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Mixed matrix membranes containing well-designed composite microcapsules for CO₂ separation

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Abstract

Hollow fillers with tailored nanostructures and functionalities have become promising candidates for advanced mixed matrix membranes (MMMs). Herein, polydopamine/poly(ethylene glycol) (PEG) composite microcapsules are synthesized by hard template method and embedded into the Pebax matrix to fabricate MMMs for CO₂ capture. As a well-known biomimetic adhesive, polydopamine in the capsule wall renders adequate polymer-filler interfacial adhesion. The template removal process produces through-wall mesopores, which allow rapid gas diffusion into the lumen, further significantly reducing the trans-membrane mass transfer resistance. The remaining PEG in the capsule wall not only increases CO₂

affinity, but also avoids excessive chain rigidification at polymer-filler interface. In this way, the composite capsules, compared with those without PEG, confer significantly enhanced separation performance on membranes. The optimal gas transport property of the resultant membranes is obtained with a CO₂ permeability of 510 Barrer and an ideal selectivity of 84.6 for CO₂/N₂ at humidified state, i.e., 108%, 98% higher than those of neat Pebax membrane, respectively. In addition, owing to dopamine-enabled strong adhesion, the MMMs exhibit better stability than Pebax membrane in the long-term test at 85 °C.

Graphical abstract

Keywords: polydopamine; microcapsule; poly (ethylene glycol); mixed matrix membrane;

CO₂ capture

1. Introduction

Over the past decades, gas separation involving polymer-based membrane technologies has

shown unique superiority over traditional processes on account of cost effective, scale-up & operation reliable, and energy saving [1-6]. However, conventional polymeric membranes are typically subject to a trade-off between permeability and selectivity [7-9]. Mixed matrix membranes (MMMs), consisting of a continuous polymer phase and a dispersed phase (usually inorganic), have revealed attractive potentials in benefiting from both phases, so as to overcome the trade-off hurdle [6, 10, 11]. The increasing growth of available polymer and filler materials provides more options and opportunities to the rational design of MMMs.

The key procedure in MMMs design is to opt for a proper filler. Most reported fillers are either porous or nonporous. Nonporous fillers are known to function by disturbing the packing manner of the polymer chains and tailoring the size of free volume cavities. Porous fillers are envisaged to provide extra transport channels with proper molecular sieving ability or favorable gas adsorption capacity. Compared with these fillers, hollow filler as an emerging concept is expected to provide much higher fractional free volume by means of the unfilled lumen. As such, the capsule structured channels are analogous to highways throughout membrane [12]. Hwang et al. [13] reported a nearly 9-times increase in CO₂ permeability after incorporation of 30 wt% hollow ZIF-8 nanoparticles into an ethylene oxide (EO) containing graft copolymer matrix, poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVC-g-POEM). Zhang et al. [14] employed hollow carbon spheres as filler and as a well-designed block copolymer as matrix, which allowed a very high filler loading up to 80 wt% and conferred a skyrocketed permeability (from 55.3 to 468.6 Barrer) on membrane (at 30 wt% loading) without compromising CO₂/N₂ selectivity. On the other hand, the fact that the capsule shell can improve selectivity has been also documented recently.

Zornoza and coworkers [12] found the incorporation of hollow silicalite-1 spheres (HZS) into a glassy polymer matrix led to an increase in H_2/CH_4 selectivity, owing to a molecular sieving effect. Roh et al. [15] synthesized poly(ethylene glycol)(PEG) modified mesoporous TiO_2 hollow nanospheres, which as fillers in PVC-g-POEM were found to slightly increase CO_2/N_2 selectivity on account of the CO_2 -philic characteristics of the grafted PEG segments.

