Journal of Membrane Science 473 (2015) 63–71

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Novel cellulose ester substrates for high performance flat-sheet thin-film composite (TFC) forward osmosis (FO) membranes

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ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form
25 August 2014
Accepted 25 August 2014
Available online 16 September 2014

Keywords:
Cellulose ester
Forward osmosis
Thin film composite membrane

ABSTRACT

A novel hydrophilic cellulose ester with a high intrinsic water permeability and a water partition coefficient was discovered to construct membrane supports for flat-sheet thin film composite (TFC) forward osmosis (FO) membranes for water reuse and seawater desalination with high performance. The performance of TFC-FO membranes prepared from the hydrophilic cellulose ester containing a high degree of OH and a moderate degree of Pr substitutions clearly surpasses those prepared from cellulose esters and other polymers with moderate hydrophilicity. Post-treatments of TFC-FO membranes using sodium dodecyl sulfate (SDS) and glycerol followed by heat treatment further enhance the water flux without compromising the selectivity. Positron annihilation lifetime analyses have confirmed that the SDS/glycerol post-treatment increases the free volume size and fractional free volume of the polyamide selective layer. The newly developed post-treated TFC-FO membranes exhibit a remarkably high water flux up to 90 LMH when the selective layer is oriented towards the draw solution (i.e., PRO mode) using 1 M NaCl as the draw solution and DI water as the feed. For seawater desalination, the membranes display a high water flux up to 35 LMH using a 2 M NaCl draw solution. These water fluxes exceeded the water fluxes achieved by other types of FO membranes reported in literatures.

1. Introduction

Forward osmosis (FO) is an emerging technology for water production [1–3]. In FO, a semi-permeable membrane, which is permeable to water while rejecting others, is used as the core of separation. The driving force for water transfer is the osmotic pressure gradient across the membrane. Comparing FO to pressure-driven reverse osmosis (RO) and thermally-driven multi-stage flash distillation (MSF) processes, FO is attractive due to (1) lower fouling propensity; [4,5] (2) higher water recovery; (3) mild operating conditions and (4) lower energy consumption if using glucose and fertilizer as draw solutes without considering regeneration or when coupled with low-pressure RO process [6–8].

Progresses on FO membranes have been made rapidly in the last decade. Various phase-inversion [9–11], thin-film composite [12–20] and layer-by-layer (LbL) membranes [21,22] have been developed. Generally, high performance FO membranes must consist of the following characteristics: (1) a thin, hydrophilic and highly porous supporting layer for better water transport and low internal concentration polarization (ICP); (2) a thin selective layer with good salt rejection and high water permeability; and (3) reasonably good anti-fouling properties. In addition, macrovoids within the membrane supports may not be desirable as they are weak mechanical points and may result in membrane failure under vibration and washing operations [16,17]. Thin-film composite (TFC) membranes synthesized on hydrophilic substrates tend to display superior FO performance compared to those on hydrophobic substrates as well as LbL membranes [17,19,20]. Since the polyamide layer in TFC membranes is formed via interfacial polymerization, this allows membrane scientists to tailor the membrane support and the selective layer separately in order to maximize the membrane performance.

So far, TFC-FO membranes were fabricated using substrates made of polysulfone [13,14], polyethersulfone [15,16], polyimide-amide [23] and their sulfonated materials [17–20]. These materials are relatively expensive. Since cellulose esters have many advantages such as vast availability, low cost, high hydrophilicity, easy fabrication and superior chlorine resistance, they may be ideal substrate materials for high-performance TFC-FO membranes. Therefore, the first objective of this study is to explore if we can combine the strengths of both cellulose esters and TFC and design superior FO membranes for water reuse and seawater desalination. Fundamental studies on membrane formation and transport properties including salt and water partition

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http://dx.doi.org/10.1016/j.memsci.2014.08.046
0376-7388/

coefficients, permeability and diffusivity, wet and dry free volume size and fractional free volume of cellulose esters comprising various functional groups such as hydroxyl (OH), acetyl (Ac), propionyl (Pr) and butyryl (Bu) have been recently reported [11,24]. The cellulose ester containing a high degree of OH and a moderate degree of Pr substitutions was chosen as the substrate material in this study because it has a water permeability of one magnitude order higher than other cellulose esters. In addition, this material possesses an extremely high water partition coefficient but a very low solubility selectivity. As a result, it would have an intrinsically high water flux with minimal ICP as the substrate material for TFC-FO membranes. A cellulose ester comprising moderate degrees of OH and Bu substitutions was also chosen for performance comparison.

The second objective of this study is to explore if we can further enhance the FO performance of the newly developed TFC membranes by post-treatments. So far, most TFC-FO membranes reported in literatures were subjected to no post-treatment or simple heat treatment after interfacial polymerization. Since glycerol and sodium dodecyl sulfate (SDS) post-treatments have shown effectiveness to augment the performance of RO membranes [25], it would be worthwhile to study their effects on FO membranes and investigate the post-treatment-induced microscopic changes on the free volume size and intensity by positron annihilation lifetime spectroscopy (PALS). To our best knowledge, this is the first report using the proposed cellulose ester as the substrate for TFC-FO membranes and also the first time examining the effects of glycerol and sodium dodecyl sulfate (SDS) post-treatments on free volume by means of PALS. These studies may open up new insights to molecularly design advanced FO membranes for water reuse and seawater desalination.

