strong black color characteristic of sulfonic acid based ionomers thermal degradation, but was extremely brittle.

Figure 5. Picture of samples obtained after compression-molding of Nafion® and Aquivion® ionomers in the acid form with no additives

The samples with azoles additives show higher thermal stability and mechanical properties due to the plasticizing and protective effect of the additives. Figure 6 shows a picture of samples obtained with Aquivion® D79-20BS sample with two additives; imidazole and 1,2,4-triazole. In general samples with imidazole additive show a light yellow coloration, due to the low degradation temperature of this additive, and probably to the unstable interaction with PFSA ionomers. Imidazole additive has the highest pKa of the series of additives selected (pKa = 14.5), compared to 1,2,4-triazole (pKa = 10) and benzimidazole (pKa = 5.3)

Figure 6. Picture of samples obtained after compression-molding at 260°C of Aquivion® D79-20BS with imidazole (Im) and 1,2,4-triazole (Tz) additives

Extruded membranes preparation and characterization

For melt-processing, imidazole additive was not considered for membranes extrusion, due on one hand to the degradation observed when samples were compression molded, and to the low boiling point of imidazole on the other hand. Furthermore, imidazole was shown to be unsuitable for fuel cell applications, due to the observed diffusion and absorption of its oxidation products on the surface of the Pt catalyst that reduces considerably the catalyst active surface (4). The high electronic density (high pKa) of imidazole ring seems to be an explanation. Azoles with lower electronic density are electrochemically stable for fuel cell applications.

Blends of Nafion® DE-2020 and Aquivion® D83 and D79 with selected additives were prepared at two additive concentrations of 15 and 20 wt%. Blends have been extruded using DSM bench-top extruder. Benzimidazole seems to be a better plasticizer than triazole at the loadings used. Thin transparent membranes were obtained with

Nafion® DE-2020 and Aquivion® D83 at both concentrations used (Figure 7). With Aquivion® D79 only 20wt% additive was processed successfully (corresponding to 1.7 mol of additive/mol of $\text{-SO}_3\text{H}$). Lower additive loading is probably not sufficient to neutralize all the acidic groups, and the viscosity remains too high. Nafion was successfully extruded with 20wt% triazole, higher loadings appear to be necessary to process Aquivion® PFSA.

Figure 7. Picture of as extruded membrane based on Aquivion D83-24B plasticized with Bz additive.

Additive loading and as a consequence the number of moles of additive per mol of sulfonic acid, is an important parameter to optimize, to achieve a significant plasticizing effect that allows the reduction of the viscosity of acidic ionomers adequately to be extruded into thin films, a process otherwise impossible without additives. For this specific study, membranes obtained were activated to ensure the removal of the additive according to the method described in the experimental section. Further characterization will be done to evaluate high temperature potential on the membranes as extruded.

Morphology. From TEM observations, activation does not seem to affect the morphology of the samples; the phase separation between hydrophilic and hydrophobic domains is preserved. Figure 8 compares extruded membranes based on Aquivion® D79 and Nafion® DE-2020 both with 20 wt% Bz additive loading. Aquivion® D79 sample shows a higher density and size of ionic domains compared to Nafion® DE-2020. This observation is in agreement with the higher IEC of Aquivion ionomers.

Figure 8. TEM images on Lead Acetate stained membranes of Nafion® and Aquivion® processed with Bz additive after activation at two magnifications x135k (left) and x580K (right)

Conductivity, IEC and dimensional stability. Ion exchange capacity and in-plane proton conductivities at RT in water were determined for extruded membranes after activation. Results are presented in Table 5. As expected samples based on Aquivion® ionomers show higher IEC, however within the same series with the same ionomer, samples extruded with benzimidazole additive, show lower IEC. This observation is in agreement with TGA observations, and confirms that benzimidazole additive has a stronger interaction with the sulfonic acid groups of the ionomers, that reduces the numbers of acidic sites available during titration. Membranes extruded with imidazole additive, might require longer activation times to completely remove the additive. Within the series of samples based on Nafion®, additive loading does not seem to affect the IEC of the final membranes as shown in Figure 9.

In-plane ionic conductivity measured by impedance spectroscopy at RT in water is relatively high for all the samples; in the range of 0.09 to 0.41 S/cm. Nafion® DE-2020 membranes extruded with 1,2,4-triazole as additive show the highest conductivities, comparison with Aquivion® ionomer processed with the same additive (sample 07-B) show lower conductivity but the thickness is very high. Measurements at higher

temperature and low relative humidity are being performed and expected to reveal more significant differences between samples.

TABLE 5. Ion exchange capacity and in-plane conductivity of extruded membranes after activation

Sample ID	Ionomer	EW	additive		IEC ^a mmol/g	σ^b S/cm	e^c (μm)
			Type	wt. %			
07-B	Aquivion® D79-20BS	790	Tz	20	1.270	2.82E-01	255
07-D	Aquivion® D79-20BS	790	Bz	20	1.083	1.06E-01	67
07-G	Aquivion® D83-24B	830	Bz	15	1.133	1.43E-01	43
07-I	Nafion® DE-2020	1000	Tz	15	0.977	3.21E-01	120
07-J	Nafion® DE-2020	1000	Tz	20	0.981	4.10E-01	177
07-K	Nafion® DE-2020	1000	Bz	15	0.770	9.11E-02	69
07-L	Nafion® DE-2020	1000	Bz	20	0.782	1.12E-01	50
Ref	Nafion® NRE-211	1000	-	-	0.895	1.12E-01	30

a: ion exchange capacity

b: in-plane ionic conductivity at room temperature in water

c: wet thickness

Figure 9. Ion exchange Capacity and in-plane conductivity obtained for activated membranes

Figure 3.10. Water uptake and dry/wet volume change measured on series of melt-extruded membranes

Figure 10 shows water uptake (WU) and dry/wet volume change (VC) measured for melt-extruded membranes and NRE-211 reference. Aquivion® based membranes show higher water uptake and volume change in agreement with their higher IEC. For Nafion® D-2020 series samples processed with benzimidazole show higher dimensional stability than those processed with 1,2,4-triazole additive.

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