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Effect of lag time in interfacial polymerization on polyamide composite membrane with different hydrophilic sub layers

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ABSTRACT

In this work, composite polyamide reverse osmosis (RO) membranes were synthesized by interfacial polymerization of trimesoyl chloride (TMC) and m-phenylenediamine (MPD) monomers over a polyethersulfone (PES) support layer. Four PES support membranes were prepared by a non-solvent-induced phase separation method using hydrophilic additives such as polyvinylpyrrolidone (PVP) and poly (ethylene glycol) (PEG). For this purpose, the influence of lag time on the properties and performance of the fabricated thin film composite (TFC) membranes was investigated. The separation performance of TFC membranes was evaluated by a cross flow flat sheet RO membrane unit. Besides, surface properties and surface morphology as well as hydrophilicity of PES support membranes and TFC membranes were examined by AFM, FE-SEM, ATR-FTIR and contact angle (CA) analyses, respectively. The results showed that adding hydrophilic agents in the PES supports improves water permeability, surface properties and pore size. The effect of lag time on the separation performance of the fabricated TFC membranes was more significant than the effect of pore size and hydrophilicity of support layer. Generally, the results confirmed that lag time plays an important role in the synthesis process and affects the separation and surface properties of the polyamide TFC membranes.

1. Introduction

The most common thin film composite (TFC) membranes used to produce drinking water from seawater, brackish groundwater, and wastewaters are aromatic polyamide (PA) membranes. The asymmetric TFC membrane is composed of a nonwoven fabric, a porous support layer and a dense thin barrier layer [1,2]. The porous support layer is usually made of polyethersulfone (PES) or polysulfone (PSf) by the phase inversion. Also, the polyamide thin layer is coated via interfacial polymerization on the porous layer. Interfacial polymerization (IP) involves reaction between a polyfunctional amine, and an acid or acid chloride which is dissolved in water and hydrocarbon solvent, respectively [3,4]. The performances of the TFC membrane are changed by the surface chemistry and morphology of the membrane. The trimesoyl chloride (TMC) and m-phenylenediamine (MPD) are two interesting monomers which have been used for the fabrication of polyamide membranes in a number of research studies [1,5].

Nowadays, a comprehensive attempt has been made to improve the performance of the TFC polyamide membrane. There are several effective parameters on the polyamide layer formation and performance of TFC membranes such as type of monomers, concentration of monomers, reaction time, curing temperature, solvents and additives [6–10]. The positions and the number of diamines and acid chlorides on the monomers determine the chain structure of the polyamide and the network formed by cross-linking [6,9]. The reaction time and curing temperature are two effective parameters on cross linking of the polyamide layer which results in the formation of a thin skin layer with low permeability and high salt rejection. Also, the monomer concentration, solvents and additives can alter the solubility and diffusivity of the amine and acid monomers into the liquid–liquid interface reaction zone and have an effect on the reaction rate [11].

In the thin film polyamide composite membrane formation, the porous support membrane was first immersed in the aqueous of amine. After a given time, the support was removed and excess amine (MPD) solution was eliminated from the top surface of the support membrane using a custom method. Then the MPD saturated support membrane was immersed in a TMC solution for interfacial polymerization. Various methods have been used to remove the excess amine solution from the different support layers such as: a) the excess solution was removed using an air knife from the membrane surface [3,12–14], b) the excess solution was then drained from the support surface in vertical position for a short time [4,15,16], and c) the excess reagent was squeezed off by a soft rubber roller [7,17–19] and decanted and allowed the membrane to remain in the air until no excess liquid exists [20,21]. According to the observation of these studies, the synthesis method affects the performance of the formed TFC membrane. One of the key parameters in

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the synthesis process is lag time which is defined as time spent for removing the excess MPD solution from the surface of the support layer until immersed in to TMC solution. However, the lag time effect on the separation performance and surface properties of polyamide TFC has not been studied.

Also, the hydrophilicity and pore size of the support layer have been studied by some researchers [12,13,22,23]. Kim and Kim [22] modified the conventional PSf support by plasma treatment with hydrophilic materials prior to interfacial polymerization of the polyamide membrane. They reported that the modification of the support layer led to an increase in the flux and rejection as well as chlorine resistance. The effect of support pore size on the TFC membrane performance was investigated by Singh et al. [23]. The results showed that PSf with higher pore size has low rejection and high water flux. Ghosh and Hoek [13] have investigated the effect of pore size and hydrophilicity of the support layer simultaneously on separation performance and surface properties of TFC membranes. They reported that the hydrophobic support layer with large pore size has highest water and salt permeability which is different with Kim and Kim [22] results. These different trends may be attributed to the lag time in interfacial polymerization. Therefore, the effect of support layer properties and lag time on the separation performance and surface properties of TFC membranes should be investigated simultaneously. Lag time is a pause time after PES support layer was wetted by MPD solution and before interfacial polymerization. Lag time is an effective parameter in the synthesized of TFC membrane which lets the MPD solution to diffuse into pore which changes the performance and surface properties of formed TFC membranes.

