eman ta zabal zazu

Universidad del País Vasco
Euskal Herriko Unibertsitatea

BCMATERIALS
BASQUE CENTER FOR MATERIALS, APPLICATIONS & NANOSTRUCTURES
ehugroup

Ionic liquid in the control of the poly(vinylidene fluoride-co-hexafluoropropylene) membranes morphology

Paula GSaiz[1], Ana Catarina Lopes[1], Simone Eizagirre[1], Roberto Fernández de Luis [1], Edurne S. Larrea[2], Arkaitz Fidalgo-Marijuan [1], María Isabel Arriortua[1,2]

[1]BCMaterials, Parque Científico y Tecnológico de Bizkaia, 48160, Derio, Spain
[2]Dpto. Mineralogía y Petrología, Universidad del País Vasco, UPV/EHU, Leioa, Spain

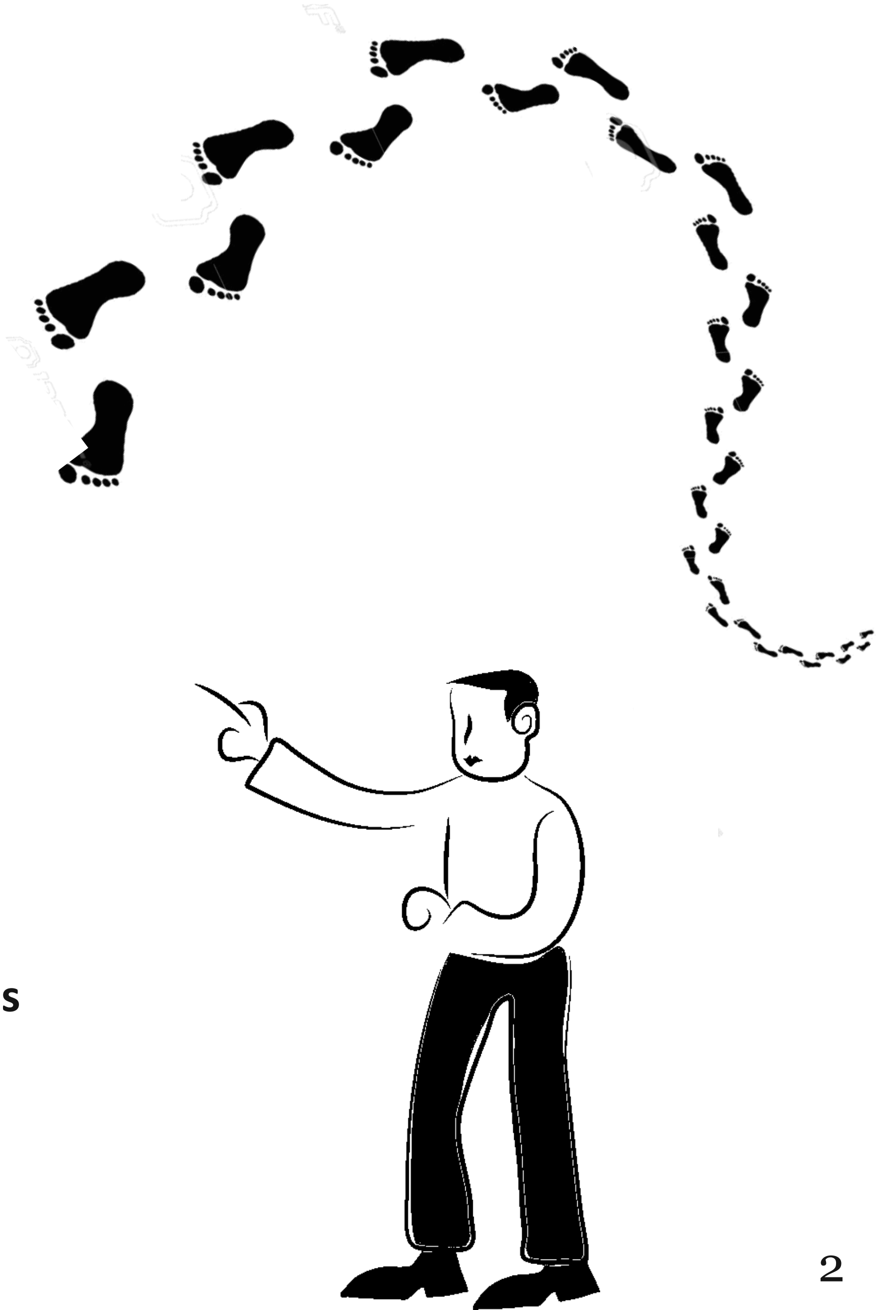
NALS

13 December
2017

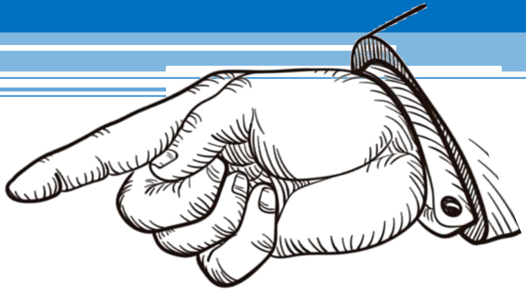
Paula GSaiz
Paula.gonzalez@bcmaterials.net
BCMaterials (Campus Leioa/
Universidad País Vasco)

