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PII: S0376-7388(18)30392-2
DOI: <https://doi.org/10.1016/j.memsci.2018.05.075>
Reference: MEMSCI16215

To appear in: *Journal of Membrane Science*

Received date: 9 February 2018
Revised date: 28 May 2018
Accepted date: 30 May 2018

Cite this article as: Yingzhen Wu, Tiantian Zhou, Hong Wu, Weixian Fu, Xinru Wang, Shaofei Wang, Leixin Yang, Xingyu Wu, Yanxiong Ren, Zhongyi Jiang and Baoyi Wang, Constructing robust and highly-selective hydrogel membranes by bioadhesion-inspired method for CO₂ separation, *Journal of Membrane Science*, <https://doi.org/10.1016/j.memsci.2018.05.075>

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Constructing robust and highly-selective hydrogel membranes by bioadhesion-inspired method for CO₂ separation

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Abstract: Water-swollen hydrogel membranes are good candidates for CO₂ separations due to the favorable solubility of CO₂ 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 CO₂ separation membranes via *in situ* generation of polydopamine (PDA) nanoaggregates within poly (vinyl alcohol) (PVA) matrix. PDA nanoaggregates entangled with PVA chains and formed

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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 CO₂/CH₄ 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 CO₂/CH₄ selectivity. Moreover, the abundant amine groups from PDA nanoaggregates could facilitate CO₂ transport. The optimized hybrid hydrogel membrane exhibited CO₂/CH₄ 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.

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

Graphical Abstract

Highlights

1. PVA hydrogel membrane was reinforced via *in situ* generation of polydopamine nanoaggregates.
2. Physical cross-linking occurred between PVA chains and polydopamine nanoaggregates.
3. Polydopamine nanoaggregates endowed hydrogel membranes with multi-transport mechanisms.
4. Modified hydrogel membranes showed enhanced CO₂/CH₄ selectivity and mechanical property.

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 CO₂ 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 CO₂ capture because the abundant polar groups on these hydrogel polymers can favorably interact with CO₂ 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 [9,10,11]. 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 CO₂ [11, 12].

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 CO₂-philic hydroxyl groups, which leads to a decreased CO₂ 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 CO₂ solubility of hydrogel membranes. Deng and Hägg prepared PVAm/PVA blend membranes with good mechanical property, operational stability and high CO₂ 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 CO₂/gas selectivity [9, 12]. For instance, the CO₂/CH₄ 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 CO₂-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 CO₂-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 CO₂ 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 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 CO₂-reactive carrier to facilitate the transport of CO₂ [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 48h.

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 (T_g) 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, $\text{CuK}\alpha$) in the range of $5\text{--}30^\circ$ at the scanning speed of $5^\circ/\text{min}$.

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 $1.0\text{ cm} \times 1.0\text{ cm} \times 1.0\text{ mm}$, 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 ($o\text{-Ps}$) lifetime (τ_3) is related to the size of free volume cavity and intensity of $o\text{-Ps}$ (I_3) is indicative of the concentration of accessible free volume cavity [30]. On assumption that the $o\text{-Ps}$ 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 equation. (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)

$$FFV = \frac{4}{3} \pi r_3^3 I_3 \quad (2)$$

2.4. Gas permeation test

Mixed gas (CO_2/CH_4 30/70 vol%) permeation measurements were conducted in a temperature range of 30-80 °C and a feed gas pressure range of 2-12 bar based on the conventional constant pressure/variable volume technique. The gas permeation apparatus has been described in our previous literatures [31]. Membranes were hydrated to form water-swollen hydrogel membrane by water vapor before use. The feed gas was humidified to saturation with water vapor by passing through a humidifier and then passed through an empty bottle to remove the condensate water. Meanwhile, N_2 as the sweep gas was humidified by pass through a water bottle at room temperature. The volumetric flow rate of sweep gas was controlled by mass flowmeters. The gases were injected into an Agilent 6820 gas chromatograph with a thermal conductive detector (TCD) to determine the compositions of permeate gas. The gas permeance (R_i , GPU, 1 GPU = $10^{-6} \text{ cm}^3 (\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$) of either gas was obtained through Eq. (3) and the final result was the average value of two

tests.

