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Crosslinking of polyimide atomic-layer-deposited on polyethersulfone membranes for synergistically enhanced performances



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ABSTRACT

Polyimide (PI) has been uniformly deposited and chemically crosslinked to form a hydrophilic and robust coating layer wrapping the skeleton of the macroporous polyethersulfone (PES) substrate membranes. PI is coated along all the exposed surfaces including the free surfaces and also the pore walls of the PES membranes by atomic layer deposition. The PI-deposited PES membranes are immersed in the excessive methanolic solution of ethylenediamine to initiate the crosslinking of PI chains. The crosslinked PES membranes exhibit synergistically enhanced performances in multiple aspects. They obtain enhanced hydrophilicity due to the formation of polar amide bonds. Control experiments on smooth PI films deposited on nonporous substrates reveal that crosslinking progressively increases the thickness of the PI films. Consequently, we are able to well control and tune the pore sizes by changing the crosslinking durations. The selectivity is enhanced by larger amplitude than the reduction of permeability as a result of reduced pore size and enhanced hydrophilicity after crosslinking. In addition, crosslinking also efficiently improves the thermal and mechanical stability and corrosion resistance of the PES membranes.

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1. Introduction

With excellent thermal resistance, chemical stability and mechanical strength, polyimide (PI) has emerged as a promising membrane material in the application of membrane separation. A number of synthetic methods including phase inversion, interfacial polymerization and vapor deposition polymerization have been used to produce PI membranes in the form of hollow fibers or flat sheets and they exhibit good permeability and selectivity to molecules of gases and organic solvents [1,2]. There are strong intra- and intermolecular interactions, for example, hydrogen bonds, among PI segments. Consequently, membranes derived from PI materials generally possess small pore sizes or even dense nonporous structures and thus find applications typically in the fields such as gas separation, pervaporation and nanofiltration [3–7]. Moreover, high temperature up to 300–400 °C is frequently required for an imidization process to enhance the thermal stability and solvent resistance of PI membranes [3]. In addition, blending or compositing PI with other polymers is also a popular approach to modify the performances of PI membranes; however, these methods typically need complex procedures and the composite membranes obtained from vapor polymerization

usually display a compact and dense bilayer structure rather than a conformal layer on the surface of the substrate membrane [8–12]. Furthermore, massive consumption of PI or its precursors as well as other organic solvents will be involved, which are considerably expensive and not environmentally benign. Considering higher cost of PI than many other membrane materials, like polyvinylidene fluoride and polysulfone, which reduces its popularity in large-scale applications, [5–8,13] it is of great significance to fabricate composite membranes combining low quantity of PI precursors with cost-efficient macroporous substrate membranes of high compatibility. In this case, the pore sizes of the PI composite membranes can be flexibly tuned in a broad range and ultimately to extend their practical applications [3,14–16].

In our previous work, the route of depositing PI on PES membranes utilizing atomic layer deposition (ALD) has been reported [17]. The surface mean pore size of PES membranes has successfully been decreased from 136 nm to 80 nm; consequently the retention rate to monodispersed silica spheres with a diameter of 23 nm increased by 60% whereas pure water flux reduces by approximately 50%. In addition, the thermal stability and mechanical strength both enhanced after the PI deposition, preliminarily demonstrating the potential of tuning the performances of macroporous membranes by PI deposition [17]. However, longer reaction time and larger amount of PI monomers are mandatory to further decrease the pore size. Moreover, due to the hydrophobic nature of

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polyimide, the surface hydrophobicity of the membranes after ALD deposition would be jeopardized as well.

In this study, to further tune the pore sizes and to improve the surface hydrophilicity of the PI-deposited PES membranes, a simple and effective treatment has been applied which only involves the immersion of the membranes in the methanolic solution of ethylenediamine to trigger the crosslinking of the deposited PI layer. Moreover, the stability and the retention rate of the polyimide-deposited PES composite membranes are expected to be progressively enhanced after such a simple treatment of crosslinking. Considering that ALD of PI is independent of the chemical nature of the substrates, we expect that ALD of PI is suitable for the functionalization and modification of many other materials given that they are tolerant to the deposition temperature.

2. Experimental

2.1. Materials

Round chips of PES membranes ($\Phi=25$ mm) with a nominal pore size of 100 nm according to the manufacturer were purchased from PALL and used as the substrate membranes. Pyromellitic dianhydride (PMDA, 99.5%, J&K Scientific) was used as one of the precursors for polyimide ALD process. Ethylenediamine (EDA, $\geq 99.5\%$, Sigma-Aldrich) was applied as both precursor and crosslinking agent in this work. Methanol (99.5%), N, N-dimethylacetamide (DMAc, 98%) and Si wafers were purchased from local suppliers. Monodispersed colloidal silica nanospheres with a diameter of 12 nm were purchased from Sigma-Aldrich with an initial concentration of 30%. The concentrated silica solutions were diluted with deionized water for 2500 times in the retention test. Bovine serum albumin (BSA) phosphate solution with the purity higher than 98% was purchased from Sigma-Aldrich.

