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Highlights

1. The effect of weight ratio of Chitosan (CH) to Pectin (PEC) is studied.
2. The methanol permeability of CH/PEC membranes decreases with the amount of Pectin.
3. Proton conductivities of CH/PEC membranes decrease until a ratio composition of 1:1.
4. DSC studies reveal excision of ionic pairs between carboxylic and ammonium groups.
5. Proton diffusion coefficients decrease one order of magnitude in CH/PEC membranes.

Influence of Pectin as a green polymer electrolyte on the transport properties of Chitosan-Pectin membranes.

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ABSTRACT

Novel blend membranes have been prepared from Chitosan (CH), Pectin (PEC) and their mixtures. The obtained samples were cross-linked and sulfonated before characterization. The results show that CH/PEC membranes display structural changes on the chemical and physical properties as a function of composition. DSC analysis reveals an endothermic peak due to the scission of the ionic pairs between carboxylic groups and ammonium groups, which produces a strong change on physical properties such as methanol permeability and proton conductivity. The methanol permeability decreases with the amount of Pectin from $(4.24 \pm 0.04) \times 10^{-6}$ cm²/s for pure Chitosan membrane to $(1.51 \pm 0.03) \times 10^{-6}$ cm²/s for blend CH/PEC membranes when the amount of Pectin is 50% (v/v). The proton conductivities of the blend membranes follow a similar behavior. For a pure CH membrane the conductivity is 2.44×10^{-3} S/cm, decreasing with pectin content until the composition 50/50 (v/v), in which the conductivity drops almost one order of magnitude.

Keywords: Biopolymeric membranes; polymer electrolyte membranes (PEM); methanol permeability; proton conductivity; differential scanning calorimetry (DSC); electrochemical techniques.

1. Introduction

The potential applications of biomaterials are numerous and involve different fields such as fibers for the textile industry, medical products, cosmetics, bioimplant, delivery of drugs, herbicides, fungicides, and so on. One of the most promising approaches to overcome the safety and environmental problems is the use of renewable resources for obtaining biodegradable polymers useful for various applications in medical, pharmaceutical, agriculture, drug release, and packaging fields. Pectin (PEC) is a structural component of the vegetal cell wall, typically isolated from plants of economic importance (citrus, sugar beet, apple, etc.). It is composed of an anionic complex polysaccharide based on chains of linear regions of (1 → 4)- α -D-galacturonosyl units and their methyl esters, interrupted in places by (1 → 2)- α -L-rhamnopyranosyl units. Fractions of these rhamnopyranosyl residues are branch points for neutral sugar side chains of (1 → 5)- α -L-arabinofuranosyl or (1 → 4)- β -D-galactopyranosyl residues (Shols & Voragen, 1994a; Shols & Voragen, 1994b). The pectin has a low cost because of their abundance in nature (Cavallaro, Donato, Lazzara, & Milioto, 2011; Pérez Espitia, Du, Avena-Bustillos, Ferreira Soares, & McHugh, 2014; Meneguín, Cury, & Evangelista, 2014). On the other hand, Chitosan (CH) is a linear copolysaccharide β -(1 → 4)-2-amine-2-deoxy-d-glucose (GlcNac) and β -(1 → 4)-2-acetamine-2-deoxy-d-glucose (GlcN). It is biodegradable, non-toxic, bio-compatible, and renewable (Croisier & Jérôme, 2013; Sevel, İkinci, & Kas, 2000; Kaminski & Modrzejewska, 1997). Also, it can be easily modified and has a noticeable ability to form many complexes with metal ions and enzymes (Schmuhl, Krieg, & Keizer, 2001; Khor, 1997). In addition to its many uses in food and agricultural applications, CH exhibits the ability to form films. In the last years CH membranes has emerged as a new alternative to get membranes with high ionic conductivity at low and moderate temperatures when the membrane is

completely or partially hydrated (Wan et al., 2003; Kordesch & Simader, 1996). Chitosan membranes or hybrid Chitosan membranes can be used for an alkaline fuel cell (AFC). The presence of polar groups on Chitosan backbone (hydroxyl and amino groups) gives a high hydrophilic character, which is a very important property for a fuel cell (Krajewska, 2001; Zawodzinski et al., 1993). The use of this kind of membranes as polymer electrolyte in a fuel cell has showed, operating at 60°C, a good performance through polarization curves (voltage-current density and power-current density). High current density values up to 35mA/cm² in a PEMFC were determined by using hydrogen as feed into the anode and air as the oxidant in the cathode (Wan et al., 2003). Further studies (Wan et al., 2006), chitosan-based composite membranes were prepared by incorporating KOH as the functional ionic source. The main problem was to hold the KOH permanently inside the composite membrane avoiding the leaching of the bulk KOH into the polymeric matrix. Nevertheless, these composite membranes achieved conductivity values up to 10⁻² S cm⁻¹ after being hydrated for 1 h at room temperature.

Microbial fuel cell (MFC) is a promising technology for wastewater treatment as well as a way to recover energy. Various polymer membranes have been developed to facilitate proton transfer between anode and cathode in MFCs (Seol et al., 2012; Chae et al., 2008; Shaari & Kamarudin, 2015). Chitosan is a cheap and environmental-friendly natural biopolymer, which is considered quite promising for its use as a polymer electrolyte in MFCs (Smitha, Sridhar, & Khan, 2004). For these reasons, the physical and chemical structure of CH must be modified to allow its use as a viable polymer electrolyte membrane (Ma & Sajhai, 2013; Tripathi & Shadi, 2011; Holder, Lee, Popuri, & Zhuang, 2016).

Blend, composites and multilayer films of PEC and CH with improved mechanical and barrier properties have been previously described (De Yao et al., 1996; Hiorth, Tho, &

Arne, 2003; Hoagland & Parris, 1996; Sriamornsak & Puttipipatkachorn, 2004; Milkova & Radeva, 2015; Pasini Cabello, Takara, Marchese, & Ochoa, 2015). However, at the best of our knowledge there is not any report on CH/PEC films functionalized with $-\text{SO}_3\text{H}$. In this paper we examine the effect of the weight ratio of CH to PEC followed by chemical functionalization on key transport properties such as methanol permeability and membrane conductivity. Also, in order to reveal the structure of films an approach based on FTIR spectroscopy and DSC analysis were performed. Water uptake, mechanical properties and ion exchange capacity were also determined.

2. Experimental

2.1 Materials

Pectin from Citrus Fruits (CAS 9000-69- degree of methyl esterification, 6.7%, MW = 30 - 100 kg mol⁻¹) was purchased from Sigma-Aldrich (Denmark). A commercial sample of CH powder with an average molecular weight 890KDa (based on viscosity) and approximately 75% deacetylation, was supplied by Sigma-Aldrich. Glutaraldehyde commercialized as 25% Grade II was purchased from Sigma-Aldrich (St. Louis, MO, USA). Glycerol, acetone, H₃PO₄, NaOH, NaCl, HCl, isopropanol and ethanol were provided by BioPack (Campana, Argentina). All solutions were prepared with Milli-Q water (resistivity < 1.8 mΩ cm). 4-formyl- 1.3-benzenedisulfonic acid disodium salt was supplied by Aldrich.