$$R_i = Q_i / (\Delta P_i A) \quad (3)$$

where Q_i is the volumetric flow rate (cm^3/s) (STP), ΔP_i is transmembrane partial pressure difference (cmHg), and A is the effective membrane area. The CO_2/CH_4 selectivity (α) was calculated by Eq. (4):

$$\alpha = R_{\text{CO}_2} / R_{\text{N}_2} \quad (4)$$

2.5. Measurement of total water, free water and bound water

Water uptake and water state in membranes were determined using the method reported in literature [6]. The membrane sample was weighed after gas permeation test to determine the “humidified” weight (m_1). Then, the membrane was heated at 100 °C in a vacuum oven for 12 h to remove free water and reweighed (m_2). After that, the membrane was again dried under vacuum at 150 °C for another 12 h to remove bound water and reweighed (m_0). The content of total water (W_t , %), bound water (W_b , %) and free water (W_f , %) were calculated based on the following equations.

$$W_t = (m_1 - m_0) / m_0 \times 100\% \quad (5)$$

$$W_f = (m_1 - m_2) / m_0 \times 100\% \quad (6)$$

$$W_b = (m_2 - m_0) / m_0 \times 100\% \quad (7)$$

3. Results and discussion

3.1. Characterization of membranes

3.1.1. TEM

TEM image of *in situ* generated PDA nanoaggregates in PVA-PDA hybrid membrane is obtained by dropping the casting solution onto the copper mesh. As shown in Fig. 1(a), *in situ* generated PDA nanoaggregates have a size of about 60 nm with a spherical shape. In contrast, the PDA nanoaggregates synthesized in the PVA-free aqueous solution show a larger size of about 140 nm (Fig. 1(b)). The confined space within the PVA matrix controls the growth of the PDA nanoaggregates. Moreover, it can be clearly seen that there are more *in situ* generated PDA nanoaggregates stacking up with each other, which could be attributed to the chains entanglement and hydrogen bonding interactions between PDA nanoaggregates and PVA matrix.

Fig. 1 TEM image of (a) the *in situ* generated PDA nanoaggregates in PVA-PDA hybrid membrane (b) PDA nanoaggregates generated in the PVA-free aqueous solution.

3.1.2. FESEM

The cross-sectional morphologies of pristine PVA membrane and PVA-PDA hybrid membranes were observed by FESEM and shown in Fig. 2. As can be seen from Fig. 2(a), the PVA layer tightly adheres to the PES layer with no visible defect voids, and the thickness

of the PVA layer is about 560 nm. After *in situ* generating PDA nanoaggregates, the PVA-PDA(0.50)/PES hybrid membranes demonstrates a rough active layer with a thickness of about 562 nm (Fig. 2 (b)). Compared with pristine PVA/PES membrane, PVA-PDA(0.50)/PES hybrid membrane has a more indistinct demarcation exists at the active layer/PES interface, indicating a better compatibility of the two layers. In order to investigate the compatibility and the distributions of PDA nanoaggregates in PVA matrix, the magnified FESEM cross-section images of free-standing membranes were observed and exhibited in Fig. 2(c-h). Pristine PVA membrane shows a very homogeneous and smooth morphology, while PVA-PDA hybrid membranes exhibit a rough cross-section morphology. The small white dots (about 60 nm) were the morphologies of PDA nanoaggregates in the membranes. Differed with the agglomeration in casting solution (Fig. 1(a)), Fig. 2(e-h) clearly exhibits that the *in situ* generated PDA nanoaggregates homogeneously disperse in PVA matrix, which was attributed to the cage effect of PVA network [32]. Moreover, no severe agglomeration or visible defect voids was found, indicating a good interface compatibility between PDA nanoaggregates and PVA matrix. The good interface compatibility can be ascribed to the physical cross-linked interactions between PDA nanoaggregates and PVA matrix.

