THICKNESS EFFECT ON MECHANICAL PROPIERTIES AND WATER LCOHOL UPTAKE IN DIRECT ETHANOL FUEL CELLS MEMBRANES

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Abstract: The mechanical properties of polybezimidazole (PBI) or modified PBI membranes, possible candidates to replace Nafion as proton exchange membranes in direct methanol fuel cells (DMFC) were studied. Phosphoric acid-doped membranes based in poly [2,5- benzimidazole] (ABPBI) were obtained by high temperature casting from methanesulphonic acid and by a new low temperature casting procedure. These membranes were studied in relation with their phosphoric acid doping level by measuring the free and bonded acid. The elastic moduli of these membranes, doped and undoped, were determined using the force spectroscopy AFM technique and compared with those determined for doped and undoped PBI (poly [2-2´-(m-fenylene)-5-5´ bibenzimidazole]) and for Nafion membranes. The water isotherms were also determined for the low and high temperature casted ABPBI membranes. It is found that a simple empirical isoterm described the water sorption of these membranes all over the water activity range (0.15 < aw < 1). Keywords: Polybenzimidazole; Nafion, Membranes, Water uptake, Elastic modulus, Acid doping,; Fuel cells.

1. INTRODUCTION

Hydrogen fed proton exchange membrane (PEM) fuel cells and direct methanol PEM fuel cells (DMPEM) fed with liquid methanol use Nafion®, a perfluorosulfonated ionomer, as electrolyte membrane (Hogarth et al. 2002), and a number of Nafion® composites have been proposed as electrolytes for this type of fuel cells (Aricó et al, 1998, 2001, 2003, 2004 and 2005; and Yang et al, 2004). Due to the dehydration that occurs at temperatures higher than 100°C and methanol crossover problem associated with the high permeability of methanol through Nafion®, that significantly lowers the electrochemical efficiency of DMPEM fuel cells, a number of alternative ionomeric materials are being tested (Jannasch, 2003). Among these materials are sulfonated polyarylene sulfones (Wang, 2002 and Lafitte ET al., 2002), polyphosphazene (Zhou et al. 2003), poly [2-2´-(m-fenylene)-5-5´ bibenzimidazole] (PBI, Celazole®) (Wainright et al, 1995), poly [2,5-benzimidazole] (ABPBI) (Asencio, 2002), and composite materials of these polymers with inorganic fillers (Aricó et al., 2002; Alberti et al., 2003 and Jang et al., 2005), whose chemical structure, along with that of PBI is shown in Fig. 1. Polybenzimidazoles are among the most promising material for DMPEM and high temperature PEM fuel cells. Commercial PBI (Celazole®) is a neutral polymer that becomes an acceptable Grotthuss proton conductor by acid doping, commonly with H3PO4. The interest in this membrane polymer is based on its high oxidative and thermal stability (Samms et al., 1996) and low methanol crossover (Wang et al.,1996). The properties of PBI membranes relevant to its use in fuel cells, such as proton conductivity, methanol crossover rate and water drag factor, have been extensively studied during the last decade and Li et al. (Li et al., 1996) have recently reviewed their properties as isolated membranes and in fuel cell tests. The proton conductivity of PBI is reported to exceed the operative range of mobile and stationary applications (0.05 S.cm-1) only above 150 oC (Kerres, 2001 and Li et al., 2004) and to improve the performance higher levels of acid doping are need, with a detrimental effect on the membrane mechanical properties(Li et al, 2004 and Carollo et al. 2006). In order to overcome this problem the inclusion of inorganic fillers and heteropolyacids, as reviewed recently by Carollo et al. (2006), or new in situ doping during casting techniques (Xiao et al., 2005) have been proposed. In addition to a suitable ionic conductivity and water/methanol sorption and transport properties, a membrane for DMFC should exhibit good mechanical strength in order to maintain its integrity during the fuel cell assembling and stack construction and to assure durability, especially under high temperature operation. In spite of that, there is a lack of information on the mechanical properties of PBI based membranes. There are several parameters than can be used to describe the mechanical behavior of a polymer (Sperling et al. 1992), but the important one for fuel cell applications is the Young´s modulus which account for the stiffness of the material, that is, the resistence of the material to be stretched or compressed. Because the membranes used in DMFC can be small in thickness (few microns) and the interphase mechanical properties of the polymers could be different from the bulk ones, the nano-indentation technique is one of the techniques that adapt to analyze these systems in a representative scale (Hodzic et al. 1999 and 2001).