2.2 Preparation of the blend membrane

The films made of Chitosan and Pectin and mixtures thereof were obtained by casting. For this, two neat polymer solutions containing CH or PEC, with a mass fraction of 2% (w/v) were prepared in distilled water containing Phosphoric Acid, 1% (v/v) at 40 °C.

With appropriate amounts of each solution, mixtures of different ratios were prepared in order to obtain films named CH/PEC 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100, respectively. 0.5% w/v of Glycerol used as plasticizer, was added to polymer solutions. Film forming solutions were cast in Petri dishes (14.5 cm internal diameter) and dried in an oven at 35°C for 48 h. After that, the films were cross-linked for 24 hours in a room temperature bath consisting of 50 mL of acetone solution containing 5% (w/v) glutaraldehyde and 1% (w/v) HCl at 25°C. Finally, the films were washed with ethanol and water. Film preparation was carried out in triplicate.

2.3. Chemical functionalization

In order to improve the ionic conductivity, sulfonic groups were added following the same procedure reported elsewhere (Mollá & Compañ, 2011). Membranes were immersed in a bath isopropanol/water (70/30 v/v) containing 0.04M 4-formyl- 1,3-benzenedisulfonic acid disodium salt and 0.1M HCl for 2 h at 50°C. Then, several washes of membranes were carried out with 0.3M HCl solution isopropanol/water (70/30 v/v) in order to eliminate possible residual sodium ions. After that, the membranes were dried at 50° C.

2.4 Chemical stability of the membranes

Vapor phase Fenton test has been developed to determine the membrane degradation as an *ex situ* accelerated test method (Delaney & Liu, 2007). Previously doped membranes with 2 ppm of aqueous solution of FeSO₄ were vacuum dried and weighted. Then using a chamber similar to reported by Delaney & Liu, 2007, samples were suspended and hydrogen peroxide added (3%) and the temperature was increased up to 80 degrees centigrade using heating tape which was wrapped around the chamber. After test period,

the chamber was allowed to reach ambient temperature and the samples were removed, dried and weighted again to determine weight loss.

3. Membranes characterization

3.1. Ionic exchange capacity (IEC)

The membranes were kept in contact with a 0.1 M HCl aqueous solution overnight. The acidic membranes obtained were further washed several times with distilled water and then equilibrated with a 1 M sodium chloride solution. The protons delivered after the ion-exchange reaction, were titrated with a 0.01 M sodium hydroxide solution. IEC was expressed as meq. H⁺ g⁻¹ of dry membrane.

3.2. Water uptake

Water uptake of the CH/PEC membranes was measured by drying H⁺-form samples in a vacuum and then weighed (W_s). For this the blend membranes were immersed in distilled deionized water overnight. After that, the membranes were removed from water, gently blotted with filter paper to remove excess surface water, and then weighed again (W_w). This operation was repeated five times. Water uptake was calculated from the difference between the weight of the blend wet and dry, by means of the expression (1). The value of water uptake was averaged from three similar membranes and the results referred to the wet membrane are given in Table 1.

$$\% \text{ Water uptake} = \left(\frac{W_w - W_s}{W_w} \right) \cdot 100 \quad (1)$$

3.3. Mechanical properties

Tensile tests of the synthesized films were performed at room temperature using a Comten Industries (Series 94 VC) device (Pinellas Park, Tampa FL, USA). Films were cut into strips with a width of 1.1 cm and length of 4.0 cm. To ensure complete relaxation of the polymeric structures and to standardize the experimental procedure, film samples were stored in a humidity- and temperature-controlled chamber for 24 h at 25°C and 75% R.H. Then, the polymeric strips were fixed between upper and lower clamps of the tensile tester and the tensile strength was determined at a constant traction speed of 5 mm/min. The mechanical parameter data include the average values from three samples of each film. The film thickness was measured using a Köfer micrometer with a precision of $\pm 1\mu\text{m}$.

3.4. Differential scanning calorimetry (DSC)

The DSC curves were obtained at 10 K/min under a nitrogen atmosphere (Melter Toledo DSC 831). Two scans were performed with each sample, being the first from -50°C to 80°C in order to remove the thermal history of the samples, and the second from -50°C to 250°C.

3.5. Methanol permeability

In order to determine the methanol permeability coefficient through the blend membranes, a typical 2-cell experimental set-up was used such as shown in a previous paper (Mollá & Compañ, 2011), where the donor chamber was filled with 2M aqueous solution of methanol, while the receptor chamber was filled with distilled water, both chambers were kept under stirring and thermostated at 50°C.

As it has been described elsewhere (Mollá & Compañ, 2015), the variation of methanol concentration with time in the receiver reservoir (C_B) was determined by means of a

densimeter (DMA-4500M). Previously, a calibration curve of the density versus methanol concentration was obtained. During those experiments, a small sample of solution from the receiver compartment was taken at certain time intervals and the density recorded. In order to avoid that the volume of liquid in the receiver reservoir (V_B) change, samples were recovered from the densimeter after each measurement. Representing the normalized methanol concentration $(C_B L V_B)/(AC_A)$ vs. time, the apparent permeability coefficient (P) of the methanol across the polymer electrolyte membranes can be determined, by mean of the expression (2)

$$C_B = \frac{P \cdot A}{L \cdot V_B} C_A \cdot t \quad (2)$$

3.6. Membrane conductivity

The conductivity of the blend membranes were measured by electrochemical impedance spectroscopy (EIS) at different temperatures, in the frequency range $10^{-1} < f < 10^6$ Hz. The experiments were performed with 0.1V amplitude, using a Novocontrol broadband dielectric Spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface. The membranes were previously equilibrated with deionized water (Milli-Q) and afterwards placed between two gold electrodes in a parallel plate liquid sample cell (BDS 1308, Novocontrol) coupled to the spectrometer. During the measurements the temperature was maintained below isothermal conditions, controlled by a nitrogen jet QUATRO from Novocontrol with a temperature error of ≈ 0.1 K during every single sweep in frequency. To obtain the conductivity of the membranes four runs were carried out. The value of the conductivity was obtained by taking the average of the four measurements and the uncertainty was the SD from the mean value.

4. Results and discussion

4.1. Water uptake and ionic exchange capacity

In general the conductivity of acidic membranes depends on the water uptake and the Ionic Exchange Capacity (IEC) of the membranes. The IEC represents the density of sulfonic acid groups into the neat and blend membranes whereas water uptake is indicative of membrane hydrophilicity. Values of the water uptake and the IEC obtained for all the studied membranes are given in Table 1. The results obtained for water uptake show that this parameter is very dependent on the amount of CH. For example, CH20/PEC80, the water uptake decreases about 80% from the value of neat Chitosan membrane while is about 60% for CH50/PEC50. It is very noticeably that blend membranes have lower water uptake than neat Chitosan and Pectin membranes. The ionic exchange capacity (IEC) decreases from 0.37 meq/g for pure Chitosan (CH/PEC 100/00) until 0.09 meq/g when the amount of Pectin is 50%. From the values given in Table 1 it can be seen that the IEC of neat membranes CH100/PEC00 and CH00/PEC100 are higher than blend membranes.

