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Synthesis of thin film composite polyamide membranes: Effect of monohydric and polyhydric alcohol additives in aqueous solution

Behnam Khorshidi[a], Babak Soltannia[a], Thomas Thundat[b], Mohtada Sadrzadeh[a,*]

[a] Department of Mechanical Engineering, 10-367 Donadeo Innovation Center for Engineering, Advanced Water Research Lab (AWRL), University of Alberta, Edmonton, AB, Canada T6G 1H9
[b] Department of Chemical & Materials Engineering, 13-287 Donadeo Innovation Centre for Engineering, University of Alberta, Edmonton, AB, Canada T6G 1H9

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ABSTRACT

Thin film composite (TFC) polyamide (PA) membranes are the most widely used membranes in current water filtration processes. Over the past decade, extensive efforts have been made to improve the permeation properties of the TFC PA membranes via different techniques. In the present work, the effect of incorporating monohydric and polyhydric alcohols into the aqueous solution on surface morphology and permeation properties of resulting TFC PA membranes was studied. The TFC PA membranes were prepared by interfacial polymerization (IP) reaction between m-phenylenediamine (MPD)-aqueous and trimesoyl chloride (TMC)-hexane solutions over polyethersulfone (PES) support. Different concentrations of ethanol (C_2H_6O), ethylene glycol ($C_2H_6O_2$), and xylitol ($C_5H_{12}O_5$) were added into the MPD-aqueous solution. The results showed that addition of alcohols with low molar volumes such as ethanol and ethylene glycol significantly improved water flux of the synthesized membranes. However, in the case of alcohols with larger molar volumes, like polyhydric xylitol, the water flux enhanced by increasing the alcohol concentration up to ~1.0 wt%, and then decreased, suggesting the presence of an optimum concentration of xylitol. This observation indicated the presence of a complex interaction between the hydrophilic hydroxyl groups and hydrophobic aliphatic carbon chain in the structure of large alcohol molecules. Furthermore, all the modified membranes showed higher rejection percentage than the original membrane which is highly desirable for fabrication of high-performance TFC membranes. The findings of this study provide insight into the synergistic effects of structural properties and surface characteristics, which are altered by the addition of alcohols, on the permeation properties of the TFC membranes.

1. Introduction

Over the past decades, the outstanding performance of thin film composite (TFC) polyamide (PA) membranes has sparked off an interest in membrane separation processes for seawater desalination and treatment of municipal and industrial wastewater [1–3]. TFC membranes consist of an ultrathin PA selective layer on top of a chemically different porous support (typically sulfone-based polymer). The ultrathin active layer controls permeability, while the thick porous layer provides mechanical support [4,5]. The multilayer feature of TFC membranes provides a significant advantage that each layer can be independently modified with the different materials and preparation protocols for a particular application of interest [6,7]. In an ideal membrane, both high permeability and selectivity are desirable since higher permeability decreases the size of the membrane modules, thereby reducing the capital cost and higher selectivity results in higher product quality.

TFC membranes are typically synthesized by interfacial polymerization (IP) reaction between polyfunctional amine (e.g. m-phenylenediamine, MPD) and acid chloride monomers (e.g. trimesoyl chloride, TMC), dissolved separately in water and an organic solvent, respectively, at the surface of a microporous substrate. It is a widely held view that the IP reaction is essentially controlled by the diffusion of amine molecules to the organic phase, and thus the reaction mainly happens on the organic side of the interface [8,9]. Therefore, any variation in miscibility of the water-organic interface is expected to affect the diffusion and partitioning of the amine molecules into the reaction zone and thus change the rate of the polymerization reaction.

A common approach for changing the miscibility of water and organic phases is to incorporate chemical additives in either of these

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* Corresponding author.
E-mail address: sadrzade@ualberta.ca (M. Sadrzadeh).

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phases. Although extensive research has been conducted to improve transport properties of the TFC membranes using surfactants, phase transfer catalysts and co-solvents [10–13], a few efforts have been made to explore the effect of polar alcohols on permselectivity and morphology of the resulting membranes [14–18]. Utilization of alcohols with polarity and miscibility between water and the organic solvent is anticipated to alter the solubility and diffusion of the reacting monomers through the water-organic interface. As a result, the rate of the polymerization reaction changes which consequently affects the surface morphology, thickness and physicochemical properties of the synthesized PA selective layer.

