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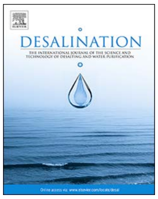
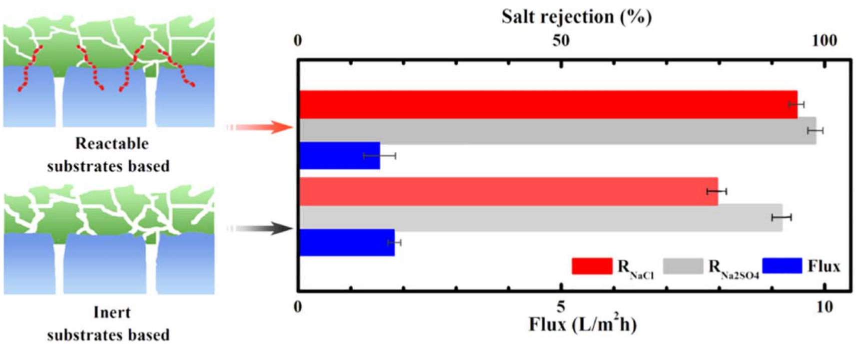


Reactable substrate participating interfacial polymerization for thin film composite membranes with enhanced salt rejection performance

Zhikan Yao[a], Hao Guo[a], Zhe Yang[a], Chuner Lin[b], Baoku Zhu[b], Yingchao Dong[c], Chuyang Y. Tang[a,*]

[a] Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong, China
[b] Key Laboratory of Macromolecule Synthesis and Functionalization (Ministry of Education, MOE), ERC of Membrane and Water Treatment (MOE), Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, China
[c] Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian, China

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we investigate the use of reactable substrates for interfacial polymerization of polyamide membranes. Two reactable group (hydroxyl group) contained substrates were prepared. Using *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) as monomers, thin film composite (TFC) membrane formed thereon displayed varying film morphology, chemical composition and separation performance. The substrate participating TFC membrane showed a thicker rejection layer with greater crosslinking density. The latter was caused by the formation of ester bonds in addition to amide bonds. This polyamide/polyester composite rejection layer had greatly enhanced NaCl and Na_2SO_4 rejection compared to the control membrane prepared on inert substrate. We further proposed a conceptual model that highlighted the important role of amphiphilic copolymers as (1) MPD enrichment loaders, (2) reactive monomers and (3) surfactants in the interfacial polymerization process.

1. Introduction

Membrane based technologies, such as reverse osmosis (RO) and nanofiltration (NF), play an increasingly important role in addressing the grand challenges of water shortage [1–4]. Most of the modern RO and NF membranes used for desalination and water reclamation are thin film composite (TFC) membranes prepared by interfacial polymerization [5–11]. In a typical interfacial polymerization process, a

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* Corresponding author.
E-mail address: tangc@hku.hk (C.Y. Tang).

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TFC membrane is obtained by forming an ultra-thin selective polyamide layer on a porous substrate through a condensation polymerization [12,13]. Water phase composition [14–18], organic phase composition [18–21], morphology and physicochemical property of substrate [22–26] and polymerization conditions [27,28] are important factors influencing the performance of TFC membrane. As the sites for the interfacial polymerization, the substrate not only provides the appropriate mechanical strength to the formed polyamide rejection layer, but also has direct impacts on the formation of the rejection layer.

The structure and surface morphology of the substrate plays a critical role on the formation of the polyamide rejection layer [10,23,24]. For example, TFC membrane formed on polysulfone substrates with small pore sizes had better salt rejection [10]. In addition, the membrane separation properties also depend strongly on the surface wetting properties of the substrate. Several studies have reported enhanced salt rejection for TFC membranes formed on hydrophilic substrates due to the formation of thicker rejection layers [7,23,25]. However, the use of hydrophilic substrates often lead to inadequate adhesion between the polyamide layer and the substrate [29].

In this work, we designed polyvinyl chloride (PVC) substrates containing reactable hydroxyl groups that can participate in the interfacial polymerization process. Specifically, the reactable groups were introduced by blending amphiphilic copolymers of methyl methacrylate and 2-hydroxyethyl methacrylate (P(MMA-*co*-HEMA)) into the PVC substrates. The separation properties of the TFC membranes prepared on these reactable substrates were systematically investigated. The findings in this study provide new insights on the role of substrate on the formation of polyamide rejection layer and thus the overall performance of TFC membranes.

2. Materials and methods

2.1. Materials

Two amphiphilic copolymers, P(MMA-*co*-HEMA), were prepared different ratios of methyl methacrylate and 2-hydroxyethyl methacrylate. Their molecular structures and the synthesis procedures are presented in Supplementary Information S1. Table 1 shows the key properties of the two copolymers, including HEMA content, molecular weight, and polydispersity index (PDI).