Fig. 2 The cross-section images of (a) PVA/PES, (b) PVA-PDA(0.50)/PES, (c and d) pristine PVA, (e and f) PVA-PDA(0.50) and (g and h) PVA-PDA(5.00).

3.1.3. FT-IR

FT-IR spectrometer was utilized to analyze the molecular interactions between PDA nanoaggregates and PVA matrix. As shown in Fig. 3, the pristine PVA membrane demonstrates two characteristic bands at 3288 cm^{-1} and 1089 cm^{-1} [33], which are assigned to hydroxyl band and -C-OH stretching band, respectively. And with the increase in PDA nanoaggregates content, the two characteristic bands of PVA shift to lower wavenumbers, indicating the formation of hydrogen bonds between the functional groups (catechol groups and the amine groups) of PDA nanoaggregates and the hydroxyl groups of PVA. Moreover, different from the chemical cross-linked PVA membrane, the intensity of the O-H stretching peak in physically cross-linked PVA-PDA membranes remains constant compared with pristine PVA membrane [14], confirming the physical cross-linking between the PDA nanoaggregates and the PVA chains via hydrogen bonds without consuming hydroxyl groups of PVA. The hydrophilic hydroxyl groups keep the hydrophilicity of membrane and ensure the CO_2 solubility of membrane. When the PDA nanoaggregates content reaches 5 mol%

(PVA-PDA(5.00)), the characteristic absorption bands for PDA nanoaggregates at 1606 cm^{-1} and 1512 cm^{-1} can be observed, which represents the overlap of the N-H bending vibrations and the C=C resonance vibration in the aromatic ring, respectively.

Fig. 3 FT-IR spectra of membranes

3.1.4. XRD

The crystalline structure of pristine PVA membrane and PVA-PDA hybrid membranes were investigated by XRD and shown in Fig. 4. Owing to the intermolecular and intramolecular hydrogen bonding interactions of PVA, pristine PVA membrane has a semicrystalline structure and exhibits the characteristic peak at around $2\theta = 19.6^\circ$ [32]. With the increase of PDA nanoaggregates content, the characteristic peak of PVA obviously becomes weaker, suggesting that part of the orderly packed crystalline regions in PVA are disrupted by *in situ* generation of PDA nanoaggregates. This variation can be explained by the presence of physical cross-linked interactions between PDA nanoaggregates and PVA matrix weaken the intrinsic intermolecular and intramolecular hydrogen bonds within PVA chains, thereby resulting in the more loosened and amorphous PVA chains. These results provide an

opportunity for improving the gas permeance property of PVA membrane.

Fig. 4 XRD patterns of membranes

3.1.5. DSC

Glass transition temperature (T_g) of the pristine PVA membrane and PVA-PDA hybrid membranes was measured by DSC and listed in Table 1. T_g often be used to reflect the chain mobility of polymer. In general, the lower T_g , corresponds to the higher chain mobility of the polymer. Due to the semicrystalline structure of PVA polymer, the PVA chains are constrained by the crystalline regions and the T_g is relatively high (43.88 °C). According to the results of XRD, the crystalline regions of PVA are destroyed by the incorporation of PDA nanoaggregates which is supposed to cause a decrease of T_g . But as shown in Table 1, with the incorporation of the PDA nanoaggregates, the T_g of PVA polymer gradually increases from 43.88 °C to 48.42 °C, which implies that the mobility of PVA chains is restricted [25]. This phenomenon can be explained that the PDA nanoaggregates physically cross-link PVA chains to generate a relatively tight PVA-PDA polymer network and constrain the mobility of PVA chains. Moreover, the physical cross-linked interaction between PDA nanoaggregates

and PVA matrix results in the formation of PVA chain rigidification at the filler-polymer interface. These results can improve the mechanical property and the gas selectivity of PVA membrane, respectively.

