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Cellulose Multilayer Membranes Manufacture with Ionic Liquid

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Abstract

Membrane processes are considered energy-efficient for water desalination and treatment. However most membranes are based on polymers prepared from fossil petrochemical sources. The development of multilayer membranes for nanofiltration and ultrafiltration, with thin selective layers of naturally available cellulose has been hampered by the availability of non-aggressive solvents. We propose the manufacture of cellulose membranes based on two approaches: (i) silylation, coating from solutions in tetrahydrofuran, followed by solvent evaporation and cellulose regeneration by acid treatment; (ii) casting from solution in 1-ethyl-3-methylimidazolium acetate ([C2mim]OAc), an ionic liquid, followed by phase inversion in water. By these methods porous supports could be easily coated with semi-crystalline cellulose. The membranes were hydrophilic with contact angles as low as 22.0° , molecular weight cut-off as low as 3000 g mol^{-1} with corresponding water permeance of $13.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. Self-standing cellulose membranes were also manufactured without porous substrate, using only ionic liquid as green solvent. This membrane was insoluble in water, tetrahydrofuran, hexane, N,N-dimethylformamide, 1-methyl-2-pyrrolidinone and N,N-dimethylacetamide.

Keywords: cellulose, membranes, 1-ethyl-3-methylimidazolium acetate, interfacial polymerization, ultrafiltration

1. Introduction

Water scarcity and access to clean water are major problems worldwide, directly affecting around 1.2 billion people, one-fifth of the world's population [1]. Even countries like Brazil known in the past for water abundance recently experienced alarming periods of drought. While seawater desalination has been an indispensable strategy in the Middle East as a source of drinking water, water treatment is essential everywhere in the world to assure sustainable life quality with high environmental standards. This includes treating municipal and agriculture wastes and recycling industrial effluents. Increasing need for safe drinking water, purification of effluents with small pollutant molecules and recovery of valuable products has placed membrane separation processes such as nanofiltration (NF) among the fastest growing technologies. The global membrane-based technology market for the treatment of industrial water and wastewater has been estimated to reach \$5.5 billion in 2015, driven by different applications and motivations in different continents [2]. With economic growth, many countries are facing an enormous challenge of water pollution. For example, 55% of the groundwater in China has been reported to have poor water quality, while 78% of urban rivers are polluted to an extent that they might not serve as drinking water source anymore [3,4]. In European countries, which have been intensively fighting to reach high level of water quality, wastewater treatment has satisfactorily reduced the content of regular pollutants, but there is an increasing concern with emerging new pollutants such as endocrine disrupters. NF is under consideration for their elimination from waste. Besides environmental aspects, water

reuse might become mandatory to bring water autonomy to desert areas in the Middle East far from the coast and therefore with restrict access to seawater. Water availability has also been a question of security and a reason for potential conflict in many countries.

For seawater desalination reverse osmosis is a well-established technology. Compared to reverse osmosis, NF membranes have higher flux with lower operational pressure, and subsequently, lower energy and lower costs are attained. NF becomes attractive when high salt rejection is not essential, for instance in applications, which do not require drinking water quality. In water scarcity areas, there is a potential for using NF to produce partially desalinated water for growing salt-tolerant crops. Besides NF, ultrafiltration (UF) is a well-established pretreatment process in water treatment and food industries. Nowadays many dairy products and beverages processing includes an ultrafiltration step [5]. The potential of membrane technology to substitute more traditional separation processes in other industrial sectors is far from being completely explored. For instance recovery of metals from mining effluents or valuable chemical products like catalysts in chemical processes using membranes could be a profitable investment if better membranes would be tailored for these applications.

Membrane technology is recognized as energy efficient, easy to scale-up and environmentally friendly, with large perspective of expanding its application with the growing need of implementing more sustainable industrial processes. Membranes have been optimized with selectivity/permeation characteristics useful for quite diverse separation tasks. However the membrane manufacture itself could be much

more sustainable and greener than it is now, as pointed out in excellent reviews recently published by Figoli et al. [6] and Szekely et al. [7].

For more sustainable membrane manufacture two aspects have to be taken into consideration: (i) the membrane material and (ii) the manufacture process. Most membrane materials are produced from petrochemical sources. The most applied membrane manufacture process involves non-solvent induced phase separation (NIPS), solution casting followed by immersion in water. Large amount of solvents like N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) or 1-methyl-2-pyrrolidone (NMP) are frequently used for phase inversion. Furthermore membranes are frequently prepared as multilayers, with the asymmetric porous support being only the substrate, which is coated by additional solutions, constituted also by solvents, which are environmentally harmful. There is an increasing discussion on the possibility of banning their application in large scale and the need for finding alternatives at least for part of the manufacture processes. One of the main motivations of this work is to substitute at least part of the solvents used in the multilayer membrane manufacture by greener alternatives. We propose new the production of membranes based on natural cellulosic materials, in which ionic liquid is employed for coatings.

