



## Development and characterisation of hybrid polysaccharide membranes for dehydration processes

Inês T. Meireles<sup>a</sup>, Rosa M. Huertas<sup>a,b</sup>, Cristiana A.V. Torres<sup>c</sup>, Isabel M. Coelho<sup>a,\*</sup>, João G. Crespo<sup>a</sup>

<sup>a</sup> LAQV/Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

<sup>b</sup> Laboratory of Membrane Processes, Instituto de Biologia Experimental e Tecnológica (iBET), apartado 12, 2780-901 Oeiras, Portugal

<sup>c</sup> UCIBIO/Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

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### ABSTRACT

The purpose of this work is the development and characterisation of new hybrid polysaccharide (FucoPol) membranes. These membranes were prepared by incorporation of a SiO<sub>2</sub> network homogeneously dispersed by using a sol-gel method with GPTMS as a crosslinker silica precursor. They were further crosslinked with CaCl<sub>2</sub> for reinforcement of mechanical properties and improvement of their permeation performance. They were characterised in terms of their structural, mechanical and thermal properties.

They presented a dense and homogeneous structure, resistant to deformation, with a T<sub>g</sub> of 43 °C and a thermal decomposition between 240 and 251 °C.

The hybrid FucoPol membranes were tested for ethanol dehydration by pervaporation and also for nitrogen dehydration. They exhibited high water selectivity values, similar to PERVAP® 4101, however they lost their stability when exposed to solutions of 10.0 wt.% water in ethanol. In contrast, these membranes were stable when applied in N<sub>2</sub> dehydration, leading to reproducible performance and very high water selectivities.

### 1. Introduction

Dehydration of organic solvents, in particular ethanol dehydration, is the most important application of pervaporation (Chapman, Oliveira, Livingston, & Li, 2008). In this process, hydrophilic membranes are used due to their high selective for water. However, they may present poor mechanical stability in the presence of high water content (Dudek, Krasowska, Turczyn, Gnus, & Strzelewicz, 2017). Therefore, several efforts have been devoted to enhance membrane stability, using different strategies, such as crosslinking, chemical modifications, use of polymer blends and development of organic-inorganic hybrid membranes, among others (Dudek et al., 2017).

Hybrid membranes have become an important research topic in membrane science because they combine the easy processing and low-cost of polymeric membranes with the high permeation fluxes and mechanical properties of inorganic membranes (Cheng et al., 2017; Wang et al., 2017). Due to their unique characteristics, they have been recognized as promising membrane materials for several applications, such as pervaporation and gas separation (Guizard, Bac, Barboiu, & Hovnanian, 2001; Zhao et al., 2013). Although these hybrid membranes generally exhibit enhanced permeability and selectivity compared to

purely polymeric membranes, their fabrication usually involves some difficulties, namely agglomeration of inorganic particles or leaching of the particles out of the membrane due to the poor compatibility between the polymeric matrix and the inorganic particles (Cheng et al., 2017; Davey, Leak, & Patterson, 2016). Among the available techniques to prepare hybrid membranes, the sol-gel process has been extensively used to provide chemical bonding between the organic and the inorganic phases, allowing the inorganic phase to disperse homogeneously in the polymeric matrix and control the concentration of precursors employed (Cheng et al., 2017; Danks, Hall, & Schnepp, 2016).

In the last years, the preparation of hybrid membranes using polysaccharides as polymer matrix has been increasing (Dudek et al., 2017; Sakai, Ono, Ijima, & Kawakami, 2002; Uragami et al., 2004). However, it is necessary to take into account the compatibility of polysaccharides in terms of solubility, pH and hydrophilicity to perform the sol-gel process, in order to obtain homogeneous materials (Spirk et al., 2013). On the other hand, in order to control the rate of degradation and mechanical properties, and avoid the excessive swelling during dehydration of solvents by pervaporation, covalent bonds are necessary. Thus, the use of silica precursors with cross linkable and favourable functional groups may increase the membrane stability, changing the

\* Corresponding author.