Table 1 Glass transition temperature (T_g)

Membrane	T_g (°C)
PVA	43.88
PVA-PDA(0.01)	45.86
PVA-PDA(0.25)	46.26
PVA-PDA(0.50)	46.85
PVA-PDA(1.00)	47.83
PVA-PDA(5.00)	48.42

3.1.6. PALS

To further investigate the microstructure of membranes, we probed the free volume characteristics of membranes by PLAS. The fractional free volume (FFV), the average radius of the free volume cavity (r_3) and corresponding intensities (I_3) of membranes are tabulated in Table 2. Compared with the pristine PVA membrane, PVA-PDA hybrid membranes have smaller fractional free volume. This phenomenon can be explained that PDA nanoaggregates acted as physical cross-linking points, constructing a relatively tight structure and significantly restricting the mobility of PVA chains, which would decrease the fractional free volume. Moreover, with the increase of PDA nanoaggregates content, the fractional free volume of hybrid membranes increases firstly and then decreases. This variation is ascribed to the comprehensive effects of PDA nanoaggregates on membrane structure. Combining the DSC, XRD and PALS characterization results, the structure change of PVA-PDA hybrid membranes is shown in Fig. 5. On the one hand, the physical cross-linking between PDA nanoaggregates and PVA significantly restricts the PVA chain mobility and decreases the fractional free volume (FFV), which is also the predominant role that PDA nanoaggregates

play in hybrid membranes to enhance the mechanical property; on the other hand, incorporating PDA nanoaggregates disrupts the crystalline regions of PVA and generates more amorphous regions and free volume cavities for gas diffusion, which is confirmed by the XRD results in Fig. 4. At low PDA nanoaggregates contents (Fig.5 (b)), the crystalline PVA chains were disrupted, PVA chains have a loose amorphous structure. Thus, the PVA-PDA(0.01) membrane has the smallest free volume cavity size (r_3) and most free volume cavities (I_3) in Table 2. With the increase of physical cross-linking point (Fig.5 (c)), the PVA chains were restricted by PDA nanoaggregates. And the loose PVA chains became dense around PDA nanoaggregates and even resulted in the PVA chain rigidification zone. Thus, with the increase of PDA nanoaggregates content, the free volume cavity size of PVA-PDA membrane increased and the free volume cavities decreased again. Above all, physical cross-linked PVA with PDA nanoaggregates may be an opportunity to enhance the mechanical property of membranes without sacrificing the gas permeance.

Table 2 Free volume properties of membranes

Membrane	τ_3 (ns)	r_3 (nm)	I_3 (%)	FFV(%)
PVA	2.124	0.296	13.27	1.440
PVA-PDA(0.01)	1.980	0.283	14.21	1.348
PVA-PDA(0.50)	2.049	0.289	13.44	1.358
PVA-PDA(5.00)	2.113	0.295	12.21	1.312

Fig. 5 Structure of pristine PVA membrane and PVA-PDA hybrid membrane

3.1.7. Mechanical property of membranes

The mechanical properties of pristine PVA membrane and hybrid membranes were probed by tensile test and summarized in Table 3. The tensile strength and modulus of pristine PVA membrane are 35.33 MPa and 0.67 GPa, respectively. The incorporation of PDA nanoaggregates can enhance the tensile strength and modulus of PVA. Meanwhile, the elongation at break was lowered with the incorporation of PDA nanoaggregates. The tensile strength and modulus of PVA-PDA(0.50) hybrid membrane reach up to 60.77 MPa and 1.50 GPa, respectively, 72.2% and 123.9% higher than pure PVA membrane.

