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PVDF Hollow Fibers Production for Seawater Desalination: Morphology, Properties and VMD Performance

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Consiglio Nazionale delle Ricerche

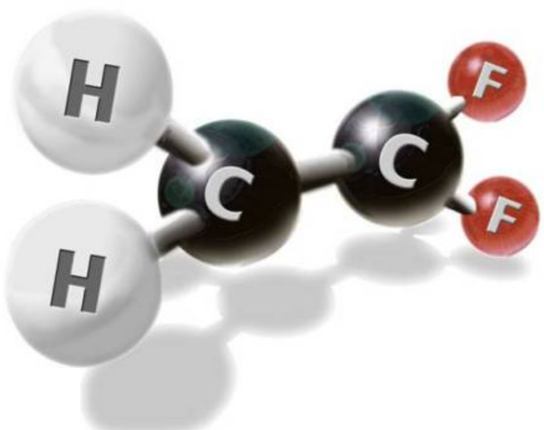
Outline

- Introduction
  - PVDF polymer and PVDF membranes in VMD
- Experimental Section
- Results and Discussion
  - Effect of spinning parameters and blend and concentration of PVDF type on membrane properties
  - Evaluation of the VMD performance
- Conclusions

PVDF properties

Poly(vinylidene fluoride) (PVDF) is a **semi-crystalline** polymer that has gained considerable attention as membrane material for many applications, due to its outstanding physical and chemical properties:

- excellent **mechanical properties**,
- outstanding **chemical resistance** to various agents (inorganic acids, weak bases, halogens, oxidizing agents, aliphatic, aromatic and chlorinated solvents),
- high **thermal and light stability** (resistant to UV light, alpha and beta radiations).



PVDF porous membranes can be prepared by immersion precipitation (non-solvent or diffusion induced phase separation, **NIPS** or **DIPS**) or by thermally induced phase separation (**TIPS**).

In this work, **PVDF hollow fiber membranes** have been prepared by **NIPS**.

PVDF for MD applications

PVDF is **widely used in literature** for preparing **membranes with optimized characteristics for MD**, due to its hydrophobicity, good chemical-physical stability.

In literature, there are **four main approaches** to produce PVDF membranes with optimized characteristics for MD:

- Use of small molecular additives and salts;
- Preparation of mixed matrix membranes (MMM), with nanofillers;
- Preparation of dual layer composite membranes;
- Use of coatings and post-treatments

PVDF commercial types

PVDF is commercialized by different companies (Solvay, Arkema, Kureha), as powder or pellets, with various trade names (Solef, Hylar, Kynar).

Solvay Solexis Solef was selected for HF preparation.

PVDF Grades	Average Molecular Weight (KDa)
1008	244
1010	352
1012	396
1015	573
6010	322
6020	687

Molecular weights of different Solef® grades

Aim of the work

The aim of this work is the optimization of the morphology and properties of hydrophobic hollow fiber membranes for enhancing the performance in VMD.

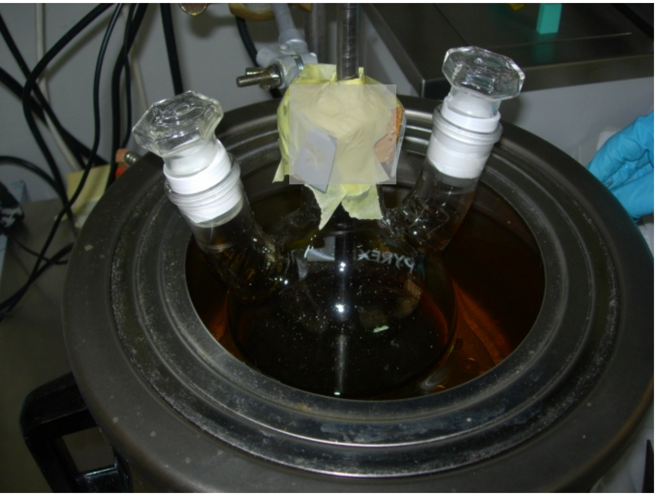
Starting from an optimized dope composition*, based on the use of **Solef 6012** as polymer, **PVP K-17** and **water** as additives, we investigated:

The effect of PVDF types (*blend of PVDF with different MW*) and concentration on fibers morphology and properties.

A. Figoli, S. Simone, A. Criscuoli, S.A. AL-Jlil, F.S. Al Shabouna, H.S. Al-Romaih, E. Di Nicolò, O.A. Al-Harbi, Drioli, Accepted in Polymer, http://dx.doi.org/10.1016/j.polymer.2014.01.035 (2014)

Preparation of HF membranes

1

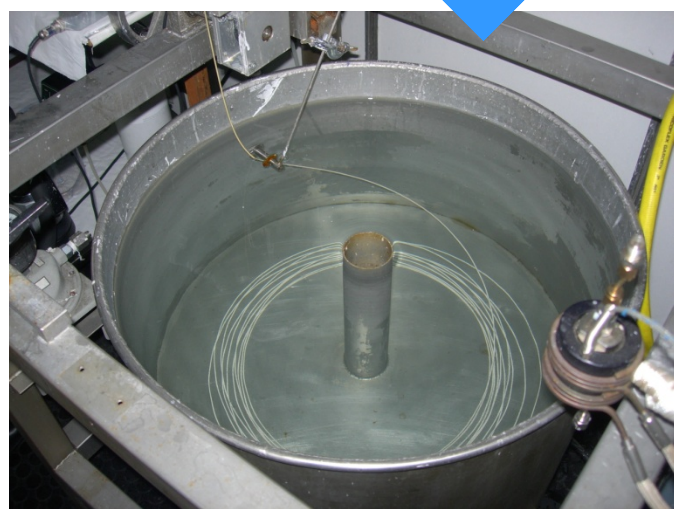


Preparation of dope solution

2

spinneret

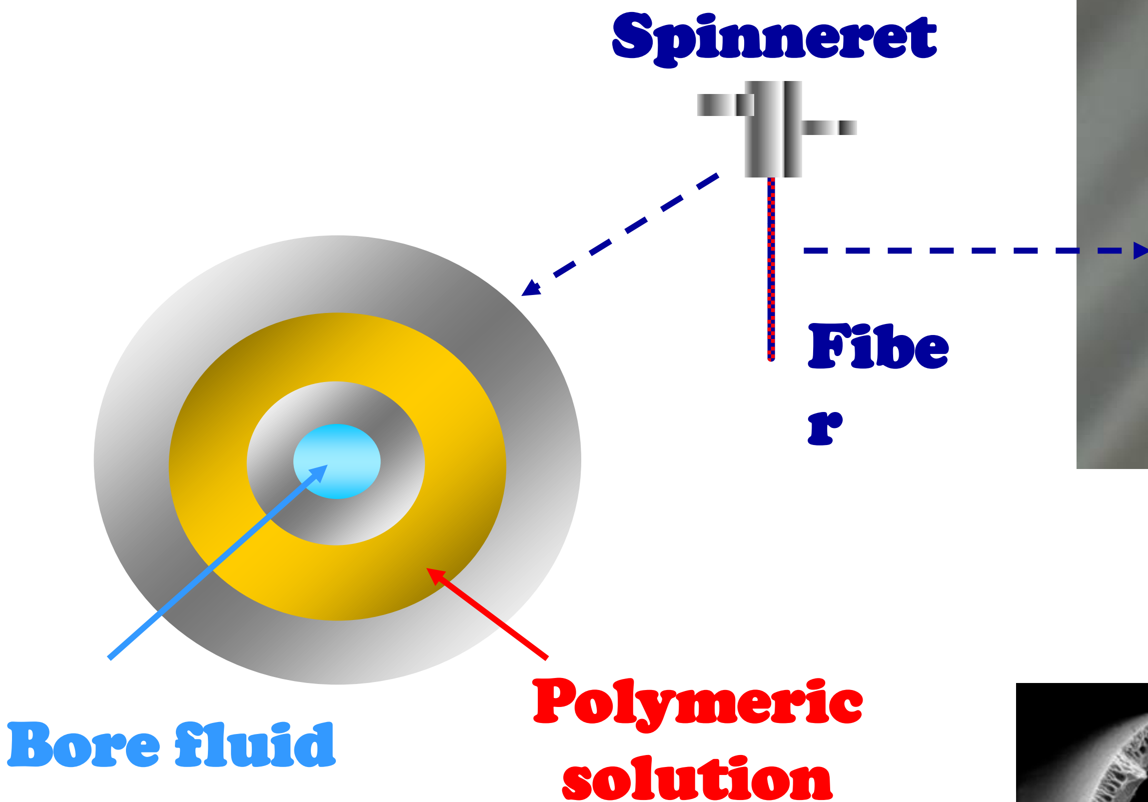
3

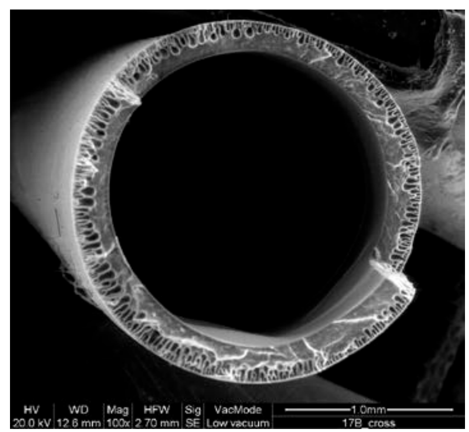


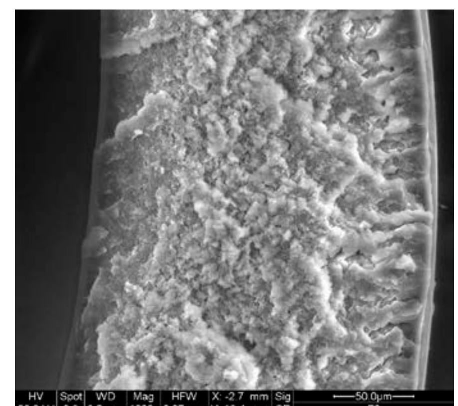
Fiber production

Simone, Figoli, Criscuoli, Carnevale, Drioli, Journal of Membrane Science 364 (2010) 219

Preparation of HF membranes







Effect of PVDF type and concentration

The effect of PVDF types (blend) and concentration on the morphology and properties of the produced PVDF hollow fibers have been evaluated and, then, tested in VMD.

