Author's Accepted Manuscript

A Catechin/Cellulose Composite Membrane for Organic Solvent Nanofiltration

Mohamed H. Abdellah, Liliana Pérez-Manríquez, Tiara Puspasari, Colin A. Scholes, Sandra E. Kentish, Klaus-Viktor Peinemann

PII: S0376-7388(18)32121-5
DOI: <https://doi.org/10.1016/j.memsci.2018.09.042>
Reference: MEMSCI16487

To appear in: *Journal of Membrane Science*

Received date: 1 August 2018
Revised date: 24 August 2018
Accepted date: 15 September 2018

Cite this article as: Mohamed H. Abdellah, Liliana Pérez-Manríquez, Tiara Puspasari, Colin A. Scholes, Sandra E. Kentish and Klaus-Viktor Peinemann, A Catechin/Cellulose Composite Membrane for Organic Solvent Nanofiltration, *Journal of Membrane Science*, <https://doi.org/10.1016/j.memsci.2018.09.042>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A Catechin/Cellulose Composite Membrane for Organic Solvent**Nanofiltration**

Mohamed H. Abdellah^{a,1}, Liliana Pérez-Manríquez^{b,1}, Tiara Puspasari^b, Colin A. Scholes^a, Sandra E. Kentish^a, Klaus-Viktor Peinemann^{b*}

^aDepartment of Chemical Engineering, The University of Melbourne, 3010 Parkville, Australia

^bAdvanced Membranes and Porous Materials Center, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia

*Corresponding author: klausviktor.peinemann@kaust.edu.sa

Abstract

In this work, a novel thin-film composite membrane composed of a polyester film on a cellulose support was successfully synthesised. The polyester film was formed from the interfacial reaction between catechin, a bio-derived poly-phenol, and terephthaloyl chloride (TPC). The cellulose support was prepared by non-solvent induced phase separation from a 12.5 wt % cellulose dope solution in 1-ethyl-3-methylimidazolium acetate ionic liquid. The composite membrane was characterized by Fourier Transform Infrared and X-Ray Photoelectron Spectroscopy to confirm the success of the interfacial reaction. Scanning electron and atomic force microscopy were used to study the surface morphology and roughness of the membranes produced. The performance of the composite membranes in terms of solvent permeance and solute rejection was investigated by studying the rejection of a broad range of different molecular weight dyes in dimethylformamide (DMF) solution. The membranes showed an average DMF permeance of $1.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with a molecular

¹ Both authors contributed equally to this work.

weight cut-off of around 500 g mol^{-1} . The membrane was stable in DMF over 30 days with no significant change in performance. The membrane has potential application in the food and pharmaceutical industries.

Keywords

Catechin, organic solvent nanofiltration, cellulose, polyphenols, interfacial polymerization

1. Introduction

Organic solvent nanofiltration (OSN) is a versatile technology that has received growing attention over recent years. This technology offers a promising alternative to conventional separation processes such as distillation and evaporation[1,2]. Organic solvent nanofiltration is distinguished by the low energy requirements as the separation occurs without phase transition [3]. Moreover, it operates at ambient temperature which obviates the thermal degradation of heat sensitive ingredients which is common in the pharmaceutical and food industries [4]. Furthermore, it is considered an environmentally favourable process, as the release of harmful vapours to the atmosphere is minimised and the carbon foot print is low [2].

The stability of polymeric OSN membranes in organic solvents is one of the main issues that prevents the commercialisation of this technology [1]. Dimethylformamide (DMF) is one such solvents that is widely used in many industries such as pharmaceutical and petrochemical production [5]. Due to its high dielectric constant and aprotic nature, DMF is a good solvent for many polymers such as polyimide (PI), polyacrylonitrile (PAN), polyurethane (PU) and polyvinylchloride (PVC) [5]. In the past few years, chemical cross-linking using aromatic diamines has been used to stabilise PI asymmetric membranes against

such polar aprotic solvents[6–11]. However, this results in a thick, dense active layer than subsequently leads to low solvent flux. PEEK membranes with high solvent and temperature stability have been introduced [12]. Recently spray-coating was proposed for membrane manufacturing [13]. It was stated that the replacement of the water-induced phase separation process makes the process greener (no contaminated waste water) and faster. In the work presented here, we use conventional production methods: water-induced phase separation for the preparation of the porous support and interfacial polymerisation for the coating, but we replaced toxic or oil-derived components by greener building blocks.