Outline

1. Introduction
2. Experimental procedure
3. Results
4. Conclusions
5. Acknowledgments

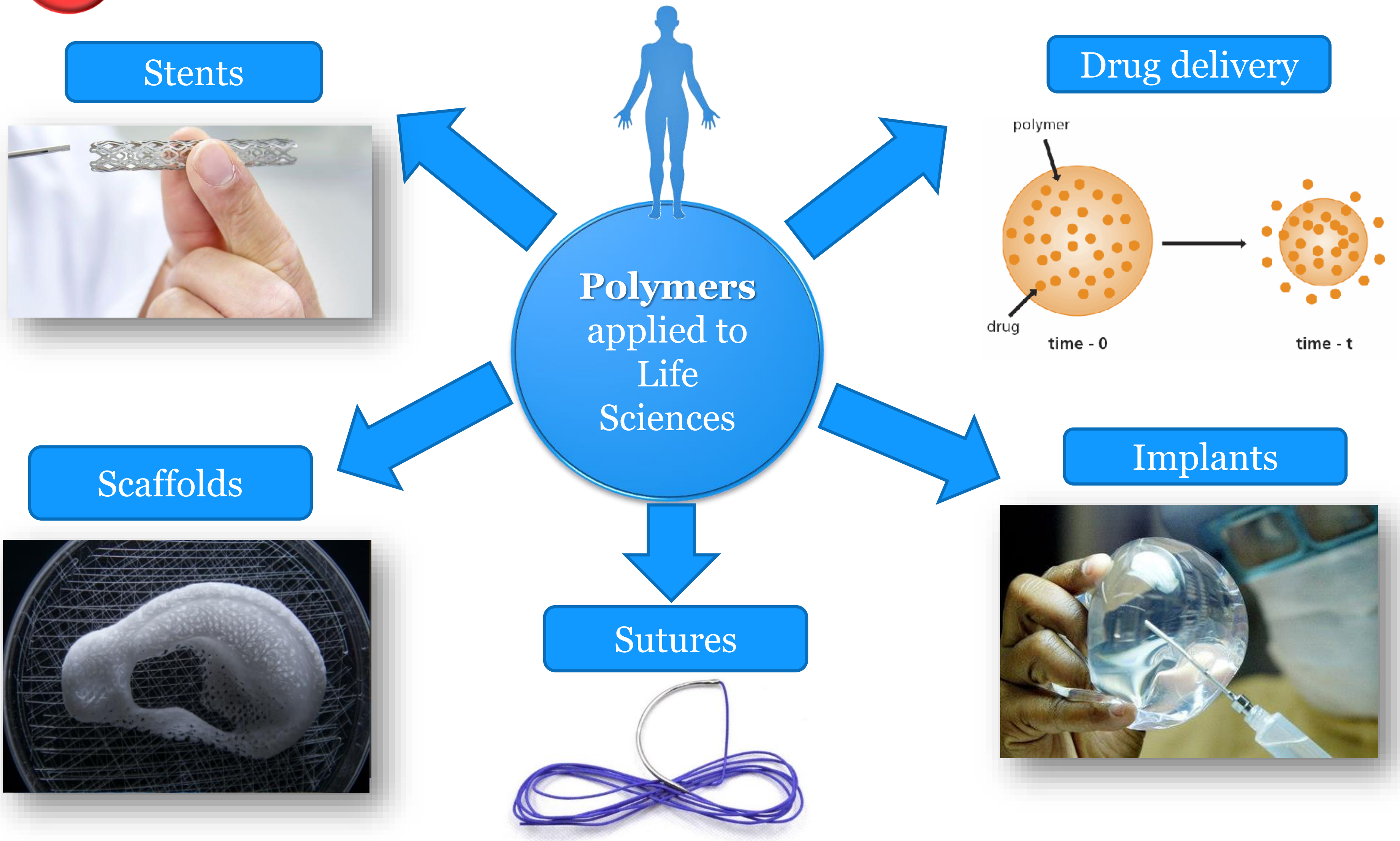


1 Introduction



- Polymers Applied to Life Sciences.
- Polymers.
- Ionic liquids.

1 *“Nanomaterials Applied to Life Sciences”*



Stents

Drug delivery

Polymers applied to Life Sciences

Scaffolds

Implants

Sutures

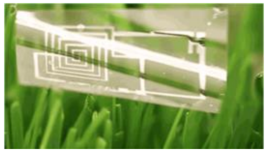
M.F. Maitz. *“Applications of synthetic polymers in clinical medicine”*. Biosurface and Biotribology, 2015, vol. 1, no 3, p. 161-176.

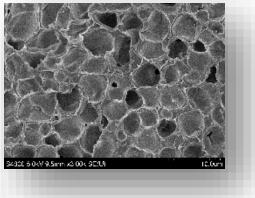
1

“Polymers Applied to Life Sciences”

Factors to consider:

- Biocompatibility
- Biodegradability
- Mechanical properties
- Morphology
- Hydrophobicity
- Thermal stability



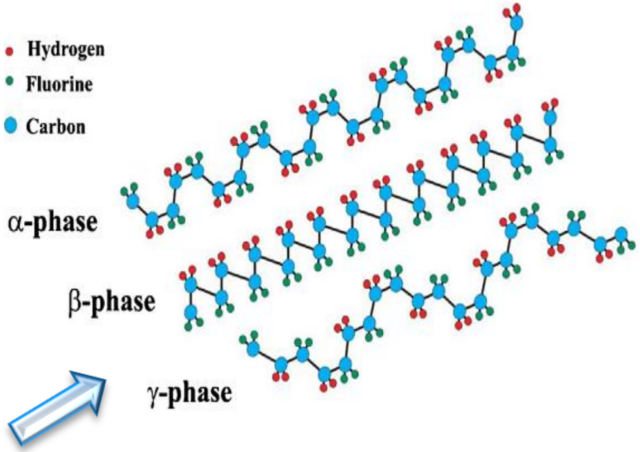


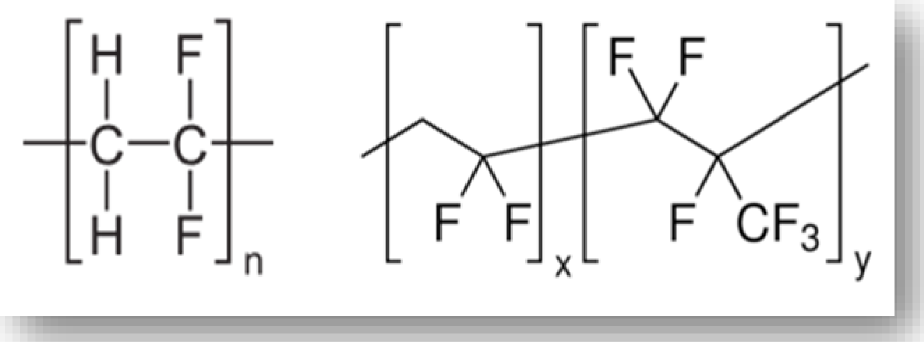
Physical and chemical properties

1 Polymers

- **PVDF** and some of its copolymers stand out for their **good properties.**

» **Biocompatibility.**
» Thermal and chemical stability.
» Highest electroactive response.
» Flexibility.
» Hidrophobic character.
» **Piezoelectricity.**