- The dope composition with Solef 6012 was taken as a reference.

- Different PVDF Solvay homopolymer grades were used, alone or in blend, for preparing polymeric dopes, while additive type and concentration, as well as all the other spinning parameters, were maintained constant on the basis of the experimental conditions already optimized.

A. Figoli, S. Simone, A. Criscuoli, S.A. AL-Jlil, F.S. Al Shabouna, H.S. Al-Romaih, E. Di Nicolò, O.A. Al-Harbi, Drioli,
Accepted in Polymer, http://dx.doi.org/10.1016/j.polymer.2014.01.035 (2014)

Results and Discussion

1) Viscosity of dope solutions

T dope solution = 40-85°C

PVDF Solef (Average Molecular Weight (KDa)

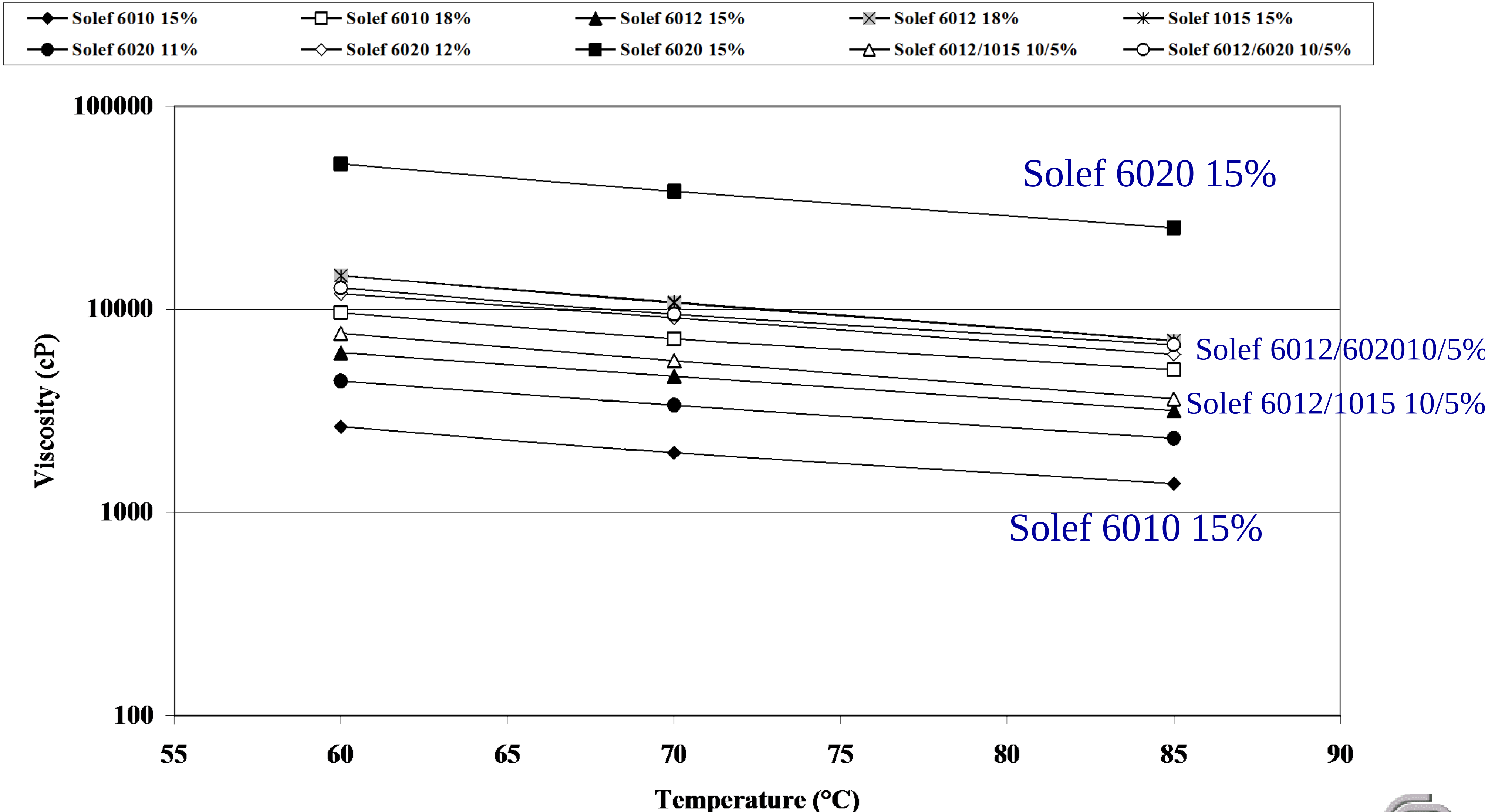
6010 (300-320)
6012 (380-400)
1015 (570-600)
6020 (670-700)
6012/1015
6012/6020

(12-18 wt.%)

+ H_2O 6 wt.% + PVP K-17 14 wt.% in NMP

Results and Discussion

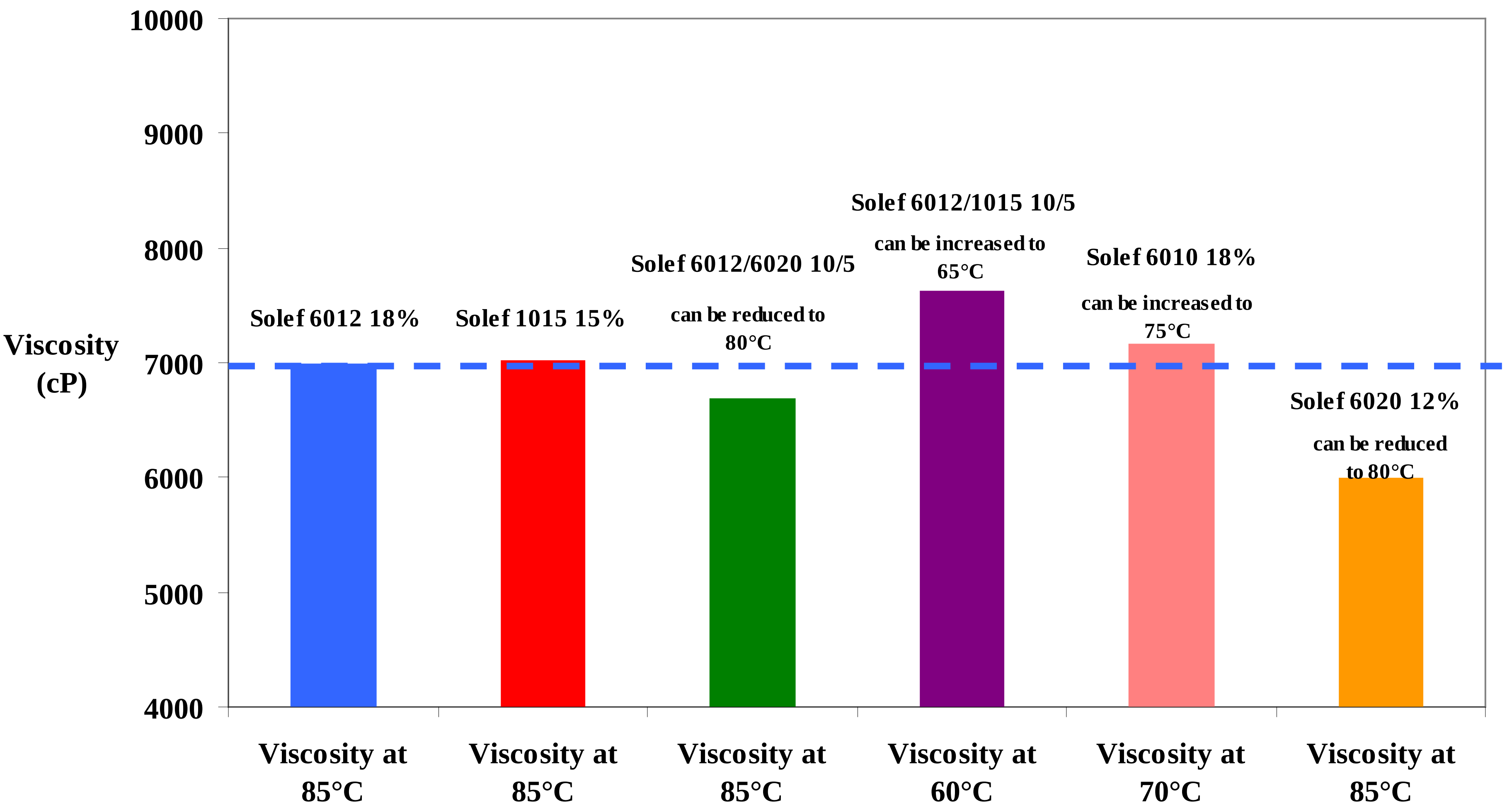
1) Viscosity of dope solutions



Results and Discussion

1) Viscosity of dope solutions

Group of PVDF/PVP K-17 14%/H_2O 6% dope solutions having the same viscosity



Results and Discussion

1) Spinning Experiments

While all the other parameters (composition and temperature of the polymeric dope, spinning rate, outer coagulant composition and temperature) are kept constant.

