Centre for Nanotechnology and Smart Materials

Preparation and characterization of polysaccharides/PVA blend nanofibrous membranes prepared by electrospinning

Carla Santos, Jose Silva, Carla Silva*, Andrea Zille

*(csilva@centi.pt)

Smart & Functional Coatings **– European Conference**
Turin, 26th September 2013

Centre for Nanotechnology and Smart Materials

Summary

- Introduction
  - Aim
- Results
- Conclusions
  - Acknowledgements

Centre for Nanotechnology and Smart Materials

Introduction

Carbohydrate Polymers
Volume 99, 2 January 2014, Pages 584–592

Preparation and characterization of polysaccharides/PVA blend nanofibrous membranes by electrospinning method

Carla Santos[a, 1], Carla J. Silva[a, 1], Zsófia Büttel[b], Rodrigo Guimarães[b], Sara B. Pereira[b], Paula Tamagnini[b, c], Andrea Zille[b, d]

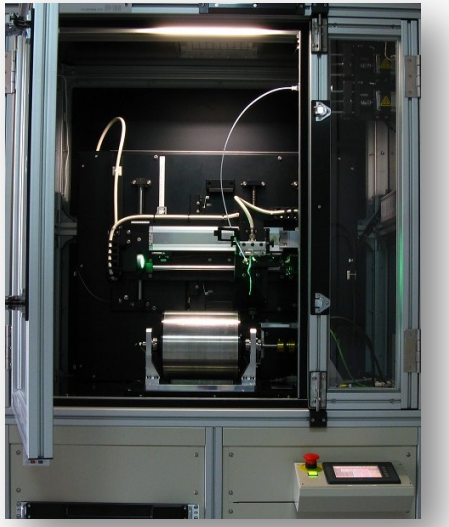
[a] Centro de Nanotecnologia e Materiais Técnicos, Funcionais e Inteligentes (CeNTI), 4760-034 Vila Nova de Famalicão, Portugal
[b] IBMC – Instituto de Biologia Molecular e Celular, Universidade do Porto, Porto, Portugal
[c] Faculdade de Ciências, Departamento de Biologia, Universidade do Porto, Porto, Portugal
[d] 2C2T – Centro de Ciência e Tecnologia Têxtil, Departamento de Engenharia Têxtil, Universidade do Minho, Guimarães, Portugal

- **Main Goal:**
  - Development of a mid-layer nanofibrous porous support for exploitable thin-film composite (TFC) membranes for water filtration

Electrospinning of a blend containing polysaccharides and polyvinyl alcohol (PVA) into a polyvinylidene difluoride (PVDF) basal microfiltration membrane.

Introduction

- **Electrospinning**:
  - 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:

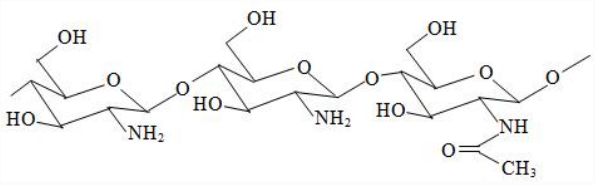
- unique structural features (e.g. high surface to volume ratio, and very good mechanical performance);
- several applications such as air and liquid filtration, tissue engineering, optical and chemical sensors.

Introduction

Polysaccharides

Chitosan (CS)

- Alkali polysaccharide
- Hydrophilic
- Gel-forming properties
- Antibacterial properties
- Heavy metal ion chelation ability



Cyanobacterial extracellular polymeric substances (EPS)

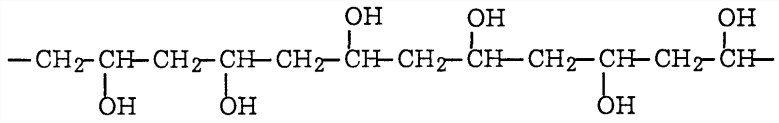
- Isolated from *Cyanothece* sp.CCY 0110 (*Mota, R., et al. Carbohyd Polym (2013) 92, 1408-1415*)
- Acidic polysaccharide
- Large number of different monosaccharides (usually 6 to 13),
- Hydrophobic
- Anti-viral properties
- Strong affinity towards metal ions

Centre for Nanotechnology and Smart Materials

Introduction

Polyvinyl Alcohol (PVA)

- synthetic polymer
- water soluble
- non-toxic
- biocompatible
- chemically and thermally stable



