PMSE Jamil Baghdachi Tuesday, April 09, 2013

454 - Fabrication and characterization of PVA, PVA/chitosan, and PVA/cyanobacterial exopolysaccharide nanofibrous composite nanofiltration membranes prepared by electrospinning

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A series of poly(vinyl alcohol) (PVA), PVA/chitosan (CS) and PVA/cyanobacterial exopolysaccharide (EPS) blend nanofibrous membranes were fabricated by electrospinning using a microfiltration poly(vinylidene fluoride) (PVDF) as a basal membrane, in order to obtain thin-layer composite (TFC) nanofiltration membranes. The morphology, diameter, structure, mechanical and thermal characteristics of electrospun nanofibers were investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), dynamical and mechanical analysis (DMA), thermogravimetry (TGA) and differential scanning calorimetry (DSC). The morphology and diameter of the nanofibers were mainly affected by concentration of the blend solution and weight ratio of the blend, respectively. Thermal and mechanical analysis demonstrated that there were strong intermolecular hydrogen bonds between the molecules of CS-PVA and EPS-PVA in the blends. The heat-treated electrospun blended membranes showed better tensile mechanical properties when compared with PVA alone, and resisted more against disintegration. Nanofiltration was successfully performed in a high pressure cell.

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Fabrication and characterization of PVA, PVA/chitosan and PVA/ cyanobacterial exopolysaccharide nanofibrous composite nanofiltration membranes prepared by Electrospinning

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INTRODUCTION

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]. Examples of electrospinning of natural polymers are limited to silk collagen, DNA, alginate, chitosan and more recently fibrinogen, gelatin and hyaluronic acid[2]. Because of the very different chain conformations, hydrodynamic responses and repulsive force in solution among the polyanions of natural polymers, the efficiency and reproducibility of the electrospinning process and the fibre uniformity remains a challenge, thus limiting their practical application[3]. The extremely high surface, bulk porosity and mechanical stability of the non-woven structures created by electrospinning overcomes the limitations of traditional membrane fabrication techniques and eases their application[4]. In the last years various nanofibres products containing the basic polysaccharide chitosan have been produced also for filtration purposes[5]. Chitosan shows singular chemical and biological characteristics such as biocompatibility, antibacterial properties, heavy metal ion chelation ability, gel-forming properties and hydrophilicity[6]. Among the acidic polysaccharides, the cyanobacterial extracellular polymeric substances (EPS) possess unique characteristics that make them very attractive for biotechnological applications, including a large number of different monosaccharides (up to 13), a strong anionic nature and affinity towards metal ions due to the presence of two different uronic acids and sulphate groups, and an hydrophobic behavior conferred by the presence of ester-linked acetyl groups, peptidic moieties and deoxysugars[7,8]. However, the information available on the rheological properties and biosynthetic pathways is still scarce, limiting their biotechnological applications[9]. In this study, anionic (EPS) and cationic (Chitosan) biopolysaccharides blended with PVA (to reduce the repulsive forces within the charged biopolymer solutions) were electrospinned into a polyvinylidene difluoride (PVDF) basal microfiltration membrane with the ultimate aim of developing a high quality mid-layer nanofibrous porous support substrate for ex[illegible] electrospinned membranes were investigated in their morphology, diameter, structure, mechanical and thermal characteristics.

MATERIAL & METHODS

- **Materials**
  - **PVA, 87-90% hydrolyzed (wt 30,000-70,000) from Sigma Aldrich (USA).**
  - **Chitosan (DD 85%), ChitoClear hqg95-43000 from Primex (Iceland).**
  - **EPS from the cyanobacterium *Cyanothece* sp. CCY 0110 (Culture Collection of Yerseke, the Netherlands).**
  - **PVDF basal disc filter (5 cm in diameter, porosity of 0.2 µm) from Sterlitech, USA.**
- **Eletrospinning**
  - **Nanon NF-103 (MECC, Japan) at room temperature. Syringes of 10 ml, needles of 0.5 mm. Electric field between 15 and 27 kV.**
- **Atomic Force Microscopy (AFM)**
- **Scanning Electron Microscopy (SEM)**
- **Dynamic Mechanical Analasys (DMA)**
- **Thermal Gravimetric Analysis (TGA)**
- **Fourier Transformed Infrared Spectroscopy (FTIR)**
- **Differential Scanning Calorimeter (DSC)**

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RESULTS & DISCUSSION

Production of PVA, PVA/Chitosan and PVA/EPS membranes

CYANOBACTERIAL EPS PRODUCTION

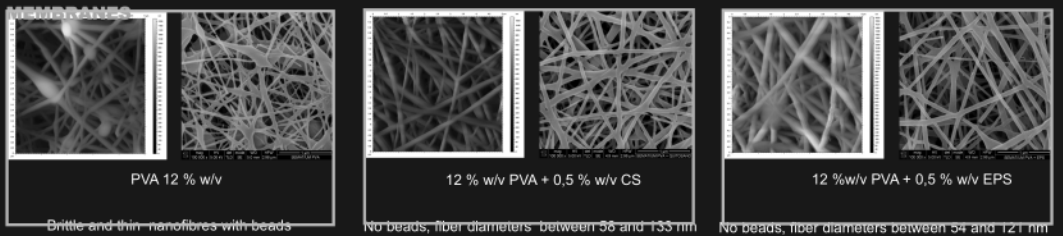
Selected strain: *Cyanothece* CCY 0110. Unicellular N_2-fixing marine strain.