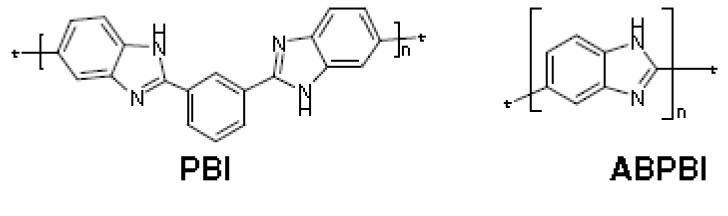


Figure 1

Here we use the atomic force microscopy (AFM) to measure the local elastic propertiesb of polymeric membranes by force spectroscopy, that is, through the relation between loading force and indentation when the AFM tip indents the membrane surface. The model developed by Stark et al.(1998) is used to obtain Young´s modulus from the linear part of the force curves.

2. EXPERIMENTAL

2.1 Membrane preparation

The Nafion membrane was a commercial Nafion 117 (Du Pont) with a thickness of around 170 µm. PBI powder (Goodfellow) was disolved in N,N-dimethylacetamid (DMA) at 70°C under stirring. PBI solution (5 wt %in DMA) was poured in a glass mold and put in a vacuum furnace at 80 °C during 4 hours in order to cast a membrane of thickness ranging from 50 µm to 150 µm. The resulting membrane was immersed in 68.8 wt % H3PO4 (10.64 M) at less 72 hours prior to use in order to protonate the imidazole ring. ABPBI was prepared by condensation of 3,4-diaminobenzoic acid (DABA) monomer in polyphosphoric acid (PPA) following the procedure reported by Gómez Romero and coworkers (2005). The resulting polymer was condensed in water, grinded, and washed with water. Then it was immersed in stirred aqueous 10 wt % NaOH during 20 hours in order to eliminate remaining polyphosphoric acid and then washed until neutral pH was attained.
Finally it was dried at 90 °C. High temperature casting ABPBI membranes were made by pouring a 5 wt % solution of ABPBI in pure methanesulphonic on a glass plate kept at about 200 °C over a heating plate inside a ventilated hood. After several hours the solvent was eliminated and the plate was immersed in water to separate the membrane. For ABPBI low temperature casting membrane preparation, a solution of 1 wt % ABPBI in formic acid was poured in a Teflon mold and the formic acid was evaporated overnight in a ventilated hood at room temperature. Then, the membrane could be easily separated from the mold. All the ABPBI membranes were doped in 10.64 M H3PO4 for 72 hours to protonate the imidazole ring.

2.2 Molecular weight measurements

The molecular weight of polybenzimidazole polymers was estimated by viscosity measurements of solutions in concentrated H2SO4 (96%). The intrinsic viscosity, [h], is defined as:

$$[\eta] = \lim_{c \to 0}\left(\frac{\ln t/t_0}{c}\right) \tag{1}$$

where c is polymer concentration in the sulfuric acid solution, in g dl-1 , t is the flow time of the polymer solution of concentration c and t0 is the flow time of 96 wt % H2SO4 . A Cannon – Fenske 150 viscosimeter was employed in the viscosity measurements. Polymer solutions of concentrations 3, 4 and 5 g.dm-3 were prepared and left several days until complete dissolution. The value of the extrapolated intrinsic viscosity at 30 °C was 2.35 dl g-1 for ABPBI, and was used to estimate the polymer molecular weight, Mw, resorting to the Mark – Houwink equation (Sperling, 1992),

$$[\eta] = KD_p^{\,a} \tag{2}$$

where Dp is the degree of polymerization and the constants K and a for ABPBI are 8.7x10-3 and 1.10, respectively (Asencio et al., 2005). The averaged molecular weight of the polymer can be calculated from the known molecular weight of the monomer unit (Mm= 116 g.mol-1), using the relationship Dp=Mw/Mp. The result, Mp = 18800 is 20% lower to that reported by Asensio et al.(2004) and approximately a half of that reported for ABPBI by Carollo et al. (2006), but the degree of polymerization is high enough for casting membranes with good mechanical stability. The value of the extrapolated intrinsic viscosity at 30ºC was 0,482 dl g-1 for PBI, and was used to estimate the polymer molecular weight, Mp, resorting to the Mark – Houwink – Sakurada equation (Bjerrum et al. 2006),

$$[\eta] = K_1 M_p^{\alpha} \tag{3}$$

where and the constants K1 and a for PBI are 1.94x10-4 and 0.791, respectively (Bjerrum ET al. 2006). The result, Mp = 19600 is somewhat lower to that reported by Bjerrum et al. (2006).

