Development of Multilayer Polyelectrolyte Thin-Film Membranes Fabricated by Spin Assisted Layer-by-Layer Assembly

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ABSTRACT: Polyelectrolyte multilayer (PEM) thin films consisting of alternate layers of two PEM systems, that is poly(diallyl dimethyl ammonium chloride)/poly(vinyl sulfate) (PDAC/PVS) and poly(allyl amine hydrochloride) (PAH)/ are successfully deposited on polysulfone (PSF) support using spin-assisted layer-by-layer assembly. The films are characterized using atomic force microscope, Fourier transform Infrared, and contact angle measurement. The salt (NaCl) rejection and water flux of the [PDAC/PVS] and [PAH/PVS] membranes are also evaluated using a crossflow permeation test cell. The permeation test shows that 120 bilayers of [PAH/PVS] on PSF substrate provide salt rejection of 53% and water flux of 37 L/m^2 h, whereas that of PDAC/PVS on PSF substrate provide salt rejection of 21% and water flux of 90 L/m^2 h for a 2000-ppm NaCl solution feed at a pressure of 40 bar and temperature of 25°C. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: spin coating; layer-by-layer assembly; multilayer thin films; permeation test; membrane

INTRODUCTION

New approaches for fabricating ultrathin film encompassing fine tuning of surface properties have been developed over the last few years. Among these, layer-by-layer (LbL) assembly provides a simple yet robust method for multilayered deposition of cationic and anionic polymer, macromolecules, colloidal objects, microorganism, or even combination of those materials. As in LbL assembly, the deposition occurs by natural adsorption, in principle, there is no restriction of using the technique with respect to substrate size and topology.[1,2] In spite of those advantages, the conventional LbL assembly (dip-LbL) is still a time-consuming process because deposition of a single layer on the substrate or previously adsorbed layer often takes several minutes. This obviously makes d-LbL is not technologically friendly. To overcome this shortage, spin-assisted layer-by-layer (SA-LbL) technique was then introduced with the main purpose of shortening processing time.[3] In SA-LbL, centrifugal force is applied during deposition which spreads the solution uniformly over the substrate and expels extra material to provide much thinner and more homogeneous films.[4,5]

There have been several publications on the application of d-LbL for fabricating multilayer film on polymeric substrate particularly for separating ions or organic substances from water including pervaporation,[6–8] nanofiltration,[9–16] and reverse osmosis.[17–21] However, to the best of our knowledge, no study has been thus far reported on the use of SA-LbL for fabricating such multilayer membranes.

Hence, in this study, we employed the SA-LbL technique to fabricate multilayer thin films from the combination of two strong polyelectrolytes poly (diallyl dimethyl ammonium chloride) (PDAC) and poly(vinyl sulfate) (PVS) and combination of weak–strong polyelectrolytes, poly(allyl amine hydrochloride) (PAH) and PVS. A commercial polysulfone (PSF) UF membrane served as the substrate.

The membrane surface roughness and surface morphology, hydrophilicity, and surface functionality were characterized by using atomic force microscope (AFM), contact angle (CA) goniometry, and attenuated total reflectance (ATR)-Fourier transform Infrared (FTIR) spectroscopy. Membranes were evaluated for their salt rejection and water permeation performance using crossflow permeation test cells. The permeation test shows that 120 bilayers of [PAH/PVS] on PSF substrate provide salt rejection of 53% and water flux of 37 L/m^2 h, whereas that of PDAC/PVS on PSF substrate provide salt rejection of 21% and water flux of 90 L/m^2 h for a 2000-ppm NaCl solution feed at a pressure of 40 bar and temperature of 25°C.

EXPERIMENTAL

Materials

PVS with M_w = 170,000 g/mol and PDAC with low molecular weight, that is M_w = 100,000–200,000 g/mol were purchased from Sigma-Aldrich, St. Louis, Missouri, USA and PAH with M_w = 120,000–180,000 g/mol was purchased from Polyscience, Warrington, Pennsylvania, USA. Molecular structure of the materials can be seen in Figure 1. All polyelectrolytes were used without further purification. Polyelectrolyte solutions at the desired concentration of 10 mmol (based on the molecular weight of the repeating unit) were prepared from 18.2 MΩ Millipore deionized (DI) water. No attempt was made to adjust the pH of PVS and PDAC because both polyelectrolytes have constant charge density over most of the pH range in water. However, the pH of PAH was adjusted at 3.5 to produce a fully ionized PAH using HCl. PSF Ultra filtration membranes (YMERSP3001, Sterlitech, Kent, Washington, USA) with MWCO of 30 kDa were used as support layer for fabricating multilayered thin-film composite membranes. This PSF support shows water flux of 325 GFD and no salt rejection at pressure of 50 psi as reported by the manufacturer.