PVDF

PVDF-HFP

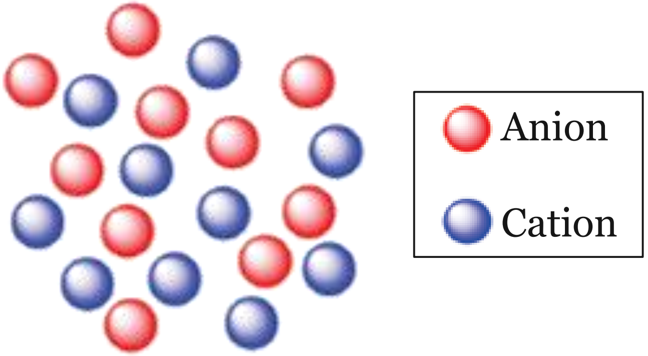
Control of the properties → **Techniques of SE, NSE, TIPS.**

Looking for other methods → **Composites polymer@ionic liquid**.

C. G. Ferreira et al. *"Tailoring microstructure and physical properties of poly(vinylidene fluoride–hexafluoropropylene) porous films"* Journal of Materials Science, vol. 50, no. 14, pp. 5047–5058, 2015..

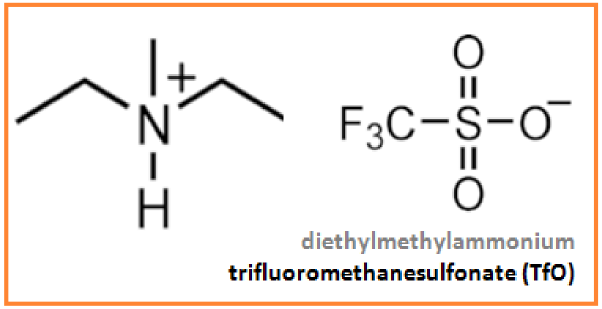
1 Ionic liquids

- ✓ Most are green solvents and biocompatible.
- ✓ Good electrochemical and thermal stability.
- ✓ Low melting point.
- ✓ Nonflammability.

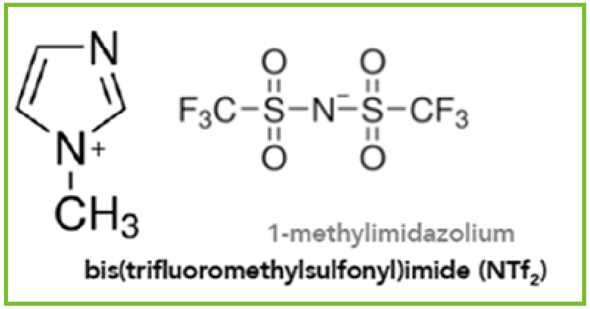


Organic cation + (in)organic anion → Hundreds of combinations

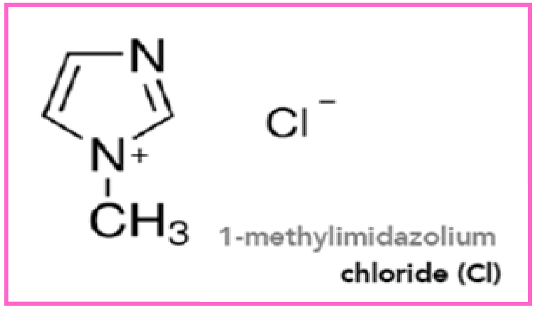
Tuneable properties


diethylmethylammonium
trifluoromethanesulfonate (TfO)

[dema][TfO]


1-methylimidazolium
bis(trifluoromethylsulfonyl)imide (NTf_2)

[MIm][NTf_2]


1-methylimidazolium
chloride (Cl)

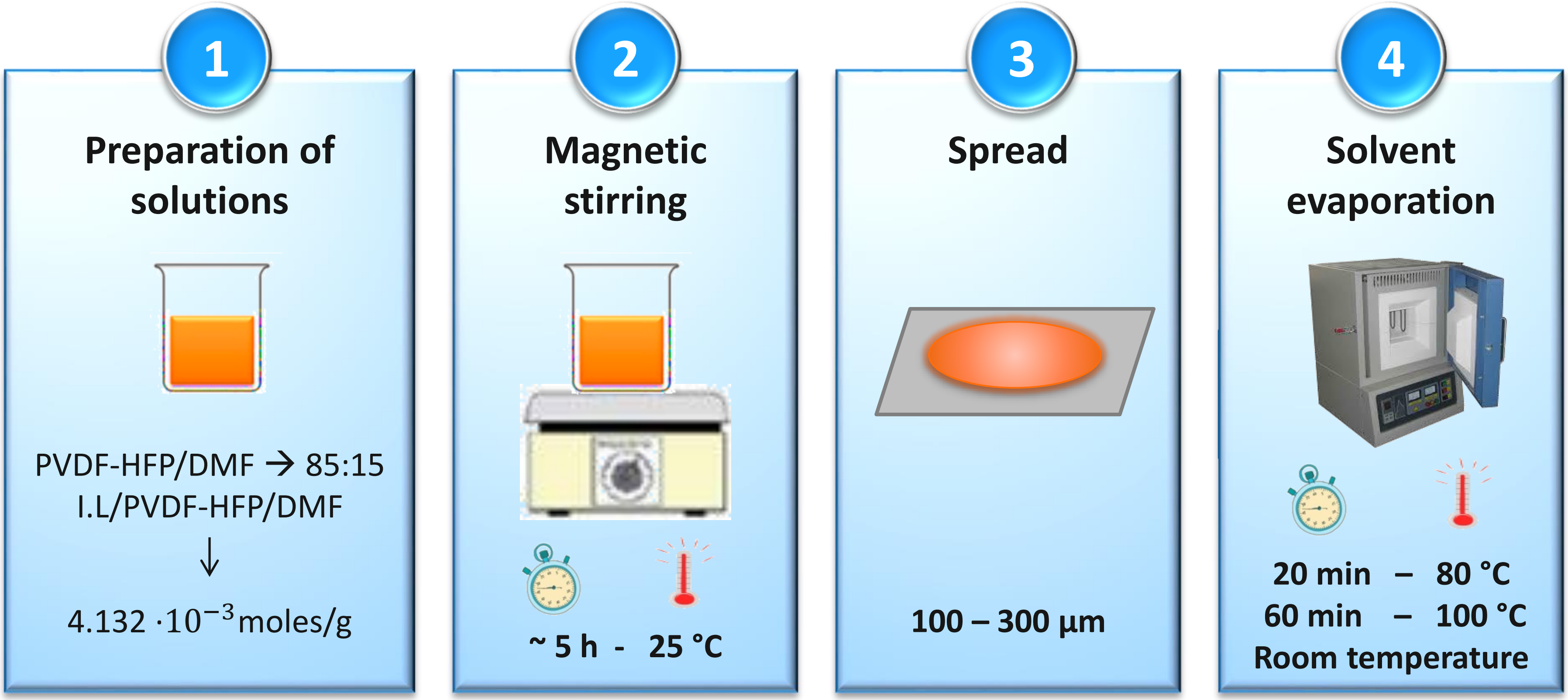
[MIm][Cl]