(Scheme 1)

Another motivation for this paper is the following. For the manufacture of multilayer membranes, by dip coating, a solvent is needed, which dissolves the coating polymer without damaging the substrate. The coating layer is usually responsible for the selectivity and the porous substrate, which is frequently made of polysulfone, poly(vinylidene fluoride) or polyacrylonitrile, improves the mechanical stability without compromising flux. Multilayer membranes have been successfully applied for gas separation, pervaporation, nanofiltration and reverse osmosis. However the application of cellulose coating for multilayer membranes has been hindered by the lack of solvent for cellulose, which would not damage the morphology of the porous polymeric support. Cellulose (Scheme 1) [8, 9] is one of the most abundant natural materials and has been used as starting material for membrane manufacture for long time. However cellulose can be hardly dissolved in common solvents due to strong hydrogen bonds and crystallinity. Chemically modified cellulose in the form of cellulose acetate has been successfully used in large scale for instance as reverse osmosis hollow fibers for seawater desalination or more recently as commercialized flat-sheet membrane for forward osmosis. However the use of cellulose itself has been restricted by the availability of industrial process for dissolution, which is currently done in aggressive medium, by chemical modification and regeneration. Cellulose fibers (e. g. viscose and rayon) and films (cellophane) are being produced for more than a century by the viscose technology, which uses a metastable solution of cellulose xanthogenate, with hazardous byproducts like heavy metals and H₂S [10]. The other well-known method for production of regenerated cellulose is the cuprammonium process also with negative environmental impacts [11]. In the 60's

cyclic amine oxides have been proposed to dissolve cellulose [12]. N-methylmorpholine-N-oxide (NMMO) has then been used for production of films and membranes [13]. The membrane manufactured with cellulose/NMMO is considered a more environmentally friendly technology [7, 14, 15].

Ionic liquids have a growing interest being considered as green solvents [16] and can dissolve lignocellulosic biomass partially or in total, depending on the subsequent addition of water and solvent. It is important to mention that the production of ionic liquids is still costly. Due to the very low vapor pressure they are expected to bring less health risks to process operators, when compared to volatile solvents, but the toxicity of some ionic liquids in water might be a cause of concern (17). Therefore for environmental and cost reasons the recovery of ionic liquids is important. Most of the recovery is done through the evaporation and precipitation processes, but a significant recovery of ionic liquid with a purity of 80%, using nanofiltration has been reported by Abels et al. (18).

Independent of the level of toxicity, ionic liquids are among the few solvents for cellulose. The dissolution of the cellulosic materials is driven by the anion of the ionic liquid, as reviewed by different groups [9, 19-23]. Anions such as halides, carboxylates and phosphates have the ability to break the hydrogen bonds within the cellulose structure. We chose 1-ethyl-3-methyl imidazolium acetate [C2mim]OAc (Scheme 1), which is liquid at room temperature and highly miscible with water [19]; it has high dissolving power even in the presence of up to 10 wt% of water and relatively low viscosity compared to other ionic liquids, and shows no corrosion against stainless steel [19]. In addition, [C2mim]OAc has low toxicity, melting point

lower than -20°C , viscosity 10 mPa s at 80°C and high hydrogen bond acceptor abilities [20, 21].

Hydrogen bond acceptor sites in the anion structure and lack of hydrogen bond donors in the ionic liquid cation favor the dissolution of cellulose. The acetate anion in the [C2mim]OAc can form hydrogen bonds with hydroxyl protons of cellulose. Heinze et al. [23] and Pinkert et al. [9] proposed that [C2mim]OAc forms even covalent bond between the glucose unit of cellulose and the imidazolium ring (Scheme 1). This is specific for acetates and not observed for the analogue chloride, although it also dissolves cellulose. Even if the covalent in Scheme 1 is formed, the ionic liquid is expected to be washed out in water, making [C2mim]OAc a good solvent for cellulose coatings.

Research regarding ionic liquids and cellulose has been mainly towards the fractionation of lignocellulosic biomass, fractionation into mono- and disaccharides as well as the usage of ionic liquids as a pretreatment for the enzymatic hydrolysis. The most exploited usage of ionic liquids in respect to cellulose is as media for homogeneous reactions in order to obtain polysaccharide derivatives from cellulosic materials [22].

As far as membrane manufacture is concerned a pioneer work has been published by Xing et al. [24, 25], based on a cellulose acetate, dissolved in [C2mim]SCN. Li et al. [14] reported so far the only work using non-modified cellulose dissolved in ionic liquid for membrane purpose. They used the ionic liquid 1-allyl-3-methylimidazolium chloride. We explore in this work [C2mim]OAc for the preparation of cellulose membranes by phase inversion.

In this work we report the preparation of multilayer membranes with selective cellulose coatings on polymeric asymmetric porous supports using solutions of (i) cellulose in [C2mim]OAc and (ii) silylated cellulose in tetrahydrofuran.

This is the first time that multilayer membranes, with a cellulose selective layer, were prepared by dip-coating solutions in ionic liquid on asymmetrically porous supports.

Preliminary results using the silylated cellulose method have been previously mentioned only in a patent of our group [26]. Silylation protects the hydroxyl groups, inhibiting H-bond formation, making the polymer hydrophobic and soluble in apolar solvents. After the coating cellulose can be easily regenerated to its original form by acid hydrolysis.