One issue often associated with MMMs is the interfacial morphology. What used to bring troubles is the poor compatibility between bulk polymer phase and inorganic filler phase, causing defective interfacial morphology, decreased separation performance and deteriorated mechanical properties [16-19]. Fortunately, it proves valid to eliminate such interfacial defects by using fillers with surface nanostructures or organic species [20, 21], and the latter has witnessed a broader range of success. The organic functionalities on filler surface afford “soft” contact with the neighboring polymer chains, as well as tunable interfacial interactions. Actually, it is not surprising to find MMMs with rigidified interfacial morphology or partial pore blockage, which was believed to do harm to permeability but has the potential of elevating selectivity. Ismail’s group has pointed out that fillers with relatively large pores (e.g. mesoporosity) might do better in enhancing the overall performance of MMMs at the presence of such interfacial morphologies [22]. Given the sufficient gain in permeability, it becomes more attractive to construct a rigidified or pore-blockage interface when designing hollow filler-based MMMs.

In recent years, muscle-inspired dopamine (DA) chemistries have attracted extensive concerns due to their wide range of applications [23]. DA has been revealed to undergo spontaneous oxidation reaction in aqueous solution to form polydopamine (PDA). The

catechol and amino groups of dopamine afford strong adhesion enabled by the full use of multiple interactions, such as hydrogen bonds, covalent bonds, π - π interactions and electrostatic interactions, etc. [24, 25]. Accordingly, we have reported that dopamine-modified fillers or dopamine aggregates themselves tend to interact strongly with various polymer chains to improve membrane cohesion and stability [26, 27]. More interestingly, Zhang and co-workers demonstrated that PDA could be deposited together with other macromolecules, such as PEG, poly(vinyl pyrrolidone) (PVP) or poly (vinyl alcohol)(PVA), without the need for a terminal covalent linker such as an amine or thiol. This finding opens up a novel avenue for assembling functional coatings [28]. It is therefore envisaged that the polydopamine coating process can be used to prepare hollow fillers, which not only allow further functionalization, but also afford the desired interfacial morphologies discussed above.

Herein, a kind of hollow polydopamine/PEG composite spheres (HDG) was synthesized as the fillers of MMMs for CO₂ capture, where PEG acted as both a CO₂ solubility enhancer and an interfacial morphology manipulator. Pebax[®] MH 1657 was utilized as the polymer matrix for its preferential CO₂ solubility, excellent mechanical stability and commercial availability. The structures of HDG and its effects on membrane structures were carefully probed. The effects of hollow structure and PEG modification to gas transport properties were separately discussed. Moreover, the influences of HDG loading, operating temperature, feed pressure and long-term stability of the Pebax-HDG MMMs are also investigated in detail.

2. Experiment

2.1. Materials

Dopamine hydrochloride (DA) was purchased from Beijing Hua Wei Rei Ke Chemical Co., Ltd. Polyethylene glycol (PEG, $M_w \sim 4000$ Da) and hydrofluoric acid (HF, 49 wt% in water) were obtained from Shanghai Aladdin biological technology. Pebax[®] MH 1657 was purchased from Arkema Co., Ltd. Tetraethyl orthosilicate (TEOS) and tris(hydroxymethyl) aminomethane (Tris) were supplied by Alfa Aesar. Anhydrous ethanol was provided by Tianjin Fengchuan Reagent Technologies Co., Ltd. Single gas (N_2 , CO_2 , He) and binary gas CO_2/N_2 (10:90 vol%) were supplied by Danlian Special Gases Company. All chemicals were used without more purification. Deionized water (DI) was used throughout the whole study.

2.2. Synthesis of hollow particles

Fig. 1. Schematic illustration of HDG microcapsules synthesis

The regular silica particles were prepared by Stöber method [29]. And hollow particles were synthesized via a modified method based upon the previously reported procedure [28]. Firstly, a certain amount of silica particles (0.4 mg/ml) was dispersed in DI (750 ml) under

ultrasonic treatment for 2 h, and then Tris (1.2 mg/ml) was added with HCl to adjust pH at 8.5. Afterward, DA and PEG were simultaneously dissolved at the mixture with magnetic stirring for 24 h. Then the suspension was centrifuged and the collected particles were repeatedly washed by de-ionized water to remove impurity. The as-synthesized core-shell particles, designated as SDG (solid dopamine/PEG composite sphere), were etched in HF solution (diluted to 10%wt with DI) for 2 h, then centrifuged, and washed with deionized water and ethanol. This obtained HDG was dried in vacuum oven at 30 °C for 48 h. Solid dopamine sphere (SDA) and hollow dopamine sphere (HDA) was also prepared for reference, almost following the same method except that no PEG was added.