Dope composition (wt.%)	PVDF/NMP/H_2O/PVP K-17 18/62/6/14
Dope flow rate (g/min)	12
Dope temperature (°C)	65-85
Bore fluid composition (wt.%)	MetOH/H_2O, EtOH/H_2O, IPA/H_2O 30/70
Bore fluid flow rate (mL/min)	13 mL/min
Bore fluid temperature (°C)	50
Outer coagulant	Tap water (room T)
Air gap (cm)	25
Spinneret dimensions (cm)	O.D./I.D. 1.6/0.6
Post treatment	NaClO 4000 ppm pH 7 overnight

Results and Discussion

2) Spinning Experiments

Spinning experiments were performed using six dopes, containing one PVDF type or polymer blends, same solvent, additive type and concentration and **same viscosity of about 7000 mPa•s**. In this way the effect of dope viscosity on liquid/liquid demixing rate should be neglected, while **the role of the polymer can be highlighted**.

Spinning experiment	PVDF-Solef®	Additives	NMP	
6012	6012 18%	H_2O 6%, PVP K-17 14%	62%	85C
6012/6020	6012/6020 10/5		65%	
6012/1015	6012/1015 10/5		65%	
6020	6020 12%		68%	
6010	6010 18%		62%	
1015	1015 15%		65%	85 C

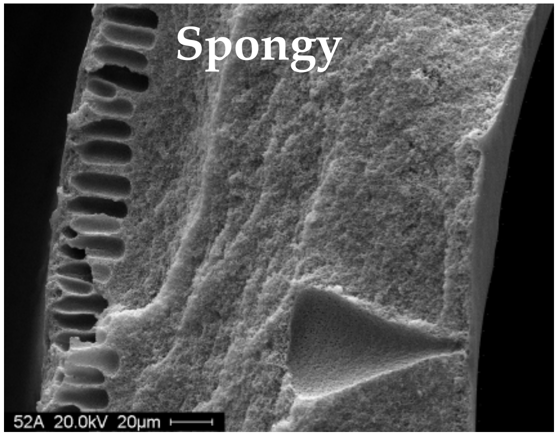
For each spinning experiment, three fiber types were produced, varying the **bore fluid**:

1. Fiber type A: NMP 30% 13 ml/min;
2. Fiber type B: EtOH 30% 13 ml/min;
3. Fiber type C: IPA 30% 13 ml/min.

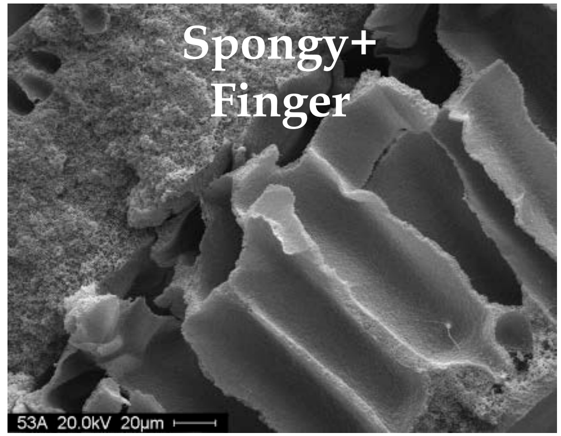
Results and Discussion

3) Fibers Morphology (NMP 30%)

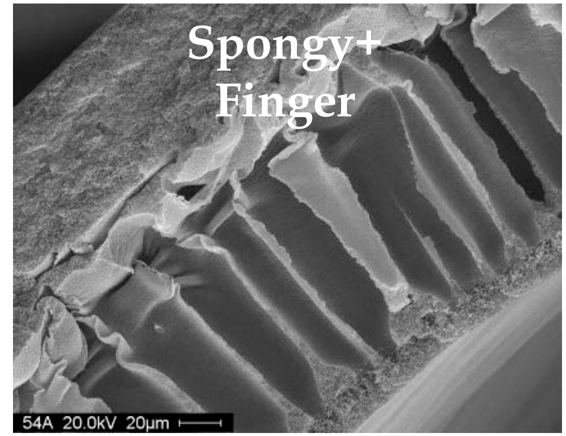
6012 **18%**



6012/6020 **10/5%**

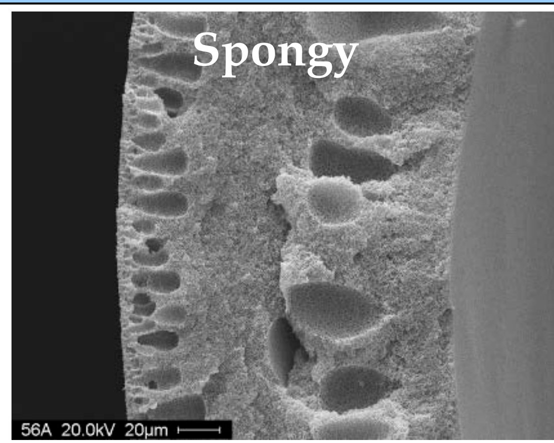


6012/1015 **10/5%**

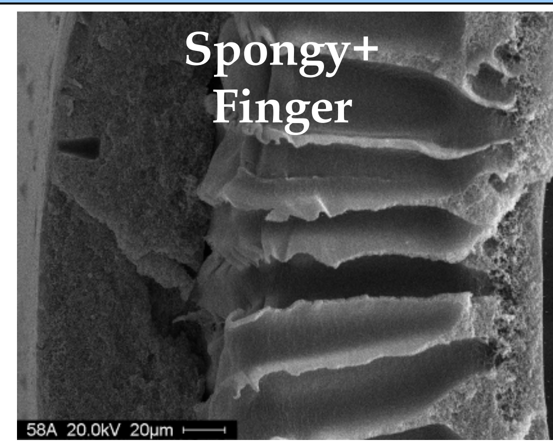


6020 **12%**

6010 **18%**



1015 **15%**



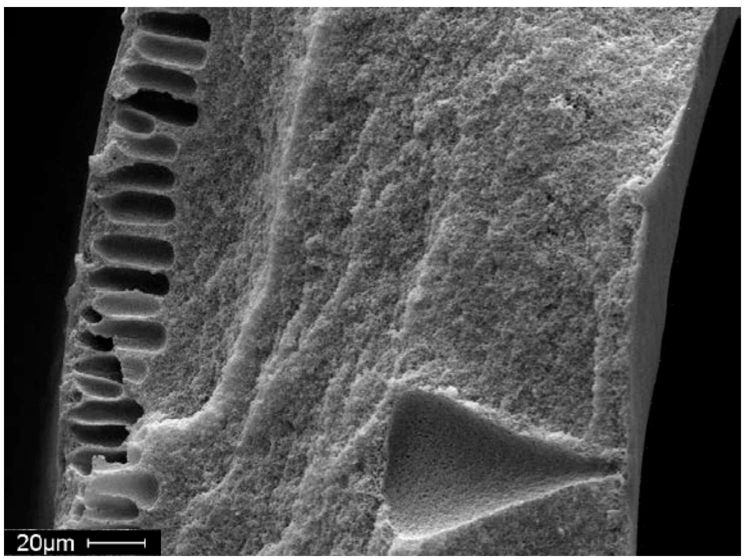
Results and Discussion

3) Fibers Morphology

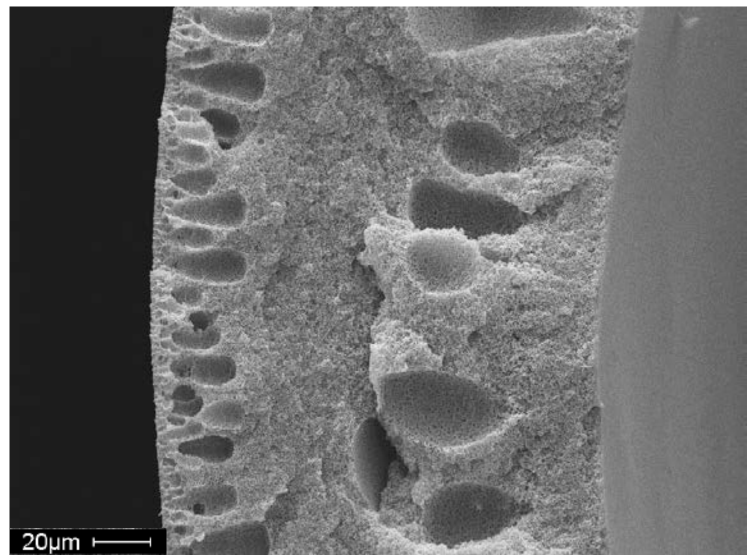
The differences observed between the morphologies of the produced hollow fiber membranes are inferred to depend mostly on **polymer concentration**.

