



## Separation performance and interfacial properties of nanocomposite reverse osmosis membranes

MaryTheresa M. Pendergast, Asim K. Ghosh<sup>1</sup>, E.M.V. Hoek\*

Department Civil & Environmental Engineering and California NanoSystems Institute, University of California, Los Angeles, California, USA

### ARTICLE INFO

#### Article history:

Received 8 February 2011

Received in revised form 3 May 2011

Accepted 3 May 2011

Available online 31 May 2011

#### Keywords:

Nanocomposite

Polyamide

Polysulfone

Reverse osmosis

Water treatment

Compaction

### ABSTRACT

Four different types of nanocomposite reverse osmosis (RO) membranes were formed by interfacial polymerization of either polyamide (PA) or zeolite A-polyamide nanocomposite (ZA-PA) thin films over either pure polysulfone (PSf) or zeolite A-polysulfone nanocomposite (ZA-PSf) support membranes cast by wet phase inversion. All three nanocomposite membranes exhibited superior separation performance and interfacial properties relative to hand-cast TFC analogs including: (1) smoother, more hydrophilic surfaces (2) higher water permeability and salt rejection, and (3) improved resistance to physical compaction. Less compaction occurred for membranes with nanoparticles embedded in interfacially polymerized coating films, which adds further proof that flux decline associated with physical compaction is influenced by coating film properties in addition to support membrane properties. The new classes of nanocomposite membrane materials continue to offer promise of further improved RO membranes for use in desalination and advanced water purification.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Mixed matrix membranes—in which a filler material is embedded within a polymeric matrix—are already used in a variety of membrane processes including fuel cells, pervaporation, and gas separations [1–5]. This concept has added a new degree of freedom in the development of membranes with novel separation performance, *i.e.*, selection of the unique properties of the filler material, which may include enhanced permeability, selectivity, stability, surface area, or catalytic activity. More recently, nanocomposite mixed matrix membranes have been explored to tailor performance and add novel functionality to membranes for water purification applications. A number of researchers have deposited nanoparticles onto the surface of reverse osmosis (RO) membranes or encapsulated them within RO membrane thin films, noting higher permeability (generally for both water and salts) and in some cases advanced functionality such as antimicrobial activity [6–10].

Jeong et al. [11] demonstrated that the incorporation of zeolite molecular-sieve nanoparticles into polyamide thin films (during interfacial polymerization) could nearly double the water flux without reducing observed rejection of sodium chloride, magnesium sulfate, and

polyethylene glycol. A key feature of these ‘thin film nanocomposite’ (TFN) membranes is that zeolite nanoparticles are roughly the same diameter as polyamide film thickness, thereby creating a “percolation threshold” through the thin film with a single particle. It is thought that zeolite molecular-sieves with 3-D interconnected pores of ~4 Angstroms improved water permeability while maintaining good salt selectivity by offering preferential flow paths for water transport; however, zeolite-polyamide coating films containing impermeable zeolite nanoparticles (internal pores filled with a polymer) at the same zeolite loading produce fluxes intermediate between the relatively low flux pure polyamide thin film composite (TFC) membrane and the relatively high flux TFN membrane. This result offered an early insight that a mechanism besides molecular-sieving could be responsible for the enhanced water flux.

Subsequently, Lind et al. [12] reported on the formation and characterization of pure polyamide TFC and zeolite-polyamide TFN membranes with seawater RO separation performance. Both TFC and TFN membranes were more permeable, hydrophilic, and rougher than a commercially available seawater RO membrane. Salt rejection by TFN membranes was consistently lower than that of hand-cast TFC membranes; however, two TFN membrane formulations exhibited better salt rejections than the commercial membrane (>99.4%). According to spectroscopic analysis, polyamide films formed in the presence of zeolite nanoparticles were less crosslinked than similarly cast pure polyamide films. At the low nanoparticle loadings evaluated, differences between pure polyamide and zeolite-polyamide membrane water and salt permeability correlated weakly with extent of crosslinking of the polyamide film, suggesting that a combination of

\* Corresponding author at: University of California Los Angeles; Department of Civil & Environmental Engineering; 5732 Boelter Hall; PO Box 951593; Los Angeles, CA, 90095–1593. Tel.: +1 310 206 3735; fax: +1 310 206 2222.