2.3. Preparation of the membranes

The films were made by solution casting method. A certain amount of capsules were dispersed in mixture solvent of 70 wt% ethanol and 30 wt% water with ultrasonic treatment for 4h. Then, Pebax[®] MH 1657 was dissolved in mixed solvent with dispersed microcapsules under 80 °C refluxing for 2h to get 3 wt% Pebax homogeneous solution. The mass concentration of capsule was controls as 0.5, 1, 5 and 10 wt%. After cooling in room temperature, the final solution was cast in Teflon molds and dried in a vacuum oven at 30 °C for 24 h then increased to 40 °C for another 24 h to remove residual solvent. The membrane

was named as Pebax-HDA-X and Pebax-HDG-Y, respectively, where X and Y represent the percentage capsule content relative to the weight of Pebax. The thickness of all membranes was controlled within the range of 60-80 μm .

2.4. Characterization of the particles and membranes

FEI TalosTM F200S was used to take transmission electron microscopy (TEM) images of the nanoparticles. The surface element valence and energy level of capsules were measured by a multifunctional imaging electron spectrometer (XPS, Thermo ESCALAB 250XI, Thermo Scientific, USA), interior label of C 1s (284.8 eV) and spot size of 20 μm , making use of monochromatic AlK α ($h\nu=1486.6$ eV) X-ray source (a wattage of 150 W) radiation. PerkinElmer Spectrum Two was used to record Fourier transform infrared spectra (FTIR) of membranes and capsules at normal temperature in the range of 4000–700 cm^{-1} with the resolution of 4 cm^{-1} . Surface area and pore size distribution of the HDA and HDG were measured by ASAP 2460 with N₂ adsorption–desorption isotherms (77 K). Cross-sectional scanning electron microscope (SEM) images of the membranes were taken from a focused ion beam scanning electron microscopy (Zeiss/Auriga FIB) after the samples were freeze-fractured in liquid nitrogen and then sputtered with gold. X-ray diffractometry (XRD) were probed to characterize packing motifs of polymer chains using a Bruker D8 Advance ECO (Germany) in the ranges of 5–70° at the scanning speed of 5°/min with a CuK α monochromatic radiation ($\lambda= 0.15406$ nm). The thermal properties of membranes were determined by differential scanning calorimetry (DSC) analysis. The membranes samples were cut into small species (< 2 mm) The detection temperature was controlled from -65 °C to

250 °C with a heating rate of 10 °C/min. The thermal stability of both capsules and membranes were studied with thermogravimetric analysis (TGA, NETZSCH STA 2500). The temperature was heated from room temperature to 800 °C at a rate of 5 °C/min. Nitrogen was used as protective gas with a flow of 50 ml/min.

2.5 Gas permeation experiments

Single gas (CO₂, N₂) and binary gas (10 vol% CO₂+90 vol% N₂) permeation experiments were conducted based on the conventional constant pressure/variable volume method (the schematic diagram of apparatus is shown in Fig. 2). Helium was selected as sweep gas in all measurements. Unless otherwise specified, the feed pressure was maintained at 2 bar and the test temperature was at 25 °C. Micron-sized water droplets were introduced into a heater through peristaltic pump, and were then mixed with feed gas through an empty bottle. Meanwhile, the sweep gas was humidified following such procedure. The flow rates of feed gas and sweep gas were controlled by two mass flowmeters at 100 ml/min and 40 ml/min, respectively. After reaching the steady state, the permeation flow rate was calculated by an ADM flow meter (G6691A, Agilent). The composition of percolated gas was measured by using gas chromatograph (GS-101, Ripuli). In addition, dry-state gas permeation experiments were conducted, in which case the feed gas and sweep gas were directly introduced into the membrane cell. All the gas permeation experiments were performed more than four times. The measurement results of four samples were averaged as the final data with deviations shown in figures as error bars.