Table 1. Water uptake and ionic exchange capacity (IEC) for the CH/PEC membranes.

Membrane	Water uptake (%)	IEC (meq g ⁻¹)
CH100/PEC00	249±4	0.37±0.01
CH80/ PEC20	172±9	0.31±0.01
CH60/ PEC 40	141±7	0.26±0.1
CH50/ PEC50	91±5	0.09±0.01
CH40/ PEC 60	56±3	0.20±0.01

CH20/ PEC80	48±3	0.30±0.01
CH00/ PEC100	149±9	0.36±0.01

The change observed in the ionic exchange capacity and water uptake of the blend membranes can be related with the formation of an ionic complex or ion pair between the carboxyl groups of PEC and the ammonium groups of CH. In neat biopolymer membranes interstitial clusters are formed, which can lead to increase of the number of ionic carriers into the matrix of the membrane. Unlike neat membranes, blend membranes show that the number of ion carriers has been reduced due to the formation of the previously cited ionic complex between CH and PEC. Thus, membranes with lower IEC and water uptake values were obtained.

4.2. Mechanical properties

Static tensile strength tests were carried out at room temperature following the experimental procedure described above. The experimental results are gathered in Table 2.

Table 2. Membrane thickness, mechanical parameters, strain at yield point ε_y (%), ultimate tensile strength σ_{ult} , and Young's modulus E measured at ambient temperature. Also, in the last column the methanol apparent permeabilities of prepared membranes measured at 50°C are informed.

%Chitosan	L(μm)	E (MPa)	ε_y (%)	σ_{ult} (MPa)	$P \times 10^6$ (cm^2/s)
100	395±2	7.2±0.4	4.9±0.6	28.7±1.1	4.24±0.04
80	277±2	7.4±0.5	7.7±0.8	29.3±0.7	3.26±0.06

60	219±2	7.6±0.3	13.8±2.2	30.3±1.5	2.29±0.02
50	222±2	5.6±0.2	6.3±1.3	34.6±1.0	1.51±0.02
40	182±2	5.5±0.1	4.4±0.7	21.7±1.8	2.33±0.06
20	193±2	5.3±0.8	1.8±0.8	19.5±1.9	3.10±0.05
0	257±2	3.9±0.8	10.2±1.9	18.6±1.7	3.90±0.04

From this Table it can be seen that the increase of pectin content in blend membranes produce changes in the mechanical properties. This could be related to the formation of the ion pair. This interaction favors the increase in the yield strength ($\epsilon(\%)$) in CH80/PEC20, CH60/PEC40 and CH50/PEC50 respect to CH100/PEC00, which can be related to the electrostatic attraction between CH-PEC polymers that form the polymeric matrix. This attraction tends to recompose the matrix to its original form before fracture. The formation of ion pairs produces an increase in the ultimate tensile strength until the amount of Chitosan/Pectin is the same (1:1). However the Young modulus increased while the amount of Chitosan decreased in CH100/PEC00, CH80/PEC20 and CH60/PEC40. For pectin concentrated membranes, the Young modulus decreased from 7.6MPa (CH60/PEC40) to 3.9MPa for neat Pectin membranes. From these results we think that membrane of CH60/PEC40 has the best mechanical properties to be used as sustainable membrane in green chemistry applications. A comparison with Chitosan membranes with both high degree of deacetylation and molecular weight reported by Wan et al., 2003 can be done. The prepared membranes reported in this work have a tensile strength and breaking elongation slightly smaller than reported by Wan et. al., 2003. The difference can be addressed to the MW and deacetylation degree values of Chitosan used. In our work, we use a Chitosan with medium MW and lower DD. Both

parameters affect the crystalline regions in CH based membranes, which determine the observed mechanical properties.

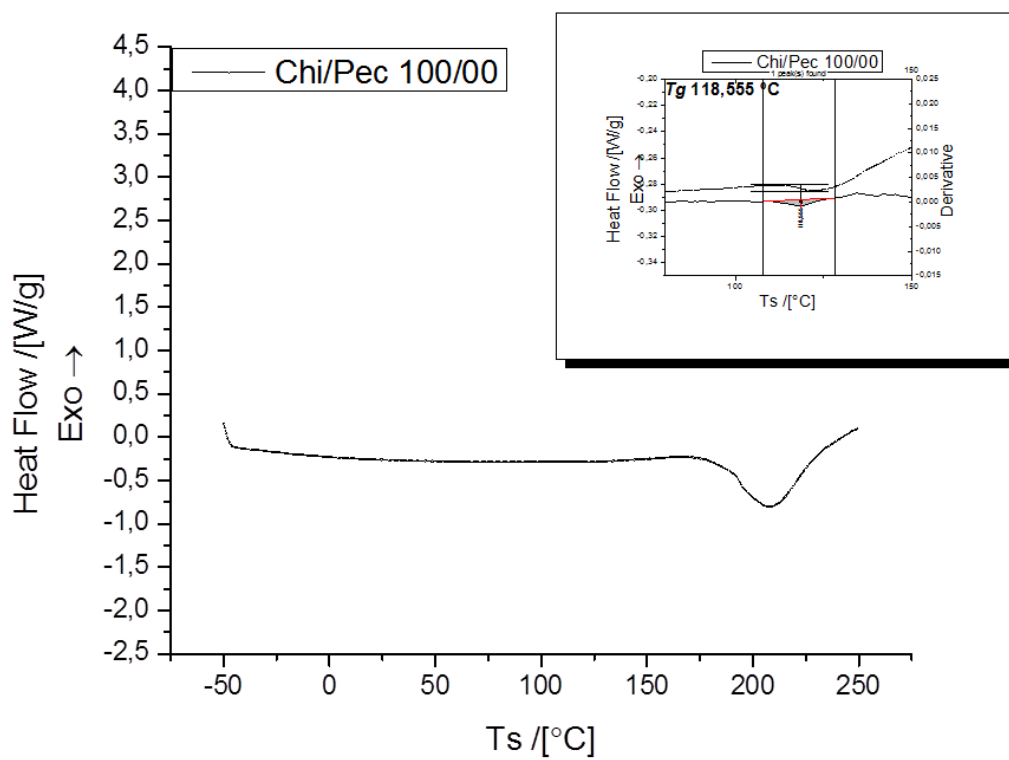
Holder et. al. 2016 have reported Sorbitol-Chitosan (S-CS) membranes and phosphorylated-Chitosan membranes (CS-P) for Microbial Fuel Cell. S-CS membranes had poor mechanical properties. Our membranes have a tensile strength 100 times higher when the amount of pectin ranges between 20-40%. On the other hand, CH/PEC membranes have a tensile strength 60% smaller than CS-P with an elongation between 3 and 5 times smaller.

