Enhanced Gas Separation Performance by Embedding Submicron Poly(ethylene glycol) Capsules into Polyetherimide Membrane

Ying-Ying Ma\textsuperscript{a}, Min Liu\textsuperscript{a}, Jing-Tao Wang\textsuperscript{a}, Bin Zhu\textsuperscript{a}, and Yi-Fan Li\textsuperscript{a,b*}

\textsuperscript{a} School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China
\textsuperscript{b} College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

Abstract

Recently, hollow filler as an emerging concept is attracting more attention in preparation of mixed matrix membranes (MMMs). Herein, poly(ethylene glycol) microcapsules (PMC) are synthesized via distillation precipitation polymerization and embedded into the polyetherimide (Ultrem\textsuperscript{a}1000) matrix to fabricate MMMs for CO\textsubscript{2} capture. The PMC exhibits a preferential hollow structure within the Ultrem matrix to furnish highways within membrane, and thus achieve high gas permeability. Meanwhile, the favorable affinity of poly(ethylene glycol) (PEG) microcapsule with ether oxygen group (EO) towards CO\textsubscript{2} enhances the CO\textsubscript{2} solubility selectivity. Such integration of physical and chemical microenvironments in the as-designed PEG microcapsule affords highly enhanced CO\textsubscript{2} separation performance. Compared to pristine Ultrem\textsuperscript{a}1000, the membrane with 2.5 wt% PMC loading exhibits 310% increment in CO\textsubscript{2} permeability and 22% increment in CO\textsubscript{2}/N\textsubscript{2} selectivity, which shows the promising prospects of designing PEG-containing microcapsules as the filler of MMMs for CO\textsubscript{2} capture.

Keywords

Mixed matrix membranes (MMMs); Poly(ethylene glycol) microcapsules (PMC); Polyetherimide (Ultrem\textsuperscript{a}1000); CO\textsubscript{2} capture

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INTRODUCTION

With the growing awareness of the reason and the detrimental sequence of greenhouse effect, rapid and selective capture of CO\textsubscript{2} from diverse gas mixtures has become an urgent demand, especially in the cases of post-combustion capture, natural gas sweetening, and precombustion capture.\textsuperscript{[1–3]} Membrane technologies have shown unique superiority in the field of CO\textsubscript{2} capture over traditional processes on account of high efficiency, low energy consumption and easy operation.\textsuperscript{[4]} Nevertheless, membrane materials with high gas separation performance, mechanical property and long-term stability are highly required to ensure practical application.\textsuperscript{[5–6]} Among various membrane materials, glassy polymers like cellulose acetate, polyimide, polyetherimide, polycarbonate, and poly(ether sulfone) are usually considered candidates for commercialization due to the satisfactory selectivity and mechanical stability. More importantly, these polymers can be fabricated into asymmetric membrane with thin selective skin layer via phase conversion method.\textsuperscript{[5–6]} However, most of these glassy polymers, especially those with abundant availability, suffer from their low intrinsic gas permeability.\textsuperscript{[9]}

In the past decades, various strategies have been proposed to improve the permeability of glassy polymers. (i) Introducing side groups with steric hindrance effect so that the chain segments can be prevented from close arrangement. (ii) Blending with highly permeable polymers such as polymers of intrinsic microporosity (PIMs). (iii) Incorporating fillers into polymers to fabricate mixed matrix membranes (MMMs).\textsuperscript{[10–14]} Among these methods, the fabrication of MMMs has raised continuous interest due to the possibility of conferring the separation performance of highly efficient fillers on membranes or producing synergic effect between polymers and fillers.\textsuperscript{[15,16]} MMMs allow any polymer to be the matrix, and there is no limitation on filler materials except the scale (usually nanometer or submicron). The increasing growth of available polymer and filler materials provides more options and opportunities to the rational design of MMMs. In particular, choosing suitable fillers could largely improve gas separation performance. For example, Yu et al. fabricated PIM-1 based MMMs by incorporating self-made porous organic frameworks material (designated as MAPDA) and reported a significant improvement in CO\textsubscript{2} permeability and CO\textsubscript{2}/N\textsubscript{2} selectivity for a representative membrane of MAPDA/PIM-1 with 15 wt% MAPDA.\textsuperscript{[17]} High porosity and molecular affinity make the predominant contribution to the enhancements of CO\textsubscript{2} permeability and CO\textsubscript{2}/N\textsubscript{2} selectivity. Sudeepa et al. tested polysulfone (PSf) based MMMs with bio-metal-organic framework (Bio-MOF-1); the gas transport properties of MMMs with Bio-MOF-1 loading up to 30 wt% were investigated, and the results showed such MMMs had a CO\textsubscript{2} permeability of 16.57 Barrer and ideal selectivity of 42.6 and 45.6 for CO\textsubscript{2}/CH\textsubscript{4} and
CO₂/N₂, respectively. This corresponds to an increase in 168% and 58% for CO₂ permeability and ideal selectivity respectively in comparison to the pristine polymer membranes. Dong et al. found that the incorporation of polydopamine-derived submicropores (PDASS) into polymers of intrinsic microporosity (PIM-1) provides a 1.6-fold enhancement in CO₂/N₂ selectivity together with acceptable gas permeability as compared to the original polymeric membrane.¹⁹