Interfacial polymerization is an elegant approach to produce thin film composite (TFC) membranes with high solvent flux [14,15]. In this method, a very thin selective film of polyamide or polyester is produced on the top of a porous support membrane by an instantaneous reaction between two reactive monomers[14–18]. These monomers are dissolved in two immiscible solvents; typically water and an organic solvent. The quality and thickness of the film produced depends on many parameters such the concentration of the aqueous and organic phases, the reaction time, and the nature and number of reactive functional groups in each of the monomers [19]. DMF-stable OSN membranes have been prepared using this approach [20]. However, the organic solvent used was hexane. According to recent European legislation (REACH), n-hexane and a broad range of other organic solvents have been classified as carcinogenic and are expected to be banned from industrial use in the future[21].

Such environment and health concerns had drawn the attention of many researchers to find more sustainable and environmentally friendly approaches to the interfacial polymerisation technique. Szekely et al. [22] outlined the main principles needed for sustainable and benign OSN technology as (a) the utilization of green solvents which account for the majority of the waste formed during the production process, (b) the use of low toxicity chemicals, (c) the use

of renewable and sustainable raw materials, (d) fabrication of the membrane at ambient temperature to reduce energy consumption and (e) the design of biodegradable membranes.

Bio-inspired polyphenols extracted from plants represent promising alternatives to hydrocarbon-based phenols for the preparation of selective polyester films [23]. Catechin (**Fig.1**) is a polyphenol that is present in many plants and fruits such as apples, blueberries, gooseberries, grape seeds, kiwi fruit and strawberries [24]. The large number of cross-linkable hydroxyl groups as well as the strong interfacial activity of polyphenols make catechin a potential substituent to commonly used harmful phenols [23]. In our previous work[25] we used Morin, a very similar polyphenol, as one of the reactants. In this work we replaced not only the Morin, but also the hydrazine cross-linked polyacrylonitrile support with an environmentally friendly biopolymer support.

Terephthaloyl chloride (TPC), a typical acid chloride, is widely used for preparation of polyamide and polyester interfacial films[15,17,18,26,27]. TPC is typically dissolved in n-hexane or cyclohexane to form the organic phase. Therefore, alternative safe solvents able to dissolve TPC are desirable. Alpha-pinene, which is extracted from plants such as rosemary, basil, pine and parsley is considered a green and sustainable alternative to n-hexane [28]. It has a very low flash point and negligible vapour pressure that eliminates the possibility of explosion, making it safe to the environment [29–31].

Cellulose is a sustainable biopolymer extracted from plants and living microorganisms[32,33]. It is characterised by chemical and thermal stability, low cost, availability and biodegradability that make it a potential alternative to hydrocarbon-based polymers as a support material [34]. Its solubility in ionic liquids has opened a new route for the preparation of cellulose membranes by the phase inversion technique [35,36]. Ionic liquids are also considered as environmentally friendly solvents due to their high thermal stability, non-flammability, negligible vapour pressure and low chemical activity [37]. A

disadvantage of ionic liquids is their high price. When used in an industrial process, they have to be recovered, which can be done by nanofiltration/distillation or by distillation alone. The objective of this work is the synthesis of OSN TFC membranes with a polyester selective layer on a cellulose support membrane through an environmentally friendly route. Using non-solvent induced phase separation, the cellulose support was prepared from a dope solution of 12.5 wt % cellulose dissolved in 1-ethyl-3-methylimidazolium acetate ionic liquid. The selective polyester film was formed on the cellulose support via interfacial polymerization between aqueous catechin and organic TPC solutions. The performance of the composite membrane produced was evaluated by the filtration of different molecular weight dyes in DMF.

Figure 1. Molecular structure of catechin

2. Experimental

2.1. Materials

Catechin, cellulose powder (Avicel PH101), alpha-pinene, dimethylformamide (DMF), terephthaloyl chloride (TPC), sodium hydroxide pellets, 1-ethyl-3-methylimidazolium acetate (EMIM Ac, purity 97 %), Sudan Orange (276 g mol^{-1}), Sudan Blue (350 g mol^{-1}), Reactive Black 5 (992 g mol^{-1}), Reactive Green 19 (1419 g mol^{-1}) were obtained from Sigma-Aldrich. Amido Black 10 B (616 g mol^{-1}) was received from MP Biomedicals, France. Thymol Blue (467 g mol^{-1}) (ACROS Organics TM) and Brilliant Blue R250 (825 g mol^{-1}) were purchased from Fisher Scientific. Non-woven polyester support was purchased from Sojitz Europe, Germany

2.2. Preparation of cellulose support membrane

The non-solvent induced phase inversion technique was used for the preparation of the cellulose support membrane [36]. Cellulose powder was dissolved in EMIM Ac at 80 °C overnight to obtain a dope solution of 12.5 % wt. Trapped air bubbles in the dope solution were removed by sonication for 1 h to minimise the potential of defect formation during the casting process. The nonwoven polyester fabric was fixed onto a clean glass plate in a horizontal position. An adjustable casting knife (BYK-Gardner) was used to create a 250- μ m thick film on the polyester support. The membrane was immediately immersed in a water bath at 23 ± 1 °C for 24 h to complete polymer precipitation. After complete precipitation, the membrane was washed and kept in deionized water until further use.

