Preparation, modification and characterization of polymeric hollow fiber membranes for pressure retarded osmosis

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1. Theory

1.1. Standard osmosis processes

The flow volumes of the draw and feed solutions were controlled using HPLC pumps (Series II; Scientific Systems Inc., USA). A back pressure regulator was installed to pressurize the draw solution passing through the active surface side of the membrane module. The active layer of the membrane was always facing the draw solution. The draw solutions were prepared 0.6 M using NaCl. In this study, the power density was calculated using the permeate flux and applied pressure.

The membrane permeate flux J_w (i.e., the volumetric flux of water) was determined by measuring the change in weight of the feed tank using an electronic balance (Mettler-Toledo, USA). The water flux Jw across the membrane is given by:

$$J_w = A(\Delta\pi - \Delta P) \quad (1)$$

where Jw is the volumetric water flux through the membrane, A is the water permeability of the membrane, $\Delta\pi$ and ΔP are the osmotic and hydrostatic pressure differences across the

membrane, respectively. PRO is an intermediate osmosis process between the FO and RO, where the hydrostatic pressure of the draw solution is lower than the osmotic pressure difference across the membrane, so that the water permeates from the feed (fresh water) side to the draw (salty water) side. In terms of energy production or consumption, which is normally evaluated based on power density defined as the product of the trans-membrane hydrostatic pressure of the draw solution and the water flux permeating across the membrane, the power density (W) versus hydrostatic pressure difference based on Eq. (2):

$$W = J_w \Delta P = A(\Delta\pi - \Delta P)\Delta P \quad (2)$$

It can be seen that pressure energy is produced in the PRO process by transferring the water from a low pressure side to a high pressure side means feed side to draw side. The energy density, which is the amount of osmotic power produced per membrane area is a major performance indicator in PRO process, as it determines the amount of membrane area and thus the size of the PRO plant for a given energy production capacity. There exists a maximum power density when the hydrostatic pressure difference is equal to the half of the osmotic pressure difference, suggesting the optimal working condition for a PRO system.

1.2. Membrane porosity

Membrane porosity refers to the void volume fraction of the membrane and defined as the volume of the pores divided by the total volume of the membrane. However all voids are not open at both ends and thus the effective porosity of the membrane is the ratio of the connected pore volume to the total void volume. There are different methods to measure the porosity including mercury intrusion and gas adsorption but the most appropriate method to measure the

effective porosity of the microporous membrane is capillary flow method based on the fluid flows through the membrane. The porosity of membrane was determined by Capillary Flow Porometer (model CFP EX. 1500, Porous Materials Inc., USA). Capillary flow porometry is an easy and suitable method to determine the pores sizes and their distribution in the membranes. The measurement of porosity and pore size distribution in the sample by the capillary flow porometer is based on the surface tension of the fluid that saturate the sample. In this method membrane sample is wetted in a fluid of known surface tension (Porwick, surface tension 18 dynes) and sealed in a chamber. The pressure of the gas on one side of the wetted membrane sample is gradually increased. When the gas pressure is sufficient to flush the fluid from the pore the gas starts flowing through the pore. The biggest pore since holds fluid with least force gas flows through the biggest pore first and as the pressure is gradually increased the liquid from biggest to smallest pore is expelled. The minimum force required to empty the fluid from the pore of the membrane was calculated using the fundamental equation of porometry.

$$d = \frac{4\gamma\cos\theta}{P} \qquad (3)$$

where P is the applied pressure, d is the diameter of the pore and γ is the surface tension of the liquid which is used to fill the pores. It is to be noted that Eq. 3 assumes that measured pore diameters are cylindrical. While this assumption is idealized for the membrane supports tested in this study, the resulting values for d calculated in Eq. 3 represent the equivalent cylindrical pore diameters of the support. It is also to be noted that the intrusion technique can detect both through and blind pores but not closed pores. For a fluid which totally wets the membrane, contact angle θ is taken 0 then Cos θ = 1.

$$d = \frac{4\gamma}{P} \qquad (4)$$

The pore size distribution provides a quantitative description of the range of pore sizes and total void volume in a given membrane sample.

