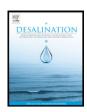
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### High flux polyamide thin film composite forward osmosis membranes prepared from porous substrates made of polysulfone and polyethersulfone blends



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#### HIGHLIGHTS

- High flux TFC FO membranes were made from polyamide on PSf/PES blend supports.
- The ratio of PSf/PES affected the porous structure and top skin section thickness.
- The initial roughness from the substrate was amplified in the interfacial copolymerization process.

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#### ABSTRACT

High water flux polyamide thin film composite (TFC) forward osmosis (FO) membranes with porous supporting substrate layers made from polysulfone (PSf) and polyethersulfone (PES) blends of varied PSf/PES ratio were prepared. The impact of PSf/PES ratio on the porous structure of the supporting substrates and resulting properties of TFC-FO membranes formed were investigated. There were three distinguished sections observed in the cross-sections of the substrates, a top dense skin section, a central porous section, and a bottom open section according to SEM images. With the joint favoring effects from maximum open bottom section percentage in the cross-section and maximum surface roughness, membrane samples made from substrates with a PSf/PES ratio of 2/3 exhibit a highest water flux of 2/3 exhibit a highest water flux of 2/3 h for 2/3 m NaCl draw solution from a de-ionized water feed solution. And their water flux reached 12.7 L/m $^2$  h under PRO mode and 10.6 L/m $^2$  h under FO mode from an ocean seawater feed solution containing 3.5 wt% of NaCl. This high flux is related to the existence of heavily populated cone shaped protrusions observed on the surfaces of formed TFC-FO membranes, resulting from amplification in initial surface roughness of the porous substrate during the active layer forming interfacial co-polymerization process.

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#### 1. Introduction

Having adequate clean water resources are critical for the wellbeing of almost all aspects of modern society including economy, public health, national security, ecosystem and others. However, with an exponentially growing population, water scarcity is becoming a serious global challenge in our time. It is reported that more than 1.2 billion people in the world are lacking access to clean and safe drinking water [1,2]. Extra incentives have been put in to search for technological approaches to produce clean water under controllable cost, e.g. desalination of seawater or brackish water [3,4] and reuse of reclaimed water [5].

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Since more than 97% of the global water resource is presented as seawater and most of the water shortage in the earth happened in the coastal heavily populated regions, desalination of sea water is becoming more and more important as an approach in generating clean and safe water to ease the global water shortage problem. Reverse osmosis (RO) is a familiar process widely used in the seawater desalination, but the applications are greatly thwarted by its high cost resulting from high energy consumption, equipment requirement, and membrane fouling propensity.

FO, as an emerging water treatment technology, has gained increasing interest in recent years. In the process, a draw solution containing specifically designed solute, e.g. ammonium bicarbonate and glucose, which have higher osmotic pressure to draw water from the feed solution such as sea water, and then clean water may be generated by separating water from the draw solution. Compared to RO, FO has many potential advantages: (1) FO process is a spontaneous low pressure process that needs lower external energy; (2) even it has

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high rejection for a wide range of contaminants, there is much less membrane fouling [6–9]. In addition, this osmotic-driven low pressure membrane separation process possesses great potential to achieve energy-efficient separations in many areas, not only for seawater desalination [10,11], but also for waste water treatment [12–14], food processing [15–17], pharmaceutical industry [18,19], electric power production [20–22] and so on.

Even though many researchers pay much attention to develop the new draw solution [23,24], one of the key issues to increase the efficiency of the process still lie in the development of high water flux FO membrane with optimized structures. M. Elimelech found that neither polyamide RO composite membrane, nor cellulose triacetate RO membrane could be used for FO processes due to low water flux of 1-2 L/ m<sup>2</sup> h [11]. He also found that commercialized cellulose triacetate (CTA) FO membranes with optimized structure showed higher water flux of 6–8 L/m<sup>2</sup> h. However, these water flux values are still far too low from what is expected for applications in practical FO systems. In a conventional RO system, the active layer of the membrane is the crux of the separation while the substrate of the membrane was mainly to provide support under higher pressure. However, in FO system, both the solute and water need to diffuse in the porous substrate before reaching the thin active layer, the structure and property of the substrate play greater role. The thin film composite membranes used for high flux FO process should have their own optimized substrate structure other than those for RO processes. Currently a lot of efforts have been put in to explore the high water flux in FO process.

