



Simulating the growth process of aromatic polyamide layer by monomer concentration controlling method



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ABSTRACT

With the wide distribution and gradual increase of TMC concentration (C_{TMC}) from 1×10^{-4} wt% to 2.5×10^{-1} wt%, the main purpose of this work is to simulate the surface structure and properties of polyamide layer of reverse osmosis membranes at its different growth stage. The surface structure and properties of the resulted membranes were then characterized by atomic force microscopy (AFM), scanning electron microscope (SEM), attenuated total reflectance infrared (ATR-IR) spectroscopy, drop shape analysis system and electrokinetic analyzer. The structure growth of polyamide layer underwent in turn three different stages including spherical aggregator, leaf-like and typical ridge-valley structure. Spherical aggregator is the intrinsic structure in the inner layer of polyamide while leaf-like structure is transitional on the outmost polyamide layer. Furthermore, to clarify the effect of the structure change on the properties of polyamide layer, contact angle and zeta potential in the surface of polyamide layer were studied. Hydrophilic surface of polyamide layer is accessible at higher TMC concentration because of the presence of negative charged groups. Performances of the membranes were further measured with an emphasis on studying its structure–performance relationship during the growth process of polyamide layer.

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1. Introduction

Polymer thin-film composites are the main membrane configurations applied in reverse osmosis (RO) and nanofiltration (NF). A typical preparation process for TFC-RO is that *in situ* synthesize polyamide active layer on the top of porous substrate *via* interfacial polycondensation (IP) of multifunctional amine and acid chloride [1,2]. Among the components of TFC-RO, the porous substrate acts as mechanical supporting layer while the active layer is responsible for the selectivity and permeability of RO membrane [3,4]. Polyamide active layer usually characters dense but thin with a thickness of nano-scale, which is pivotal to the success of TFC-RO membranes. The advantages of TFC-RO membranes have enabled them to extensively apply in seawater desalination, wastewater treatment and so on.

In the past decades, various techniques such as ATR-IR [5–7], scanning electron microscopy [8–10], transmission electron microscopy [11,12], X-ray photoelectron spectroscopy [13], small-angle neutron scattering [14] and AFM [15–18] have been employed to characterize TFC-RO membranes. The results have

disclosed that the surface of the active layer has structural diversity, which was closely related to the chemo-physical properties of porous substrate [19–21], monomers [3,22,23], hydrocarbon solvent [24] and post-curing treatment [8,24,25]. The selectivity and permeability of TFC-RO membranes could be well adjusted *via* the control of its surface structure [26–28]. One of the most reported structures in the active layer surface is ridge-and-valley structure forming at the interface facing to organic phase [10,29]. It was the direct contributor for surface roughness and surface area of TFC-RO membranes [10]. Furthermore, the intrinsic structure of the active layer was electrically double-layer, in which the dense inner barrier layer was positively charged and responsible for selectivity. The outmost layer was relatively loose and negatively charged as compared to the inner layer [11]. These results were well in accordance with the formation kinetics of the active layer postulated by model-based simulation [30]. More recent, Liu et al. have figured a more clear-cut profile on the microstructure of the active layer according to their creative investigations. They proposed a three-layer structure model, in which the dense middle layer was observed to have intrinsic cross-linked structure with over 86.0% of –CONH– and below 14.0% of –COOH [6]. Definitely, although the above conclusions were consistent to some extent concerning the structure of the active layer and its formation kinetic, most of the others are still mutually controversial. Two factors, that is, the rapid

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and delicate reaction process and the very thin structure, constitute the main obstacle for a deeper understanding on the above issues. It has greatly limited one to design and synthesize more cost-effective TFC-RO membrane with precise and high ion selectivity.

Herein, we present a systematical study on the structural features of polyamide layer at its different growth stage by means of concentration controlling method. Since the interfacial polymerization is too fast to perform an in-situ monitoring, our approach is to control the polymerization process *via* a wide change in the acyl chloride concentration. Compared to the time variable applied in most of previous studies [2,30,31], the monomer concentration in the interface region is a more reliable and stable variable in the control of IP process. The structure of the nascent active layer from different growth stage was analyzed by AFM, SEM, drop shape analysis system, electrokinetic analyzer and ATR-IR etc. The results would deepen the fundamental understanding on polyamide growth and its structure evolution.

2. Experiment

2.1. Materials

Solvents and reagents in analytical grade were purchased from commercial sources. Polysulfone supported membranes were our commercial production and used as is. Trimesoyl chloride (>98%) and *m*-phenylenediamine (MPDA) (>99%) were purchased from Sigma-Aldrich.

