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A robust thin film composite membrane incorporating thermally rearranged polymer support for organic solvent nanofiltration and pressure retarded osmosis

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ABSTRACT

Thin film composite (TFC) polymer membranes are ubiquitous in membrane-based liquid separation processes, especially in reverse osmosis (RO). While the ultrathin polyamide separating layer employed in TFC membranes has exhibited excellent performance in many liquid separation processes, the polymer support has been identified as a bottleneck to practical applications. In this work, we report a highly porous, thermally and chemically robust support comprising a thermally rearranged polymer which is combined with a polyamide active layer to form a thermally rearranged, thin film composite (TR-TFC) polymer membrane for general use in liquid separation, and for environmentally-friendly power generation. The precursor polymer has good processability for scale-up of synthesis and membrane fabrication. After thermal rearrangement, the developed TR-TFC membranes containing polybenzoxazole-*co*-imide can be utilized in separations in any organic liquids, including under harsh environments such as dimethyl formamide even at elevated temperatures, with a remarkable performance. Moreover, the membrane achieves 40 W m^{-2} of power density through pressure retarded osmosis using a concentrated brine, similar to those obtained from RO plants. These results points to the possibilities for next-generation TFC polymer membranes for general use in liquid separation and power generation.

1. Introduction

Ultrathin polyamide active layers of current thin film composite (TFC) membranes exhibit excellent performance in most liquid separation applications. In particular, reverse osmosis (RO) has been successfully commercialized through applications of the TFC membranes [1–5]. In recent years, post-treatments of the polyamide active layer have given rise to further advances in general membrane-based liquid separation by enhancing the membrane permeance (by up to four times) without significantly compromising rejection [6,7]. The post-treatment of the polyamide layer is conducted *via* microphase swelling with pure dimethyl formamide (DMF) which enhances the permeance in both aqueous and organic solvent system [6–10]. However, these high permeance TFC membranes must be fabricated on the surface of either an anodized alumina or crosslinked polyimide asymmetric membranes as the support layer, to provide DMF resistance [6,7]. The alumina support has limitations, including cost and difficult handling and scale-up, and the crosslinked polyimide membrane exhibited aging phenomena in DMF and under elevated temperature [3,6,7,11]. While the formation of the thin film active layer of TFC membranes has been comprehensively investigated, the conventional polymer support membranes continue to suffer pore collapse, accelerated aging and limited chemical and thermal stability under harsh operating conditions as well as high mass transport resistance [2,3,12–16]. In recent years, a poly(ether-ether-ketone) (PEEK) asymmetric membrane, which can operate under harsh conditions without undergoing aging, was introduced and contrasted with crosslinked polybenzimidazole (PBI) and crosslinked polyimide (PI) membranes [11]. However, these had permeances typically < 1 L m^{-2} h^{-1} bar^{-1}. Given that membrane operation under harsh conditions (*e.g.* operating temperature > 60–90 °C) is required for many industrial applications such as geothermal brackish water, nanofiltration, bleaching and dyeing applications, there is a need for more robust polymer membranes capable of operating at processes conditions [11,17–22].

In addition, in osmotically driven processes, many different kinds of nanofibrous membranes (NFMs) have been recently introduced for

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replacing the conventional support layer in TFCs in an attempt to reduce mass transfer resistance [14,23–27]. These NFMs, usually fabricated by electrospinning techniques, can effectively reduce internal concentration polarization through the membrane, consequently maximizing the driving force and generating higher power density *via* pressure retarded osmosis process [28–30]. Though NFMs reported to date (*e.g.* poly(vinylidene fluoride) (PVDF), polyethersulfone (PES), Nylon 66, and poly(etherimide)) exhibited excellent membrane performance due to their highly porous and interconnected structures, the mechanical strength and solubility in aprotic solvents of the current polymeric nanofibrous membranes were not desirable to withstand harsh operating conditions, such as a high operating pressure and temperature, organic solvents, and acid and base solutions. Therefore, we conjecture that highly porous, thermally and chemically stable polymers are desirable for next-generation support membranes as they will permit microphase swelling of the active layer by DMF during membrane fabrication; by withstanding harsh environments, they will be operable under real process conditions at elevated solvent temperatures; and they will reduce the support layer mass transport resistance which is so critical in osmotically driven processes.

In this study, we report for the first time a thermally rearranged thin film composite membrane (TR-TFC) consisting of an ultra-thin polyamide layer and a thermally rearranged nanofibrous polymer support coated with polydopamine (PDA) (TR-NFM coated with PDA, referred to as TR-PDA), specifically for use in organic solvent nanofiltration (OSN) performing molecular separations in organic liquids, and pressure retarded osmosis (PRO) for sustainable power generation.

2. Experimental

2.1. Materials

4,4′-oxydiphthalic anhydride (ODPA), 3,3′-dihydroxy-4,4′-diaminobiphenyl (HAB), and 4,4′-oxydianiline (ODA) from Sigma-Aldrich Chemical Co. (Milwaukee, WI, USA) were used for the synthesis of hydroxy polyimide (HPI), a precursor of thermally rearranged polybenzoxazole-co-imide (TR-PBOI). *N*-methyl-2-pyrrolidone (NMP), *o*-xylene, and *N*,*N*-dimethylacetamide (DMAc) were purchased from Sigma-Aldrich to synthesize and fabricate a nanofibrous membrane (NFM) with HPI *via* the electrospinning technique. Dopamine chloride and tris(hydroxymethyl) aminomethane hydrochloride (Sigma-Aldrich) were used for the hydrophilic treatment of the thermally rearranged nanofibrous membranes (TR-NFM) to aid the formation of the polyamide active layer. *m*-phenylene diamine (MPD, > 99%) and 1,3,5-bezenetricarbonyl trichloride (TMC, 98%) were obtained from Sigma-Aldrich to fabricate the ultra-thin polyamide layer on the hydrophilic treated TR-NFM. All organic solvents used to investigate the organic solvent nanofiltration (OSN) performance were purchased from Sigma-Aldrich. Deionized water was obtained *via* an ultrapure water purification system (Milli-Q® Direct, Merck Millipore, Darmstadt, Germany).