2.3. Synthesis of the TFC membrane by interfacial polymerization

The polyester/cellulose composite membrane was fabricated by the interfacial polymerization reaction between catechin and TPC. Due to the acidic nature of phenols, a 20 g L⁻¹ catechin solution was prepared in sodium hydroxide solution at pH 12.4 due to its limited solubility at lower pH conditions [38,39]. A 2 g L⁻¹ TPC solution was prepared in alpha-pinene. To begin the synthesis, the wet cellulose support membrane was cut and fixed between a plate and frame (open area of 7 × 7 cm²) with a rubber gasket in between to avoid any leakage of the reacting solutions. 15 mL of the catechin solution was poured into the frame and left in contact with the cellulose support for 15 mins. Then, the residual catechin solution was removed and the setup dismantled. To avoid defect formation in the selective top film, the residual droplets of catechin solution on the surface of the cellulose support were removed by gently pressing the membrane on a filter paper using a rubber roller. The membrane was then fixed between the plate and frame and 15 mL of the TPC solution were poured inside the frame and left for 3 h. Afterwards, the excess solution was drained and the membrane was rinsed with pure alpha-pinene to remove unreacted monomers. The membrane was left to dry

under ambient conditions for 10 min before it was annealed at 50 °C under atmospheric pressure for 5 min. The resulting membrane was kept in dry conditions until use.

2.4. Membrane characterisation

2.4.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrometer (Nicolet iS10) was used to confirm the successful interfacial reaction between the reacting monomers and examine both the composite membrane and the cellulose support. The measurement was conducted in the range of 3700-900 cm^{-1} . Prior to the analysis, membrane samples were dried overnight under vacuum at 30 °C.

2.4.1.2. X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was conducted in a Kratos Axis Supra spectrometer equipped with a monochromatic Al Ka X-ray source ($h\nu = 1486.6 \text{ eV}$) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of $\sim 10^{-9}$ mbar. High-resolution spectra were recorded using an aperture slot of 300 μm x 700 μm , a pass energy of 20 eV and a step size of 0.1 eV. Membrane samples were mounted in floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s binding energy of Sp^2 hybridized carbon taken to be 284.5 eV.

2.4.1.3. Scanning Electron Microscopy (SEM)

An FEI Magellan XHR SEM microscope with a voltage of 1 kV was used to obtain high-resolution surface and cross-sectional images of the composite membrane. The membrane samples were snapped in liquid nitrogen after removing the nonwoven polyester packing to obtain sharp and well-defined cross-section images. The samples were then mounted on an aluminium stub and sputtered with 2-nm thick iridium layer.

2.4.1.4. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM, Agilent 5500 SPM) was used to estimate the surface roughness and the topography of membranes from 2D/3D images of $5 \times 5 \mu\text{m}$. The equipment was operated under atmospheric air in acoustic AC mode.

2.5. Permeation experiments.

The filtration experiments were carried out in the setup shown in **(Fig. 2)**. A dead end-flow cell (STERLITECH) with a membrane active area of 12.6 cm^2 was connected to a high-pressure N_2 cylinder to apply the required pressure, measured by a pressure gauge mounted on the connection line. To minimise concentration polarisation effects, the feed solution was stirred during filtration by placing the cell on a magnetic stirrer plate. All experiments were conducted at room temperature ($23 \pm 1 \text{ }^\circ\text{C}$) and 10 bar using DMF solvent. A new membrane coupon was used for each experiment. Prior to the filtration experiments, the membrane was conditioned by permeating 50 ml of DMF at 10 bar. Then, 75 ml of each dye solution ($35 \mu\text{mol L}^{-1}$) was loaded into the cell and the feed pressure was adjusted at 10 bar. A sample of 5 ml of the permeate was collected in triplicate for analysis, after discarding the first 10 ml. The composite membrane performance was evaluated in terms of DMF permeance and the rejection of different molecular weight dyes. The membrane permeance was calculated as follows,

$$P = \frac{V}{A \Delta P t} \quad \text{L m}^{-2} \text{ bar}^{-1} \text{ h}^{-1} \quad (1)$$

where $V \text{ (m}^3\text{)}$ is the permeate volume collected within time ($t, \text{ h}$), A is the membrane active area (m^2), ΔP is the transmembrane pressure across the membrane (bar)

For rejection calculations, the concentration of the dye in the retentate and permeate solutions was measured using a NanoDrop 2000/2000c spectrophotometer (Thermo-Fisher Scientific).