M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, and B. Scrosati, *"Ionic-liquid materials for the electrochemical challenges of the future"* Nature Materials, vol. 8, no. 8, pp. 621–629, 2009.

2 Experimental procedure

- Samples Preparation.
- Characterization.

2 Samples preparation



1
Preparation of solutions

PVDF-HFP/DMF → 85:15
I.L/PVDF-HFP/DMF
↓
$4.132 \cdot 10^{-3}$ moles/g

2
Magnetic stirring

~ 5 h - 25 °C

3
Spread

100 – 300 µm

4
Solvent evaporation

20 min – 80 °C
60 min – 100 °C
Room temperature

C. G. Ferreira et al. *"Tailoring microstructure and physical properties of poly(vinylidene fluoride–hexafluoropropylene) porous films"* Journal of Material Sciences, vol. 50, no. 14, pp. 5047–5058, 2015.

② Characterization

- **Morphology** → SEM measures.

- **Hidrophobicity** → Contact angle measures.

- **Mechanical properties** → Stress-strain curves.

- **Thermal characterization** → TGA.

- **Phase content** → FTIR-ATR spectroscopy.

3 Results

Morphology.
Hydrophobicity.
Mechanical properties.
Thermal characterization.
Crystallization-phase characterization.

3 Morphology / hidrophobicity

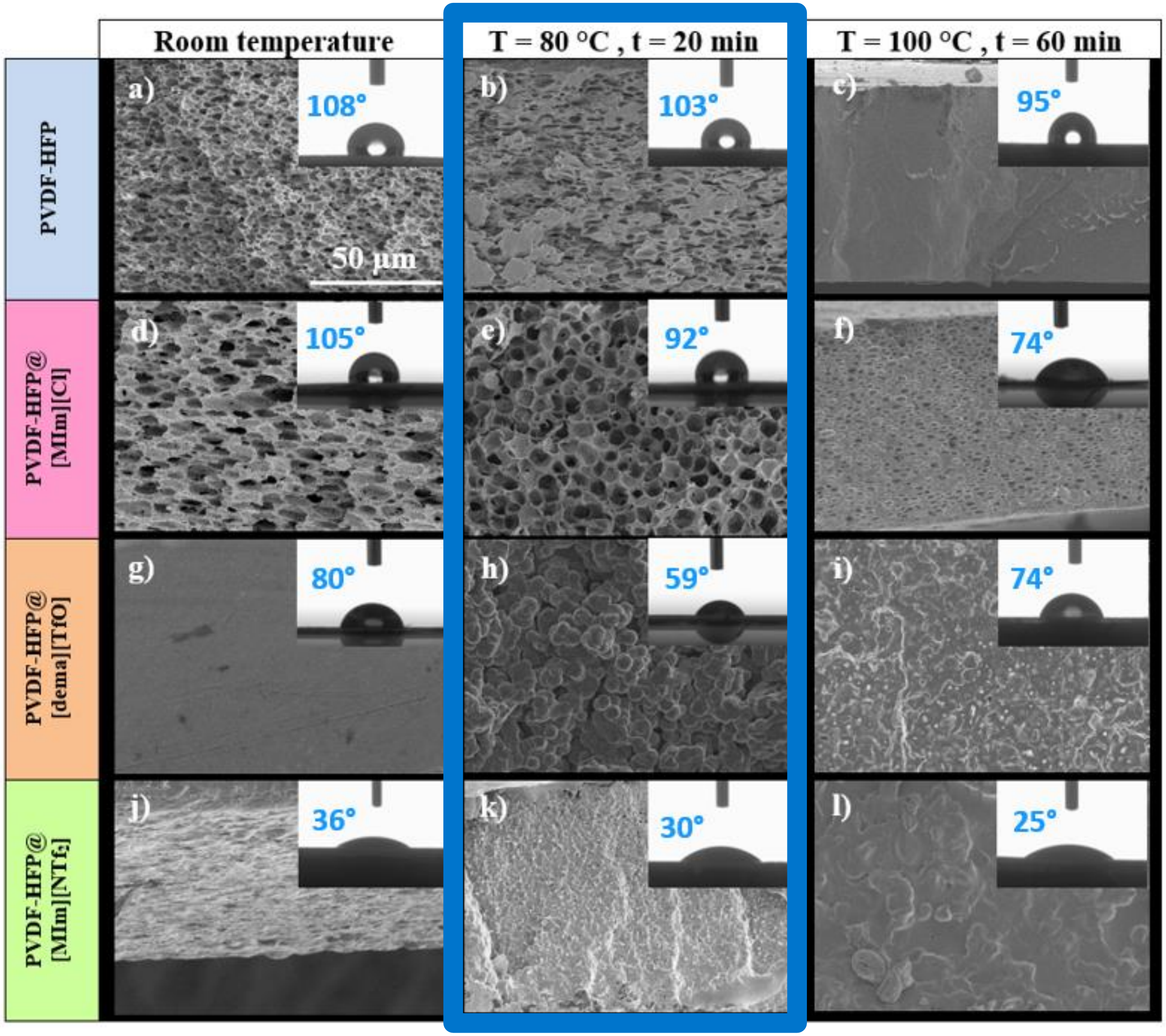


Figure 1. SEM (cross–section) and contact angle images for the different samples.

Dependence with the solvent evaporation process and **with the type of ionic liquid.**

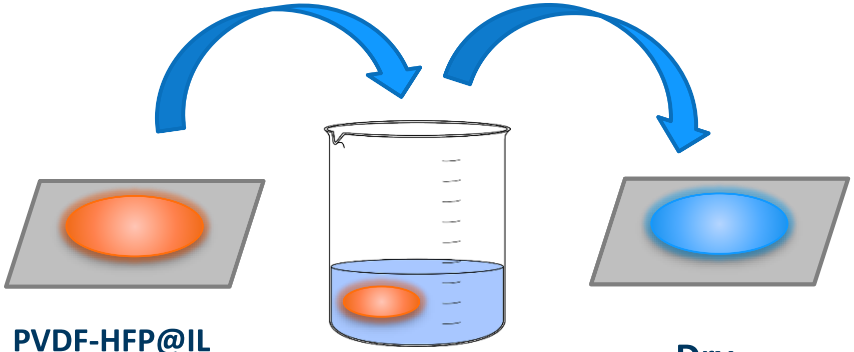
- Porous
- Non-porous
- With spherulites

- Hydrophobic
- Hydrophilic

3 Morphology

Immersion in water

- Is the ionic liquid expelled?
- What effects does it have on the properties of the membrane?



PVDF-HFP@IL membrane

48h in H_2O

Dry

¡Morphology is maintained!

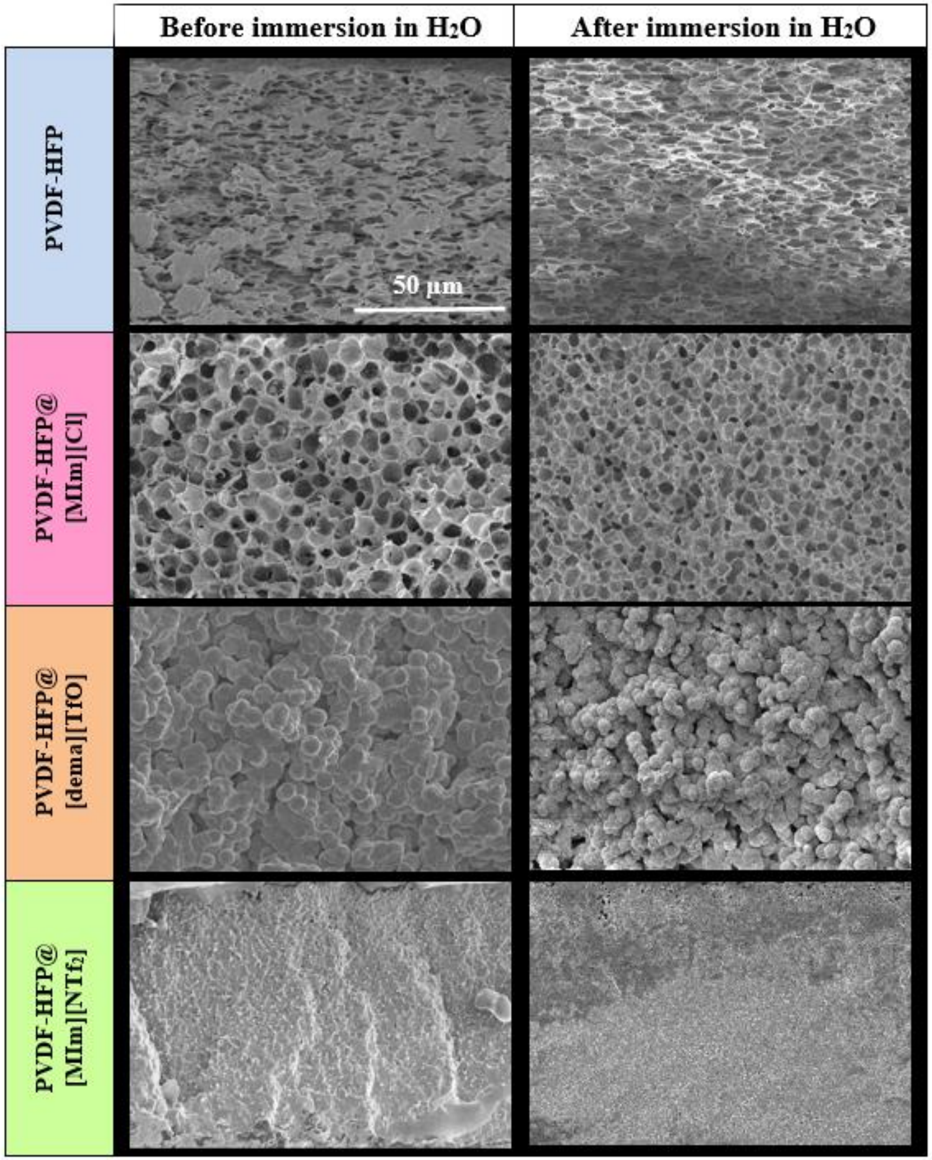


Figure 2. SEM (cross-section) images of the samples dried at 80ºC before and after immersion in water for 48h.

