

Castor Oil and Commercial Thermoplastic Polyurethane Membranes Modified with Polyaniline: A Comparative Study

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The study of conducting polymeric membranes is decisive in some areas, as in fuel cells and electro dialysis. This work aims the study of membranes using conventional and conductive polymers blends. Two types of polyurethane were used as conventional polymers, commercial thermoplastic polyurethane and polyurethane synthesized from castor oil and 4-4-dicyclohexylmethane isocyanate. Two kinds of conducting polymers were used, polyaniline doped with organic acid and a self doped polyaniline. The polymers and the membranes were characterized by electrical conductivity, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). The synthesis of the membranes produced was proper, featuring a complete reaction, analyzed by FTIR. The membranes also showed good mechanical properties and thermal stability (≈ 220 °C). Among the membranes studied, the polyaniline doped with p-toluenesulphonic acid obtained higher thermal and viscoelastic properties. Thus they can be used in separation techniques using membranes.

Keywords: *membranes, thermoplastic polyurethane, conducting polymer*

1. Introduction

Commercial ion selective membranes have undergone a rapid growth during the last two decades. The interests for membranes have increased concurrently with new processes and new applications. The main processes of separation by membranes are: microfiltration, ultrafiltration, reverse osmosis, electro dialysis, and others. Membrane processes are increasing its utilization in many fields, such as water and wastewater treatment. The utilization of membrane technology in the development of processes to treat wastewater is generally limited due to its high price of the membranes¹.

The membrane can be defined as a permeable or semi-permeable phase allowing the passage of some species and restricts the movement of others. Usually, membranes are thin layers which may have different structures, however all have in common the selectivity in transport behavior for different components². Synthetic membranes are commonly prepared by polymer materials with varied chemical and physical characteristics. The preparation can be homogeneous or heterogeneous, where the homogeneous membranes feature good electrochemical properties but poor mechanical behavior, whereas the heterogeneous membranes show high mechanical properties and low

electrochemical properties. In the literature review^{2,3} some studies can be found using polymer nanocomposites based on others polymer matrices such as epoxy resin, polystyrene, polypropylene, polyethylene and polyurethane³.

In this way, conducting polymers has been applied, for instance, for corrosion protection⁴, organic electroluminescent diodes⁵, electrical devices^{6,7}, smart windows⁸ and ion-exchange membranes^{9,10}. Polyaniline (PAni) is the conducting polymer most widely used in blends with conventional polymers due to its good environmental stability, easy obtaining and low cost. However, PAni has low mechanical properties. Among the conventional polymers, polyurethanes (PUs) show good mechanical properties, such as stiffness and flexibility¹¹⁻¹³. Polyurethanes are segmented polymers with microphase separated morphology¹⁴. It is noteworthy in the engineering thermoplastic PU application the morphology of this material. Morphology depends on factors such as chemical composition, segment size, segment functionality, glass transition temperature (T_g) and others¹⁵.

Previously works as Amado et al.¹⁶ used HIPS (high impact polystyrene) as base polymer, forming HIPS/PAni blends. They obtained that the HIPS/PAni membranes can be processed in a temperature around of 200 °C and the infrared spectroscopy (FTIR) showed a peak at 1034 cm^{-1}

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regarding the S=O group. Whereas Singh et al.¹⁷ realized the synthesis and characterization of conducting polymer composites based on PANi/polyethylene with glycol/zinc sulfide system. They concluded that this combination can be useful for light-harvesting for solar cells due to the good absorption ultraviolet-visible region for the hybrid system studied. Since Milanese et al.¹⁸ studied the flexural properties of sisal/castor-oil based PU with sisal fibers in natural conditions and thermally treated (at 60 °C for 72 hours) and achieved a good interface adhesion sisal/castor-oil based PU.

Castor oil has been used in their synthesis, replacing the polyol¹⁹⁻²¹. The castor oil also is used in the PU synthesis due to its good thermal stability in different conditions of pressure and temperature. Therefore these PU and PANi blends can be an inexpensive alternative to produce cation-exchange membranes. The conducting polymer would have a function of acting as ion exchange agent in the blend. The PANi can be sulfonated and the production of a PU with PANi sulfonated blend allows obtaining a membrane with good mechanical properties and high diffusion coefficient^{17,18}. Sulfonated PANi (SPAN) can be used as exchange groups, once the sulphonic groups are chemically linked to polymer chains, as well as in the commercial membranes.

In this work, PANi was doped with different organic acids. Also, membranes of PU/PANi have been developed. Thus, the aim of this study was to synthesize the PANi, preparing the membrane and characterize and compare the membranes produced using doped PANi with the membranes produced using SPAN. Lastly, also was investigated the influence of the thermoplastic PU (TPU) and the results were compared with that PU produced with castor oil (CAPU)²².

2. Experimental

2.1. Material

Amomnium peroxodisulfate ((NH₄)₂S₂O₈) (Synth) and hydrochloric acid (Nuclear) were used in the aniline polymerisation. Chlorosulfonic acid (HClSO₃) (Vetec), 1,2-dichloroethane (Synth) and acetone (Nuclear) were used in the polyaniline sulfonation, while p-toluenesulfonic acid was used for the doping of the polyaniline. 4,4-diciclohexilmethane diisocyanate (Bayer) and castor oil (Delaware) were used in the polyurethane synthesis. Regarding that all chemicals products were used without any further purification.