The instrument was set at the wavelength (λ_{max}) corresponding to the maximum absorption of the corresponding dye (**Table 1**). The percentage rejection was calculated as follows,

$$\% R = \frac{C_r - C_p}{C_r} \times 100 \quad (2)$$

Where C_r and C_p are the dye concentration in the retentate and the permeate solution, respectively.

Figure 2. The dead-end filtration setup used for the experiments

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

Generally, phenols in solutions behave like weak acids that have a low reactivity toward acylation, the characteristic reaction that occurs during interfacial polymerization[40]. Upon reacting with strong bases such as sodium hydroxide they convert to more reactive phenoxide ions[41]. These phenoxide ions react easily with TPC monomers through the interfacial reaction to form the polyester film according to the proposed reaction scheme shown in **Fig. 3**. The success of this reaction was confirmed by the FTIR spectra of the cellulose support and the composite membrane exhibited in **Fig. 4**. In comparison with the cellulose spectrum,

there is a strong additional peak in the composite membrane spectrum at a wavenumber of 1730 cm^{-1} . This peak corresponds to the carbonyl group ($\text{C}=\text{O}$), the functional group of esters, which forms as a result of the reaction between the acyl group in the TPC and phenoxide ion (**Fig. 3**). There is also another strong peak in the composite membrane spectrum at 1250 cm^{-1} which does not appear in the cellulose spectrum. This peak represents the sp^2 hybridised carbon ($\text{C}=\text{C}$) of the benzene rings. No significant change can be detected in the intensity of the OH peak for the cellulose support and the composite membrane.

Figure 3. The reaction scheme for the interfacial reaction between catechin and TPC to form the polyester film

Figure 4. FTIR spectra of the cellulose support and the polyester TFC composite membrane

3.2. X-ray infrared spectroscopy (XPS)

Further confirmation of the interfacial polymerisation reaction was provided by an analysis of the C1s and O 1s XPS peaks of both the cellulose support and the composite membrane. **Fig. 5A** and **B** depicts the deconvolution of the C 1s core level XPS peak the cellulose support and the composite membrane, respectively. For both samples, the peaks appear at binding energies of 284.8, 286.3 and 288 eV representing the C-C, C-O and O-C-O functional groups, respectively. The extra peak observed in the composite membrane (**Fig. 5B**) at a binding energy of 289 eV corresponds to the ester functional group (O=C-O) which results from the interfacial reaction between catechin and TPC (**Fig. 3**). The deconvolution of O 1s XPS peaks for cellulose and the composite membrane is presented in **Fig. 6A** and **B**. The common peak observed at a binding energy of 531.8 eV in both samples represents the C-O functional group. The new extra peak, which appears in the composite membrane at a binding energy of 532.9 eV (**Fig. 6B**) confirms the existence of the ester functional group (O=C-O) and the successful formation of the polyester film on the top of the cellulose support.

Figure 5. A high-resolution C 1s core -level XPS spectrum of A) the cellulose support and B) the polyester/cellulose composite membrane

Figure 6. A high-resolution O 1s core -level XPS spectrum of A) the cellulose support and B) the polyester/cellulose composite membrane

3.3. Scanning Electron and Atomic Force Microscopy

Fig. 7A shows a surface image of the cellulose support where many pores (average size = 36 ± 8 nm) can be observed. **Fig 7B** and C shows surface and cross-sectional images of the polyester composite membrane. A continuous uneven surface of the polyester layer can be clearly seen on the top of a porous cellulose sublayer. This rough morphology is known as the “ridge and valley” structure which is a characteristic feature of membranes prepared by interfacial polymerization [42–47]. The ‘protuberances’ can be attributed to the rapid diffusion of catechin molecules into the organic phase, which is then hindered by the equally rapid formation of the interfacial film[46–48] .

Figure 7. SEM images of A) cellulose support (surface), B) the composite membrane (surface) and C) the composite membrane (cross-sectional)

Atomic force microscopy analysis was used to measure the surface roughness of the cellulose support and the composite membrane (Figure S1, Supplementary Information). The root-mean roughness (RMS) was 3.5 nm for the cellulose support and 15.2 nm for the composite membrane. Although the ridge and valley structure is clearly seen in the SEM images (**Fig. 7 B and C**) the RMS value for this composite membrane is lower than values reported by others for membranes formed with *m*-phenylene diamine (MPD) (40 – 190 nm) [51,52]. It is comparable to the roughness for membranes made with semi-aromatic amines such as piperazine (< 20nm) [49]. These differences reflect the relative diffusion rates of the respective amine monomers.