Methods

The SA-LbL deposition technique involves sequential deposition of dilute polyelectrolyte solutions with drying and rinsing between each deposition step. Ultra filtration PSF membrane was pretreated by using UV at wavelength of 256 nm to increase the surface charge and hydrophilicity, following the procedure described by Nyström and Jörvinen.[22] After this pretreatment, PDAC layer was deposited on PSF support using the SA-LbL system (Spin grower[TM] from Absolute Nano, Ann Arbor, Michigan, USA). To eliminate the effect of ramp speed during the deposition,[23] the deposition was commenced after the speed reached the desired spin speed of 3000 rpm. PDAC was deposited at a rate of 0.4 mL/s for 7 s and the film was subsequently spun dried for 20 s. The dry film was then rinsed with DI water at a rate of 0.4 mL/s for 14 s to remove weakly bound polyelectrolyte. The rinsed PDAC film was once again spun-dried for 20 s. PVS was then deposited on the PDAC layer in a similar manner to complete the bilayer deposition. This PDAC/PVS bilayer deposition cycle was repeated until the prescribed number of bilayers was deposited on PSF substrate to produce PDAC/PVS membrane. PAH/PVS film was also deposited on PSF substrate in a similar manner to fabricate the PAH/PVS membrane.

Characterization

Contact mode PicoSPM LE (Agilent, Santa Clara, California, USA) was used to examine the surface morphology of the SA-LbL films deposited on PSFultrafiltration membrane. AFM scanning probes with spring constant of 0.02–0.77 N/m were employed during the characterization. Surface roughness and morphology was taken for scan size of 20 μm by 20 μm and RMS surface roughness reported in this study is the average value from three different locations. Sessile drop CA measurement was carried out by using DM-501 (Kyowa Interface Science, Japan) to examine the change of hydrophilicity of SA-LbL membrane before and after coating. DI water as much as 1 μL was used for this measurement. The smart iTR[TM] ATR-FTIR Nicolet 6700 Model (Thermo Scientific) was used to investigate functional groups of polyelectrolyte multilayer film and the support.

Permeation Test

Permeation test was performed using CF042 (Sterlitech, USA) crossflow permeation test cell. Permeation cell tested an active membrane surface area of 42 cm^2. Feed water consisting of 2000 ppm of sodium chloride was passed through the SA-LbL-fabricated membrane at a pressure of 40 bar and a temperature of 25°C. After the permeation cell condition reached steady state, the permeate flow rate and conductivity measurement was continually taken for every 1 h. Permeation test was conducted for 7 h including time to reach steady state.