2.2. Polyaniline synthesis

The chemical oxidative polymerization of aniline was carried out according to a standard method^{23,24}. The obtained PANi was filtered, washed with a diluted HCl solution and dried at 60 °C for 24 hours. SPAN was obtained as previously described²⁵ using three different sulfur and nitrogen ratios (S/N), which were 1.5, 2.0 and 3.0. PANi also was doped with p-toluenesulphonic acid, to improve the solubility in dimethylformamide, and denominated as PANi_{TSA}^{26,27}.

2.3. Membrane preparation

The membranes were prepared by mixing PU with conducting polymers. Two different mixing methods were tested to evaluate the effect of production methods:

In the first method, CAPU/SPAN and CAPU/PANi_{TSA} mixture preparations were carried out at 70 °C under nitrogen atmosphere by first mixing castor oil and PANi. After this step, diciclohexilmethane isocyanate was added to react with the polyol (castor oil) to form the PU. PU isocyanate/hydroxyl molar ratio (NCO/OH) was 1.5 and the reaction medium was kept under mechanical stirring for 90 minutes. The membranes were obtained by pouring the mixture over the glass plates and spreading them until a uniform thickness was achieved. The membranes were kept in an oven at 60 °C for 6 hours, and the temperature was increased to 120 °C for 18 hours in order to promote the cure of PU. The amount of PANi in the membrane composition was 10 wt.%.

In the second method, the Commercial TPU (Texin® Bayer) and PANi_{TSA} were dissolved in dimethylformamide, a common solvent for both materials. After dissolution, the PANi_{TSA} was dispersed in a TPU polymeric matrix for 30 minutes. 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 was slowly evaporated during 24 hours, at room temperature. The amount of PANi in the membrane composition was 10 wt.%.

2.4. Polymer and membrane characterization

The electrical conductivity of membranes was measured according to the four-probe standard method using a Cascade Microtech CS 4-64 equipment, associated to a Keithley 2400 Source Meter²⁸. Pure PANi was previously homogenized in a mill and dried to make a KBr disc. The amount of KBr in the disc composition was 99 wt.%. The film membranes were directly analyzed. All samples were analyzed by FTIR (Perkin Elmer spectrometer, model Spectrum 1000). The spectra were recorded in the spectral range of 400-4000 cm⁻¹.

The thermal stability of the membranes was evaluated by thermogravimetric analyses (TGA) using a TA Instruments model TGA 2050 Analyzer, in a temperature range of 25 to 1000 °C, under N₂ atmosphere at a heating rate of 20 °C.min⁻¹. The dynamic mechanical analysis of the membranes were performed in a TA Instruments model DMA 2980 Analyzer, in the range of -125 to 150 °C at a heating rate of 5 °C.min⁻¹, strain amplitude of 0.1%, frequency of 1 Hz and operating in a single cantilever mode.

Micrographs of the membranes surfaces were obtained using a Scanning Electron Microscope (SEM) model Philips XL20. The samples were previously sputter-coated with gold.

3. Results and Discussion

3.1. Electrical conductivity

Table 1 shows the electrical conductivity values (performed in triplicate) of a SPAN sample prepared with different ratios between sulfur and nitrogen (S/N). Also the conductivity of PANi_{TSA} was analyzed. It was observed that PANi_{TSA} has a much higher conductivity than SPAN. This behavior possibly is associated to the self-doping

Table 1. Electrical conductivity of PANi samples sulfonated in different molar ratios of sulfur and nitrogen (S/N) and PANi_{TSA}.

| Sample | Conductivity (S.cm ⁻¹) |
|---------------------|---|
| SPAN 1.5 | $3.7 \times 10^{-2} \pm 1.5 \times 10^{-2}$ |
| SPAN 2.0 | $2.4 \times 10^{-3} \pm 1.3 \times 10^{-3}$ |
| SPAN 3.0 | $1.7 \times 10^{-5} \pm 7.5 \times 10^{-6}$ |
| PAni _{TSA} | $1.1 \pm 6.1 \times 10^{-1}$ |

effect, which happens in conducting polymers, and can be explained because when dopants species located inside the polymeric matrix helps in the process of internal charge compensation. This self-doping causes changes in the polymer characteristics²⁹.

