Ionic liquids in the control of the poly(vinylidene fluoride-cohexafluoropropylene) membranes morphology

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INTRODUCTION

The development of **polymer membranes** with **tailored micro-morphology** and wettability is a demand in the areas of filtration, sensors or tissue engineering, among others. Poly(vinylidene fluoride-cohexafluoropropylene) (**PVDF-HFP**) is a thermoplastic copolymer and one of the most interesting polymers to be used in these areas due to its good properties. However, the control of the morphology is a complicated task and is mostly restricted to the use of solvent evaporation (SE) techniques [1]. In this way, ionic liquids (**ILs**), molten salts with melting points lower than 100 °C, which stand out for their good properties, such as high thermal stability or nonflammability, are a promising alternative for the **control of morphology** in certain materials since the large number of ionic liquids that exist allows to tailor the most suitable combination in order to meet the desired properties [2-3]. In this work, the production and the characterization of PVDF-HFP@ionic liquid **composite membranes** using different



The composite properties were analyzed by Scanning Electron Microscopy - SEM (JEOL JSM-7000F), Contact Angle (NEURTEK OCA 15EC DATAPHYSICS), Mechanical Test (Shimadzu AGS-500NJ), Thermogravimetric Analysis - TGA (NETZSCH STA 449F3) and Infrared Spectroscopy – FTIR (Jasco FT/IR-6100 spectrometer).

ionic liquids and methodologies are described in detail (figs. 1-6).







0 -Room temperature 20min 80°C 60min 100°C

Figure 4: Elastic module estimated for the samples.

* After immerse the membranes in water for 48h.

Figure 3 : Images of the Contact Angle Measurements as a function of time of the different samples dried at 80°C (before and after immersion in H_2O).

Different morphologies and properties in function of the ionic liquid present in the membrane.

54500 5 OkV 9 3mm v1 00k SEIM

Figure 1 : SEM (cross–section) and contact angle images for the different samples.

\$4000 5 0KV 9 3YMN 41.00K SE(M)

a) 100 100 80 80 ▲ ≫ 60 8 60 Mass Ξ 40 40 20 20 PVDF-HFP -PVDF-HFP_H₂O PVDF-HFP@[MIm][Cl PVDF-HFP@[MIm][CI]_H₂O PVDF-HEP@[dema][Tf0 PVDF-HFP@[dema][TfO]_H₂O PVDF-HFP@[Mlm][NTf₂ - PVDF-HFP@[MIm][NTf₂]_H₂O 400 500 400 500 600 200 300 600 700 100 800 200 300 700 100 Temperature / °C Temperature / °C

Figure 5 : Thermogravimetric curves for the membranes dried at 80 °C, (a) before immersion in water (b) after immersion in water.

After immerse the membranes in water we can appreciate a higher hydrophobicity on the membranes, nonetheless, the membranes morphology is not affected. The percentage of polymer piezoelectric β -phase is mantained or even increased.





Figure 6 : FTIR-ATR spectra of the different membranes dried at 80 °C, (a) before immersion in water (b) after immersion in water.

DISCUSSION & CONCLUSIONS

- The polymer membrane properties can be **tuned using ILs.**
- Morphology, wettability or mechanical properties change depend on the production methodology employed as well as on the type of ionic liquid used.
- After the immersion of membranes in water, the morphology is maintained, but it recovers its hydrophobic properties as well as its thermal stability until temperatures higher than 400 °C. The percentage of piezoelectric β-phase is mantained or even increased.
- The possibility to tailor the membranes morphology by the variation of the IL type opens new possibilities in the area of membranes production, since the

wide range of different IL structures predicts a huge variety of different membrane structures.

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