2.3 Acid doping level measurements

For acid doping level measurements, PBI and ABPBI membrane samples previously doped in 10.64 M aqueous H3PO4 were equilibrated at 25ºC by keeping the membranes in the vapor phase of 10.64 M aqueous H3PO4 in capped and sealed (Parafilm) polypropylene flasks termostatized, and were weighted periodically until a constant weight was obtained. Each membrane sample was then immersed in 0.1 M KCl at 25ºC and the initial pH of the solution was measured with a 682 Titroprocessor (Metrohm) using a combined pH glass electrode (Metrohm 6-0204-100) with N2 bubbling. The evolution of the pH was monitored as a function of time until a final pH value was reached. The difference between the final and initial pH allowed us to calculate the free acid content (not bonded to imidazole group) in the membrane. Afterwards, the solution with the membrane inside was titrated, drop by drop, with 0.1 M NaOH enabling enough time to neutralize the membrane bonded acid. The total tritration time was about 4 hours. Finally, the membrane sample was removed from the titration vessel, washed with water and dried at 130 ºC for 12 hours in order to obtain its dry weight. The total H3PO4 uptake was calculated from the volume of NaOH solution added between each of the two step pH jumps, corresponding to the equilibria:

$$H_2PO_4^- = HPO_4^{-2} + H^+ \tag{4}$$
$$HPO_4^{-2} = PO_4^{-3} + H^+ \tag{5}$$

The degree of acid doping, that is, the moles of acid per imidazol ring, was calculated as:

$$\lambda_a = \frac{VcM_m}{w_o} \tag{6}$$

where V is the averaged volume of NaOH solution added for the neutralization of the first and second protons in cm3, c is the NaOH concentration in mol cm-1, wo is the membrane dry weight in g and Mm is 116 g mol-1 for ABPBI, corresponding to the molecular weight of the monomer unit; and 142 g mol-1 for PBI, considering that 284 g mol-1 is the molecular weight of the monomer unit and there are two imidazol ring in each monomer unit of PBI. The free acid content, expressed as a fraction of total H3PO4 inside the membrane is calculated as:

$$\lambda_f = \frac{V(c - c_f)}{Vc} \tag{7}$$

$$c_f = 10^{pH_i - pH_f} \tag{8}$$

where pHi is the initial pH value and pHf is the final pH value reached after the membrane sample immersion in the 0.1 M KCl solution.

2.4 Water uptake measurements

The water uptake pf PBI and ABPBI doped membranes were measured in the relative humidity range from 0.15 to 1. The membrane samples were first equilibrated in vapor phase with H3PO4 10.64M in capped and sealed (Parafilm) polypropylene flasks thermostated at 25 °C and weighted daily until a constant weight was obtained. Then they were maintained in isopiestic equilibrium, suspended over saturated salt solutions, in capped and sealed vessels thermostatized at 30 °C, and weighted twice a day until constant weight was attained. In order to obtain the dry weight of membrane samples, they were washed several hours in boiling water until neutral pH to remove all the doping acid and finally dried at 130°C about 6 hours until constant weight was attained. The water content in doped membranes was expressed by means of two hydration numbers defined as lwa and lw, the first being the number of water molecules per molecule of acid, and the second the number of water molecules per imidazol ring. Thus, the acid based hydration number was calculated as,

$$\lambda_{wa} = \frac{w_w M_a}{w_a M_w} \tag{9}$$

where M_w and M_a are water and acid molecular weight, respectively; and w_w and w_a are the mass of water and acid in the membrane, respectively, calculated as:

$$w_w = w - w_o - w_a \tag{10}$$

$$w_a = VcM_a \tag{11}$$

being w the doped membrane mass. The dry polymer based water content, λ_w, was calculated as:

$$\lambda_w = \frac{w_w M_m}{w_o M_w} \tag{12}$$

where the symbols have the same meaning as before and Mm corresponds to the molecular weight of the monomer unit per imidazol ring (142 g mol-1 for PBI and 116 g mol-1 for ABPBI).All the reagents analytical grade were used as received N,N-dimethilacetamide (Merck), H3PO4 (Merck), H2O2 (Merck), H2SO4 (Baker Analized), NaOH (Merck), KCl (Merck), 3,4- diaminobenzoic acid, 97% (Aldrich), Polyphosphoric acid 85% (Aldrich), methanesulfonic acid 99.5+% (Aldrich) and methanol (J.T.Baker). Water was deionized and passed through a Millipore filter.