The permeability (P_i , Barrer, 1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹) of either gas

was obtained by the following equation:

$$P_i = \frac{Q_i l}{\Delta p_i A}$$

Where Q_i is the volumetric permeation flow rate of gas “i” (cm³/s) at standard temperature and pressure (STP), l is the membrane thickness (cm), Δp_i is the transmembrane partial pressure difference of gas “i” (cm Hg), and A is the effective membrane area (15.9 cm²). The ideal and mixed-gas selectivity (α_{ij}) was calculated by the following equation:

$$\alpha_{ij} = \frac{P_i}{P_j}$$

where P_i and P_j are the permeability of gas “i” and “j”, respectively.

Fig. 2. Schematic diagram of the gas permeation apparatus

3. Results and discussion

3.1. Characterizations of nanoparticles

Fig. 3. a,b,c) TEM images of different particles: (a) SiO₂, (b) SDG and (c) HDG. d) FTIR spectra of spheres. e) BJH pore size distribution curves of HDA and HDG. f) high-resolution XPS spectrum of C 1s. g) TGA curves of capsules and PEG.

Herein, SiO_2 is utilized as hard-templates and synthesized by a reformative sol-gel method reported in previous work [30]. The morphologies of nanoparticles are explored with TEM (Fig. 1(a)-(c)). Fig. 3a shows that prepared SiO_2 has a uniform shape with a radius 100-140 nm. According to Fig. 3b, core-shell structure is clearly observed, the dark section is SiO_2 and the gray section is co-deposition layer of DA and PEG of which thickness is about 25~35 nm. After etching SiO_2 , the capsules still maintain well-defined structure in Fig. 1c and hollow lumen is created. It is noted that morphology of capsules are not changed with the PEG incorporated compared with SDA and HDA shown in Fig. S1.

In FT-IR spectra of Fig. 3d, it should be noted that there is a strong Si-O-Si stretching vibration in 1060 cm^{-1} , while the signal disappeared in the HDA and HDG proving that inner core is removed. The broad band around 3250 cm^{-1} is attributed to N-H/O-H stretching vibrations and catechol groups. It can be seen that the bands located at 1592 cm^{-1} and 1507 cm^{-1} respectively correspond to the C=C in aromatic ring and N-H bending vibrations [26]. The characteristic band at 1285 cm^{-1} indicates the typical vibration of phenolic C-OH bending in dopamine [31].

The pore-size distribution of HDA and HDG is shown in Fig. 3e. BET surface areas of HDA and HDG are 21.94 and $9.27\text{ m}^2/\text{g}$, respectively. The decrease of surface area is probably due to the flexibility of the PEG molecular chain, which cannot afford the formation of permanent nanoporosity.. The observation of mesopores of $\sim 4\text{ nm}$ hints the results of PEG loss during etching. The larger mesopores with the size around $\sim 25\text{ nm}$ might reflect the release of a small fraction of dopamine aggregates during etching, because the co-deposition

process does not involve the so-called secondary treatment reactions. The broad distribution with the peak value at 90 nm accords well with the template size and the varieties of inter-particle spacing. N₂ adsorption–desorption isotherms of particles are exhibited in Fig. S2, which also indicates complex pore structure of fillers.

Table 1 The chemical composition of HDA and HDG.