PVDF 18%

Solef 6012



Solef 6010

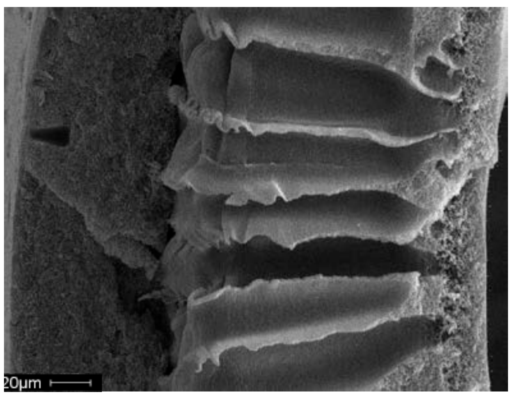
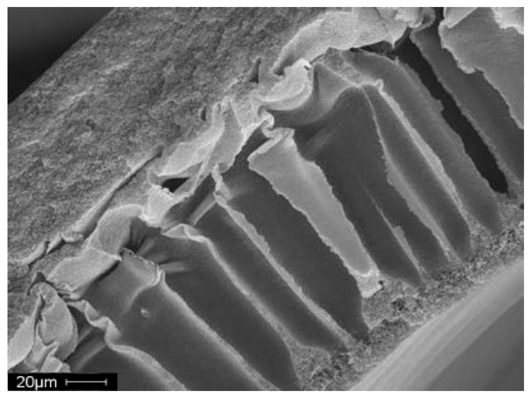
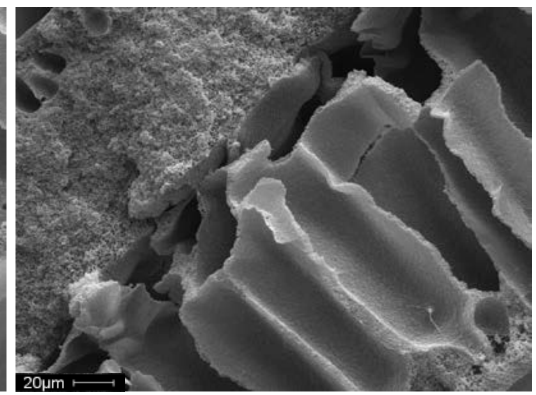


Results and Discussion

3) Fibers Morphology

The differences observed between the morphologies of the produced hollow fiber membranes are inferred to depend mostly on **polymer concentration**.

PVDF 15%

Solef 1015	Solef 6012/1015	Solef 6012/6020
		

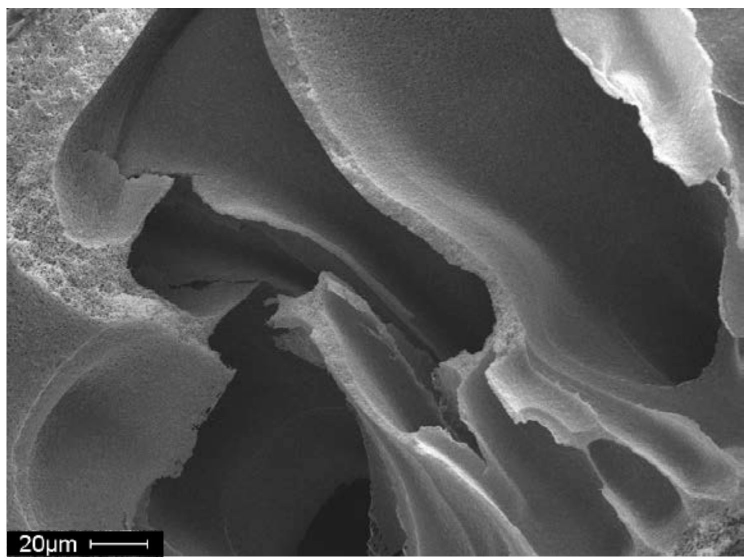
Results and Discussion

3) Fibers Morphology

The differences observed between the morphologies of the produced hollow fiber membranes are inferred to depend mostly on **polymer concentration**.

PVDF 12%

Solef 6020



Results and Discussion

3) Fibers Morphology

The morphology shown in the SEM pictures confirms that, in our case, **membranes are obtained by nucleation of the polymer lean phase**. However, **droplet coalescence depends on polymer concentration**.

- At **lower polymer concentration**, droplet coalescence takes place much more before solidification of the polymer-rich phase, thus resulting in **large tear-drop macrovoids**.
- These structures **reduce** to parallel finger-like or **disappear** and turn into sponge-like structure **when increasing polymer concentration**.
- **This is in agreement to what observed in literature (Smolders).**

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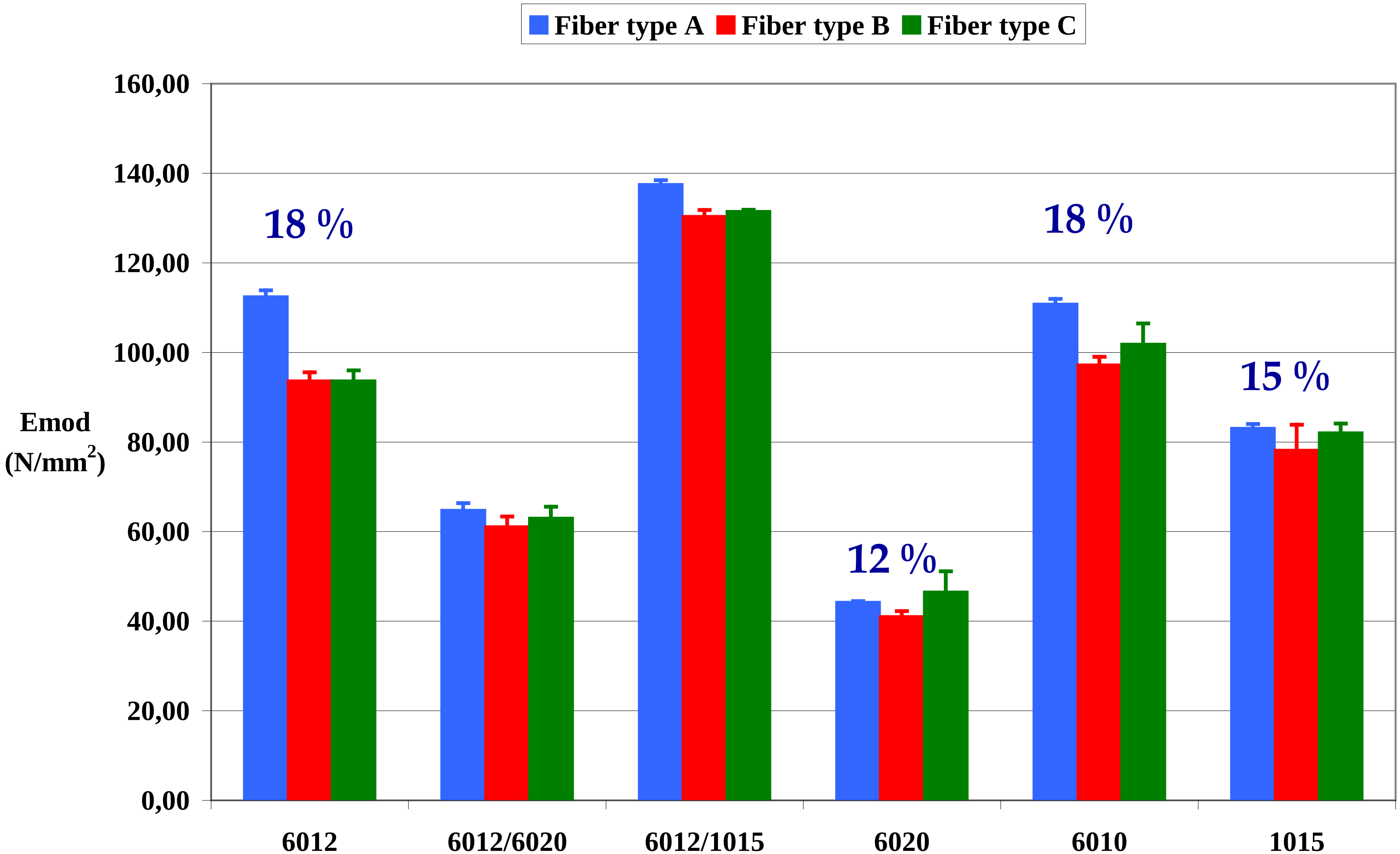
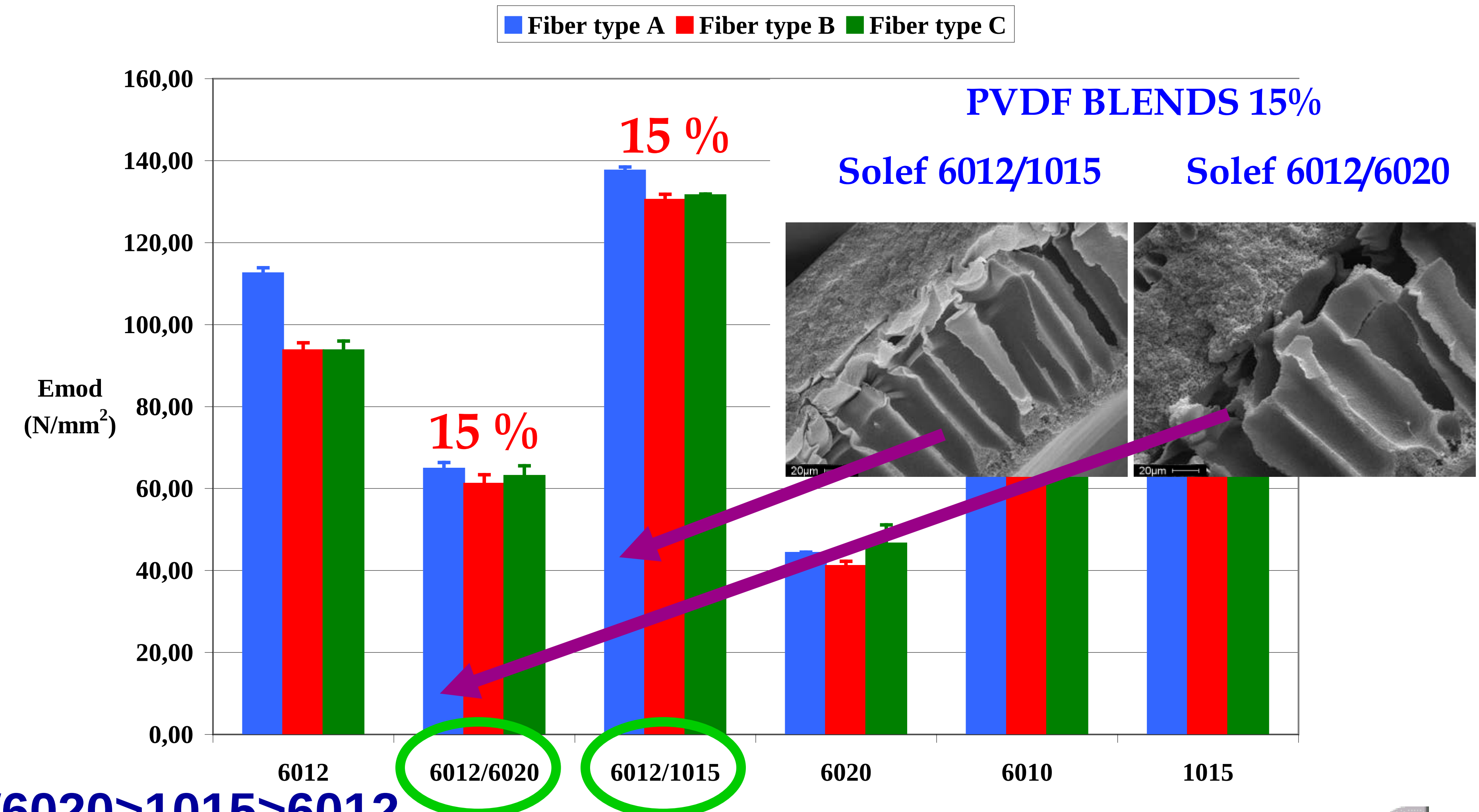
Results and Discussion