Recently, hollow filler as an emerging concept attracts more attention in preparation of MMMs due to much higher fractional free volume by means of the unfilled lumen, furnishing highways within membrane. For instance, Ding et al. filled the hollow polyamide nanoparticles into liquid acrylate monomers to form the MMMs via the UV-induced photo-polymerization, which shows a maximum CO₂ permeability of 1898 Barrer and a maximum CO₂/N₂ permselectivity of 43.9 at 1 wt% nanofiller loading.²⁰ Lee et al. synthesized hollow ZIF-8 (H-ZIF) polyhedral nanocrystals and distributed it in an amphilphile poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVCH-g-POEM) graft copolymer matrix to form MMMs for CO₂/CH₄ separation.²¹ The MMMs exhibit an approximately fivefold increase in CO₂ permeability compared to pristine PVCH-g-POEM membrane with a CO₂/CH₄ selectivity of 14.3, which is close to upper bound reported by Robeson in 2008. Zhu et al. successfully prepared polydopamine/poly(ethylene glycol) (PEG) composite microcapsules into the Pebax matrix to fabricate MMMs for CO₂ capture.²² The optimal gas transport property of the resultant membranes is obtained with an excellent CO₂ permeability and CO₂/N₂ selectivity, i.e., 108% and 98% higher than those of neat Pebax membrane, respectively.

Interfacial morphology is a prominent issue in preparation of MMMs when glassy polymers are used as matrix. Non-selective interfacial voids exist in the filler/polymer interface region due to poor interface compatibility between polymer and inorganic fillers, which reduces the selectivity of the membrane. Due to the strong rigidity of the filler and poor interfacial compatibility between polymer and fillers, the presence of the fillers disrupts chain packing, creates interfacial voids between the two phases and generates interface defect.²³ Common measures to eliminate this defect include the following aspects: (i) Modifying the filler surface. Griselda et al. found that the incorporation of clinoptilolite-type natural zeolite modified with three alkylamines into polyisulfone increased the permeability of CO₂ and the selectivity of CO₂/CH₄.²⁴ At 0.345 MPa, MMMs shows an enhancement up to 30% on the CO₂ permeability (22.79 Barrer) and 55% on the CO₂/CH₄ selectivity (45.78) in comparison with the polymeric membrane (CO₂ permeability 17.34 Barrer; CO₂/CH₄ selectivity 29.38). (ii) Utilizing framework fillers with organic moieties, such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). Ma et al. incorporated hydroxy MOFs in a polylime matrix for CO₂ capture and hydrogen purification.²⁵ The MMMs exceed present Robeson upper bounds with a H₂ and CO₂ permeability of 907 and 650 Barrer, respectively, with a H₂/CH₄ and CO₂/CH₄ selectivity of 45 and 32, respectively. The unparalleled performance results from intimate interactions at the boundary of hydroxyl MOFs and carboxylic polymers via intensive hydrogen bonds. (iii) Designing "soft" fillers without inorganic constituent. For example, Wang et al. prepared poly(ethylene glycol)-containing polymeric sub-microspheres (PEGSS) and found that the CO₂ permeability and the CO₂/N₂ selectivity of PEGSS/PM MMMs with a filler loading of 20 wt% can be enhanced by factors of 35% and 104%, respectively.²⁶ This method is expected to thoroughly solve the interfacial defects arising from compatibility. However, the permeability of the filler phase can be higher to push the membrane performance to a higher level.

Herein, we report a series of MMMs containing poly(ethylene glycol) microcapsules (PMC) for CO₂ capture. The microcapsule provides favorable physicochemical microenvironments to construct CO₂ transport channels: the unique hollow structure of microcapsules provides a short transfer channel, which reduces the resistance by shortening the transfer path, and therefore increases the permeability of membrane.²⁷⁻²⁹ In addition, the favorable affinity of PEG microcapsule with ether oxygen group towards CO₂ molecules enhances the CO₂ solubility selectivity. Ultem™1000 as a benchmark matrix polymer was selected so as to better evaluate the effect of fillers.³¹⁻³⁴

**EXPERIMENTAL**

**Materials**

Tetraethyl orthosilicate (TEOS) and poly(ethylene glycol) methacrylate (PEGMA, M₄, 360) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. Acetonitrile and anhydrous ethanol were obtained from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Ammonia water (NH₃·H₂O, 25%) and N,N-dimethyl formamide (DMF) were supplied by Fengchuan Chemistry Co., Ltd. (Tianjin, China). Hydrofluoric acid (HF) was provided by Sigma-Aldrich. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Xiya reagent (Chengdu, China). 3-(Methacryloylo)propyltrimethoxysilane (MPS) and ethylene glycol di-methacrylate (EGDMA) were supplied from Alfa Aesar. Methacrylic acid was obtained from Xiya reagent (Shandong, China). Poly(ethylene glycol) (PEG, M₄, 400) was purchased from Aladdin Reagent (Shanghai) Co., Ltd. Single gases (N₂, CO₂) were supplied by Dalian Special Gases Company. Deionized water was used throughout the experiment. All chemicals were used without further treatment.

