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Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Synthesis and characterization of a layered-hybrid membrane consisting of an organosilica separation layer on a polymeric nanofiltration membrane



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ARTICLE INFO

Article history:

Received 8 May 2014

Received in revised form

9 August 2014

Accepted 13 August 2014

Available online 23 August 2014

Keywords:

Layered hybrid

Organosilica

Spin-coating

Polymer support

Vapor permeation

ABSTRACT

In this study a new type of layered hybrid membrane was fabricated. This new membrane consisted of a thin organically bridged silica separation layer deposited onto the surface of a flexible polymeric membrane, NTR-7450 (Nitto Denko, Japan), and was comprised of a sulfonated polyethersulfone top layer and a porous polysulfone support. Using 1,2-bis(triethoxysilyl)ethane (BTESE) as a precursor, a continuous and defect-free BTESE separation layer was deposited onto the surface of a polymeric nanofiltration membrane via a facile, reproducible and scalable sol-gel spin-coating and low-temperature curing process. First, the optimal preparation conditions were established, which included the curing temperature and the spin-coating cycles. The membranes were then used for the vapor permeation dehydration of isopropanol-water solutions, and showed a stable water flux of 2.3 kg/(m² h) and an improved separation factor of about 2500, which was an increase of approximately 5-fold compared with that of a polymeric nanofiltration membrane. In addition, single-gas permeance through this membrane was also discussed and a modest H₂/N₂ selectivity of 26 was obtained, which approximated the performance of ceramic-supported BTESE-derived silica membranes.

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1. Introduction

Membrane-based separations have received considerable amount of attention in chemical industries due to their low energy consumption, low operating costs and steady-state operation [1]. Due to simple operation and control, reliable performance and low energy requirements, the use of these membranes is an attractive separation technique for energy-intensive processes such as the separation of azeotropic or close-boiling point mixtures, recovery of organic compounds from water, and the dehydration of organic solvents via either pervaporation (PV) or vapor permeation (VP) [2].

Various membrane materials including polymers such as polyvinyl alcohol [3,4], polyamide [5], polycarbonate [6], and inorganic materials such as zeolite and silica [7] have been frequently studied and used for VP or PV processes. These membranes, however, have shown shortcomings or defects in a variety of applications. For example, many polymeric membranes generally exhibit low stability under harsh conditions such as exposure to

aggressive solvents, high water content in the feed, or high temperatures. Moreover, the performance of polymeric membranes has also been subject to limitations due to an intrinsic trade-off between permeability and selectivity [8,9]. On the other hand, it is well known that some types of zeolite membranes are not stable in acidic solutions due to a degradation of the zeolite structures [10], and amorphous silica membranes generally lack stability in aqueous systems due to a low degree of hydrothermal stability [11]. At present, there is a general trend in research towards improving the stability of membranes under more complex and harsh conditions that includes the application of more aggressive organic solvents, higher water content and lower pH values in solutions. Therefore, the development of more robust and stable membranes is a constant pursuit by membrane developers.

Recently, organic-inorganic hybrid silica membranes consisting of covalently bonded organic and inorganic moieties have attracted considerable amount of attention due to high degrees of thermal and chemical stability under various harsh conditions, and to their excellent molecular sieving abilities [12–14]. For example, a promising organosilica membrane prepared by the hydrolysis and condensation of the bridged precursor 1,2-bis(triethoxysilyl)ethane (BTESE), has

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shown an unparalleled lifetime of 1000 days for the pervaporative dehydration of *n*-butanol at 150 °C [15]. Reportedly, even in aprotic solvents or at a pH as low as 2, these membranes continue to be very stable. In our previous report, a highly permeable hydrogen separation membrane with improved hydrothermal stability was developed successfully via a “spacer” technique that was used to design the pore size of a BTESE-derived silica membrane [16]. Moreover, our research group applied BTESE membranes to the pervaporative dehydration of acetic acid aqueous solutions [17] and water desalination via reverse osmosis [18], confirming an excellent degree of acid and chlorine resistance. However, all of these organosilica membranes were fabricated on flat or tubular ceramic supports [11–19], which limits the applications of them due to the high cost of the support materials and complex fabrication processes, which results in scale-up difficulties.

A new concept in polymer-supported membrane fabrication is now being proposed—the fabrication of a high-performance inorganic separation layer on polymer supports. For example, Nair and co-workers have reported the fabrication of modified mesoporous silica and zeolitic imidazolate framework (ZIF) membranes on polymeric hollow fibers [20,21], which they applied to gas separation and to the separation of hydrocarbons by pervaporation, respectively. The separation performances of these membranes have been equal to, or even better than, those of previous ceramic-supported membranes. Subsequent reports on the fabrication of zeolite membranes on porous polysulfone have shown high H₂/CH₄ (10.5) and H₂/N₂ (12.4) selectivities in the separation of gas mixtures [22]. Moreover, a more promising polymer-supported, BTESE-derived silica membrane was prepared by Ngamou et al. via an expanding thermal plasma chemical vapor deposition (ETP-CVD) technique [23]. Unfortunately, the carbon bridges, Si–C–C–Si in a BTESE molecular structure, were decomposed by the abundant reactive oxygen species, because of a thermally enhanced oxidation reaction during plasma deposition. Reportedly, only 30% of the Si–C–C–Si bridges were retained in the BTESE networks, which is the most important structure to improve the hydrothermal stability of an organosilica membrane.

