DESARROLLO DE MEMBRANAS DE INTERCAMBIO PROTÓNICO BASADAS EN COMPOSITES POLÍMERO@LÍQUIDO ÍONICO

(Development of proton exchange membranes based in polymer@ionic liquid composites)

Trabajo de Fin de Máster
para acceder al

MÁSTER EN NUEVOS MATERIALES

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Resumen

Los líquidos iónicos (IL), sales líquidas a temperatura ambiente, son de gran importancia en diferentes aplicaciones debido a las buenas propiedades que poseen, como su alta estabilidad química y térmica, su alta conductividad iónica o su nula volatilidad. Estos materiales se pueden combinar con una gran variedad de polímeros para producir membranas sólidas que combinen las buenas propiedades mecánicas de los materiales poliméricos con las propiedades de los líquidos iónicos. Una de las aplicaciones de interés de estos composites es el desarrollo de membranas de intercambio protónico (PEM), las cuales presentan alta conductividad protónica, buena resistencia mecánica y alta estabilidad térmica.

Este trabajo se centra en el desarrollo de composites polímero@líquido iónico, utilizando distintos líquidos iónicos. En particular, se ha utilizado el polímero PVDF-HFP y tres líquidos iónicos próticos diferentes (Diethylmethylammonium trifluoromethanesulfonate, 1-Methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-Methylimidazolium chloride). Las membranas se han sintetizado en diferentes condiciones y, posteriormente, han sido caracterizadas por diversas técnicas (SEM, ángulo de contacto, ensayos mecánicos, TGA, FTIR y medidas eléctricas) con el fin de comparar las propiedades y seleccionar las más apropiadas para determinadas aplicaciones. A partir de los resultados logrados se ha podido observar cómo cambian aspectos como la morfología, la hidrofobicidad, la conductividad o las propiedades mecánicas dependiendo del procedimiento de síntesis empleado y del tipo de líquido iónico utilizado.

Palabras clave: Membranas, composites, PVDF-HFP, líquidos iónicos, pilas de combustible.

Abstract

Ionic liquids (IL), liquid salts at room temperature are being explored in different applications due to their good properties such as high chemical and thermal stability, high ion conductivity or non volatility. IL can be combined with a wide variety of polymers for the production of solid membranes which combine the good mechanical properties of the polymeric materials with the properties of the ionic liquids previously mentioned. One of the most interesting applications of these composites is the development of proton exchange membranes (PEM) with high proton conductivity in dry and wet states, good mechanical strength and thermal stability.

This work focuses on the development of polymer@ionic liquid membranes using different types of ionic liquids. In particular, the study was focused on the use of PVDF-HFP and three different protic ionic liquids (Diethylmethylammonium trifluoromethanesulfonate, 1-Methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-Methylimidazolium chloride). The membranes were synthesized under different conditions and posteriorly characterized by several techniques (SEM, contact angle, mechanical tests, TGA, FTIR and electrical measurements) in order to compare the properties of the membranes with the different ionic liquids and select the most appropriate for specific applications. From the results, it has been observed how aspects such as morphology, hydrophobicity, conductivity or mechanical properties change depending on the synthesis procedure employed and on the type and amount of ionic liquid used

Keywords: Membranes, composites, PVDF-HFP, ionic liquids, fuel cells.

1. Introduction

1.1. Composites

In today's society, the development of new materials and devices is a demand to solve problems in various fields such as energy, medicine and technology. For this reason, the research in the field of materials is in continuous growth.

The search for materials with novel properties leads to the development of composite materials, which consist on a mixture of two or more elements and the combination of their particular characteristics in order to obtain new or better properties. That is the case of the increase of the resistance or the lightness of a material when mixing it with other elements. Therefore, these materials are developed in order to reduce the negative properties and maximize the positive ones of each of the elements that compose them [1]. Composites have generated a great interest in the field of materials since they can present unique properties that are not presented when the elements appear separately. Currently, they are produced and applied in several fields such as energy [2], aerospace [3], construction [4] or medicine [5].

The term composite is often used to refer to synthetic materials; however, these materials also exist naturally (eg, wood or bones are composite materials).These materials are usually formed by a *matrix* which is reinforced by another element called *reinforcement*, which is usually immersed in the matrix. Based on this, composite materials are usually classified according to the type of matrix (metallic, ceramic or polymeric) or the type of reinforcement (fibers, sheets or particles) [1][6].

Among the composite materials, the polymer matrix composites stand out because of its good mechanical and corrosion resistance properties. In these compounds, the polymer matrix may be thermoplastic, thermostable or an elastomer, depending on the required properties. Particularly, in this project we have worked with thermoplastic polymer@ionic liquid composites [7]. Membranes based on proton ionic liquid incorporated into a polymer matrix have been developed in order to take advantage of the properties of each of the materials employed, such as the good mechanical properties of the polymeric material and the proton conduction properties of the ionic liquid.

1.2. Ionic liquids

Ionic liquids (ILs) or room temperature ionic liquids (RTILs) are materials of great importance due to its interesting properties. They are defined as molten salts that have melting points (T_m) lower than 100 °C, this is, most are liquids at room temperature. Normally, they are formed by an organic cation and an organic or inorganic anion. Ionic liquids greatly differ from ionic solutions. While ionic solutions consist of ionic salts on a solvent (Figure 1-*a*), ionic liquids do not contain a solvent, they are formed entirely by ions (Figure 1-*b*). These materials stand out for their good properties, such as high ionic conductivity, good thermal and electrochemical stability (T_d >300°C), low vapor pressure or nonflammability, in addition to their ability to act as solvents of various materials [8-9].

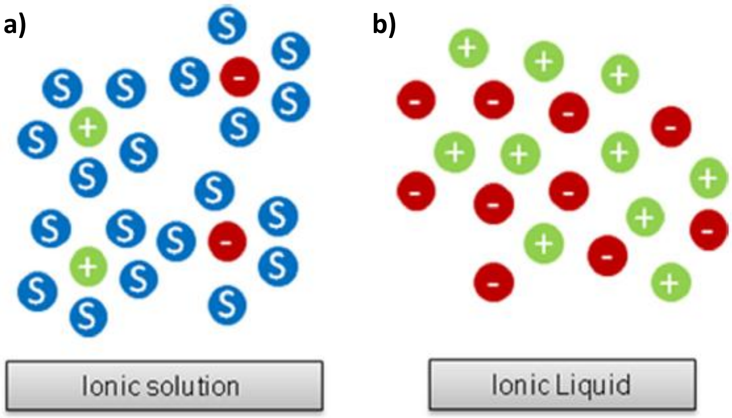


Figure 1. Difference between: (a) ionic solution and (b) ionic liquid. Cation (+), anion (-) and solvent (S).

ILs are formed by an organic cation (where MIm, EMIm or dema are frequently used) and by an organic or inorganic anion (where NTf_2, TfO or Cl are some of the most used). Due to the large number of possible combinations of cations and anions, currently, there exist more than 10^3 different ionic liquids. The large number of possibilities allows to tailor the most suitable combination to meet the desired properties for specific applications, since the chemical and physical properties are dependent from the used cations and anions. For example, the conductivities of ionic liquids at room temperature range from $1 \cdot 10^{-4}$ to $1.8 \cdot 10^{-2}$ S/cm depending on the cations and anions in which they are based [10-12]. Due to its good properties, ionic liquids are used on a wide variety of applications like for example, as solvents, on energy storage and conversion, on gas separation, and even in biochemical processes [9].

Ionics liquids are usually classified into two main groups: Aprotic ionic liquids (AILs) and protic ionic liquids (PILs). The first (AILs), that are more common and have always been more studied, are usually obtained by the quaternization of an amine followed by an anion exchange reaction. This type of ILs don´t have exchangeable protons. On the other hand, on the last years, the interest on the other type of ionic liquids (PILs) has grown since they have interesting properties for certain applications such as the development of proton exchange membranes due to the reactivity of the exchangeable (mobile) protons located on the cation. This type of ILs are formed by a transfer of a proton between a Brönsted acid and a Brönsted base (is the classical acid-base neutralization reaction) [8][13].

One of the most widely used ionic liquid for the synthesis of proton conduction membranes is the diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) (Figure 2), which stands out for its high thermal stability (with a decomposition temperature of T_d = 360°C), its low melting point (T_m = −6°C), its high ionic conductivity (53 mS cm^{-1} at 160°C under anhydrous conditions and 10 mS cm^{-1} even at room temperature) or its open circuit voltage (OCV) greater than 1V (1.03 V at 150 °C, under anhydrous conditions) [14-15].

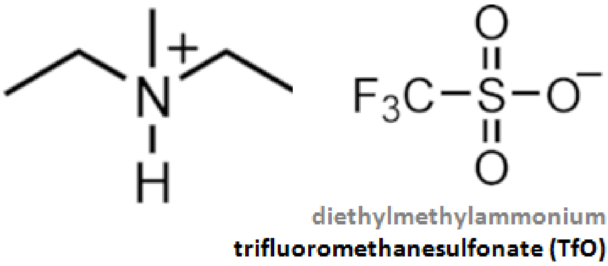


Figure 2. Structure of [dema][TfO].

ILs can be mixed with organic or inorganic compounds in order to improve their physical and chemical properties. Due to their high ionic conductivity, ionic liquids are being investigated in the area of electrolytes. However, its liquid state is a limitation. To achieve the desired solid film state, ionic liquid is mixed with a polymer that provides the necessary mechanical sustainability. In this case, compatibility between ILs and polymers is crucial for the preparation of polymer@ionic liquid composites [8][16].

The mixture of ionic liquids and polymers on a solid film results in a modification of the ion transport properties and of the mechanical properties. In this blend, ionic conductivity is increased as increasing the amount of ionic liquid and it's about finding a compromise between the mechanical stability and the proton transport properties [10][17].

1.3. Polymers (PVDF-HFP)

In order to develop these polymeric@ionic liquid membranes, several polymers can be used (such as Nafión, polyvinylidene-fluoride, polyimides, polybenzimidazole or polyethylene glycol among others). These polymeric materials stand out for their good mechanical properties [10][17].

One of the most commonly used polymer on the development of polymer composites is the polyvinylidene fluoride (PVDF), as well as its copolymers. PVDF is a semicrystalline thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. It is a material widely used because of its good properties such as her good chemical stability, high polarity (high dielectric constant), excellent mechanical and thermal properties, low density, hydrophobic nature or biocompatibility. But especially, polyvinylidene fluoride and its copolymers stand out for having the highest dielectric constant and the highest electroactive response among the polymers. PVDF can exhibit five crystalline phases, being the most common the α, β and γ phases (Figure 3). The β-phase is, among the mentioned phases, the one with the highest dipolar moment [18-20].

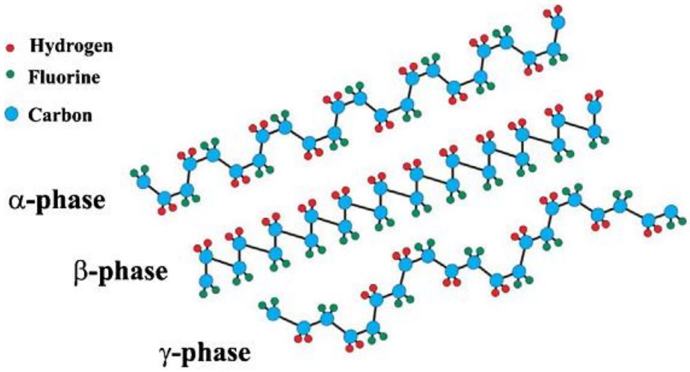


Figure 3. Representation of some phases of PVDF.

Because of its good properties, these materials are used in a wide range of applications such as energy generation and storage [21], actuators and sensors [22], separators and filtration membranes [23] or even biomedical sciences [24], among others. In many of these applications, PVDF should be in one of its electroactive phases (β or γ), what can be controlled by the method of production [20].

The polymeric material used in this work has been the poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), which is a copolymer of the PVDF. On this polymer, the inclusion of hexafluoropropylene (HFP) in the structure involves an increase on the fluorine atom content and a decrease on the degree of crystallinity with respect to the homopolymer (Figure 4) [19]. This compound is very interesting due to its interesting properties, since it contains both semicrystalline (PVDF) and amorphous (HFP) phase. Whereas the amorphous phase allows higher ionic conduction, the crystalline phase provides the mechanical strength essential for the membranes. Moreover, it presents a high thermal stability ($T_d \approx 475$ ºC) [25].

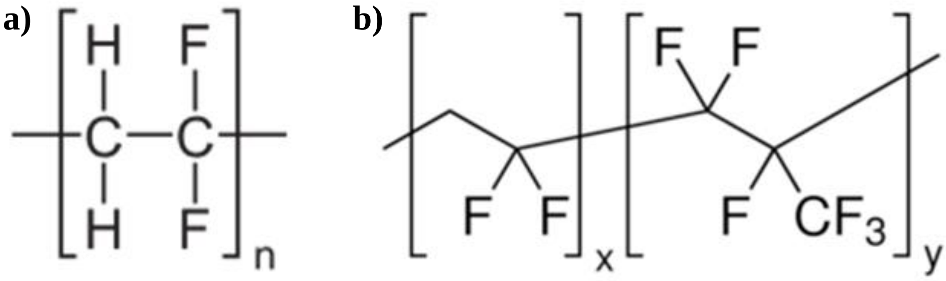


Figure 4. Structure of: (a) PVDF and (b) PVDF-HFP.

1.4. Applications – Fuell cells

The combination of the previously mentioned materials (PVDF-HFP as polymeric matrix plus ionic liquid dispersed on it) allows to obtain membranes (composites) with a series of properties (mechanical strength, ionic conduction, chemical and thermal stability, ease of manufacture...). These properties make the PVDF-HFP@IL composites suitable for their applications in storage and power generation [14] where these membranes act as solid electrolytes (for example in fuel cell electrolytes [26], dye-sensitized solar cell electrolytes [27], lithium battery electrolytes [28] or double layer capacitors [29]) or as gas separation membranes [30], among others.

Among all the possible applications of these proton exchange membranes, it is worth mentioning their use in fuel cells. Fuel cells are electrochemical devices, that is, they transform chemical energy into electrical energy through oxidation and reduction reactions. Fuel cells typically use hydrogen as fuel, which is introduced in the negative electrode (anode) where it undergoes an oxidation reaction and is dissociated into protons and electrons. On the other hand, in the positive electrode (cathode) oxygen is reduced and dissociated into O_2^-. Afterwards, electrons, protons and O_2^- react in the cathode forming water as the only byproduct. The redox reactions that occur in the cell are given by [31]:

$$\text{Anode: } H_2 \rightarrow 2H^+ + 2e^- \qquad (1)$$

$$\text{Cathode: } \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (2)$$

Current energy sources present problems for the environment since they require the use of fossil fuels which will eventually run out. It is a demand to look for alternatives. Fuel cells provide an efficient and clean energy conversion mechanism and have several advantages such as high efficiency and capacity, being a promising alternative to current energy sources. For these reasons, a great development of this technology is expected in a close future. Anyway, there are still many aspects to improve since they still present some problems such as the high costs, the low durability, the low power, the rapid degradation or the low conductivity of materials. It is clear that new materials and devices are necessary for the development of new fuel cell electrolyte membranes and, in general, for a future sustainable society [32-33].

Currently, there is a wide range of designs for fuel cells that mainly differ in the chemical characteristics of the electrolyte. Among the different types, the proton exchange membrane fuel cells (PEMFCs) stands out for its high efficiency. In this type of cells the electrolyte consists on a proton exchange polymer membrane (PEM) that allows the circulation of protons through it (from the anode to the cathode of the cell) and avoids the circulation of electrons, which are forced to flow through an external circuit generating electricity in the process, and also acts as separation device of the gaseous reactants [31]. The efficiency and the long service life of PEMFC is highly dependent of the performance of this membrane, making it one of the critical components of the system.

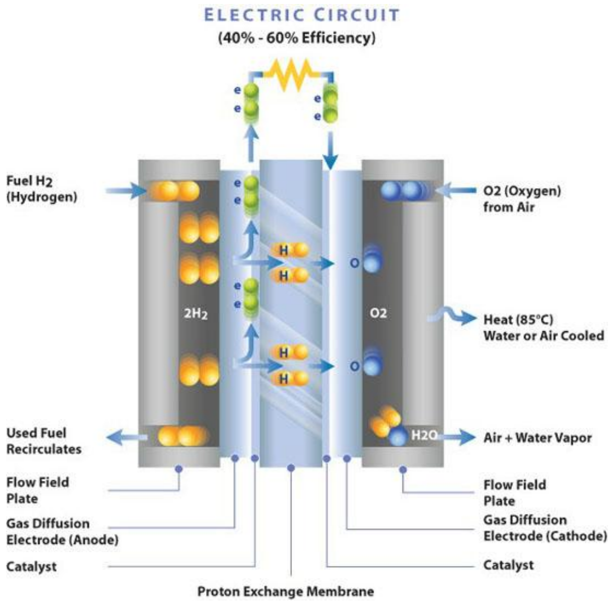


Figure 5. PEMFC scheme.

The PEMFC (Figure 5) has three main components: two electrodes (anode and cathode) and the above cited polymer electrolyte located between the two electrodes. In addition these devices have other elements such as the gas diffusion layers or the interconnectors, among others. Since the potential of a single cell is too small for most practical applications, these devices are typically composed of a stacking of several unit cells connected in series to form what is known as a fuel cell stack. This system is more complex than a single unit cell, due to the requirements for current collection, thermal management, cell and gas separation, structural support and the distribution of oxidants and fuels [34].

Various types of polymeric materials can be used to develop these proton exchange membranes (perfluorinated, non-fluorinated, partially fluorinated, with ionic liquids...), each one with their advantages and disadvantages. Among all possibilities, membranes composed of Nafion, which is a perfluorinated polymer, are the most widely used as electrolyte in PEMFCs because of its excellent chemical stability, good mechanical strength and high proton conductivity [13][35]. However, this material presents a loss of efficiency when operating at temperatures above 100°C, since the ionic conductivity drops in the absence of water (wetness is critical for proton conductivity). Moreover, the traditional PEMs also presents problems related to the high cost of production and the high fuel crossover [10].

In this way, there is a great interest in the search for new materials able to improve the existing electrolyte membranes. A promising alternative to the traditionally used Nafion are the membranes formed by polymers and ionic liquids, since these last ones present a high proton conductivity even in the absence of humidity and, therefore, can be used as proton conductors for non-humidified intermediate temperature fuel cells. In order to use the electrolytes in fuel cells, these membranes must satisfy certain properties such as high proton conductivity in both wet and dry environments, low fuel and oxygen crossover, mechanical strength, dimensional stability or thermal and electrochemical stability under the operating conditions, among other [10][36].

1.5. Objectives of the work

The aim of this work is to develop polymer@ionic liquid composites by tuning several parameters of the synthesis (temperature and time of evaporation of the solvent, type and quantity of ionic liquid, thickness of membranes...) in order to study how the properties of the samples (such as thermal stability, morphology, mechanical strength or conductivity) depend on these parameters.

The membranes obtained will be characterized in order to know their properties and consider possible applications. Particularly, it will be analyzed which have better properties to be used as proton exchange membranes for fuel cells.

2. Experimental proccedure

The procedures carried out for the preparation of the proton exchange membranes as well as the characterization techniques used are described below. In this work, we used different protic ionic liquids and some parameters of the synthesis have been varied (evaporation temperature of the solvent, percentage of ionic liquid, thickness of the samples...) in order to compare the properties of each sample (morphological, mechanical, thermal and electrical properties, among other).

2.1. Materials

The ionic liquids Diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]), 1-Methylimidazolium bis(trifluoromethylsulfonyl)imide ([MIm][NTf_2]) and 1-Methylimidazolium chloride ([MIm][Cl]) were obtained from Iolitec (Germany) with stated purity of 98 %. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, SOLEF® 21216/1001 from Solvay (Belgium)) was used as polymer matrix and N,N-dimethylformamide (DMF) (99.8%) (supplied by Sigma Aldrich) as solvent. The structures of the ionic liquids used are shown in the Figure 6.

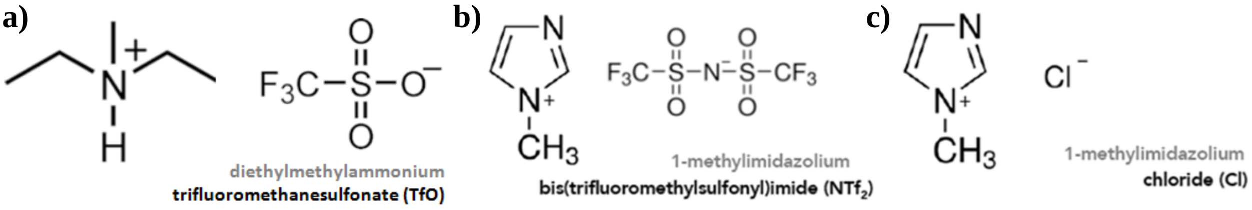


Figure 6. Structure of: (a) [dema][TfO], (b) [MIm][NTf_2] and (c) [MIm][Cl].

2.2. Samples preparation

The membranes have been prepared by solvent casting and evaporation of the solvent at different temperatures. Figure 7 shows a scheme of the preparation procedure of the composite membranes. 6 mL of solvent per gram of polymer have been used, what corresponds to a weight polymer:solvent ratio of (85:15). In order to compare properties, equivalent molar quantities of each ionic liquid were used. Starting with a 60% and 80% wt of [MIm][NTf_2], the equivalent molar quantities of the other liquids were taken (Table 1). The solvent, the polymer and the selected ionic liquid were mixed in the desired weight ratios and placed into magnetic stirring (200 rpm) at room temperature until the complete dissolution of the polymer. Then, the homogeneous solution was spread on a glass substrate and the solvent was evaporated either at room temperature or in the oven at a specific temperature for a certain time.

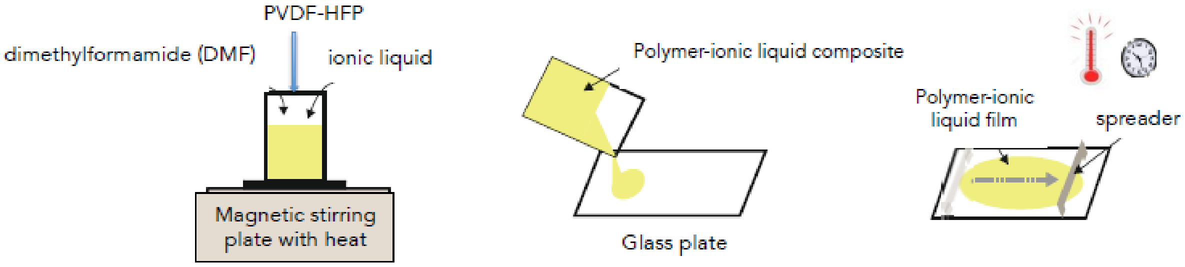


Figure 7. Scheme of the synthesis proccedure.

The effect of different parameters in the properties of the samples was analyzed. Among the parameters studied are included the temperature and time of solvent evaporation, the percentage of ionic liquid and the thickness of the prepared membrane. The characteristics of all the prepared materials are summarized in the Table 1.

Table 1. Characteristics of the prepared samples.

Polymer	I.L.	Sample	%wt I.L.	T / ºC	t / min
PVDF-HFP	-	PVDF-HFP (T_{room})	0	T_{room}	-
		PVDF-HFP (80ºC-20min)		80	20
		PVDF-HFP (100ºC-60min)		100	60
	[MIm] [Cl]	PVDF-HFP@[MIm][Cl] (T_{room})	33.0	T_{room}	-
		PVDF-HFP@[MIm][Cl] (80ºC-20min)		80	20
		PVDF-HFP@[MIm][Cl] (100ºC-60min)		100	60
		PVDF-HFP@[MIm][Cl] (< %wt)			
		PVDF-HFP@[MIm][Cl] (> %wt)	56.6		
	[dema] [TfO]	PVDF-HFP@[dema][TfO] (T_{room})	49.5	T_{room}	-
		PVDF-HFP@[dema][TfO] (80ºC-20min)		80	20
		PVDF-HFP@[dema][TfO] (100ºC-60min)		100	60
		PVDF-HFP@[dema][TfO] (< %wt)			
		PVDF-HFP@[dema][TfO] (> %wt)	72.3		
	[MIm] [NTf$_2$]	PVDF-HFP@[MIm][NTf$_2$] (T_{room})	60.0	T_{room}	-
		PVDF-HFP@[MIm][NTf$_2$] (80ºC-20min)		80	20
		PVDF-HFP@[MIm][NTf$_2$] (100ºC-60min)		100	60
		PVDF-HFP@[MIm][NTf$_2$] (< %wt)			
		PVDF-HFP@[MIm][NTf$_2$] (> %wt)	80.0		

Firstly, different processes of evaporation of the solvent (temperature and time) were tested. The solvent evaporation process was performed at room temperature, in the oven at 80 °C for 20 minutes, in the oven at 100 °C for 1 hour and in the oven at 180 °C for 15 minutes. The 180 °C process was ruled out due to the degradation of the PVDF-HFP@[MIm][Cl] composite at that temperature. From the SEM images and using the Image J program, it was observed that the obtained samples present a thickness value that varies from 100 to 300 µm, depending on the method of production and type of IL used. However this thickness is too high for membranes used in PEMFCs. In this way, after the characterization of all the previously prepared samples, the method that results in good mechanical properties and non-porous films (1h at 100 °C) was used to prepare new samples of higher percentage of IL with lower thickness (between 20 and 60 µm). The electrical characterization presented in this work was performed over these last prepared samples.

2.3. Characterization of the composite membranes

In order to study the properties of the synthesized samples different measurements were carried out. The morphology of the composite membranes was studied using a scanning electron microscopy (SEM, JEOL JSM-7000F) with an accelerating voltage of 5kV. Samples were analyzed both in surface and in cross section (samples were cut after their submersion in liquid nitrogen). Prior to analysis, samples were coated with a gold layer of 15 nm using a sputter coating.

On the other hand, to study the hydrophilicity of the samples, contact angle measurements have been carried out using the NEURTEK OCA 15EC DATAPHYSICS instrument and deionized water drops of 2µL. Five different measurements were performed in each membrane and then, the average value was calculated.

The mechanical properties of the membranes were analyzed by the trace of the stress-strain curve of each membrane using the traction machine (Shimadzu AGS-500NJ). Measurements were taken in the tensile mode. Samples with lengths and widths of 10 mm were stretched at a rate of 1 mm/min.

The thermal properties of the membranes were studied by a thermogravimetric analysis (TGA), with the NETZSCH STA 449F3 instrument. These measurements were obtained in a temperature range of 25 to 800 °C at a heating rate of 5°C/min. Aluminum oxide (Al_2O_3) pans have been used due to their excellent chemical and thermal resistance.

Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR) measurements have been carried out in order to determine the phase content of the composite membranes. The spectra was taken in the range between 600 and 4000 cm^{-1} with a Jasco FT/IR-6100 spectrometer.

Finally, the ionic conductivities and the transport properties of the membranes were studied by electrochemical impedance spectroscopy (EIS) using an Agilent E4980A Precision LCR Meter instrument. The measurements were carried out in the frequency range of 20 to 2000000 Hz. To perform the measurements, the electrodes were made by depositing a gold layer of 40 nm thickness and 5.48 mm diameter on each side of the sample by sputtering with the QUORUM Q150T ES instrument. These measurements were carried out in the samples without humidity and heat treatment, for the wet samples (15 min under vapor) and for the dry samples (20 min at 60 degrees in the oven), in order to compare the ion transport properties. All the results obtained are shown in the following section of the work.

3. Results and analysis

As discussed above, the prepared composite membranes have been subjected to various analysis in order to characterize their properties (morphological, hydrophilicity, mechanical, thermal and electrical properties). Some of the results obtained are shown and discussed below.

3.1. Morphological characterization and hydrophilicity

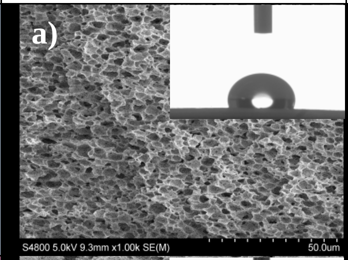
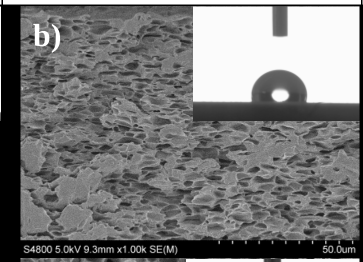
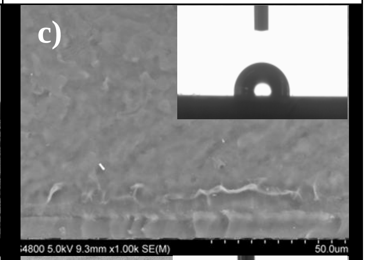
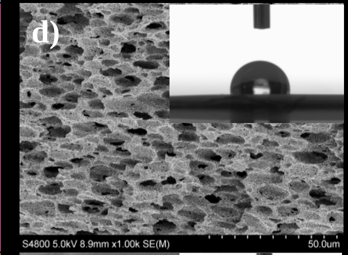
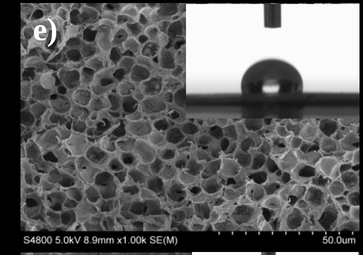
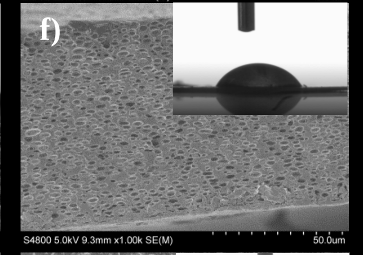
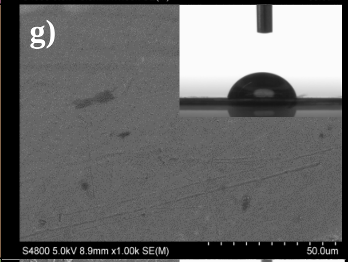
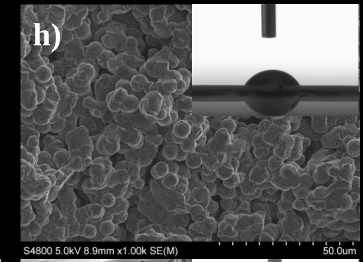
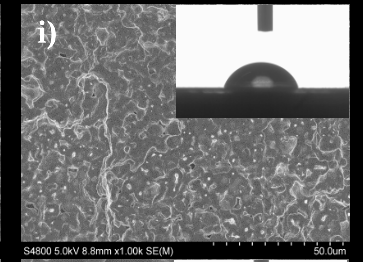
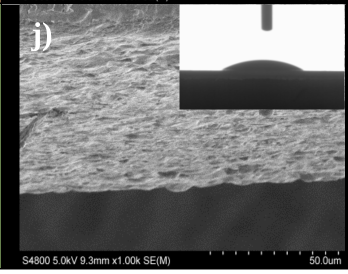
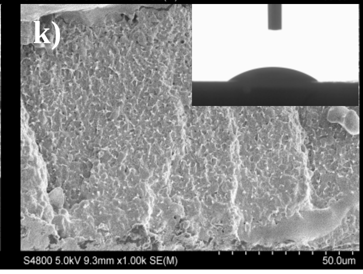
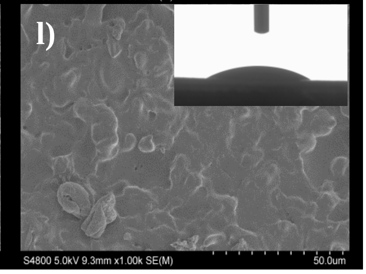
Representative cross-sectional SEM images of the membranes as well as images of static contact angle measurements are shown in the Table 2. SEM images were taken in order to compare the morphology of the different samples. The results reveal the existence of different morphologies (porous, not porous or spherulites) which depend on the processing conditions and the ionic liquid used.

The temperature and time of solvent evaporation play an important role on the morphology obtained. It is observed that in the samples of neat PVDF-HFP and PVDF-HFP@[MIm][Cl] the pore size decreases as the temperature and time of solvent evaporation increase. In the neat PVDF, the pore is formed by a phase separation between the solvent and the polymer [19]. At higher temperatures, the DMF in the polymer evaporates more quickly, leading to a lower pore size in the sample. When the solvent evaporates slowly, the process of phase separation is completed, resulting in a larger pore size [37]. A similar behavior is observed in the PVDF-HFP@[MIm][Cl] composite.

However, this behavior was not observed in all the prepared composites, which evidences the influence of the type of IL in the polymer/solvent interaction and, consequently, in the morphology of the composite. Contrary to the membranes of PVDF-HFP and PVDF-HFP@[MIm][Cl] that show a high degree of porosity along the thickness of the samples, the membranes formed by PVDF-HFP@[MIm][NTf_2] do not present porous. Moreover, in the PVDF-HFP@[dema][TfO] composite a structure formed by spherulites can be observed, especially in the sample dried at 80 °C.

The possibility to tailor the membranes morphology by the variation of the IL type opens new possibilities in the area of membranes production, since the wide range of different IL structures predicts a huge variety of different membrane structures.

Table 2. SEM (cross–section) and contact angle images for the different samples.

	Room temperature	**T = 80 °C , t = 20 min**	**T = 100 °C , t = 60 min**
PVDF-HFP			
PVDF-HFP@ [MIm][Cl]			
PVDF-HFP@ [dema][TfO]			
PVDF-HFP@ [MIm][NTf$_2$]			

The hydrophobic properties of the membranes have also been analyzed in order to know how they respond to the presence of water, since these properties may play an important role in certain applications such as battery and fuel cell electrolytes. Table 3 shows the results obtained for the contact angle measurements performed on the different samples. Depending on the contact angle, the membranes can be classified as hydrophilic or hydrophobic. Generally, a surface is called hydrophilic when its contact angle is lower than 90° and hydrophobic when the contact angle is higher than 90°. Moreover, surfaces can be defined as superhydrophobic when its contact angle is higher than 150° or as superhydrophilic when the contact angles is lower than 10° [38].

Table 3. Contact angle estimated for the samples.

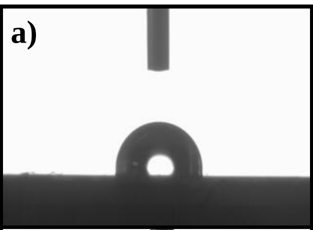
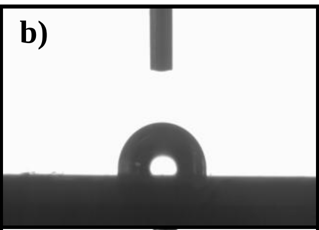
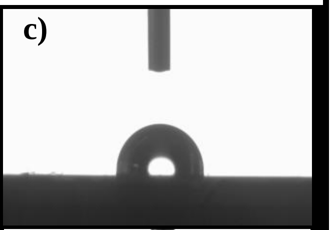
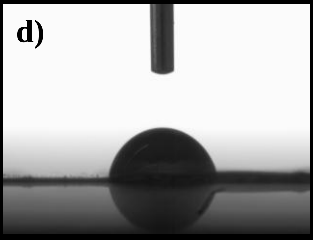
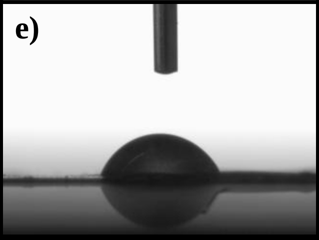
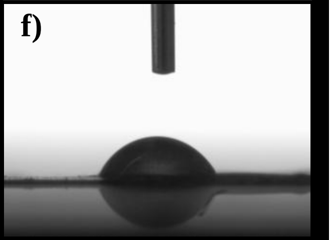
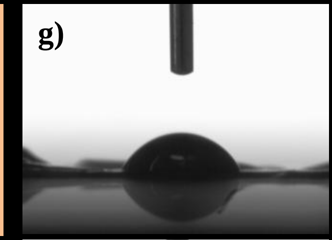
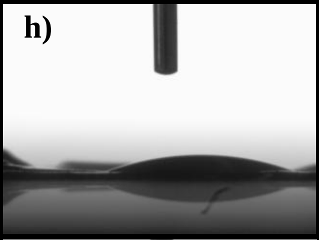
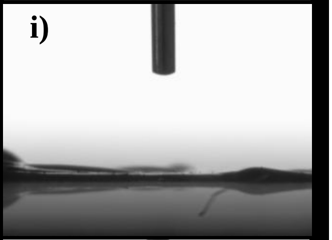
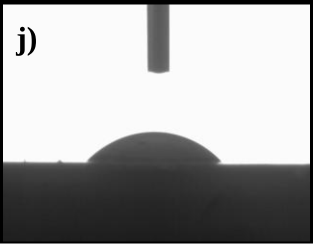
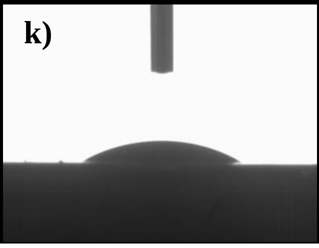
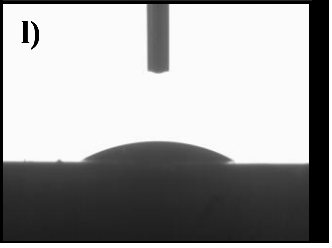
Sample	Processing	Contact angle (°)
PVDF-HFP	Room temperature	108 ± 5
	T = 80 °C, t =20 min	103 ± 3
	T = 100 °C, t = 60 min	95 ± 5
PVDF-HFP@[MIm][Cl]	Room temperature	105 ± 5
	T = 80 °C, t =20 min	92 ± 9
	T = 100 °C, t = 60 min	74 ± 9
PVDF-HFP@[dema][TfO]	Room temperature	80 ± 4
	T = 80 °C, t =20 min	59 ± 9
	T = 100 °C, t = 60 min	74 ± 1
PVDF-HFP@[MIm][NTf$_2$]	Room temperature	36 ± 5
	T = 80 °C, t =20 min	45 ± 6
	T = 100 °C, t = 60 min	25 ± 1

Observing the results of the contact angle measures, immediately after the contact of the drop with the membrane surface, it is shown that some membranes have a hydrophobic character while others have hydrophilic character. Membranes composed of PVDF-HFP@[MIm][Cl], as well as those of pure PVDF-HFP present higher values of contact angle, that is, they are apparently more hydrophobic than the PVDF-HFP@[dema][TfO] and PVDF-HFP@[MIm][NTf$_2$] membranes.

Moreover, it is observed that in the pure PVDF-HFP and in the PVDF-HFP@[MIm][Cl] the contact angle decreases with increasing the drying temperature, as does the porosity of the sample. The hydrophobicity of a material is generally increased by the presence of surface textures and it was observed that the roughness of the prepared samples surface increase as the surface porosity increase [18]. In contrast, composites of PVDF-HFP with the other two ionic liquids ([MIm][NTf$_2$] and [dema][TfO]), which are non porous and present a smoother surface, do not show this behaviour. Particularly in the case of the membrane with spherulites (PVDF-HFP@[dema][TfO] at 80 °C), a higher hydrophilic character than the other samples of PVDF-HFP@[dema][TfO] can be observed. Regarding to samples of [MIm][NTf$_2$], it was concluded that these samples are clearly the most hydrophilic ones.

However, the values obtained for the static contact angle are not directly related with the wettability of the membrane. Table 4 shows the images of the contact angle measurements as a function of the time for the samples with higher % wt of ionic liquid prepared at 100ºC. In these images, it can be appreciated the different ways in which the membranes absorb water depending on the type of ionic liquid used. It was demonstrated that the wettability of the sample is highly dependent from the type of IL incorporated in the composite. All of them are able to absorb water, but the composite prepared with [dema][TfO] stands out for the significant and rapid capacity of absorption.

Table 4. Images of the Contact Angle Measurements as a function of time of the different samples with higher % wt of ionic liquid.

	At t = 0 s	At t = 10 s	At t = 30 s
PVDF-HFP			
PVDF-HFP@[MIm][Cl]			
PVDF-HFP@[dema][TfO]			
PVDF-HFP@[MIm][NTf$_2$]			

3.2. Mechanical characterization

The different morphologies obtained in the different samples of our work can be also appreciated at the macroscopic scale, where changes in the appearance of the membranes (transparency or opacity) and in the mechanical properties of them are observed.

In this section, the results of the tensile tests performed on the different samples, as well as the elastic modules obtained from the tensile curves, are presented. These curves have been measured for samples synthesized with a lower % wt of ionic liquid in order to analyze the effect of the ionic liquid and of the solvent evaporation process in the mechanical properties of the samples, which are very important in a large variety of applications. Stress-strain curves obtained are shown in the Figure 8.

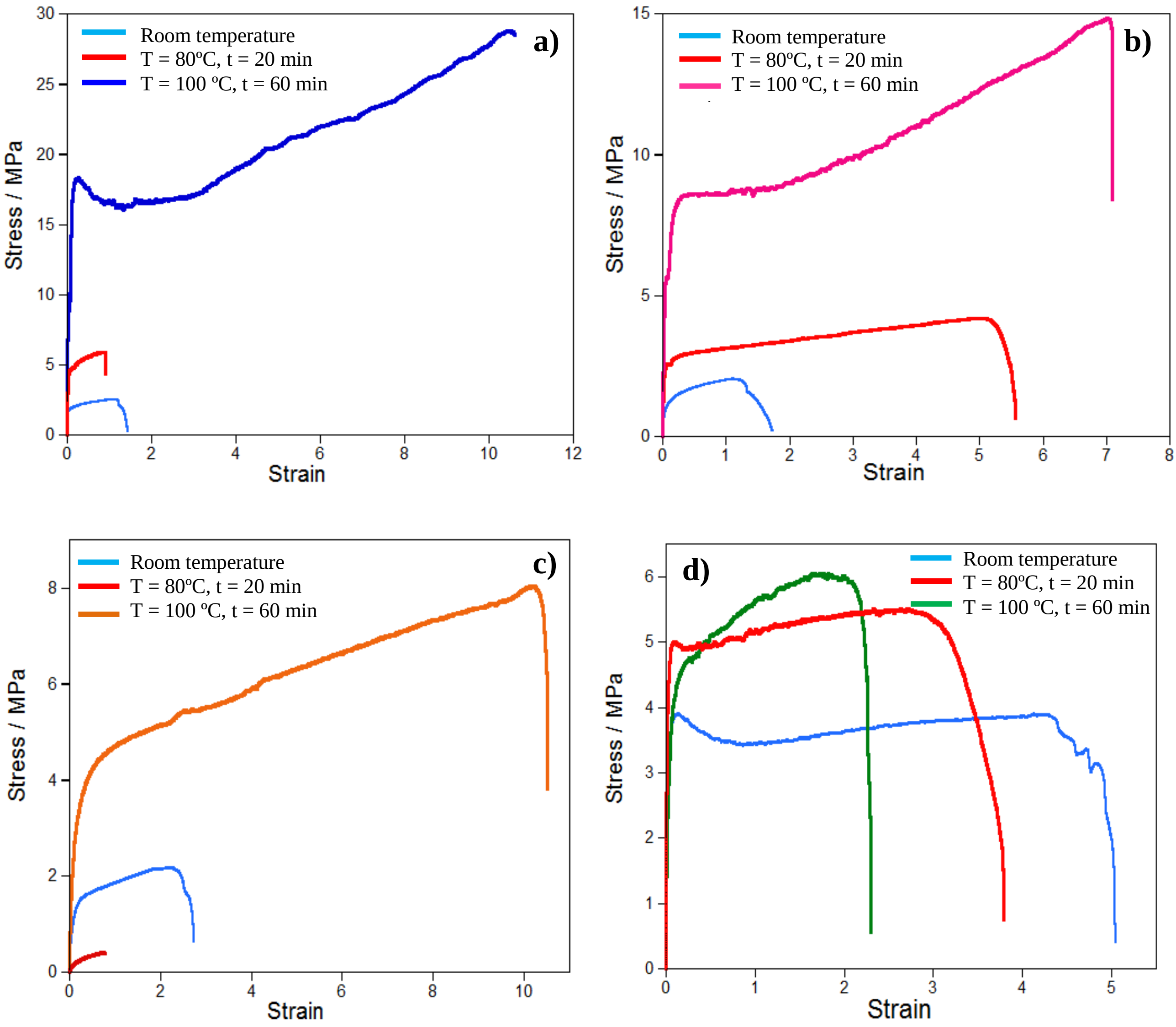


Figure 8. Stress-strain curves of the membranes of (a)PVDF-HFP@[MIm][Cl], (b)PVDF-HFP@[dema][TfO], (c) PVDF-HFP@ [MIm][NTf2] and (d) PVDF-HFP, all samples with lower % wt of ionic liquid.

In the stress-strain curve two main characteristic zones are presented. The first zone presents a linear behavior that corresponds to the elastic regime and the second zone presents a plastic behavior until the breaking point is reached. From the linear zone of the curves, the elastic modulus (or Young's modulus) (E) of each sample can be obtained through the Hooke's law [19]:

$$E = \sigma / \varepsilon \qquad (3)$$

where σ is the applied stress and ε is the deformation produced in the material. The results obtained for the Young's modulus of each sample are shown in Figure 9**.**

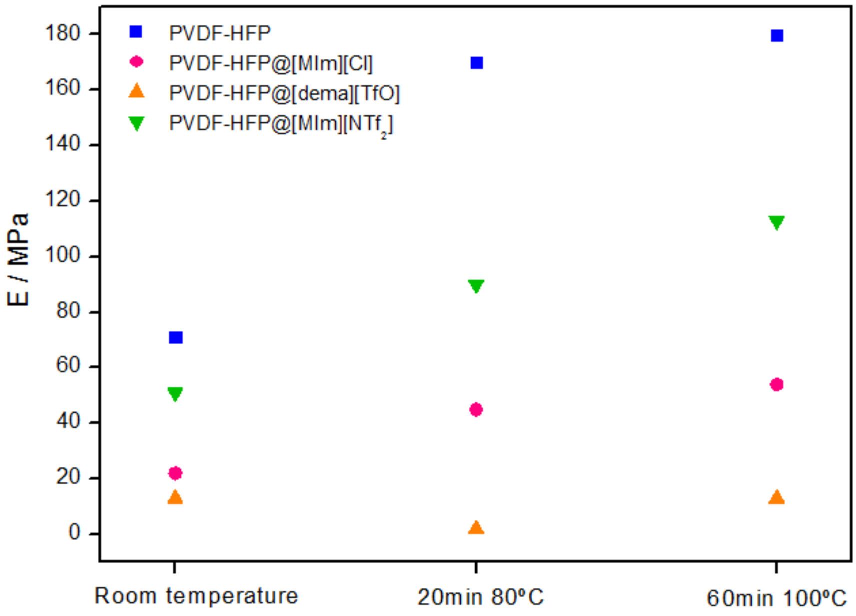


Figure 9. Results of elastic module estimated for the samples whose stress-strain curves are shown in previous figure.

As can be seen, for the PVDF-HFP, PVDF-HFP@[MIm][Cl] and PVDF-HFP@[MIm][NTf_2] membranes the Young's modulus increases as the porosity of the sample decreases. This is not the case for the membranes of PVDF-HFP@[dema][TfO]. For the sample dried at 80 °C, a very small Young's modulus is obtained (2 MPa) what is related with the spherulitic-based structure of this membrane, which originates a higher number of fragile breakpoints. From these results, it is evident that both the morphology and the ionic liquid used greatly influence the mechanical properties of the membranes [19].

3.3. Thermal characterization

To further understand the thermal behavior of the samples and the polymer@IL interactions, in Figure 10 are represented the thermogravimetric curves of neat PVDF-HFP and of the composites with the two different concentrations of IL, all for the samples dried at 100 °C for 1 hour. In this case, it was analyzed how the degradation temperatures of the membranes change according to the different ionic liquids used.

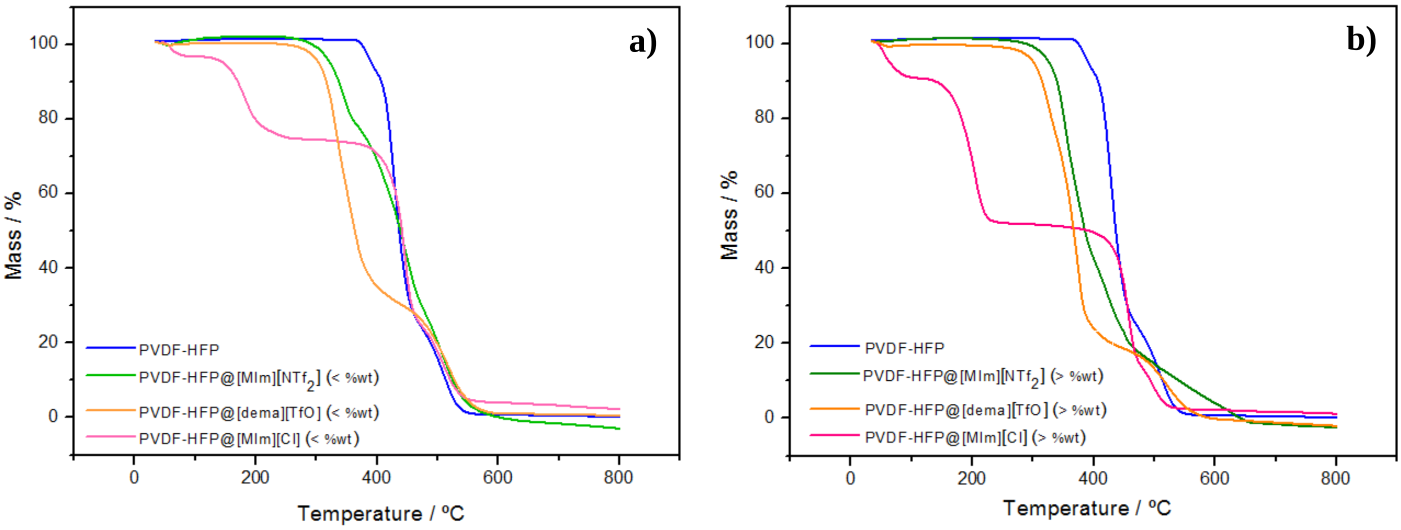


Figure 10. Thermogravimetric curves for the membranes with: (a) less % wt of ionic liquid (b) greater % wt of ionic liquid.

TGA measurements demonstrate that the pure PVDF-HFP membrane is thermally stable until temperatures close to 450 ºC. At this moment, the carbon-hydrogen bonds of the polymer chain break, and the formation and loss of hydrogen fluoride along the polymer chain occurs [39]. On the other hand, in the polymer@IL composites other weight losses previously occur. This change in the degradation temperatures of the different samples is due to the interaction between the polymer and the different ionic liquids [40].

For the PVDF-HFP@[dema][TfO] and PVDF-HFP@[MIm][NTf$_2$] composites the more significant weight loss presents an onset temperature above 300°C. That temperature is lower than the degradation temperature of pure PVDF-HFP, but is high enough for most applications, including fuel cell electrolyte membranes applications. In addition, for the sample of PVDH-HFP@[dema][TfO] a small initial weight loss is observed at lower temperatures, around 100°C, what most likely corresponds to the loss of the water present in this IL structure.

However, thermal stability is lower for the PVDF-HFP@[MIm][Cl] composite. For the sample with lower % wt of [MIm][Cl] an initial mass loss, corresponds to the loss of the water present in the composite, is about 3% of the total mass, while for the sample with higher % wt of [MIm][Cl] it corresponds to a value of around 9 %. Moreover, contrary to the other composites, the one with [MIm][Cl] presents another mass loss step below 200 ºC, that is followed by the last degradation process at temperatures around 450 ºC. This anticipation of degradation process is typical in samples containing

Cl ions. Previous studies suggest that it is caused by the interactions of the polymer with the degradation products of chloride ILs [41].