2.5 Membrane AFM images

The AFM images of the membranes were acquired using the tapping mode. The AFM parameters to obtain the images were carefully set to minimize the pressure of tip on the membrane fibers, and the silicon surface also could enhance the non-deformability of fibers against the tip pressure (D. Alliata et al, 1996). The commercial Si tip was used, which was an anisotropic geometry in shape with the nominal radius <10 nm, resonant frequency nominal of 300 kHz (315.27 kHz measured), a nominal spring constant of 40 N/m (36.50 N/m measured) (MPP-11100 – Veeco Probes – Santa Bárbara - California). Standard images were obtained over non-supported membranes prepared in the conditions they are used in fuel cells Membrane Electrode Asseblies (MEA). On the other hand, high resolution images of the polymer fibers were acquired in order to obtain structural data on the organization of the fibers in the membranes prepared by different casting procedures. In order to diminish the deformation by interaction with the tip, very thin membranes were formed over a silicon chip, having a very flat surface, employing diluted solutions (~1:5000) of the different polymers.

2.6 Force spectrometry measurement of local elastic properties

A commercial AFM was employed for the measurements (Veeco - DI Multimode Nanoscope IIIa) with 150 µm lateral scan range and a 5 µm z-scanner. The elasticity measurements were done with a Si3N4 tip with a spring constant of 0.46N/m (Nano Devices, Veeco Metrology, Santa Barbara, California, pyramidal tip shape, cone half angle a=18°, tip curvature radius r <10 nm, resonant frequency nominal: 57 kHz, measured: 47.50 kHz). For control experiments a stiff mica surface was employed before the measurements to assure the correct operation of the tip, and to verify a suitable spring constant. The setpoint was 60% of the free oscillation far away from the surface. All measures were carried out in a N2 atmosphere, and allowing to stabilize during 1 hour, to avoid the effect of the adsorbed water over the membranes surfaces. A series of force curves were obtained for each membrane in different positions in order to obtain representative data of the surface. To avoid structural damage of the membranes sample at the point of interest, the tip was first approached carefully to the sample surface. Then, the tip was retracted by adjusting the setpoint to the lowest possible value. Subsequently, the force curve measurements were performed in different points. This procedure was necessary to assesses changes in the shape of the force curves due to sample deterioration induced by the tip. For force curve acquisition the upper force limit was set to 75 nN. Before and after the measurements on each membrane, the sensor response was calibrated on the mica substrate. The z-approach speed was 1.74 µm/s

3. INDENTATION DATA ANALISYS

The indentation of an AFM tip fixed to a cantilever (spring constant k) into a soft sample (Young's modulus E, Poisson's ratio n) can be modeled using Hertzian contact mechanics (Hertz, 1882). This theory provides a very simple but direct approach to the material elasticity for a sample with a semi-infinite thickness. For an infinitely hard body indenting (indentation d) into an elastic half space with a normal force F this theory leads to:

$$F = \xi d^{m} \frac{E}{1-\nu^{2}} \qquad (13)$$

where x is a constant dependent on the tip geometry. The exponent m characterizes the indentation behavior. For the indentation of a sphere the exponent is m=3/2 (provided that d << sphere radius). A conical indenter with a half angle a leads to m=2. When the tip exerts a pressure on the sample, the force curve exhibits a certain slope, whose value depends on the stiffness of the sample. Considering the indentation d(z), the cantilever deflection, d (z), for soft samples becomes,

$$\delta(z) = \begin{cases} -(z - z_o) - d(z), & z < z_o \\ 0 & z \geq z_o \end{cases} \qquad (14)$$