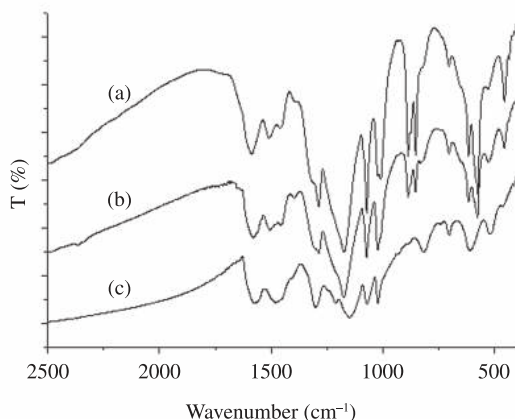
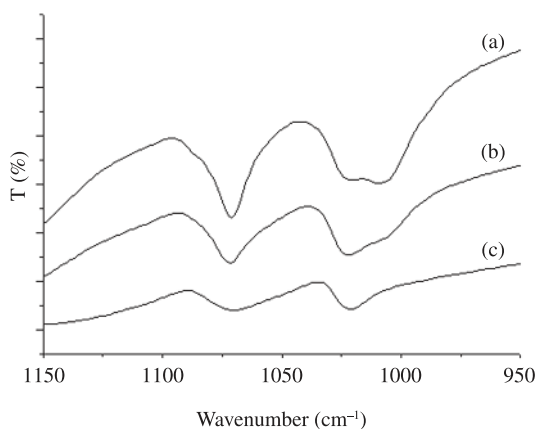
For the SPAN, the results showed that the increase in molar ratio S/N decreases the PANi conductivity. These results corroborating with Ito et al.²⁵, when the molar ratio S/N increases, the conductivity decreases; however the solubility of SPAN in polar solvents like water increases. The values for electrical conductivity of all produced membranes (CAPU/SPAN, TPU/PAni_{TSA} and CAPU/PAni_{TSA}) are smaller than 5.10^{-5} S.cm⁻¹, limit of the measurement unit used, probably because PANi doping can happen during the membrane production (due to the alkalinity of the solvent employed) or due to insufficient dispersion of the PANi into the PU.

3.2. Infrared spectroscopy

The “SPANs” spectra are similar to the one described in literature. But the intensity of these peaks may vary. Figure 1 shows the SPANs spectra, where the variation of the ratio S/N used in the synthesis can be observed. Peaks at 1467 cm⁻¹ and 1560 cm⁻¹ are related to benzenoid and quinoid rings respectively. The SPANs spectra showed peaks at 1171 cm⁻¹ and 1074 cm⁻¹ due to asymmetric and symmetric stretching of S=O=S. The peak at 1020 cm⁻¹ corresponds to S=O bond stretching and that at 702 cm⁻¹ related to S–O bond. The absorption peak at 813 cm⁻¹ is related to out-of-plane bending of 1,2,4-trisubstituted aromatic ring and that at 609 cm⁻¹ is attributed to the C–S bond. It is possible to observe the intensity difference in the area of the peaks in 1074 cm⁻¹ and 1020 cm⁻¹. This fact was attributed to the PANi sulfonation. Other important information regarding to sulfonation degree is the peaks area, which increases with the sulfonation degree.

Figure 2 shows a highlighted region, (between 1150 and 950 cm⁻¹) where the areas can be compared. The SPAN 3.0 (Figure 2a) presents the largest area showing that is possible to quantify the sulfonation degree and this way differentiates the PANi's by FTIR.

Figure 3 shows the spectra of the two kinds of PU used in this work. In Figure 4a were observed the peaks corresponds to the CAPU. Peak at 2957 cm⁻¹ corresponds to an angular deformation of CH₃ and at 1645 cm⁻¹ there is a peak attributed to the stretching of C=O groups. Other peak at 1075 cm⁻¹ is attributed to the stretching of C–O–C groups. The peak at 2269 cm⁻¹ corresponding to the N=C=O residual groups and it only appears for CAPU, indicating that the reaction is not still complete or that the proportions are not

**Figure 1.** FTIR spectrum of (a) SPAN 3.0, (b) SPAN 2.0 and (c) SPAN 1.5.**Figure 2.** FTIR spectrum of the a highlighted region (a) SPAN 3.0, (b) SPAN 2.0 and (c) SPAN 1.5.

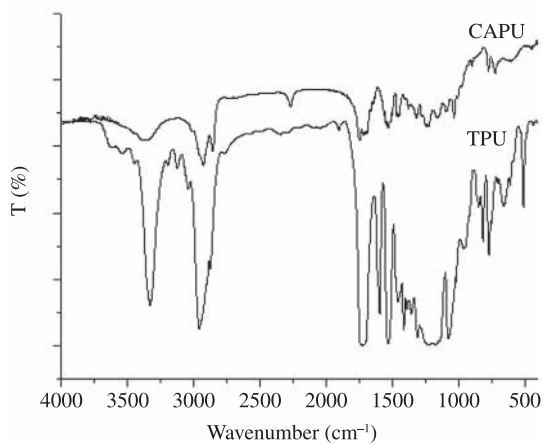
adjusted. The peaks at 1753 cm⁻¹ and 1700 cm⁻¹ (1665 cm⁻¹ for TPU) are attributed to the C=O free and H-bond (C=O) urethane respectively^{11,30} and that at 3345 cm⁻¹ N-H group stretch.