E-mail address: [emvhoek@ucla.edu](mailto:emvhoek@ucla.edu) (E.M.V. Hoek).

<sup>1</sup> Current address: Desalination Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India.

molecular-sieving, crosslinking, and thin film defects likely governs transport through zeolite-polyamide TFN membranes.

More recently, composite RO membranes were formed by interfacial polymerization of polyamide thin films over pure polysulfone and nanocomposite-polysulfone porous support membranes [13]. Nanocomposite supports were formed from four different sized amorphous non-porous silica nanoparticles, a zeolite A nanoparticle, and a surface-modified (hydrophobic) zeolite A nanoparticle. Nanocomposite-supported RO membranes generally had higher initial permeability and experienced less initial flux decline than pure polysulfone supported membranes. Cross-sectional SEM images verified that this decline was due to significant reduction in thickness of pure polysulfone supports, whereas minimal compaction was seen in nanocomposites due to enhanced mechanical stability imparted by the nanoparticles. A conceptual model was proposed to explain the mechanistic relationship between support membrane compaction and observed changes in water flux and salt rejection. As the support membrane compacts, surface (*i.e.*, skin layer) pore constriction increases the effective path length of diffusion through polyamide thin films, thereby reducing both water and salt permeability. Nanocomposites that resist compaction also resist irreversible flux decline.

This study uses nanocomposite membrane materials to elucidate and decouple the potential roles of coating film and support membrane in RO membrane compaction, and offers a potential route to improved RO membrane performance by eliminating flux decline due to physical compaction. Four different types of nanocomposite RO membranes were formed by interfacial polymerization of either polyamide (PA) or zeolite A-polyamide nanocomposite (ZA-PA) thin films over either pure polysulfone (PSf) or zeolite A-polysulfone nanocomposite (ZA-PSf) support membranes. The hand-cast membranes are described as (a) thin film composite (TFC = PA/PSf), (b) nanocomposite supported thin film composite (nTFC = PA/ZA-PSf), (c) thin film nanocomposite (TFN = ZA-PA/PSf), and (d) nanocomposite supported thin film nanocomposite (nTFN = ZA-PA/ZA-PSf). Membrane interfacial properties, separation performance, and compaction resistance are presented and discussed.

## 2. Materials and methods

### 2.1. Membrane preparation

Support membranes were prepared by dissolving 18 g of polysulfone (PSf) beads ( $M_n$ -26,000 from Aldrich, St. Louis, Missouri, USA) into 72 mL of *N*-methyl pyrrolidone (NMP) (Acros Organics, Morris Plains, New Jersey, USA) in airtight glass bottles. For nanocomposite membranes, 3.6 g of 250 nm Linde Type-A zeolite nanoparticles (NanoH<sub>2</sub>O Inc., Los Angeles, California, USA) were dispersed in NMP prior to PSf addition. The suspensions were then agitated for several hours until complete polymer dissolution was achieved to form the casting solutions. Casting solutions were spread via knife-edge over a polyester non-woven fabric (NanoH<sub>2</sub>O Inc., Los Angeles, California, USA), previously adhered to a glass plate. The glass plate was immediately immersed into a coagulation bath of 18 MΩ laboratory deionized water maintained at room temperature to induce polymer precipitation. After 30 minutes the non-woven fabric supported polysulfone and nanocomposite membranes were removed from the water bath, separated from the glass plate, washed thoroughly with deionized water, and stored in deionized water in a laboratory refrigerator at 5 °C to inhibit biogrowth.