3 Hidrophobicity

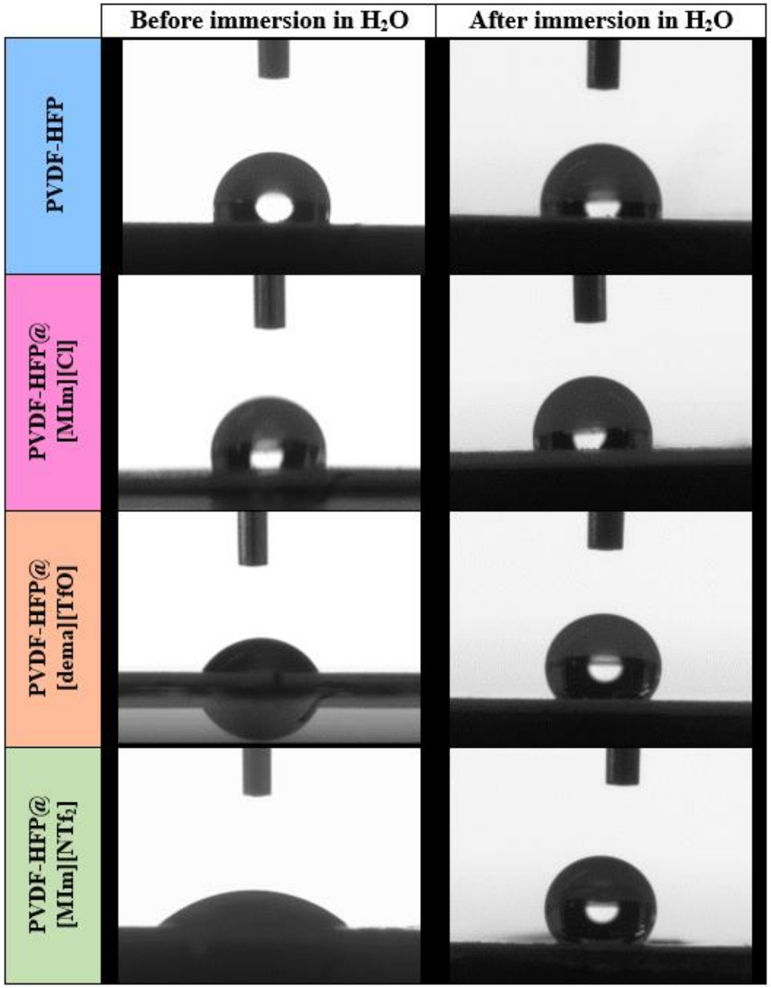


Figure 3. Contact angle measurements before and after immersion in water.

Hydrophobicity

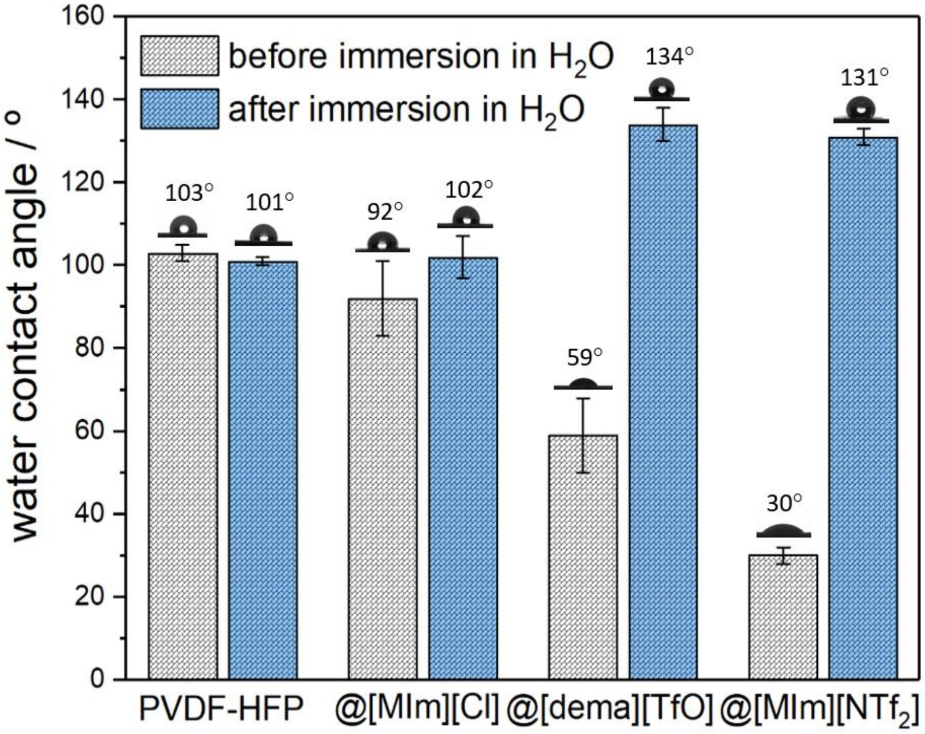


Figure 4. Contact angle of the prepared samples before and after immersion in water.

