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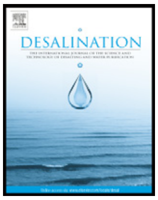

Interfacially polymerized polyamide thin film composite membranes: Preparation, characterization and performance evaluation

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ABSTRACT

The formation of polyamide thin film composite (TFC) membranes via interfacial polymerization (IP) of *m*-phenylenediamine (MPD) in water with trimesoyl chloride (TMC) in hexane was studied. Parametric studies were conducted by varying reaction time, curing time and curing temperature. It is evident from the results that increasing the polymerization time results in decreasing the membrane surface roughness and increasing solid–liquid interfacial energy. Also with increasing the polymerization time, surface morphology changes from "nodular" and "leaf like" morphology to "hill and valley". The other involving parameters were the thin film thickness, which the results indicated that PA thin film thickness increased with polymerization time and moreover the acidic feature of PA film varied during polymerization process. Increasing polymerization time led to decreasing membrane water flux and increasing salt rejection since the PA layer became thicker and the extent of cross-linking increased. Also, it was shown that the curing conditions affect on membrane performance and with increasing curing time and temperature, salt rejection was increased and flux was decreased.

1. Introduction

Several methods can be carried out in desalination and industrial water treatment. Reverse osmosis (RO) is one of these methods which are simple to operate in comparison with other separation processes are widely used in chemical, environmental and food industries [1–6]. Most of the commercially successful RO and nanofiltration (NF) membranes are thin film composite (TFC) membranes which consist of a barrier active dense layer and a porous sublayer. This active layer is usually formed via interfacial polymerization (IP) technique which can provide good selectivity and high water permeation rate.

One of the successful TFC membranes is polyamide (PA) composite membranes. PA active layer polymerized interfacially on top of polysulfone (PS) and polyethersulfone (PES) porous support membrane [7–11]. Between a wide range of reactive monomers used in IP process to produce PA layer, m-phenylene diamine (MPD) and trimesoyl chloride (TMC) have special importance since they provide aromatic cross-linked PA layer and hence provide high water flux. In this IP process, the immiscible aqueous and organic phases brought together and a thin film immediately formed between two phases at the organic side of the interface due to low solubility of acid chloride in water and fairly good solubility of amines in organic solvents [12,13].

The interfacial polymerization time is very fast and many factors such as reaction time, reaction temperature, curing conditions and monomer concentration can affect PA structure. Also, the produced film is extremely thin so its characterization by common methods used in the bulk polymer characterization is not possible and therefore use of surface analysis methods is necessary. TFC membranes preparation has been studied by different groups of researchers who focused on several fields such as effect of PA molecular structure on membrane properties and performance [14], mechanical properties of thin film layer [15], surface feature [16], transport modeling and mathematical modeling of interfacial polymerization [17,18] and use of nanozeolite particle in thin film nanocomposites [19].

In this study, PA TFC membranes were prepared by interfacial polymerization of MPD and TMC as two important and widely used monomers in IP process on top of the PES porous support membrane which prepared by non-solvent induced phase separation. PES has been studied thoroughly and is well known for its proper properties such as favorable mechanical strength, thermal and chemical stability and excellent biocompatibility [20–24]. Several TFC were prepared under different polymerization conditions such as polymerization time, curing time and curing temperature. The effect of polymerization time as one of the important kinetic parameters on active layer thickness, morphology, structure, hydrophilicity, roughness and thermal properties were investigated by scanning electron microscopy (SEM), attenuated total

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reflectance infrared spectroscopy (ATR-IR), contact angle measurement (CA), atomic force microscopy (AFM) and differential scanning calorimetry (DSC). Finally, the performance of the TFC membranes was characterized.

2. Experimental

2.1. Preparation of TFC membranes

Polymeric solution was prepared by dissolving 15 wt.% PES (Ultrason E6020P, BASF) and 2.5 wt.% polyvinylpyrrolidone (PVP, Mw = 40,000 g/mol, Aldrich) as a pore former polymeric additive in N, N-Dimethylacetamide (DMAc, Merck) as a solvent at 25 °C with continuous stirring. The well mixed bubble free solution was cast on a glass plate followed by immersion and coagulation in distilled water as non-solvent bath. After coagulation, membranes were moved to the second water bath for 24 h until morphology became set and most of solvent and water-soluble polymer were removed.

Microporous PES support membranes was taped onto an Al plate and immersed in aqueous solution containing 2 wt.% MPD (Aldrich) and soaked for 2 min. Then the membrane surface was rolled out with a soft rubber roller and followed by hanging the soaked membrane to eliminate remaining bubble and excess solution. Next, the membrane was dipped into organic solution containing 0.1 wt.% TMC (Aldrich) in n-hexane (Merck) for 15, 45, 90 and 180 s. The resulting TFC membranes were dried in a controlled temperature during specific period of time and temperature. The TFC membrane preparation conditions are presented in Table 1.