In this paper, polyamide composite membranes are fabricated by interfacial polymerization on the various PES porous membranes as support layers. For this purpose, the effect of PEG 600 and PVP k90 hydrophilic additives on the PES porous support layer is investigated and the surface properties, hydrophilicity, water permeability and morphology of the prepared support layers were characterized by atomic force microscopy (AFM), attenuated total reflectance (ATR), contact angle and a field-emission scanning electron microscope (FESEM). Also, the effects of the lag time on the properties and performance of the polyamide TFC membranes are studied. Finally, the TFC membranes are analyzed to evaluate their separation performance, thickness, hydrophilicity and morphology.

2. Materials and methods

2.1. Materials

n-Hexane, sodium chloride (NaCl), N,N-dimethylacetamide (DMAc), trimesoyl chloride (TMC), m-phenylenediamine (MPD) and poly(ethylene glycol) (PEG 600) were purchased from Merck Co. Ltd.(Darmstadt, Germany). The polyvinylpyrrolidone (PVP-K90) was supplied by Fluka (Milwaukee, USA). The commercial polyethersulfone (Ultrason E 6020 P) provided by BASF (Ludwigshafen, Germany) was also used. All of the materials were dried at 80 °C for at least 5 h before use.

2.2. Membrane preparation and synthesis

The porous support layers were prepared by the phase inversion technique in the PES/hydrophilic additive/DMAc/water system. The PES and hydrophilic additives were dissolved into the DMAc solvent. The prepared solution was stirred vigorously at 80 °C for 4 h, and then mixed at room temperature over night to obtain a clear homogenous solution. Afterwards, the polymer solution was de-aerated by a vacuum process for 2 h. This solution was cast on a polyester nonwoven fabric supported by a glass plate with a 300 μm knife gape. The glass plates were then immersed in a de-ionized water bath at room temperature. After 10 min, the formed PES porous support layer was washed with de-ionized water for several times and stored in a water bath for 24 h. The PES porous support layer was dried at room temperature for 2 days before the use.

The TFC membrane was prepared by interfacial polymerization on the PES porous support layers. The PES membrane that was taped to a glass plate was placed in an aqueous solution of 2% (w/v) MPD for approximately 2 min. The excess solution was removed from the top surface of the PES support layer by the rubber roller. After that, the saturated PES sample was placed in dry air, blowing for a given time and then immersed in a solution of 0.1% (w/v) TMC in hexane at 25 °C for 1 min. After that, the saturated PES support layer was placed in dry air for a given time which is named lag time and then immersed in a solution of 0.1% (w/v) TMC in hexane at 25 °C for 1 min. This lag time lets the MPD solution to diffuse into pores which changes the performance and surface properties of formed TFC membranes. The resulting membranes are cured by heating in an oven at 70 °C for 6 min, washed thoroughly with de-ionized water and stored in lightproof containers at 5 °C. The experimental conditions were used to fabricate various polyamide TFC membranes and the nomenclature to define the membrane samples is presented in Table 1.

2.3. Membrane characterization

2.3.1. Separation performance

The flux and salt rejection of the TFC membranes were measured by a cross flow flat sheet membrane module with filtration area of 35 cm^2 at temperature of 25 °C and operating pressure of 176.4 psi (~12 bar). The same procedure was used to determine the separation performance of the PES porous membrane at operating pressure of 29.4 psi (~2 bar). A scheme of the experimental RO setup is depicted in Fig. 1. The volumetric pure water flux, J_v, was calculated using the following equation:

$$J_v = \frac{v}{A \times t} \tag{1}$$

where v is volume of the collected permeate (L), A is the membrane area (m^2) and t is time duration of the experiment (h). Salt rejection (R) of TFC membranes was calculated by measuring rejection of 0.2 wt.% of NaCl which was analyzed with the conductivity of the feed and product solutions using a calibrated conductivity meter (DiST®4 (HI98304), HANNA instruments®, Inc., Italy) as follows:

$$R = 1 - \frac{C_p}{C_f} \tag{2}$$

Mean pore radius, r_p, (μm) of the PES support membrane was determined using the filtration velocity method. Mean pore radius could be experimentally determined by the Guerout–Elford–Ferry equation [24]:

$$r_p = \sqrt{\frac{(2.9-1.75\varepsilon) \times 8\eta hQ}{\varepsilon \times \Delta P}} \tag{3}$$

Table 1
The experimental conditions were used to fabricate various polyamide TFC membranes and the nomenclature was utilized to define the membrane samples.

Condition	Name [a]						
	A	B	C	D	1	2	3
PES (wt.%)	20	15	15	15	–	–	–
PEG (wt.%)	–	5	–	2.5	–	–	–
PVP (wt.%)	–	–	5	2.5	–	–	–
Lag time (min)	–	–	–	–	0	4	8

[a] A, B, C and D letters illustrate PES support layer with various formulations, namely D shows a support layer that contains 15% PES, 2.5% PEG and 2.5% PVP. The number after the letter indicates the lag time, for example: D1 shows TFC membrane sample with experimental conditions of PES = 15%, PEG = 2.5%, PVP = 2.5%, and lag time of 0 min as well as A2 shows TFC membrane sample with experimental conditions of PES = 20%, wet support layer and lag time of 4 min.