By FTIR analysis of the utilized PUs was possible to verify that the bands of PU made with castor oil resemble the bands of the commercial TPU. Membranes spectra (Figure 3b) showed peaks of SPAN, PAni_{TSA} and PU due to SPAN 2.0 and PAni_{TSA} incorporation into the PU matrix. The N=C=O group absorption present in the CAPU spectrum in 2269 cm⁻¹ disappeared in the CAPU/SPAN 2.0 membrane spectrum (Figure 3b) and also disappears in the CAPU/PAni_{TSA} membrane, probably due to its reaction with the amine groups of SPAN and PAni_{TSA}³¹. Table 2 shows the FTIR attribution of the polymers studied.

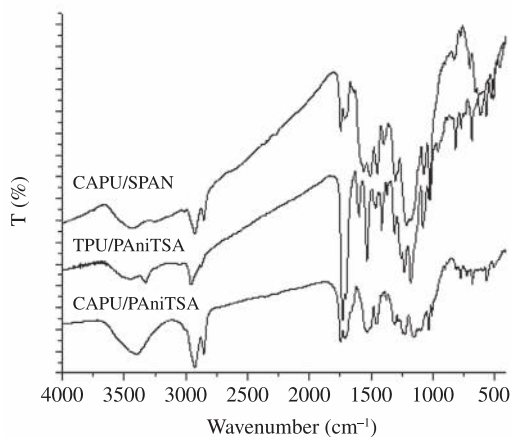
3.3. Thermal analysis

The thermal stability was studied aimed to determinate the limits for the membranes utilization; once these membranes can be used in several separation processes; also thermal stability can be associated with the morphological characteristics. In the Figure 4 it can be visualized the

thermograms of the polymers used in the membranes production. The several SPAN thermograms (Figure 4) present a first thermal event below 100 °C due to evaporation of the water molecules in the polymers. A second thermal



(a)



(b)

Figure 3. FTIR spectrum of (a) CAPU and TPU and (b) spectrum of CAPU/SPAN, TPU/PAni_{TSA} and CAPU/PAni_{TSA} membranes.

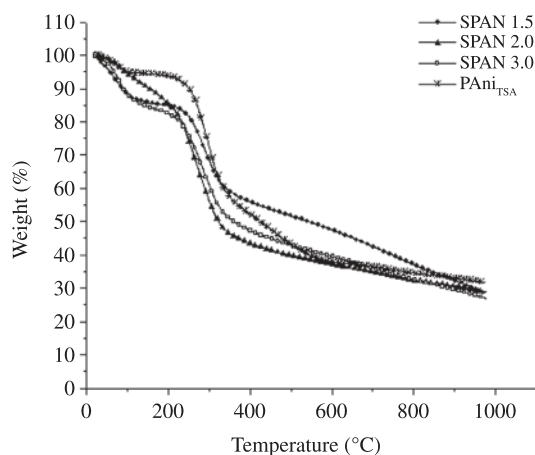


Figure 4. Thermogravimetric analysis of self doped pani (span) and PAni_{TSA}.

event of the SPAN begins around 220 °C and it is attributed to $-\text{SO}_3\text{H}^-$ group linked to the aromatic ring. Polymer main chain degradation starts around 300 °C and displays a process of continuous degradation until 1000 °C.

Figure 4 also shows that the amount of residue decreases with the increase of the amount of $-\text{SO}_3\text{H}^-$ groups. This phenomenon can be attributed to the low stability of the $-\text{SO}_3\text{H}^-$ groups linked to the main chain, because as larger is the number of $-\text{SO}_3\text{H}^-$ groups, lower is the polymer stability, and consequently the smaller is the residue. For this same Figure 4, the PAni_{TSA} shows a first mass loss below 100 °C due to residual humidity of the polymer synthesis. The second mass loss at 200 °C is due the loss of dopants molecules from the polymer structure. The third mass loss from 370 °C can be attributed to the degradation of the polymeric chain.

Figure 5a presents the CAPU, TPU, CAPU/PAni_{TSA} and CAPU/SPAN 2.0 thermograms. It shows a first thermal event beginning around 330 °C, and a slight inflection around 400 °C characterizing two events of weight loss. However, it can be observed that the insertion of SPAN 2.0 in the CAPU does not modify the CAPU degradation profile. However the CAPU/PAni_{TSA} membrane did not show this behavior, suggesting the occurrence of H-bonds between PAni amines and CAPU.

Figure 5b shows the peak temperatures where the decomposition rate is maximum, obtained by differential thermogravimetric (DTG) curves for CAPU, CAPU/SPAN and CAPU/PAni_{TSA} membranes. For CAPU and CAPU/SPAN 2.0 it is possible to observe two different peaks related to the mass losses, which are attributed to the cured and uncured CAPU respectively. In the TPU sample is possible to observe the same behavior.