4.3. Differential scanning calorimetry (DSC)

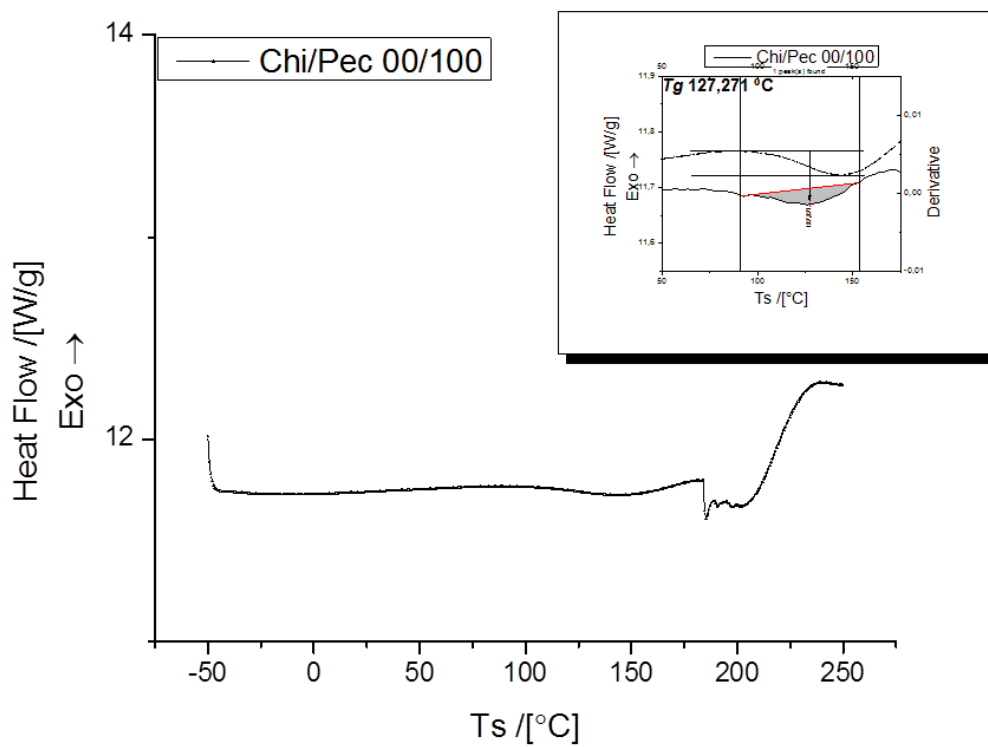
DSC thermograms of sulfonated CH/PEC membranes with compositions 100/00, 60/40, 50/50, 40/60 and 00/100 are shown in Figures 1a, 1b and 1c. CH/PEC 100/00 presents the typical Tg(I) and Tg(II) endothermic trials as it has been reported when the second scan is performed (Mucha & Pawlak, 2005). Tg(I) at 118°C refers to water-plasticized chitosan macromolecules. Tg(II) at ~ 190°C is attributed to unplasticized chitosan macromolecules. As Mucha & Pawlak have pointed out, referred to Tg (II), this event is a broad jump at 170-220°C, which can be recognized as their Tg, reflecting the increase of molecular movement due to dissociation of hydrogen bonds and to start of molecular chain scissions. However, those researchers have performed their analysis with uncrosslinked chitosan. Other researchers (Neto et al., 2005; Thacharodi & Panduranga, 1993; Jen & Wen, 2011) have addressed the endothermic peak circa 170°C to the glutaraldehyde use as a crosslinking agent. They informed that there were only endothermic events at 168°C using a single scan. The authors suggested that glutaraldehyde can react with amine groups of chitosan. Thus, water molecules will be bound to hydroxyl groups instead of amino groups, which are less electronegative than

hydroxyl ones. Therefore, the endothermic peak was shifted from 133°C to 168°C for uncrosslinked and crosslinked chitosan, respectively. In our study this explanations are complementary. The thermal behavior of pectin samples has been previously described by Einhorn-Stoll et al. (Einhorn-Stoll, Kunzek, & Dongowski, 2007; Einhorn-Stoll & Kunzek, 2009a; Einhorn-Stoll & Kunzek, 2009b). These researchers mentioned that pectin thermal behavior depends on the chemical composition and on state transitions, occurring during processing, as well as on the interdependence of both factors. Some pectin samples showed an exothermic degradation peak between 180-270°C. Also, an endothermic pre-peak appeared before the degradation peak, corresponding to a conformational change that might be the transformation from the more stable 4C_1 chair conformation of the galacturonan ring via a boat conformation ${}^{1,4}B$ to the inverse 1C_4 chair conformation. Other researchers have also observed that this conformational change has a higher free energy G (Marszalek et al., 1999; Jarvis, 2002; Zhang & Marszalek, 2006; Haverkamp, Marshall, & Williams, 2007; Williams, Marshall, Anjukandi, & Haverkamp, 2007). These thermal events are present in the DSC thermograms of CH/PEC 0/100. The pure pectin thermogram shows an exothermic degradation peak at 234°C, and there is an endothermic pre-peak at 205°C. Also, at $T=127^\circ\text{C}$ another endothermic event similar to CH is observed related to water-plasticized pectin macromolecules and the sulfonic groups are incorporated by the functionalization of the reaction with 4-formyl-1-3-benzenedisulfonic acid.

From Figure 1 we can see that the thermograms of blend membranes are different from those of pure polymers.



(a)



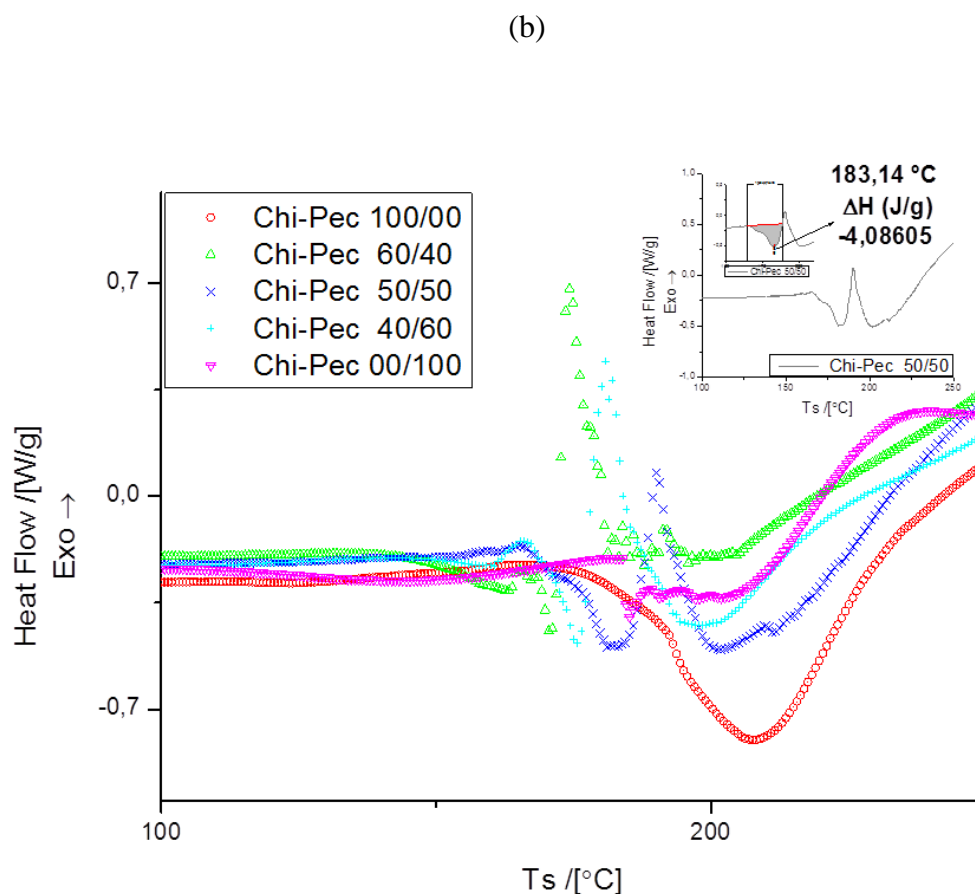


Figure 1. DSC thermograms of: a) CH100/PEC00, b) CH00/PEC100 and c) DSC of CH/PEC blend membranes.

