Journal of Membrane Science 469 (2014) 397–409

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Fabrication and characterization of a novel poly (amide-urethane@imide) TFC reverse osmosis membrane with chlorine-tolerant property

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ARTICLE INFO

Article history:
Received 24 December 2013
Received in revised form
11 June 2014
Accepted 15 June 2014
Available online 2 July 2014

Keywords:
Reverse osmosis membrane
Poly(amide-urethane@imide)
Two-step interfacial polymerization
Chlorine-tolerant
Ultrathin polyimide film

ABSTRACT

A novel poly(amide-urethane@imide) reverse osmosis (RO) composite membrane with chlorine-tolerant property was prepared on a polysulfone supporting film through two-step interfacial polymerization. The crosslinking agent – 5-choroformyloxyisophaloyl chloride (CFIC) was first reacted with 4-methyl-phenylenediamine (MMPD) via interfacial polymerization to get the nascent poly(amide-urethane) base membrane (CFIC–MMPD) without curing treatment. Then the resultant base membrane contacted again with the second aqueous solution containing functional secondary amine – N,N′-dimethyl-*m*-phenylenediamine (DMMPD) to obtain the poly(amide-urethane@imide) TFC RO membrane (MMPD–CFIC@CFIC–DMMPD). X-ray photoelectronic spectroscopy (XPS) was combined with attenuated total reflectance infrared (ATR-IR) to verify that the ultrathin polyimide film (CFIC–DMMPD) has been successfully grafted on the surface of the MMPD–CFIC base membrane. The images of scanning electronic microscopy (SEM) and atomic force microscope (AFM) showed that the poly(amide-urethane@imide) membrane has much smoother, more hydrophilic surface than the poly(amide/imide-urethane) membrane (MMPD/DMMPD–CFIC) prepared by conventional one-step interfacial polymerization of CFIC and composite MMPD/DMMPD. However, the permeation experiment revealed that the poly(amide-urethane@imide) membrane has a slight loss in both salt rejection and water flux than the poly(amide/imide-urethane) membrane and conventional commercialized polyamide membrane (MPD–TMC), but exhibits better chlorine-tolerant property due to the introduction of ultrathin polyimide film (CFIC–DMMPD) on the outmost surface of the TFC RO membrane, and the combination of IR and XPS analyses shows a good agreement with the chlorine exposure results of membranes.

1. Introduction

Reverse osmosis (RO) membrane technology is increasingly used in seawater desalination, ultrapure water production, wastewater treatment and reuse [1–4]. Various polymers have been tested for their suitability in the production of thin-film composite (TFC) RO membranes [5–13]. Due to the excellent separation performances including water flux and salt rejection, aromatic polyamide (PA) membranes have been widely accepted as the optimal among such RO membranes [6,14]. However, oxidation and fouling are currently two major obstacles for the aromatic polyamide RO membranes, which deteriorate membrane performance and shorten membrane lifetime; ultimately, increasing the energy demand and cost of RO membrane plants [15–20]. To address the two problems, various approaches have been performed, which generally involves pretreatment of the RO feed solution (e.g., addition of bactericide, acidification, antiscalant, lime softening, filtration, etc.), development of new TFC RO membrane materials, surface modification of commercial RO membrane (e.g., hydrophilicity, roughness and charge), optimization of process conditions, and periodic cleaning (like osmotic back-washing or chemical cleaning) [21–35]. Even after more than four decades of commercial development, however, chlorine intolerance remains the main hurdle for RO membrane technology to overcome

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http://dx.doi.org/10.1016/j.memsci.2014.06.029
0376-7388/

the severe performance limitations imposed by biological fouling of conventional aromatic PA membranes [18–20].

It is generally considered that the chlorination of conventional aromatic polyamide attributes to the N-chlorination by substituting the hydrogen on amide nitrogen, followed by ring-chlorination via Orton rearrangement [36–38]. Based on this understanding, some strategies of preventing chlorination have been conducted to improve the chlorine resistance of aromatic polyamide RO membrane, such as introduction of electron-withdrawing groups (like chlorine, bromine, fluorine, carboxyl and sulfonic) in the aromatic benzene ring [39,40], increase in steric hindrance of aromatic amide bond with ortho-position methyl group [41], or substitution of the N-position hydrogen atom by methyl group on the aromatic amide bond [42–44], and surface modification by coating with high chlorine-resistance polymers (like poly(N,N-dimethylaminoethyl methacrylate [19], multi-hydroxyl containing cross-linking monomers (MHX) [45], hydantoin derivative [46], imidazolidinyl urea (IU) [47] and hexafluoroalcohol containing aromatic diamine (HFA-MDA) [48]). It is well known that there are a lot of residual unreacted acyl chloride groups (–COCl) and a few unreacted polyfunctional acyl chloride monomer on the nascent membrane surface without heat curing after interfacial polymerization [46,48,49]. It is thus hypothesized that membrane properties and performances (e.g., smoother and more hydrophilic surface, less susceptible to chlorine, etc.) may be enhanced through a second polymerization reaction such as a special functional amino monomer with residual acyl chloride groups and/or monomers due to the introduction of a large mount of amino groups on the membrane surface or ultrathin functional polymeric film [49]. For example, Zou et al. [49] first prepared the conventional polyamide RO membrane with TMC and MPD via interfacial polymerization technique without post-treatment, and then modified in situ by using tetraethylenepentamine (TEPA) via the second interfacial polymerization method. The modified RO membrane has larger contact angle than the unmodified membrane, and similarly both the salt rejection and water flux decreased with the increase in pH value of the feed due to the introduction of amino group (–NH_2) and imino group (=NH), while the ummodified membrane was just opposite due to the existence of carboxyl (–COOH). However, to our best knowledge, it has not been reported that the introduction of ultrathin polyimide chlorine-tolerant film on the polyamide-urethane base membrane surface to improve the chlorine-resistant ability of the TFC RO membrane through the second interfacial polymerization. Therefore, in the current study, the two-step interfacial polymerization technique was proposed to fabricate the chlorine-tolerant poly (amide-urethane@imde) TFC reverse osmosis membrane.

