



Tuning the molecular structure, separation performance and interfacial properties of poly(vinyl alcohol)–polysulfone interfacial composite membranes

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ABSTRACT

Interfacial composite membranes were prepared by dip-coating poly(vinyl alcohol) hydrogels on polysulfone ultrafiltration support membranes. Ultra-thin poly(vinyl alcohol) films were cast using multi-step coating procedure with dilute poly(vinyl alcohol) aqueous solutions and stabilized by a novel *in situ* cross-linking technique using five different cross-linking agents. A previously developed film casting technique allowed a constant film thickness of 200–300 nm to be maintained while varying cross-linking degree and cross-linking agent. The effects of crosslinking on the molecular structure, separation performance, and interfacial properties of poly(vinyl alcohol)–polysulfone composite membranes were probed experimentally and with molecular dynamic simulations. Higher degrees of cross-linking correlated strongly with lower PVA film crystallinity and decreased hydrophilicity. Experimentally determined solvent and solute permeability data correlated almost perfectly with molecular dynamics simulated fractional free volumes of the cross-linked poly(vinyl alcohol) membranes, demonstrating the importance of polymer free volume (*i.e.*, steric exclusion and hindered diffusion) in solvent and solute transport through nanofiltration membranes and suggesting that predictive, *in silico* design of cross-linked PVA coating films may be practical.

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1. Introduction

The inherent hydrophilicity of poly(vinyl alcohol) (PVA) along with its excellent thermal, mechanical and chemical stability make it an attractive polymer for fabricating water treatment membranes [1]. However, historically PVA has not produced membranes with competitive water permeability because it has a semi-crystalline structure due to strong hydrogen bonding interactions. In addition, the hydrophilicity leads to high water uptake and swelling in water, which requires PVA to be cross-linked to maintain stability and to produce adequate selectivity in molecular separations [2].

Cross-linked PVA membranes are appropriate for pressure-driven separations designed for a variety of water treatment applications including microfiltration [3] (for particle and bacteria removal), ultrafiltration [4,5] (for virus and macromolecule removal), nanofiltration (NF) [6] (for organic acid, small molecule

and divalent metal removal), and reverse osmosis (RO) [7–10] (for desalination). In addition, cross-linked PVA membranes have been commercialized for dehydration of organic solvents by pervaporation; such membranes are prepared by coating a thin cross-linked PVA layer over polyacrylonitrile ultrafiltration membranes [11,12]. While there have been many previous attempts to develop cross-linked PVA membranes for RO [7–9,13–18] and NF applications [10,19,20], none of these past formulations achieved commercial success because the membranes exhibited relatively low permeability and selectivity due to defect formation, improper cross-linking, or excessive thickness of PVA coating layers. These results were most commonly observed for surface cross-linking and dip-coating methods.

In this study, we employed a multi-step coating procedure followed by *in situ* cross-linking to prepare interfacial composite membranes with ultra-thin, defect-free PVA coating films. To develop composite PVA membranes with NF-like separation performance, cross-linked PVA hydrogels were coated over polysulfone ultrafiltration membranes and cross-linked using several different dicarboxylic acids and dialdehydes. The effects of cross-linking degree, cross-linking agent, and dry curing conditions on the molecular structure and transport properties of PVA–Psf composite nanofiltration membranes was investigated using molecular

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Table 1
Cross-linking agents investigated.

Common name	Chemical formula	Chemical structure	M_w
Succinic acid	C ₄ H ₆ O ₄	HOOCCH ₂ CH ₂ COOH	118.09
Maleic acid	C ₄ H ₄ O ₄	HO ₂ CCH=CHCO ₂ H	116.07
Malic acid	C ₄ H ₆ O ₅	HOOCCH ₂ CH(OH)COOH	134.09
Glutaraldehyde	C ₅ H ₈ O ₂	OHC(CH ₂) ₃ CHO	110.12
Suberic acid	C ₈ H ₁₄ O ₄	HOOC(CH ₂) ₆ COOH	174.19

dynamics simulation, infrared spectroscopy, X-ray diffraction, and separation performance studies.

2. Molecular dynamics simulations

Molecular models of uncross-linked PVA and cross-linked PVA polymers using different cross-linking agents (Table 1) were constructed in this study. The developed PVA model and PVA–succinic acid, PVA–maleic acid, PVA–malic acid, PVA–glutaraldehyde, PVA–suberic acid cross-linked polymer models were constructed using the Amorphous cell module (see Supporting Information). Three types of cross-linking potentially existed in the cross-linked PVA membranes: (1) cross-linking of PVA between –OH groups of PVA polymer chains, *i.e.*, self cross-linking; (2) cross-linking between one carboxylic group of succinic acid and an –OH group in PVA polymer chain, *i.e.*, partial cross-linking; (3) cross-linking between both carboxylic groups of succinic acid and –OH groups in PVA polymer chains, *i.e.*, complete cross-linking [21]. Simulations assumed a cross-linking degree of 20% calculated from

$$\chi_{CL}[\%] = \frac{W_{CL} \times MW_{PVAunit} \times 2}{W_{PVA} \times MW_{CL}} \times 100, \quad (1)$$

where W_{CL} , W_{PVA} , $MW_{PVAunit}$, and MW_{CL} represented the weight of cross-linking agent, the weight of PVA, the molecular weight of one PVA unit (CHOHCH₂), and the molecular weight of the cross-linking agent, respectively. The cross-linking degree only indicates the molar ratio of cross-linking agent to PVA monomeric units used as a starting point for MD simulations; Eq. (1) makes no assumptions about the three types of cross-linking described above. The ultimate structure of cross-linked PVA was determined by the MD simulation. The resulting atomistic structures were subsequently optimized as described previously [22–24].

The simulated atomistic models allow an accurate determination of geometrical quantities characterizing the structure. The fractional free volume (FFV) of the equilibrated uncross-linked PVA membranes and cross-linked PVA membranes were determined by a hard spherical probe. The atoms composing the membranes are represented by hard spheres with van der Waals radius (C = 1.55 Å; H = 1.10 Å; O = 1.35 Å). The probe molecules were modeled as spheres with radii of 1.6 Å. The Connolly surface was determined from the probe molecule rolling over the van der Waals surfaces created by the polymer atoms; polymer free volume was defined as the empty volume within the Connolly surface. The fractional free volume was the ratio of polymer free volume to the total volume modeled. It should be mentioned that the free volume obtained by this method excluded the volume that could not be accessed by the probes, but this volume is also largely inaccessible by water molecules.

3. Experimental

3.1. Chemicals and materials

Mowiol® PVA 6-98 with average molecular weights of 47,000 g/mol, respectively, 98.0–98.8% hydrolyzed, was purchased from Sigma-Aldrich Company (St. Louis, MO, USA) for the formation of active layers of the NF composite membranes. Commercial

polysulfone ultrafiltration membranes (NanoH₂O Inc., Los Angeles, CA, USA) were used as supports on which the PVA films were cast. Cross-linking agents succinic acid (>99%), maleic acid (>99%), malic acid (>99%), glutaraldehyde (25% aqueous solution) and suberic acid (>99%) were used as received from Sigma–Aldrich company (St. Louis, MO, USA) (Table 1).

3.2. Membrane preparation

Poly(vinyl alcohol) powder was dissolved in DI water at 90 °C using mechanical stirring (Fisher Scientific, Pittsburgh, PA, USA) for about 60 min to make PVA aqueous solutions. Unless otherwise specified, the PVA molecular weight was 47 kDa and the PVA concentration was 0.10 wt%. Next, PVA solutions were cooled to room temperature and the cross-linking agent was added along with 2 M HCl as catalyst under continuous stirring to produce the PVA casting solution. Cross-linking agent concentration was selected to produce a theoretical cross-linking degree of 20 percent (as calculated by Eq. (1)) unless otherwise specified.

Poly(vinyl alcohol) casting solutions were coated onto polysulfone ultrafiltration membranes for three times. First, the casting solution was poured onto the PSf support and let sit for 10 min. Then, the solute was drained and the remaining water was allowed to evaporate at room temperature for 24 h. Next, the coated membrane was doped into the same PVA solution for 10 s and then taken out, and air-dried for 24 h again. The 10-s coating and drying was repeated a third time to produce defect-free ultra-thin PVA coating films. The PVA coated polysulfone membranes were then cured at 100 °C for 10 min.

3.3. Membrane characterization

The extent of cross-linking of PVA coating layers was confirmed by attenuated total reflection infrared spectroscopy (ATR-IR) performed on a Jasco FTIR 670 plus with variable angle ATR attachment coupled to a germanium crystal operated at an angle of 45°. Prior to the ATR-IR measurement, the samples were dried in a desiccator for a minimum of 24 h. Crystallinity of PVA coating films was characterized by X-ray diffraction, XRD (Brüker AXS D8 diffractometer, Germany, using Cu K α radiation).

The membrane surface hydrophilicity, surface tensions, and interfacial free energies were determined from measured contact angles using an automated contact angle goniometer (DSA0 KRÜSS GmbH, Hamburg, Germany). At least twelve equilibrium contact angles were measured for each sample. The highest and lowest values were discarded before taking the average and standard deviation. Contact angle measurements for deionized water (polar liquid), diiodomethane (apolar liquid) and glycerol (polar liquid) enables determination of surface tension parameters using the extended Young–Dupre equation [25]. Here, as elsewhere [26,27], we define “wettability” from the surface roughness corrected solid–liquid interfacial free energy, $-\Delta G_{13}$, and “hydrophilicity” from the surface roughness corrected interfacial free energy of cohesion, ΔG_{131} .

3.4. Separation performance

The separation performance of PVA–PSf composite membranes was evaluated in a bench scale crossflow membrane filtration system equipped with six parallel membrane cells (effective membrane area is 12.9 cm² for each membrane cell). The system was described in detail elsewhere [26]. Pure water flux of polysulfone and PVA–PSf membranes were determined using 18 M Ω laboratory de-ionized water at 25 °C and applied pressures of 173 and 1034 kPa (25 and 150 psi), respectively. The crossflow Reynolds number was maintained at 312 without a mesh spacer in the feed

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