Analysis of the DSC curve for the CH/PEC mixtures showed a pair of endothermic and exothermic peaks below 200°C. Blend membranes have an endothermic peak at 171.2, 175.8 and 183.1°C for CH60/PEC40, CH40/PEC60 and CH50/PEC50, respectively, like are showed in Table 3. The detected endotherm peak is attributed to the evaporation of water tightly linked through polar interactions to ionic groups (Ribeiro, Silva, Ferreira, & Veiga, 2005) and can be assigned to the excision of an ion pair between the carboxylic group (-COOH) of the Pectin and the ammonium group (-NH₃⁺) of the

Chitosan. All this is confirmed by the fact that the peak is shifted to the higher temperature as the composition of the membranes tends to be 1:1.

Table 3. Values of temperature and enthalpy corresponding to endothermic and exothermic peaks of blend membranes and pure polymers. In the last column we give the relative average molecular weight of membranes.

Membrane	Endothermic peak			Exothermic peaks			M_w
	T (°C)	ΔH (J/g)	ΔH (kJ/mol)	T (°C)	ΔH (J/g)	ΔH (kJ/mol)	
100-00	-	-		-	-		250000
60-40	171.2	-1.62	-285.01	174.3	5.2	915.2	176000
50-50	183.1	-4.09	-643.55	190.0	3.59	565.5	157500
40-60	175.8	-2.29	-317.74	180.9	7.36	1023.1	139000
00-100	-	-		-	-		650000

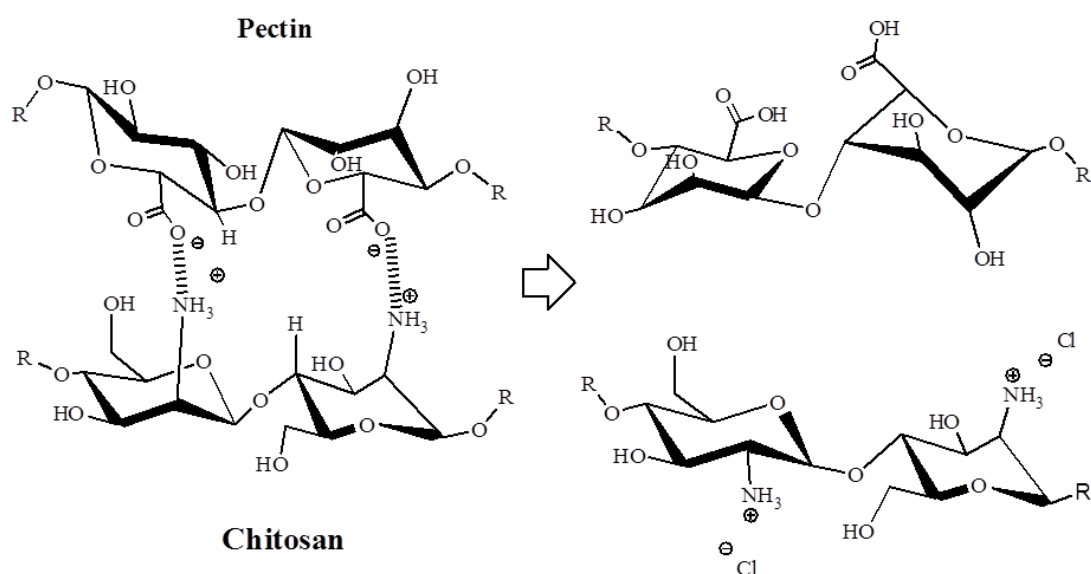


Figure 2. Reaction to the excision of an ion pair between the carboxylic group ($-\text{COOH}$) of the Pectin and the amine group ($-\text{NH}_3^+$) of the Chitosan.

The representation of the reaction of the ionic complex ion between the two polymeric components of the CH/PEC membranes is shown in Figure 2, where the thermograms of blend membranes also shows the exothermic peaks corresponding to the subsequent relaxation of the molecular polymeric matrix. The peaks are centered at around 174.3, 180.9 and 190.0°C for CH60/PEC40, CH40/PEC60 and CH50/PEC50, respectively, which could be assigned to the formation of an ionic pair between the carboxylate group ($-\text{COO}^-$) of pectin and the amine group $-\text{NH}_3^+$ of chitosan due to dehydration during the DSC scan. Similar results were found in CH/PEC, chitosan/alginate and chitosan/carboxycellulose blends (Ghaffari, Navaee, Oskoui, Bayati, & Rafiee-Tehrani, 2007; Mayur, Rajashree, Jolly, & Vijay, 2007; Ostrowska-Czubenko & Gierszewska-Drużyńska, 2009; Rosca, Popa, Lisa, & Chitanu, 2005). From the area of the

endothermic peaks we calculated the enthalpy of the process the excision of an ion pair supposing that the relative average molecular weight of Chitosan and Pectin are 250000 and 65000, respectively. The values obtained are 285.0 kJ/mol (1.62 J/g), 317.7 kJ/mol (2.29 J/g) and 643.5 kJ/mol (4.09 J/g) for CH60/PEC40, CH40/PEC60 and CH50/PEC50, respectively. These results confirm the greater formation of complex ions when membrane composition is tending to 1:1, point where it is necessary to give more temperature and energy to break the complex. Finally in the thermograms we can see that around 235°C of temperature the degradation of the Pectin begins to occur. Similar results have been found by Gümüşoğlu et al. (Gümüşoğlu, Albayral, & Deligöz, 2011), where the ionic interaction of the base polyelectrolyte complexes (PEC) membranes formed by Chitosan and poly(acrylic acid (PAA) produce an enhancement of their mechanical properties at least until 230°C.

4.4. Methanol permeability

The Methanol permeability has been measured analyzing the change of methanol concentration in the receptor chamber. The Figure 3 shows the function $(C_B \cdot L \cdot V_B / A \cdot C_A)$ versus time measured at 50°C for CH/PEC membranes. Linear trends are obtained and the slopes estimated. The values obtained from the slope of the plots permit to obtain the apparent methanol permeability of the membranes by means of eq.(2). In Table 2 the results obtained for the apparent permeabilities of CH/PEC membranes are shown. Data show that the lowest methanol permeability value $(1.51 \pm 0.04) \times 10^{-6} \text{ cm}^2/\text{s}$ correspond to CH50/PEC50 membrane. This coefficient is higher when the membrane is pristine Chitosan $(4.24 \pm 0.04) \times 10^{-6} \text{ cm}^2/\text{s}$ and pristine Pectin $(3.90 \pm 0.04) \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. In the case of membranes where the amount of each polymer is different,

such as CH60/PEC40 or CH40/PEC60, the apparent permeabilities are practically the same.