**Synthesis of Fillers**

**Synthesis of silica core**

The silica core was prepared by the Stöber method.³⁵ In brief, the mixture of deionized water (20 mL) and ammonia solution (NH₃·H₂O, 25%, 10 mL) was added into anhydrous ethanol (200 mL) with vigorous stirring for 5 min. Then TEOS (11 mL) was added drop by drop at 30 °C and heated for 24 h with a magnetic agitator. The suspension was directly used to prepare core-shell composite spheres without separating silica particles.

**Synthesis of PEGSS**

The core-shell PEG-containing polymeric sub-microspheres (PEGSS) were synthesized by distillation-precipitation polymerization method.³⁶ MPS (1 mL) was added into the silica spheres solution aforementioned suspension and stirred for 24 h at 30 °C followed by centrifugal separation and repeated washing. The nanoparticles with the size of 200–250 nm were dried at 40 °C in vacuum for 48 h, and the collected MPS modified
SiO₂ was obtained and named as SiO₂-MPS. Subsequently, SiO₂-MPS (0.2 g), PEGMA (0.6 mL), MAA (0.3 mL), EGDMA (0.6 mL) and AIBN (0.036 g) were dispersed in acetonitrile (80 mL) and heated to a boiling state to evaporate half of the acetonitrile. The PEGSS was collected by centrifugation and washed with anhydrous ethanol several times, and then dried at 40 °C in vacuum for 48 h.

**Synthesis of PMC**

The synthesis of PMC is based on a hard template method. The as-synthesized core-shell particles (PEGSS) were etched in HF solution for 2 h. Afterward, the product was collected by centrifugation and washed with deionized water several times until neutral pH. Finally, the PMC was dried at 40 °C in vacuum for 48 h.

**Preparation of Membranes**

The membranes were prepared by solution casting method. Ultem®1000 (0.8 g) was dissolved in DMF with vigorous stirring at 50 °C for 3 h. Then, a certain amount of PMC was dispersed in DMF, followed by sonication and stirring for 0.5 h. The obtained PMC suspension was mixed with Ultem®1000 solution by sonication and stirring under 30 °C for 1.5 h. The loading amount of PMC was varied from 0 wt% to 5.0 wt %. The final mixed solution was casted on a clean glass plate. After the evaporation of DMF in vacuum oven at 80 °C for 12 h followed by 120 °C for another 12 h, the prepared MMMs were ripped off carefully from the substrate. The resultant membranes were named as Ultem-PMC-X, where X (X=0, 1.25, 2.5, 5) represents the weight ratio of the PMC to Ultem®1000. The thickness of all membranes was controlled within the range of 60–90 μm.

**Characterization of PMC and Membranes**

The morphologies of SiO₂-MPS, PEGSS and PMC were detected by transmission electron microscopy (TEM, FEI Talos™ F200S). The surface chemical compositions of SiO₂-MPS and PMC were measured by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, Thermo Scientific, USA). Fourier transform infrared (FTIR) spectra were recorded at room temperature by PerkinElmer Spectrum Two in the range of 4000–500 cm⁻¹ with the resolution of 4 cm⁻¹. The thermogravimetric analysis (TGA, NETZSCH STA 2500) was used to test thermal stability of the fillers and membranes, and the samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperature (Tg) was determined by differential scanning calorimetry (DSC), and the detection temperature was controlled in 30–400 °C with a heating rate of 10 °C/min. The cross-section of Ultem and Ultem-PMC(X) was tested by scanning electron microscopy (SEM, Zeiss/Auriga FIB) after the samples were freeze-fractured in liquid nitrogen and then sputtered with gold. X-ray diffractometry (XRD) was performed to characterize the crystal structure of the membranes and packing motifs of polymer chains using a Bruker D8 Advance ECO (Germany) in the ranges of 5°–80° at the scanning rate of 5 °/min with a Cu Ka monochromatic radiation (λ = 0.15406 nm). Surface area and pore size distribution of the PMC were measured by BK 100-1 with N₂ adsorption-desorption isotherms (77 K).