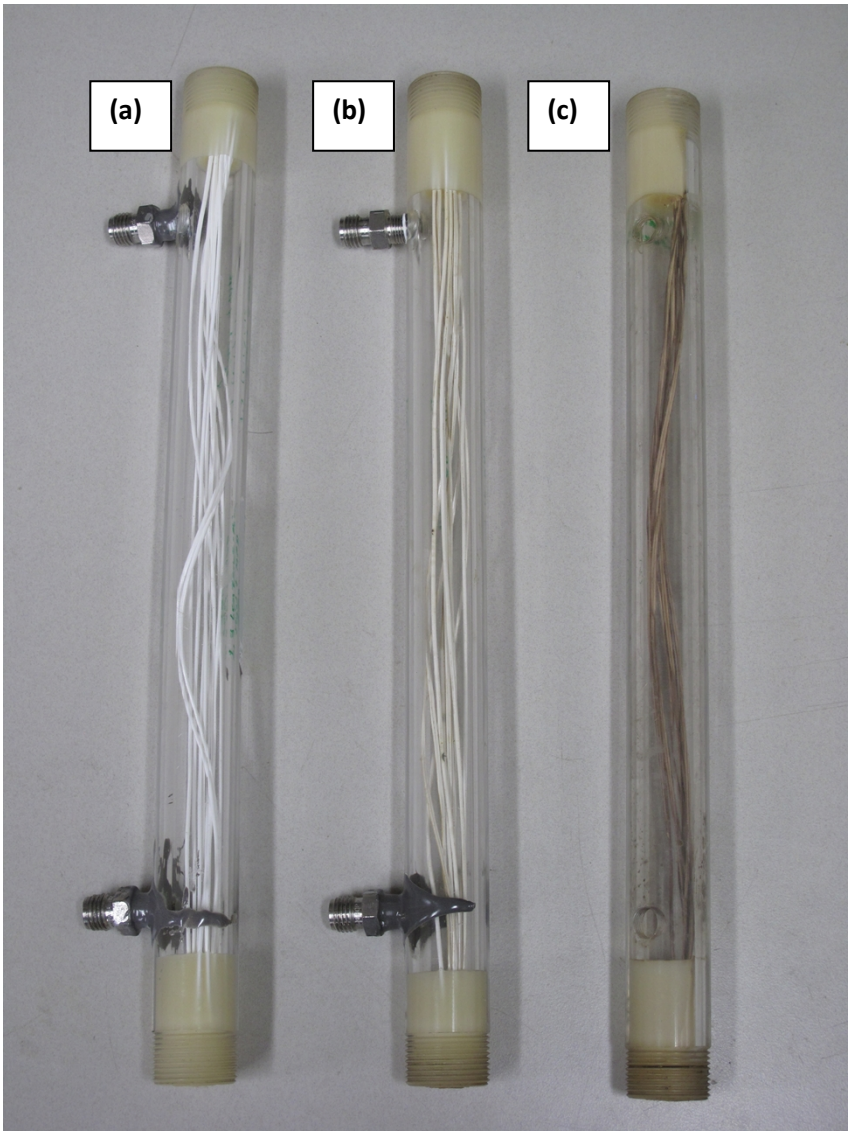

Fig. S1. The images presented the (a) PES/PA-M1, (b) PDA/PA without additive- M2 and (c) PDA/PA with additive- M3 PDA coated hollow fiber membranes module**.**

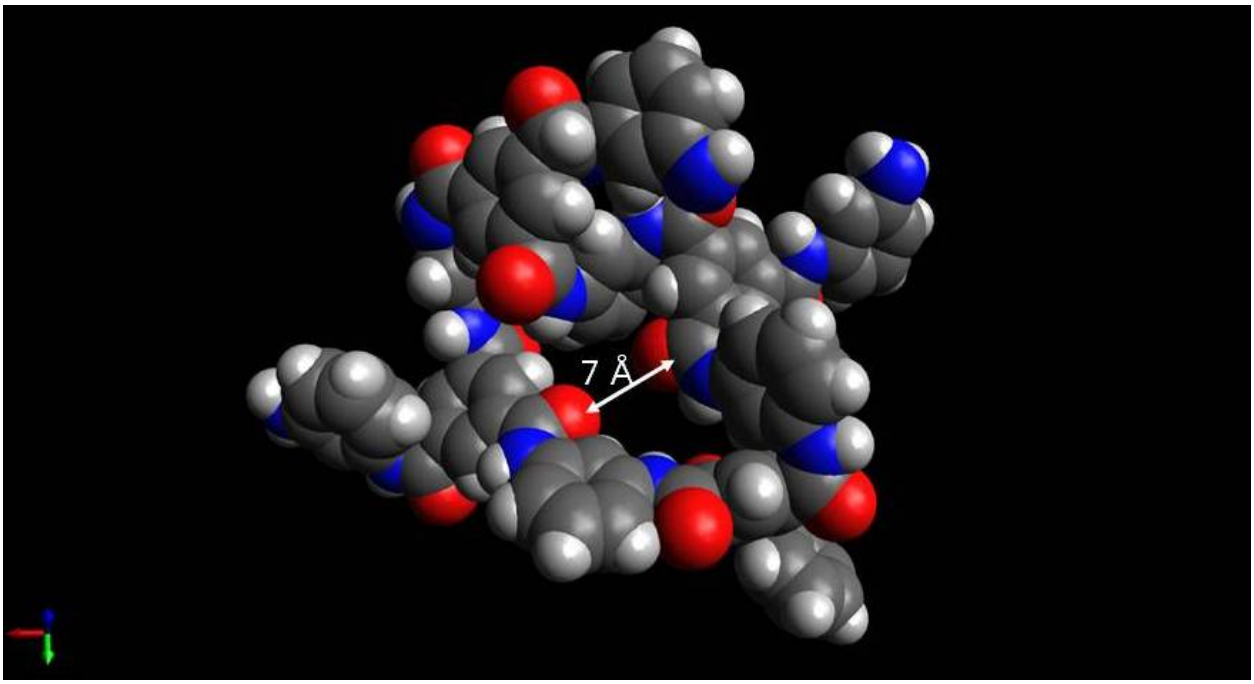

Fig. S2. The simulation image of MPD and TMC thin film composite structure on the PDA coated PES hollow fiber membrane.

Figure S2 shows a snapshot of the MD simulation system. The system consists of two square membranes (3.3 nm long in the x and y directions and 1.5 nm thick in the z direction) separating two KCl solutions of different concentrations. The membrane atoms are located in a face centered cubic fashion in the xy plane. Membrane consists of a semipermeable pore (only water can go through the pore and ions do not go through the pore) of diameter 7 Å at the center of the membrane.