where z_0 is the z piezo position when the tip hits the sample (contact point). The force curves on soft samples can be calculated directly from the Hertz model in Eq. (1). Assuming a cone as a model for the AFM tip, the cantilever deflection *vs.* indentation relation is,

$$d(z) = \left(k\delta(z) \frac{2}{\pi \tan\alpha} \frac{1-\nu^2}{E} \right)^{1/2} \qquad (15)$$

where $F(z)=k\delta(z)$ is the loading force, and k is the spring constant. Replacing Eq. (2) for the cantilever deflection in soft samples in Eq. (3), and solving the quadratic equation, the expression for the force curve on an elastic sample is

$$\delta(z) = \begin{cases} -(z - z_o) \pm \left[\frac{a^2}{K^2} - 2\frac{a}{K}(z - z_o) \right]^{1/2}, & z < z_o \\ 0 & z \geq z_o \end{cases} \qquad (16)$$

with $a = \frac{k}{\pi \tan\alpha}$, and $K = \frac{E}{1 - \nu^2}$.

It is important to consider that for a very thin sample, the deflection of the cantilever is influenced by the substrate, which restricts the validity of the model. To avoid this type of problems, sufficiently thick membranes were used, so that the influence of the substrate is considered null.

4. RESULTS AND DISCUSSION

4.1 Phosphoric acid uptake

The degree of acid dopping, la, of the membranes are summarized in Table 1, along with their free acid content, lf, and the acid based hydration number, lwa. These results correspond to membranes doped with doped in 10.64 M aqueous H3PO4 and in isopiestic equilibrium with the same acid solution at 25ºC (aw » 0.32).

Table 1. Doping degree (λ_a), free acid content (λ_f), and water content (λ_{wa}) at 25 ºC for PBI and ABPBI membranes doped in 10.64 M aqueous H_3PO_4.

Membrane	λ_a	λ_f	λ_{wa}
ABPBI – low T	3.5	0.098	1.4
ABPBI – high T	2.8 2.9^a	0.093	0.8
PBI	1.9 2.5^a 2.0^b	0.095	1.0 0.9^b

The phosphoric acid uptake in ABPBI membranes is higher than in PBI ones, when compare per imidazol ring. On the other hand the acid uptake of low T cast ABPBI membranes is higher than the acid uptake of the high T cast ABPBI membranes. The doping degree was compared with that reported for PBI and ABPBI (high T casting) by Asensio et al. (2004). It could be observed that the agreement is rather good taking into account the differences in the degree of polymerization. Also, a good agreement is found with the reported phosphoric acid and water content for PBI membranes reported by Lobato et al. (2006). Only a small fraction of the total up taken acid, about 10%, is not bonded to polymer imidazole groups. The calculated water molecule per phosphoric acid molecule is 0.8 for the high T cast ABPBI, in good agreement with the values found in PBI (see Table 1), while this number is almost double (1.4) for low T cast ABPBI. This excess of water linked with the doping acid in the case of the low T cast ABPBI membranes could only be related with the supramolecular packing of the ABPBI chains during the casting process, which probably yield to a less compact structures than that formed in the high T casting.

4.2 Water uptake

The water uptake of polymer membranes from vapour phase is of great importance, since water is involved in the electrode reactions and species transport mechanism through the fuel cell membrane. The water uptake of PBI and ABPBI (low and high T casting) doped membranes from vapor phase at 30 ºC, expressed as lw (Eq. (12)), and as m, the mass of water uptaked per 100 grams of dry membrane (ww/100wo), are summarized in Table 2 at different water activities. The sorption isotherms for water have the form of type III in the Brunauer classification (Brunauer et al., 2006), characteristic of weak interaction between adsorbate and surface. It is also observed that at water activity higher than 0.2 the water uptake by ABPBI membranes is higher than in PBI membranes, and ABPBI membranes cast at low T has higher water uptake than the membranes cast at high T, which is also consistent with the higher acid doping level in the low T cast membranes.