2.2. Membrane preparation

The membranes were prepared based on the traditional interfacial polymerization approach described elsewhere [1]. First, polysulfone supported membranes taped to stainless steel plates were immersed in an aqueous solution containing 3.5 wt% MPDA and 0.01 wt% NaOH, for 10 s. Subsequently, MPDA soaked supporting membranes were placed on a rubber sheet and the excess aqueous solution on its surface was removed by a nitrogen knife. The MPDA saturated polysulfone membranes were then immersed in a hexane solution of TMC with designed concentration for 10 s. The TMC concentrations applied in this study are arranged from 2.0×10^{-4} wt% to 2.5×10^{-1} wt%. The resulted membranes were naturally dried in ambient temperature for a few minutes to completely remove the excess hexane solution. Finally, the obtained RO membranes were stored in deionized (DI) water for further use.

2.3. Membrane characterization

Surface microstructures of the RO membranes were imaged by tapping mode in air using a commercial Nanoscope[®]V Multi-Mode viii AFM (Bruker). It was equipped with an *E* scanner which possesses the maximum *xy* range of 15.0 μm . The topographies were obtained at the scan size of 2.0 or 5.0 μm (data collection at 512×512 pixel) and the scan frequency of 1.0 Hz by a silicon nitride cantilever.

Surface microstructures of the RO membranes were observed by a field emission scanning electron microscope with SEM of Hitachi S-4300. Magnifications up to 50,000 were obtained at 5 kV.

Contact angle measurements of the dried RO membranes were performed by a drop shape analysis system (DSA 30, Krüss GmbH, Germany). DSA 4 software was used to analyze the equilibrium contact angle of the samples which is the average of the left and right contact angles. The reported value for each sample was averaged from ten measurements of the equilibrium contact angles.

Zeta potential of the membranes was determined by a streaming current electrokinetic analyzer (SurPass, Anton Paar GmbH, Graz, Austria) according to the procedure described by Luxbacher [32]. For zeta potential measurements, 10 mM KCl was used as a

background electrolyte solution and solution pH keeps at 6.8. The reported value for each sample was averaged from five parallel measurements.

The applied ATR-IR instrument is a Nicolet IS10 Fourier transform infrared spectrometer (Thermo scientific) equipped with a Barnes model 300 continuously variable ATR accessory. For ATR-IR studies of the membrane samples, the germanium crystal was fixed at 45 °C angle of incidence, which gave a probing depth of about 0.4 μm in the chemical infrared region of interest. The spectra were collected at 4 cm^{-1} resolution and 64 scans, and were baseline-corrected using the OPUS software. All of the samples used for ATR-IR study were pre-dried in vacuum at 80 °C for 6 h. The samples were taken at random from the flat sheet films, and were placed in direct contact with Ge ATR crystal.

2.4. Performance test

Using a cross-flow type apparatus, all tests for thin film composite RO membranes performance were conducted in 4000 ppm NaCl solution at room temperature and 225 psi. Both permeate and retentate were recycled back to the feed tank during the tests. Rectangle membrane samples were placed in the test apparatus with the active skin layer facing the feed water. The effective membrane area was around 19 cm^2 . All of the membrane samples were prepared and tested at least quintuplicate, results of which were then averaged. The permeating volume collected for 1 h was used to describe flux in terms of gallons per square feet per day (gfd). A standardized conductivity meter was used to measure NaCl concentrations in the feed and product water for determining membrane selectivity as given below:

$$\text{salt rejection}(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (1)$$

in which C_f and C_p are the feed and permeating concentration of NaCl, respectively.

The flux of polysulfone membrane was determined by using a stirred cell under dead-end type. Prior to test, the samples were shaped into circular with diameter of 50 mm and installed in the cell. The effective area of the sample for the test is 37.4 cm^2 . After filled with about 300 ml distilled water, the cell was connected with a nitrogen tank and the test was performed under the pressure of 0.2 MPa. A 200 ml cylinder was used to measure the permeate for 60 s. Each value shown in this paper was averaged from five parallel tests.

3. Results and discussion

Fig. 1 presents AFM height images of the surface of polysulfone membrane which was used as porous supporting layer to prepare RO membranes. Polysulfone membrane has a typical particle-aggregated structure. The surface roughness is 3.47 nm, indicating a quite smooth surface of our supporting membrane. The contact angle at its fully dried state is about 83°. The water flux of polysulfone membrane is about 446 GFD at 0.2 MPa.

Fig. 2 shows AFM height images of polyamide layer obtained from different C_{TMC} . The spherical aggregators can be found in Fig. 2A–C, which formed at very small C_{TMC} . The spherical structure is tightly aggregated and no obvious porous structure is observed at the applied resolution. Meanwhile, with the increase of C_{TMC} from 2.0×10^{-4} wt% to 2.0×10^{-2} wt%, the size of spherical structure grows from ~20 nm to ~60 nm. The result indicates that, increasing C_{TMC} can result in a continuous growth of the spherical structure. It is interesting to denote that, at C_{TMC} of 2.0×10^{-2} wt%, the spherical structure in the up part of the layer are tend to aggregate to form a relatively loose leaf-like structure (Fig. 2C). It becomes mature

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