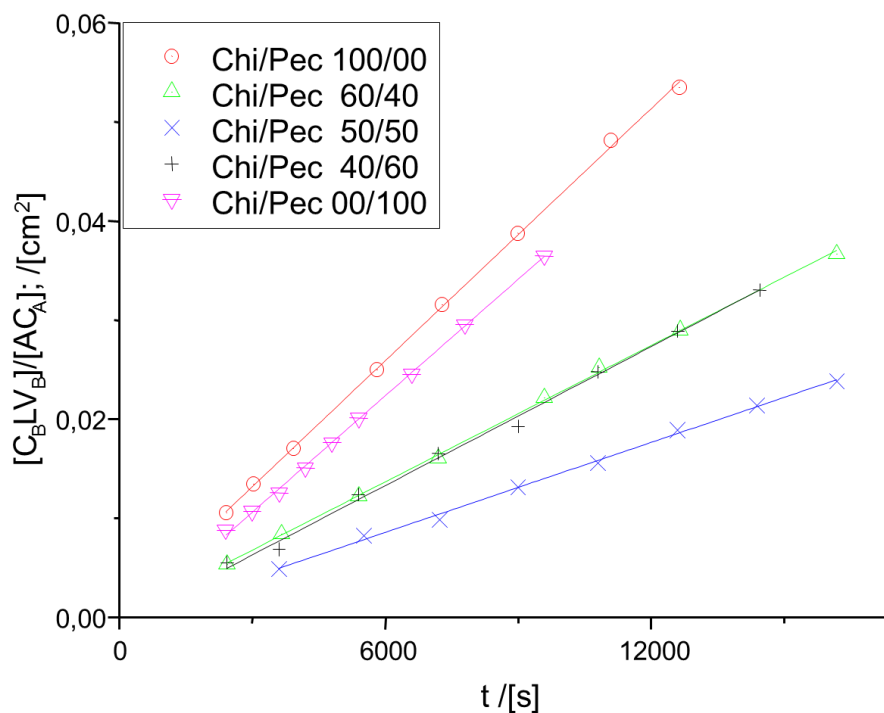


Figure 3. Representation of $(C_B \cdot L \cdot V_B / A \cdot C_A)$ versus time of the CH/PEC blend membranes. The slope equates to the apparent methanol permeability.

These values found in our work are quite similar to the values found for pristine Nafion® and Alginate90% /Carrageenan10% membranes where the apparent methanol permeabilities are about 2.2×10^{-6} and 4.0×10^{-6} cm^2/s , respectively, but eight times higher than neat Alginate membranes (Pasini-Cabello et al., 2014). The lowest methanol permeability value found for CH50/PEC50 can be attributed to the ion pair formation mentioned that partially hinder the methanol diffusion into the membrane matrix.

4.5. Conductivity results

Impedance spectroscopy measurements were carried out for CH/PEC membranes with compositions 100/00, 80/20, 60/40, 50/50, 40/60, 20/80 and 00/100 at different temperatures in order to obtain the conductivity and the diffusion coefficient of ionic charge carriers. All the impedance measurements were done after hydration of the blend membranes. From the dielectric measurements, the electrical conductivity σ can be obtained from the imaginary part of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) where $\varepsilon'' = \sigma / (\varepsilon_0 \omega)$, being ε_0 the permittivity of vacuum and ω the angular frequency of the applied electric field. The region where the slope of $\log \varepsilon''$ versus $\log \omega$ is equal to -1 allows extrapolate to low frequencies and the intercept of this straight line is the dc-conductivity (σ_{dc}). Alternatively, the data obtained can be analyzed in terms of the Bode diagram (Compañ, Riande, Fernández-Carretero, Berezina, & Sytcheva, 2008; Paddison, Kruer, & Maier, 2006). Typical plots of Bode diagram are shown in Figure 4. This figure reveals that the real part of the conductivity increases with the frequency and tends to a constant value when the phase angle, φ , reaches a maximum, for each temperature.

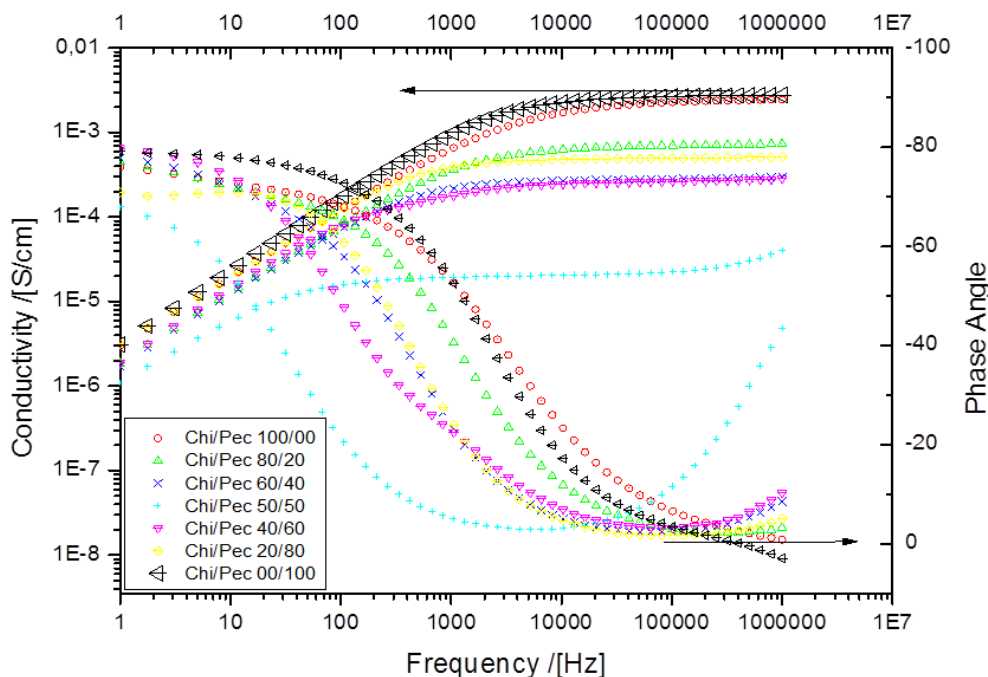


Figure 4. Bode diagram for the CH/PEC membranes obtained at 30°C of temperature.

As it can be seen in Figure 4, all the samples, at 30°C of temperature, shown a plateau in the plot of the real part of the conductivity vs frequency in the region of moderate and high frequencies (10^3 to 10^6 Hz) coexisting with the peak of the phase angle or the tendency to the value zero. The value of the conductivity for which ϕ reaches a value practically equal to zero can be taken as the proton conductivity of the membrane. Values of the conductivity for all the membranes of CH/PEC are given in Figure 5.