Table 3 mechanical property of membranes

Membrane	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PVA	35.33 $\pm$ 4.7	0.67 $\pm$ 0.06	153.73 $\pm$ 7.7
PVA-PDA(0.01)	47.84 $\pm$ 4.9	1.30 $\pm$ 0.09	124.70 $\pm$ 6.2
PVA-PDA(0.25)	54.86 $\pm$ 5.6	1.44 $\pm$ 0.05	115.12 $\pm$ 5.6
PVA-PDA(0.50)	60.77 $\pm$ 6.2	1.50 $\pm$ 0.04	108.24 $\pm$ 4.1
PVA-PDA(1.00)	66.41 $\pm$ 5.1	1.59 $\pm$ 0.08	97.54 $\pm$ 3.2
PVA-PDA(5.00)	68.44 $\pm$ 4.8	1.68 $\pm$ 0.12	74.68 $\pm$ 2.7

Table 4 shows the comparison of mechanical properties of PVA composites reinforced with various methods. In general, PVA can be reinforced by chemical cross-linking with glutaraldehyde [34]. The covalent bonds are inserted in PVA chains lead to a significant increase in the mechanical property. Moreover, incorporating reinforcement materials in PVA can also improve the tensile strength and modulus based on the simple mixing rules of the composite [35]. Compared with other reinforced methods, *in situ* generation of PDA nanoaggregates in PVA shows the higher capability of improving tensile strength and modulus than most of the methods. The increase of the mechanical property can be attributed to the formation of physical cross-linking between PVA and PDA nanoaggregate through

hydrogen bonding interactions and chains entanglement.

Table 4. Comparison of mechanical properties of PVA composites

PVA composites	Optimal content	Tensile strength (MPa)		Tensile modulus (MPa)		Ref.
		Pure PVA Matrix	Composite (increment)	Pure PVA Matrix	Composite (increment)	
PVA cross-linked by glutaraldehyde	4 wt%	8.6	13.8 (60.5%)	6.4	12.5 (95.31%)	[36]
PVA/MWNTs	4 wt%	8.6	21.4 (148.8)	6.4	18.3 (185.9%)	[36]
PVA/CS	50 wt%	2.7	5.5 (103.7%)	92	168 (82.6%)	[37]
PVA/GO	2.0 wt%	25.4	37.8 (48.8%)	27.6	67.3 (143.8%)	[35]
PVA/rGO	0.7 wt%	96	140 (45.8%)	4100	4900 (19.5%)	[38]
PVA/PDA	0.5 mol%	35.3	60.8 (72.2%)	670	1500 (123.9%)	This work

3.1.8. Thermostability of membranes

It has been reported that polydopamine is a kind of synthetic melanins which exhibits similar physical and chemical properties to natural melanins, such as photoprotection [39] and radical scavenging properties [40]. Herein, we also measured the thermal stability of pristine PVA membrane and PVA-PDA hybrid membranes by TG as shown in Fig. 6. The pristine PVA membrane reveals a typically three-stage weight loss [41]. The first stage weight loss between 40 and 150 °C is ascribed to the evaporation of free water and bound water. The second stage weight loss from 204 to 330 °C is mainly due to the elimination of the hydroxyl group of PVA. And the last stage, a breakdown of PVA backbone began at 350 °C. Compared with pristine PVA membrane, the thermal stability of PVA-PDA hybrid membranes is increased. The onset decomposition temperature of PVA shift from 204 to 243 °C with the content of PDA nanoaggregates increases from 0.01 % to 5.00 %. Firstly, the improvement in the thermal stability of PVA-PDA hybrid membranes can be ascribed to the constrained mobility of polymer chains caused by the physical cross-linked interaction between PVA and PDA nanoaggregates. Moreover, many studies suggested that PDA nanoaggregates could

scavenge the radicals generated by the elimination of the hydroxyl group in PVA through radical addition or a one-electron-transfer process. Therefore, incorporation of PDA nanoaggregates can hinder the elimination reactions of the hydroxyl group of PVA, which delays the onset decomposition temperature of PVA from 204 to 243 °C [40]. But, at the higher temperature above 350 °C, the degradation of PVA mainly via vigorous random chain-scission of PVA, which is not affected by the PDA nanoaggregates. Thus the second decomposition temperature of PVA is invariant with the increase of PDA nanoaggregates content.