RESULTS AND DISCUSSION

In this study, thin film composite membranes fabricated from two polyelectrolyte systems were investigated. First system consists of the combination of strong/strong polyelectrolytes that is PDAC/PVS,
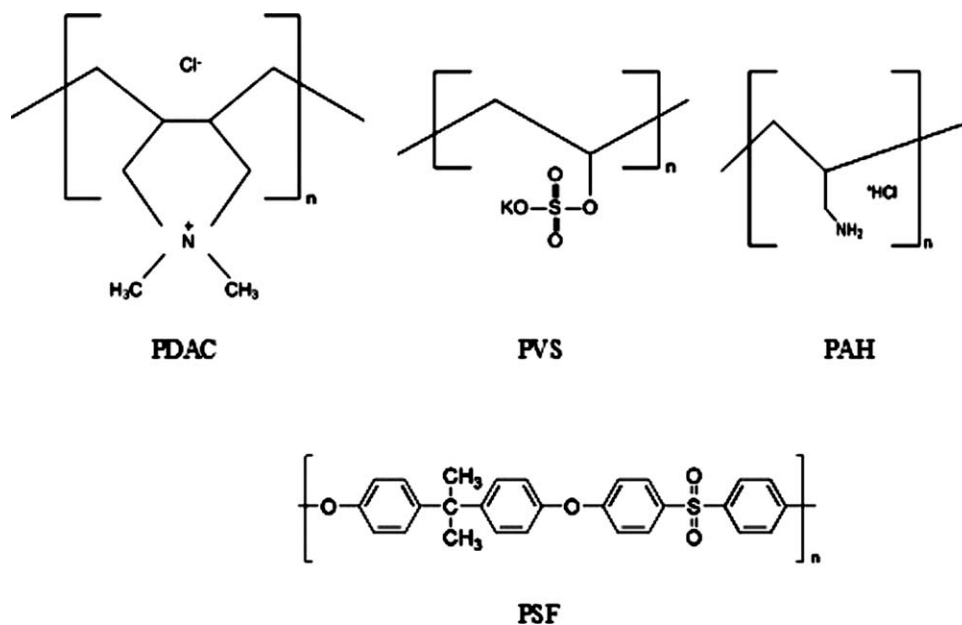
Figure 1 Molecular structure of materials used in this study.

whereas the second one consists of weak/strong polyelectrolytes PAH/PVS. As is well known, the degree of dissociation of weak polyelectrolyte is mainly determined by its pH. In the case of PAH, it is reported that PAH with pK_a of 8.5 starts gaining protons at pH lower than 6.[24,25] In this study, pH of 3.5 was selected for PAH deposition to ensure PAH is in its fully ionized state. Unlike weak polyelectrolyte, charge density of PDAC and PVS remains constant over most of pH range in water. It is reported that PDAC has pK_b of 11.8,[23] whereas PVS has pK_a < 2.[26] It is also reported that complex formation from PDAC and PVS showed stoichiometric chemistry, meaning that all potential ionic bonds between the two are most likely formed.[27] The PSF UF membrane is used here as support because this membrane has also been widely used as support in TFC NF/RO membrane and has been known for its outstanding chemical, thermal, and mechanical stabilities.

SA-LbL assembly produces multilayer thin film with different mechanisms from traditional dip-LbL assembly. In the case of dip-LbL, layer is formed by natural adsorption of polyelectrolytes on the substrate or previously adsorbed layers. Initially, this adsorption form islands of adsorbate on the substrates. This initial stages are sometime called induction period. As the number of layer increases, the islands are bridged and connected one another and start forming bigger islands until all substrate surface is covered.[28,29] In the case of SA-LbL, forced adsorption occurs instead of natural adsorption because of applied centrifugal force during the deposition. Water molecules that usually screen the interaction between layers are removed because of the centrifugal force. Therefore, SA-LbL assembly results in much faster film formation with complete surface coverage over the substrate because no more barrier between layers.[4] The film then builds up based on the overcharged compensation mechanism. In general, charges of previously adsorbed layer must be compensated by subsequent layer. However, the excess amount of polyelectrolytes is required to compensate owing to many other weaker interactions between previously adsorbed layer and subsequent layer. This excess amount of polyelectrolyte in fact results in surface charge reversal from positive to negative or vice versa.[30]

