The effect of production method on the properties of high impact polystyrene and polyaniline membranes

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Abstract
In this study, different membranes were prepared using conventional polymer (high impact polystyrene) and polyaniline to evaluate their use in electrodialysis. Two different preparation modes were tested: chemical mixture with subsequent solvent evaporation; and mechanical mixture with subsequent pressing under heating. The purpose was to understand the effect of production methods on membrane microstructure and ionic transport. Membranes were characterized by swelling study, Fourier transformed infrared spectroscopic, scanning electron microscopy, thermogravimetric analysis and dynamic mechanical analysis. Ionic transport through the membranes was evaluated using a three-compartment cell. The results of the produced membranes were compared with those of the commercial Nafion 450 membrane.

1. Introduction
The concern about the preservation of water resources has grown in the last decades. Industrial activities have led to widespread heavy metal contamination of soils and natural waters. Of the different sources of water contamination, one of the most important is the electroplating industry because it generates a considerable volume of effluents containing high concentrations of metal ions. Another aggravating factor is that the traditional process for the treatment of these effluents – not very efficient and in some cases totally inefficient – produces a dangerous solid waste (electroplating sludge), which should, therefore, be disposed of in appropriate landfills.

In the last decades, separation techniques using membranes have been studied for the treatment of public-supply water and, more recently, for the treatment of industrial effluents. The separation of ionic species through membranes is an alternative to the conventional treatment used in electroplating. Electrolysis may be an attractive alternative to effluent treatment because the electrochemical apparatus is compact and requires less electric power than other techniques, like reverse osmosis [1–3]. Compared with the conventional process of wastewater treatment, electrodialysis has the advantage of not generating any electroplating sludge.

One of the most important applications of electrodialysis in wastewater treatment systems is its use in processing rinse waters from the electroplating industry. In the treatment of rinse waters, electrodialysis can be used for the recovery of electroplating baths, which increases their lifetime due to the removal of contaminants [4–7].

The progress of electrodialysis has been basically associated with the development of new ion-selective membranes and the changes made to commercially available membranes to improve their transport properties.

Conducting polymers are a new class of polymers used in the production of membranes. Conducting polymers have some advantages over conventional polymers, such as their electric conduction when in the doped state. However, these polymers do not have good mechanical properties, and should be used together with a conventional polymer in membrane preparation [8–10].

The use of polyaniline is limited by the fact that it cannot be melted in its conducting, protonated state, nor dissolved in organic solvents used in conventional polymer processing. Great progress was made in this area with the development of a polyaniline (PAni) dissolution method by Heeger and coworkers [11]. This method is based on the use of functionalized protonic acids that form a compound with the polymer and simultaneously promote doping and solubility of polyaniline in several organic solvents.
2. Experimental

2.1. Membrane preparation

The membranes were prepared by mixing conventional polymer (HIPS) with conducting polymers (PAni). Two different mixing methods were tested to evaluate the effect of production method. Also used three different dopants in polyaniline and polyaniline to obtain conducting blends for different purposes [13–15].

Other method to blend polyaniline and conventional polymers, is the mechanical mixture using a rotary mixer or a screw extruder is the most common [16]. In these processes, conductivity is strongly dependent on the miscibility and rheological properties of the blend components. The temperature should be sufficiently high to allow the material to flow, and sufficiently low to prevent polymer degradation. The aim of this study, is to investigate the effect of two different preparation methods on membrane properties.

2.1.1. Method 1: mechanical mixture in screw extruder

HIPS and PAni were mechanically mixed in a single screw extruder (Ciola MPE 18V) operated at 180 °C and 30 rpm, and then pelleted. The amount of polyaniline used was 20 wt%. For film preparation, pellets were pressed in a heating press (Carver) at 160 °C to avoid polyaniline decomposition. The material was then pelleted in a Seibt ACS 300 unit.

2.1.2. Method 2: solvent dissolution

The same amount of HIPS and PAni used in the previous method were dissolved in 20 mL of tetrachloroethylene, a common solvent for both materials. After dissolution, PAni was dispersed in an HIPS polymeric matrix for 30 min. This dispersion was performed at 1000 rpm in a mixer (Fisaton). The membranes were molded on glass plates using a laminator to keep thickness constant, and the solvent evaporated slowly for 24 h under room temperature.