2.2. ALD of PI on PES membranes and crosslinking of PI by ethylenediamine

Substrate PES membranes were first placed in the chamber of a home-made ALD reactor. The chamber was heated to 160 °C and pumped to ~ 2 Torr. PMDA and EDA vapors were alternatively pulsed into the reactor for the duration of 2.5 and 0.05 s with the exposure time of 10 and 5 s, respectively to ensure the sufficient adsorption and reaction between the precursors and the substrates. Nitrogen with a flow rate of 50 sccm was used to purge the by-product and unabsorbed/unreacted precursors out of the reactor. The purge time for PMDA and EDA was 40 and 15 s, respectively. One ALD cycle can be described as PMDA pulse/exposure/ N_2 purge/EDA pulse/exposure/ N_2 purge. After 1500 ALD cycles, the PI-deposited membranes were immersed into 15 mL of methanolic solution with 2 wt% EDA for crosslinking at the temperature of 30 °C for 1 h, 6 h, 8 h, 11 h and 15 h, respectively. The crosslinked membranes were immersed in water for 12 h to remove the residual solvent and dried at 60 °C in air overnight. We deposited PI on the smooth surface of Si wafers with the same ALD process and then crosslinking for comparison with that deposited on PES membranes.

2.3. Characterizations

The surface morphologies of membrane samples were examined under a Hitachi S4800 field emission scanning electron microscope (FESEM) operated at 5 kV. A thin layer of Pt/Pd alloy sputtering was coated on the samples to avoid surface charging during SEM observations. The distribution of the nitrogen element on the cross section of different membrane samples was obtained from an energy dispersive X-ray (EDX, Oxford INCA 350) microanalysis system

attached to the SEM. Surface pore size distribution and mean pore size were determined by the software of Nano Measurer based on SEM images and at least 60 pores on the surface were measured to calculate the average diameter. A spectroscopic ellipsometer (Complete EASEM-2000U, J. A. Woollam) with the wavelength range of 246.1–999.8 nm in an incidence angle of 65° was used to measure the thickness of the PI films deposited on silicon wafer before and after crosslinking. The thickness of initial SiO_2 layer on Si wafer has been subtracted. The average thickness of initial SiO_2 layer has been determined by spectroscopic ellipsometer as 2.5 nm. More than 10 spots on the surface of Si wafer were selected and the thickness was correspondingly measured. The Fourier Transformation Infrared (FTIR) spectra were obtained from a Nicolet 8700 FTIR spectrometer in the mode of attenuated total reflection (ATR). Thermo gravimetric analyses (TGA) and differential scanning calorimetry (DSC) were both performed on a TA TG449F thermal analyzer in nitrogen atmosphere with a heating rate of 10 °C/min. TGA measurement was carried out at the temperature from 30 °C to 800 °C and DSC from 30 °C to 400 °C. A contact angle goniometer (Dropmeter A-100, Maist) was applied to obtain the dynamic water contact angle. For each sample, at least 3 sites were tested and the average water contact angle was acquired. The corrosion resistance was compared on the basis of residual mass of the membranes after immersing into the DMAc solvent for 24 h. The residual mass was tested for 3 times and the average value was reported. To test the mechanical stability of the deposited and crosslinked membranes, we treated them with ultrasonication oscillation at the power of 120 W for 30 min and then checked the presence of cracks on their surfaces by SEM. The fouling resistance of the original PES membranes and the crosslinked membranes was compared by the extent of their static adsorption of proteins. The membrane samples were placed separately into 10 mL of 0.5 g/L bovine serum albumin (BSA) phosphate solution without agitation for 12 h at 25 °C. The concentrations of the BSA solutions determined by UV–vis spectroscopy at 280 nm (NanoDrop 2000c, Thermo) before and after the adsorption were used to calculate the value of protein adsorption.

2.4. Permeation performance of modified PES membranes

The pure water flux and the retention to 12-nm silica nanospheres of the original, PI-deposited and crosslinked PES membranes were performed on a stirred filtration cell (Amicon 8010, Millipore Co., Billerica, MA) at the pressure of 0.01 MPa. The retention rates were calculated by comparing the concentrations of Si element in the feed and permeate solutions. An inductive coupled plasma emission spectrometer (ICP, Optima 7000DV, Perkin-Elmer) was used to measure the Si element concentrations.

3. Results and discussion

3.1. Crosslinking of PI layers ALD-deposited on Si wafers

To have a direct understanding on the crosslinking behavior of ALD-deposited PI thin layers, we first ALD-deposited PI layers on nonporous, planar Si substrates and performed crosslinking treatment on them. Such deposited PI films exhibited smooth surfaces before and after crosslinking (Fig. S1) and their thickness can be reliably determined by ellipsometry. The crosslinked PI films gained increased thickness because of the incorporation of EDA molecules into the PI chains. The increase in thickness can be used to evaluate the degree of crosslinking of the PI films. As shown in Fig. 1, the increase in film thickness was relatively faster before the crosslinking duration reached 8 h and thereafter the thickness increased very slightly. The thickness of the P film deposited on Si substrate before crosslinking was 123 nm, and it was increased to

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