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Novel hydrophilic nylon 6,6 microfiltration membrane supported thin film composite membranes for engineered osmosis

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ABSTRACT

Previous investigations of engineered osmosis (EO) concluded that hydrophobic support layers of thin film composite membrane causes severe internal concentration polarization due to incomplete wetting. Incomplete wetting reduces the effective porosity of the support, inhibiting mass transport and thus water flux. In this study, novel thin film composite membranes were developed which consist of a poly(piperazinamide) or polyamide selective layer formed by interfacial polymerization on top of a nylon 6,6 microfiltration membrane support. This intrinsically hydrophilic support was used to increase the "wetted porosity" and to mitigate internal concentration polarization. Reverse osmosis tests showed that the permselectivity of our best poly(piperazinamide) and polyamide thin film composite membranes approached those of a commercial nanofiltration and a commercial reverse osmosis membrane, respectively. The osmotic flux performance of the new polyamide thin film composite membrane showed matched water flux, 10 fold lower salt flux and 8–28 fold lower specific salt flux than the standard commercial cellulose triacetate forward osmosis membrane from Hydration Technology Innovations^{TM}. The relatively good performance in osmotic flux tests of our thin film composite membranes was directly related to the high permselectivity of the selective layers coupled with the hydrophilicity of the nylon 6,6 support. These results suggest that these nylon 6,6 supported thin film composite membranes may enable applications like forward osmosis or pressure retarded osmosis.

1. Introduction

Clean water and energy are essential for public health and economic prosperity. Engineered Osmosis (EO) is an emerging platform technology that has the potential to sustainably produce clean drinking water and electric power. It has therefore garnered great interest amongst the membrane science community within the past half-decade [1–3]. Unlike hydraulically driven membrane processes, EO exploits the natural phenomenon of osmosis, which occurs when two solutions of differing concentration are placed on two sides of a semi-permeable membrane. The generated osmotic pressure difference drives the permeation of water across the membrane from the dilute solution to the concentrated solution. EO has applications in direct osmotic concentration (DOC) for concentrating high-value solutes, forward osmosis (FO) for seawater desalination and pressure retarded osmosis (PRO) for electric power generation [4–6].

Despite the potential to address water and energy scarcity, EO processes have not yet become commercialized on a large scale. One major obstacle to commercialization is the lack of an appropriately designed membrane. Early work concluded that thin film composite (TFC) membranes specially designed for nanofiltration (NF) and reverse osmosis (RO) membranes, the best salt rejecting membranes commercially available, were unsuitable for osmotic separations due to their poor flux performance [4–6]. A typical RO membrane is comprised of an aromatic polyamide thin film formed in-situ on top of an asymmetric polysulfone (PSu) mid-layer casted by phase inversion over a polyester (PET) nonwoven backing layer [7–9]. TFC-NF or TFC–RO membranes fail to perform well in EO processes because the thick support layers that, while necessary to withstand large hydraulic pressures in NF or RO, create resistance to solute mass transfer in FO or PRO. This mass transfer resistance is known as internal concentration polarization (ICP) and occurs within the thick support layers. ICP adversely affects the performance by reducing the osmotic pressure difference across the TFC membranes [2,4,6,10–13]. ICP may even be enhanced by the hydrophobic nature of typical TFC support layers. The intrinsic hydrophobicity of the PSu and PET layers prevent complete wetting of the pore structure. The unwetted areas of the support layer are not available for solute and

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water transport [14]. Existing commercial FO membranes from Hydration Technology Innovations^{TM} (HTI) are specifically designed for EO processes with minimized ICP, which is achieved by eliminating the thick backing layer and using hydrophilic cellulose triacetate (CTA) to make the membranes [15]. However, due to its integrated membrane structure and chemistry, these commercial FO membranes have relatively low permeability and salt rejection. Additionally, CTA is also susceptible to hydrolysis under basic conditions and high temperature [8].

A membrane designed for an osmotically driven process should have a combination of characteristics. It must have a permselectivity to reject most solutes and produce high water fluxes. This is common in today's RO membranes which have a highly selective polyamide layer. For applications in EO, however, this selective layer must also be supported by a thin, highly porous, non-tortuous and hydrophilic support layer to minimize effective ICP [16,17]. For EO applications involving hydraulic pressure (like PRO) the membranes must be able to tolerate the mechanical stresses during operation, though all membranes will need to have a minimum strength requirement for fabrication and installation into elements and modules.

One option is to design a TFC membrane with an RO-type selective layer supported by a hydrophillic porous support. Such a membrane would retain the high permselectivity of a commercial RO membrane and exhibit low resistance to mass transfer during osmotic flow due to improved hydrophilicity of the support.

