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Optimizing the preparation of multi-layered polyamide membrane via the addition of a co-solvent

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ABSTRACT

Polyamide membranes with controlled surface morphology were prepared by the interfacial polymerization of 1,3-phenylenediamine (MPD) with 1,3,5-benzenetricarbonyl trichloride (TMC) on polysulfone ultrafiltration supports. The addition of co-solvents (acetone, ethyl acetate, and diethyl ether) into the organic phase was used to control both the surface morphology and the polyamide network structures. The as-prepared membranes had multi-layered polyamide structures, which consisted of large (1 μm) and ordinal (100–300 nm) ridge-and-valley formations. Permeate flux and rejection reactions were successfully controlled by the types and amounts of co-solvents that were added. The optimal membrane conditions included the addition of 3 wt% ethyl acetate, with a NaCl rejection of more than 99% and a permeate flux of more than 1.8 m^3/(m^2 d) at 1.5 MPa, which was more than three times higher than the membranes prepared without a co-solvent.

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1. Introduction

Reverse osmosis (RO) and nanofiltration (NF) membranes currently are the most remarkable separation technologies due to their high removal properties with low amount of energy consumption [1]. RO membranes were developed to obtain safe and clean water and for application to various types of separation targets. Separation targets of RO membranes include inorganic monovalent ions, and RO membranes have the highest level of rejection of solutes among the separation membranes, such as monovalent ion, hardness components (ex. calcium, magnesium) and organic matters (ex. trihalomethane precursor, pesticides and deodorants). Several types of RO membranes have been developed and operated at pressures of approximately 0.5~6.0 MPa [1–3]. NF membranes possess an odd set of characteristics in which the removal of solutes is inferior to that of RO membranes, but the water permeability is superior. Furthermore, NF membranes are superior to RO membranes for the selective removal of solutes. For example, NF membranes can show a high degree of rejection toward bivalent electrolytes such as MgSO$_4$ and low rejection of monovalent electrolytes (NaCl), while RO membranes rejects almost all types of solutes from feed water because of their high removal properties [2]. Furthermore, the application of NF membranes is expected to expand in new directions, such as the pre-treatment of seawater for desalination and process separations such as the purification of pharmaceuticals, water purification and color removal from

soy sauce [1–3]. In order to expand the application of RO and NF membranes, the characteristics of these membranes, such as removal properties, water permeability, and resistance to chemicals and heat must be improved. In particular, the degree of water permeability could lead to a lowering of both the energy costs and impact on the environment.

In general, composite RO and NF membranes are divided into three layers. A bottom layer of polyester unwoven cloth with an approximate thickness of 100–200 μm is used for mechanical strength in the PA separation layer. The middle layer, which is composed of polysulfone (PSf) or polyethersulfone (PES) with an approximate thickness of 30–50 μm, is used to support the top layer. A top layer of polyamide (PA) or polyetherimide (PEI) with an approximate thickness of 100–200 nm is used for the separation of some solutes from feed water [3]. In particular, it is the top layer characteristics, such as solute removal and water permeability, that affects the membrane performance.

One method to achieve a high degree of water permeability is to improve monomer reactivity with additives in the water phase. For example, Hirose et al. reported that adding alcohol and ether in the water phase led to higher water permeability and higher salt rejection [4,5]. Zhao et al. also reported that adding hydrophilic additives such as o-aminobenzoic acid in the water phase led to higher water permeability and higher salt rejection [6]. But only a few papers have ever reported about the membranes fabricated with additives in the organic phase.

Recently, we were the first to report that a high degree of water permeability could be obtained with polyamide composite membranes by adding a co-solvent into the organic phase, which makes
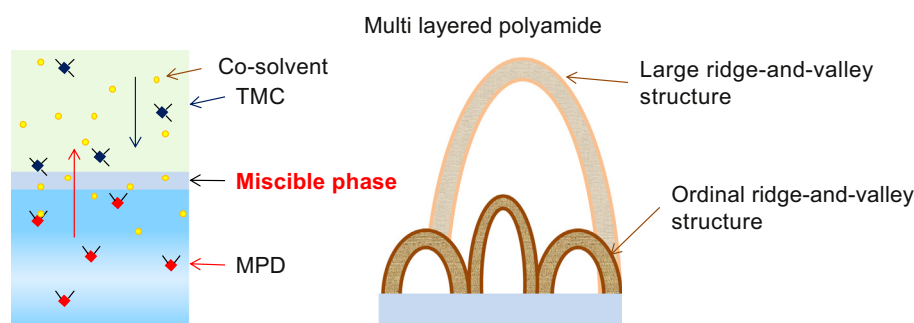
Multi layered polyamide

Fig. 1. Schematic model for the formation of a polyamide membrane using a co-solvent.

