High-performance reverse osmosis membranes fabricated on highly porous microstructured supports

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GRAPHICAL ABSTRACT
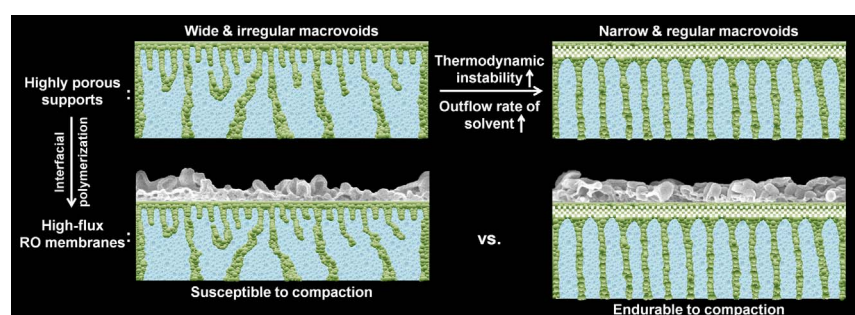
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ABSTRACT

Increasing the surface porosity of a support membrane has been proposed as an effective way to improve the water permeability of thin-film composite (TFC) reverse osmosis (RO) membranes by reducing the diffusion pathway in the active layer. In this work, we prepared a highly porous microstructured (HPμS) support membrane with a suitable mechanical strength to enhance the water permeability of an RO membrane. The HPμS support membrane was prepared by increasing the thermodynamic instability of a 10 wt% polymer solution and thereby facilitating rapid desolvation. The rapid desolvation formed the narrow and regularly arranged pore structure in the sublayer, and we proposed the mechanism for the sublayer structure formation based on analyses of the thermodynamic properties of such a binary system. Owing to the narrow and regular structure, the HPμS support membranes showed the exceptional mechanical strength, which was comparable to the strength of support membranes used for conventional RO membranes. Also, the HPμS support membranes successfully endowed an in-house RO membrane with the performance (water permeability of $4.68\,\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ and NaCl rejection of 98.3%) surpassing commercial RO membranes and thin-film nanocomposite membranes recently reported in the literature.

1. Introduction

Since Reid and Breton announced a symmetrical cellulose acetate membrane with 99% salt rejection in the late 1950s [1], many studies have focused on improving the membrane permeability as high as $4.6 \times 10^{-3}\,\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ [2]. For example, Loeb-Sourirajan developed an asymmetric cellulose acetate membrane with water flux that was an order of magnitude higher than that of the symmetric cellulose

acetate membrane [3]. Subsequently, Cadotte reported a thin-film composite (TFC) reverse osmosis (RO) membrane prepared via an interfacial reaction as an alternative to the cellulosic membranes [4]. Since then, there have been several approaches such as the proper selection of monomers used in polymerization or the control of morphology during polymerization reactions to attain further improvement of the membrane transport properties [2]. As a result, these approaches have resulted in about a 10^3-fold improvement in flux over the past decades [2]. Eventually, these technological advances in achieving higher water permeability, along with energy-efficient pumps and pressure exchangers, led to a dramatic reduction in the specific energy consumption for seawater desalination from ~16 to 2 kWh m^{-3} [5,6].

Although the energy saving achievable by further increasing the water permeability has become marginal, high-flux membranes are still desirable to reduce the membrane area required, the footprint of overall system, the use of chemical cleaning agents and the membrane replacement cost [2]. As such, many researchers have attempted to enhance the water permeability of RO membranes without compromising the salt rejection. To this end, various methods of surface modification have been employed to render a hydrophilicity on the membrane surfaces such as photochemical-, radical-, radiation-, redox-, and plasma-induced grafting as well as a physical coating of hydrophilic materials [2]. Alternatively, organic or inorganic nanomaterials such as graphene oxide (GO), carbon nanotubes (CNTs) and zeolites have been used to increase the hydrophilicity of membrane as well as to facilitate the diffusion of water molecules via well-defined pore channels [7–9]. In spite of these efforts, it is still hard to find the RO membranes achieving the water permeability higher than 4 L m^{-2} h^{-1} bar^{-1} with NaCl rejection above 98% because the modification of the active layer for improving water permeability inevitably entails the sacrifice of salt rejection.