	Element composition (at.%)			C1s species composition (area%)			
	C	N	O	C-C/C-H	C-N/C-O	C=O	C=N
HDA	68.50	10.29	21.21	50.52	29.54	9.88	10.06
HDG	71.47	7.59	20.93	55.12	27.72	11.72	5.44

The chemical composition variations of HDA and HDG are detected by high-resolution XPS. The spectrum of HDA and HDG both shows strong C 1s, O 1s and N 1s signals (Fig. S3), while no F 1s and Si 2p signals are found, coinciding with the result of FT-IR (Fig. 3d). The deconvolution of C 1s band (Fig. 3f) and alteration of atomic ratios (Table 1) validate the co-deposition of DA and PEG, implying a significant change of surface property of HDA after PEG modification. In addition, according to the C/N atomic ratio of HDA, it can be inferred that there are some Tris molecules mixed in the polymerization of dopamine. Furthermore, thermogravimetric analysis of HDG (Fig. 3g) displays distinct decrease after 300 °C as compared to HDA because of the degradation of PEG, from which the mass ratio of introduced PEG is calculated to be about 12 wt%.

3.2. Characterizations of membranes

Fig. 4. a,b,c) Cross-section images of membranes: (a) Pebax, (b) Pebax-HDG-1, (c) partial enlargement of Pebax-HDG-1. (d) and (e) FTIR spectra of Pebax and Pebax-HDG membranes. (f) XRD patterns of Pebax and Pebax-HDG membranes.

The morphology of polymer-particle interface of MMMs is analyzed in detail. Fig. 4(a,b,c) shows the cross-sectional morphologies of membranes before and after HDG loading. The smooth morphology agrees with the rubbery-like characteristic of Pebax. The microcapsules maintain the pristine structure and are evenly distributed in Pebax matrix. When the loading increased to 5 wt%, HDGs are shown to tend to agglomerate (Fig. S4), which may restrict the full use of embedded microcapsules. Thanks to the partially broken shell caused during sample preparation in liquid nitrogen, the large lumens can be clearly observed. The absence of distinct boundary at the polymer-filler interface (Fig. 4c) indicates fairly good interfacial adhesion, which can be further attributed to the tight interactions between dopamine and polymeric chains. This changes the stability of Pebax-HDG membranes, as evidenced by

thermogravimetric analysis (Fig. S5). Typically, such a uniform dispersion of filler particles into the continuous polymer matrix is crucial to the formation of defect-free membranes and improving overall gas separation performance.

The result of membrane FT-IR spectra is showed in Fig. 4d. In neat Pebax, peaks at 3301 cm^{-1} and 1098 cm^{-1} are attributed to stretching vibration of C-O-C in PEO segment and N-H in PA6 segment, respectively. And the peak at 1732 cm^{-1} corresponds to the O-C-O in saturated ester. The peak at 1639 cm^{-1} is attributed to H-N-C=O group. It is obvious that all typical bands assigned to the Pebax polymer are observed in all Pebax-HDG films, which suggests that the chemical structure of the Pebax polymer matrix was maintained in the MMMs with an increase of HDG loading. Compared with the original Pebax membrane, there is no significant change in the IR peak of the MMMs and no additional peak appears, indicating that the HDG and Pebax are physically bound without strong chemical interactions. It is noteworthy that the peak at 1097 cm^{-1} in pristine Pebax has a distinct shift to lower frequency in Pebax-HDG membranes, providing the evidence of hydrogen bonding between N-H in filler and C-O-C in EO segment.

Table 2 Thermal properties of Pebax and Pebax-HDG membranes

Membrane	T_g ($^{\circ}\text{C}$)	PEO		PA6	
		T_m ($^{\circ}\text{C}$)	X_c (%)	T_m ($^{\circ}\text{C}$)	X_c (%)
Pebax	-51.78	15.94	20.31	204.01	35.81
Pebax-HDG-0.5	-51.19	14.15	18.59	198.63	37.52
Pebax-HDG-1	-50.52	14.46	10.35	200.98	38.67
Pebax-HDG-5	-50.15	13.02	11.64	203.33	36.91
Pebax-HDG-10	-43.55	12.45	11.15	202.01	36.14