2. Experimental

2.1 Material

Avicel® PH-101 microcrystalline cellulose (MW=160,000-560,000 g mol⁻¹) (Scheme 1) and hexamethyldisilazane (≥97.0%) were purchased from Fluka Analytical, latter produced by Wacker Chemie AG, Burghausen, Germany, both used as received. Hexane (95%, anhydrous) was supplied by Sigma Aldrich®. Hydrochloride acid (HCl, 36.5-38.0%) and sodium chloride (99%) were purchased from Alfa Aesar®. Poly (ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) of different molecular weights (0.2, 1.5, 3, 6, 10, 35, 100, 300 and 600 Kg mol⁻¹), and the ionic liquid 1-ethyl-3-methylimidazolium acetate (≥90%) (Scheme 1) were

purchased from Sigma Aldrich®, produced by BASF. Milli-Q® water (Millipore) with specific resistivity 18.2 MΩ cm at 26.1°C was used for membrane preparation and testing. Solvents N,N-dimethylformamide (DMF, anhydrous, 99.8%), N,N-dimethylacetamide (DMAc, CHROMASOLV® Plus, for HPLC, ≥99.9%) and 1-methyl-2-pyrrolidinone (NMP, ACS reagent, ≥99.0%) were purchased from Sigma Aldrich® and used as received. Tetrahydrofuran (THF, ≥99.5%, for synthesis) was purchased from ROTH® and used as received. The asymmetric porous supports based on polyetherimide (PEI), polyacrylonitrile (PAN), polysulfone (PSU) and polyvinylidene fluoride (PVDF) were prepared at KAUST by phase inversion using continuously operating machine. The nonwoven polyester fabric used for the preparation of cellulose/ionic liquid membranes was purchased from Hirose Paper, Japan.

2.2 Preparation of trimethylsilyl cellulose

Cellulose (3 g) was swollen in 150 ml water and 30 ml DMAc, followed by filtration, further dissolution in 300 ml DMAc and heating at 165°C for 30 min under reflux. After cooling the solution to 100°C, 15 g of LiCl was added and stirred until complete dissolution. After cooling down to room temperature a clear solution was obtained after stirring for 8 h to 12 h stirring. 45 ml of HDMS was then slowly added to the solution at 80°C in 3 h. The hot solution was precipitated in methanol, filtered, thoroughly washed and dried in vacuum oven at 60°C over night.

2.3 Preparation of cellulose multilayer membrane

Two methods were applied for the manufacture of cellulose multilayer membranes:

Method 1: Regenerated silyl cellulose

Silylated cellulose was dissolved in THF and used as coating solution. As porous substrate PAN, PSU, PEI or PVDF asymmetric porous membranes, previously manufactured by phase inversion in a continuous machine were used. They were dip coated with 0.6 wt% to 1.9 wt% silylated cellulose solutions in THF and dried with briefly hot air. The dried membrane was then immersed in 1 M hydrochloric acid aqueous solution for 15 to 30 minutes to regenerate the cellulose. The 1 M hydrochloride acid was prepared from 36.5-38.0% hydrochloride acid purchased from Alfa Aesar®.

Method 2: Cellulose/ionic liquid

The unmodified cellulose was dissolved in the ionic liquid [C2mim]OAc, at 80°C during 24 h. The cellulose concentration was 2, 5 and 10 wt%. The solutions were then cast after cooling down to 23°C, with the doctor blade adjusted to 150 µm gap, on asymmetric porous supports (PAN, PEI, PSU or PVDF) and polyester nonwoven, respectively, or directly on glass plates. After casting, the membranes were immersed for 2 h to 4 h in deionized water to induce phase separation and dried in air.

Preparation of multilayer membranes with polyamide selective layer

Thin film composite membranes with a selective polyamide layer were prepared using interfacial polymerization (IP) [27] with m-phenylenediamine and trimesoyl chloride as reactants in aqueous and organic phase, respectively. The polymerization was directly performed on asymmetric porous supports or on cellulose membranes prepared as described above.

2.4 Characterization of cellulose membranes

2.4.1 Chemical characterization

The functional groups of unmodified cellulose, silylated cellulose and regenerated cellulose as well as a non-modified support were analyzed by attenuated total reflectance mode (ATR) using Fourier Transform Infrared Spectroscopy (FTIR) Perkin Elmer Spectrometer. The number of scans for each sample was 16 with the resolution of 4 cm⁻¹, conducted at room temperature using the ATR unit with a nominal incident angle of 45°.

¹H NMR spectrum was recorded on Bruker Avance III 400 MHz spectrometer using CCl₃D as a solvent.

2.4.2 Membrane morphology

For the surface and cross-section membrane characterization FEI Nova Nano 630, FEI Magellan, FEI Quanta 200 or 600 field emission scanning electron microscopes (FESEM) were used. To reduce surface charging, the samples were coated with either iridium or platinum inside K575X or Q150ES (Quorum technologies, UK) sputter coaters.