2.2. Membrane characterization

The membranes were prepared according to preparation method and dopant. Table 1 shows the characteristics of the membranes produced. Only MCS and MCE membranes were characterized by FTIR, SEM, TGA and DMA because the behavior of the other membranes was the same as that of MCS or MCE.

2.2.1. Infrared spectroscopy (FTIR)

The samples were prepared with potassium bromide (KBr) powder. Pure polyaniline was previously homogenized in a mill and dried to make a KBr pellet. All samples were analyzed using a spectrometer (Spectrum 1000, PerkinElmer FTIR). The spectrum was recorded in the spectral range of 400–4000 cm⁻¹.

2.2.2. Morphology

Scanning electron micrographs of the membranes surface were obtained using a microscope (Philips XL20) after the samples were sputter-coated with gold.

2.2.3. Thermogravimetric analysis (TGA)

The membranes were analyzed using a thermogravimetric analyzer (TGA 2050, TA Instruments) at a temperature ranging from 25 to 1000 °C under N₂ atmosphere. Heating rate was 20 °C/min for all samples.

2.2.4. Dynamic mechanical analysis (DMA)

The membranes were analyzed using a dynamic mechanical analyzer (DMA 2980, TA Instruments) at a temperature ranging from 150 °C to 200 °C. Heating rate was 5 °C/min at a frequency of 1 Hz. The samples measured 200 mm × 70 mm × 0.26 mm.

2.2.5. Swelling

Membranes were placed in deionized water at room temperature for 24 h for swelling equilibrium. Excess water was removed with filter paper. The membranes were weighed, kept in an oven at 80 °C for 6 h, and then weighed again. Water uptake was determined by the mass difference between the wet and dried membranes (after heating at 80 °C). Water absorption is expressed in percentages [1,8].

2.2.6. Electrodialysis

Tests were conducted using a three-compartment cell [8,9]. Platinumized titanium electrodes were used as anode and cathode. The volume in both compartments was 200 mL. The membranes were immersed in the working solutions for 48 h to reach equilibrium between membrane and solution. A pseudo stationary state was achieved with a pre electrodialysis for 20 min. After this period solutions were replaced by new ones and the experiment was restarted. Solutions were prepared with distilled and deionized water.

The anionic membrane was an AMT (Asahi Glass Co.) membrane, and the cationic membranes were the ones synthesized in this study and a Nafion 450 (DuPont de Nemours Co.) membrane, which was used for comparisons. The effective area of the membranes was 16 cm².

Tests were conducted by applying a current density of 10 mA/cm². The tests lasted 180 min and were all conducted at room temperature. Table 2 shows the distribution of solutions in the different compartments.

Test 1 evaluated the transport of Na⁺ ions through the membranes. Test 2 checked membrane selectivity and the transport of Cl⁻ ions. In test 2, the membranes produced in this study were placed in the anionic position, and the Nafion 450 membrane was used as the cationic membrane.

The ions extractions were evaluated in percentages, as:

\[
\% \text{ extraction} = \frac{C_f - C_i}{C_i} \times 100
\]

where \(C_i\) is initial concentration; and \(C_f\) is final concentration.

The standard deviation in ions extractions is 2%.

Table 1

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Preparation method</th>
<th>Dopant type</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCE</td>
<td>Method 1: mechanical mixture in screw extruder</td>
<td>CSA</td>
</tr>
<tr>
<td>MCS</td>
<td>Method 2: solvent dissolution</td>
<td>CSA</td>
</tr>
<tr>
<td>MDE</td>
<td>Method 1: mechanical mixture in screw extruder</td>
<td>DBSA</td>
</tr>
<tr>
<td>MDS</td>
<td>Method 2: solvent dissolution</td>
<td>DBSA</td>
</tr>
<tr>
<td>MTE</td>
<td>Method 1: mechanical mixture in screw extruder</td>
<td>p-TSA</td>
</tr>
<tr>
<td>MTS</td>
<td>Method 2: solvent dissolution</td>
<td>p-TSA</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Test</th>
<th>Compartment</th>
<th>Cathodic</th>
<th>Intermediary</th>
<th>Anodic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 M Na₂SO₄</td>
<td>0.1 M Na₂SO₄</td>
<td>0.1 M Na₂SO₄</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.1 M K₂SO₄</td>
<td>0.1 M NaCl</td>
<td>0.1 M K₂SO₄</td>
<td></td>
</tr>
</tbody>
</table>
The electric resistance of the membranes was measured using a three-compartment cell, as previously described [17,18]. Membrane potentials were measured using two reference calomel electrodes connected to Luggin capillaries, as schematically shown in Fig. 1. The solution to be analyzed was in the central compartment and inside Luggin capillary B. A sodium sulfate solution (0.1 M Na₂SO₄) was placed in the external compartments. The variation in the potential was monitored at 2-min intervals under continuous increase of the current.