**Gas Permeation Test**

The single gas (CO₂, N₂ and CH₄) permeation experiment was conducted based on the test principle of time-lag method to measure the permeability, diffusivity and solubility of the gases in membrane. The effect of operation pressure on gas separation performance is 0.4 MPa and the test temperature was at 30 °C. Before analysis, the membranes were evacuated at least 8 h to remove previously residual air from the system and dissolved gases from the sample. Any membrane was measured at least 3 times to get reliable results. The ideal selectivity (a₁₂) was calculated by the following equation:

\[
a_{ij} = \frac{P_i}{P_j}
\]

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

**RESULTS AND DISCUSSION**

**Characterizations of Nanoparticles**

As revealed by the TEM images, Fig. 1(a) shows that silica spheres have a smooth surface and relatively uniform size in the range of 200–250 nm. According to Fig. 1(b), the core-shell PEG-containing polymeric sub-microspheres (PEGSS) synthesized by distillation-precipitation polymerization method are clearly observed, and the dark section is SiO₂ and the gray section is the polymer layer of which thickness is about 100 nm. It is noted that after etching SiO₂ with HF, the color of the middle region changes from dark to light while the morphology of the capsules is not changed as shown in Fig. 1(c), which means that the shell and lumen structures were successfully created.

The pore-size distribution of PMC is shown in Fig. 2(a). The observation of mesopores of ~3.2 nm hints the results of polymer loss during etching. And Brunauer-Emmett-Teller (BET) specific surface area of PMC is 762.4 m²/g as determi-

Fig. 1 TEM images of the prepared different particles: (a) SiO₂-MPS, (b) PEGSS and (c) PMC.

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ined by nitrogen adsorption/desorption isotherm (Fig. 2b). PMC with larger BET surface area could provide more adsorption sites and improve adsorption ability of macromolecule microcapsules, which could function largely as a resource to increase the CO$_2$ solubility.

To demonstrate the successful synthesis of microcapsule, TGA was performed in Fig. 3(a). There was a weight loss stage of nanoparticles before 200 °C, which is attributed to the dehydration by the adsorbed water evaporation. For SiO$_2$-MPS and PEGSS, the following weight loss stage (200−500 °C) was caused by the oxygen-containing functional groups. For PMC, the second stage represented the decomposition of polymer, which started from 200 °C. As the degradation was basically complete, the content of polymer microcapsules was calculated to be about 75.7 wt%. The differences of three nanoparticles on TGA indicate the successful synthesis of the microcapsules to some extent. In addition, the chemical structures of SiO$_2$, SiO$_2$-MPS and PMC were analyzed by FTIR spectra and the spectra are shown in Fig. 3(b). The broad band in the region of 3800−2850 cm$^{-1}$ (O−H stretching vibrat-
ons) and the band at about 1733 cm$^{-1}$ (C=O stretching vibrations) represent the presence of MAA. The band at about 1637 cm$^{-1}$ (C=C stretching vibrations) indicates the presence of MPS. The absorption band at 947 cm$^{-1}$ is assigned to the stretching vibration of Si–OH. The stretching vibration bands at 1110 and 808 cm$^{-1}$ correspond to the asymmetric stretching vibration and symmetric stretching vibration of Si–O–Si. The signal disappears in the spectrum of PMC, demonstrating that inner core is removed. To further certify the chemical structure of the microcapsule, the element composition of the nanoparticles was obtained by XPS. As shown in Figs. 3(c) and 3(d), the spectra of PMC display peaks at around 529 and 282 eV, corresponding to O1s and C1s and in accord with the element composition of PMC. The characteristic signals of O1s at 529 eV represent $\equiv$O$\equiv$CH$_2$CH$_2$– while those of C1s at 288, 286 and 284.8 eV correspond to ester base, ether oxygen group from PEGMA and C–C, respectively, which confirms the chemical structure of the PEG microcapsules.

Characterizations of Membranes
The internal morphologies and filler dispersion of the MMMs were exhibited by cross-section SEM images. As shown in Fig. 4, cross section of membranes is impacted by the incorporation of the PMC, which reveals that the neat membrane presents a dense and defect-free structure while MMMs become rougher (Figs. 4b–4d). The distribution of filler within the membrane could be observed more obviously with the increase of PMC loading. The PMC is uniformly distributed in the membrane and no obvious aggregation is observed. However, the agglomeration of microcapsules is clearly observed when the PMC loading increased to 5 wt%, which might decrease the effective adsorptive sites for CO$_2$. At the same time, the locally aggregated microcapsules might produce more tortuosity in transfer pathways, which impedes gas diffusion.