4) Fibers mechanical properties



Results and Discussion

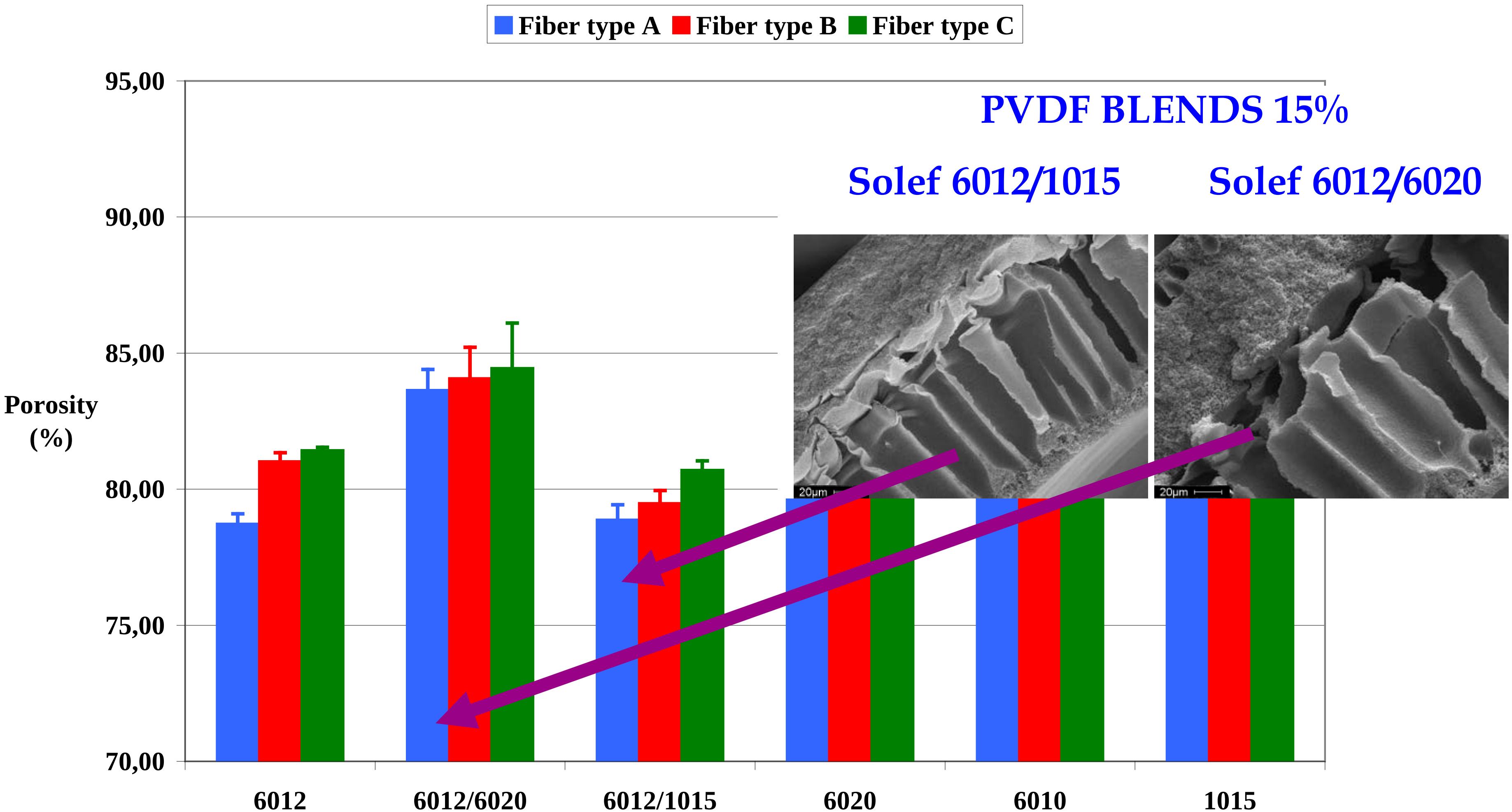
4) Fibers mechanical properties



MW6020>1015>6012

Results and Discussion

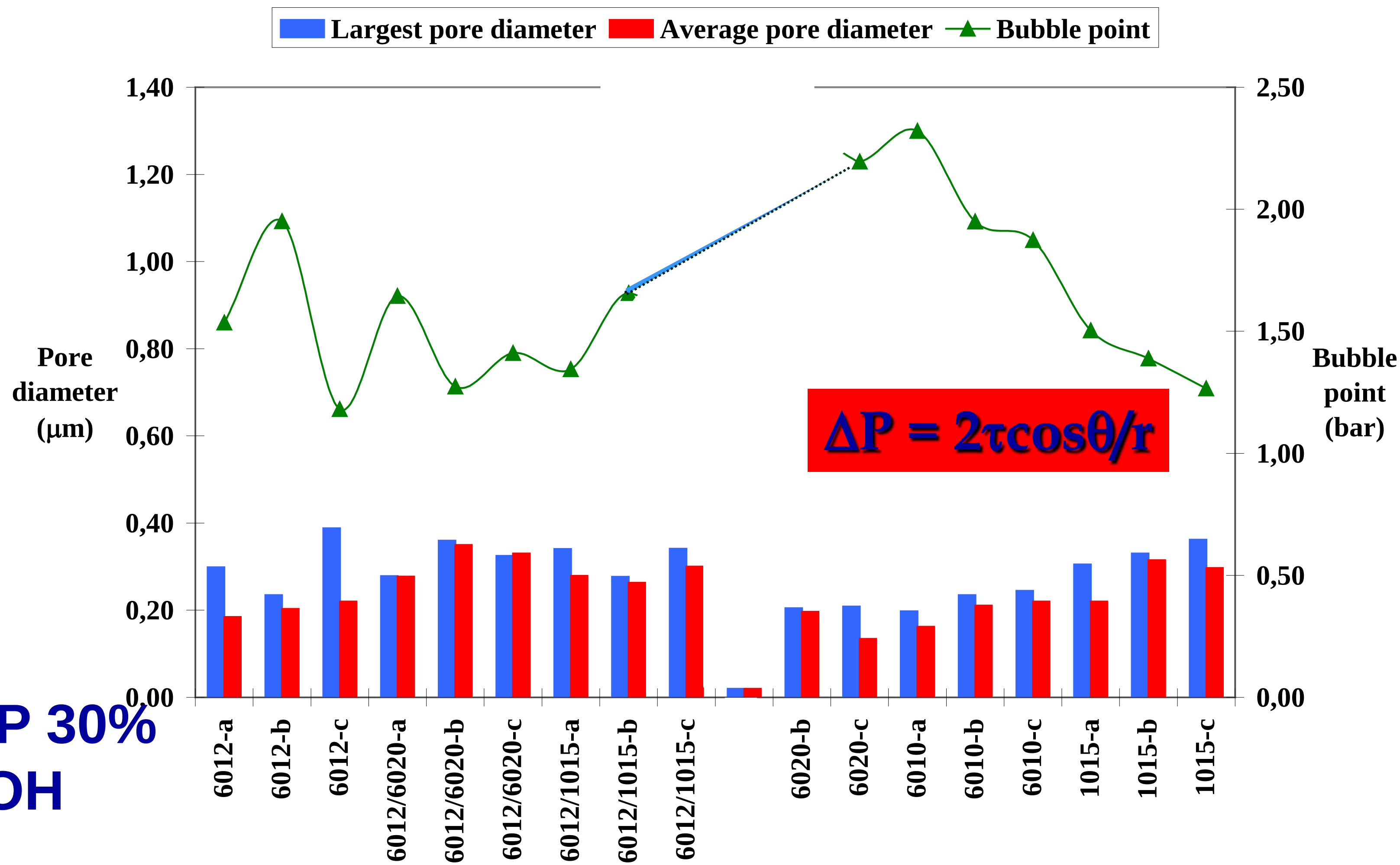
5) Fibers Porosity



"Typical" trade-off with mechanical properties

Results and Discussion

6) Bubble point and pore size distribution

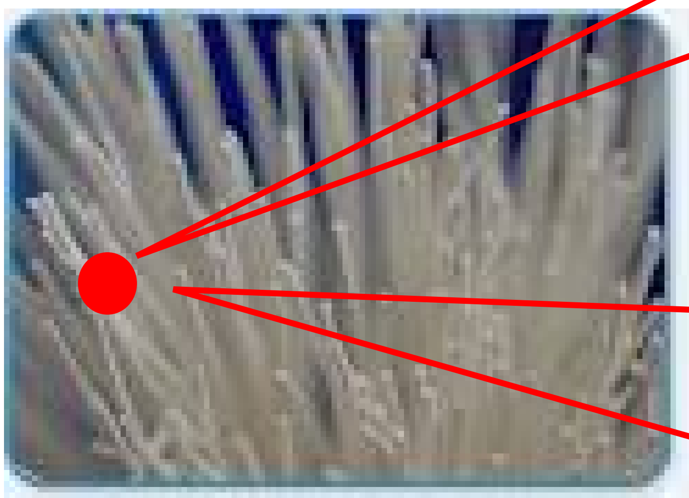