3. Results

3.1. Study of the membrane properties

3.1.1. Infrared spectroscopy

To assess the incorporation of PANi in the polymeric matrix, samples of PANi/CSA and HIPS, as well as membrane samples, were analyzed. Fig. 2 shows the FTIR spectra of PANi/CSA, HIPS and the MCE membrane. The MCS spectrum was similar to that of the MCE membrane.

The polyaniline spectrum was similar to the one described in the literature [19]. Peaks at 1467 cm⁻¹ and 1560 cm⁻¹ were associated with benzenoid and quinoid rings. The peak at 1299 cm⁻¹ was associated with an angular deformation of the C–N group. The doping of polyaniline was observed at 1122 cm⁻¹ in the formation of the H⁺N=Q–NH⁺ polarons. A peak at 1034 cm⁻¹ showed that S=O groups were associated with the sulfonic acid used as dopant.

In the HIPS spectrum, different peaks were observed. The peak at 2948 cm⁻¹ corresponded to an angular deformation of CH₃. At 1731 cm⁻¹, there was a peak attributed to the stretching of C=O.
groups. Peaks at 1645 cm$^{-1}$ and 1554 cm$^{-1}$ corresponded to N-H stretching. Peaks at 1075 and 1140 cm$^{-1}$ were associated with the stretching of C-O-C groups.

The spectrum of the MCE membrane showed peaks of PANi and HIPS spectra, which demonstrated the incorporation of PANi into the plastic matrix. Some of the peaks overlapped at the stretching of N-H groups at approximately 3430 cm$^{-1}$.

### 3.1.3. Thermogravimetric analysis

The analysis of the thermogravimetric curve (Fig. 5) revealed that the initial degradation of the polymeric chain of MCE membranes occurred at about 220 °C. The degradation of MCS membranes began earlier, at about 150 °C. This difference was probably associated with the method used to produce the membranes. A solvent was used to prepare MCS membranes; some residue of this solvent may have been retained inside the membrane and may have evaporated before the polymer [22]. This weight loss cannot be attributed to PANi, because PANi degradation begins at about 220 °C.

Another important finding was the difference in amount of residue between the membranes at 1000 °C. This difference is probably due to the greater stability of the connections of aromatic rings in the polyaniline chain. This chain does not decompose at high temperatures or under an N$_2$ atmosphere.

### 3.1.4. Dynamic mechanical analysis

Modulus is defined as the ratio of tension to deformation. Fig. 6 shows the mechanical strength through the storage modulus, which was associated with the elastic fraction of the material as a function of the temperature of the MCS and MCE membranes [23].

MCE membranes display higher modulus compared to MCS membranes probably due to solvent molecules entrapped into MCS structure. Both membranes have shown two $T_g$, similarly to the $T_g$ of HIPS that are −75 °C for polybutadiene phase and 103 °C for polystyrene phase, respectively. Preparation methods and polyani-
line addition are able to modify morphology of membranes but do not modify phase transitions of the materials. Therefore, the modulus at room temperature, where the membranes are used, is different: for MCS (about 1000 MPa) and MCE (about 1600 MPa). This fact is associated with membrane mechanical resistance: the higher the modulus, the greater the membrane resistance to deformation, which means that more energy is required to deform the membrane.

Fig. 7 shows the DMA results of MCE membranes after several electrodialysis tests, which totaled about 600 h of work. DMA results showed that these membranes had a decrease in their mechanical properties. Peaks of loss modulus clearly show that the glass transition temperature (Tg) of polybutadiene (PB) is about −75 °C, and of polystyrene (PS), about 103 °C.

The decrease of the modulus from 1600 MPa to 1000 MPa at room temperature showed that less energy was necessary to deform the membrane because of the reduction of its mechanical resistance.