U.PORTO FACULDADE DE CIÊNCIAS UNIVERSIDADE DO PORTO
IBMC INSTITUTO DE BIOLOGIA MOLECULAR E CELULAR INSTITUTE FOR MOLECULAR AND CELL BIOLOGY
Universidade do Minho
2C2T CENTRO DE CIÊNCIA E TECNOLOGIA TÊXTIL
INVISIBLE NETWORK project
FCT Fundação para a Ciência e a Tecnologia
UNIÃO EUROPEIA Fundo Europeu de Desenvolvimento Regional
QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL
COMPETE

Experimental

PVDF basal filter

(5cm ∅, 0.2mm porosity)

PVA 12%wt (in H_2O)

or

PVA 12%wt + **Chitosan (CS)** 0.5%wt (in 1% Acetic acid aq. solution)

Alkali polysaccharide DD ~85

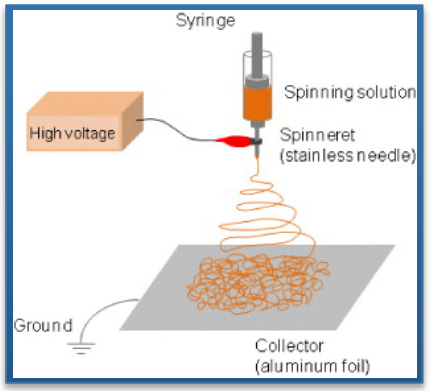
or

PVA 12%wt + **cyanobacterial extracellular polymeric substances (EPS)** 0.5%wt (50/50 DMSO:H_2O)

Acid polysaccharide

Experimental

Electrospinning:



http://iopscience.iop.org/1468-6996/13/1/015003/article

Conditions:

- Room temperature
- 10mL syringe with needles of 0.5mm of inner diameter
- Electric field: 20 to 23kV
- Feed rate: 0.2mL/h
- Conductivity and viscosity of the polymer solutions:

Polymer blend (%wt)	Conductivity (μS cm^{-1})	Viscosity (cP)
12% PVA	874 ± 9	96 ± 3
12% PVA + 0.5% EPS	1149 ± 26	563 ± 3
12% PVA + 0.5% CS	1274 ± 20	442 ± 12

Experimental

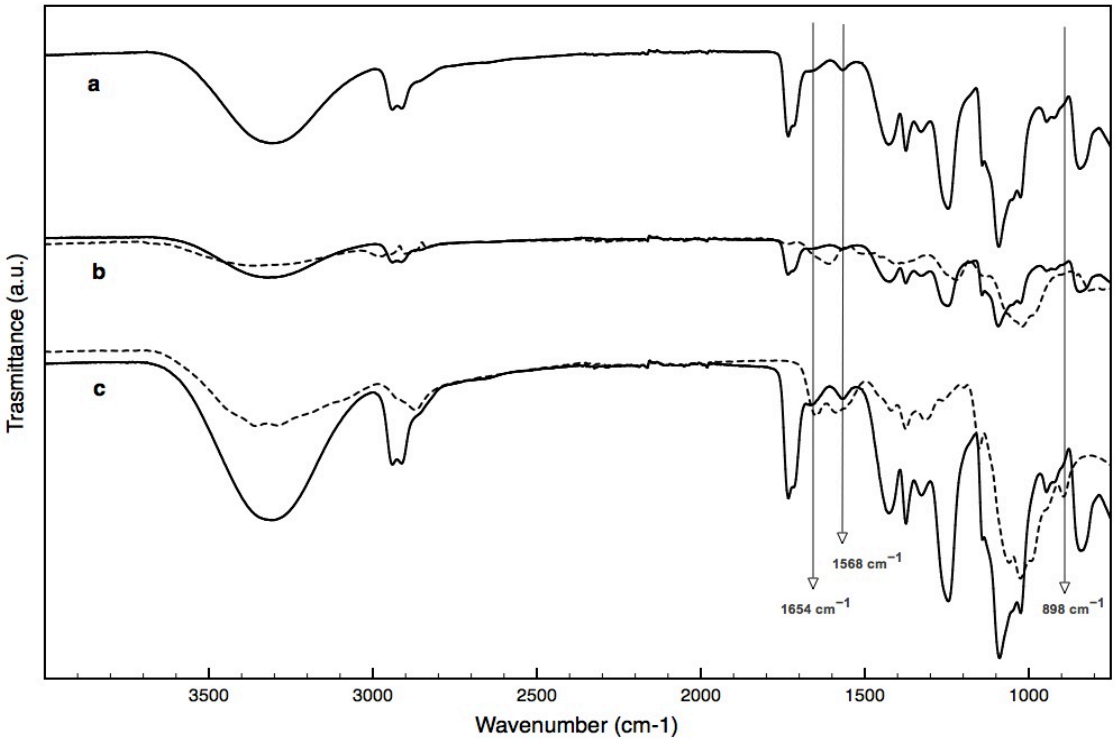
Characterization of electrospinned PVA and PVA/polysaccharides membranes