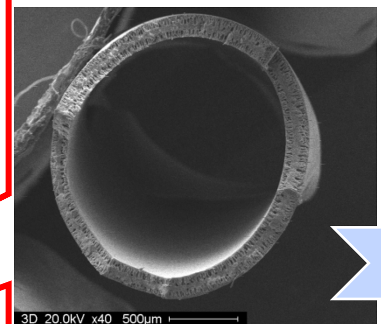
a) NMP 30%
b) ETOH
c) IPA

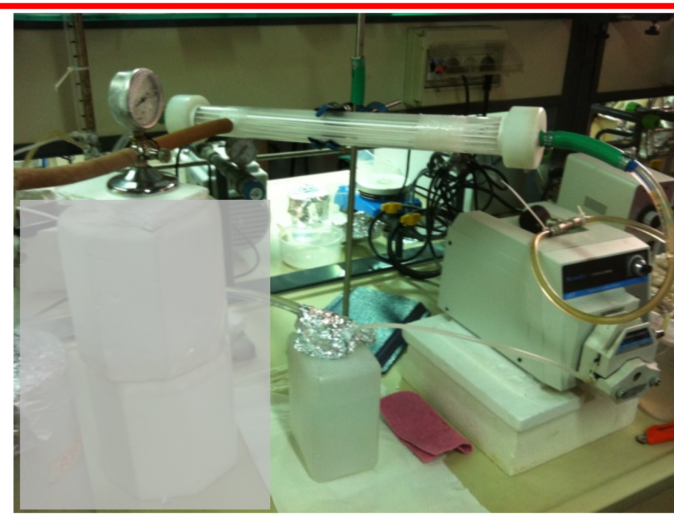
I) Effect of bore fluid composition and flowrate

VMD

From hollow fibers to modules

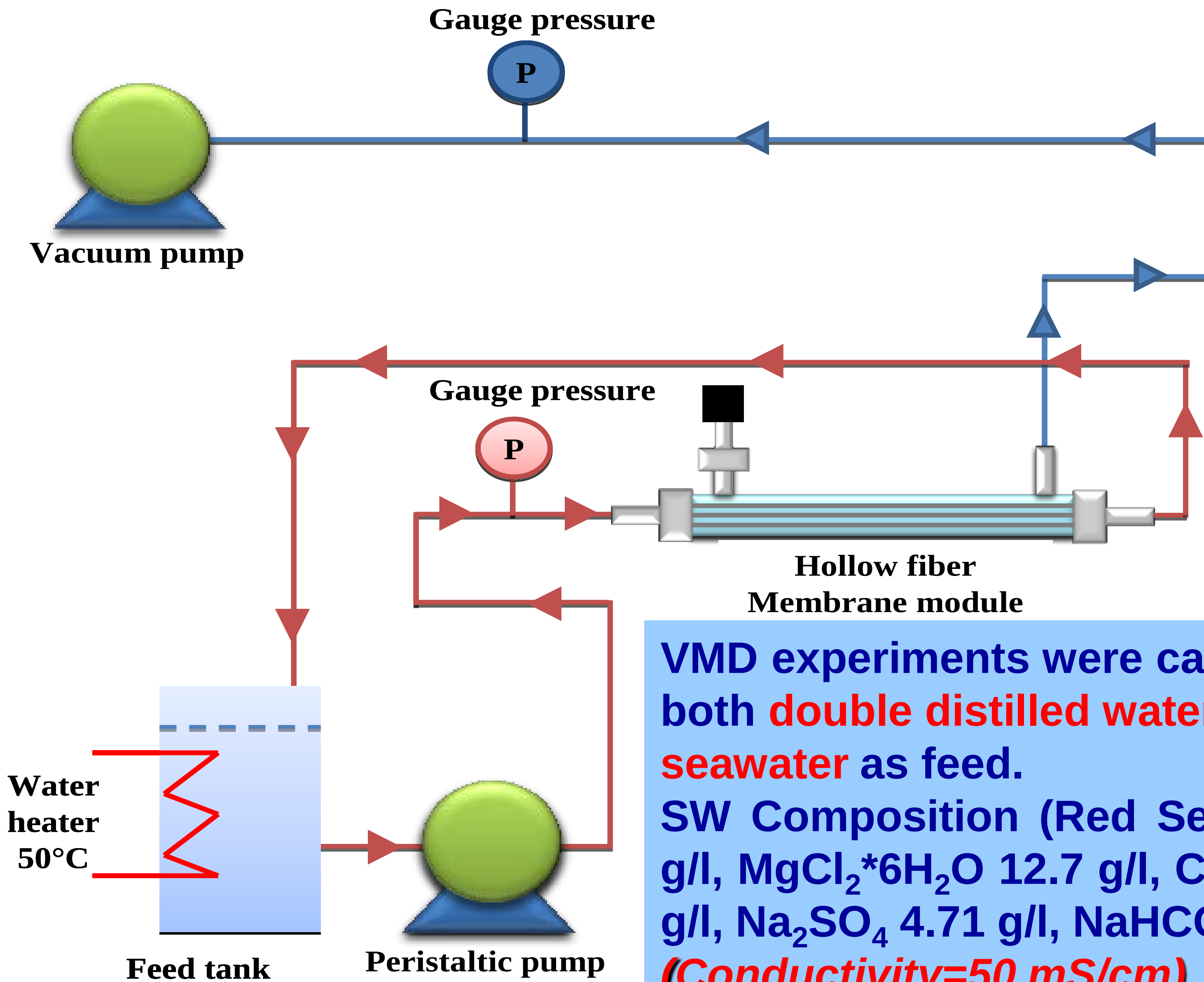






A= 38 cm^2 and 0,1 m^2

VMD Plant



VMD experiments were carried out using both double distilled water and synthetic seawater as feed.