3.4. Fourier Transform Infrared Spectroscopy

The results obtained for the FTIR measurements are shown in the Figure 11. From the FTIR spectra, the percentage of the crystalline phases (α and β) present in the membranes was estimated. This parameter, that for many applications is irrelevant, is a crucial factor in the area of sensors and actuators.

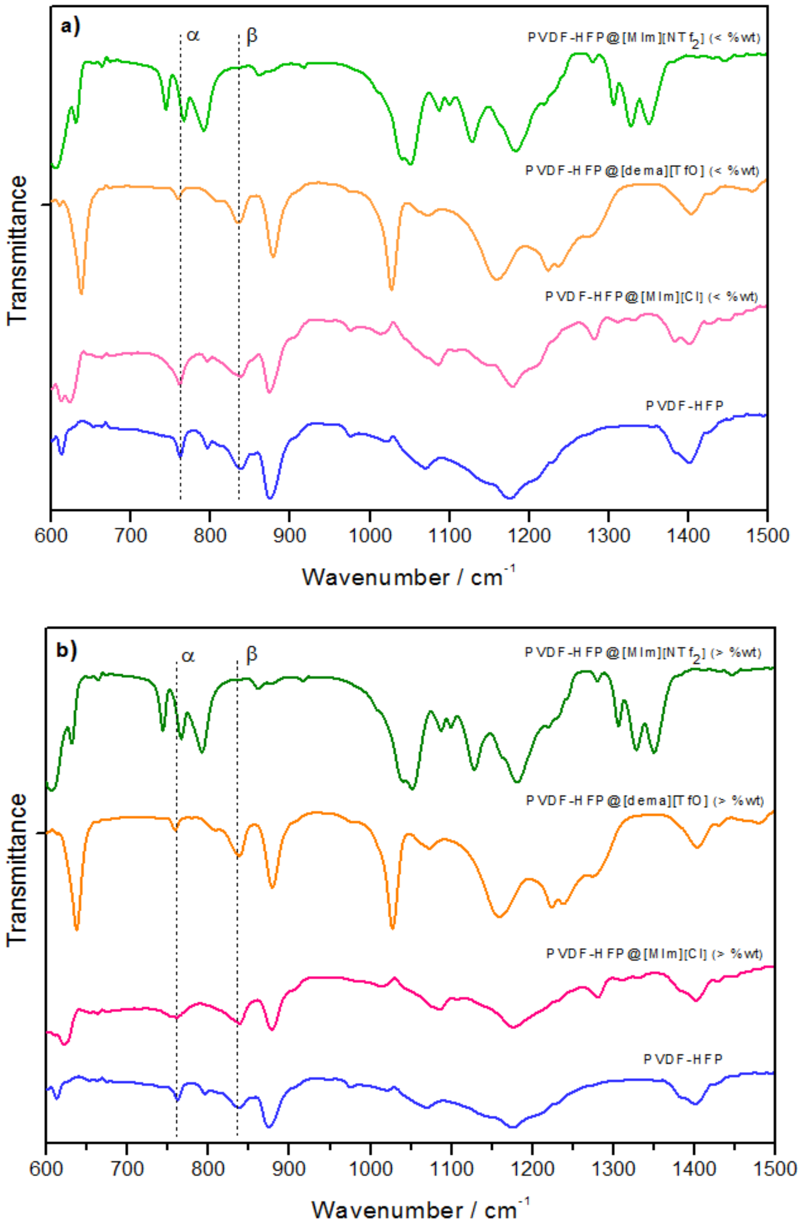


Figure 11. FTIR-ATR spectra of the different membranes with: (a) less % wt of ionic liquid (b) higher % wt of ionic liquid.

Looking at the Figure 11, it can be observed that the spectra of the membranes of PVDF-HFP@[dema][TfO], PVDF-HFP@[MIm][Cl] and pure PVDF-HFP are very similar, whereas the FTIR spectrum of the PVDF-HFP@[MIm][NTf$_2$] is very different. This fact indicates that, probably, the interaction of the [MIm][NTf$_2$] IL and the polymer chains prevents its crystallization , originating an amorphous membrane.

On the other hand, in the FTIR-ATR spectra of the PVDF-HFP, PVDF-HFP@[dema][TfO] and PVDF-HFP@[MIm][Cl], there are two strong absorption bands over 763 and 839 cm^{-1} characteristics of the α and β-phases of the PVDF-HFP, respectively. From these bands it is possible to calculate the percentage of each crystalline phase present in the sample using the equation (4) and assuming that only the α- and β-phases are present in the membranes, since they are the most common phases in which the PVDF-HFP crystallizes [42].

$$\%\ (\beta\text{-phase}) = \frac{A_\beta}{(K_\beta/K_\alpha)\cdot A_\alpha + A_\beta} \cdot 100 \qquad (4)$$

Where A_α and A_β are the absorbance of the α and β-phases (at 763 and 839 cm^{-1}, respectively) and K_α and K_β are the absorption coefficients ($K_\alpha = 6.1\cdot10^4$ cm^2/mol and $K_\beta = 7.7\cdot10^4$ cm^2/mol) [42]. The results obtained for the calculation of the percentage of the piezoelectric β-phase present in the membranes are shown in Table 5.

Table 5. Percentage of beta phase in the different samples.

Sample	% (β-phase)
PVDF-HFP	38.2
PVDF-HFP@[MIm][Cl] (< %wt)	31.1
PVDF-HFP@[MIm][Cl] (> %wt)	62.5
PVDF-HFP@[dema][TfO] (< %wt)	65.1
PVDF-HFP@[dema][TfO] (> %wt)	65.7
PVDF-HFP@[MIm][NTf$_2$] (< %wt)	0
PVDF-HFP@[MIm][NTf$_2$] (> %wt)	0

In view of the results, we can see that the type and amount of ionic liquid used in the composite influence significantly the percentage of β-phase content in the sample. The percentages of β-phase obtained for the composite membranes formed by PVDF-HFP and the ionic liquids ([dema][TfO] and [MIm][Cl]) is higher than for pure PVDF-HFP, except in the case of PVDF-HFP@[MIm][Cl] composite with lower %wt of ionic liquid, which percentage of β-phase is slightly lower when compared with pure PVDF-HFP. For the PVDF-HFP@[MIm][NTf$_2$] sample the percentage of beta phase is null.

3.5. Electrical characterization

To conclude with the block of results, the electrical measurements were performed on the different samples and are shown below. From these measures we intend to study the effect of the quantity and type of ionic liquid as well as the humidity in parameters such as conductivity. First, the conductance of the samples as a function of frequency was measured. The a.c. conductivity (σ) was obtained from the following equation:

$$G = \sigma \cdot \frac{A}{d} \qquad (5)$$

Where *G* is the conductance, *A* is the area of the electrodes and *d* the separation between them. The results obtained for the measurement of the conductivity in the membranes with higher percentage of ionic liquid as well as in the membrane of pure PVDF-HFP are shown in the Figure 12.

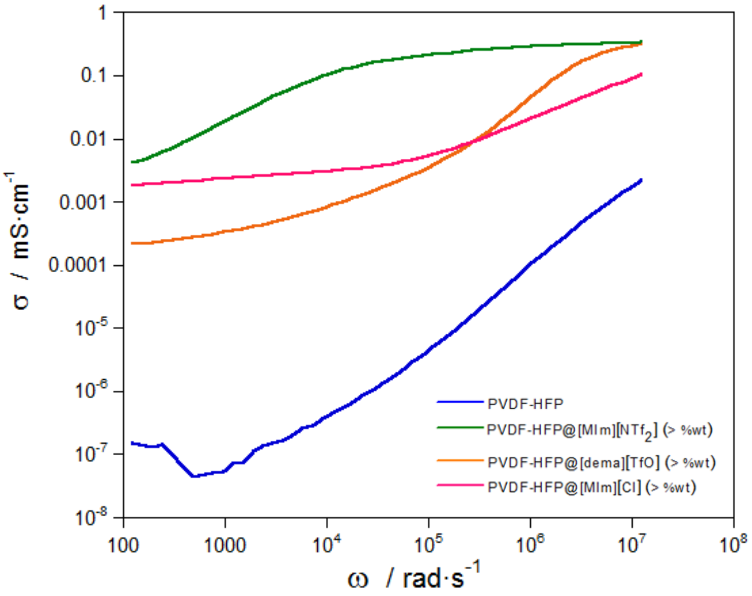


Figure 12. Ionic conductivity as a function of angular frequency for the sample of pure PVDF-HFP and for the composite samples with higher %wt of IL.