E-mail address: [imrc@fct.unl.pt](mailto:imrc@fct.unl.pt) (I.M. Coelho).

polymer structure and leading to better performing membranes (Su, Buss, McCloskey, & Urban, 2015). In particular, (3-Glycidyoxypropyl) trimethoxysilane (GPTMS) has been explored as one of the most commonly used organic silanes that forms covalent bonds between organic and inorganic networks (Gabrielli et al., 2013). The three hydrolysable alkoxy groups and high reactive epoxide ring present in GPTMS can create covalent bonding with the hydroxyl groups of polysaccharides, leading to a SiO<sub>2</sub> network. Peng, Lu, Sun, and Jiang (2006) reported that poly(vinyl alcohol) (PVA) + GPTMS hybrid membranes exhibited improved transport properties for the separation of benzene/cyclohexane mixtures. Also, Pandis et al. (2014) found an improvement of the mechanical properties of chitosan + TEOS (tetraethylorthosilicate) + GPTMS hybrid membranes. Other works reported the use of hybrid polysaccharide (chitosan, alginate or cellulose) membranes for alcohol dehydration by pervaporation, using different inorganic materials, such as graphene oxides (Dharupaneedi, Anjanapura, Han, & Aminabhavi, 2014; Zhao et al., 2016), silica particles (Choudhari, Premakshi, & Kariduraganavar, 2016; Pandey & Shahi, 2013) and titanium particles (Zhu et al., 2012).

The purpose of this work is the development and characterisation of a new hybrid polysaccharide membrane, using GPTMS as precursor of a sol-gel reaction and the exopolysaccharide – FucoPol – produced by *Enterobacter* A47 (Freitas et al., 2011). The chemical, thermal and mechanical properties of the membrane developed were analysed, as well as its morphological structure, swelling and biological degradability. These membranes were then applied for ethanol dehydration by pervaporation and also for gas (nitrogen) dehydration, in order to evaluate their potential for dehydration processes.

## 2. Experimental

### 2.1. Materials

(3-Glycidyoxypropyl) trimethoxysilane (GPTMS) purchased from Sigma-Aldrich (USA) and acetic acid glacial (99–100%) purchased from J.T. Baker (USA) were used as precursor and acid catalyst, respectively, in the sol-gel process. Calcium chloride (CaCl<sub>2</sub>) (> 93.0%) was obtained from Fluka Analytical (USA) and ethanol absolute (99.99%) was obtained from Fisher Chemical (USA). Magnesium nitrate hexahydrate (98.0%) was supplied by Alfa Aesar (UK). Nitrogen (99.99%) and helium (99.99%) used in gas dehydration tests were obtained from Irmasolda (Portugal).

### 2.2. Polysaccharide production and purification

FucoPol was produced by *Enterobacter* A47 using glycerol as carbon source, in a 10 L bioreactor with controlled temperature (30 °C) and pH (7). The bioreactor was operated in a batch mode (initial glycerol concentration of 40 g L<sup>-1</sup>) during the first 10 h of cultivation, followed by a fed-batch mode for 3 days (feeding with a 200 g L<sup>-1</sup> glycerol solution at a rate of 20 g L<sup>-1</sup> h<sup>-1</sup>). The aeration rate (0.125 vvm, volume of air per volume of reactor per minute) was kept constant throughout the cultivation, while the dissolved oxygen (DO) concentration was maintained below 10% during the fed-batch phase (Freitas et al., 2014).

FucoPol extraction and purification consisted on several steps as described by Ferreira et al. (2014). The diluted broth (1:5 v/v) was centrifuged (8875 G for 30 min) to remove bacterial cells and the supernatant was submitted to thermal treatment (70 °C, 1 h) to guarantee the inactivation of bacterial enzymes. Then, it was centrifuged (8875 G for 30 min) again, to remove precipitated proteins and remaining cells. After this procedure, the supernatant was submitted to a dia-ultrafiltration process, using a crossflow membrane cassette (Hydrosart Ultrafiltration Cassettes, Sartorius Stedim Biotech GmbH, Germany) with a molecular weight cut-off of 100 kDa and a surface area of 0.6 m<sup>2</sup>, operated at a transmembrane pressure of 0.4 bar, to remove low molecular weight contaminants, e.g. salts, glycerol and proteins. The

treated supernatant containing FucoPol was concentrated 5 times, using the same membrane module, switching to an ultrafiltration processing mode. The solution obtained was freeze dried (Martin Christ, model Epsilon 2–40, Germany) during 48 h.