For the Figure 6 it is possible to observe in the loss modulus that the membrane produced with TPU presents smaller modulus, presenting rubber behavior, with a plateau before T_g defined, showing rigid behavior due to the chains interlacements. In the curve is possible to visualize T_g around -30 °C. In the curve for CAPU membrane is not possible to visualize the T_g clearly; because the same does not present

Table 2. FTIR attribution of the polymers studied.

| SPAN (cm ⁻¹) | PU (cm ⁻¹) | Attribution |
|--------------------------|------------------------|--|
| 1560 | | quinoid ring |
| 1467 | | benzenoid ring |
| 1171 | | asymmetric stretching of S=O=S |
| 1074 | | symmetric stretching of S=O=S |
| 1020 | | S=O bond stretching |
| 702 | | S-O bond |
| 609 | | C-S bond |
| | 3345 | N-H stretch |
| | 2957 | angular deformation of CH ₃ |
| | 2269 | N=C=O |
| | 1753 | C=O free urethane |
| | 1700 and 1665 | H-bond (C=O) urethane |
| | 1645 | stretching of C=O groups |
| | 1075 | stretching of C-O-C groups |

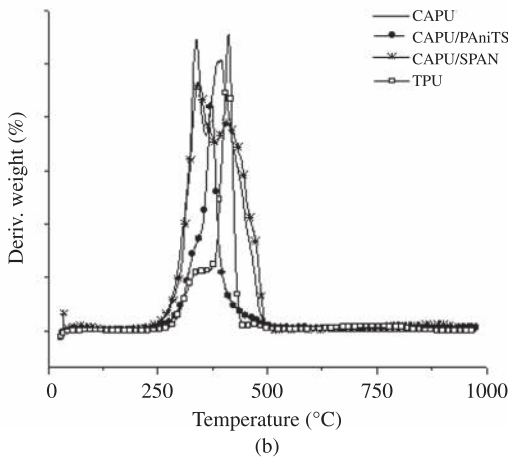
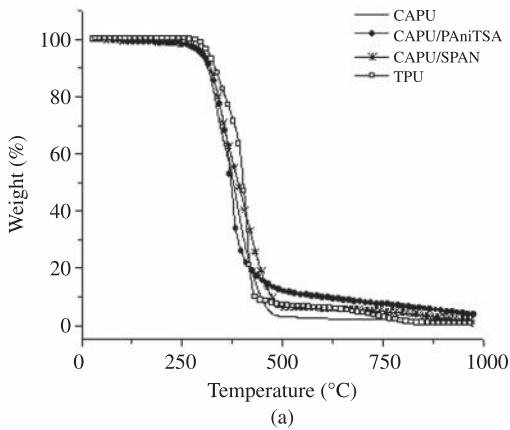


Figure 5. TGA (a) and DTG (b) of CAPU, TPU and CAPU/SPAN, CAPU/PAniTSA membranes.

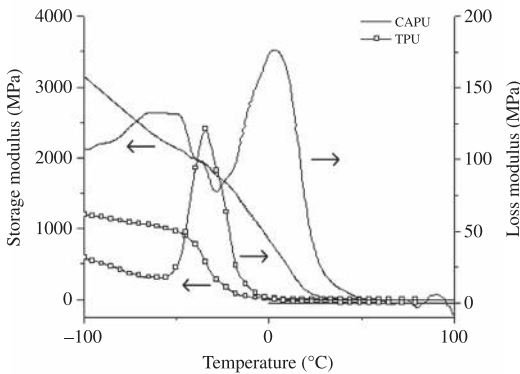


Figure 6. Storage and loss moduli of CAPU and TPU membranes.

very defined plateau. For the CAPU sample, a peak around $-50\text{ }^{\circ}\text{C}$ probably is related to the polyurethane uncured during the reaction. A peak is also observed at around $3\text{ }^{\circ}\text{C}$ which is related to the T_g .

The DMA curves (Figure 7) of PU, CAPU/SPAN 2.0 and CAPU/PAniTSA shown the membranes T_g . The PAni incorporation increases the T_g from $3\text{ }^{\circ}\text{C}$ to $18\text{ }^{\circ}\text{C}$ for CAPU/SPAN 2.0 membranes and from $3\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$ for

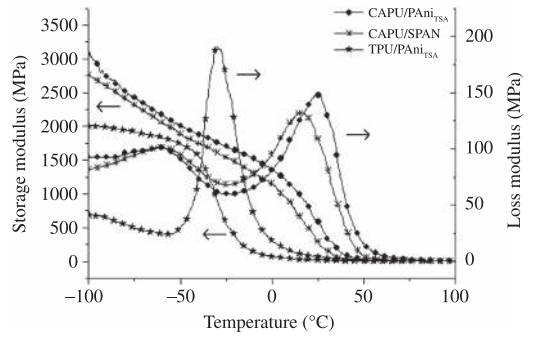
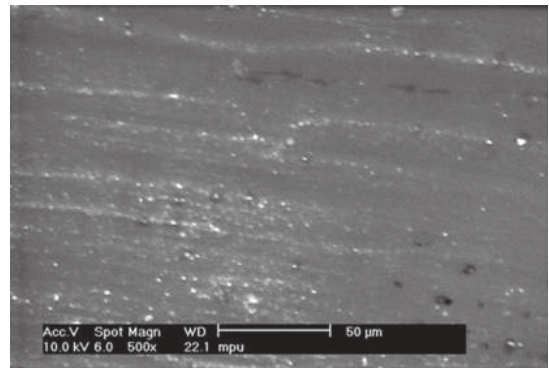
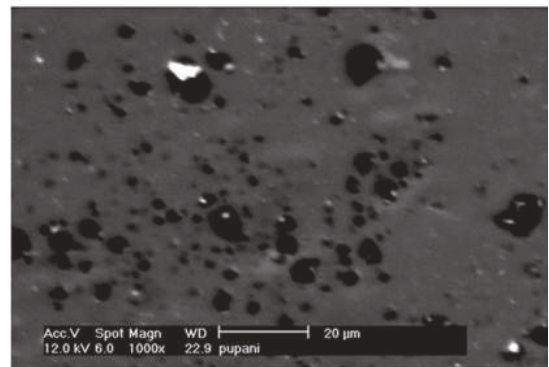