The polymer chain mobility is reflected by the changes of glass transition temperature (T_g)

through DSC. There are two endothermic peaks observed in all membranes around 13 °C and 205 °C for the melting peak of PEO and PA6 chain segments, respectively. It is generally accepted that the increased interfacial interaction at the filler-polymer interface and the rigidification of the polymer chain lead to an increase in T_g . As shown in Table 2, the T_g value of PEO segments increases from -51.6 °C to -43.5 °C with the HDG loading increasing from 0.5% to 10%, demonstrating strong interaction between polydopamine and Pebax matrix, as consistent with what has been reported in literature [32]. Compared with pristine Pebax, all Pebax-HDG membranes display a remarkably lower degree of PEO crystallinity (X_c) and slightly lower melting temperature (T_m), which manifests that the incorporation of hollow filler efficiently interrupts the ordered chain packing of the PEO segment in Pebax. By comparing the change of crystallinity degree for the PEO and PA6 segments, it can be further concluded that the fillers have more influence on PEO segment than that on PA6 segment.

The stacking motifs of polymer chain were investigated by wide-angle X-ray diffraction (XRD) and shown in Fig. 4f. Generally, the more ordered the structure is, the sharper and more intense the peak will be. Pebax is one kind of block copolymer with partial microphase separation due to the difference between rigid PA6 segments and flexible PEO segments. Accordingly, there are two major peaks in neat Pebax XRD pattern. The broad one at $2\theta=15^\circ$ reveals the amorphous phase region for irregular packing of the polymer chains, and the much sharper one at $2\theta=24^\circ$ is known to arise from the crystalline PA6 block via interchain hydrogen bonding. For MMMs, no evident change in the broad peak was observed suggesting the matrix structure maintained with little transformation, but the intensity of PA6 peak increases significantly with HDG filler loading. Particularly at a loading of 1%, the

crystallinity of the PA6 segment is the strongest. That is probably because a reasonable amount of hydrogen bonding induced the re-arrangement of PA6 chains and prompted their crystallization [33, 34]. The crystallization of PA6 further helped to facilitate the microphase separation of the two blocks of Pebax, which may be beneficial to the formation of PEO continuous phase and accelerate the transport of CO₂ molecules. However, excessive amount of hydrogen bonding at high HDG loading are believed to cause severe rigidification of the segment rather than inducing the regular arrangement of the polymer chain, as evidenced by glass transition temperature in Table 2.

3.3. Gas separation performance test

3.3.1. Effect of filler types on gas permeation

Fig. 5. Effect of different fillers (1 wt %) on gas transport properties of MMMs. Pure gas permeation test was at 0.2 MPa and 25 °C. Feed gas was saturated with water vapor.

The effect of filler type is firstly investigated, and results are shown in Fig. 5. Filler loading is controlled at 1wt% except SDG, of which the content is determined by the same volume ratio as HDG (Fig. S6). Pebax-HDA membrane exhibits negligible changes compared with original Pebax membrane. Considering the non-porous structure of HDA, it demonstrates that

gas molecules will find difficulty in diffusing through the shell, leaving the lumen starved. Besides, on account of abundant hydroxyl group and amine group, HDA could form strong hydrogen-bond interaction with Pebax matrix so as to restrict the flexibility of polymer chain, which would do harm to gas diffusion and resulted in a slight drop of the Pebax-HDA membrane permeability. In contrast, a distinct increase of both permeability and selectivity can be observed for Pebax-HDG. The increased CO_2 permeability and selectivity are attributed to two reasons: first, the unique structural advantages of HDGs, particularly the functionalized shell and the opened lumen, can greatly facilitate gas transport. Second, the addition of PEG improves CO_2 affinity and permeability of the capsule wall. Furthermore, a significant increase in permeability and selectivity is found when comparing Pebax-SDG with Pebax-HDG, which further proves the effect of the hollow structure. For comparison, the three membranes were also tested under dry state (Table S1), and the same tendency is found for them.

3.3.2. Effect of filler contents on gas separation performance

Fig. 6. Effect of filler content on binary gas separation performance at 0.2MPa and 25 °C. Feed gas was saturated with water vapor.

