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Polyamide thin film composite membrane prepared from *m*-phenylenediamine and *m*-phenylenediamine-5-sulfonic acid

Zhou Yong [a], Yu Sanchuan [b], Liu Meihong [c], Gao Congjie [b,*]

[a] *College of Material Science and Chemical Engineering, Zhejiang University, Hangzhou, 310027 China*
[b] *The Development Center of Water, Treatment Technology, SOA, Hangzhou 310012, China*
[c] *Zhejiang University of sciences, Hangzhou 310028, China*

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Abstract

Thin film composite (TFC) membranes based polyamide were prepared with *m*-phenylenediamine (MPD), *m*-phenylenediamine-5-sulfonic acid (SMPD) and trimesoyl chloride (TMC) through interfacial polymerization technique on the polysulphone supporting film. The membranes were characterized using permeation experiments with salt water, attenuated total reflectance infrared (ATR-IR) and X-ray photoelectronic spectroscopy (XPS) as well as scanning electronic microscopy (SEM). This study has shown that the active layer of TFC membrane is aromatic polyamide, including sulfuric acid function group (-SO_3H) according to the result of ATR-IR and XPS. The NaCl rejection of RO membranes decreased and the flux increased when W_{SMPD}/W_{MPD} increased from 0 to 1, and the linear part with pendant -COOH in membrane barrier layer increased with the increase of SMPD content, but the surface of membrane becoming smoother and smoother with the increase of SMPD content. So the membranes performance mainly was determined by chemical structure in their barrier layer.

Keywords: Polyamide; Thin-film composite membrane; Trimesoyl chloride; *m*-Phenylenediamine; *m*-Phenylenediamine-5-sulfonic acid

1. Introduction

Interfacial polymerization is copolymerization of two reactive monomers dissolved in two immiscible solutions, respectively. The monomers can meet and react only at the interface of the solutions when two solutions are contained in a reaction chamber. As reaction continues, polymer film is formed at the interface. The film is usually very thin because the growing interfacial polymer behaves as a barrier to diffusion of the two monomers, and the polymerization levels off at a limiting thickness, typically of the order of micrometre (μm) or less. To provide durability to the fragile films, the interfacial polymerization was frequently carried out at the surface of a microporous substrate, in which case the result is called a thin-film composite membrane [1].

The current worldwide expansion and diverse application of the RO technology has resulted from the introduction of thin-film-composite (TFC) membranes by interfacial polymerization in 1972 [2]. Most of thin skin layer in commercial are aromatic polyamides or their derives [3]. The material used to produce the skin layer included the aliphatic or aromatic diamines or the mixture of them [4].

In the previous research, how membrane performance is related to the molecular structure of aromatic polyamides had been studied too. Hirose et al. [5] studied the relationship between the surface structure of skin layers of crosslinked aromatic poly amide RO membranes and their RO performance. Seung-Yeop Kwak [6] characterized the RO permeability in conjunction with the macromolecular structures and inherent polymer properties for crosslinked and linear model aromatic polyamides by cross polarization/magic angle spinning (CP/MAS). Juhn et al. [7] proposed the mechanical strength of the barrier layer should be an important factor determining its performance. Permeation experiments were

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* Corresponding author. Tel.: +86 571 88935362.
E-mail address: zhouyong771014@163.com (G. Congjie).

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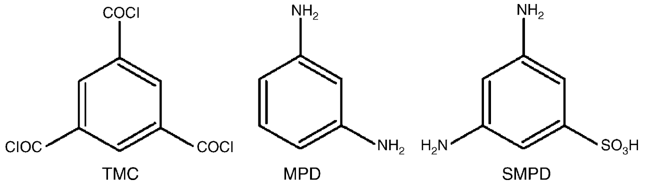

Fig. 1. Monomers for prepared TFC membranes.

then performed to correlate the mechanical strength to the permeation performance of the composite membranes. The experiments indicated that the permeation behavior of composite membranes with a high rupture strength barrier layer agreed well with the solution-diffusion transport mechanism.

It is known that low water permeability of the membranes fabricated from the various aromatic polyamides stemmed from the rigid cross-linked structure [8]. Incorporation of various polymers such that poly(vinylalcohol) and poly(vinylphenol) to the aromatic polyamides have been studied to the mitigate cross-linked barrier with bulky groups in polymer backbone or side chain [9–11].