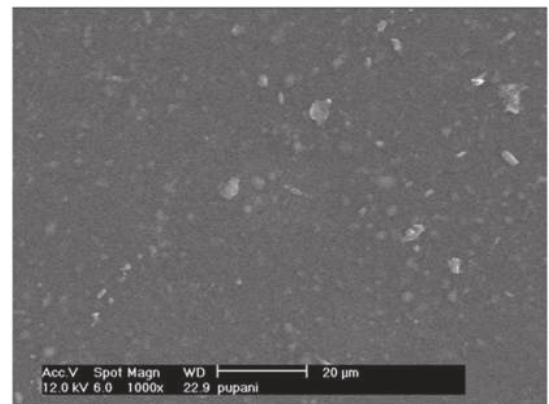
Figure 7. Storage and loss moduli of TPU/PAniTSA, CAPU/SPAN and CAPU/PAniTSA membranes.



(a)



(b)



(c)

Figure 8. SEM micrographs of membranes (a) CAPU, (b) CAPU/PAniTSA, and (c) TPU.

the CAPU/PAni_{TSA} membranes. The increase on T_g due to the PANi incorporation can be explained considering the formation of H-bonds^{30,32} between PANi amine groups and PU urethane groups as shown in Figure 6. The difference between CAPU/SPAN 2.0 and CAPU/PAni_{TSA} temperatures can be explained by the stronger steric effect in the SPAN 2.0 than in the PANi_{TSA} due to sulphonic group linked chemically to the aromatic ring, which would disfavor the formation of the H-bonds.

For the TPU/PAni_{TSA} membrane can be observed that the storage modulus has lower modulus, showing behavior of viscoelastic materials, with an elastomeric plateau before the T_g , to rubbery behavior and viscous, when the modulus is zero^{33,34}.

3.4. Morphological analysis

For the application in electro dialysis it is important that the membranes should have good thermal, chemical and mechanical strength, besides of structural homogeneity. This way, the membrane should present a constant thickness and that the blend should have a homogeneous distribution between PU and PANi. Figure 8 shows the membranes micrographics. A small difference among the morphologic structures of CAPU and TPU membranes was observed. It also can be observed that these membranes present agglomerates. These agglomerates possibly correspond to the presence of PANi in the membranes, indicating that a good dispersion of PANi in PU was not achieved. This fact has negative influence in the mechanical properties and in the diffusion efficiency¹¹.

References

- Leiknes T. Membrane technology in environmental engineering – meeting future demands and challenges of the water and sanitation sector. *Desalination*. 2006; 199:12-14. <http://dx.doi.org/10.1016/j.desal.2006.03.132>
- Scott K. Introduction to membrane separations. In: Handbook of industrial membranes: introduction to membrane separation. 2nd ed. Elsevier Advanced Technology; 1995. p. 3-185.
- Jeziórska R, Klepka T and Paukszta D. Polycarbonate/maleic anhydride grafted polyethylene/graphite composites. *Polimery-W*. 2007; 52:294-298.
- Meneguzzi A, Pham MC, Ferreira CA, Lacroix JC, Aeiayach S and Lacaze PC. Electroactive poly(aromatic amine) films deposited on mild steel. *Synthetic Metals*. 1999; 102:1390-1391. [http://dx.doi.org/10.1016/S0379-6779\(98\)01020-0](http://dx.doi.org/10.1016/S0379-6779(98)01020-0)
- Tang CW and Vananslyke SA. Organic electroluminescent diodes. *Applied Physics Letters*. 1987; 51:913-915. <http://dx.doi.org/10.1063/1.98799>
- Gazotti WA, Nogueira AF, Girotto EM, Gallazzi MC and de Paoli MA. Flexible photoelectrochemical devices based on conducting polymers. *Synthetic Metals*. 2000; 108:151-157. [http://dx.doi.org/10.1016/S0379-6779\(99\)00272-6](http://dx.doi.org/10.1016/S0379-6779(99)00272-6)
- de Paoli MA, Nogueira AF, Machado DA and Longo C. All-polymeric electrochromic and photoelectrochemical devices: new advances. *Electrochimica Acta*. 2001; 46:4243-4249. [http://dx.doi.org/10.1016/S0013-4686\(01\)00684-3](http://dx.doi.org/10.1016/S0013-4686(01)00684-3)
- Nishikitani Y, Kobayashi M, Uchida S and Kubo T. Electrochemical properties of non-conjugated electrochromic

4. Conclusions

In this work types of membranes were produced and characterized. The analysis of the membranes synthesis (CAPU/SPAN and CAPU/PAni_{TSA}) was satisfactory, since the characteristic peaks of the CAPU, SPAN and PANi_{TSA} were present in the FTIR spectra. This technique also demonstrated the complete reaction between isocyanate and secondary amines from SPAN and PANi_{TSA}, as NCO peaks disappeared from the membrane spectra.