Low Temperature SEM experiments were carried out using a PP2000T cryo transfer system (Quorum Technologies, UK) attached to a FEI on Nova Nano 630 SEM with field emission source and through-the-lens detector. To examine the top surface or cross section morphology of membranes, the samples (approximately 2 mm x 5 mm) were mounted either flat onto an aluminum stub using aluminum tape or vertically inside slot and secured mechanically between two parallel jaws. The stub was then secured on the cryo specimen holder, rapidly plunged into the liquid nitrogen slush and transferred under vacuum into a PP2000T cryo preparation chamber precooled at -180°C . To obtain fractured surface of membrane cross section, the sample temperature was raised to -150°C and the top part of the vertically mounted membrane was hit with a knife precooled at -150°C . In order to remove residual ice contamination and further reveal the structure of the surface and the fractured plane, samples were sublimed inside the SEM chamber at -90°C . To avoid charging problems, samples were transferred back to the preparation chamber and sputter coated with 5 nm-thick platinum in an argon atmosphere at -150°C . The samples

were then transferred back to SEM cryo stage, held at -130°C , and high quality SEM images were captured. In all cases, the imaging was performed using an accelerating voltage of 2-3 kV and working distance of 5 mm.

Atomic Force Microscopy (AFM) image was obtained using a 5500 Scanning Probe Microscope (5500 SPM, Agilent Technologies, USA) in tapping mode. The cantilever had force constant of 0.5 N/m to 9.5 N/m (NANOSENSORS), resonance frequency 45 kHz to 115 kHz and was Pt/Ir-coated on tip and detector side.

2.4.3 X-Ray Diffraction Analysis

The degree of crystallinity and crystallization form of the non-modified cellulose and deposited coatings was characterized using a Bruker D8 Advance diffractometer with Cu-K α radiation source ($\lambda=1.5406 \text{ \AA}$) at 40 kV and 40 mV. The data was collected using the range of 2θ from 5° to 50° , step size 0.01° and scan speed of 0.4 second per step.

2.4.4 Water permeance

Water permeances of non-modified PAN, PEI, PSU asymmetric porous supports and cellulose multilayer membranes were measured using a dead-end set-up at 5 bar, with effective membrane area of 14.6 cm^2 and using Milli-Q® water as the feed.

2.4.5 Molecular weight cut-off

Gel permeation chromatographs for the determination of molecular weight cut-off (MWCO) were measured using the GPC System-Agilent 1200 Series. The GPC/SEC columns were used together, Agilent PL aquagel OH 60 8 μm and Agilent PL aquagel OH 40 8 μm . Columns were calibrated with polyethylene oxide/glycol EasiVial PEG/PEO (4 ml), the standard for SEC. Three EasiVial PEG/PEO standards cover the molecular range from 106 g mol⁻¹ to 1,258,000 g mol⁻¹.

To measure the MWCO of the membranes, PEG solutions (0.1 wt% single solutions or 0.5 wt% of a mixture of 5 PEG molecular weights) were used as feed in dead-end filtration experiments at 5 bar with an effective membrane area of approximately 14.6 cm². The chosen PEG molecular weights were 200, 1500, 3000, 6000, 10000, 35000, 100000 and 300000 g mol⁻¹. The solute rejection was calculated from the concentrations of the solute in the feed and permeate, analyzed by GPC.

Rejections were calculated by the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (1)$$

where C_p and C_f are solute concentrations in permeate and feed, respectively. The MWCO is defined as the smallest molecular weight with 90 % rejection.

2.4.6 Salt rejection

Salt rejection was measured for selected membranes, with 2000 ppm sodium chloride solution used as feed in a dead-end set-up under pressure of 5 bar with effective membrane area of 14.6 cm². The salt concentration was evaluated by measuring conductivity with a WTW ProfiLine Cond 3310 equipment. The feed initial volume was 300 mL, the permeation was conducted for 30 min before collecting samples for conductivity measurement.

2.4.7 Solvent resistance

Two types of cellulose membranes without porous support, prepared from 5 and 10 wt% cellulose/[C2mim]OAc solutions, were used for evaluating their resistance to common organic solvents. The membranes were immersed in five organic solvents, THF, hexane, DMF, NMP and DMAc for 1 h, 12 h, 24 h and one week. Subsequently, the membranes were immersed in methanol to assure complete removal of high boiling point residual solvents and the membranes were dried before weighting. The resistance was evaluated by measuring the weight difference before (m_1) and after (m_2) the test.

$$w_L = (m_1 - m_2) \times 100 \% \quad (2)$$

2.4.8 Contact angle

Contact angles (θ) were analyzed by an Attension Theta Optical Tensiometer (KSV Instruments) at room temperature. The 0.1 μ l drop of DI water was dropped out onto the membrane using the sessile drop method. Each sample was measured 3 times.

3. Results and discussion

Two methodologies were explored for the manufacture of multilayer or integrated cellulose membranes. The advantages and characteristics of the membranes obtained were evaluated by chemical and morphological analysis, resistance to organic solvents and performance in the filtration of aqueous solutions containing a mixture of solutes of different sizes.