2.2. Characterization of TFC membranes

The chemical characterization and thickness measurement of PA layer of TFC membranes were accomplished by ATR-IR spectroscopy instrument (EQUINOX55, LSI) using multiple internal reflectance apparatus and ZnSe ($n = 2.43$) prism as an internal reflection element was fixed at a 45° angle of incidence [25].

Top surface morphology of TFC membranes was evaluated by SEM (Philips XL 30). For SEM evaluations, the membranes were coated by a thin layer of gold under vacuum condition. Surface roughness (RMS) and relative surface area (Δ) were characterized for a 10 × 10 μm quadrangle sample by AFM DualScope C-21(DME, Denmark) in contact mode in the air.

The water contact angle (CA) of the TFC membranes surface was measured by sessile drop method (OCA-20, DataPhysics Instruments GmbH, Germany) at room temperature. De-ionized water was used as a probing liquid for several different points of membrane surface and the average of measured value was reported as a CA of membrane surface. Also, the solid–liquid interfacial free energy which is the better determination of surface hydrophilicity than CA [10,26], was evaluated using Eq. (1):

$$-\Delta G_{SL} = \gamma_L[1 + \cos\theta / \Delta] \qquad (1)$$

Table 1
TFC membrane preparation conditions.

Sample number	Reaction time (s)	Curing time (min)	Curing temperature (°C)
1	15	7	55
2	45	7	55
3	90	7	55
4	180	7	55
5	45	7	35
6	45	7	85
7	45	3	55
8	45	15	55
9	45	30	55

θ and γ_L are the average contact angle and the liquid surface tension (for pure water at 25 °C is 72.8 mJ/m^2), respectively [10].

DSC measurement of dried samples was carried out under nitrogen atmosphere using NETZCH, 200 F3. The flow rate of nitrogen gas was 20 ml/min and the heating rate was 10 °C/min from 25 °C to 300 °C.

2.3. Membrane performance evaluation

The performance test of TFC NF membranes were conducted with a cross-flow cell (Fig. 1) using solution of pure sodium chloride with 1000 ppm concentration in distilled water under constant pressure (6 bar) and temperature (25 °C). Quadrangular membrane samples (4 × 5 cm^2) were placed in cell with the active layer facing the incoming feed. The flux and the solute rejection were determined by measuring the volumetric permeate flow directly (L/m^{2}h) and ion conductivity (Hanna) of permeation by using conductivity–concentration curve, respectively. Solute rejection calculated by following equation:

$$\text{Rejection}(\%) = 100 \times \left(C_f - C_p\right) / C_f \qquad (2)$$

Where C_f and C_p are the ion-conductivity of feed solution and permeate, respectively.

3. Results and discussion

3.1. Surface properties

Effect of polymerization time as one of the important kinetic parameters on surface feature of TFC membrane which play critical role in membrane performance, was studied by using CA, SEM and AFM analysis. Water contact angle of membrane surface can evaluate surface hydrophilicity and free energy. Results showed that adding PA layer on top of the PES microporous support layer CA decreased from 69° for PES support membrane due to the presence of amide, carboxylic and hydroxyl functional groups which increased surface hydrophilicity and surface free energy (Table 2). But polymerization time didn't influence much on water contact angle of TFC membranes because TFC membranes have rough surface and this roughness can produce some errors on CA measurements whereas surface free energy provide better understanding about surface hydrophilicity. TFC membrane surface CA changed between 57° and 68° and surface free energy increased with increase of polymerization time.

Top surface morphology of TFC membranes was investigated by SEM method. As shown in Fig. 2, surface morphology is a function of polymerization time. During the first stage of polymerization process (15 s), “nodular” and “leaf like” morphology were observed. However, as polymerization time increased, surface morphology changed to “hill

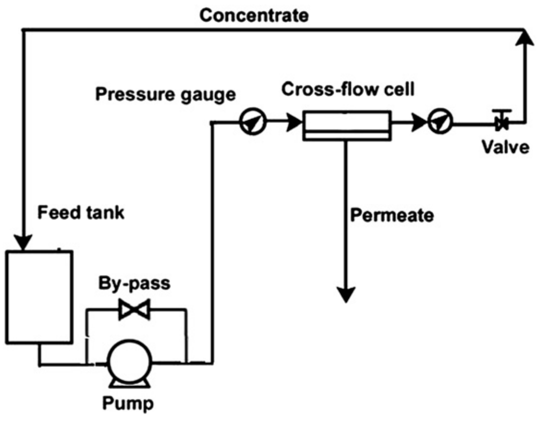

Fig. 1. The cross flow system for water treatment process.