Unless specified otherwise, all other chemicals were used without further purification. PVC (Mn ~ 47,000), *N*,*N*-dimethylacetamide (DMAc, 99%), *n*-hexane (for HPLC, ≥95%), lithium chloride (LiCl, anhydrous, 99%), *m*-phenylenediamine (MPD, 99%) and trimesoyl chloride (TMC, 1,3,5-benzenetricarbonyl trichloride, 98%) were purchased from Sigma-Aldrich. Polyethylene glycol 400 (PEG400), trisodium phosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$), sodium chloride (NaCl) and sodium sulfate (Na_2SO_4, anhydrous) were all analytical reagents and obtained from Dieckmann company. Deionized water used throughout this work was supplied from a Milli-Q system (Millipore).

2.2. Preparation of membrane substrates

The reactable substrates M1 and M2 were prepared by the traditional non-solvent induced phase separation (NIPS) method by blending copolymer-1 and copolymer-2 into the PVC dope solution, respectively (Table 2). In a typical casting, a dope solution was spread into a thick film by an automatic film applicator (Elcometer 4340, Elcometer, adjusted at a gate height of 150 μm). The nascent film was coagulated in a deionized water bath at room temperature (about 25 °C) and the formed substrate was stored in deionized water before further use. A control substrate of M0 was also casted without the addition of any reactable copolymers.

Table 1
Molecular weight and HEMA content for the synthesized copolymers.

ID	HEMA content (wt%)[a]	Mn[b]	Mw[b]	PDI[b]
Copolymer-1	36.1	38,200	68,700	1.80
Copolymer-2	54.9	37,200	58,800	1.58

[a] Calculated from ^{1}HNMR measurement.
[b] Calculated from GPC result.

Table 2
The compositions of casting solution for membrane substrates.

ID	PVC (wt%)	Copolymer-1 (wt%)	Copolymer-2 (wt%)	PEG400 (wt%)	LiCl (wt%)	DMAc (wt%)
M0	12	–	–	3	1	84
M1	14	1.5	–	1	0.5	83
M2	14	–	1.5	1	0.5	83

2.3. Interfacial polymerization

MPD and TMC were used as monomers to form rejection layer on the reactable substrate by interfacial polymerization following a reported procedure [15]. In summary, an aqueous solution of 1% (*w/v*) MPD with 0.6% (w/v) Na_3PO_4 as the acid acceptor was poured onto a substrate surface and allowed to contact the surface for 1 min. After draining off the excess MPD solution, the residual droplets of MPD solution were removed from the substrate by rolling a rubber roller across the surface. Afterwards, the organic phase solution with 0.05% (*w/v*) TMC in *n*-hexane was poured onto the substrate surface for 30s. After removing excess organic solution, the membrane was rinsed using *n*-hexane to wash away residual reagents. The resulting membrane was immersed in deionized water at 50 °C for 10 min for further polymerization. Finally, the prepared membrane was stored in deionized water before characterization. The membrane prepared on M0, M1 and M2 were then denoted as TFC-0, TFC-1 and TFC-2, respectively.

2.4. Membrane characterization

Membrane surface and cross-section (fractured in liquid nitrogen) morphologies were imaged by a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi) after sputter-coated with a thin layer of gold (SCD 005, BAL-TEC). SEM images were analyzed to calculate the surface pore size of the substrate using image analysis software (Image-Pro Plus, Media Cybernetics, Inc.). Atomic force microscopy (AFM, Multimode 8, Bruker) was applied to exam the surface roughness of membrane, in which R_a (average roughness) and roughness ratio were analyzed by software Nanoscope Analysis (Bruker) with 5 μm × 5 μm scanning range. The water contact angle (WCA) of the substrates and TFC membranes were measured with an optical instrument (Attension Theta, Biolin Scientific) equipped with video capture for predicting hydrophilicity. X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA system, PHI Co.) was used to measure the composition of a membrane surface. Al Ká radiation (1486.6 eV) was adopted as X-ray source and run at a power of 250 W (14.0 kV, 93.9 eV) with an electron take off angle of 30° relative to the sample plane. The data were analyzed using the AugerScan 3.2 software provided by RBD Enterprises, Inc. SurPASS electrokinetic analyzer (SurPASS™ 3, Anton Paar) equipped with an adjustable gap cell was utilized to evaluate the surface charge properties (zeta potentials) and isoelectric point (IEP) of the membranes, following a standard operation using 1 mmol/L KCl aqueous solution as the testing solution [30].

2.5. Filtration performance tests

A laboratory-scale cross-flow membrane filtration setup was applied to evaluate the pure water flux and salt rejection of the prepared