3.1.5. Thickness, swelling and electrical resistance

The swelling capacity of the membrane affects not only its dimensional stability but also its selectivity, electric resistance and hydraulic permeability. Dimensional stability increases as the polymer affinity for water decreases. Conversely, as polymer affinity for water increases, ionic transport resistance decreases [1,10].

Table 3 shows the thickness, swelling and electrical resistance of the membranes produced for this study and of the Nafion 450 membrane, as well as anionic membrane.

Membranes that use CSA as doping acid have slightly greater swelling than other membranes. However, the Nafion membrane showed a much greater swelling than the synthesized membranes. This difference may be associated with the fact that Nafion is a supported membrane and is thicker than the membranes under study.

Table 4 Percent extraction of sodium and chloride through the membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pe Na⁺ (%)</th>
<th>Pe Cl⁻ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCE</td>
<td>27.7</td>
<td>2.1</td>
</tr>
<tr>
<td>MCS</td>
<td>43.8</td>
<td>0.2</td>
</tr>
<tr>
<td>MTE</td>
<td>30.4</td>
<td>2.5</td>
</tr>
<tr>
<td>MTS</td>
<td>33.0</td>
<td>2.9</td>
</tr>
<tr>
<td>MDE</td>
<td>23.9</td>
<td>5.2</td>
</tr>
<tr>
<td>MDS</td>
<td>30.4</td>
<td>1.7</td>
</tr>
<tr>
<td>Nafion 450</td>
<td>43.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Moreover, the membranes produced after mixing in an extruder (method 1: mechanical mixture in screw extruder) had greater electric resistance than the membranes produced in solution (method 2: solvent dissolution). The MDS membrane had the lowest resistance of all the membranes produced with HIPS and PAni, because PAni DBSA chains are present in a more extended conformation increasing the chance of forming the conducting network [21].

In the membrane production by method 2, occurs the microtubules formation, show in the micrographs. The formation of such a microtubule may explain the electrical behavior of these blends.

The MCE membrane had the greatest resistance, and this fact was associated with the preparation method and the doping acid used.

3.1.6. Sodium and chloride extraction

Table 4 shows the percentage of sodium and chloride ions extracted through the membranes. The results show a effect of the production method and of the type of acid used as polyaniline dopant on sodium transport through the membrane and on membrane selectivity.

Membranes produced in solution (method 2: solvent dissolution) showed greater transport of sodium ions and greater selectivity than the membranes produced using method 1 (mechanical mixture in screw extruder). The MCS membrane had the best transport of all membranes produced for this study when compared with the commercial Nafion membrane. The results of sodium transport also confirmed the effect of the acid structure used as polyaniline dopant. Two aspects must be taken into account here. First, TSA and DBSA are aromatic acids, and CSA is a cyclic acid. This difference may affect the interactions between the (HSO₃⁻) groups from the dopant acid and nitrogen from polyaniline, which may affect ionic transport through the membrane. Second, the substitute for the aromatic ring of the DBSA acid is much larger than that of the TSA acid, and this may increase space limitations during transport, which causes a decrease in transport for this membrane, as our results demonstrated.

It is believed that the best percent extraction of the prepared membranes for the method 2, probably due the formation of the microtubule structures in accordance with the micrographs.

4. Conclusion

The evaluation of membrane properties showed that the production method and the structure of the polyaniline dopant affect ionic transport as well as thermal, chemical and mechanical properties.

The MCE membrane (HIPS/CSA/extrusion) had greater thermal stability than the MCS membrane (HIPS/CSA/solution) because its degradation began at higher temperatures. The MCE membrane had a greater storage modulus and, consequently, greater mechanical resistance than the MCS membrane.

The analysis of membrane morphology showed that PAni mechanically mixed with HIPS had a different conformation from PAni used in the mixture with solvent, which had a fibrous structure.
All the membranes produced for this study had good selectivity, which was confirmed by low chloride transport through the membranes.

The analysis of sodium ionic transport showed that transport was excellent for all membranes produced for this study. Sodium transport through MCS membranes was similar to that found for the Nafion 450 membrane.

In conclusion, the differences in properties found in this evaluation of membranes indicate that, because of their lower resistance and better transport properties, membranes processed with solvent can be more widely used than those processed by mechanical mixture. Of all the membranes in this study, the MCS showed the best results.

Acknowledgements

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References