Composite RO membranes were then formed via interfacial polymerization atop the phase inverted structures. Pure polysulfone support membranes were used for TFC and TFN membranes and nanocomposite support membranes were used for nTFC and nTFN membranes. Support membranes were immersed in an aqueous solution of *m*-phenylenediamine (MPD) (1,3-diaminobenzene, Sigma-Aldrich, Milwaukee, Wisconsin, USA), triethyl amine (TEA), (+)-10-champhor sulfonic acid (CSA), sodium lauryl sulfate (SLS), and isopropanol (IPA) for 15 seconds. The

MPD solution contained MPD:TEA:CSA:SLS:IPA in ratios of 2.0:2.0:4.0:0.02:10 w/v%. Excess MPD solution was removed from the support membrane surfaces using laboratory gas forced through a custom fabricated air knife. Aqueous MPD saturated support membranes were then immersed into 0.1 wt% trimesoyl chloride (1,3,5-tricarbonyl chloride, Sigma-Aldrich, Milwaukee, Wisconsin, USA) in a proprietary isoparaffin (ExxonMobil Isopar G, Gallade Chemicals, Inc., Santa Ana, California, USA) at 30 °C for 15 seconds to initiate polymerization. The resulting composite membranes were heat cured at 82 °C for 10 minutes, washed thoroughly with deionized water, and stored at 5 °C in opaque containers of deionized water. Both TFN and nTFN membranes were formed by dispersing 0.2 w/w% zeolite-A nanoparticles in the TMC solution as previously described [11,12].

### 2.2. Membrane characterization

The surface (zeta) potentials of hand-cast UF and RO membranes were determined using the Helmholtz-Smoluchowski equation and measured streaming potentials in 10 mM NaCl solution at an unadjusted pH of  $5.8 \pm 0.2$  (Zeta PALS, Brookhaven Instrument Corp., New York, New York, USA). Sessile drop contact angles of deionized water were measured on membrane samples in an environmental chamber mounted to a contact angle goniometer (DSA10, KRÜSS GmbH, Hamburg, Germany). The equilibrium values were taken as steady-state averages of left and right angles. Surface roughness of synthesized membranes was measured via AFM (Nanoscope IIIa, Digital Instruments, Santa Barbara, California, USA).

Mechanical strength of polysulfone and nanocomposite membranes was characterized by the ultimate tensile strength ( $\sigma$ ) measured with a mechanical testing instrument (Instron® 5540 Series Single Column Testing Systems, Instron, Norwood, Massachusetts, USA). In this test, a membrane specimen (4 cm × 1.5 cm) was stretched at a constant rate (0.5 mm/min) until breakage. The ultimate tensile strength is calculated from the maximum load applied at breakage divided by the original cross-sectional area of the test piece. The cross-sectional area was determined by micro-caliper measurements of film thickness and the sample width. The non-woven polyester fabric contributed an ultimate strength of 16.2 MPa.

### 2.3. Membrane performance experiments

Polysulfone and nanocomposite support membrane performances were evaluated using a high-pressure chemical resistant dead-end filtration cell (HP4750 Stirred Cell, Sterlitech Corp., Kent, Washington, USA) at room temperature (~20 °C) under applied pressure of 140 kPa (20 psi). Pure water permeability was determined by filtering deionized water through the support membranes. The molecular weight cutoff (MWCO) of these membranes was determined from the separation of a series of dextran solutions. Dextran concentrations in the feed and permeate were analyzed with a total organic carbon analyzer (Apollo 9000, Tekmar Dohrmann, Cincinnati, Ohio, USA). MWCO is defined as the molecular weight dextran molecule that was rejected 90% or more.

The separation performances of synthesized TFC and TFN membranes were evaluated in terms of water flux and salt rejection. Membranes were washed thoroughly for 45 min under applied pressure of 1550 kPa (225 psi). The permeability was monitored during initial stages of compaction to gain an understanding of the mechanical stability of each. Pure water flux was then measured at room temperature by normalizing the volume of pure water collected in 30 min increments by the active membrane area (13.85 cm<sup>2</sup>). For all thin film membranes formed, rejection tests were applied by challenging the membranes with a 10 mM NaCl solution and repeating the permeation test.

Download English Version:

<https://daneshyari.com/en/article/624161>

Download Persian Version:

<https://daneshyari.com/article/624161>

[Daneshyari.com](https://daneshyari.com)