Culture was grown in ASNIII medium 10 L bioreactors at 30 ºC under continuous light regimen (40 µE m^{-2} s^{-1}), with aeration (5 L min^{-1}) and magnetic stirring (150 rpm). The cells were removed by centrifugation. The supernatant dialyzed and the EPS precipitated in cold ethanol and lyophilized.

EPS showed a complex heteropolysaccharide composition: 9 different monosaccharides (including two uronic acids, two pentoses and two deoxyhexoses), the presence of sulfate groups and peptides.

This type of acidic exopolysaccharides have putative antimicrobial and antiviral properties and a particular affinity to bind metal ions.

ATOMIC FORCE MICROSCOPY AND SCANNING ELECTRON MICTOSCOPY IMAGES OF ELECTROSPUN MEMBRANES



PVA 12 % w/v — Brittle and thin nanofibres with beads

12 % w/v PVA + 0,5 % w/v CS — No beads, fiber diameters between 58 and 133 nm

12 %w/v PVA + 0,5 % w/v EPS — No beads, fiber diameters between 54 and 121 nm

EDS ANALISYS FOR CONFIRMATION OF ELECTROSPUN FIBERS CONTAINING CS OR EPS

Element	PVA		PVA + Quit		PVA + EPS	
	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

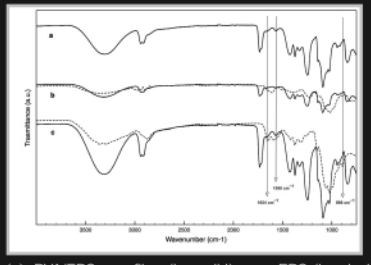
➡ Nitrogen appears from the chitosan's amine and acetylamine groups

➡ Sulphur content derives from the EPS

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

Characterization of PVA, PVA/Chitosan and PVA/EPS membranes

ATF-FTIR SPECTRA OF NANOFIBER MATS



1654 cm-1 carbonyl streching of the secondary amide band [3]

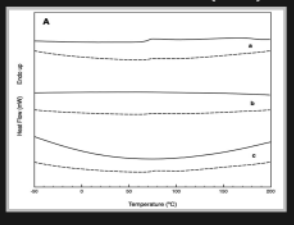
898cm-1 faint shoulder is the characteristic of the saccharide structure

1568 cm-1 intensities of the carboxyl band attribute to the acetate group of the PVA show a relative diminution

Reaction of the PVA with EPS and CS has indeed occurred by forming acetal bridges [4

(a), PVA/EPS nanofiber (b - solid), pure EPS (b - dashed), PVA/CS nanofiber (c - solid), pure chitosan (c - dashed).

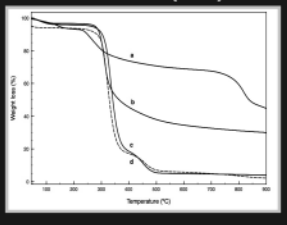
TERMOGRAVIMETRY (TGA) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSIS



DSC. Solid: PVA (a), EPS (b) and CS (c) polymers. Dashed: PVA (a), PVA/EPS (b) and PVA/CS (c) nanofibers.

No crystallization or fusion peaks only T_g of PVA at 70 ºC

Slight positive shift in T_g for PVA/CS and PVA/EPS nanofiber indicates presence of a miscible phase

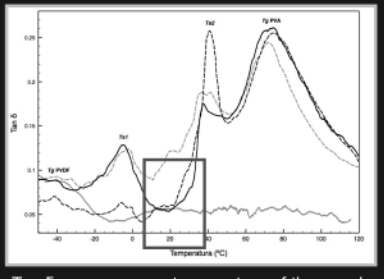


TGA. EPS (a), Chitosan (b), PVA (c) and nanofibers (d)

Three steps degrdation for EPS and PVA and two steps degradation for CS.

Degradation profiles of nanofibers fit the degradation profile of PVA

DYNAMIC MECHANICAL ANALYSIS (DMA)



The two main α-relaxation peaks at about -42 ºC and 72 ºC are related to the T_g of PVDF and PVA

Peak between -10 and −5 ºC (Ts1) attributed to the secondary β-relaxation of PVA and polysaccharides in dry state

Secondary relaxation temperature peaks between 35 and 45 ºC (Ts2) associated with the local molecular motions or conformational changes of PVA side groups and increase of residual water mobility in chitosan.

Significant enhancing of the elastic properties of the membrane in a temperature range (10 and 30 °C) important for the membrane performance in water filtration applications.

Tan δ curves versus temperature of the membranes. PVDF (solid grey), PVDF coated PVA nanofibers (dashed grey), PVDF coated PVA/CS nanofibers (dashed black), PVDF coated PVA/EPS nanofibers (solid black)

ONGOING WORK & FUTURE PROSPECTIVES

- **Final assembling of the TFC nanofiltration membrane by the application of a crossilinked PVA ultra-thin selective barrier top layer**
- **Further characterization of membranes, nanofiltration tests with sythetic seawater**
- **Testing antifouling activity and biofilm formation on membranes**
- **Increase antibacterial activity by the addition of silver nanoparticles to the blend solutions**