2. Materials and methods

2.1. Fabrication of cellulose ester membrane supports

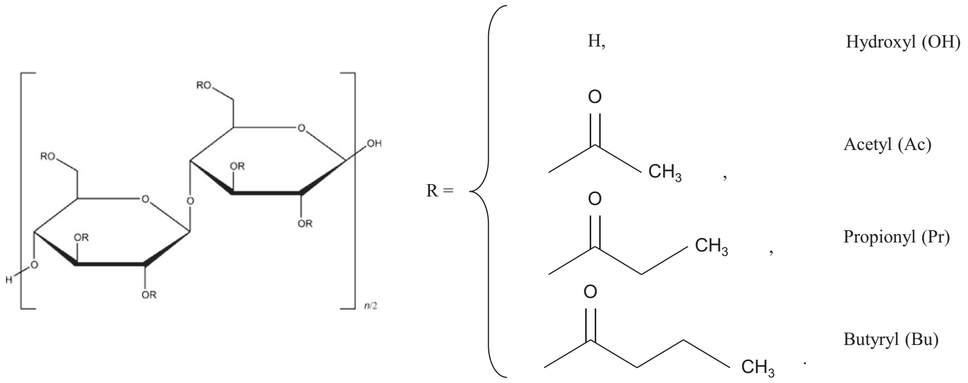
As aforementioned, the cellulose acetate propionate (CAP) containing a high degree of OH and a moderate degree of Pr substitutions (referred to as CAP-O thereafter) and the cellulose acetate butyrate (CAB) comprising moderate degrees of OH and Bu substitutions (referred to as CAB-M) were synthesized by Eastman Chemical Company (USA) and used for the fabrication of membrane supports. Fig. 1 shows their chemical structures, and basic properties. *N*-methyl-2-pyrrolidone (NMP, > 99.5%, Merck), polyethylene glycol 400 (PEG, Mw = 400 g mol^{-1}, Sigma-Aldrich) and deionized (DI) water were used as the solvent and additives, respectively. DI water was produced by a Milli-Q unit (Millipore, USA) at a resistivity of 18 MΩ cm. The cellulose ester polymers were dried at 120 °C overnight in a vacuum oven prior to use. *m*-Phenylenediamine (MPD, lenediaminevacuum oven prior to use. at 120ly. DI water was produced by a Milli-Q usulfate (SDS, ≥ 99.0%, Sigma-Aldrich), glycerol (≥ 99.5%, Sigma-Aldrich) and hexane (> 99.9%, Fisher Chemicals) were used during interfacial polymerization and post-treatments. For forward osmosis (FO) tests, sodium chloride (NaCl, ≥ 99.5%, Merck) was used to prepare the draw solutions and model seawater by dissolution in DI water.

The casting solutions consisted of 10 wt% cellulose ester, 42 wt% *N*-methyl-2-pyrrolidone (NMP) as the solvent, 42 wt% PEG400 and 6 wt% deionized (DI) water as additives. Thin layer of cellulose ester membranes was cast on a smooth and hydrophilic glass plate using a 100 μm casting knife and then immersed immediately in a water coagulant bath at room temperature for phase inversion. The as-cast membranes were gently peeled off from the glass plate and then soaked in a tap water bath at room temperature overnight to remove the residual solvent and additives. The membrane supports were then preserved in a 50 wt% glycerol aqueous solution for 1 day before interfacial polymerization.

2.2. Interfacial polymerization and post-treatment methods of flatsheet TFC-FO membranes

The cellulose ester membrane support was first immersed in a 2 wt% MPD aqueous solution for 2 min. After that the excess MPD solution was removed by purging a sweeping air for 30 s. The membrane support top layer was contacted with TMC dissolved in hexane with a concentration of 0.05 wt% for 2 min for polymerization to occur. After removing the TMC solution, the membrane was dried in air for 2 min before storing in DI water prior to testing.

Some of the TFC-FO membranes were subjected to two different post-treatment methods. The post-treatment method 1 involves the immersion of the TFC-FO membranes in a (0.3 wt%/1 wt%) SDS/glycerol aqueous solution for 15 min. The post-treated TFC membranes were then immersed in DI water before testing. Some membranes were subjected to the post-treatment method 2 by firstly immersing the SDS/glycerol treated TFC-FO membranes in DI water for 1 min to rinse off SDS and glycerol followed by heat treatment at 60 °C for 1 min in an oven. The treated TFC membranes were stored in DI water prior to use.



Cellulose ester	DS(OH)	DS(Ac)	DS(Pr)	DS(Bu)	T_g (°C)	Density (g/cm^3)
CAP-O	1.10	1.31	0.59	-	187	1.28
CAB-M	0.83	1.49	-	0.68	180	1.28

Fig. 1. The chemical structures, compositions and basic properties of cellulose esters used in this work.