Figure 2(a) shows highly porous membrane with porosity of few tens of nanometer size, such morphology is common for PSF UF membrane. Figure 2(b,c) show the membrane after deposition of 60 bilayers of PAH/PVS and PDAC/PVS, respectively. These AFM images provide clear evidence that the deposition was successful as the rough and porous PSF substrate surface is seen covered completely with a rather smooth and nonporous film. It should be noted that the bare PSF substrate showed RMS roughness of 28.18 nm, whereas the surface roughness measured by AFM for [PAH/PVS]$_{60}$ and [PDAC/PVS]$_{60}$ membranes showed RMS roughness of 15.35 and 13.45 nm, respectively. The lower surface roughness of PDAC/PVS film compared to that of PAH/PVS film is related to chain flexibility and charge density. It is known that PDAC is stiffer and has lower charge density than PAH[31] and as such, PDAC can adopt more conformation flattening than PAH.
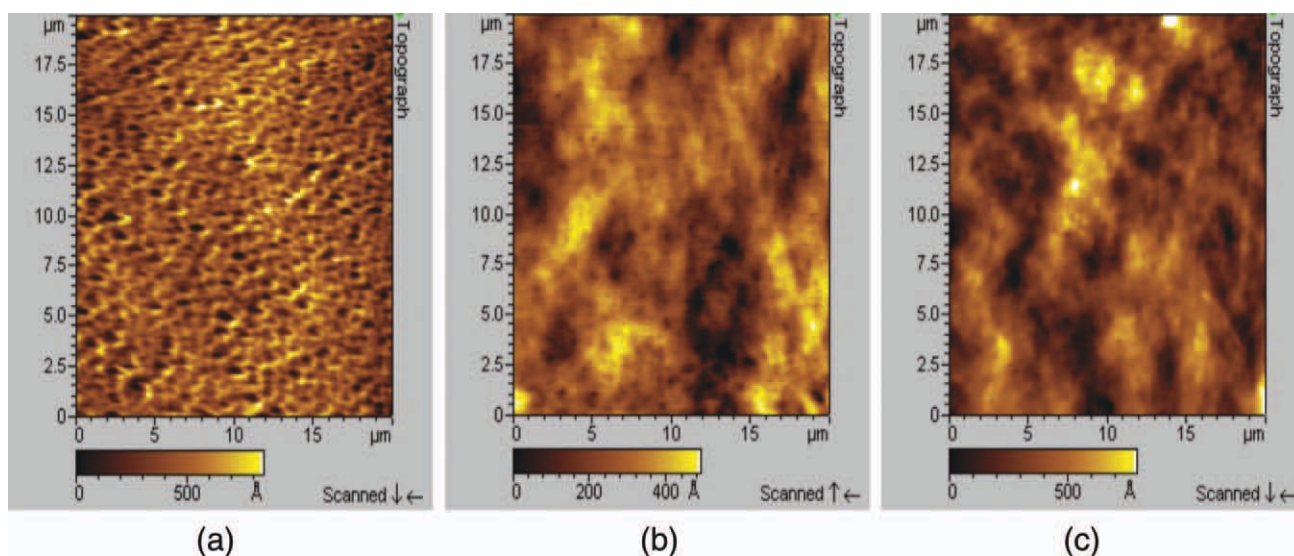
Figure 2 AFM images with scan size of 20 μm × 20 μm: (a) uncoated PSF; (b) [PDAC/PVS]$_{60}$; (c) [PAH/PVS]$_{60}$.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It must be pointed out that although the deposited films appear more or less uniform and homogeneous, few dark spots can still be seen in the deposited films as displayed by the AFM images shown in Figure 2(b,c). One may think that the dark spots are pores or defects; however, if it is the case, then the flux will be extremely high and the rejection must be extremely low close to the value reported for PSF ultrafiltration support (**Materials** section). Therefore, we believe that the dark spots are just sort of valley

features that do not provide any direct access from the surface to the substrate.

Figure 3 shows the FTIR results within functional groups of the bare and coated membranes. The three peaks appearing at wavelength of 2930s cm^{-1} belong to CH, CH$_2$, and CH$_3$ stretch which are present in all materials used in this study. Meanwhile, strong broad peak appearing at wavelength of 3360 cm,^{1} for PSF may come from O—H group, which may have formed in PSF as a result from chain scission