Fig. 6 The TGA curves of membranes

3.1.9. Water content and state in membranes

According to the different thermodynamic properties of water in hydrogel membranes, water molecules are generally classified into two states: bound water and free water [9, 10, 13]. The content of the total water, bound water and free water of PVA-PDA hybrid hydrogel membranes were measured and shown in Table 5. Bound water refers to the water that bound to polymer matrix via hydrogen bonding, and its content depends on the number of polar

groups [12]. With the increases of PDA nanoaggregates content, the amount of bound water increases from 3.03% to 5.96%. This phenomenon proves that the hydrophilicity of PVA is not reduced by physical cross-linking, and on the contrary, the incorporation of PDA nanoaggregates increases the number of polar groups in membrane and leads to the increase of membrane hydrophilicity. Free water has the same property as bulk water, and its content depends on the fractional free volume of hybrid hydrogel membrane. As shown in Table 5, the amount of free water first decreases and then increases, which is in agreement with the variation of fractional free volume (FFV) revealed by PLAS (Table 2). In gas separation process, free water in the free volume cavities to help generate interconnected CO₂ transport passageways. Bound water combined with polar groups in PDA nanoaggregates can promote the CO₂ reacts with the amine group in PDA nanoaggregates. In summary, incorporation PDA nanoaggregates can reinforce the hydrogel membranes while maintaining the hydrophilicity and water uptake capacity of membranes.

Table 5 water content and state in different membranes

Membrane	W _f (%)	W _b (%)	W _t (%)
PVA	312.41	3.03	315.44
PVA-PDA(0.01)	241.12	3.06	244.18
PVA-PDA(0.25)	249.36	3.63	252.99
PVA-PDA(0.50)	273.32	4.63	277.95
PVA-PDA(1.00)	252.21	5.02	257.23
PVA-PDA(5.00)	217.64	5.96	223.60

3.2. Gas permeation test

3.2.1. Effect of PDA nanoaggregates content on separation performance

To investigate gas separation performance of the membranes, the mixed gas CO₂/CH₄ (30/70 vol%) separation experiments are performed at 30 °C and 0.2 MPa under humidified

condition. As shown in Fig. 7, pristine PVA/PES hydrogel membrane has a CO₂ permeance of 17.2 GPU and CO₂/CH₄ selectivity of 31.5, which is comparable to the reported literatures [14, 42]. As the percentage of the DA increases to 0.50 mol%, the CO₂ permeance is nearly constant, but the CO₂/CH₄ selectivity significantly increases from 31.5 to 43.8. And as the DA content further increases, the CO₂ permeance and the CO₂/CH₄ selectivity decrease simultaneously.

Generally speaking, the cross-linked membranes usually have a lower gas permeance and higher selectivity in comparison with uncross-linked membranes [43-45]. But in fact, PVA-PDA/PES hybrid hydrogel membranes not only have a higher selectivity but also maintain the intrinsic high permeance of PVA polymer at a relatively low cross-linking degree. This phenomenon is ascribed to the multiple effects of the incorporation of PDA nanoaggregates into PVA [25, 46]. Firstly, the physical cross-linked interaction between PDA nanoaggregates and PVA polymer generates a relatively tight polymer structure, restrains the mobility of polymer chains and even results in the rigidification of polymer chain. Hybrid hydrogel membranes have a greater mass transport resistance, which leads to the decrease of gas permeance. And as the kinetic diameter of CO₂ (0.33 nm) is smaller than that of CH₄ (0.38nm), smaller gases will undergo less transport resistance than larger gases, thus the CO₂/CH₄ selectivity will be increased [47]. Secondly, the rich amine groups on PDA nanoaggregates can act as CO₂ facilitated transport carriers, which can facilitate CO₂ transportation in the humidified state, leading to the increase of CO₂ permeance and CO₂/CH₄ selectivity [28, 29]. Thirdly, the presence of PDA nanoaggregates suppresses the crystallinity of PVA, resulting in a relatively amorphous structure and more free volume cavities, which