3.4. Stability of cellulose support in DMF

The initial DMF permeance through the fresh membranes was 18 ± 3 and $1.7 \pm 0.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for the cellulose support and the composite membrane, respectively. The significantly lower DMF permeance through the composite membrane is expected and attributed to the dense polyester film formed on the porous cellulose support. The characteristics of the cellulose support and the composite membrane are presented in **Table.1**.

Table 1. Characteristics of the cellulose support and the catechin/ cellulose composite membrane.

	Cellulose support	Composite membrane
Top layer thickness (nm)	9443 $\pm$ 442	340 $\pm$ 17
Pure DMF permeance (L m ⁻² h ⁻¹ bar ⁻¹)	18 $\pm$ 3	1.7 $\pm$ 0.1
Roughness (RMS) (nm)	3.5	15.2

The stability of both the cellulose support and the composite membrane was then studied by soaking the membranes in DMF at ambient temperature over a period of 30 days. The permeance of both membranes was unchanged after this treatment, with values of 19.1 $\pm$ 0.5 and 1.7 $\pm$ 0.4 L m⁻² h⁻¹ bar⁻¹ for the cellulose support and the composite membrane, respectively. This confirms the stability of both the cellulose and the composite membrane in DMF. Visual inspection of the samples revealed no variation in either the color or the texture of the membranes.

3.5. Membrane performance

The rejection of the cellulose support was evaluated with Reactive Black dye solution and found to be 15 %. This low rejection value is expected due to the porous nature of the cellulose support. The composite membrane showed an average DMF permeance of 1.2 $\pm$ 0.2 L m⁻² h⁻¹ bar⁻¹ and a molecular weight cut-off around 500 g mol⁻¹ (**Fig. 8**). The digital photographs taken for the cellulose support (Figure S2, Supplementary Information) before

and the after the filtration experiment showed colouring of the membrane with the dye colour. This implies that the rejection observed was mainly due to adsorption effects. On the other hand, those photographs of the composite membrane (Figure S1, Supplementary Information) remained unchanged that confirms that the rejection observed was due to solute repelling rather than adsorption effects.

The performance of the catechin/cellulose composite membrane developed in the present work and those developed in the literature is reported in **Table 2**. Fontananova et al. [53] reported $0.7 \text{ l L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ DMF permeance with 46 % rejection of Solvent Blue 35 (350 g mol^{-1}) through crosslinked polyimide integrally skinned asymmetric membranes. Using polypyrrole/hydrolysed PAN composite membrane, Li et al.[54] reported a DMF permeance of $0.05 \text{ l L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ combined with 91 % rejection of Rose Bengal (1017 g mol^{-1}). Jimenez et al.[20] reported a DMF permeance of $1.5 \text{ l L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ through a polyamide/polyimide (P84) TFC and a molecular weight cut-off of 236 g mol^{-1} . Taking into account the environmental friendly route used, the polyester/cellulose TFC membranes fabricated here are considered as a new class of OSN membranes that can compete with those prepared through conventional approaches.

Table 2. DMF permeance and rejections of the our catechin/cellulose composite membrane and those reported in the literature

Membrane type	Membrane material	Marker	DMF permeance ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	Rejection (%)	Reference
TFC by interfacial polymerisation	PA/Cellulose	Amido-Black (617 g mol^{-1})	1.4	92	This work
	PA/ cross linked P84 PI	Polystyrene oligomers (236-1200 g mol^{-1})	1.5	91 (236)	[16]
	PA/cross linked PAN	Brilliant blue R250 (826 g mol^{-1})	1.1	95	[55]
	PA/ Cellulose	Methyl Orange (327 g mol^{-1})	2.4	90	[18]
TFC via coating	Polypyrrole/ hydrolyzed PAN	Rose Bengal (1017 g mol^{-1})	0.05	91	[54]
	Pebax 1657/ Crosslinked PAN	Brilliant Blue 250 (826 g mol^{-1})	1	95	[56]
Polymeric ISA	Cross linked P84 PI/ P84 PI	Solvent Blue 35 (350 g mol^{-1})	0.7	46	[53]
	Cross linked Matrimid PI	Polystyrene oligomers (236-1200 g mol^{-1})	1	90 (500)	[57]
	Cross linked polyaniline	Polystyrene oligomers (236-1200 g mol^{-1})	0.6	95 (300)	[58]

Figure 8. DMF permeance and rejection values of different molecular weight dyes through catechin/cellulose TFC membranes

Conclusions

A novel composite polyester/cellulose OSN membrane was successfully synthesised via the interfacial polymerisation reaction between bio-derived catechin and TPC. The cellulose porous support was prepared by non-solvent induced phase separation from a dope solution of cellulose dissolved in an environmentally friendly ionic liquid. The hydrocarbon-based solvent for the interfacial polymerisation was replaced by bio-derived alpha-pinene. The composite membrane showed a good DMF permeance of $1.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with a MWCO of 500 g mol^{-1} measured from the rejection of different molecular weight dyes. The cellulose support and the composite membrane showed stable performance over a period of 30 days. The results obtained from this study show potential for the utilization of these membranes in the food and pharmaceutical industries.