3.1 Method 1: Regenerated silyl cellulose

Multilayer membranes were obtained by dip coating of asymmetric porous polymeric supports based on PSU, PEI, PAN and PVDF. The MWCO in the range of ultrafiltration are usually prepared by phase inversion from solutions in polar solvents like DMAc, DMF or NMP. Deposition of a second polymer layer is an important method for preparing nanofiltration, forward osmosis or gas separation membranes. Cellulose is soluble in DMAc/LiCl, however this would also solubilize or at least

damage most of the mentioned polymeric supports. When silylated, cellulose becomes apolar and soluble in hexane or THF, which do not affect commonly used polymeric supports. After coating, the cellulose can be regenerated to its hydrophilic and less soluble original form by acid treatment.

The success of different steps of silylation and regeneration were proven by spectroscopic methods of characterization. Non-modified microcrystalline cellulose and silylated cellulose as well as the cellulose regenerated by acid treatment were characterized by ATR-FTIR. The FTIR spectra in Figure 1 indicates the structural changes of the pristine cellulose into trimethylsilylcellulose due to the etherification with OH groups substituted by O-Si(CH₃)₃ groups. The peaks for the substituted groups that reflect the valence vibrations in the trimethylsilyl cellulose can be seen at 760 cm⁻¹, 1260 cm⁻¹ (Si(CH₃)₃) and 850 cm⁻¹ (Si-C). The peaks representing the deformation vibrations can be identified at 970 cm⁻¹ (Si-O) and 1470 cm⁻¹ (SiCH₃). Characteristic absorption band associated to the OH valence vibration at ~ 3500 cm⁻¹ is much lower in the silylated trimethylsilylcellulose, but some unreacted OH group still remained.

(Fig. 1)

Regeneration of OH groups after treatment by HCl is proven by the increase of the broad band at 3400 cm^{-1} , which is related to OH stretching vibration. The peak has higher intensity than for the pristine cellulose, indicating the regeneration of cellulose. A band at 2900 cm^{-1} is due to the CH stretching vibration. In the case of amorphous cellulose this band would be shifted or not present.

The silanization was confirmed by NMR ^1H (Fig. 2). The most obvious shift is the appearance of the peak at 0.21 ppm, which refers to the proton in the methyl group in the trimethylsilyl structure. The peak at 1.25 ppm is relative to the silane with the methyl groups. A group of peaks with lower intensity from 3.18 ppm to 3.48 ppm are typical shifts for the anhydroglucose unit. Chemical shifts detected at 2.08 ppm, 2.94 ppm and 3.08 ppm are most likely from DMAc used in the preparation of silylated cellulose.

The contact angles for non-modified porous supports and those coated by regenerated silyl cellulose are shown in Table 1. For the latter the value is 32.6° , clearly lower than that of unmodified porous supports. However the contact angle is still higher than for coatings obtained by dissolving cellulose in ionic liquid. This could indicate that the cellulose is not completely regenerated, still containing some rest of silyl hydrophobic groups on the surface, which can however not be detected by FTIR.

The surface morphology indicating order and possible crystallization of the regenerated cellulose layer coating is visible in Fig. 3a. To confirm it, X-ray experiments were conducted. The diffractograms of cellulose before the silylation and after the regeneration are shown in Fig. 3b and 3c, respectively.

(Fig. 2)

Cellulose can exist in 6 different cellulose polymorphs, which can be interconverted [28]. Cellulose I is commonly found as native cellulose. Cellulose IIII or IIII can be obtained by treatment of cellulose I or II with liquid ammonia while cellulose IVI and IVII are observed by heating cellulose IIII or IIII, respectively.

Crystallinity was confirmed in all cases. The angles corresponding to the peak maximum in different diffractograms are shown in Table 2. For each case the probable polymorph was identified, based on previous cellulose characterization reports (Isogai et al. [29]). The cellulose coating prepared by silylation and treatment with acid is probably polymorph type II, following the same pattern reported before for cellulose regenerated by other procedures [12, 19, 29].

Table 1. Contact angle of investigated membranes

Membrane	Contact Angle (°)
PSU	86.0 ± 1.6
PEI	73.0 ± 7.9
PAN	51.2 ± 0.5
1 wt% Cellulose (regenerated)/ PAN	32.6 ± 0.4
1 wt% Cellulose (regenerated)/ PAN/IP	62.7 ± 0.8
2 wt% Cellulose/ [C2mim]OAc/ Nonwoven	26.1 ± 1.8
2 wt% Cellulose/ [C2mim]OAc/ PEI	25.7 ± 0.9
2 wt% Cellulose/ [C2mim]OAc/ PSU	22.0 ± 1.8

(Fig. 3)

Table 2. Cellulose diffractogram and polymorphs

Material and/or Membrane	2 θ			Cellulose Polymorph
	1st Peak	2st Peak	3st Peak	
Non-modified cellulose	14 °	16 °	22 °	I
Regenerated cellulose	12 °	20 °	22 °	II
Cellulose/[C2mim]OAc	12 °	20 °	22 °	II

The performance of regenerated cellulose membranes, prepared from silylated cellulose on PAN asymmetric porous supports, can be seen in Table 3 and Fig. 4, including rejection of PEG with different molecular weights and water permeance. The thickness of coating layer was increased with higher cellulose concentration in THF, consequently reduced the water permeability and MWCO, but increased salt and PEG rejection. Higher cellulose concentrations led to thicker coatings of lower water permeances. The lowest MWCO was 5,000 g/mol, reached with 1.6 wt% cellulose in THF, corresponding to a water permeance of 8.1 Lm⁻² h⁻¹ bar⁻¹.