- **ATR-FTIR** (Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy)
- **EDS** (Energy Dispersive X-ray Spectroscopy)
- **AFM** (Atomic Force Microscopy)
- **SEM** (Scanning Electron Microscopy)
- DMA (Dynamic Mechanical Analysis)
- TGA (Thermal Gavimetric Analysis)
- DSC (Differential Scanning Calorimeter)
- **Metal Chelation Efficiency**

→ Investigation of the morphology, diameter, structure, mechanical and thermal properties.

Results

- **ATR-FTIR**



(a) PVA nanofiber and pure polymer

(b) PVA /EPS nanofiber (*solid line*) and pure EPS polymer (*dashed line*)

(c) PVA/CS nanofiber (*solid line*) and pure CS polymer (*dashed line*)

Results

EDS analysis

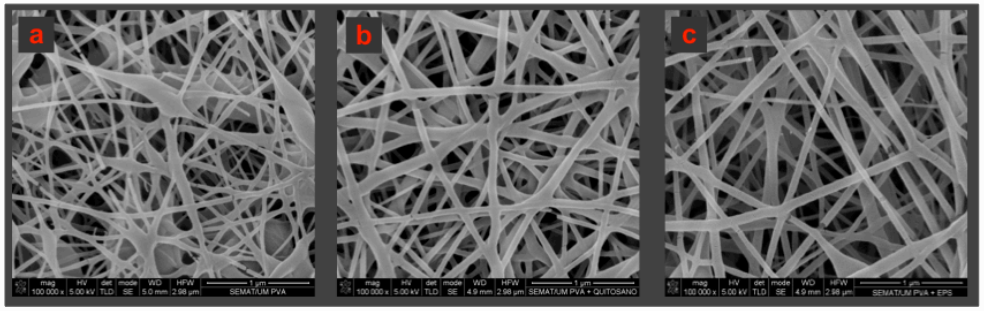
Variation of weight and atomic percentages of the atoms C, O, N and S in the electrospun nanofibres

	PVA		PVA/CS		PVA/EPS	
Element	Wt %	At %	Wt %	At %	Wt %	At %
C	44.30	51.44	42.27	49.26	37.32	44.25
O	55.70	48.56	55.84	48.85	61.97	55.40
N	-	-	1.89	1.89	-	-
S	-	-	-	-	0.71	0.35
Total	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*

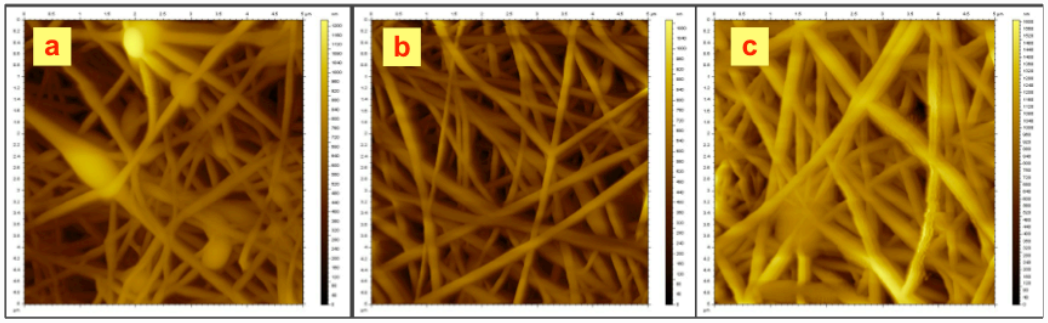
Centre for Nanotechnology and Smart Materials

Results

- **SEM** (amplification 100.000x)



- **AFM** (scanned area 5x5μm)



Electrospun membranes:

(a) 12%wt PVA

(b) 12%PVA and 0.5%CS

(c) 12%PVA and 0.5%EPS

PVA/polysacharides membranes (*b*,*c*):

- Uniform and smooth morphology
- No beads formation
- Narrow diameter distribution from ~50 to 130nm.