The water sorption of the doped PBI and ABPBI membranes is much higher than the corresponding to Nafion membranes in its protonated form. Weng et al.(1995) have shown that when equilibrated in 85% H3PO4, that is, at acid concentration close to that used for doping our membranes, acid taken up by the Nafion membrane is about two moles per sulfonic acid group, and the water sorption of the Nafion/H3PO4 membranes increases roughly a factor two as compared with Nafion. Because these measurements were performed at 125 oC we did not compare them with our measurements. As expected by the form of the isotherms, which clearly indicate that they are not of the BET type, we fail to fit these isotherms using this isotherm. Therefore, we analyzed the data using two alternative isotherms. First, the modified BET equation (Anderson, 1946) in its linear form,

$$\frac{a_w}{m(1-a_w)} = \frac{1}{m_0 C} - \frac{1}{m_0}\ln(1-a_w) \qquad (17)$$

where m = ww/100wo, mo is the mass of water in the monolayer per 100 grams of dry membrane, aw the water activity, and C a parameter related to the energy of the sorption. Secondly, we used the empirical isotherm proposed by Iglesias and Chirife (1978) to describe the sorption of water in high-sugar food:

$$\ln\left[m + (m^2 + m_{0.5})^{1/2}\right] = A + Ba_w \qquad (18)$$

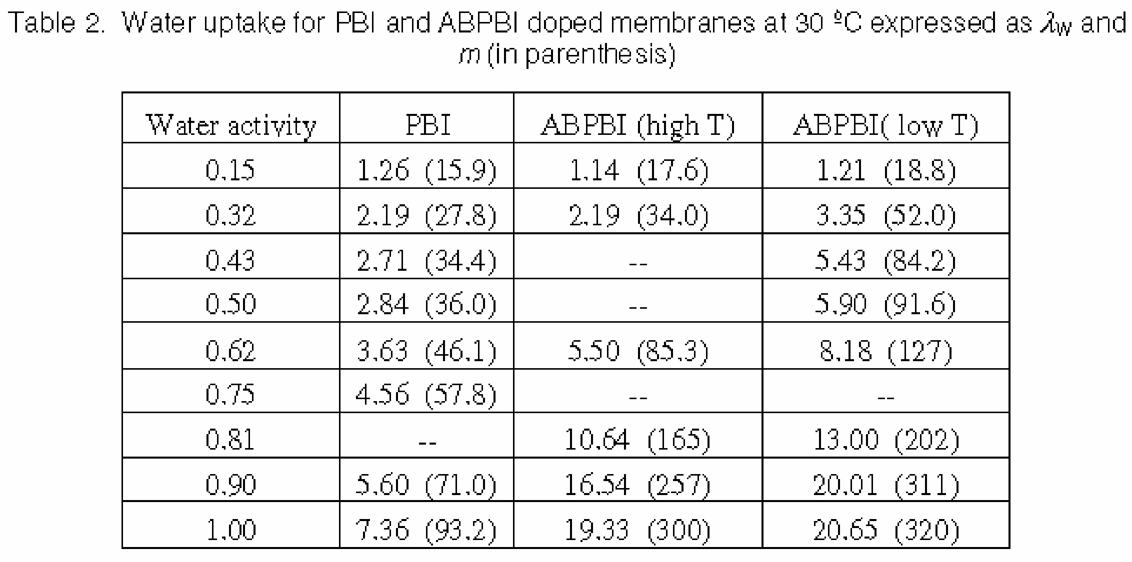


Table 2. Water uptake for PBI and ABPBI doped membranes at 30 ºC expressed as λ_W and m (in parenthesis)

Water activity	PBI	ABPBI (high T)	ABPBI(low T)
0.15	1.26 (15.9)	1.14 (17.6)	1.21 (18.8)
0.32	2.19 (27.8)	2.19 (34.0)	3.35 (52.0)
0.43	2.71 (34.4)	--	5.43 (84.2)
0.50	2.84 (36.0)	--	5.90 (91.6)
0.62	3.63 (46.1)	5.50 (85.3)	8.18 (127)
0.75	4.56 (57.8)	--	--
0.81	--	10.64 (165)	13.00 (202)
0.90	5.60 (71.0)	16.54 (257)	20.01 (311)
1.00	7.36 (93.2)	19.33 (300)	20.65 (320)

where the m0.5 represents the water sorption at aw= 0.5, A and B are empirical parameters. It can be observed that both equations describe reasonably well the experimental data on the entire range of water activities, being the standard deviation a slightly lower in the case of the isotherm given by Eq. (14). The parameters of this isotherm for the three membranes are summarized in Table 3. While the validity of Eq. (14) is restricted to 0.1 < aw < 0.8 in fruits and related products (Anderson, 1978), it was extended up to aw = 0.9 in the water sorption by polyaramide blend fabrics (Genç et al., 2006) and it was applied all over the water activity range in this work (0.15 < aw < 1.0) without any serious deterioration of its performance.