The thermogravimetric analysis showed that the membrane presented thermal stability until 220 °C. The DTG analysis showed a higher reticulation degree of the CAPU/PAni_{TSA} when compared with the CAPU/SPAN membrane and only CAPU. Membranes produced with CAPU and SPAN, CAPU and PANi_{TSA} may be used in electro dialysis tests regarding on its mechanical properties, since these membranes have a high mechanical behavior, as showed in dynamic mechanical analysis, through in the storage modulus.

Evaluating the two membranes can be concluded that the CAPU/PAni_{TSA} membrane presented better performance compared the other membranes studied, as it can be visualized in the dynamic mechanical and thermogravimetric analysis.

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- polymers derived from aromatic amine derivatives. *Electrochimica Acta*. 2001; 46:2035-2040. [http://dx.doi.org/10.1016/S0013-4686\(01\)00411-X](http://dx.doi.org/10.1016/S0013-4686(01)00411-X)
- Amado FDR, Ferreira CA, Gondran E, Ferreira JZ and Rodrigues MAS. Synthesis and characterization of high impact polystyrene/polyaniline composite membranes for electro dialysis. *Journal of Membrane Science*. 2004; 234:139-145. <http://dx.doi.org/10.1016/j.memsci.2004.01.017>
 - Tran-Van F, Carrier M and Chevrot C. Sulfonated polythiophene and poly(3,4-ethylenedioxythiophene) derivatives with cations exchange properties. *Synthetic Metals*. 2004; 142:251-258. <http://dx.doi.org/10.1016/j.synthmet.2003.09.013>
 - Swamy BKK, Siddaramaiah, Somashekarappa H and Somashekar R. Structure-property relationship of PANi filled chain extended polyurethane. *Polymer Engineering and Science*. 2004; 44:772-778. <http://dx.doi.org/10.1002/pen.20069>
 - Chwang CP, Liu CD, Huang SW, Chao DY and Lee SN. Synthesis and characterization of high dielectric constant polyaniline/polyurethane blends. *Synthetic Metals*. 2004; 142:275-281. <http://dx.doi.org/10.1016/j.synthmet.2003.09.012>
 - Amado FDR, Rodrigues LF Jr, Rodrigues MAS, Bernardes AM, Ferreira JZ and Ferreira CA. Development of polyurethane/polyaniline membranes for zinc recovery through of electro dialysis. *Desalination*. 2005; 186:199-206. <http://dx.doi.org/10.1016/j.desal.2005.05.019>
 - Patel MR, Shukla JM, Patel NK and Patel KH. Biomaterial based novel polyurethane adhesives for wood to wood and metal to metal bonding. *Materials Research*. 2009; 12(4):385-393. <http://dx.doi.org/10.1590/S1516-14392009000400003>