In this study, the key crosslinking agent – 5-choroformyloxyisophaloyl chloride (CFIC) with trifunctional groups (including –OCOCl and –COCl) was reacted successively with 4-methylphenylenediamine (MMPD) and modified functional diamine N,N′-dimethyl-*m*-phenylenediamine (DMMPD) via two-step interfacial polymerization technique to obtain the chlorine resistant poly (amide-urethane@imide) (MMPD–CFIC@CFIC–DMMPD) thin-film composite reverse osmosis membrane, and compared with the poly (amide/imide-urethane) (MMPD/DMMPD–CFIC) and the conventional commercialized polyamide (MPD–TMC) membranes prepared by conventional one-step interfacial polymerization method. The chemical composition and morphology of the resultant membranes surface were investigated via attenuated total reflectance mode Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), scanning electronic microscopy (SEM) and atomic force microscopy (AFM). The hydrophilicity of the resultant membranes was analyzed by contact angle measurement. The membrane separation performance was measured by RO permeation experiment. Meanwhile, the chlorine-resistant property of the resultant membranes was evaluated through free chlorine exposure experiment, which was further elucidated by combination of IR and XPS analyses.

2. Experimental

2.1. Materials and reagents

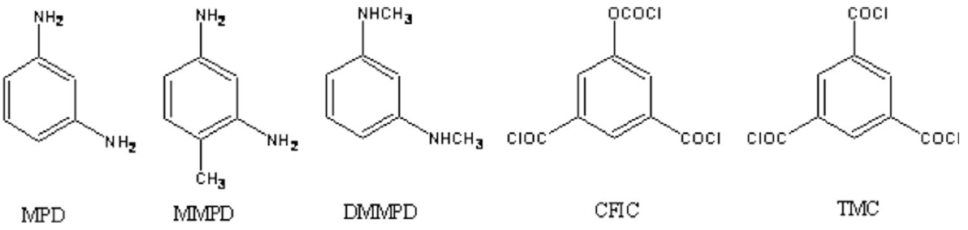
5-choroformyloxyisophaloyl chloride (CFIC, Scheme 1) was synthesized via triphosgene (BTC) method in the presence of composite catalyst imidazole-pyridine [50], and N,N′-dimethyl-*m*-phenylenediamine (DMMPD, Scheme 1) was prepared by the reduction method with composite $NaBH_4$-I_2 [51]. Chemical used to fabricate the RO membrane, including monomers trimesoyl chloride (TMC, purity > 99.5%), m-phenylenediamine (MPD, purity > 99.5%) and m-phenylenediamine-4-methyl (MMPD, purity > 99.5%) as well as aqueous phase additives triethyl amine (TEA), (+)-10-champhor sulfonic acid (CSA) and sodium dodecyl sulfate (SDS), were purchased from J&K Scientific Ltd. Sodium hypochlorite solution (NaClO, 5 wt% free chlorine) used in chlorine exposure experiment was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). All other reagents such as n-hexane and sodium chloride (NaCl) are analytic purity grade unless otherwise specified and used as received without further purification. Deionized (DI) water with conductivity less than 5 μS/cm was produced by a two-stage reverse osmosis system.

2.2. Fabrication of TFC reverse osmosis membrane

2.2.1. The conventional polyamide membrane

The polysulfone (PS) microporous membrane with molecular weight cut-off about 100,000 g/mol and water permeability of approximately 80.0 l/m^2 h bar (supplied by the Development Center of Water Treatment Technology, Hangzhou, China) was used as support film to fabricate the thin-film composite RO membrane. The reference conventional polyamide membrane (MPD–TMC) was fabricated by conventional interfacial polymerization of TMC in n-hexane and MPD in aqueous solution.

First, the PS support membrane was clamped between two Teflon frames (thickness: 0.8 cm; inner length: 20 cm; and inner width: 15 cm), and then the MPD (2.0 wt%) aqueous solution with triethyl amine (TEA, 3.0 wt%), sodium dodecyl sulfate (SDS, 0.15 wt%) and (+)-10-champhor sulfonic acid (CSA, 4.0 wt%) was poured into the top surface of the PS support membrane for soaking. After 2 min, the



Scheme 1. Chemical structure of the used functional monomers.