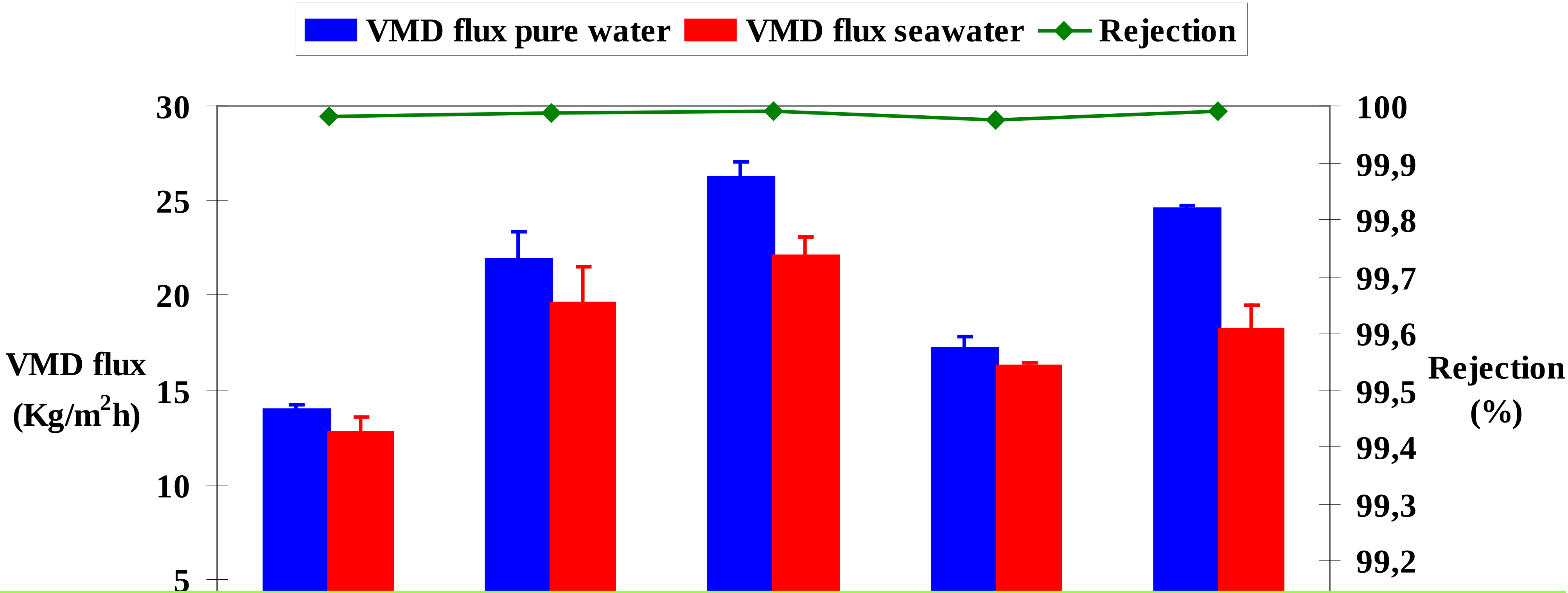
SW Composition (Red Sea): NaCl 27.85 g/l, $MgCl_2 \cdot 6H_2O$ 12.7 g/l, $CaCl_2 \cdot 2H_2O$ 1.79 g/l, Na_2SO_4 4.71 g/l, $NaHCO_3$ 0.207 g/l)

(Conductivity=50 mS/cm)

Figoli et al, Polymer 2014

Results and Discussion

7) VMD



The VMD fluxes measured during tests on synthetic seawater are slightly lower than those measured when feeding pure water. The salt rejection, calculated on the basis of the electrical conductivity of feed (~54 mS) and distillate samples collected at the end of each test, is in the range 99.98-99.99%.

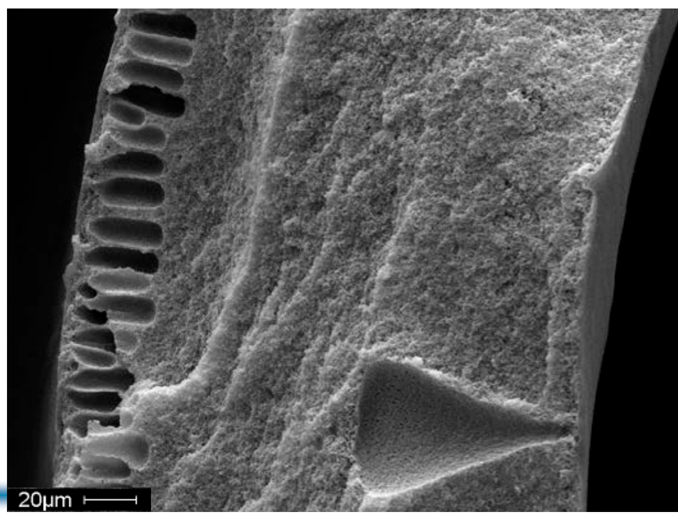
Results and Discussion

7) VMD

In agreement to what observed in literature: the VMD flux is strongly affected by membrane porosity. Membrane porosity, in turn, is connected to membrane morphology and depends on composition of the polymeric dope.

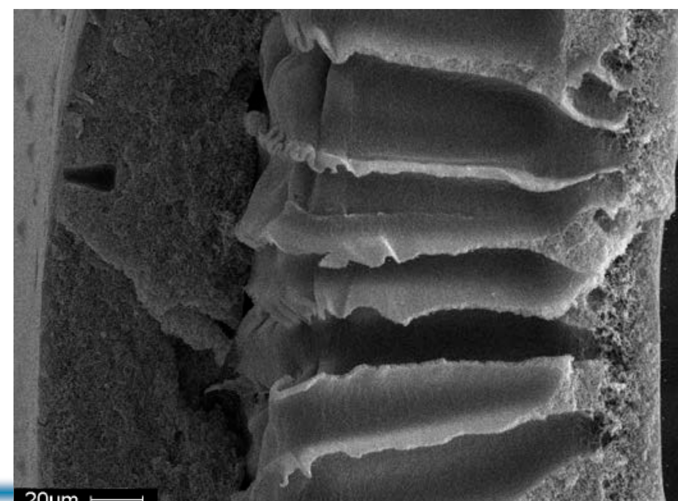
PVDF 18%-Spongy

VMD Flux (H_2O): 13.93 Kg/m^{2}h



PVDF 15%-Asymmetric

VMD Flux (H_2O): 24.55Kg/m^{2}h



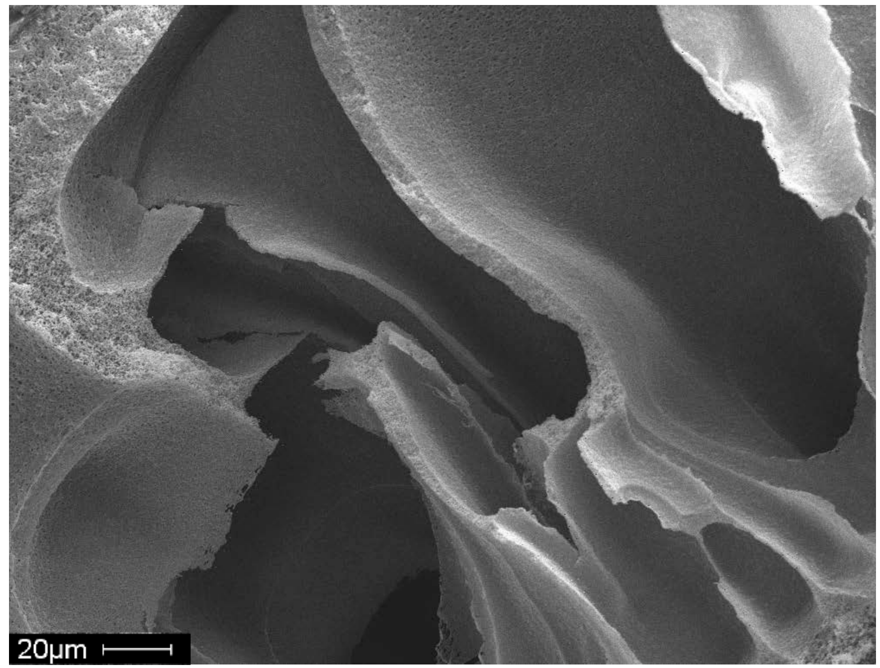
Results and Discussion

7) VMD

Fibers spun from dopes containing the **lowest polymer percentage** show **water leakage** from the feed to the distillate side during VMD experiments. This is due to their morphology and to their **low bubble point** (corresponding to larger pore size).