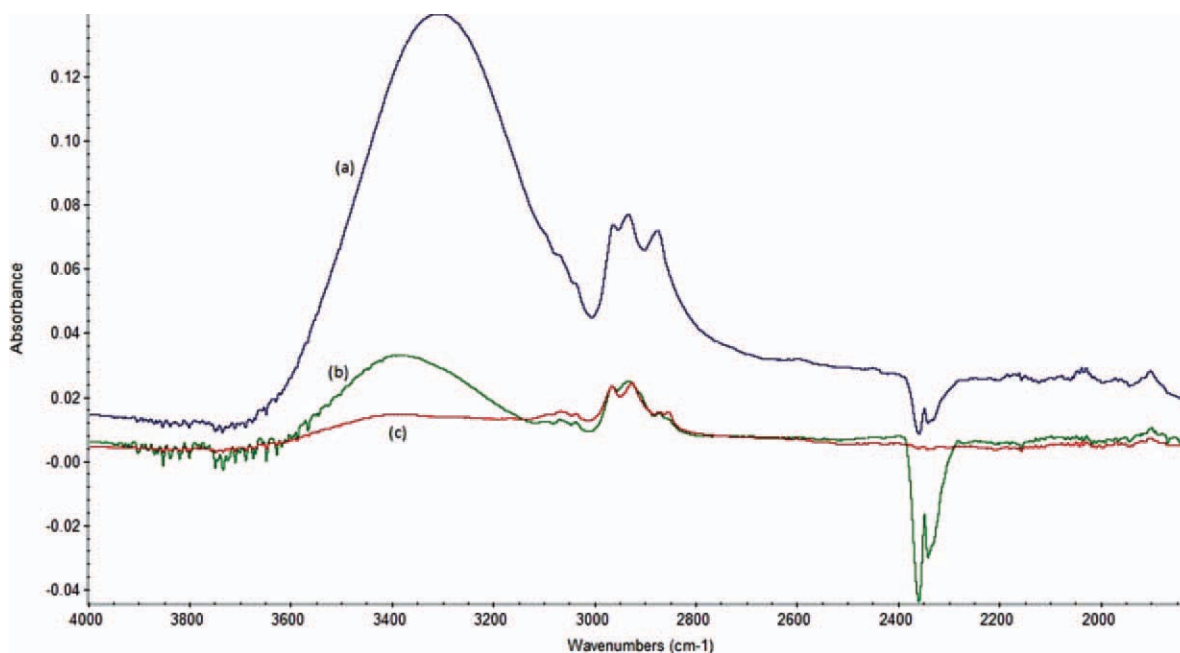**Figure 3** FTIR characteristic peak for bare and coated PSF within functional group region. (a) Commercial PSF; (b) [PDAC/PVS]$_{60}$; (c) [PAH/PVS]$_{60}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
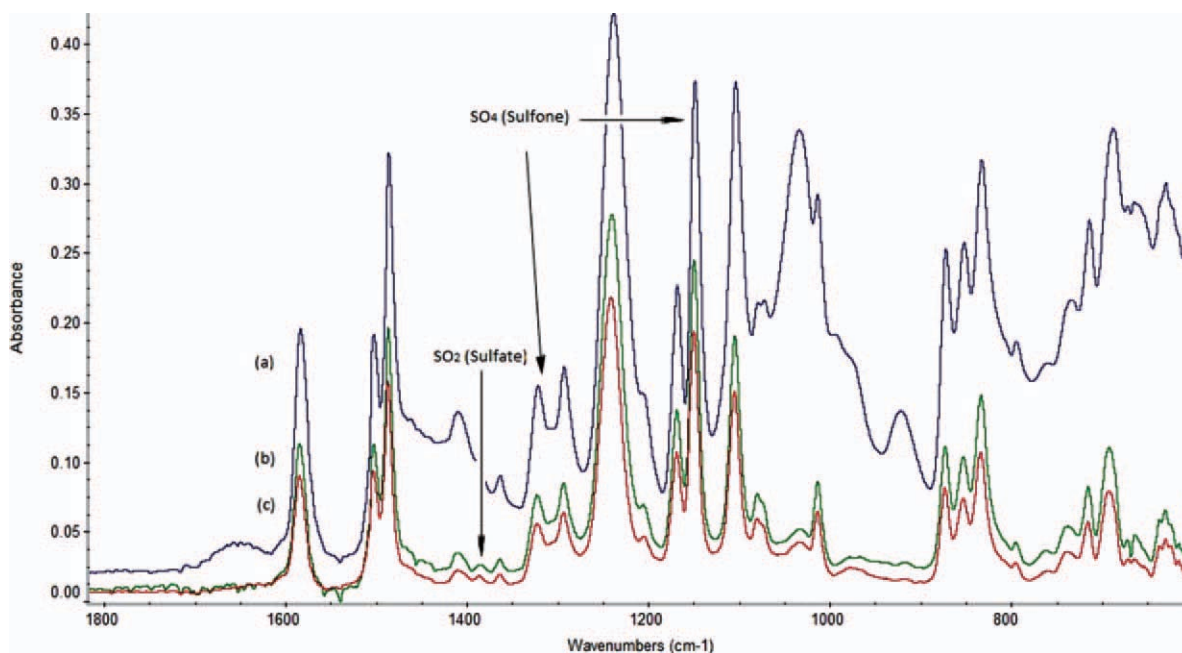
Figure 4 FTIR characteristic peak for bare and coated PSF within finger print region. (a) Commercial PSF; (b) [PDAC/PVS]$_{60}$; (c) [PAH/PVS]$_{60}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of PSF during UV irradiation.[32] Weaker peaks appear at wavelength of almost 3390 cm^{-1} for [PDAC/PVS]/PSF and [PAH/PVS]/PSF are also most likely assigned for O—H.