has been testified by XRD (Fig. 4) and PALS (Table 2) [48]. Hence, more free water will exist in the hydrogel membranes to construct more water channels, which can preferentially pass through CO_2 [7]. For these three aspects, the hybrid hydrogel membranes show a significant increase of CO_2/CH_4 selectivity and a slight decrease in the permeance at a relatively low cross-linking degree (PVA-PDA(0.01), PVA-PDA(0.25)). According to the analysis of FFV in Table 2, the PVA-PDA(0.50) hydrogel membrane should have higher permeance than PVA-PDA(0.01) hydrogel membrane due to the higher FFV, it remains unchanged since the PVA chain rigidification zone forms around PDA nanoaggregates with the increase of the physical cross-linking points which would hinder the CO_2 molecules to access and trigger the CO_2 transport sites on PDA nanoaggregates. This chain rigidification zone is favorable to selective diffusion of CO_2 , so the PVA-PDA(0.50) hydrogel membrane has higher CO_2/CH_4 selectivity. As the PDA nanoaggregates content increase, the physical cross-linking effect of PDA nanoaggregates dominates the performance of hybrid hydrogel membranes. Physical cross-linking effect generates a tight polymer structure that obviously decreases free water content of hybrid hydrogel membranes. The decrease of water channels leads to the sharp decrease of both CO_2 permeance and CO_2/CH_4 selectivity.

Fig. 7 Effect of PDA nanoaggregates content on gas separation performance of hydrogel membranes.

3.2.2. Effect of feed pressure on gas separation performance

To investigate the effect of feed pressure, the gas separation performances of PVA/PES hydrogel membrane and PVA-PDA(0.50)/PES hydrogel membrane were tested at the pressure range of 2-12 bar at 30 °C under the humidified condition and were plotted in Fig. 8. It is obvious that the CO₂ permeance and CO₂/CH₄ selectivity of pristine PVA/PES hydrogel membrane slightly increase with the increase of feed pressure. The solubility of polar CO₂ gas molecules in water increases with the increase of pressure, leading to the increase of CO₂ solubility coefficient of hydrogel membrane [49]. Unlike CO₂ molecule, CH₄ is a kind of nonpolar permanent gas molecules, its solubility coefficient is independent of the pressure. The slight decrease of CH₄ permeance can be ascribed to the compaction effects of swelling polymer chains at high pressure.

Compared with PVA/PES hydrogel membrane, the CO₂ permeance and CO₂/CH₄

selectivity of PVA-PDA(0.50)/PES hydrogel membrane decrease sharply with the feed pressure increasing from 2 to 6 bar and then decrease slightly at higher pressures. This phenomenon implies that PDA nanoaggregates endow hybrid hydrogel membranes with multi-transport mechanisms. As discussed in the previous section, the facilitated transport mechanism in PVA-PDA(0.50)/PES hybrid hydrogel membrane compensate the decrease of CO_2 permeance which is caused by cross-linking effect [29]. But with the increase of feed gas pressure, the carriers on PDA nanoaggregates are saturated, and the reversible reaction reaches to a balance. Therefore, the membrane cannot maintain the high permeance. Meanwhile, CH_4 gases molecules through membrane only follow the solution-diffusion mechanism, thus the slight decline of CH_4 permeance results from the polymer compaction. In this case, the CO_2/CH_4 selectivity of PVA-PDA(0.50)/PES hybrid hydrogel membrane exhibit a decreasing trend.

Fig. 8 Effect of feed pressure on gas separation performance of pristine PVA/PES hydrogel membrane and PVA-PDA(0.05)/PES hydrogel membrane (a) CO_2 permeance, (b) CH_4 permeance and (c) CO_2/CH_4 selectivity of membranes.