The cross-section SEM images of the near Ultem membrane and MMMs with different PEGSS loadings are shown in Figs. 5(a)–5(d). The EDS-mapping in Figs. 5(a1)–5(d1) further reveals the distribution of the PEGSS nanoparticles in MMMs with the distribution of silicon (Si). The above results are consistent with transmission electron microscopy (TEM). It could be clearly observed that the nanoparticles were well-distributed in MMMs. To clarify whether they were still hollow capsules or just phase-separated micro-globes, a control experiment with similar molecular weight linear PEG filler ($M_n$ 400) was carried out to clarify this point (Figs. 5a2–5d2). With the increase of the PEG filler, the random patterns and even cracks become obvious, significantly different from the micro-
spheres or microcapsules within MMMs. TEM images also confirm the well-maintained morphologies of microcapsules within MMMs (Fig. 6).

Fig. 7(a) displays the FTIR spectra of the prepared membranes. As for pristine Ultem, the characteristic bands at 1779, 1719 and 717 cm$^{-1}$ refer to the asymmetric stretching, symmetric stretch and the bending vibration peak of C=O in Ultem membrane, respectively. Also, stretching vibration of C=N in the imide group is observed at 1355 cm$^{-1}$.[38,39] The characteristic band at 1072 cm$^{-1}$ corresponds to the stretching vibration of C−N−C. Compared with the pristine Ultem, similar infrared spectra of MMMs with different filler contents show no new band, indicating that no new chemical bonds were formed as the PMC loading increased from 0 wt% to 5 wt%. XRD was utilized to further investigate the crystalline structure of the as-prepared membranes and the results are shown in Fig. 7(b). The pristine Ultem membrane reveals a strong and broad characteristic peak at 2θ=17.5°, which indicates the semi-crystalline structure of the membrane.[38,39]

When filling PMC into the polymer matrix, it can be seen that the crystallinity of MMMs decreases, which leads to the en-


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"mages of membranes with different PEGSS loadings: (a) Ultem, (b, d) Ultem-PEGSS-1.25, (c) high-resolution TEM image corresponding to the marked zone in (b), (e) Ultem-PEGSS-2.5, (f) Ultem-PEGSS-5.

There is a weight loss stage of MMMs before 300 °C, which is attributed to the dehydration by the adsorbed water evaporation. The following weight loss stage (300−500 °C) is caused by the decomposition of polymer. The incorporation of PMC imparts MMMs higher decomposition temperature around 520 °C, while the neat Ultem membrane begins to degrade at a lower temperature around 500 °C. In addition, it can be seen that the degradation temperature of the membrane increases more obviously with the increase of fillers, which should be attributed to the interaction between Ultem and PMC that increases the required energy for polymer chains movement or segmentation. This is consistent with the DSC result.

Mechanical properties of the membranes in term of their stress-strain curves are shown in Fig. 8. Ultem control mem-

brane, Ultem PMC-1.25, Ultem PMC-2.5, and Ultem-PMC-5 were chosen as representatives. Fig. 8 suggests that Ultem control membrane displays the tensile strength of 34.1 MPa at the elongation of 3.9%. The incorporation of PMC slightly enhances the mechanical stability of MMMs and significantly enhances the elongation at break, demonstrating the contribution from soft organic filler and the good interfacial adhesion. When the amount of fillers reaches 5%, the tensile strength and the elongation decrease sharply, indicating the effect of the agglomeration of microcapsules.

**Gas Separation Performances**

*Pure gas permeation properties of MMMs*

The performance of the MMMs containing PMC was tested by pure gas (CO$_2$, CH$_4$ and N$_2$). Tables 1 and 2 summarize the gas permeation properties of pristine Ultem membrane and MMMs at 0.4 MPa and 30 °C. Considering the kinetic diameter CO$_2$ (0.330 nm) is smaller than those of N$_2$ (0.364 nm) and CH$_4$ (0.380 nm), the permeability of CO$_2$ is higher than N$_2$ and CH$_4$ for these membranes. Compared with the pristine membrane, Ultem PMC-2.5 membrane, with 2.5 wt% PMC loading, shows the highest permeability of CO$_2$ and exhibits increment of 310%, and
separation performance exhibits CO\textsubscript{2}/N\textsubscript{2} selectivity increment of 22\%, CO\textsubscript{2}/CH\textsubscript{4} selectivity increment of 9\%. The increase of CO\textsubscript{2}/N\textsubscript{2} selectivity is more remarkable than CO\textsubscript{2}/CH\textsubscript{4}. This may be because the critical temperature difference between CO\textsubscript{2} (304.1 K) and N\textsubscript{2} (126.2 K) is larger than that of CO\textsubscript{2} and CH\textsubscript{4} (190.6K). Hence, it is reasonable to assume that the increase of gas permeability and selectivity of MMMs is attributed to the favorable physicochemical microenvironments of microcapsule.\cite{29,30,41} Firstly, the unique hollow structure of microcapsule and permeable capsule wall provide a fast transfer channel, which reduces the resistance by shortening the transfer path and increases the permeability of membrane. Secondly, the favorable affinity of microcapsule with ether oxygen group towards CO\textsubscript{2} molecules enhances the CO\textsubscript{2} permeability via solution-diffusion mechanism. Such hypothesis is consistent with the XRD and DSC results. XRD results show decreased crystallinity in MMMs because the interactions between Ultem and PMC disrupt the chain packing and increase the chain spacing of the polymer in the membrane, which is anticipated to create more free volume and may enhance gas diffusivity coefficients.\cite{42} Besides, the reduction of \( T_g \) value in DSC indicates moderate mobility of Ultem chains without the generation of interfacial rigidification morphology. Further, gas diffusivity and solubility coefficients of membrane are calculated to investigate the transport properties of MMMs and the result is consistent with the analysis above. In addition to the aforementioned explanation that the improvement of performances arises from gas diffusivity coefficients, another important reason may lie in the solubil-