Recently, interesting works focusing on using novel materials from copolymerization, grafting, surface modification and polymer blend, have been reported in optimizing the porous structures of TFC membranes substrate for higher water flux FO processes [25–27]. Compared to the development of new membrane materials, modifying the existing materials is relatively simple and effective. Among them, blending a novel component into existing one during the pore formation process, adjusting the porous structure and properties of the supporting substrate simultaneously, has become one of the research focuses in the search for high flux FO membranes. Here, we reported our recent results in the efforts to prepare high water flux polyamide TFC-FO membranes by blending less polar polyethersulfone (PES) component into polysulfone (PSf) component in the porous supporting structures. Morphologies and physical characteristics of the resulting PSF/PES blending membranes were investigated. It is demonstrated that high water flux FO membrane with stable high salt rejection may be obtained with minimum twist from the current TFC membrane preparation process.

#### 2. Experimental

#### 2.1. Materials

Polysulfone (PSf, P-3500 LCD MB7, Mn = 80,000) and Polyethersulfone (PES, veradel3000P, Mn = 62,000) were purchased from Trump Chemical Corp., China, and dried in a vacuum oven at 80 °C for 24 h before use. N-methyl-2-pyrrolidone (NMP, anhydrous, >99%), polyethylene glycol 600 (PEG600, anhydrous, >99%), 1,3-phenylenediamine (MPD, >99.5%), 1,3,5-benzenetricarbonyl trichloride (TMC, 98%), n-hexane (97%), NaCl (crystals) were all purchased from Aladdin Reagent Co., Ltd., China.

#### 2.2. Membrane preparation and characterization

#### 2.2.1. Fabrication of membrane substrates

Polymer mixtures of PSf/PES with the weight ratios of 5/0, 4/1, 3/2, 2/3, 1/4 and 0/5, were prepared and named as M1s, M2s, M3s, M4s, M5s and M6s, respectively. To fabricate membrane substrates for interfacial polymerization, polymer casting solutions containing 18 wt.% of the above polymer mixtures and 10 wt.% of PEG were prepared using NMP as solvent.

The casting solutions were de-aerated under reduced pressure for 1 h before casting onto a glass plate with a casting knife of 130  $\mu m$  in thickness. The nascent membranes were then immersed into a water coagulation bath immediately at room temperature. After residual solvent was removed by washing in a DI water bath for 1 h, the samples were kept in another DI water bath before interfacial polymerization was carried out.

#### 2.2.2. Interfacial polymerization of TFC-FO membrane

The PSf/PES substrates were first immersed in an aqueous solution of 2 wt.% MPD for 2 min. A filter paper was used to remove the excess MPD solution. Next, the membrane was immersed into a 0.1 wt.% TMC in n-hexane solution for 1 min. The composite membranes were then cured at 95 °C for 3 min, followed by cooling in the air for 1 min. Thereafter the fabricated TFC-FO membranes were rinsed thoroughly to remove the residual solvent and stored in DI water at room temperature. We named the composite membranes after polymerization as M1c, M2c, M3c, M4c, M5c and M6c corresponding to M1s to M6s respectively.

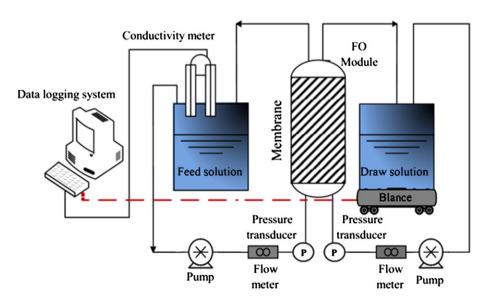


Fig. 1. Schematic diagram of FO system.

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