Reverse osmosis (RO) membranes based polyamide were prepared with *m*-phenylenediamine (MPD), *m*-phenylenediamine-5-sulfonic acid (SMPD) and trimesoyl chloride (TMC) through interfacial polymerization technique on the polysulphone supporting film. We tried to enhance the flux by addition of SMPD to MPD. Fig. 1 was the chemical structure of three monomers. The membranes were characterized using permeation experiments with salt water, attenuated total reflectance infrared (ATR-IR), and X-ray photoelectronic spectroscopy (XPS) as well as scanning electronic microscopy (SEM). The relation of RO performance and chemical structure, morphology of membranes was elucidated.

2. Experimental

2.1. Synthesis of polyamide and their water absorption

Water adsorption of membrane material has been used to study the correlation of material structure and membrane flux [12]. The same method was used to synthesize the polyamide powders of MPD/TMC, MPD + SMPD/TMC. The aqueous solution contained 2% MPD, mixture of MPD and SMPD ($W_{\mathrm{SMPD}}/W_{\mathrm{MPD}}$ is from 0.1 to 1) and the organic solution was IP1016 solution (isoparaphin type hydrocarbon oil made by IDEMITSU Chemical Co. Ltd.) containing 0.10% (w/v) of TMC.

Water uptake of the dried polyamides was measured as follow: samples of polyamide powder were heated in tared glass pan at 100 °C under partial vacuum 12 h. The samples were weighed and then were placed in a humidity and temperature controlling chamber (Chang Zhou institute of testing equipment, China). The reading was 95% RH at 30 °C. Sample weights were determined twice a day.

2.2. Preparation of TFC membrane

To fabricate the TFC membrane, support membrane composed of microporous polysulphone (The Development Center of Water Treatment Technology, SO A, China) was clamped between two Teflon frames that were 0.8 cm high and inner cavity 15 cm × 20 cm in an assembly clean room. An aqueous solution of *m*-phenylenediamine (MPD, Shang Hai AMINO-CHEM CO. LTD, purity >99.5%) and *m*-phenylenediamine-5-sulfonic acid (SMPD, Shang Hai AMINO-CHEM CO. LTD, purity >99.0%) was poured on top of the support membrane and allowed to soak in 2 min. The surface was rolled with a soft rubber roller to eliminate some little bubble during soaking procedure. Excess solution was drained off the surface by standing the holder on the top and bottom edge until no excess liquid exists. The holder was then held at a 30° and the organic solution of trimesoyl chloride (TMC, Qin Dao Ocean Chem. Co, purity >99.0%) was poured into the frame from top to bottom; the holder was then lowered quickly. After a 20 s residence time, the excess organic solution was poured off the surface, and the frame with membrane was held at 80 °C in a hot air dryer for 5 min so that a skin layer was formed on the supporting membrane. The composite reverse osmosis membranes were washed in pure water (<2 μs/cm) and kept in 1% $NaHSO_3$ solution.

The aqueous solutions in this study contained total 2.0% (w/v) of MPD and SMPD mixture and $W_{\mathrm{SMPD}}/W_{\mathrm{MPD}}$ is from 0.1 to 1, 3.0% of triethylamine, camphor sulfonic acid used to regulate pH 8.5 to absorb the hydrochloric acid (HCl) from the interfacial reaction. The organic solution was IP 1016 solution (isoparaphin type hydrocarbon oil made by IDEMITSU Chemical Co. Ltd.) containing 0.10% (w /v) of TMC.

2.3. Membrane performance evaluation

The membrane samples were picked carefully under a fluorescent lamp to avoid some obvious deficits before test. All tests for RO performance were conducted at 1.5 MPa using a 2000 mg/L NaCl solution (pH 7.0) at 25 ± 2 °C (with fluxes corrected to 25 °C) in cross-flow cells (Fig. 2). Circular membrane samples with a diameter of 40mm were placed

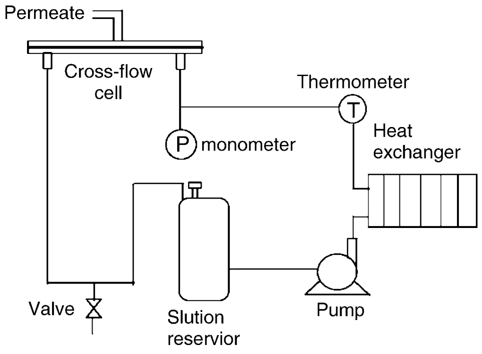

Fig. 2. Permeation test rig.