3 Mechanical properties

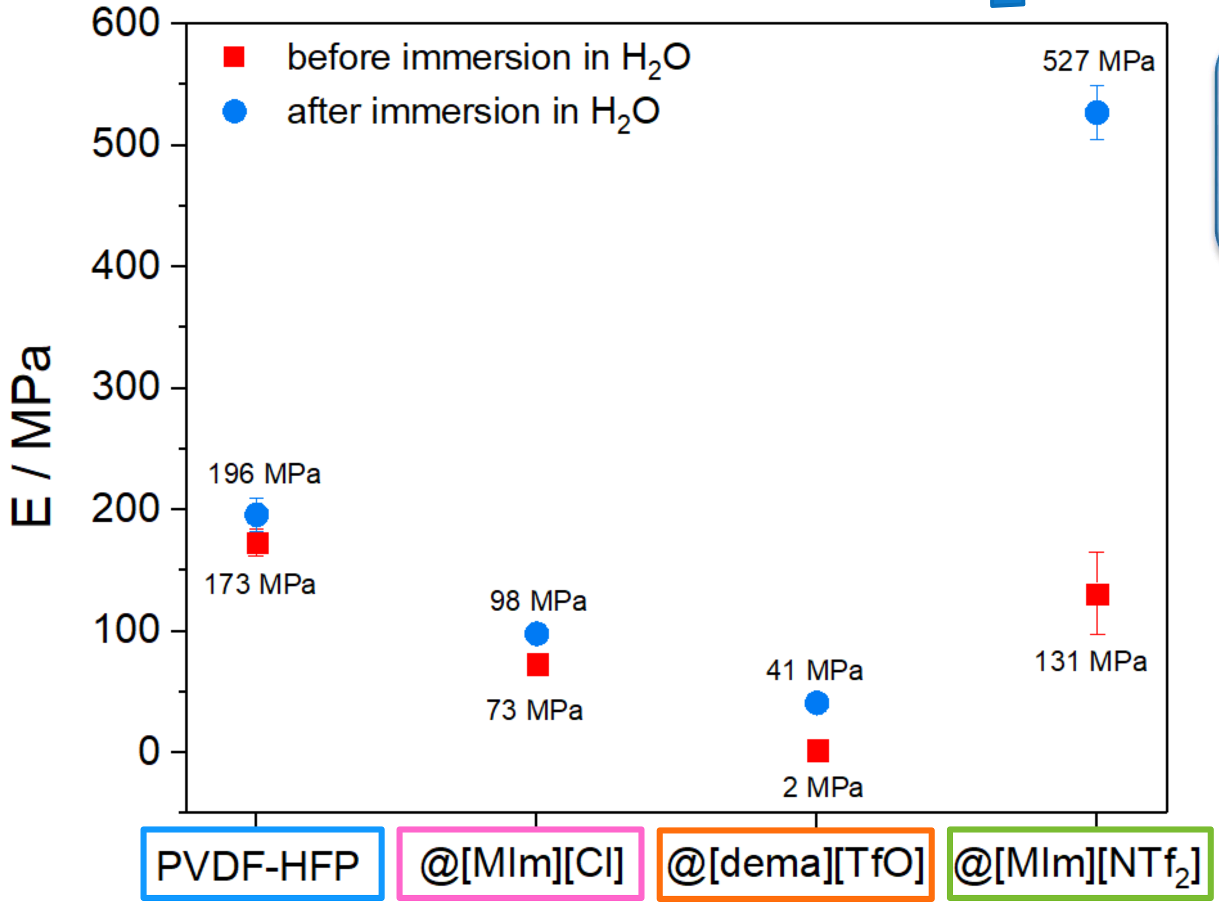


Figure 5. Results of elastic module estimated for the different samples dried at 80 ºC during 20 min before and after the immersion in water.

- **Spherulitic character →** Young modulus lower.
- **Non porosity →** Young modulus higher

After immersion in water

Young modulus ↑ ✓

ILs act as plasticizers

3 Thermal characterization

PVDF-HFP the highest T_d > 450 °C

T_d depends on the ionic liquid

T_d of the neat PVDF-HFP is reached after the immersion in water

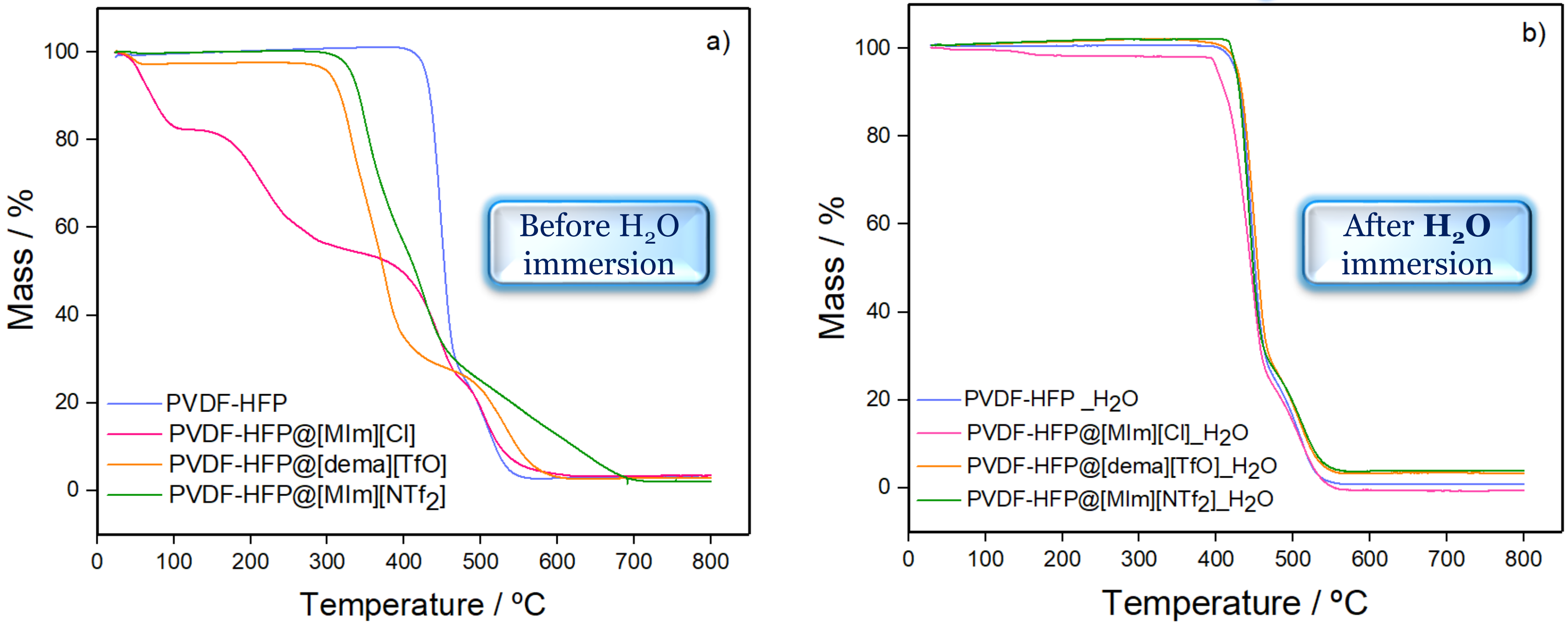
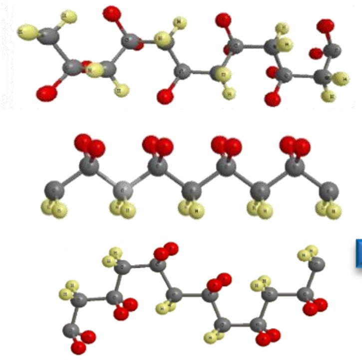


Figure 6. Thermogravimetric curves for the membranes dried at 80 °C, (a) before immersion in water (b) after immersion in water.