In part of the membranes, a top polyamide selective layer was formed on the cellulose coating by interfacial polymerization. For comparison, the interfacial polymerization was also performed directly on the porous PAN and PVDF supports without cellulose. The morphology of the polyamide layer directly on the porous supports is respectively shown in Fig. 5 and 6 and on cellulose is shown in Fig. 7. A clear difference was observed, depending on the substrate.

Detailed investigation of thin polyamide film membranes by scanning or transmission electron microscopy have been reported by different groups before [30-35]. Ferlita et

al. [36] reported a freeze fracture method for FESEM investigation. The investigated membranes were imaged mostly dry. Freger et al. [30] used AFM to characterize the surface of wet membranes. As far as we are aware of, this is the first time that cryo scanning electron microscopy has been used for the characterization of thin film polyamide membranes. The investigation of wet membranes by cryo SEM allows a better observation of the detailed structure since the method does not require staining, dehydration or embedding in resin as used in careful TEM imaging work reported before by Freger et al. [30] and Pacheco et al. [35]. Details of the nodules and larger pockets on PAN and PVDF imaged by cryo microscopy are depicted in Fig. 5 and 6. Small nodules and semicircular ones have been detected before for analogous systems using an optimized procedure for TEM [35], but they are less evident in regular SEM. Particularly the smaller nodules are frequently hidden by the larger pocket structures.

(Fig. 4)

Table 3 Performance of membranes prepared from silylated cellulose/THF solution on PAN porous support, followed by regeneration in acid.

Coating Solution (wt% Cellulose)	Coating Thickness (μm)	Water Permeance ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	MWCO (Kg mol^{-1})	NaCl Rejection ^b (%)
0	0	102.5	90	0
0.6	0.3	28.1 ± 0.6	47	1.8
1.0	1.0	16.8 ± 2.7	10	2.2
1.6	1.8	8.1 ± 0.3	5	3.1
1.9	2.0	5.7 ± 1.4	5	9.1

^aEstimated by FESEM; ^b2000 ppm NaCl as feed solution

(Fig. 5)

The images in Fig. 5 and 6 also reveal the effect of the support on the morphology of the interfacial polymerized layer. PVDF is more hydrophobic and has larger and more scattered pores, while PAN is hydrophilic and has higher density of smaller pores. The polyamide layer is more homogenous with smaller nodules when prepared on PAN. The influence of the porous support on the polyamide layer has been pointed out before by Li et al. [14], Gosh et al. [32] and Pacheco et al. [35]. The dense (non porous) areas of the membranes locally obstruct the growth of the interfacial polymerized layer, while the contact between organic and aqueous phase is favored through the pores. Li et al. [36] explained that large pores during the interfacial polymerization lead to a rapid transport of amine from the aqueous phase, filling the membrane pores, and the organic phase to react with trimesoyl chloride. Convection due to Marangoni effect leads then to turbulent mixture of monomers and formation of larger globules.

(Fig. 6)

Interfacial polymerization was also performed on a membrane coated with cellulose. Well-distributed small pockets were seen in Fig. 7 a, b. A significant difference was observed between images obtained for the dry membrane with regular SEM and the wet membrane by cryo microscopy. The wet multilayer membrane has a more swollen polyamide layer (Fig. 7 c, d) indicating that water is kept below it. The polyamide thin film layer seems to be less adhered to the substrate in the case of regenerated cellulose support. In addition, the polyamide thin film is smoother than those on PAN and PVDF porous supports (Fig. 5, 6 and 7). The reason for the unexpected morphology observed in Fig. 7c can be understood as following. The cellulose layer on the porous support probably absorbs and better holds the amine solution also during the interfacial polymerization process. The diffusion of amine from the cellulose layer to the organic phase is gentler, resulting in a smoother polyamide thin film layer. When the interfacial polymerization is conducted on a hydrophobic support with large pores, like the PVDF membranes shown in Fig. 6, there is a turbulent amine transport into the organic phase to react with trimesoyl chloride and immediately form a rough polyamide layer. The probable mechanism for the thin polyamide layer formation on substrates of different porosity is illustrated in Fig. 8, based in a model proposed by Li et al. [37]. Additionally the swelling of the highly hydrophilic cellulose layer itself with water might also affect the cryo image in Fig. 7.

