Preparation of high flux thin film composite polyamide membrane: The effect of alkyl phosphate additives during interfacial polymerization

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HIGHLIGHTS

► TBP and TPP were added during an interfacial polymerization for polyamide membranes.
► The membranes using TBP showed a remarkably increased flux and a reduced rejection of NaCl.
► From SEM and AFM data, the surface morphologies of the NF membranes were considerably changed.

GRAPHICAL ABSTRACT

SEM images of the surface morphologies of the TFC polyamide membranes with (a) no TBP and (b) 0.6 wt. % TBP as an additive in the organic solution.

ABSTRACT

Thin film composite (TFC) polyamide membranes have been used and progressed for desalination and pressure retarded osmosis. A preparation method of TFC polyamide nanofiltration (NF) membranes with enhanced flux is reported. The polyamide TFC NF membrane was fabricated by adding tributyl phosphate (TBP) and triphenyl phosphate (TPP) to an organic solution containing trimesoyl chloride (TMC) during an interfacial polymerization process. The membrane test was performed using a 2000 ppm of sodium chloride solution and a cross-flow permeation cell. The addition of TBP to the TMC organic solution exhibited much higher water flux than that of TPP. The resulting membrane using TBP showed a remarkably increased water flux and a slightly reduced rejection of sodium chloride. From SEM and AFM data, the surface morphologies of the TFC polyamide NF membranes were considerably changed compared to the membrane prepared without addition of TBP in the TMC organic solution.

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1. Introduction

The role of membrane technology in sustainable development of energy and water is becoming more and more evident. Due to the ability of the thin film composite (TFC) membrane to retain salts and organics dissolved in water with high efficiency, desalination [1–3], pressure retarded osmosis [4–7] and industrial water reuse via such a membrane are possible. For the last several decades a thin film composite polyamide reverse osmosis (RO) or nanofiltration (NF) membrane has been developed by an interfacial polymerization method [8–12]. Commercially available TFC membranes are composed of interfacially polymerized polyamide film as a selective layer and porous polysulfone membrane as a support layer. The
performance of the TFC membrane is generally determined during the interfacial polymerization. Since Cadotte and co-workers published a paper on the interfacial synthesis of RO membranes [13], a great amount of effort has been devoted to enhancing the performance of the TFC membrane [14–16]. For example, using nanoparticles during the preparation of the TFC polyamide membrane can enhance the performance of the membrane [17,18]. Tarboush et al. reported that the incorporation of a hydrophilic surface modifying macromolecules increased the NaCl separation ability and the stability of the TFC polyamide membrane [19]. Yoon et al. investigated the effect of membrane support on the resulting interfacially polymerized polyamide membrane [20]. The water flux of the TFC membranes based on a polyacrylonitrile nanofibrous support was much better than that of a commercial membrane.

The addition of different additives in the aqueous phase has been attempted to improve the water flux of the TFC membrane without a significant loss of its salt rejection capability. Kuehne et al. reported that the addition of the organic salt of triethylamine with camphorsulfonic acid could considerably increase the water flux, with no loss of salt rejection [21]. The addition of alcohols in the aqueous phase was another feasible means of increasing the TFC polyamide membrane performance. Kong et al. could increase the water flux of the TFC polyamide membrane by adding acetone in the organic phase [22].

In this study, a high flux thin film composite polyamide membrane synthesized by an interfacial polymerization method is reported. The effect of phosphate additives in the organic phase on the membrane performance to improve the water flux was investigated. The interaction between tributyl phosphate and aromatic acid chloride in the organic phase was found to change the surface morphology and the membrane performance.

2. Experimental

2.1. Materials

Polysulfone (PSF) ultrafiltration (UF) membranes were provided by Woongjin Chemical Co., Ltd. in Korea. The membranes were used as support for interfacial polymerization. 1,3-phenylene diamine (MPD) was purchased from DuPont. 1,3,5-Benzenetricarbonyl trichloride (TMC), triethylamine (TEA), 2-ethyl-1,3-hexanediol (EHD), camphorsulfonic acid (CSA), dimethylsulfoxide (DMSO), tributyl phosphate (TBP), and triphenyl phosphate (TPP) were purchased from Sigma-Aldrich. Isoparaffin (ISOL-C) was provided by SK Chemical in Korea. All chemicals were used as received. The deionized (DI) water used here was produced with a Milli-Q system (Millipore).