The FTIR technique is widely used to study some changes that take place on the polymer surface during a modification process. Unfortunately, this method is too insensitive in many cases because of the large sampling depth of the ATR-FTIR spectroscopy. This sampling depth is usually much greater than the thickness of the modified layer and the absorption bands of introduced functionalities might show very low intensity. Figure 4 shows the ATR-FTIR results from the finger print regions of the membrane systems. As shown in Figure 4, the characteristic peak of PSF appears at wavelengths of 1323 and 1151 cm^{-1}. Owing to large sampling depth, both PSF characteristic peaks also appear in coated sample but their lower intensity provides evidence of the presence of coating or thin-deposited layer on PSF substrate. A weak peak appearing at wavelength of 1385 cm^{-1} shows the sulfate functional group for PVS which does not appear in the spectra of bare PSF. This peak thus provides the proof that PVS was successfully deposited on PSF. Another peak characteristic at 1411 cm^{-1} belongs to CH$_2$ band (Fig. 5).

CA measurements indicate that the LbL-coated membranes are more hydrophilic than that of bare PSF substrate. [PDAC/PVS]$_{60}$ and [PAH/PVS]$_{60}$ showed CA of 57.8 and 57.9°, respectively. In comparison, the CA of bare PSF is reported to be 80.5°. This higher hydrophilicity of the coated PSF results
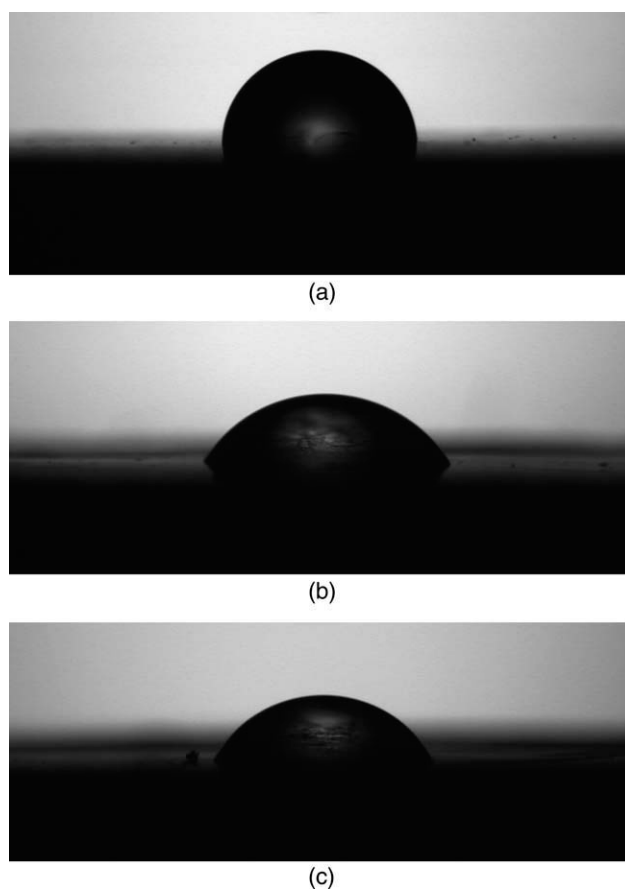