3.2.3. Effect of operating temperature on gas separation performance

To explore the effect of operating temperature, the gas separation performance was investigated at different temperatures in the range of 30-80 °C. As shown in Fig. 9(a), both the PVA/PES hydrogel membrane and PVA-PDA(0.50)/PES hydrogel membrane show a significant increase in CO_2 permeance with the increase of operating temperature. The

variation can be explained that the mobility of gases molecules is enhanced and polymer chains become looser at the higher temperature, so that the transport resistance decreases and the CO₂ permeance increases sharply [6, 50]. And it is worth noting that the increasing rate of CO₂ permeance for PVA-PDA(0.50)/PES hydrogel membrane with increasing temperature is smaller than that of PVA/PES hydrogel membrane. Compared with PVA/PES hydrogel membrane, the physical cross-linking in PVA-PDA(0.50)/PES hydrogel membrane constructs a relatively tight polymer structure, constrains the mobility of PVA chains and enhances the transport resistance, resulting in a comparatively low CO₂ permeance. Moreover, due to the stronger heat effect of CO₂ sorption in the hydrogel membrane, the CO₂/CH₄ selectivity significantly decreases with increasing temperature (Fig. 9(b)).

Fig.9 Effect of operating temperature on gas separation performance of pristine PVA/PES hydrogel membrane and PVA-PDA(0.05)/PES hydrogel membrane.

3.2.4 Long-term operation stability

As shown in Fig. 10, the stability test of PVA-PDA(0.50)/PES hydrogel membrane was tested up to 150 h under the humidified condition at the temperature of 30 °C and the feed pressure of 2 bar. The CO_2 permeance and CO_2/CH_4 selectivity remain constant during the testing time with a permeance of 16-17 GPU and a selectivity of 42-44. The desirable long-term stability of PVA-PDA(0.50)/PES hydrogel membrane is ascribed to the physical cross-linking effect, which generates a more stable PVA-PDA polymer structure.

Fig. 10 Long-term operation stability of PVA-PDA(0.50)/PES hybrid hydrogel membrane.

4. Conclusion

In this study, a bioadhesion-inspired approach is developed to reinforce hydrogel membrane and enhance gas separation performance. PVA-PDA/PES hybrid hydrogel membranes were fabricated by *in situ* generation of multi-functional PDA nanoaggregates in PVA matrix for CO₂/CH₄ separation. On one hand, the bioadhesive PDA nanoaggregates physically cross-linked PVA chains *via* chains entanglement and hydrogen bonding, which could enhance the mechanical property and long-term stability of hydrogel membranes. Compared to pristine PVA membrane, the tensile strength and tensile modulus of the PVA-PDA(0.50) hybrid membrane increased by 72.2 % and 139.9 %, respectively. On the other hand, the strong interfacial interaction between PVA matrix and PDA nanoaggregates caused a polymer chain rigidification region near the polymer-filler interface which enhanced the CO₂/CH₄ selectivity. Additionally, the PDA nanoaggregates containing abundant amine carriers facilitated the CO₂ transport through a reversible reaction. Thus, the PVA-PDA(0.50)/PES hybrid hydrogel membranes exhibited a 43.85% higher CO₂/CH₄

selectivity than PVA/PES hydrogel membrane without scarifying CO₂ permeance. This bioadhesion-inspired approach may evolve a platform technology for designing and preparing hydrogel membranes with tunable separation performance and mechanical property. Furthermore, the increase of CO₂ transport sites and incorporation of porous nanofillers will be viable approaches to further intensify the CO₂ separation performance.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Key R&D Program of China (2017YFB0603400), the National Natural Science Foundation of China (No. 21576189, 21490583 and 21621004), Natural Science Foundation of Tianjin (16JCZDJC36500), the National Science Fund for Distinguished Young Scholars (No. 21125627), Program of Introducing Talents of Discipline to Universities (B06006), State Key Laboratory of Organic-Inorganic Composites (oic-201701004).

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