(Fig. 7)

(Fig. 8)

Table 4. Water permeance of membranes constituted by layers of interfacial polymerized polyamide on regenerated cellulose and on PAN porous support

Coating solution (wt% Cellulose) ^a	Water permeance (L m ⁻² h ⁻¹ bar ⁻¹)	MWCO (g mol ⁻¹)	Na Cl Rejection ^b (%)
0	0.6 ± 0.7	< 200	58 ± 22
0.6	3.2 ± 0.8	< 200	5.4 ± 0.4
1.0	1.7 ± 0.1	< 200	19 ± 1
1.6	1.4 ± 0.2	< 200	36 ± 3
1.9	1.1 ± 0.1	< 200	82 ± 6

^a Solution in THF; ^b 2000 ppm NaCl as feed solution, 5 bar

Table 4 summarizes the permeances, MWCO and NaCl rejections of multilayer membranes prepared with cellulose and polyamide. The rejection of PEG molecules with molecular weight of 200 g mol⁻¹ was higher than 90% for all membranes. A 5-fold increase of water permeance was observed when introducing a thin cellulose layer, keeping the MWCO below 200 g mol⁻¹, but with much lower salt rejection (only 5.4 %). This kind of membrane could be useful for separation of mixed organic/inorganic waste streams in pharmaceutical, food and agrochemical industries. For instance in biotechnology, reactions or treatments using micro-organisms in many cases requires salt removal, since they can not withstand the osmotic pressure caused by high salt concentration [38].

A significant improvement of salt rejection was obtained with a thicker cellulose interlayer (coating solution concentration 1.9 wt%). In this case the salt rejection was 41 % higher and at the same time the water permeance was 83 % higher than when the polyamide layer prepared directly on PAN. Also the reproducibility was higher.

It is important to note that this comparison was done using the same monomers, same PAN support and under the same preparation conditions. Changing the support, monomers and/or further optimization of the interfacial polymerization preparation conditions might lead to other tuned salt rejection and permeance values.

The reason for the larger permeance with cellulose interlayer might be the following. In the case of polyamide cast directly on porous supports (Fig. 5 and 6) probably only the part of the layer forming pockets or globular nodules coming out of the pores will be available for water transport. The areas of the polyamide layer between the pores are strongly adhered to the PVDF or PAN dense surface and are practically impermeable to water. The hydrophilic cellulose swells with water, which can then freely permeate the whole polyamide layer above it without restrictions (Fig. 8, right). The effective total area for water permeation is therefore larger with the cellulose layer.

3.2 Method 2: Cellulose/ionic liquid

The second method chosen for the preparation of cellulose membranes was based on the dissolution of cellulose in ionic liquids and does not require additional solvents other than [C2mim]OAc and water as coagulation bath. For this reason the method can be considered greener than method 1 or any other processes involving cellulose dissolution in aggressive solvents. The cross sections of multilayer cellulose membranes prepared on PSU and PEI supports are shown in Fig. 9. Thicknesses of 0.4 μm to 5.6 μm were obtained by coating cellulose/[C2mim]OAc solutions with

different concentrations on asymmetric porous supports. Thicker cellulose membranes were prepared directly on polyester nonwoven. High magnification of the cellulose coating (Fig. 9c) image shows a regular structuration parallel to the surface. FESEM and AFM images of the coating surface prepared from cellulose/[C2mim]OAc solutions are shown in Fig. 10. The surface is slightly different from regenerated silyl cellulose prepared by Method 1. The corresponding X-ray diffractogram is also depicted in Fig. 10, confirming the crystallinity of the cellulose coating. Peaks appear in the same scattering angles, indicating that the same form of cellulose, i.e. cellulose polymorph II predominates in both regenerated celluloses from the silylation process and the dissolution in ionic liquid. Amorphous cellulose has a broad peak with a maximum around 20° to 22° [39]. There is an overlap of the broad amorphous peak and the sharper one for the crystalline form II in this region at 20° . Similar is observed for the regenerated cellulose obtained by silylation and acid treatment. However, the peak for the regenerated silyl cellulose at 20° is broader than for that obtained for coatings from dissolved cellulose in ionic liquid, indicating lower crystallinity, smaller crystallites and/or non-uniformity within the crystallites. Cellulose crystallites are normally small (< 5 nm), the exact determination of the crystal lattice by XRD is not always possible and the degree of crystallinity might have a large variation for the same sample [40, 41].

The contact angles of coatings obtained from cellulose/[C2mim]OAc solutions were 22.0° to 26.1° , lower than for regenerated silyl cellulose (Table 1), confirming the total availability of OH groups for interaction with water.

The performance of membranes prepared from cellulose/[C2mim]OAc solutions is summarized in Table 5 and Fig. 11. The increase of cellulose concentration resulted in lower MWCO with simultaneous reduction of the water permeance and increase of coating thickness. PSU as a porous support led to the highest water permeance and lowest MWCO.

One of the advantages of cellulose is the lack of solubility in water and most of the organic solvents. Regenerated cellulose coatings obtained from 5 wt% and 10 wt% solutions in [C2mim]OAc without any support were immersed in THF, hexane, DMF, NMP and DMAc for 1 h, 12 h, 24 h and for one week and the weight loss was measured by measuring the weight before and after the experiment. The membranes showed no visible change and no weight loss, indicating that the cellulosic membranes are resistant in these solvents.