Almost simultaneously, our research group was proposing the sol–gel processing of a layered hybrid membrane where the organosilica separation layer was deposited onto a polysulfone (PSF) film and 100% of Si–C₂H₄–Si bridge networks could be retained [24]. In addition, we applied the layered hybrid membranes to the vapor permeation dehydration of isopropanol–water solutions, which exhibited good stability and an improved separation performance [25]. However, there was extensive penetration by the coating sol into the porous PSF support since the relatively large pore sizes (~50 nm) of the support were difficult to coat to a uniform thickness, which often led to pinholes and the formation of defects. In order to form a continuous and complete organosilica film on the porous PSF surface, a high concentration of coating sol (10 wt% BTESE) and multiple spin-coating cycles (at least 3 spin-coated cycles) were required during the spin-coating process, which inevitably led to the formation of a thicker organosilica film, thereby increasing the transport resistance of water molecules [25]. Therefore, for the development of an advanced separation membrane with good stability and separation performance as well as a simplified fabrication process and low cost, particularly in the preparation process, the choice of more appropriate polymer supports with suitable pore size distribution and properties will be important.

In this paper, sol–gel spin-coating was applied to the fabrication of layered hybrid membranes by coating a thin BTESE-derived silica separation layer onto a polymeric nanofiltration membrane, which consisted of a thin sulfonated polyethersulfone (SPES) skin layer and a porous polysulfone (PSF) support. First, we investigated the fabrication conditions of the BTESE separation layer that would be coated onto this support. Then, polymer-supported,

BTESE-layered hybrid membranes were employed for the vapor permeation dehydration of an isopropanol–water (90/10 wt%) solution at 105 °C. Furthermore, the single-gas permeation of this membrane was also investigated.

2. Experimental

2.1. Materials

A nanofiltration membrane (NTR 7450, Nitto-Denko, Japan) with an ultrathin sulfonated polyethersulfone (SPES) skin layer on the surface of a porous polysulfone (PSF) support was used for the polymer support. The average pore size of the SPES skin layers was approximately 1.4 nm, as estimated based on the molecular weight cut-off (MWCO) [26,27]. The 1,2-bis(triethoxysilyl)ethane (BTESE) precursor was purchased from Gelest, Inc (Germany). All the chemicals were of reagent grade and used without further purification.

2.2. Fabrication of a BTESE membrane onto a polymer support

BTESE polymeric sols were prepared by the hydrolysis and polymerization reaction of BTESE in 1-propanol according to a method established in our previous report [24]. Briefly, BTESE was mixed with 1-propanol, and then distilled water and HCl were successively added dropwise to this solution under continuous stirring. The molar composition of the reactants was BTESE/H₂O/HCl = 1: 60: 0.1, and the BTESE concentration was kept at 5.0 wt% after the addition of 1-propanol, which proved to be the lowest concentration of sol to effectively form a complete and continuous BTESE film on a polymer surface using a spin-coating process [25]. After stirring for 1.5 h in a closed glass bottle at room temperature, the BTESE sols were used to prepare the separation layer on the nanofiltration membrane (NTR 7450) support.

Layered hybrid membranes consisting of the BTESE separation layers on NTR supports (BTESE/NTR) were fabricated via a sol–gel spin-coating process that is described elsewhere [25]. For the first step in the spin-coating process, the NTR support (diameter: 2.5 cm) was fixed onto a macroporous stainless plate (Pore diameter: 100 μm, porosity: 50%). Subsequently, approximately 200 μL of BTESE sol was dispensed onto the NTR support surface, and then the spin speed was immediately increased to 6000 rpm in 5 s and was held for 30 s (spin-coating process). Finally, the obtained samples were cured at temperatures that varied from 100 to 200 °C for 25 min (curing process). One spin-coating cycle included both spin-coating and curing processes.

2.3. Characterizations

Several methods were used to characterize the NTR-7450-supported BTESE membrane (BTESE/NTR). The surface morphology and cross-sections of NTR and BTESE/NTR membranes were examined using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The surface chemical bonding and compositions of BTESE/NTR layered hybrid membranes were measured using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT/IR-4100, JASCO, Japan) and X-ray photoelectron spectroscopy (XPS, ESCA3400, Shimadzu, Japan), respectively. For XPS, the depth profiles of the concentrations of C, S, Si and O were obtained in the membrane from the C 1s, S 2p, Si 2p and O 1s energy bands by sputtering with 0.6 keV Ar⁺ at 80 nm min⁻¹ (based on SiO₂).

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