Jegal et al. [19] studied the effect of different concentration of n-propanol in amine-water solution on permeation properties and morphology of PA TFC membranes. The addition of n-propanol up to 20 wt% in amine-water solution increased the water flux with a constant rejection of polyethylene glycol (PEG) 200 Da (~90%). However, higher concentrations of n-propanol in aqueous solution resulted in dramatic decrease in salt rejection (~25%). The change in permeation properties of the synthesized membranes was attributed to a change in the miscibility of water and organic solvent (hexane) that affected the polymerization reaction and the final structure of the polymerized membrane. Liu et al. [20] used different concentrations of isopropyl alcohol in aqueous solution to modify the IP reaction between MPD and 5-chloroformyloxyisophthaloyl chloride (CFIC). They reported that the water permeability and salt rejection of the synthesized membranes improved at lower concentrations of the isopropyl alcohol (less than 6.0 wt%). In contrast, at higher isopropyl concentrations, the increase in water flux was accompanied with a significant decrease in salt rejection. This salt rejection decline was ascribed to the formation of a loose PA film due to the high concentration of alcohol additive during the IP reaction. Qui et al. [21] showed that the incorporation of isopropanol into the amine-water solution enhanced the permeation flux, while the salt rejection remained constant. The increase in water flux was mainly attributed to the fast reaction between hydroxyl groups of the alcohol and the functional groups of the acid chloride monomer that led to the formation of ester structure within the PA network. The swelling of PA film with isopropanol alcohol, as well as the change in polarity of the water-alcohol system, were also mentioned as the possible reasons for the water flux enhancement. Despite existing reports in the literature regarding the modification of IP reaction using alcohol additives, more investigation is required to provide a clear understanding of the influence of size and functionalities of alcohols (i.e. number of hydroxyl groups and chain length) on the kinetics of the IP reaction and consequently the physicochemical properties of the resulting TFC membranes.

In the present work, the effect of using monohydric and polyhydric alcohol additives with different chain length and hydroxyl group on the surface morphology and permeation properties of the resulting TFC PA membrane was studied. Different concentrations of ethanol (C_2H_6O), ethylene glycol ($C_2H_6O_2$), and xylitol ($C_5H_{12}O_5$) were added into the MPD-aqueous solution. The physicochemical characteristics of synthesized PA TFC membranes such as surface morphology, wettability, and chemical composition were analyzed and linked to their permselectivity (pure water flux and salt rejection) properties. The addition of alcohols into MPD-aqueous solution was found to enhance the water flux by changing the miscibility of water and the organic phase during IP reaction which significantly altered the surface morphology and permeation characteristics of the PA active layer. The number of hydroxyl groups and the chain length of the alcohols were also identified as significant influential factors on the permeation properties of the synthesized membranes.

2. Materials and methods

2.1. Chemicals and reagents

MPD (≥99%) and TMC (98%) were obtained from Sigma-Aldrich and used as reacting monomers. Hexane (≥99%), sodium dodecyl sulfate (SDS) and triethylamine (TEA) was purchased from Fisher Scientific. Ethanol (C_2H_6O), ethylene glycol ($C_2H_6O_2$), and xylitol ($C_5H_{12}O_5$) were all obtained from Sigma-Aldrich and utilized as hydrophilic additives in the MPD-aqueous solution. All the materials were used as they were received from suppliers. Microporous polyethersulfone (PES) support with average pore size of 100 nm was purchased from Sterlitech Co. (WA, USA).

2.2. Synthesis of thin film composite (TFC) membranes

The TFC membranes were prepared via IP reaction between 2.0 wt% MPD in water and 0.15 wt% TMC in hexane at the surface of the PES substrate. The PES support was first immersed in the MPD solution, containing 0.2 wt% SDS and 1.0 wt% TEA and different concentration (1.0–6.0 wt%) of alcohol (ethanol, ethylene glycol and xylitol), for 10 min. Afterward, the PES support was removed, and excess diamine solution was squeezed off the surface using a soft rubber roller. The impregnated PES substrate was then brought into contact with the TMC solution to allow the polymerization reaction at the surface for 30 s. The resulting TFC membranes were then cured in a digital oven (Thermo Scientific Heratherm™, USA) for 4 min at 60 °C. Finally, the membranes were carefully washed with deionized (DI) water to remove any residual reactants from the surface and then kept in DI water bath until characterization tests were performed. The chemical formula of the reacting monomers and the synthesized PA film are illustrated in Fig. 1. The list of the synthesized TFC membranes and the concentration of the alcohols used as the additives in the MPD-water solution are presented in Table 1.

2.3. Characterization of TFC PA membranes

Surface morphology of the TFC membranes was studied using Field Emission Scanning Electron Microscope (FESEM, Zeiss Sigma 300 VP). All membranes were carbon coated and imaged at a magnification up to 30,000. Transmission Electron Microscope (TEM, Philips/FEI Morgagni 268, Netherlands) was used to capture the cross-sectional image of the TFC membranes. Stained membranes in uranyl acetate and lead citrate, was embedded in Spurr's resin and then cut into ultrathin sections using ultramicrotome (Reichert-Jung Ultracut E, USA). Surface topography of the synthesized membranes was obtained using Atomic Force Microscopy (AFM, Bruker Dimension Icon, USA). An area of 10 µm ×10 µm of the TFC membranes was scanned three times using tapping-mode at a scanning rate of 1.0 Hz at ambient

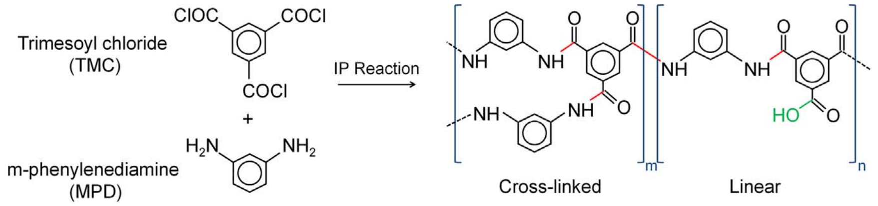

Fig. 1. Chemical structure of the polyamide film synthesized by interfacial polymerization (IP) reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC).