Journal of Membrane Science 563 (2018) 229–237

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Constructing robust and highly-selective hydrogel membranes by bioadhesion-inspired method for CO_2 separation

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ARTICLE INFO

Keywords:
Polydopamine nanoaggregates
Poly (vinyl alcohol)
Physical cross-linking
Carbon dioxide separation

ABSTRACT

Water-swollen hydrogel membranes are good candidates for CO_2 separations due to the favorable solubility of CO_2 in water. However, the excessive amount of water often causes the poor mechanical property and low selectivity. Herein, we propose a bioadhesion-inspired method to construct robust and high-performance CO_2 separation membranes *via in situ* generation of polydopamine (PDA) nanoaggregates within poly (vinyl alcohol) (PVA) matrix. PDA nanoaggregates entangled with PVA chains and formed hydrogen bonding with hydroxyl groups from PVA chains. Physical cross-linking occurred between PVA chains and PDA nanoaggregates. Compared with the PVA membrane, the PVA-PDA hybrid membrane with the dopamine content of 0.5 mol% exhibited a 1.7-fold increase in tensile strength and a 2.2-fold increase in the tensile modulus. The membranes were used for CO_2/CH_4 separation. The physical cross-linking resulted in a PVA chain rigidification region around PDA nanoaggregates, which hindered the penetration of larger-size gas molecules and thus enhancing the CO_2/CH_4 selectivity. Moreover, the abundant amine groups from PDA nanoaggregates could facilitate CO_2 transport. The optimized hybrid hydrogel membrane exhibited CO_2/CH_4 selectivity of 43.2, which was 43.85% higher than that of the PVA membrane. The bioadhesion-inspired method opens up new opportunities to exploit the potential application of hydrogel membranes.

1. Introduction

Energy-efficient separation of carbon dioxide from other gases such as nitrogen, methane and hydrogen has become a worldwide concern [1]. Compared with conventional technologies, membrane gas separation shows great potential in CO_2 capture due to its low energy consumption, low maintenance and easy operation [2]. Among polymeric membrane materials, hydrogel polymers such as poly (vinyl alcohol) (PVA) [3,4], polyvinyl amine (PVAm) [5] and chitosan (CS) [6] have been proved to be a very attractive class of membrane materials for CO_2 capture because the abundant polar groups on these hydrogel polymers can favorably interact with CO_2 and thus leading to a high solubility selectivity [7].

PVA is a commercially available hydrogel polymer which has been used to fabricate gas separation membranes due to its excellent film-forming and chemical-resistant property [3,8]. However, the abundant polar groups on PVA chains usually result in high polymer cohesion energy and a low free volume, which dramatically increases the mass transport resistance and leads to low gas permeabilities [7]. It has been found that the gas permeability of PVA polymer would be significantly increased when they were swelled by water [9–11]. This kind of hydrophilic polymer membrane can be hydrated in the presence of water to form water-swollen hydrogel membrane (hydrogel membrane) [12]. On one hand, water acts as a plasticizer to weaken the polymer cohesion energy, significantly increase the inter-chain distance and free volume, thus effectively decreasing the mass transport resistance [6,10]. On the other hand, an appropriate content of water can generate additional gas transport pathways in water-swollen hydrogel membranes, especially for relatively high soluble gas molecules like CO_2 [11,12].

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https://doi.org/10.1016/j.memsci.2018.05.075
Received 9 February 2018; Received in revised form 28 May 2018; Accepted 30 May 2018

However , high water content often brings about undesirable poor mechanical property and operational instability which severely limit the industrial application of hydrogel membranes [7,13]. In this regard, exploring an effective approach to reinforce the mechanical property of hydrogel membranes while preserving the water content is highly challenging. Chemical cross-linking is a commonly used method to reinforce PVA hydrogel membranes [14,15]. However, chemical cross-linkers may consume the CO_2-philic hydroxyl groups, which leads to a decreased CO_2 solubility and water content in the membrane [14]. Physical cross-linking is another method to reinforce hydrogel membrane including chain entanglement, hydrogen bonding, crystallite formation and hydrophobic interaction [15,16]. Though physical cross-linking usually does not form permanent junctions, it is sufficient to maintain the mechanical property of hydrogel membrane in water vapors [17]. Moreover, physical cross-linking does not consume the polar groups on hydrogel membranes, which ensures the hydrophilicity and the CO_2 solubility of hydrogel membranes. Deng and Hägg prepared PVAm/PVA blend membranes with good mechanical property, operational stability and high CO_2 permeability [18,19]. In PVAm/PVA blend membranes, physical cross-linking reinforces the hydrogel membranes *via* hydrogen bonding and chains entanglement between PVAm chains and PVA chains [17]. Another undesirable problem of water-swollen hydrogel membranes is the excessive swelling that limits CO_2/gas selectivity [9,12]. For instance, the CO_2/CH_4 selectivity of water-swollen hydrogel membranes is approximately equal to that in bulk water (only about 21), which is far from the demand for practical application. Incorporating CO_2-reactive carriers into hydrogel membranes has been proved to be an effective method to enhance the selectivity [1,5,20,21]. Thus, it can be reasonably expected that incorporation of CO_2-carrier containing polymers to form physical cross-linking with hydrogel chains will offer an effective approach to achieving sufficient robustness and high-performance simultaneously for hydrogel membranes.

Inspired by the unique wet adhesion capability of mussel adhesive proteins, we attempt to incorporate the mussel-inspired adhesive polymer into hydrogel membrane to enhance the mechanical property and CO_2 separation property. Dopamine (DA) is a kind of mussel-inspired adhesive polymer containing both a catechol group and an amino group. Under weakly alkaline conditions, dopamine can aggregate e into polydopamine (PDA) nanoaggregates and firmly adhere to virtually all kinds of materials [22,23]. Previously, we applied various dopamine nanoaggregates to tune the microstructures of membranes [24–26]. In this study, we prepared a series of hybrid hydrogel membranes *via in situ* generation of PDA nanoaggregates in PVA matrix. During the generation of PDA nanoaggregates, the entanglement or interpenetrating structure between PDA chains and PVA chains would be achieved, which is beneficial for mechanical performance. The catechol groups and amino groups on PDA nanoaggregates could generate hydrogen bonding with hydroxyl groups on PVA [27]. Thus, physical cross-linking occurred between PVA chains and PDA nanoaggregates. Moreover, abundant amino groups on PDA nanoaggregates are also good CO_2-reactive carrier to facilitate the transport of CO_2 [28,29]. The influence of PDA nanoaggregates on the morphology, free volume characteristics, structure, water content, water state, mechanical property, stability, and thermal stability of membranes was investigated. The effect of the PDA nanoaggregates content, operating pressure and temperature on the membrane performances were investigated.

2. Experiment

2.1. Materials and chemicals

Poly (vinyl alcohol) (degree of polymerization 1750 ± 50), ethanol and 1.0 M sodium hydroxide (NaOH) standardized solution were purchased from Tianjin Jiangtian Technology Development Co., Ltd. (China); dopamine hydrochloride was obtained from Wuhan Yuancheng Technology Development Co., Ltd. (China); poly (ether sulfone) (PES) ultrafiltration membranes (molecular weight cutoff of 50000) were purchased from Jiangsu Synder Membrane Technology Co. Ltd. (China). All chemical reagents were of analytical grade and used without further purification. Deionized water purchased from the Millipore system (Milli-Q) was used in the whole experiment.

2.2. Preparation of membranes

Hybrid hydrogel membranes were prepared *via in situ* generation PDA nanoaggregates in PVA matrix. PVA was dissolved in deionized water under mild mechanical stirring at 90 °C for 6 h to obtain 3 wt% PVA solution. After cooling to ambient temperature, a certain amount of dopamine hydrochloride powder was added into 15 g PVA solution. The pH value of the solution was regulated to 8.5 by adding 1.0 M NaOH standardized solution [22]. Subsequently, the mixture was stirred under 50 °C water bath for 30 min to generate PDA nanoaggregates. After cooling down to room temperature, the brown-colored casting solutions with different DA content were spin-coated on the PES substrates. Finally, the membranes were dried at room temperature for 24 h. The resultant composite membranes were designated as PVA-PDA(X)/PES, where X (= 0.01, 0.25, 0.50, 1.00 and 5.00) referred to the mole percentage of the DA to PVA. And pristine PVA/PES composite membrane was also prepared by spin coating pristine PVA solution onto the PES substrate. During the gas separation process, the membranes would be rehydrated to form PVA-PDA(X)/PES hydrogel membranes.

For characterizations, the free-standing pristine PVA membrane and PVA-PDA hybrid membranes were also prepared by the solution-casting method. The casting solvent was cast onto a glass plate to the desired thickness and dried at room temperature for 48 h.

2.3. Characterizations

The size and morphology of the *in situ* generated PDA nanoaggregates in casting solution were observed with a PHILIPS TECNAI G2 F20 transmission electron microscope (TEM). The cross-section morphology of the membranes was observed by a Nanosem 430 scanning electron microscope (SEM). The BRUKER Vertex 70 Fourier transform infrared (FT-IR) spectrometer was used to measure the chemical structures of composite membranes. The glass transition temperature (*Tg*) of membranes was measured by a Netzsch 204F1 differential scanning calorimetry (DSC). The thermal gravimetric analysis (TGA) was used to analyze the thermal stability of membranes by a NETZSCH 209F3 instrument. The mechanical property of membrane was tested using an instron mechanical tester (Changchun Kexin WDW-02). The crystallinity structure of membranes was examined by X-ray diffraction (XRD, D/MAX-2500, CuKα) in the range of 5–30° at the scanning speed of 5°/min.

The free volume property of the membranes was detected by positron annihilation lifetime spectroscopy (PALS) with an EG&G ORTEC fast-fast coincidence system (resolution 210 ps). Two samples to be tested were 1.0 cm × 1.0 cm × 1.0 mm, which were placed on either side of the ^{22}Na positron source. The integral statistics for each spectrum was equal to 2 million coincidences and was resolved by LT-v9 program. The ortho-positronium (*o*-Ps) lifetime (τ_3) is related to the size of free volume cavity and intensity of *o*-Ps (I_3) is indicative of the concentration of accessible free volume cavity [30]. On assumption that the *o*-Ps is localized in a spherical potential well surrounded by an electron layer of thickness Δr equal to 0.1656 nm. The radius of the free volume cavity (r_3) was obtained by a semiempirical Eq. (1):

$$\tau_3 = \frac{1}{2}\left[1 - \frac{r_3}{r_3 + \Delta r} + \left(\frac{1}{2\pi}\right)\sin\left(\frac{2\pi r_3}{r_3 + \Delta r}\right)\right]^{-1} \quad (1)$$

The fractional free volume (*FFV*) could be calculated by Eq. (2)