3 Crystallization-phase

- **α-phase**: At 763 cm^{-1}
- **β-phase**: At 840 cm^{-1}
  1279 cm^{-1}
- **γ-phase**: At 840 cm^{-1}
  1234 cm^{-1}



Increase on the **piezoelectric phases** after immersion in water

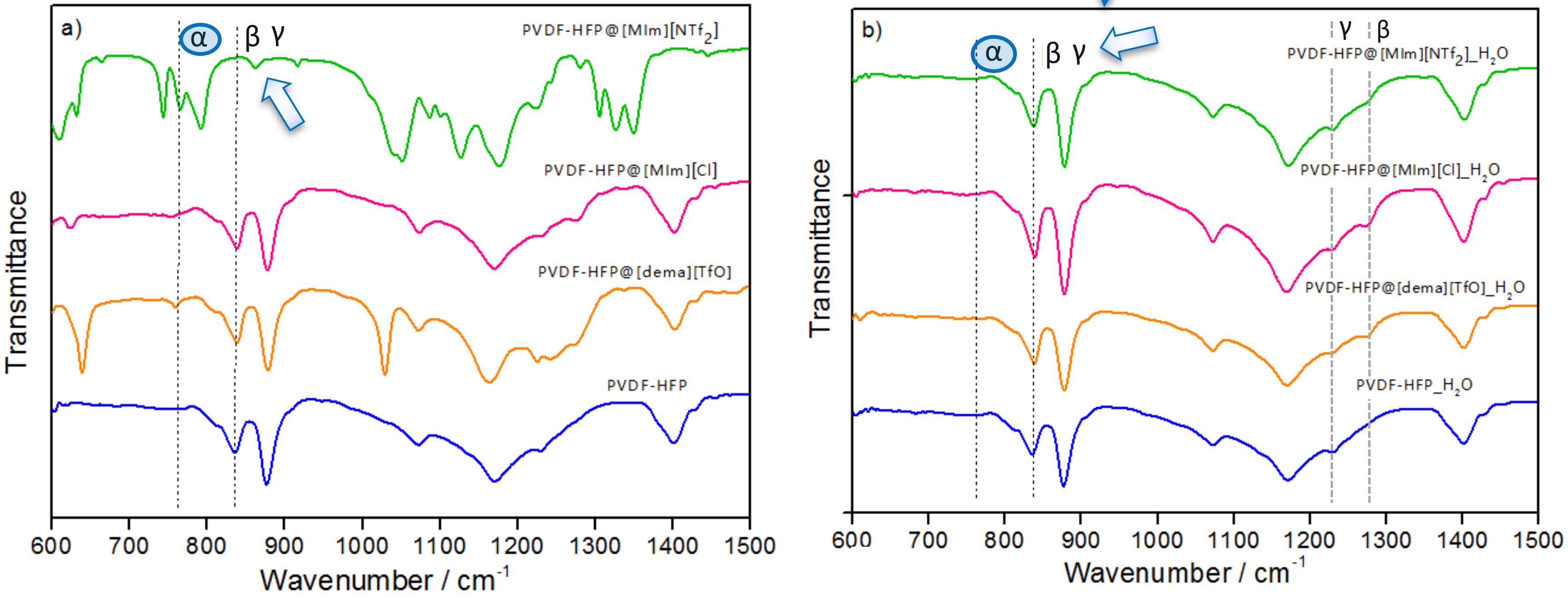


Figure 7. FTIR-ATR spectra for the membranes dried at 80 °C, (a) before immersion in water (b) after immersion in water.

4 Conclusions

4 Conclusions

- ✓ Membranes of PVDF-HFP@IL have been successfully developed through the solvent casting and evaporation method.
- ✓ ILs have been shown to serve as **properties controllers** on the synthesis of PVDF-HFP membranes.
- ✓ The possibility to **tailor** the PVDF-HFP **membranes morphology** by the variation of the IL opens new possibilities.
- ✓ It is possible to recover some of the typical properties of neat PVDF-HFP membranes **keeping** the new membrane **morphology** after the IL removal.

5 Acknowledgments

eman ta zabal zazu

Universidad del País Vasco
Euskal Herriko Unibertsitatea

UC
UNIVERSIDAD DE CANTABRIA

BCMATERIALS
BASQUE CENTER FOR MATERIALS, APPLICATIONS & NANOSTRUCTURES
ehugroup

sgiker
Ikerkuntzarako Zerbitzu Orokorrak
Servicios Generales de Investigación

EUSKO JAURLARITZA
GOBIERNO VASCO

(KK-2016/00095-LISOL, program Elkartek)

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA, INDUSTRIA Y COMPETITIVIDAD

(MAT2016-76739-R(AEI/FEDER, UE))

(INDESMOF H2020 - MSCA-RISE 778412)

MARIE CURIE ACTIONS

(BIDMAG- MSCA-Individual Fellowship 701852)

NALS 2017

Thank you very much for your kind attention!!!

Paula GSaiz
Paula.gonzalez@bcmaterials.net
BCMaterials (UPV/EHU,
Campus Bizkaia, Leioa)

Mirador Tina Menor (Cantabria)

Cuevas de Altamira (Cantabria)