the organic (hexane) and water phases miscible [7,8]. The concept is quite different from that of additives in the aqueous phase. By the addition of co-solvent, "miscible phase" which is a place where MPD and TMC are able to exist together, is reportedly formed at the interface [7,8], and we reported that the properties of adding co-solvent into the organic phase were quite important in determining RO performance [7,8]. Fig. 1 shows a schematic model for the formation of polyamide membranes. During the first period of interfacial polymerization for membranes with a co-solvent, the addition of the co-solvent in the organic phase formed a "miscible phase" between the hexane and the water phases. By forming a "miscible phase", MPD and TMC reacted with each other in the miscible phase to form large ridge-and-valley structures. As the co-solvent added in the organic phase was soluble in water, it diffused to the water phase, and consequently the miscible phase would disappear. Therefore, after forming large ridge-and-valley structures, the MPD and TMC in the interface reacted with each other near the interface and formed ordinal sizes of ridge-and-valley structures. As a result, smooth and widespread polyamide structures were formed in the organic phase.

In a previous paper, we reported that the formation of a multi-layered polyamide structure depends on the concentrations of acetone as a co-solvent that was added into the organic phase [8]. The SEM images confirmed that a smooth, widespread, and loose polyamide structure was formed over an ordinal ridge-and-valley polyamide structure. These multi-layered structures had a high degree of water permeability while maintaining a high degree of rejection, which was controlled by the types of co-solvents that were added into the organic phase.

In the present study, novel RO membranes, which had high values for both salt rejection and high water permeability, were developed with the addition of co-solvents into the organic phase. We selected three types of organic solvents, including acetone, ethyl acetate, and diethyl ether, to use as co-solvents. Salt rejection and water permeability were examined in order to optimize the preparation conditions such as the types and concentrations of solvents. For these membranes, FT-IR (for amide content), SEM surface morphology, and desalination performance were evaluated using different types and concentrations of added organic solvents.

2. Experimental

2.1. Fabrication of a multi-layered polyamide membrane

Polyamide membranes were fabricated on ultrafiltration polysulfone (PSf) supports with approximate top-surface diameter of 20–30 nm [9] via the interfacial polymerization of 1,3-phenylenediamine (MPD) with 1,3,5-benzenetricarbonyl trichloride (TMC). The detailed process of membrane preparation was as follows [7,8]. First, the PSf supports were placed in an aqueous solution of 2 wt% MPD and 0.15 wt% sodium lauryl sulfate for 2 minutes, and

then the excess solution was removed. Subsequently, the PSf supports were immersed in a hexane solution containing 0.1 wt% TMC with 0.5–5 wt% co-solvent. In the present study, three types of solvents, acetone, ethyl acetate, and diethyl ether, were selected and added as co-solvents. After a polymerization reaction of approximately 60 seconds, the TMC solution was poured off, and the membrane was dried in air for 5–10 minutes. Finally, the as-prepared membranes were rinsed with deionized (DI) water.

2.2. Characterization

All the membranes used for the morphology characterization of the active layer were rinsed several times with deionized water, and were then dried under vacuum at 30 °C for 12 hours. FE-SEM images were obtained using a S-4500 (HITACHI, Japan) [4,10,11]. Cross-section TEM images were obtained using a H-7650 (HITACHI, Japan) [7,9]. The FT-IR spectra were collected using a Spectrum One (PerkinElmer, USA) [12]. The water contact angle was collected using a DM-500 (KYOWA Interface Science, Japan) [13,14,15].

Desalination performance was measured using RO/NF evaluation equipment [4,7,8]. The effective membrane area was approximately 44 cm^2. Rejections of probe molecules and permeate fluxes were measured through the as-prepared polyamide membranes. RO performance was evaluated with NaCl, MgSO$_4$ and IPA aqueous solutions, the concentrations of which were 2000, 2000, and 500 ppm, respectively, using a stainless-steel cross-flow filtration cell of custom-made equipment at a pressure of 1.5 MPa with a feed flow rate of 4–5 L/min, a pH of 6.5–7.0, and a temperature of 25 °C. Values of electrical conductivity for the concentrations of electrolyte and organic solutes were evaluated using a conductivity meter GM-117 (KYOTO ELECTRONICS, Japan), and gas chromatography, GC-17A (SHIMADZU, Japan), respectively. Rejection and permeate flux were calculated using the following equations:

$$\text{Rejection} = (1 - C_p/C_f)100$$

$$\text{Permeate flux} = \Delta V/(\Delta ts)$$

where C_p (mg/l) is the permeate concentration, C_f (mg/l) is the feed concentration, ΔV is the permeate volume (m^3), Δt is permeation time (s), and s is the effective membrane area (m^2). The precision in permeability and rejection measurements was estimated to be within $\pm$ 10% and $\pm$ 1%, respectively.

3. Results and discussion

3.1. Surface morphology

The surface morphologies of the as-prepared polyamide membranes were observed using SEM micrographs of the samples and magnifications of 50,000 in Figs. 2–4. The morphologies of the polyamide membranes that were prepared without a co-solvent