References

- [1] P. Marchetti, M.F. Jimenez Solomon, G. Szekely, A.G. Livingston, Molecular Separation with Organic Solvent Nanofiltration: A Critical Review, *Chem. Rev.* 114 (2014) 10735–10806.
- [2] P. Vandezande, L.E.M. Gevers, I.F.J. Vankelecom, Solvent resistant nanofiltration: separating on a molecular level, *Chem. Soc. Rev.* 37 (2008) 365–405.
- [3] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Application of membrane separation processes in petrochemical industry: a review, *Desalination*. 235 (2009) 199–244.
- [4] C. de Moraes Coutinho, M.C. Chiu, R.C. Basso, A.P.B. Ribeiro, L.A.G. Gonçalves, L.A. Viotto, State of art of the application of membrane technology to vegetable oils: A review, *Food Res. Int.* 42 (2009) 536–550.
- [5] J.A. Marsella, Dimethylformamide, in: *Kirk-Othmer Encyclopedia of Chemical Technology*, American Cancer Society, 2013: pp. 1–9.
- [6] K. Vanherck, P. Vandezande, S.O. Aldea, I.F.J. Vankelecom, Cross-linked polyimide membranes for solvent resistant nanofiltration in aprotic solvents, *J. Membr. Sci.* 320 (2008) 468–476.
- [7] I. Soroko, Y. Bhole, A.G. Livingston, Environmentally friendly route for the preparation of solvent resistant polyimide nanofiltration membranes, *Green Chem.* 13 (2011) 162–168.
- [8] Y.H. See Toh, F.W. Lim, A.G. Livingston, Polymeric membranes for nanofiltration in polar aprotic solvents, *J. Membr. Sci.* 301 (2007) 3–10.
- [9] K. Vanherck, A. Cano-Odena, G. Koeckelberghs, T. Dedroog, I. Vankelecom, A simplified diamine crosslinking method for PI nanofiltration membranes, *J. Membr. Sci.* 353 (2010) 135–143.
- [10] Y.H. See-Toh, M. Silva, A. Livingston, Controlling molecular weight cut-off curves for highly solvent stable organic solvent nanofiltration (OSN) membranes, *J. Membr. Sci.* 324 (2008) 220–232.
- [11] K. Hendrix, K. Vanherck, I.F.J. Vankelecom, Optimization of solvent resistant nanofiltration membranes prepared by the in-situ diamine crosslinking method, *J. Membr. Sci.* 421–422 (2012) 15–24.
- [12] J. da Silva Bural, L. Peeva, A. Livingston, Negligible aging in poly (ether-ether-ketone) widens application range for solvent processing, *J. Membr. Sci.* 525 (2017) 48–56
- [13] J. H. Kim, M. Cook, S. H. Park, S. J. Moon, J. F. Kim, A. Livingston, J. M. Lee, A compact and scalable fabrication method for robust thin film composite membranes, *Green Chem.* 20 (2018) 1887–1897
- [14] S. Karan, Z. Jiang, A.G. Livingston, Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation, *Science*. 348 (2015) 1347–1351.
- [15] L. Pérez-Manríquez, A.R. Behzad, K.-V. Peinemann, Sub-6 nm Thin Cross-Linked Dopamine Films with High Pressure Stability for Organic Solvent Nanofiltration, *Macromol. Mater. Eng.* 301 (2016) 1437–1442.
- [16] M.F. Jimenez Solomon, Y. Bhole, A.G. Livingston, High flux hydrophobic membranes for organic solvent nanofiltration (OSN)—Interfacial polymerization, surface modification and solvent activation, *J. Membr. Sci.* 434 (2013) 193–203.
- [17] L. Pérez-Manríquez, P. Neelakanda, K.-V. Peinemann, Tannin-based thin-film composite membranes for solvent nanofiltration, *J. Membr. Sci.* 541 (2017) 137–142.
- [18] M.H. Abdellah, L. Pérez-Manríquez, T. Puspasari, C.A. Scholes, S.E. Kentish, K.-V. Peinemann, Effective Interfacially Polymerized Polyester Solvent Resistant