15. Martin DJ, Warren LAP, Gunatillake PA, McCarthy SJ, Meijs GF and Schindhelm K. New methods for the assessment of in vitro and in vivo stress cracking in biomedical polyurethanes. *Biomaterials*. 2000; 21:1021-1029. [http://dx.doi.org/10.1016/S0142-9612\(99\)00271-9](http://dx.doi.org/10.1016/S0142-9612(99)00271-9)
16. Amado FDR, Rodrigues MAS, Morisso FDP, Bernardes AM, Ferreira JZ and Ferreira CA. High impact polystyrene/polyaniline membranes for acid solutions treatment by electro dialysis: preparation, evaluation and chemical calculation. *Journal of Colloid and Interface Science*. 2008; 320:52-61. PMID:18222464. <http://dx.doi.org/10.1016/j.jcis.2007.11.054>
17. Singh A, Singh NP, Singh P and Singh RA. Synthesis and characterization of conducting polymer composites based on polyaniline-polyethylene glycol-zinc sulfide system. *Journal of Polymer Research*. 2011; 18:67-77. <http://dx.doi.org/10.1007/s10965-010-9392-6>
18. Milanese AC, Cioffi MOH and Voorwald HJC. Flexural behavior of sisal/castor oil-based polyurethane and sisal/phenolic composites. *Materials Research*. 2012; 15(2):191-197. <http://dx.doi.org/10.1590/S1516-14392012005000019>
19. Nayak P, Mishra DK, Parida D, Sahoo KC, Nanda M and Nayak PL. Polymers from renewable resources. IX. Interpenetrating polymer networks based on castor oil polyurethane poly(hydroxyethyl methacrylate): Synthesis, chemical, thermal and mechanical properties. *Journal of Applied Polymer Science*. 2006; 63:671-679. [http://dx.doi.org/10.1002/\(SICI\)1097-4628\(19970131\)63:5<671::AID-APP15>3.0.CO;2-X](http://dx.doi.org/10.1002/(SICI)1097-4628(19970131)63:5<671::AID-APP15>3.0.CO;2-X)
20. Amado FDR, Rodrigues LF Jr, Forte MMC and Ferreira CA. Properties evaluation of the membranes synthesized with castor oil polyurethane and polyaniline. *Polymer Engineering and Science*. 2006; 46:1485-1489. <http://dx.doi.org/10.1002/pen.20602>
21. Prashantha K, Pai KVS, Sherigara BS and Prasannakumar S. Interpenetrating polymer networks based on polyol modified castor oil polyurethane and poly(2-hydroxyethylmethacrylate): Synthesis, chemical, mechanical and thermal properties. *Bulletin of Materials Science*. 2001; 24:535-538. <http://dx.doi.org/10.1007/BF02706727>
22. Valero MF, Pulido JE, Ramírez A and Cheng Z. Síntesis de poliuretanos a partir de polioles obtenidos a partir del aceite de higuera modificado por transesterificación con pentaeritritol. *Química Nova*. 2008; 31:2076-2082. <http://dx.doi.org/10.1590/S0100-40422008000800031>
23. MacDiarmid AJ and Epstein AJ. Polyanilines: a novel class of conducting polymers. *Faraday Discussion of the Chemical Society*. 1989; 88:317-332. <http://dx.doi.org/10.1039/dc9898000317>
24. Campos TLA, Kersting DF and Ferreira CA. Chemical synthesis of polyaniline using sulphanic acid as dopant agent into the reactional medium. *Surfaces and Coating Technology*. 1999; 122:3-5. [http://dx.doi.org/10.1016/S0257-8972\(99\)00399-0](http://dx.doi.org/10.1016/S0257-8972(99)00399-0)
25. Ito S, Murata K, Teshima S, Aizawa R, Azako Y, Takahashi K et al. Simple synthesis of water-soluble conducting polyaniline. *Synthetic Metals*. 1998; 96:161-163. [http://dx.doi.org/10.1016/S0379-6779\(98\)00074-5](http://dx.doi.org/10.1016/S0379-6779(98)00074-5)
26. Neoh KG, Pun MY, Kang ET and Tan KL. Polyaniline treated with organic acids: doping characteristics and stability. *Synthetic Metals*. 1995; 73:209-215. [http://dx.doi.org/10.1016/0379-6779\(95\)80018-2](http://dx.doi.org/10.1016/0379-6779(95)80018-2)
27. Li S, Cao Y and Xue Z. Soluble polyaniline. *Synthetic Metals*. 1987; 20:141-149. [http://dx.doi.org/10.1016/0379-6779\(87\)90553-4](http://dx.doi.org/10.1016/0379-6779(87)90553-4)
28. Jousseume V, Morsli M, Bonnet A and Lefrant S. X-ray photoelectron spectroscopy of conducting polyaniline and polyaniline-polystyrene blends. *Journal of Applied Polymer Science*. 1998; 67:1209-1214. [http://dx.doi.org/10.1002/\(SICI\)1097-4628\(19980214\)67:7<1209::AID-APP7>3.0.CO;2-K](http://dx.doi.org/10.1002/(SICI)1097-4628(19980214)67:7<1209::AID-APP7>3.0.CO;2-K)
29. Yue J, Wang ZH, Cromack KR, Epstein AJ and MacDiarmid AG. Effect of sulfonic acid group on polyaniline backbone. *Journal of the American Chemical Society*. 1991; 113:2665-2671. <http://dx.doi.org/10.1021/ja00007a046>
30. Yilgor E, Burgaz E, Yurtsever E and Yilgor I. Comparison of hydrogen bonding in polydimethylsiloxane and polyether based. *Polymer*. 2000; 41:849-857. [http://dx.doi.org/10.1016/S0032-3861\(99\)00245-1](http://dx.doi.org/10.1016/S0032-3861(99)00245-1)
31. Jeevananda T and Siddaramaiah. Synthesis and characterization of polyaniline filled PU/PMMA interpenetrating polymer networks. *European Polymer Journal*. 2003; 39:569-578. [http://dx.doi.org/10.1016/S0014-3057\(02\)00272-0](http://dx.doi.org/10.1016/S0014-3057(02)00272-0)
32. Ho KS, Hsieh KH, Huang SK and Hsieh TH. Polyurethane based conducting polymer blends. I. Effect of chain extender. *Synthetic Metals*. 1999; 107:65-73. [http://dx.doi.org/10.1016/S0379-6779\(99\)00144-7](http://dx.doi.org/10.1016/S0379-6779(99)00144-7)
33. Cassu SN and Felisberti MI. Comportamento dinâmico-mecânico e relaxações em polímeros e blendas poliméricas. *Química Nova*. 2005; 28:255-263. <http://dx.doi.org/10.1590/S0100-40422005000200017>
34. Almeida Júnior JHS, Ornaghi Júnior HL, Amico SC and Amado FDR. Study of hybrid intralaminar curaua/glass composites. *Materials and Design*. 2012; 42:111-117. <http://dx.doi.org/10.1016/j.matdes.2012.05.044>