PVDF 12%

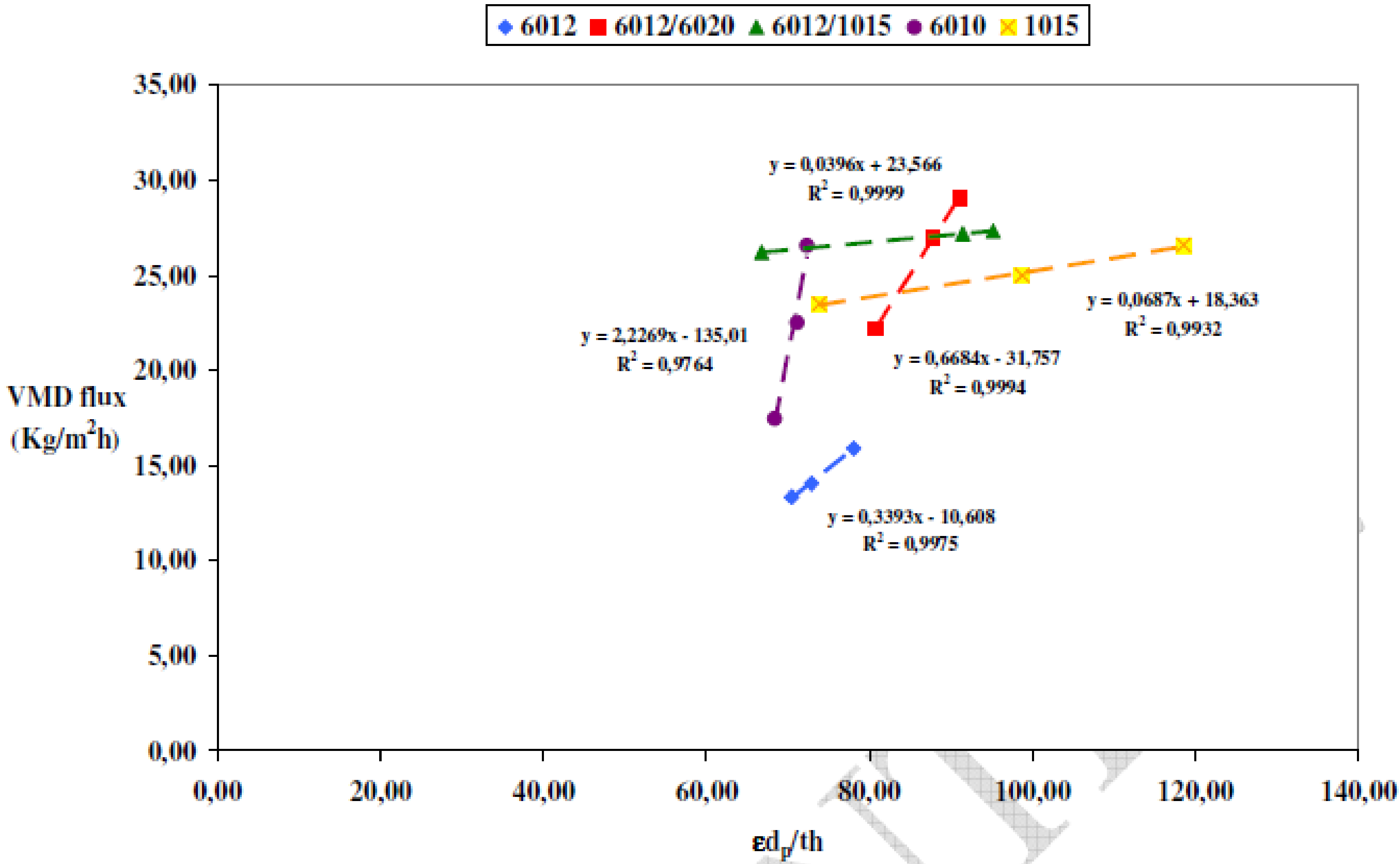
Solef 6020



J. Membr. Sci. 323 (2008) 85; Desalination 287 (2012), 326

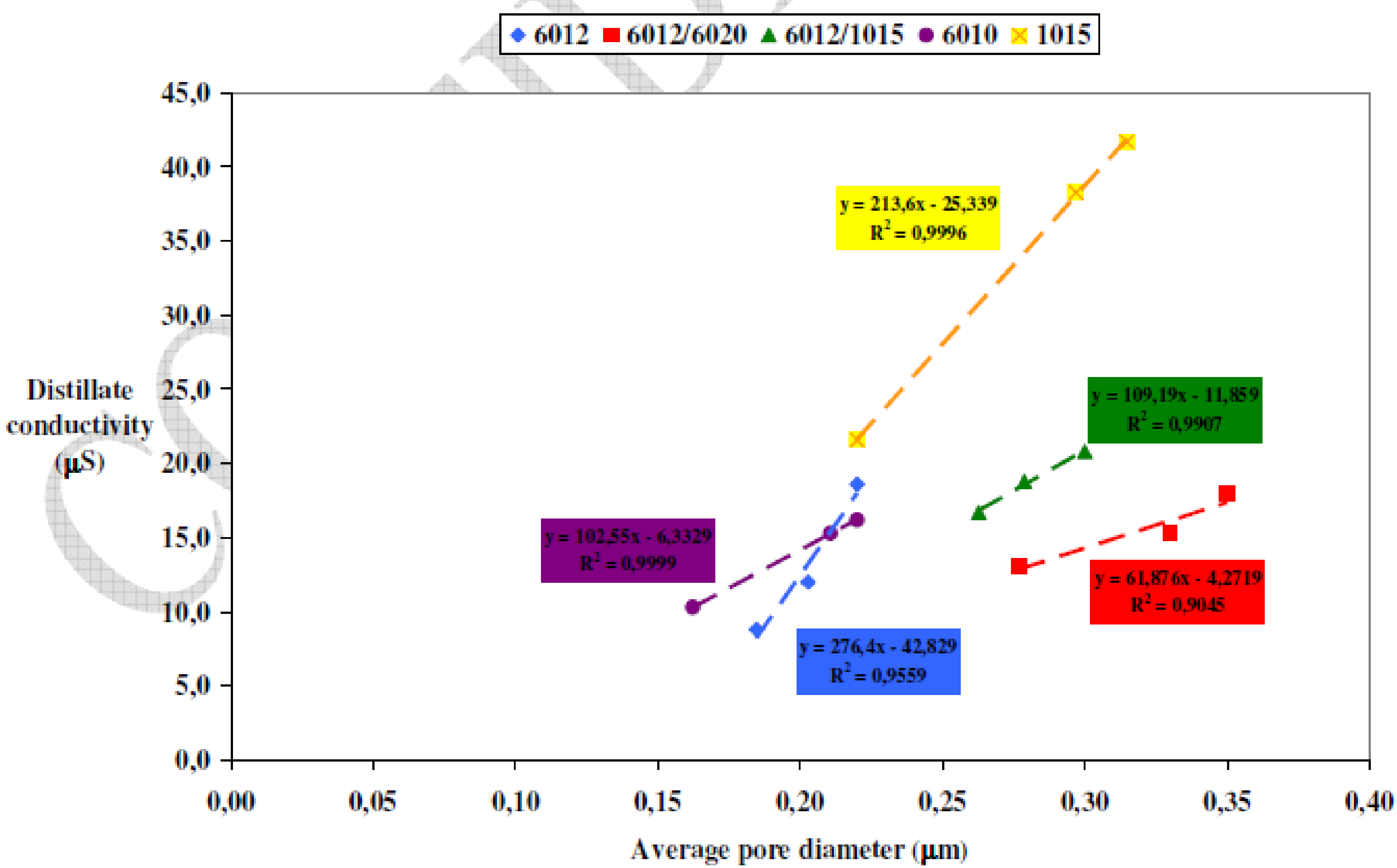
Results and Discussion

Dependence of water vapour flux on "morphology factor"



Results and Discussion

Dependence of electrical conductivity of distillate on Pore diameter

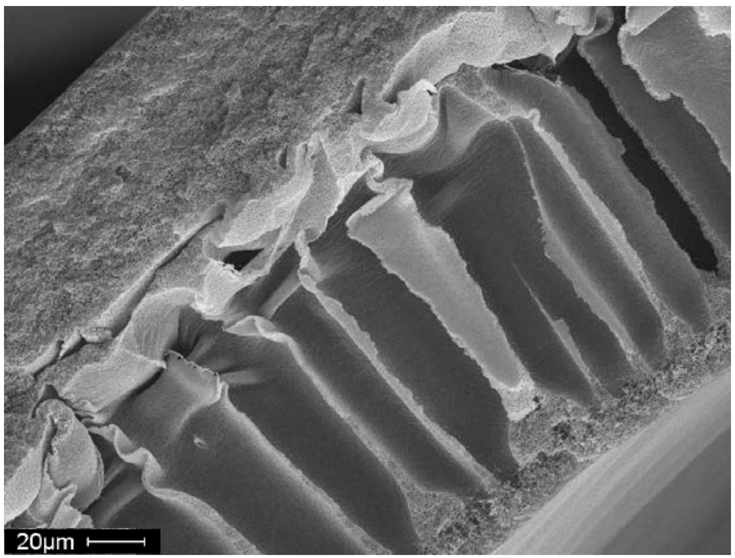


Higher conductivity → lower is the rejection of salts

Summary

The PVDF hollow fibers produced using a blend 6012/1015 showed the best couple in terms of flux and selectivity, with performance comparable to that of commercial PP fibers (H_2O: 23.29 Kg/m^2h, Synthetic Seawater: 23.26 Kg/m^2h, Rejection: 99.99%)

BLEND Solef 6012/1015



VMD flux
22.09 kg/m^2h
with synthetic seawater

selectivity
99.99%

Conclusion

- The porosity has the main influence of water vapour flux in VMD in all the cases studied ⟶ Asymmetric structure

- Water vapour flux obtained with salty solution is always sligthly lower than with distilled water

- Higher permeate conductivity is obtained at higher pore size (lower salt rejection)

- Membranes with PVDF homopolymer or blended polymer allowed to taylor membranes with similar morphologies

Acknowledgment

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للعلوم والتقنية KACST

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Solvay Specialty Polymers is also gratefully acknowledged for providing the polymer used throughout this study.