U.PORTO FACULDADE DE CIÊNCIAS UNIVERSIDADE DO PORTO · IBMC INSTITUTO DE BIOLOGIA MOLECULAR E CELULAR · Universidade do Minho · 2C2T CENTRO DE CIÊNCIA E TECNOLOGIA TÊXTIL · INVISIBLE NETWORK project · FCT Fundação para a Ciência e a Tecnologia · UNIÃO EUROPEIA Fundo Europeu de Desenvolvimento Regional · QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL · COMPETE

Centre for Nanotechnology and Smart Materials

Results

Metal Chelation Test

Dead-end filtration of a standard solution of hexavalent chromium (2mg/mL) prepared using potassium dichromate ($K_2Cr_2O_7$)

Before filtration, electrospun membranes were cross-linked with glutaraldehyde (GA) to maintain its morphology and prevent it from dissolution during filtration.

Increase in chromium binding capacity of ~5% in both PVA/polysaccharide blended membranes

→ Remarkable result given the low amount (0.5%) of added polysaccharides.

U.PORTO FACULDADE DE CIÊNCIAS UNIVERSIDADE DO PORTO · IBMC INSTITUTO DE BIOLOGIA MOLECULAR E CELULAR · Universidade do Minho · 2C2T CENTRO DE CIÊNCIA E TECNOLOGIA TÊXTIL · INVISIBLE NETWORK project · FCT Fundação para a Ciência e a Tecnologia · UNIÃO EUROPEIA Fundo Europeu de Desenvolvimento Regional · QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL · COMPETE

Centre for Nanotechnology and Smart Materials

Final Remarks

- Successful preparation of electrospun PVA/polysaccharides (CS or EPS) blend nanofibrous membranes
- Presence of intermolecular hydrogen bonds between the polysaccharides and PVA (indicated by thermal and mechanical analysis)
- Electrospun PVA/polysaccharides blended membranes showed better tensile mechanical properties when compared with PVA alone, and resisted more against disintegration in the temperature range 10-50 ºC.
- In ***future work***, these membranes will be further coated with an ultra-thin selective top layer.

U.PORTO FACULDADE DE CIÊNCIAS UNIVERSIDADE DO PORTO
IBMC INSTITUTO DE BIOLOGIA MOLECULAR E CELULAR
Universidade do Minho
2C2T CENTRO DE CIÊNCIA E TECNOLOGIA TÊXTIL
INVISIBLE NETWORK project
FCT Fundação para a Ciência e a Tecnologia
UNIÃO EUROPEIA Fundo Europeu de Desenvolvimento Regional
QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL
COMPETE

Centre for Nanotechnology and Smart Materials

Acknowledgements

- FCT and FEDER (COMPETE Programme): projects PEst-C/SAU/LA0002/2011, PTDC/CTM/100627/2008 and PTDC/EBB-EBI/099662/2008; and grants SFRH/BPD/37045/2007 and SFRH/BPD/72400/2010.
- Project INVISIBLE NETWORK nº. 13857 * SI I&DT Mobilizador

Centre for Nanotechnology and Smart Materials

Thank you for your attention !

CeNTI - Intelligent technology designed for you!

csilva@centi.pt

www.centi.pt

www.facebook/centinetwork

U.PORTO FACULDADE DE CIÊNCIAS UNIVERSIDADE DO PORTO · IBMC INSTITUTO DE BIOLOGIA MOLECULAR E CELULAR INSTITUTE FOR MOLECULAR AND CELL BIOLOGY · Universidade do Minho · 2C2T CENTRO DE CIÊNCIA E TECNOLOGIA TÊXTIL · INVISIBLE NETWORK project · FCT Fundação para a Ciência e a Tecnologia MINISTÉRIO DA CIÊNCIA E DO ENSINO SUPERIOR · UNIÃO EUROPEIA Fundo Europeu de Desenvolvimento Regional · QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL PORTUGAL 2007-2013 · COMPETE PROGRAMA OPERACIONAL FACTORES DE COMPETITIVIDADE