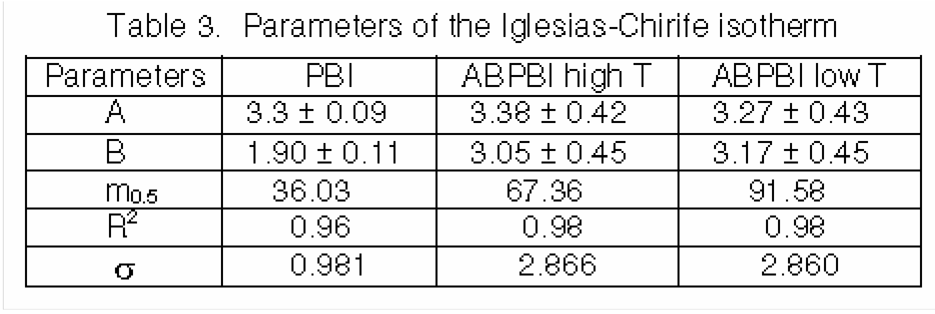


Table 3. Parameters of the Iglesias-Chirife isotherm

Parameters	PBI	ABPBI high T	ABPBI low T
A	3.3 ± 0.09	3.38 ± 0.42	3.27 ± 0.43
B	1.90 ± 0.11	3.05 ± 0.45	3.17 ± 0.45
$m_{0.5}$	36.03	67.36	91.58
R^2	0.96	0.98	0.98
σ	0.981	2.866	2.860

It is found that the water uptake for the PBI membrane doped with 1.95 moles of acid per imidazole group (3.9 moles of acid per monomer unit) shows higher water uptake that the reported by these authors for doping grades between 1.7 and 5.7 moles of acid per monomer unit in the range 0.4 < aw < 0.8. However, at aw close to 0.9 the water uptake seems to follow the expected trend. The observed behavior could be due to differences in membrane properties such as polymer molecular weight and / or undoped membrane pre-treatment.

4.3 High Resolution AFM Images

In Fig. 2 (a-c), a big difference is observed in the thickness of the membrane fibers depending of the casting method used to prepare them. In the case of LT-ABPBI (Fig. 2a), the fibers are around 25nm in diameter, while in the HT-ABPBI (Fig. 2b), the polymer fibers seems to form bunches of around 200nm. This morphology differences could explain not only the different behavior in mechanical properties of the membranes, but also, differences in methanol crossover, water (and H3PO4) sorption, proton conductivity, etc., which are fundamental factors for his utilization in fuel cells. Water uptake in ABPBI membranes shows that the LT-ABPBI absorbs more water (and H3PO4) than HT-ABPBI. This can be explain considering that larger inter-fiber spaces exist among the smaller fibers in LT-ABPBI as compared to HT-ABPBI, consequently, a bigger number of fibers are exposed to water. In the case of PBI (Fig. 2c), it can be seen that the fibers have a diameter of around 40nm, and they are much more knotted than in ABPBI, which could originate some of the differences between PBI and ABPBI (LT and HT), respect to water and acid sorption, young's modulus, etc.