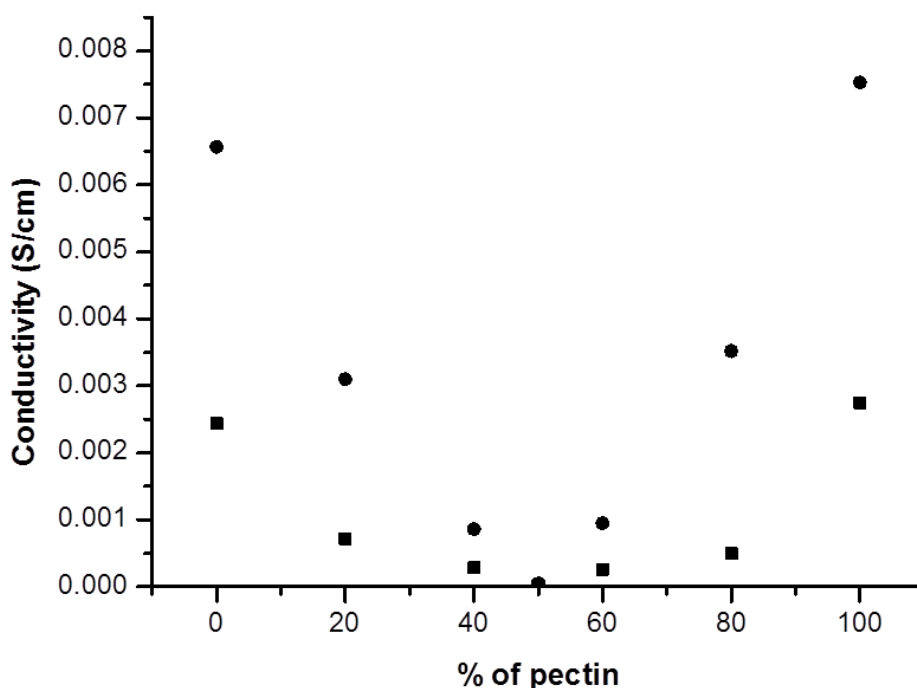


Figure 5. Conductivity of CH/PEC membranes with respect to the amount of pectin measured at 30°C (■) and 50°C (●), respectively.

As we can see, the conductivity for pristine Chitosan (CH100/PEC00) was 2.44×10^{-3} S/cm and 6.57×10^{-3} S/cm at 30 and 50°C respectively, decreasing when the amount of pectin increases up to the proportion of Chitosan and Pectin in the membrane is 1:1, where its conductivity is about two orders of magnitude smaller. These values are higher than estimated for membranes based on Chitosan crosslinked with glutaraldehyde (around 1.3×10^{-4} S/cm) (Majsztrik, Satterfield, Bocarsly, & Benziger, 2007), but lower than membranes of Chitosan crosslinked in sulphuric acid (about 1.83×10^{-2} S/cm) (Bass & Freger, 2008). On the other hand, our CH membranes have values of conductivity quite similar to the value found by Shirdast et al. 2.2×10^{-3} S/cm (Shirdast, Sharif, & Abdollahi, 2016), and lower than usually reported by others

researchers (Wan et al., 2006; Khiar, Puteh, & Arof, 2006). However our results are more satisfactory due to our membranes have lower IEC (0.37 meq/g) than Shirdast et al. 2016, which its value was around 0.97 meq/g. The small differences found in conductivity can be attributed to lower degree of deacetylation of Chitosan of this work (around 75%), in comparison with those used by others (between 80 and 90%). On the other hand, our membranes have values higher of IEC than obtained by others (Holder et al., 2016), where CH and Sorbitol-Chitosan (S-CH) membranes had values of 0.24 and 0.30 meq/g, respectively. Note that the abbreviation of Chitosan in other references (Holder et al., 2016; Shirdast et al., 2016) is CS in place of CH used in our manuscript. The conductivity for pristine chitosan membranes varies from 2.75×10^{-3} S/cm at 30°C and 7.53×10^{-3} S/cm at 50°C to the value of 5×10^{-5} S/cm for CH50/PEC50 membranes. The conductivities of our membranes are one order of magnitude higher than the ionic conductivity found in hydrated Chitosan membranes prepared from various degrees of deacetylation (DDA) and different molecular weights from aqueous solutions of Chitosan and acid acetic (Wan et al., 2003). This may be due to increased degree of crystallinity that has these Chitosan based membranes. A higher crystallinity degree in the membrane diminishes the mobility of protons.

A comparison between the conductivities of our blend membranes and those CH, S-CH and phosphorylated-Chitosan (CH-P) membranes prepared by other authors (Holder et al., 2016) showed that our blends have an internal resistance comprised between 500 and 4500 Ω . These values are in the same order of magnitude than Chitosan (464 Ω), Sorbitol-Chitosan (804 Ω) and Sorbitol-Phosphorylated-Chitosan membranes (2984 Ω) (Holder et al., 2016).

Electrochemical performance of CH, S-CH and CH-P membranes investigated in single microbial fuel cells (MFCs) for bioelectricity generation have shown an excellent

behavior. The results of the performance and durability show that during bath cycle of MFC operating with CH membrane, a maximum voltage of 152.6 mV was reached at day 5 out of 7 days it took to reach cycle completion. The results are better when the membrane used was S-CH, where this membrane was able to sustain a bath cycle for 12 days with maximum voltage of 464 mV with a power density of 94.59 mW/m². These results are even better in the case of membranes of CH-P where the maximum voltage was 504 mV and the maximum power density 130.03 mW/cm². When the membrane S-CH-P was situated in the MFC system took 15 days to reach the maximum voltage of 294 mV (Holder et al., 2016). That means that this kind of membranes can sustain themselves a lot of days until reach the end of cycle. These results allow us to think that our membranes can also to be used as PEM in fuel cells such as PEMFC, DMFC or MFCs.

The most important parameters to characterize and estimate the ionic transport in polymers and membranes is the mobility associated to the total charge carrier concentration. However, they are in general difficult to quantify and it is still at the present time a matter of discussion in the scientific literature (Compañ et al., 2008). To give an estimation of the diffusivity from the dielectric spectra we have considered the model described previously based on the analysis of the dielectric spectra of the electrode polarization where it is consider neglected the ion-ion interactions and convection flux. Considering in first approximation that all the ionic capacity into the membrane is involved in the distribution of ions that can move freely through the membrane, the proton conductivity and ion diffusivity can be expressed according the Einstein relation (Paddison et al., 2006), but a misprint in eq.(4) of this reference F was written instead of F², now the equation (3) is correctly stated as:

$$\sigma = \frac{c_+ F^2 D_+}{RT} \quad (3)$$

Where R is the universal gas constant, F the Faraday constant, T the absolute temperature, c_+ the ionic exchange capacity and D_+ the proton diffusion coefficient. The expression (3) permits us to obtain the diffusivity of the protons through the CH/PEC membranes from the values of conductivity obtained from the Bode diagram and the values measured for the ionic exchange capacity given in Table 1. The results found for the diffusion coefficient shows that vary in proportion to the ratio (σ /IEC). The values obtained at 30°C are 1.70×10^{-6} cm²/s and 2.0×10^{-6} cm²/s for pristine Chitosan and Pectin membranes, where this value decreases for the blend membranes until the lowest value of around 0.6×10^{-7} cm²/s is reached, corresponding to the CH50/PEC50 membranes. These values are quite close to that found in Nafion[®] 117 (Wan et al., 2006; Khiar et al., 2006), perfluorinated nanocomposite membranes modified by polyaniline (Compañ et al., 2008) and bio-polymeric membranes of Alginate-Carrageenan, but in such cases the membranes had less IEC and water uptake than this one (Pasini-Cabello et al., 2014). At it is known the IEC and swelling of the membranes will affect the ionic permeability through the membrane. In this sense the high degree of swelling into the membrane will allow ions to move through the membrane increasing its diffusivity in the swollen state. Such is shown in Table 1 the values of pristine membranes have higher values of IEC and swelling than blend membranes. This produces a significant increase in conductivity. This behavior could be due to the strong interaction from the intramolecular hydrogen bonds between hydroxyl groups and amine groups which are harder than intermolecular hydrogen interactions bonds between polar groups and water.