As an alternative, support membranes have recently received a vast amount of attention as an important factor allowing enhanced water permeability in TFC membrane without sacrificing the salt rejection. Theoretically, an increased surface porosity of support can shorten the effective diffusion paths of permeating species, namely water and salts, in the active layer which is formed on the support [10–13]. As the reduction of diffusion paths can give the same effect of reducing the thickness of the active layer, the water flux can be enhanced without scarifying the salt rejection. Indeed, this behavior was experimentally demonstrated by a few studies [14–16]. As an instance, Lee et al. [14] demonstrated that a highly porous support membrane reinforced by single-layer GO sheets provided an in-house RO membrane with a higher water flux without decreasing salt rejection when compared to commercial RO membranes and those prepared via modification of the active layer. Pore-forming agents such as CNTs and SiO$_2$ nanoparticles were also employed to increase the porosity of support, resulting in improved water permeability without sacrificing the salt rejection [15,16]. However, tailoring the structure of support membrane using functional nanomaterials requires additional processes where oxidizing agents such as H$_2$SO$_4$ or HNO$_3$ are often used to disperse the nanomaterials, which could eventually lead to adverse environmental effects. Furthermore, the use of such nanomaterials unavoidably increases the cost of the membrane.

To address the issues aforementioned, we prepared a support membrane with high porosity and suitable mechanical strength by adjusting the thermodynamic instability of the polymer solution and thereby changing the morphology of the support membrane. Based on the previous work in which a highly porous support membrane was successfully fabricated with a 10 wt% polymer solution [14], we first prepared six kinds of 10 wt% polysulfone (PSf) polymer solutions by tailoring the composition of the solvent mixtures containing *N*-methyl-2-pyrrolidinone (NMP) and *N, N*-dimethylformamide (DMF), which have different affinities for PSf. Subsequently, we confirmed that desolvation of the polymer solutions was facilitated by increasing their thermodynamic instability, which formed narrow and regular pore

structures in the sublayer of the support membrane. This hypothesis was supported by our analyses of the thermodynamic properties of the polymer solutions along with in situ observations of the phase separation. The highly porous microstructured (HPµS) support membrane with the regular structure showed exceptional mechanical strength, which was comparable to the strength of support membranes used for conventional RO membranes. Furthermore, the HPµS support membrane was used to produce a compaction-endurable TFC membrane with higher water permeability and comparable salt rejection.

2. Materials and methods

2.1. Preparation of support membranes with different morphologies

Unless otherwise noted, all chemicals were purchased from Sigma-Aldrich and were used as received. To produce PSf (Udel® P 3500 MB7, Solvay Korea, Seoul) support membranes with distinctive morphologies, six types of support membranes were fabricated by varying the ratio of NMP and DMF in the solvent mixtures used to prepare a polymer solution of 10 wt%. The solvent mixtures had the following ratio of DMF with respect to NMP: 0, 0.25, 0.5, 0.75, 0.875 and 1. Other than the solvent composition, all the procedures for non-solvent induced phase separation (NIPS) were performed as explained previously [17]. Briefly, the polymer solutions were sonicated for 1 h to remove bubbles and were cast on a non-woven fabric with a casting knife set at a gate height of 200 µm. Then, the polymer solutions were immersed in tap water for solidification at room temperature. Each support membrane was marked as N1D0, N3D1, N1D1, N1D3, N1D7, and N0D1 based on the ratio of each solvent. For an effective comparison, the 15 wt% support membrane (15 wt% PSf and 85 wt% NMP) was also prepared as a control in the same way as the 10 wt% PSf support membranes (Fig. S1) since support membranes prepared from 15 to 25 wt% polymer solutions are commonly used for conventional RO membranes [14].

2.2. Preparation of thin-film composite membranes comprising support membranes with different morphologies

Among the as-prepared support membranes, the N1D0, N1D1 and N1D7 membranes were used to fabricate the TFC membranes via interfacial polymerization. For interfacial polymerization, two kinds of solutions were used: an aqueous solution containing 2 wt% *m*-phenylenediamine (MPD), 4 wt% camphor sulfonic acid, 1 wt% dimethyl sulfoxide, and 2 wt% triethylamine (Alfa Aesar, USA); and an organic solution of 0.1% (w/v) trimesoyl chloride (TMC) and n-hexane (Merck, Germany). Except for the composition of the additives used for interfacial polymerization, all the procedures were conducted as described previously [14]. Briefly, the support membranes were immersed in an MPD solution including several additives for 1 min. The excess MPD solution was removed from the membrane surface with a rubber roller. After that, the MPD-soaked support membranes were dipped in a TMC solution for 1 min. The as-prepared TFC membranes were cured at 60 °C for 10 min and were marked as TFC-N1D0, TFC-N1D1, and TFC-N1D7. To compare the separation performance and the long-term stabilities, the 15 wt% support membrane was also employed to prepare the TFC membrane using the same conditions as described above. The TFC membrane prepared using the 15 wt% support membrane was marked as a TFC-15 membrane.

2.3. Measurement of the viscosity and determination of the intrinsic viscosity

The viscosities of the polymer solutions were measured three times at room temperature using a rheometer (Physica MCR 101, Anton Paar, Austria). These values were used to determine the intrinsic viscosities, which can be used to estimate the solvent power for polymers. The