Alkali and acid polysaccharides blend nanofibrous membranes prepared by electrospinning



C.Santos¹, C.J.Silva^{1*}, Z. Büttel², R.Guimarães², P. Tamagnimi^{2,3}, A.Zille^{2,4}

¹ CeNTI - Centro de Nanotecnologia e Materiais Técnicos, Funcionais e Inteligentes, Rua Fernando Mesquita 2785, 4760-034 V. N. Famalicão, Portugal.



³ Faculdade de Ciências, Departamento de Biologia, Universidade do Porto, Rua do campo Alegre, Edifício FC4, 4169-007 Porto, Portugal.

⁴ 2C2T – Centro de Ciência e Tecnologia Têxtil, Departamento de Engenharia Têxtil, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal















* csilva@centi.pt









Introduction

Electrospinning allows the production of polymer fibres with diameters in the sub-micron size range, through the application of an external electric field, keeping intact the bulk properties of the polymers. Electrospun membranes possess some unique structural features, such as a high surface to volume ratio and very good mechanical performance, properties that are determinant to their use in several applications such as air and liquid filtration, tissue engineering, optical and chemical sensors [1].

In this work, alkali and acid biopolysaccharides blended with polyvinyl alcohol (PVA) were electrospinned into a polyvinylidene difluoride (PVDF) basal microfiltration membrane, with the goal of developing a mid-layer nanofibrous porous support for exploitable thin-film composite (TFC) membranes for water filtration. The alkali and acid biopolysaccharides chosen were, respectively, chitosan (CS), a cationic polyelectrolyte (in this case with deacetylation degree around 85), and cyanobacterial extracellular polymeric substances (EPS), an acidic polysaccharide isolated from *Cyanothece* sp.CCY 0110 [2].

The electrospun blended nanofibrous membranes were fully characterized in order to investigate their morphology, diameter, structure, mechanical and thermal properties. The results showed that these membranes have great potential for filtration purposes [3].



Experimental



PVDF basal filter (5cm \emptyset , 0.2 μ m porosity)

PVA 12%wt (in H₂O)

or

PVA 12%wt + Chitosan (CS)

0.5%wt (in 1% Acetic acid aq. solution)

Alkali polysaccharide

or

PVA 12%wt + cyanobacterial extracellular polymeric substances (EPS) 0.5%wt (50/50 DMSO:H₂O)

Acid polysaccharide

High voltage

http://iopscience.iop.org/1468-

6996/13/1/015003/article

Spinning solution

(stainless needle)



Electrospinming

Conditions:

- Room temperature
- 10mL syringe with needles of 0.5mm of inner diameter
- Electric field: 15 to 27kV
- Feed rate: 0.1 to lmL/h
- Viscosity and conductivity of the polymer solutions:

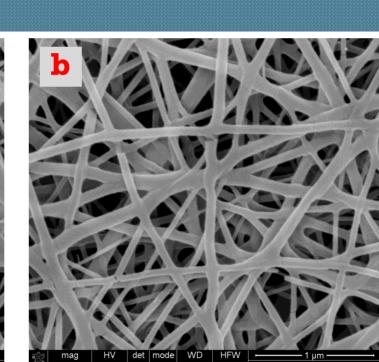
Conductivity ((μ S cm -1)	Viscosit	y (cP)
874 9	9	96	3
1149 2	26	563	3
1274 2	20	442	12
	874 S 1149 2	Conductivity (μS cm ⁻¹) 874 9 1149 26 1274 20	1149 26 563

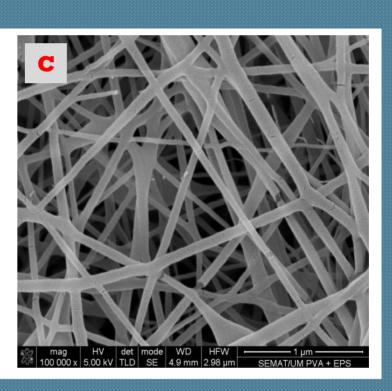
Characterization of electrospinned PVA/polysaccharides membranes:

AFM, SEM, EDS, DMA, TGA, DSC, ATR-FTIR

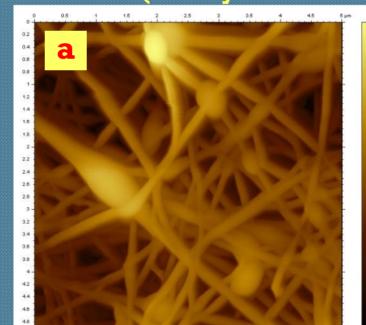
Results

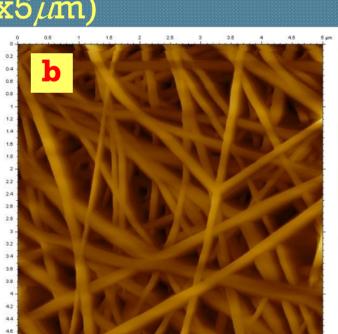
a





AFM (analysis area 5x5μm)





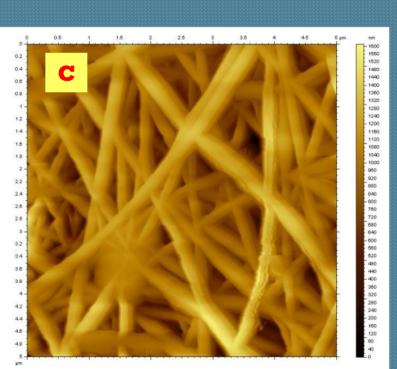


Figure 1: SEM and AFM images of PVA/polysaccharide blended electrospun fibres using (a) 12%wt PVA, (b) 12%PVA and 0.5%CS, and (c), 12%PVA and 0.5%EPS solutions.