The interest of CH is the tendency to acquire high hydrophilicity, very easy chemical modification and good mechanical and thermal resistance. The CH with amino groups present a polycationic character and form ionic cross links in presence of acidic groups

(Osugi, Dong, Hexig, & Inoue, 2007) producing polyelectrolytes complexes membranes solving the dopant migration to give effective performance in DMFCs for prolonged periods (Göktepe, Çelik, & Bozkurt, 2008). The main concern of this type of membranes is the possible degradation, during cell operation conditions. In this way some authors (Gümüşoğlu, Albayral & Deligöz, 2011), have investigated the oxidative and hydrolytic stability of Chitosan and poly(acrylic acid) membranes found that can be suitability for use in fuel cells such as DMFCs in which diluted methanol were used. In this way hydrolytic and oxidative stability of the CH/PEC membranes were tested to investigate the convenience for use as PEM in fuel cells. The hydrolytic stability of this type of membranes was characterized controlling the time duration until membrane broken after immersion in hot water. The results found for our membranes were around 125 hours quite similar to PEC membranes which were more than 120 hours. These results show that both kinds of membranes are suitable for fuel cells applications.

Several works have reported results from an *ex situ* vapor phase hydrogen peroxide test (Delaney & Liu, 2007; Hommura, Kawahara, Shimohira, & Teraoka, 2008) and found that gas phase hydrogen peroxide is very aggressive toward perfluorosulfonated (PFSA) membrane, causes chain scissions in the backbone and in the side chain (Endoh, 2008).

In our membranes the *ex situ* vapor phase hydrogen peroxide test has allowed observe the weight retention of our membranes as function of time, such as is shown in Figure 6. A close inspection of this figure shows that the weight of each membrane decreases gradually. On the other hand, we can observe that pure chitosan membranes (CH/PEC 100/00) are completely degraded after 24 h. This behavior has also been reported by other researchers (Tian, Liu, Hu, & Zhao, 2004) and they have mentioned that this type of change in the fundamental

chitosan structure appears to be possible due to the role of the amine group in the degradation of polysaccharides by hydrogen peroxide. The glycoside bonds are more susceptible to split since there is an amine group adjacent to the C₂ pyranose ring.

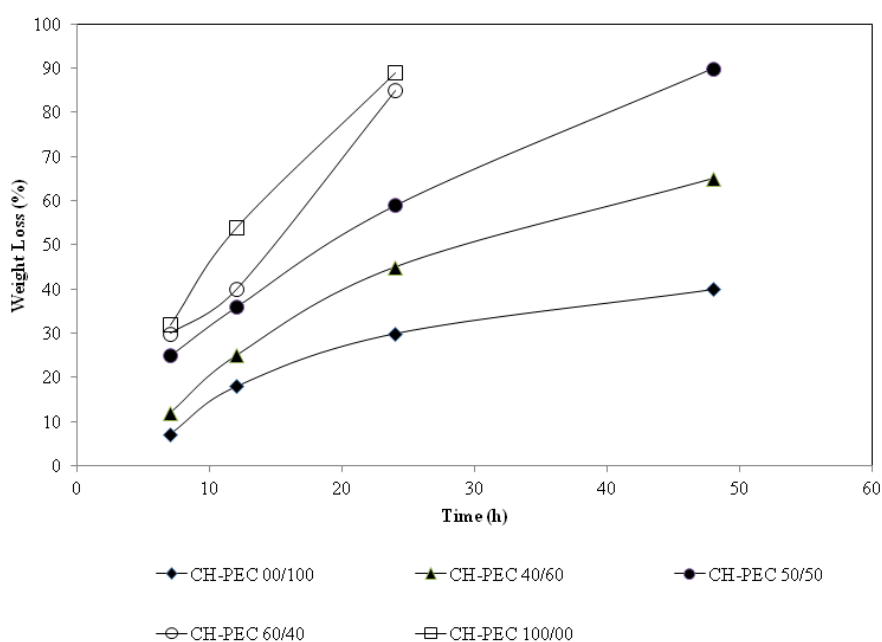


Figure 6. Chemical stability studies of CH/PEC membranes from Fenton test.

However, Pectin based membranes are more resistant to this test such as we can observe from Figure 6 where an increase of amount of PEC produces a significant increase of membranes durability. On the other hand, CH/PEC membranes allow fairly good chemical stability as the sulfonation degree decreases, i.e the IEC decrease.

5. Conclusions

To summarize, blend membranes of Chitosan and Pectin were obtained and characterized. The pristine Chitosan and Pectin membranes showed higher proton conductivities, IEC, water uptake and methanol permeability than blend membranes of CH/PEC. This is due to the formation of an ionic complex, which compacts the polymer matrix reducing the channel hydrophilicity.

When the ion pair between the carboxylic group (-COOH) of the Pectin and the amine group (-NH₃⁺) of the Chitosan reacts, it is produced a diminution of content of free amine and carboxylic groups decreasing the hydroxyl groups and hence the hydrophilicity and swelling of the membranes. When the content of the blend membrane is 50:50 wt, the ionic strength fraction of the ions is practically the same, reducing around two orders of magnitude its properties with respect to the ionic transport. Our results showed that the methanol permeability was reduced due to ion pair formation. This strong interaction hinders the diffusion of methanol molecules through the membrane lowering permeability value about three times when such value is compared to pristine membranes. On the other hand, the blend membranes with a content 50/50wt have ultimate tensile strength σ_{ult} higher than the others blends due to the channels become more compacted.

The *ex situ* vapor phase hydrogen peroxide test has allowed observe that the weight of each membrane decreases gradually. Pristine chitosan membranes (CH/PEC 100/00) are completely degraded after 24 h. This behavior can be possible due to the role of the amine group in the degradation of polysaccharides by hydrogen peroxide. The glycoside bonds are more susceptible to split since there is an amine group adjacent to the C₂ pyranose ring.

However, PEC based membranes are more resistant to Fenton's test where a increasing of PEC produce a significant increase of membranes durability. On

the other hand, CH/PEC membranes allow fairly good chemical stability as the sulfonation degree decreases.

CH/PEC membranes merits further studies to obtain membranes with good performances for use as proton exchange membranes for MFCs and DMFCs, using dilute methanol or ethanol as fuel. Additionally, the methodology presented in this work may be extendable to other applications considering the influence of the amount of each component into the blend membrane as consequence of the formation of the ionic complex.

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