However, research using hydrophilic polymers in TFC membrane supports is still in its infancy at the time of this writing. Recent efforts on designing TFC flat sheet and hollow fiber membranes for EO [17–19] focus on support structures but not support chemistry. Hydrophobic PSu and polyethersulfone (PES) are used in these studies. Several groups are also considering the fabrication of integrated asymmetric EO membranes using hydrophilic polymers such as polybenzimidazole and cellulose acetate (CA) [20–22]. However, hydrophilic polymers are not conventionally used to support TFC membranes, even in RO applications. This is due to differences in the fabrication process and the likelihood of plasticization in aqueous environments.

An issue that needs to be considered in making hydrophilic polymer supported TFC membrane is support swelling [23]. Water molecules might plasticize the hydrophilic support more severely than the rigid polyamide selective layer, causing post-fabrication perforation or delamination of the selective layer. Additionally, the mechanical stability of hydrophilic supports may be impacted by a swelling–deswelling equilibrium in the presence of high concentration of salt ions [24]. Choosing a suitable hydrophilic support with low swelling propensity is essential but also challenging.

In this work, a nylon 6,6 microfiltration membrane from 3M^{TM} was used as the support for TFC membranes for the first time. Nylon 6,6, a common polymer for textile and plastic industry has good mechanical, thermal and chemical properties due to its semi-crystalline structure. Additionally, it is much more hydrophilic than conventional PSu support but has less swelling propensity than other common hydrophilic polymers, such as cellulose acetate [25].

We selected both poly(piperazinamide) and polyamide as the selective layer in order to suit different types of draw solutes. Poly(piperazinamide) is usually used to fabricate NF membranes, which has high rejection to divalent salts, such as $MgSO_4$, with relatively high permeate flux [26]. It may therefore be suitable for osmotic processes using draw solutions composed of divalent salts. Polyamide, on the other hand, is usually used to fabricate RO membranes, which has high rejection to monovalent salts like NaCl [26] and might be applied in EO with monovalent salt draw solutions.

This investigation demonstrates the performance of both classes of TFC membranes supported by a commercial hydrophilic nylon 6,6 microfiltration (MF). Salt rejection and pure water permeability of the newly fabricated TFC poly(piperazinamide) and polyamide membranes are comparable to commercially available nanofiltration (NF) and reverse osmosis (RO) membranes, respectively. The osmotic flux performance of polyamide TFC membrane is also evaluated and is shown to meet or exceed the performance of the standard commercial FO membranes. We hypothesized that hydrophilic nylon 6,6 that supports the membrane selective layer should enhance osmotic flux by minimizing ICP due to improved wetting.

2. Experimental

2.1. Materials

A multi-zoned nylon 6,6 MF membrane designated BLA010 was provided by 3M Purification Inc. (Meriden, CT) as the support for TFC EO membranes. This MF membrane has three regions: (1) a large pore region at the upstream side of the membrane that usually faces the feed in MF as a pre-filter by capturing larger particles; (2) a nonwoven scrim used as a mechanical support and to facilitate manufacturing; and (3) a small-pore region on the downstream side of the membrane that faces the permeate in MF to provide the retention of small contaminents. The mean pore sizes of the small-pore region and large-pore region are 0.1 μm and 0.45 μm, repectively, according to the manufacturer.

Diamine monomers piperazine (PIP) and m-phenylenediamine (MPD) were purchased from Acros Organic and Sigma-Aldrich, respectively. Acid chloride monomer trimesoyl chloride (TMC) and acid acceptor triethylamine (TEA) were purchased from Sigma-Aldrich. Hexane, the solvent for TMC, was purchased from Fisher Scientific. Deionized water (DI) obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA) was used as the solvent for diamine monomers. Sodium chloride and magnesium sulfate were purchased from Fisher Scientific.

Commercial asymmetric cellulose triacetate (HTI-CTA) FO membrane (Hydration Technology Innovations Inc., Albany, OR), TFC NF membrane NF270 and TFC seawater RO membrane SW30-XLE (Dow Water & Process Solutions Company, Midland, MI) were acquired for comparison.

2.2. Interfacial polymerization of TFC membrane

The monomers used for in situ interfacial polymerization of poly(piperazinamide) were PIP and TMC. PIP was dissolved in Milli-Q water at varying concentrations ranged from 0.25% to 3% (w/v). An equivalent amount of TEA was added into aqueous solution as an acid acceptor [27]. PIP has been reported to react slowly to form the poly(piperazinamide) layer because of its inefficient partitioning capacity into the organic phase and tendency to react with hydrochloride. Addition of acid acceptor drives the reaction toward the formation of poly(piperazineamide) [28]. A 0.15% (w/v) solution of TMC in hexane was prepared. All solutions were stirred at room temperature for at least 3 h prior to using.

A nylon 6,6 microfiltration membrane was first taped onto a glass plate with the smaller pore side facing up. The support was then immersed into an aqueous PIP solution for 120 s. Excess PIP solution was removed from the support membrane surface using a rubber roller. The membrane was then dipped into a TMC/hexane solution for 60 s to form an ultrathin poly(piperazineamide) film. The resulting composite film was air dried for 120 s and subsequently cured in an air-circulation oven at 80 °C for 5 min for