



Novel insights into the interplay between support and active layer in the thin film composite polyamide membranes



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ABSTRACT

Fundamental problems in thin film composite (TFC) reverse osmosis (RO) membranes in terms of the interfacial adhesion between the support and the active layer, the impact of support surface pore characteristics on the active layer formation process and the accordingly obtained active layer properties were investigated. Paper studies mainly includes following aspects: Five types of polysulfone (PSF) supports with varied surface pore characteristic properties were prepared and characterized; Thin film composite (TFC) polyamide (PA) reverse osmosis (RO) membranes were fabricated on these supports via in situ interfacial polymerization (IP) technology under identical IP protocols, and the performance and properties of the obtained TFC membranes were investigated systematically; Three types of these supports produced TFC membranes with both good salt rejection and high water flux. On the other hand, two types of them produced TFC membranes with inferior salt rejection attributed to the delaminated active layer from the support; The root cause for the delamination was explored and a speculated mechanism model for it and for the impact of support surface pore characteristic on the active layer formation was proposed. Furthermore, profilometer was used for the first time to measure the accurate thickness of individual active layer to overcome the shortcomings of the conventional electron microscope technologies. The basic understanding of the interplay between the support and the active layer provides important information for developing of thin film composite (TFC) membranes with improved performance.

1. Introduction

Although reverse osmosis (RO) and nanofiltration (NF) membranes have become the dominant technology for desalination of seawater and brackish water nowadays [1], some fundamental problems influencing the membrane performance and properties are not very clear. Membranes used in such systems are usually the standard designed thin film composite (TFC) polyamide (PA) membranes [2], which are composed of two main functional layers beside the non-woven fabric mechanical strengthening layer [3,4]: a porous ultrafiltration support (tens of micrometers in thickness) usually prepared from polysulfone (PSF) through the Loeb-Sourirajan phase inversion method [5], and upon which an ultra-thin polyamide (PA) film (10 to more than 200 nm in thickness) as active separation layer fabricated via the in situ interfacial polymerization (IP) technique [6]. It is generally considered that the active layer is responsible for the main salt rejection and water permeation properties. Comprehensive attempts have been made to tune the physicochemical properties of the active layer through employing different types of monomers [7,8], additives [9,10], co-

solvents [11,12], post-treatment procedures [13,14], surface coating [2,15], and introducing of mixed-matrix composition [16,17], etc. However, recent reports indicated that the support property also has non-negligible impact on the resultant TFC membrane performance and features [18,19]. Ghosh et al. [20] proposed a conceptual model based on the capillary phenomenon to describe the impacts of support properties on the IP reaction process, and concluded that highly porous, relatively hydrophobic support produced more permeable composite membrane. Despite broad interest in finding proper support or active layer fabrication protocols, the study focusing on the interplay between the support and the active layer is still new.

The adhesion between the supporting layer and the active layer is the most obvious issue. However, the study about it has never been reported, speculating due to the fragility of the ultra-thin active layer making it challenging to be investigated as that in macroscopic multi-layer system [21]. In practice, delamination of active layer from support was often experienced by anyone preparation of TFC membrane in laboratory. When the active layer delaminated from the support, it could be partially torn under high hydraulic pressure during

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filtration operation. The torn sites would lead to a bulk flow of brine, and deteriorated the membrane rejection. Alsvik et al. [22] stated the delamination of PA active layer from the hydrophilic support due to the unfavorable interaction between the two layers of different hydrophilicity. Yan et al. [23] carried out an “inverse” interfacial polymerization to obtain PA membrane and found that the adhesion between the “inverse” PA film and the PSf support was much weaker than that in the conventional case. Soice et al. [24,25] proposed the major cause of performance decline of RO membranes caused by chlorination was not due to polymer chain cleavage but physical separation of the PA skin layer from the PSf support layer. However, little study has been reported on the root cause for the delamination or versus the mechanism of adhesion between the active layer and the support.

The surface property of support may influence the IP process and the resultant active layer feature. In a typical IP operation, the porous support was firstly impregnated by the multifunctional amine monomer aqueous medium, and then the loosely bound aqueous phase solution was drained by a rubber roller or air stream. The amount of residual aqueous phase solution is a key factor impacting the quality of the resultant PA film. It is the surface properties of the support that governs the amount of residual aqueous phase solution and the subsequent diffusion to the organic phase to form PA barrier layer. This is mainly related to both the hydrophilicity and pore characteristics of the supports. Traditionally, it has been studied from the point of view of the hydrophilicity. Chao et al. [26] studied the effect of the surface property of the PTFE supporting membrane on the formation of active layer, and found that the position of the densest structure of the active layer was decided by the hydrophilicity of the support used. Ghosh et al. [20] explained that hydrophilic support gave rise to more PA formation deeper within support membrane pore, and resulted in less permeable membrane. Hermans et al. [27] stated that the support membrane porosity factor had a significant effect on the TFC membrane performance. However, the role of the support surface pore on the formation mechanism of PA active layer is not known.