- Nanofiltration Membrane from Bioderived Materials, *Adv. Sustainable Syst.* 2 (2018) 1800043(1–7).
- [19] P.W. Morgan, Interfacial Polymerization, in: *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc. New York, 2002.
- [20] M.F. Jimenez Solomon, Y. Bhole, A.G. Livingston, High flux membranes for organic solvent nanofiltration (OSN)—Interfacial polymerization with solvent activation, *J. Membr. Sci.* 423 (2012) 371–382.
- [21] REACH - ECHA, (2016). <http://echa.europa.eu/regulations/reach> (accessed April 14, 2016).
- [22] G. Szekely, M.F. Jimenez-Solomon, P. Marchetti, J.F. Kim, A.G. Livingston, Sustainability assessment of organic solvent nanofiltration: from fabrication to application, *Green Chem.* 16 (2014) 4440–4473.
- [23] D.G. Barrett, T.S. Sileika, P.B. Messersmith, Molecular diversity in phenolic and polyphenolic precursors of tannin-inspired nanocoatings, *Chem. Commun.* 50 (2014) 7265–7268.
- [24] A.A. Zanwar, S.L. Badole, P.S. Shende, M.V. Hegde, S.L. Bodhankar, Chapter 21 - Antioxidant Role of Catechin in Health and Disease, in: *Polyphenols in Human Health and Disease*, Academic Press, San Diego, 2014: pp. 267–271.
- [25] L. Pérez-Manríquez, P. Neelakanda, K.-V. Peinemann, Morin-based nanofiltration membranes for organic solvent separation processes, *J. Membr. Sci.* 554 (2018) 1–5.
- [26] S. Konagaya, M. Tokai, Synthesis of ternary copolyamides from aromatic diamine (m-phenylenediamine, diaminodiphenylsulfone), aromatic diamine with carboxyl or sulfonic group (3,5-diaminobenzoic acid, 2,4-diaminobenzenesulfonic acid), and iso- or terephthaloyl chloride, *J. Appl. Polym. Sci.* 76 (2000) 913–920.
- [27] K.C. Gupta, Synthesis and evaluation of aromatic polyamide membranes for desalination in reverse-osmosis technique, *J. Appl. Polym. Sci.* 66 (1997) 643–653.
- [28] F. Chemat, M.A. Vian, eds., *Alternative Solvents for Natural Products Extraction*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2014.
- [29] C. Dejoye Tanzi, M. Abert Vian, C. Ginies, M. Elmaataoui, F. Chemat, Terpenes as Green Solvents for Extraction of Oil from Microalgae, *Molecules.* 17 (2012) 8196–8205.
- [30] C. Dejoye Tanzi, M. Abert Vian, F. Chemat, New procedure for extraction of algal lipids from wet biomass: a green clean and scalable process, *Bioresour. Technol.* 134 (2013) 271–275.
- [31] Z. Li, K.H. Smith, G.W. Stevens, The use of environmentally sustainable bio-derived solvents in solvent extraction applications—A review, *Chin. J. Chem. Eng.* 24 (2016) 215–220.
- [32] S.J. Eichhorn, Cellulose nanowhiskers: promising materials for advanced applications, *Soft Matter.* 7 (2011) 303–315.
- [33] T. Ward, Biopolymers, in: *Van Nostrand's Encyclopedia of Chemistry*, John Wiley & Sons, Inc., New York, 2005.
- [34] J. Zhou, J. Chen, M. He, J. Yao, Cellulose acetate ultrafiltration membranes reinforced by cellulose nanocrystals: Preparation and characterization, *J. Appl. Polym. Sci.* 133 (2016) 43946(1–7).
- [35] T. Puspasari, H. Yu, K.-V. Peinemann, Charge- and Size-Selective Molecular Separation using Ultrathin Cellulose Membranes, *ChemSusChem.* 9 (2016) 2908–2911.
- [36] S. Livazovic, Z. Li, A.R. Behzad, K.-V. Peinemann, S.P. Nunes, Cellulose multilayer membranes manufacture with ionic liquid, *J. Membr. Sci.* 490 (2015) 282–293.
- [37] M. Freemantle, *An Introduction to Ionic Liquids*, Royal Society of Chemistry, Cambridge, 2010.