2.2. Preparation of a precursor polymer and NFM

Hydroxy polyimide (HPI) was synthesized *via* polycondensation and azeotropic imidization with two diamines (4,4′-oxydianiline and 3,3′-dihydroxy-4,4′-diamino-biphenyl) and one dianhydride (4,4′-oxydiphthalic anhydride) with *N*-methyl-2-pyrrolidone and *o*-xylene as a solvent and azeotropic agent, respectively. Using a multi-nozzle electrospinning apparatus (M-tek, Gyeonggi-do, Republic of Korea), 40 ml of HPI solution (dissolved in *N*,*N*-dimethylacetamide with 8–10 *wt*%) was electrospun onto the drum type collector (0.21 m^2) using 16 needles (23 gauge) and 4.0 ml h^{-1} of feed rate. After fabrication, the membranes were pressed 3 times at 150 kg f cm^{-2} and 130 °C for 2–3 s. Further details of the synthesis and fabrication are described in Fig. S1 and Section S1 (Supporting information), as well as our previous studies [31,32].

2.3. Fabrication of TR-TFC membrane

HPI-NFM (hydroxy polyimide) was converted to TR-NFM (thermally rearranged polybenzoxazole-*co*-imide) in a furnace at 400 °C for 2 h under an argon atmosphere. The PDA coating solution was prepared with 2 g dopamine chloride in 1 L of a 10 mM tris(hydroxymethyl) aminomethane hydrochloride aqueous solution. The solution pH was adjusted to 8.5 with 1 M $NaOH_{aq}$ to induce the polymerization of dopamine. The coating was conducted by dip-coating overnight with stirring at 300 rpm. The polyamide active layer was fabricated on the surface of TR-PDA *via* interfacial polymerization using a 3.5 wt% MPD aqueous solution and 0.15 wt% TMC hexane solution for 1 min of reaction time. The DMF activation was conducted by immersing a membrane in DMF solution at certain time. The detailed descriptions of the thermal rearrangement, PDA coating, and TFC fabrication are presented in Fig. S2, and Section S1, S2, and S3 (Supporting information).

2.4. Characterization

Five specimens of each sample were immersed in each solvent overnight. Using a dead-end cell (HP4750 stirred cell, Sterlitech Corp., WA, USA), the pure solvent permeances (PSPs) of the TR-NFMs were measured at 1 bar with N_2 gas. Duplicate specimens were prepared (2 × 5 cm^2) and the change in membrane area (in-plane) and weight was measured before and after immersing in each solvent for 1 day. Digital photographs were obtained right after taking the samples from each solvent and putting the membrane between glass plates and analyzed with the *ImageJ* open-source program. The SEM images and AFM images of TR-NFM were observed with field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Tokyo, Japan) and atomic force microscopy (AFM, Veeco, NY, USA) using a silicon probe (Nanosensors, Neuchatel, Switzerland) with a force constant of 1.2–20 N m^{-1}. The details of the characterization and PSP test are described in Section S4 and S5 (Supporting information).

2.5. Organic solvent nanofiltration (OSN) test

The multi-cell cross-flow Imperial apparatus was utilized for evaluating the performance of TR-TFCs at 30 bar and 30 °C with 50 L h^{-1} using a 2 g L^{-1} of polystyrene oligomers (standard polystyrene molecular weight 580 and 1150, Agilent Technology, CA, USA) feed solution. To conduct filtration tests at elevated temperatures, the high-temperature Imperial rig was used at three temperatures (30, 60, and 90 °C) with same conditions. The feed and permeate samples were injected into an Agilent HPLC system with a UV/Vis detector set at a wavelength of 264 nm and an ACE 5-5C18-300 column (Advanced Chromatography Technologies, ACT, UK) with methanol and THF containing 0.1 vol% trifluoroacetic acid (9:1, *v/v*) as mobile phase. To confirm the polystyrene rejection, three different dyes were chosen as follows: Chrysoidine G (C.S.G., 249 g mol^{-1}, '+' charge), Methyl Orange (M.O., 327 g mol^{-1}, '-' charge), and Brilliant Blue (B.B., 826 g mol^{-1}, '-' charge). The Hanyang OSN apparatus was used to find the correlations between solvent properties and membrane permeance with the only difference being the flow rate is smaller at 1 L h^{-1}. Further details for OSN test are well-described in Section S6 (Supporting information).

2.6. Pressure retarded osmosis (PRO) test

A lab-scale cross-flow system (Sepratek, Daejeon, Republic of Korea) was used to determine both membrane intrinsic properties and PRO performance. Firstly, the membrane was compacted with D.I. water at 15 bar for at least 5 h. After compaction, the feed concentration was adjusted to 2000 ppm $NaCl_{aq}$ solution and membrane intrinsic