2.2. Preparation of polyamide membranes

Polyamide membranes were prepared by interfacial polymerization on a PSF UF membrane. The PSF membrane was dipped into an aqueous solution containing MPD, TEA (2–3 wt.%), DMSO (1 wt.%), EHD (0.2–0.3 wt.%), and CSA (1–2 wt.%) in DI water, after which the excess solution was removed by squeezing with a soft rubbery roller after 1 min. The PSF membrane was then immersed in a solution of 0.1 wt.% TMC and different concentrations of TBP or TPP in isoparaffin. After 1 min of reaction, the membrane was dried in air for 5 min. The membrane was rinsed with a 0.2 wt.% Na2CO3 solution.

2.3. Membrane characterization

The Fourier transform infrared spectra (FT-IR) of the TMC solution were obtained by a FT-IR spectrophotometer (NICOLET 5700, Thermo Electron Corporation, USA). The surface morphologies were observed by means of scanning electron microscopy (SEM, XL30S, PHILIPS, Netherlands) and atomic force microscopy (AFM, Nanoscope IV, Digital Instruments, USA).

2.4. Permeation tests

The water flux and salt rejection capabilities of the membranes were measured with 2000 ppm of NaCl at a pressure of 225 psi and a temperature of 25 °C. A conductivity meter was used for the salt rejection test. The effective membrane area was 18 cm².

3. Results and discussion

3.1. Membrane performance with different additives

A relatively high flux polyamide TFC membrane could be fabricated by variation of the additive concentrations of EHD, CSA and DMSO in an aqueous solution. The water flux of the membrane was significantly increased from 8 to 40 gal/ft² day without loss of NaCl rejection due to the effect of additives in an aqueous MPD solution, as shown in Table 1. The rejection levels were similar for all of the membranes, at 97.5–98.5%. The water flux increase results from the complex formation between MPD and EHD. The hydroxyl group of EHD facilitates a hydrogen bonding interaction with the amine group of MPD. The hydrophobic alkyl group of EHD transports MPD more to the organic solution, which builds up the concentration of MPD in the interface of organic and aqueous phases. The build-up of MPD–EHD complex in the interface can increase the surface area of the TFC polyamide membrane. In the case of CSA, organic salts between the sulfonic acid group of CSA and the amine group of TEA are formed and the organic salts may not hinder the interfacial polymerization between MPD and TMC from Table 1. The water soluble organic salts can be washed out after polymerization. The wash-out of the organic salts increases water flux due to the enhanced porosity of the resulting polyamide membrane. DMSO in MPD aqueous solution can also affect the performance of the TFC polyamide membrane. DMSO can swell the polysulfone support membrane. The MPD aqueous solution can be easily penetrated into the swelled support membrane, which can increase the water flux of the resulting TFC polyamide membrane. However, DMSO addition in the MPD aqueous solution without the addition of EHD or CSA could not influence the membrane performance. DMSO addition in the MPD solution containing EHD or CSA considerably enhanced the water flux with slight loss of the salt rejection.