- [38] K. Srinivas, J.W. King, L.R. Howard, J.K. Monrad, Solubility of Gallic Acid, Catechin, and Protocatechuic Acid in Subcritical Water from (298.75 to 415.85) K, *J. Chem. Eng. Data.* 55 (2010) 3101–3108.
- [39] J. Cuevas-Valenzuela, Á. González-Rojas, J. Wisniak, A. Apelblat, J.R. Pérez-Correa, Solubility of (+)-catechin in water and water-ethanol mixtures within the temperature range 277.6–331.2K: Fundamental data to design polyphenol extraction processes, *Fluid Phase Equilib.* 382 (2014) 279–285.
- [40] F.A. Carey, *Organic Chemistry*, McGraw-Hill, New York, 2000.
- [41] T.W.G. Solomons, C. Fryhle, *Organic Chemistry*, John Wiley & Sons, New York, 2009.
- [42] J.-E. Gu, S. Lee, C.M. Stafford, J.S. Lee, W. Choi, B.-Y. Kim, K.-Y. Baek, E.P. Chan, J.Y. Chung, J. Bang, J.-H. Lee, Molecular Layer-by-Layer Assembled Thin-Film Composite Membranes for Water Desalination, *Adv. Mater.* 25 (2013) 4778–4782.
- [43] S.G. Kim, S.Y. Park, J.H. Chun, B.-H. Chun, S.H. Kim, Novel thin-film composite membrane for seawater desalination with sulfonated poly(arylene ether sulfone) containing amino groups, *Desalin. Water Treat.* 43 (2012) 230–237.
- [44] J. Lee, A. Hill, S. Kentish, Formation of a thick aromatic polyamide membrane by interfacial polymerisation, *Sep. Purif. Technol.* 104 (2013) 276–283.
- [45] A.K. Ghosh, B.-H. Jeong, X. Huang, E.M.V. Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, *J. Membr. Sci.* 311 (2008) 34–45.
- [46] G. Hurwitz, G.R. Guillen, E.M.V. Hoek, Probing polyamide membrane surface charge, zeta potential, wettability, and hydrophilicity with contact angle measurements, *J. Membr. Sci.* 349 (2010) 349–357.
- [47] L. Mh, W. Dh, Y. Sc, G. Cj, Influence of the polyacyl chloride structure on the reverse osmosis performance, surface properties and chlorine stability of the thin-film composite polyamide membranes, *J. Membr. Sci.* 326 (2009) 205–214.
- [48] P.W. Morgan, S.L. Kwolek, Interfacial polycondensation. II. Fundamentals of polymer formation at liquid interfaces, *J. Polym. Sci.* 40 (1959) 299–327.
- [49] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Probing the nano- and micro-scales of reverse osmosis membranes—A comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements, *J. Membr. Sci.* 287 (2007) 146–156.
- [50] S.-Y. Kwak, S.G. Jung, Y.S. Yoon, D.W. Ihm, Details of surface features in aromatic polyamide reverse osmosis membranes characterized by scanning electron and atomic force microscopy, *J. Polym. Sci. Part B Polym. Phys.* 37 (1999) 1429–1440.
- [51] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes: I. FTIR and XPS characterization of polyamide and coating layer chemistry, *Desalination.* 242 (2009) 149–167.
- [52] A. Widjaya, T. Hoang, G.W. Stevens, S.E. Kentish, A comparison of commercial reverse osmosis membrane characteristics and performance under alginate fouling conditions, *Sep. Purif. Technol.* 89 (2012) 270–281.
- [53] E. Fontananova, G.D. Profio, F. Artusa, E. Drioli, Polymeric homogeneous composite membranes for separations in organic solvents, *J. Appl. Polym. Sci.* 129 (2012) 1653–1659.
- [54] X. Li, P. Vandezande, I.F.J. Vankelecom, Polypyrrole modified solvent resistant nanofiltration membranes, *J. Membr. Sci.* 320 (2008) 143–150.

- [55] L. Pérez-Manríquez, J. Aburabi'e, P. Neelakanda, K.-V. Peinemann, Cross-linked PAN-based thin-film composite membranes for non-aqueous nanofiltration, *React. Funct. Polym.* 86 (2015) 243–247.
- [56] J. Aburabie, K.-V. Peinemann, Crosslinked poly(ether block amide) composite membranes for organic solvent nanofiltration applications, *J. Membr. Sci.* 523 (2017) 264–272.
- [57] I. Soroko, M.P. Lopes, A. Livingston, The effect of membrane formation parameters on performance of polyimide membranes for organic solvent nanofiltration (OSN): Part A. Effect of polymer/solvent/non-solvent system choice, *J. Membr. Sci.* 381 (2011) 152–162.
- [58] X.X. Loh, M. Sairam, A. Bismarck, J.H.G. Steinke, A.G. Livingston, K. Li, Crosslinked integrally skinned asymmetric polyaniline membranes for use in organic solvents, *J. Membr. Sci.* 326 (2009) 635–642.

Accepted manuscript

Highlights:

A catechin/cellulose composite nanofiltration membrane has been developed.

The membrane made from bio-derived materials is stable in dimethylformamide.

The cross-linked catechin selective layer exhibits high DMF fluxes.

The membrane rejects molecules with a molecular weight higher 500 g/mol.

Accepted manuscript