| Membrane       | \( P_{\text{CO}_2} \) | \( P_{\text{CH}_4} \) | \( P_{\text{N}_2} \) | \( P_{\text{CO}_2}/P_{\text{N}_2} \) | \( P_{\text{CO}_2}/P_{\text{CH}_4} \) |
|----------------|-------------------|------------------|------------------|-----------------|-----------------|
| Ultem          | 2.0               | 0.069            | 0.074            | 27.0            | 29.0            |
| Ultem-PMC-1.25 | 7.8               | 0.21             | 0.22             | 35.7            | 37.1            |
| Ultem-PMC-2.5  | 8.2               | 0.26             | 0.25             | 33.0            | 31.5            |
| Ultem-PMC-5    | 3.6               | 0.15             | 0.13             | 27.5            | 24.0            |

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Membrane | $D_{\text{CO}_2}$ | $D_{\text{CH}_4}$ | $D_{\text{N}_2}$ | $S_{\text{CO}_2}$ | $S_{\text{CH}_4}$ | $S_{\text{N}_2}$ | $D_{\text{CO}_2}/D_{\text{CH}_4}$ | $D_{\text{CO}_2}/D_{\text{N}_2}$ | $S_{\text{CO}_2}/S_{\text{N}_2}$ | $S_{\text{CO}_2}/S_{\text{CH}_4}$
--- | --- | --- | --- | --- | --- | --- | --- | --- | --- | ---
Ultem | 0.59 | 0.08 | 0.18 | 3.4 | 0.9 | 0.40 | 3.2 | 7.38 | 8.4 | 3.76
Ultem-PMC-1.25 | 1.15 | 0.13 | 0.30 | 6.9 | 1.52 | 0.72 | 3.8 | 8.85 | 9.5 | 4.54
Ultem-PMC-2.5 | 1.43 | 0.21 | 0.53 | 5.8 | 0.91 | 0.47 | 2.7 | 6.81 | 12.3 | 6.37
Ultem-PMC-5 | 0.70 | 0.16 | 0.31 | 5.1 | 0.84 | 0.41 | 2.3 | 4.38 | 12.2 | 6.07

Table 2 Gas diffusivity and solubility coefficients of pristine Ultem and MMMs (tested at 0.4 MPa, 30 °C).

| Number | Filler (wt%) | Normalized CO$_2$ permeability | Normalized CO$_2$/N$_2$ selectivity | Testing conditions | Ref. |
|--- | --- | --- | --- | --- | --- |
a | Carbon molecular sieve (35) | 1.89 | 1.03 | 35 °C, 0.345 MPa | [4] |
b | ZIF-8 (10)$^*$ | 1.86 | 1.20 | Mixed gas (20 vol% CO$_2$), 35 °C, 0.690 MPa | [44] |
c | ZIF-90A (15) | 2.07 | 1.02 | 35 °C, 0.45 MPa | [45] |
d | NH$_3$-MIL-53 (15)$^*$ | 2.53 | 1.37 | 25 °C, 0.5 MPa | [46] |
e | PIM-1 (10) | 2.67 | 0.92 | 35 °C, 0.35 MPa | [47] |
f | PIM-1 (30) | 6.26 | 0.90 | 35 °C, 0.35 MPa | [47] |
g | Halloysite nanotube (0.5) | 1.27 | 1.08$^*$ | 25 °C, 1.5 MPa | [48] |
h | Ag-halloysite nanotube (0.5) | 1.52 | 0.91$^*$ | 25 °C, 1.5 MPa | [48] |
i | HSSZ-13 zeolite (10)$^*$ | 0.97 | 0.98 | 35 °C, 0.159 MPa | [49] |
j | Grignard treated HSSZ-13 zeolite (10)$^*$ | 0.58 | 1.15 | 35 °C, 0.159 MPa | [49] |
k | Graphene oxide (0.25) | 1.16 | 1.59$^*$ | 25 °C, 1 MPa | [50] |
l | PEG microcapsule (1.25) | 3.9 | 1.32 | 30 °C, 0.4 MPa | This work |
m | PEG microcapsule (2.5) | 4.1 | 1.22 | 30 °C, 0.4 MPa | This work |

Table 3 Comparison of gas transport properties of other Ultem-based MMMs with those in current work.