Accurate measurement of the active layer thickness is still challenging now, due to its ultra-thin thickness and integrity structure with the support. It was conventionally measured by electron microscope techniques such as scanning electron microscopy (SEM) or transmission Electron Microscopy (TEM), based on observation of the cross-sectional view of the active layer attached to support. However, the interface between these two layers was often blurry. Furthermore, the thickness had to be measured in a very small window due to the high magnification needed to ensure enough resolution. The active layer thickness usually has a certain deviation in different positions. As a result, artifacts may often be introduced by these electron microscope methods.

In the present study, TFC membranes were fabricated on five types of PSf supports with different surface pore characteristic using an identical interfacial polymerization protocol, respectively. The obtained TFC membranes exhibited distinct performance, with two of inferior salt rejection due to the delamination of active layer from support, and the other three of both good salt rejection and high water flux comparable to the commercial ones. The properties of supports and active layers were studied through a number of analysis techniques including atomic force microscopy (AFM), scanning electron microscopy (SEM), infrared spectrum (IR), etc. Profilometer as a tool enable to verify the precise thickness of thin films across the wafer surface down to nanometer scale, was used for the first time to measure the thickness of PA active layer in a millimeter scale window to overcome the shortcomings of electron microscope methods. To the best of our knowledge, it is the first time to systematically investigate of the delamination issue in TFC membranes and the interplay between the support and the active layer.

2. Experiments

2.1. Materials and reagents

Polysulfone (PSf) (Udel P-3500) was purchased from Solvay Specialty Polymers Co. The resin was dried overnight at 120 °C before use. Analytical purity grade trimesoyl chloride (TMC), m-phenylenediamine (MPDA), camphorsulfonic acid (CSA), triethylamine (TEA), 1-Methyl-2-pyrrolidinone (NMP) and N,N-dimethyl-formamide (DMF) were purchased from Sigma–Aldrich Inc. Anodic alumina oxide (AAO) membranes with pore size range of 20–30, 40–70, and 80–100 nm were purchased from Pu-Yuan Nanotechnology limited company. The Dow-Corning 730 solvent resistant adhesive was used to fix the composite membrane to a silicon wafer to facility the characterization of active layer backside properties. Water used in all the studies was freshly produced from a reverse osmosis system. All other reagents were obtained from commercial sources and used as received.

2.2. Polysulfone (PSf) supports preparation

The polysulfone (PSf) asymmetric membranes were prepared using varied polymer concentration of 20 wt%, 18 wt%, 16 wt%, 14 wt% and 12 wt% through the classical phase inversion process [3]. In a typical step, dry polysulfone (PSf) resin was dissolved in DMF to form homogeneous solution firstly. Preparation conditions for all the supports were provided in Table 1. After filtered with a stainless steel filter and degassed with a vacuum pump. The viscous solution was spread on a non-woven fabric with desired thickness using a casting machine. After a 5 s evaporation period, the casting films were immersed in water. Then, the membranes were kept in water bath overnight to wash out the residual solvent. The membranes were then washed thoroughly with and stored in water until they were used.

2.3. Thin film composite (TFC) polyamide membranes preparation

The polyamide active layer of the RO membranes was fabricated on the above prepared PSf supports using the same interfacial polymerization protocol. First, the aqueous phase solution containing MPDA (2.0%, w/v), TEA (1.0%, w/v) and CSA (2.0%, w/v) was poured on top of the polysulfone supports and allowed to soak for 3 min. Excess solution was drained from the support surface and air-dried for about 5 min until no observed droplets. Afterwards, the organic phase solution with TMC (0.1%, w/v) dissolved in Isopar G was poured on top of the aqueous phase immersed supports and allowed to contact for 20 s. After removing the excess organic solution, the nascent membranes were cured in an oven at 90 °C for further polymerization. Finally, the membranes were rinsed thoroughly with water and stored in 1% NaHSO₃ solution before used. All the above operations were performed in an assembled clean room with constant temperature at 23–28 °C and relative humidity of 35–50%.

Table 1
Preparation conditions and basic properties of the supports.

Support	Casting solution (wt%)		Thickness (μm)	Contact angle (°)	$P_{Overall}$ (%)	Water flux (L/m ² h)
	PSf	DMF				
S-1	20.0	80.0	39–42	75.2 ± 1.4	62.9	140 ± 17
S-2	18.0	82.0	40–43	78.8 ± 0.6	67.4	210 ± 32
S-3	16.0	84.0	42–44	76.2 ± 1.3	70.7	340 ± 65
S-4	14.0	86.0	40–42	74.6 ± 1.2	72.0	510 ± 69
S-5	12.0	88.0	40–42	73.0 ± 1.8	80.2	680 ± 87

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