Figure 5 Water droplet images for CA measurement of PEM film on top of PSF membrane. (a) Bare PSF substrate; (b) [PDAC/PVS]$_{60}$ membrane; (c) [PAH/PVS]$_{60}$ membrane.
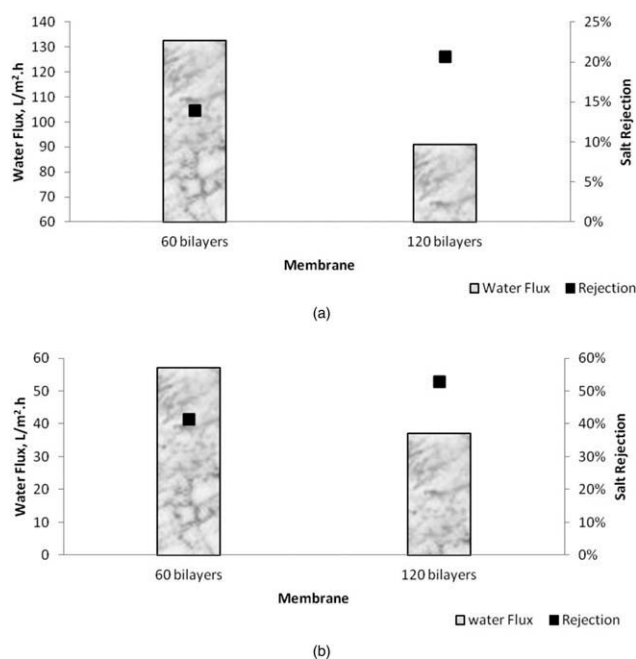
(a)

(b)

Figure 6 Permeation test result for different number of bilayers ($n = 60$ and 120). (a) [PDAC/PVS]$_n$; (b) [PAH/PVS]$_n$.

from the presence of more hydrophilic PVS as the outermost layer in the TFC membranes.

Figure 6 shows the results of the permeation test for the [PDAC/PVS]$_n$ and [PAH/PVS]$_n$ membranes containing various numbers of bilayers. Based on our previous study reported elsewhere,[33] the thickness of one bilayer of either [PDAC/PVS] or [PAH/PVS] measured using ellipsometer on silicon wafer substrate is around 2–3 nm. Thus, 60-bilayer polyelectrolyte multilayer film is expected to have thickness of 120–180 nm, whereas 120-bilayer is expected to have thickness of 240–360 nm. As it can be seen, the flux decreases as the number of bilayers is increased. This is to be expected because water flux is inversely proportional to the film thickness and with increase in the number of bilayers the film thickness increases and results in the flux decline. Similarly, as the number of bilayer increases, the permeability of salt decreases which obviously leads to the decrease of the salt flux. The decrease in salt flux means fewer amounts of salt passes through the membrane and results in higher salt rejection.

Figure 6 also shows that PDAC/PVS multilayer membrane has higher water flux and lower salt rejection compared to PAH/PVS multilayer membrane at a given number of layers. Although both membranes have quite similar morphology prior to membrane testing as suggested from AFM images (Fig. 2), in fact, PDAC/PVS film swells more than PAH/PVS does especially when it is exposed to salt solution. This swelling obviously results in larger pore size which causes much more water and salt

molecules pass through the membrane. It was reported that thin film consists of PDAC coupled with another polyions that is poly(styrene sulfonate) (PSS) showed higher swelling degree, whereas PAH/PSS demonstrated much more stable film.[34] Hence, it can also be concluded that PDAC/PVS multilayer film will also swell more than PAH/PVS multilayer film.

CONCLUSIONS

Two polyelectrolyte multilayer systems that is PDAC/PVS and PAH/PVS were successfully deposited as multilayer thin films via SA-LbL assembly to create active layers on top of commercial PSF UF membranes.

This study establishes that SA-LbL processing can be successfully used to fabricate thin-film composite membranes via the process of depositing alternate nanothin layers on a given support scaffold. The [PDAC/PVS] and [PAH/PVS] thin-film membranes fabricated by SA-LbL provide high flux and moderate salt rejection. For example, [PDAC/PVS]$_{120}$ membrane showed water flux of about 90 L/m^2 h and salt rejection of 21%, whereas [PAH/PVS]$_{120}$ membrane showed water flux of 37 L/m^2 h and salt rejection of 53%. [PAH/PVS] membrane thus performs better than PDAC/PVS membrane in salt rejection of almost two times higher and a reasonable water flux.

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