EDS Analysis PVA PVA/CS PVA/EPS Wt % Wt % At % At % **Element** 44.30 37.32 42.27 49.26 44.25 51.44 55.70 48.85 61.97 48.56 55.84 55.40 O 1.89 $\bigcirc .71$ 0.35 100.00 100.00 100.00 100.00 100.00 100.00 Total

Table 1: Variation of weight and atomic percentages of the atoms C, O, N and S in the electrospun nanofibres

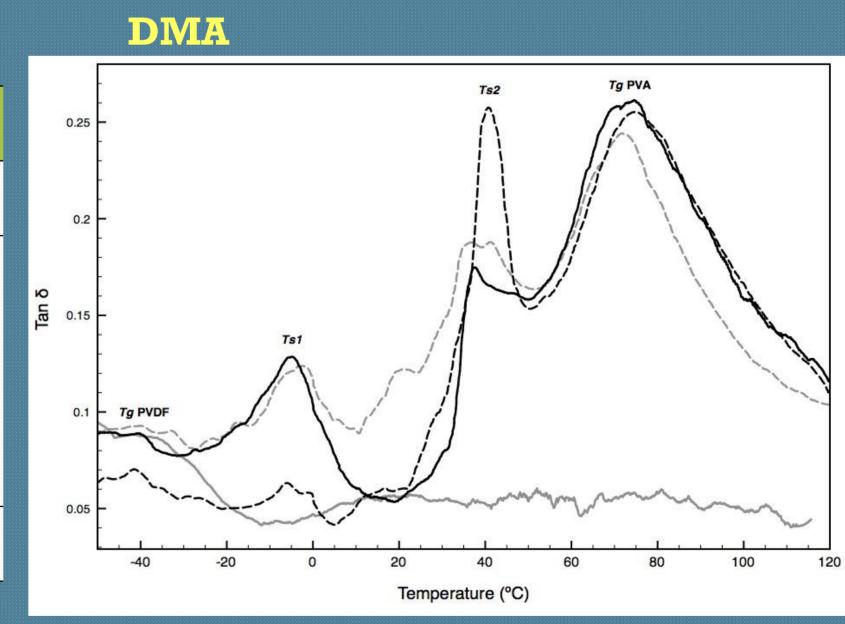


Figure 2: $Tan \delta$ curves versus temperature of the membranes. PVDF (solid grey line), PVDF coated with PVA nanofibres (dashed grey line), PVDF coated with PVA/CS nanofibres (dashed black line), and PVDF coated with PVA/EPS nanofibres (solid black line).

Conclusion

- Electrospun PVA/alkali polysaccharide (CS) and PVA/acid polysaccharide (EPS) blend nanofibrous membranes were successfully prepared, with an uniform and smooth morphology, and narrow diameter distribution from ~50 to 130nm.
- Thermal and mechanical analysis demonstrated the presence of intermolecular hydrogen bonds between the polysaccharides and PVA.
- The electrospun PVA/polysaccharides blended membranes showed better tensile mechanical properties when compared with PVA alone, and resisted more against disintegration in the temperature range between 10 and 50 °C.
- In future work, these membranes will be further coated with an ultra-thin selective top layer.

References:

[1] Liu, Y., Wang, R., Ma, H. Y., Hsiao, B. S., Chu, B. (2013) High-flux microfiltration filters based on electrospun polyvinylalcohol nanofibrous membranes. *Polymer*, 54, 548-556.

[2] Mota, R., Guimarães, R., Büttel, Z., Rossi, F., Colica, G., Silva, C. J., Santos, C., Gales, L., Zille, A., De Philippis, R., Pereira, S. B., Tamagnini, P. (2013) Production and characterization of extracellular carbohydrate polymer from Cyanothece sp. CCY 0110. Carbohydrate Polymers, 92, 1408-1415.

[3] Santos, C., Silva, C. J., Büttel, Z., Guimarães, R., Pereira, S. B., Tamagnini, P., Zille, A. (2014) Preparation and characterization of polysaccharides/PVA blend nanofibrous membranes by electrospinning method. *Carbohydrate Polymers*, 99, 584-592

Acknowledgments:

This work was funded by FEDER funds through the Operational Competitiveness Programme – COMPETE and by National Funds through FCT – Fundação para a Ciência e a Tecnologia under the projects FCOMP-01-0124-FEDER-022718 (PEst-C/SAU/LA0002/2011), FCOMP-01-0124-FEDER-009389 (PTDC/CTM/100627/2008) and FCOMP-01-0124-FEDER-009697 (PTDC/EBB-EBI/099662/2008), and the grants SFRH/BPD/37045/2007 and SFRH/BPD/72400/2010.

The authors also thank to the project <code>INVISIBLE NETWORK</code> n° . <code>13857 * SI I&DT Mobilizador</code>.