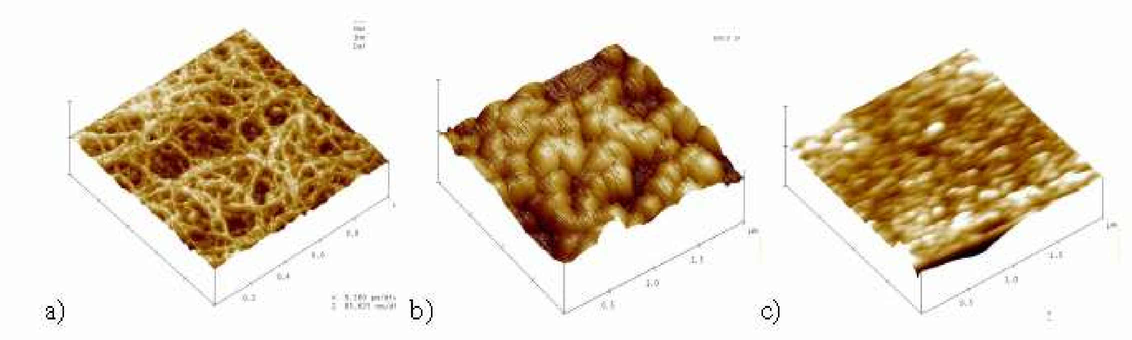


Figure 2

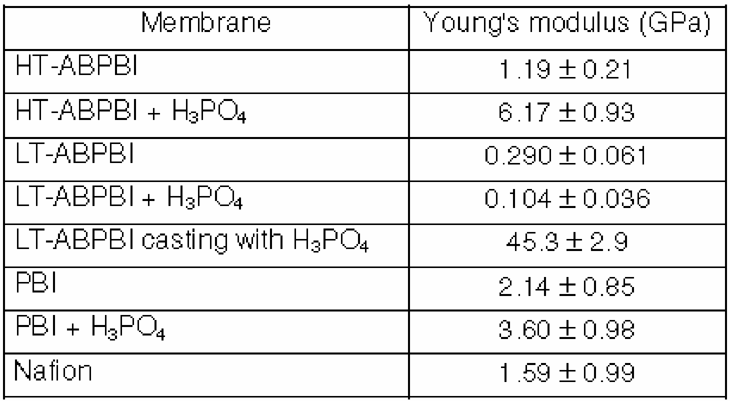
4.4 Normal resolution images

It can be seen that all the membranes have similar Root Mean Square (RMS). Both, LTand HT-ABPBI, exhibit larger roughness when doped. This behavior seems to be strongly dependent on the casting method employed. In the case of the LT-ABPBI the doped membrane has higher RMS that the undoped membrane and the roughness is even larger when the casting was performed in the presence of H3PO4. This could indicate that the roughness of the membrane depends on the uptake of H3PO4, which is expected to be larger for the membrane whose casting was realized in the presence of H3PO4 than for the LTABPBI membranes doped after the casting. The HT-ABPBI presents a dramatic change in RMS upon doping, very different with the LT-ABPBI behavior. This difference can be explained considering the differences of the fiber thickness mentioned above. In the case of the PBI membrane, the roughness falls on doping is remarkable, this could be due to the differences in the conformation of fibers with respect to ABPBI (HT and LT) that can be seen in the Fig. 2.

4.5 Young's modulus measurent by force spectrometry analysis

All indentation experiments can be described by the mechanical contact theory (Eq. 4) and the indentations deeps were shorter than 120nm. The values of Young's modulus obtained are presented in Table 4, each with their respective uncertainty. The Young's modulus for LT-ABPBI membranes casted in the presence of H3PO4, is significantly higher that doped and undoped LT-ABPBI membranes, probably as a result of the higher inter-molecular interactions mentioned above. The Young's modulus decreases when doped with phosphoric acid for LT-ABPBI membranes, but increases for HT-ABPBI and PBI membranes. These results agree with the behavior observed in the laboratory when the casted membranes are handled. A hypothesis that would account for these findings requires to consider two opposite effects; first, the increase in the size of the fiber by the incorporation of acid, which diminishes the packing of fibers in polymer; and second, the increase of the packaging by increase of the interactions between fibers due to doping. It is important to consider that the LT-ABPBI (before and after being doped) presents much more water absorption (and of acid) that the other membranes that were studied, which is an effect that supports the theory indicated above.

Table 4. Young's modulus of the studied membranes



Membrane	Young's modulus (GPa)
HT-ABPBI	1.19 ± 0.21
HT-ABPBI + H_3PO_4	6.17 ± 0.93
LT-ABPBI	0.290 ± 0.061
LT-ABPBI + H_3PO_4	0.104 ± 0.036
LT-ABPBI casting with H_3PO_4	45.3 ± 2.9
PBI	2.14 ± 0.85
PBI + H_3PO_4	3.60 ± 0.98
Nafion	1.59 ± 0.99

The roughness differences mentioned before between PBI, ABPBI (LT and HT) could be, in principle, an explanation of the differences presented in terms of elasticity, and the fact that the Young's modulus of the LT-ABPBI whose casting was realized in the presence of H3PO4 is about 100 times greater than the LT-ABPBI with doped subsequent to casting; if we considered that when being all the doped fibers, the forces of interaction between fibers would be higher and these would pack more, giving like result membranes more rigid.

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