In order to demonstrate the effect of the additives in an organic solution on the membrane performance, the concentrations of TBP and TPP were varied under the same condition to that of the aqueous solution. The water flux and NaCl rejection of the membranes with additives of TBP and TPP in the TMC organic solution at different concentrations are shown in Fig. 1. For the membranes using TBP as an additive in the organic solution, an increase in the water flux was observed with no significant loss of salt rejection when the amount of TBP in the organic solution was increased up to 0.9 wt.%. However, it was found that with the increase in TPP concentration in the TMC organic solution, the water flux was slightly decreased without loss of salt rejection.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Flux (gal/ft² day)</th>
<th>Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPD without additives</td>
<td>8.33</td>
<td>97.69</td>
</tr>
<tr>
<td>DMSO (1 wt.%)</td>
<td>7.76</td>
<td>98.19</td>
</tr>
<tr>
<td>CSA (1 wt.%)</td>
<td>11.25</td>
<td>97.84</td>
</tr>
<tr>
<td>EHD (0.3%)</td>
<td>12.4</td>
<td>98.6</td>
</tr>
<tr>
<td>DMSO/CSA (1 wt.%/1 wt.%)</td>
<td>36.5</td>
<td>97.94</td>
</tr>
<tr>
<td>DMSO/CSA/EHD (1 wt.%/1 wt.%/0.3 wt.%)</td>
<td>41.12</td>
<td>97.57</td>
</tr>
</tbody>
</table>

Table 1: The effect of additives in MPD solution on the performance of TFC polyamide membranes.
The effect of TBP and TPP on the TFC polyamide membrane was confirmed by FT-IR. Fig. 2 shows the FT-IR spectra of the two TMC organic solutions using TBP and TPP as additives. The addition of TBP into the TMC organic solution shifted the peak at 1772.5 cm\(^{-1}\), which is assigned to the absorption peak of the benzoyl chloride group to 1760.2 cm\(^{-1}\). In the case of TPP in the TMC organic solution, this peak shifted less (1771.6 cm\(^{-1}\)) than that of TBP. This red shift can be explained in terms of the interaction between the additives and TMC. The phosphate group of TBP is believed to have formed a complex with the carbonyl chloride group of TMC in the organic solution due to the dipole–dipole interaction between the two groups from the red shift of benzoyl chloride of TMC, as shown in Fig. 2. Mickols et al. [23] reported that the phosphate was capable of forming “associations” with TMC and the term “associations” was intended to include covalent bonds, complexes, weak bonds and other interactions which form between the phosphate and the TMC. However, in our study, it was confirmed that the alkyl group of the phosphate is very important for the complex formation between the phosphate and the TMC. In the case of TPP, the steric hindrance of the phenyl group of TPP reduces the possibility of complex formation between TPP and TMC compared to that of TBP additive. The dipole–dipole complex formation between TMC and TBP generates concentration polarization of TMC in the organic solution. TMC with no complex becomes more hydrophilic than TMC with a complex due to three butyl groups of TBP. This implies that the concentration of the TMC on the interface is lower than the concentration in the bulk during the interfacial polymerization. Moreover, the carbonyl chloride group of TMC will be shielded due to the complex between the phosphate and TMC. This shield effect decreases the reactivity of TMC to MPD, which results in a slight loss of salt rejection.

3.2. Membrane morphology

The surface morphologies of the TFC polyamide membranes prepared with TBP as an additive in the TMC organic solution are shown in Fig. 3. Both membranes show a unique ridge-and-valley
structure. With the addition of TBP into the TMC organic solution, the surface morphology of the membrane prepared without TBP addition was changed. The addition of TBP in the TMC organic solution during interfacial polymerization tends to increase the ridge portion of the polyamide TFC membrane. Most of the ridge film covers the valley film.

AFM images are shown in Fig. 4. The AFM image of the membrane with no TBP addition shows a ridge-and-valley structure. The membrane with the addition of 0.6 wt.% TBP in the TMC organic solution indicates that the surface of the TFC polyamide film has a broad ridge and a loose structure compared to the membrane without TBP addition. The AFM images show similar morphology to those noted in the SEM photographs.

4. Conclusion

TFC polyamide membranes were synthesized by an interfacial polymerization method. The aqueous solution composition was optimized for a high flux polyamide membrane. TBP and TPP were added to a TMC organic solution to enhance the performance of the TFC polyamide membrane. TBP as an additive in the TMC organic solution considerably improved the water flux compared to that without TBP addition. TBP as an additive has much better performance than TPP due to the complex formation between TBP and TMC in an organic solution, as revealed from FT-IR spectra. SEM and AFM revealed that the membrane with the TBP addition had a broad ridge structure compared to the membrane without TBP addition.

References

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