The effects of filler content on HDA-filled and HDG-filled MMMs can be elucidated based on Fig.6. Interestingly, both CO₂ permeability and CO₂/N₂ selectivity of HDG-filled MMMs increase first and then decrease with the increment of filler content, and the optimal loadings for both of them are found to be 1%. Similar tendency was observed for Pebax-based MMMs in the literature [35-37], whereas the underlying mechanism was not thoroughly discussed. As a matter of fact, due to the absence of molecular sieving capacity for HDG, such phenomenon can be only interpreted by the solubility enhancement effect, according to the classical tradeoff theories [38, 39]. However, the low filler content is unlikely to significantly contribute to the preferential CO₂ sorption. It is hence reasonable to assume that the PEO segments of Pebax might become more separated from PA6 segments, and thus the CO₂ philic regions are better connected. Such hypothesis is consistent with the analysis of DSC and XRD data, where the lowest crystallinity of PEO and highest crystallinity of PA6 are also found at 1% loading. The decrement of PEO and increment of PA6 crystallinity enlarge the difference in rigidity between PEO and PA6, and therefore better nanophase separation can be expected. More PEO chains are released from crystalline regions and become more flexible, providing more efficient domains to interact with CO₂ and facilitate its diffusion. Another interesting finding is the sharp difference between HDA-filled and HDG-filled MMMs. Obviously, the embedding of HDA does not bring any positive effect to membrane performance. Both CO₂ permeability and CO₂/N₂ selectivity continuously decreases with HDA content increasing. In addition to the aforementioned explanation that HDA is not permeable, another important reason may lie in the chain rigidification interfacial morphology. Although it cannot be directly observed, it is easy to conclude that HDG possess far less “sticky” surface than HDA

because of the partial coverage of PEG chains. That is, HDA is more likely to cause too strong interfacial adhesion, which will not only restrict the chain mobility, but also reduce the CO₂ binding capacity of the ether-oxygen bonds.

3.3.3. Effect of operating temperature on gas separation performance

Fig. 7. Effect of feed temperature on CO₂/N₂ separation property of Pebax-HDG-1 at 0.2 MPa with binary gas. Feed gas was saturated with water vapor.

The effects of operating temperature on the gas separation performance about the pristine Pebax and Pebax-HDG-1 membranes are plotted in Fig. 7. Obviously, CO₂ permeability is significantly enhanced with the increase of operating temperature, resulting from both the increase of the average kinetic energy of gas molecules and the flexibility of polymer chains.[40]. However, there is a falling tendency of selectivity, reflecting the tradeoff between chain rigidity and interchain spacing. Notably, Pebax-HDG-1 membrane shows higher CO₂ permeability and selectivity than that of neat Pebax membrane within the whole temperature range from 25 to 85 °C. Besides, Arrhenius equation is used to describe the temperature

dependence of CO₂ permeability and the activation energy for CO₂ permeation is calculated by following equation:

$$\ln P_{CO_2} = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A)$$

where P_{CO_2} represents the permeability of CO₂ (Barrer), E_a is the activation energy (kJ·mol⁻¹), R is the universal gas constant (J·mol⁻¹·K⁻¹), T is the absolute temperature (K) and A is the pre-exponential factor (Barrer). The calculated CO₂ apparent activation energy value of neat Pebax (12.3 kJ·mol⁻¹) is larger than that of Pebax-HDG-1 membrane (11.3 kJ·mol⁻¹) in the temperature range of 25 to 85 °C, which indicates that the energy barrier of CO₂ permeation for Pebax-HDG-1 membrane is lower than neat Pebax membrane.

3.3.4. Effect of feed pressure on gas separation performance

Fig. 8. Effect of feed pressure on CO₂/N₂ separation property of Pebax-HDG-1 at 25 °C with binary gas. Feed gas was saturated with water vapor.