Comparison with other Ultem-based MMMs

To acquire an overview of CO$_2$ and N$_2$ permeation properties, the results of this work were compared with those representative Ultem-based MMMs reported in literature (Table 3 and Fig. 9). After such comparison, though only moderate CO$_2$/N$_2$ selectivity is acquired in this study, the MMMs described here placed themselves among the best records of CO$_2$ permeability enhancement. Therefore, it can be inferred that not only the unique structural advantages of microcapsules but also the favorable affinity of PEG microcapsule with ether oxygen group towards CO$_2$ molecules enhances the CO$_2$ permeability. Conclusively, the incorporation of polymeric capsules in this study provides an efficient approach to enhance the gas separation performance of glassy polyimide membranes.

CONCLUSIONS

In the present study, novel PMC was utilized as an efficient filler of MMMs for CO$_2$ separation. The unique hollow structure of microcapsules and permeable capsule wall provide a fast transfer channel, which reduces the resistance by shortening the transfer path and increases the permeability of membrane. The favorable affinity of microcapsule with ether oxygen group towards CO$_2$ molecules enhances selective CO$_2$ sorption and permeation. Moreover, the interactions between Ultem and PMC disrupt the chain packing and increase the chain spacing of the polymer, which is anticipated to create more free volume and may enhance gas diffusivity coefficients. Besides, the hydrogen bond between PEG microcapsule and polymer as...
well as the flexibility of PEG chains contributes to the desired interface morphology without severe non-selective voids or chain rigidification, and it is helpful to improve the interface transfer characteristics of the membrane, and realize the synergistic strengthening of solution-diffusion mechanism. Compared to the pristine Ultem membrane, Ultem-PMC-2.5 membrane exhibits 310% increment in CO₂ permeability and 22% increment in CO₂/N₂ selectivity, which hints that such kind of microcapsules might become very promising candidate fillers in designing advanced MMMs.