(Fig. 9)

(Fig. 10)

Table 5. Water permeance and solute rejection for multilayer membranes prepared from Cellulose/[C2mim]OAc

Coating solution (% Cellulose)	Support	Thickness of cellulose layer (μm) ^a	Water permeance ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	Rejection of PEO ^b (%)	MWCO (Kg mol^{-1}) ^c
0	PSU	0	$(1.1 \pm 0.2) \times 10^3$	100	92
2	PSU	0.4	262.9 ± 3.9	95	81
5	PSU	0.9	25.6 ± 0.3	95	60
10	PSU	2.3	13.8 ± 1.0	100	3
0	PEI	0	$(1.3 \pm 0.2) \times 10^3$	48	275
5	PEI	0.7	9.9 ± 0.1	100	67
10	PEI	3.9	1.75 ± 0.05	100	7
5	Polyester nonwoven	3.5	11.4 ± 0.9	97	46
10	Polyester nonwoven	6.8	1.2 ± 0.05	100	5

^aEstimated by FESEM (Figure 9); ^b PEO with $\text{MW} 100 \text{ Kg mol}^{-1}$;

^cEstimated by GPC data from Figure 11

(Fig. 11)

4. Conclusion

We manufactured multilayer membranes based on thin cellulose coatings on porous polymeric supports, by using two different approaches: (i) cellulose silylation and regeneration by acid treatment and (ii) cellulose dissolution in the ionic liquid [C2mim]OAc. Regenerated cellulose membranes prepared by silylation led to MWCO as low as $5,000 \text{ g mol}^{-1}$ measured with non-ionic poly (ethylene glycol) with $8.1 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ water permeance and only 3% NaCl rejection. Membranes prepared from dissolved cellulose in [C2mim]OAc had MWCO as low as $3,000 \text{ g mol}^{-1}$ and $13.8 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ water permeance. The cellulose layer was confirmed to be

partially crystalline, the contact angle was 22.0° , clearly more hydrophilic than for the uncoated porous membrane, which had 51° to 86° and a MWCO higher than $90,000 \text{ g mol}^{-1}$. Cellulose membranes were also prepared without any support and confirmed to be insoluble in water, tetrahydrofuran, hexane, N,N-dimethylformamide, 1-methyl-2-pyrrolidinone and N,N-dimethylacetamide. This makes cellulosic membranes potentially suitable also for application in solvent medium. Furthermore interfacial polymerization performed on the cellulose layer led to MWCO lower than 200 g mol^{-1} , extending the application to the nanofiltration range. The morphology of the multilayer membranes was investigated by FESEM and AFM. The wet membrane was imaged by cryo FESEM to demonstrate the influence of the sublayer on the morphology of the thin polyamide selective layer. Cellulose promoted a smoother interface polymerization and at the same time due to its hydrophilicity, it swells with water and increases the permeance.

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6. References

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Figure Captions

Scheme 1. Schematic representation of cellulose and 1-ethyl-3-methylimidazolium acetate [C2mim]OAc covalent binding.

Fig. 1. FTIR spectra of non-modified microcrystalline cellulose (black), silylated cellulose (blue) and regenerated cellulose (red); inset: expanded spectra at low wavelength range.

Fig. 2. NMR ^1H spectrum of trimethylsilyl cellulose (silylated cellulose).

Fig. 3. Surface FESEM image and X-ray diffractograms of a) dry polyacrylonitrile porous membrane coated with 1 wt% silylated cellulose in THF, followed by regeneration with acid treatment; X-Ray diffractograms of (b) unmodified cellulose and (c) regenerated cellulose.

Fig. 4. PEG rejections of cellulose membranes prepared by coating with different concentrations of silylated cellulose on PAN porous supports, followed by regeneration with acid solutions: (a) cellulose coating and (b) cellulose coating with polyamide layer.

Fig. 5. Surface (FESEM image) of a dry (a) PAN porous membranes and (b, c) the same membrane coated with polyamide by interfacial polymerization: (b) dry and (c) cryo images of wet membranes.

Fig. 6. Surface (FESEM image) of (a) PVDF porous membranes and (b, c) the same membrane coated with polyamide by interfacial polymerization: (b) dry and (c) cryo images of wet polyamide/PVDF membrane.

Fig. 7. FESEM images of membranes prepared by interfacial polymerization on asymmetric porous polyacrylonitrile supports coated with 1 wt % regenerated cellulose: (a) cross section and (b, c, d) surface images of (a, b) dry and (c, d) cryo wet membranes.

Fig. 8. Thin polyamide layer formed by interfacial polymerization on supports of different porosities: (a) PAN, (b) PVDF and (c) cellulose coating on porous PAN. Membrane soaked in diamine aqueous solution (yellow) in contact to trimesoyl chloride organic solution (green). Right: Probable water permeation path.

Fig. 9. Cross section (FESEM) images of membranes prepared from (a) 2, (b) 5 and (c) 10 wt% cellulose solutions in [C2mim]OAc by casting on polysulfone asymmetric porous supports and immersion in water.

Fig. 10. X-Ray diffractogram of cellulose after dissolution in [C2mim]OAc and immersion in water; inset: AFM and FESEM images of coating surfaces prepared with 5 wt% cellulose/[C2mim]OAc solution.

Fig. 11. PEG rejections of cellulose membranes prepared from solution in [C2mim]OAc coated on PSU and PEI porous supports or directly on polyester nonwoven.

Figure 1

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11