The effect of operation pressure on gas separation performance is studied by enhancing feed pressure from 2 to 6 bar. As shown in Fig. 8, with the increase of feed pressure, the CO₂

permeability of neat Pebax membrane slightly decreases and CO_2/N_2 selectivity increases, which can be explained by the compressing-caused polymer densification. However, for the Pebax-HDG membrane, a far more rapid increase of CO_2/N_2 selectivity with pressure increment could be observed. Fortunately, such results can be reasonably interpreted by the modified interfacial theory for large-pore fillers based MMMs by Ismail and co-workers [22], and hence become a meaningful evidence of it. According to this theory, three cases of pore blocking morphology of MMMs are likely to occur. If the pore blockage is not severe, then, most likely, simultaneous increase of permeability and selectivity can be observed, which should have been the case of perfect interface according to the classical non-ideal interfacial morphology theory proposed by Koros et al. [16]. If the pore blockage exceeds a certain extent, permeability tends to decline, whilst selectivity is expected to become higher than the neat polymer matrix one. Once pore blockage becomes too severe that a dramatic decline in permeability combined with a slight rise or no significant change in selectivity are the characteristics of this morphology.

By reviewing the decreasing permeability and increasing selectivity in Fig. 8, with the large pores on the shell of HDG taken into account, the second case is believed to approach the truth. As feed pressure increases, pore blockage is expected to become more severe, and the increase of selectivity is not that remarkable when the pressure reaches 6 bar. Feed pressure-dependent curve are also plotted for the corresponding thin-film composite membranes (Fig. S7). The one with Pebax-HDG-1 as the active layer records a CO_2 permeance of ~ 200 GPU and a CO_2/N_2 selectivity of ~ 40 , better than pristine Pebax composite membrane.

3.3.5. Long-term operation stability

Fig. 9. Long term operation stability of Pebax-HDG-1. Binary gas permeation test was at 0.2 MPa and 85 °C. Feed gas was saturated with water vapor.

Long term operation test of mixed-gas permeation is processed in 2 bar and 85 °C to further investigate the structural stability of Pebax-HDG membranes. The permeability data start to be recorded when the steady-state operation is achieved. As shown in Fig. 9, during the entire test period of over 100 h, the Pebax-HDG membrane exhibits stable separation performance with average CO₂ permeability of 720 Barrer and CO₂/N₂ selectivity of 65. And neat Pebax shows a slow decline in both CO₂ permeability and CO₂/N₂ selectivity. The constant membrane separation performance is attributed to superior thermal properties of HDG capsules and strong interfacial polymer–filler adhesion. This result shows that the Pebax-HDG membrane has the potential to be applied in elevated temperature, further broadening the adaptability of the membrane.

4. Conclusion

In summary, we designed polydopamine/PEG composite microcapsules as efficient

fillers of MMMs for CO₂ separation. Compared to the relatively dense wall structure of polydopamine microcapsules without PEG addition, the composite microcapsules exhibit mesoporous wall so that the lumens become highways for gas transport. On the other hand, PEG functionalities not only increase CO₂ affinity of the microcapsule, but also avoid excessive chain rigidification at polymer–filler interface. In this way, interestingly, a proper content of polydopamine/PEG composite microcapsules brings one-fold enhancement for both CO₂ permeability and selectivity compared to Pebax, while polydopamine microcapsules slightly reduce the performance of Pebax. Moreover, the long-term operation stability of MMMs filled with composite microcapsules at high temperature is found superior to that of Pebax membrane, owing to the polydopamine-enabled interfacial adhesion. One pity of this study lies in the absence of further permeability enhancement at elevated capsule loading, which might result from the solubility-controlled CO₂ separation mechanism of Pebax. However, the data of this study has revealed that the co-existence of polydopamine and PEG is likely to effectively tune the interfacial morphology together with filler functionalization, hinting that such kind of composite microcapsules might become very promising candidate fillers in designing advanced MMMs.

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Highlights:

- Hollow polydopamine/PEG composite nanoparticles (HDGs) are prepared as MMMs fillers.
- Both CO₂ permeability and selectivity of the MMMs are doubled compared to Pebax.
- The roles of the lumen and PEG moieties in gas transport are separately discussed.
- Membrane stability at 85 °C is improved due to the strong adhesion of Pebax to HDGs.