A strong increase of the electrical a.c. conductivity is observed in all the composite samples with respect to the pure PVDF-HFP which in turn also depends on the type of the ionic liquid. As can be observed, the best results for the conductivity measurements are obtained for the sample of PVDF-HFP@[MIm][NTf$_2$], for which a value of 0.33 mS·cm^{-1} is reached at high frequencies. The lower value of conductivity was observed for the sample of PVDF-HFP@[MIm][Cl], which may be related with the porosity of the sample that difficult the ionic diffusion. On the other hand, it can be observed that at low frequencies the conductivity of the samples of PVDF-HFP@[MIm][NTf$_2$] and PVDF-HFP@[dema][TfO] is very different whereas at higher frequencies the conductivity of the PVDF-HFP@[dema][TfO] composite approaches that of the PVDF-HFP@[dema][TfO] membrane, indicating that the conductivity can be originated by different processes.

To study the effect of the humidity on the electrical behavior, a sample was submitted to a dry (20 min a 60 °C) and humidification (15 min under vapor) process just before the performance of the electrical measurements. Due to the higher values obtained with PVDF-HFP@[MIm][NTf_2] composite, this sample was chosen to study this effect. The obtained results are shown below (Figure 13).

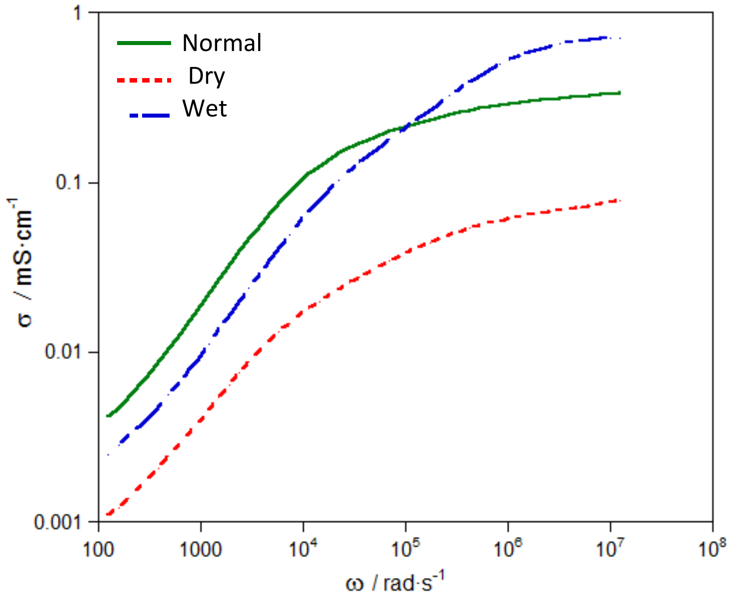


Figure 13. Ionic conductivity of the samples of PVDF-HFP@[MIm][NTf_2] with higher %wt submitted to a dry and humidification process.

As can be seen, the presence of humidity on the sample increases the conductivity of the sample to more than double at high frequencies. On the other hand, this value is lower when the sample is dry. The results indicate that the presence of water facilitates the transport of charge at higher frequencies leading to higher conductivity. That is, the membrane absorbs the water and thus increases the conductivity which is related to the water absorption properties of the membranes studied previously and represented in Table 4.

On the other hand, the capacitance (C) was also measured and from the parallel plate capacitor equation it was obtained the value of the dielectric constant of the medium (ε_r) [43]:

$$C = \varepsilon_r \cdot \varepsilon_0 \cdot \frac{A}{d} \qquad (6)$$

Where ε_0 is the absolute permittivity whose value is of $8.85 \cdot 10^{-12}\ C^2/N \cdot m^2$. The results obtained for the measurement of the dielectric constant on the different samples are shown in the Figure 14.

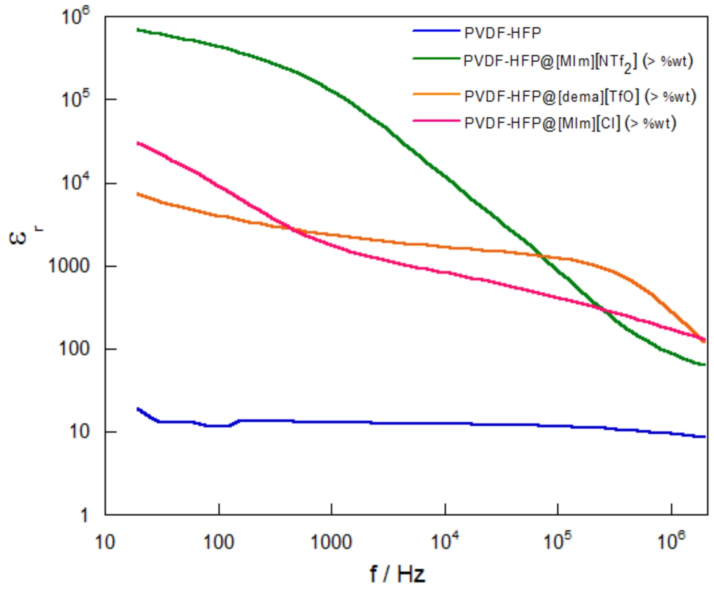


Figure 14. Dielectric constant as function of the frequency for the sample of pure PVDF-HFP and for the composite samples with higher %wt of IL.

Also on this case, the dielectric constant of the composite samples presents a higher dielectric constant in comparison with the pure PVDF-HFP. Particularly, the dielectric constant of PVDF-HFP@[MIm][NTf$_2$] sample is higher at low frequencies but then, at high frequencies, becomes smaller than for the other samples.

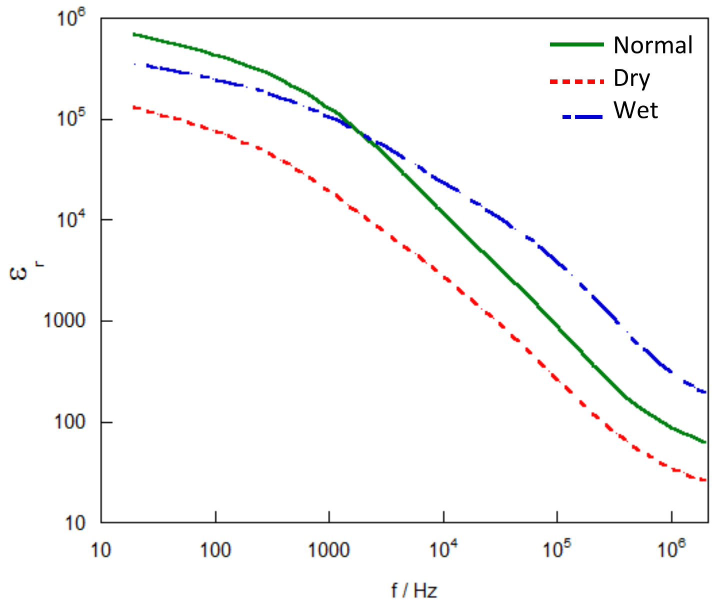


Figure 15. Dielectric constant of the sample of PVDF-HFP@[MIm][NTf$_2$] with higher %wt submitted to a dry and humidification process.

In the Figure 15 can be seen again that the presence of humidity on the sample leads to higher values of dielectric constant.

4. Conclusions and future directions

Composite membranes of PVDF-HFP and different ionic liquid were successfully prepared by the solvent casting method. Several membranes with different properties were obtained by modifying certain parameters in the synthesis procedure. For example, it was observed how the morphology or the mechanical strength of the membranes changes depending on the type of ionic liquid and the solvent evaporation temperature.

In view of the obtained results, it can be concluded that the best candidates for proton exchange membranes for intermediate-temperature fuel cell systems would be the PVDF-HFP@[MIm][NTf$_2$] membranes, since they are not porous and have mechanical strength, thermal stability and high conductivity (even in the absence of moisture). On the other hand, the use of the PVDF-HFP@[MIm][Cl] membranes for this type of application is ruled out due to its high porosity, lower conductivity and poor thermal stability.

Moreover, due to the different properties of the samples, they can be used in other applications. For instance, the control of morphology and porosity of the sample can be used in gas separation applications or in the adsorption of gases. The increase in the percentage of electroactive β-phase when using certain ionic liquids is also interesting in piezoelectric sensors and actuators applications. In addition, the mechanical strength and thermal stability of the membranes, which are very good, suggest their viability for other applications.

A complete characterization of the obtained membranes was done. However, there is still a lot of work to do until the application of these membranes in devices such as fuel cells, since there are various aspects to be improved such as the mechanical strength or the conductivity of them. In collaboration with Tecnalia research center, we are already working on testing these membranes in fuel cells (PEMFCs) in order to analyze their efficiency. Moreover, it would be interesting to achieve an even higher conductivity, which would require the increase of the Ionic liquid content in the membranes or the test of other type of ionic liquids. Finally, it would be also interesting to continue analyzing how the morphology or the mechanical properties of the samples can be tailor with the type of ionic liquid and with the synthesis procedure since, as stated before, the wide range of different IL structures predicts a huge variety of different membrane structures.

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6. References

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