The sugar composition of FucoPol polymer was 37.0%mol of fucose, 34.0%mol of glucose, 23.0%mol of galactose and 6.0%mol of glucuronic acid, obtained by liquid chromatography (HPLC) using a CarboPacPA10 column (Dionex) as described in our previous work (Meireles, Portugal, Alves, Crespo, & Coelho, 2015).

### 2.3. Membrane preparation

Five membranes with different calculated amounts of silica precursor (Eqs. (1) and (2)) were prepared as described by Huertas et al. (2014) to obtain final concentrations of SiO<sub>2</sub> (3.0, 5.0, 7.0, 7.5 and 8.0 w/w%) and a molar ratio between GPTMS SiO<sub>2</sub> precursor and glacial acetic acid of 2.6:1.

The Eqs. (1) and (2) are defined as:

$$m_{\text{SiO}_2} = \frac{x\text{SiO}_2 \cdot m_{\text{polymer}}}{1 - x\text{SiO}_2} \quad (1)$$

$$n_{\text{GPTMS}} = \frac{m_{\text{SiO}_2}}{M_{\text{SiO}_2}} \quad (2)$$

where xSiO<sub>2</sub> is the weight fraction of SiO<sub>2</sub> to be introduced into the polymeric matrix, m<sub>SiO<sub>2</sub></sub> is the mass of silica to be added, M<sub>SiO<sub>2</sub></sub> is the molecular weight of silica (60.08 g/mol), considering the complete condensation of GPTMS, and n<sub>GPTMS</sub> is the number of moles of GPTMS precursor.

The hybrid membranes were prepared by dissolution of 1.5 w/v% of the dried FucoPol in distilled water during 8 h, at room temperature. Then, glacial acetic acid was added as acid catalyst, for obtaining acidic conditions (pH 3–4) during the sol reaction, in order to functionalise the biopolymer with the silica precursor of GPTMS (Gabrielli et al., 2013). After this, the calculated amount of GPTMS was added dropwise under vigorous magnetically stirring to the aqueous solution, to develop a good dispersion of the silica particles in the polymeric matrix. This procedure was carried out in order to obtain hybrid membranes with a final SiO<sub>2</sub> content of 3.0, 5.0, 7.0, 7.5 and 8.0 w/w%, with respect to the biopolymer. These solutions were maintained under stirring overnight at room temperature (22.0 ± 1.0 °C) and then, sonicated during 25 min before casting the membranes in Teflon Petri dishes. They were dried at 30.0 °C in an oven during 72 h, for completing dehydration and condensation reaction of SiO<sub>2</sub> and promoting linkages with FucoPol chains.

The membranes prepared with optimized molar ratios were immersed for crosslinking reaction with a solution of calcium chloride (2 g/100 ml) during 5 min. The excess liquid was removed using a tissue paper and the membranes were dried at ambient temperature and relative humidity (T = 22.0 °C and RH = 48%).

### 2.4. Characterisation of the hybrid polysaccharide membranes

#### 2.4.1. Fourier transform infrared (FT-IR) spectroscopy

Fourier Transform Infrared Spectra (FT-IR) of the hybrid polysaccharide membranes and of pristine FucoPol were recorded using attenuated total reflectance (ATR) on a Bruker Spectrometer IFS 66/S FT-IR instrument (USA) equipped by H-ATR with a ZnSe crystal. The chemical structure of the membranes was checked by analysing normalized spectra obtained in the range of wave numbers from 4000 to 550 cm<sup>-1</sup> during 120 scans with 2 cm<sup>-1</sup> resolution.

#### 2.4.2. Thermogravimetry analysis (TGA)

The thermal stability of the hybrid polysaccharide membranes developed and pristine FucoPol was studied by thermogravimetric analysis using a TA TGA Q-50 analyser (TA Instruments, USA). The TGA

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