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REFERENCES
1 Du, N.; Park, H. B.; Dal-Cin, M. M.; Guiver, M. D. Advances in high permeability polymeric membrane materials for CO₂ separations. Energy Environ. Sci. 2012, 5, 7306–7322.
2 Sanders, D. F.; Smith, Z. P.; Guo, R.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.; Freeman, B. D. Energy-efficient polymeric gas separation membranes for a sustainable future: a review. Polymer 2013, 54, 4729–4761.
3 D’Alessandro, D. M.; Smit, B.; Long, J. R. Carbon dioxide capture: prospects for new materials. Angew. Chem. Int. Ed. 2010, 49, 6058–6082.
4 Vu, D. Q.; Koros, W. J.; Miller, S. J. Mixed matrix membranes using carbon molecular sieves-I Preparation and experimental results. J. Membr. Sci. 2003, 211, 311–334.
5 Jamil, A.; Koh, P. C.; Shariﬀ, A. F. Polyetherimide-montmorillonite mixed matrix hollow ﬁbre membranes: effect of inorganic/organic montmorillonite on the CO₂/CH₄ separation. Sep. Purif. Technol. 2018, 206, 256–267.
6 Jeong, M. K.; Park, J. H.; Nam, S. Y. Fabrication of PEG-polyimide copolymer hollow ﬁber membranes for gas separation. J. Nanosci. Nanotechnol. 2017, 17, 7490–7496.
7 Yong, W. F.; Li, F. Y.; Xiao, Y. C.; Chung, T. S.; Tong, Y. W. High performance PIM-1/Matrimid hollow ﬁber membranes for CO₂/CH₄, CO₂/N₂, and CO₂/O₂ separations. J. Membr. Sci. 2013, 443, 156–169.
8 Dong, G. X.; Li, H. Y.; Chen, V. Factors affect defect-free Matrimid (R) hollow ﬁber gas separation performance in natural gas puriﬁcation. J. Membr. Sci. 2010, 353, 17–27.
9 Park, H. B.; Jung, C. H.; Lee, Y. M.; Hill, A. J.; Pae, S. J.; Mudie, S. T.; van Wagner, L.; Freeman, B. D.; Cookson, D. J. Polymers with cavities tuned for fast selective transport of small molecules and ions. Science 2007, 318, 254–258.
10 Zhang, C.; Liu, B.; Wang, G.; Yu, G.; Zou, X.; Zhu, G. Small-pore CAU-21 and porous PIM-1 in mixed-matrix membranes for improving selectivity and permeability in hydrogen separation. Chem. Commun. 2019, 55, 7101–7104.
11 Yeong, Y. F.; Kho, T. S. Fabrication of amino-functionalized CAU-1/cellulose acetate mixed matrix membranes for CO₂/N₂ separation. Key Eng. Mater. 2019, 797, 39–47.
12 Hassain, I.; Nam, S. Y.; Rizzuto, C.; Barbieri, G.; Tocci, E.; Kim, T. H. PIM-polyimide multiblock copolymer-based membranes with enhanced CO₂ separation performances. J. Membr. Sci. 2019, 574, 270–281.
13 Bernabe, D. P.; Caparanga, A. R.; Hu, C. C.; You, S. J.; Lee, K. R.; Lai, J. Y. MOF-modified high permeability polyimide membrane for gas separation. Key Eng. Mater. 2019, 801, 313–318.
14 Swaidan, R.; Ghanem, B. S.; Litwiller, E.; Pinnau, I. Pure- and mixed-gas CO₂/CH₄ separation properties of PIM-1 and an amidoxime-functionalized PIM-1. J. Membr. Sci. 2014, 457, 95–102.
15 Guan, W.; Dai, Y.; Dong, C.; Yang, X.; Xi, Y. Zeolite imidazolate framework (ZIF)-based mixed matrix membranes for CO₂ separation: a review. J. Appl. Polym. Sci. 2020, 48968.
16 Sabatghytham, A.; Liu, X.; Benzaqui, M.; Gkaniatsou, E.; Orsi, A.; Loziniska, M. M.; Sicard, C.; Johnson, T.; Steunou, N.; Wright, P. A.; Serre, C.; Gascon, J.; Kapteijn, F. Influence of filler pore structure and polymer on the performance of MOF-based mixed-matrix membranes for CO₂ capture. Chem. Eur. J. 2018, 24, 7949–7956.
17 Yu, G. L.; Wang, Z. Y.; Liu, X. T.; Zhu, G. S.; Zou, X. Q. Mixed matrix membranes derived from nanoporous polymeric frameworks for permeable and selective CO₂ separation. J. Membr. Sci. 2019, 591, 117343.
18 Ishaq, S.; Tamime, R.; Bilad, M. R.; Khan, A. L. Mixed matrix membranes comprising of polysulfone and microporous Bio-MOF-1: preparation and gas separation properties. Sep. Purif. Technol. 2019, 210, 442–451.
19 Dong, G.; Zhang, J.; Wang, Z.; Wang, J.; Zhao, P.; Cao, X.; Zhang, Y. Interfacial property modulation of PIM-1 through polydopamine-derived submicroporous for enhanced CO₂/N₂ separation performance. ACS Appl. Mater. Interfaces 2019, 11, 19613–19622.
20 Ding, X.; Tan, F.; Zhao, H.; Hua, M.; Wang, M.; Xin, Q.; Zhang, Y. Enhancing gas permeation and separation performance of polymeric membrane by incorporating hollow polyamide nanoparticles with dense shell. J. Membr. Sci. 2019, 570–571, 53–60.
21 Lee, J. H.; Kwon, H. T.; Bae, S.; Kim, J.; Kim, J. H. Mixed-matrix membranes containing nanocage-like hollow ZIF-8 polyhedral nanocrystals in graft copolymers for carbon dioxide/methane separation. Sep. Purif. Technol. 2018, 207, 427–434.
22 Zhu, B.; Liu, J.; Wang, S.; Wang, J.; Liu, M.; Yan, Z.; Shi, F. L.; Li, J. Y. Mixed matrix membranes containing well-designed composite microparticles for CO₂ separation. J. Membr. Sci. 2019, 572, 650–657.
23 Xiao, Y. C.; Low, B. T.; Hosseini, S. S.; Chung, T. S.; Paul, D. R. The strategies of molecular architecture and modification of polyimide-based membranes for CO₂ removal from natural gas-a review. Prog. Polym. Sci. 2009, 34, 561–580.
24 G. Castruita-de León, Yeverino-Miranda, C. Y.; Montes-Luna, A. D. J.; Meléndez-Ortiz, H. I.; Alvarado-Tenorio, G.; García-Cerda, L. A. Amine-impregnated natural zeolite as filler in mixed matrix membranes for CO₂/CH₄ separation. J. Membr. Sci. 2019, 457, 129–139.
25 Ma, C.; Urban, J. J. Enhanced CO₂ capture and hydrogen purification by hydroxyl metal-organic framework/polyimide mixed matrix membranes. ChemSusChem 2019, 12, 4405–4411.
26 Wang, S. F.; Feng, J. Y.; Wu, H.; Li, Y. F.; Liu, Y.; Li, X. Q.; Xin, Q. P.; Jiang, Z. Y. Enhanced CO₂ separation properties by incorporating polyethylene glycol-containing polymeric submicropores into polyimide membrane. J. Membr. Sci. 2015, 473, 310–317.
27 Zhang, H.; Guo, R.; Zhang, J.; Li, X. Facilitating CO₂ transport across mixed matrix membranes containing multifunctional nanocapsules. ACS Appl. Mater. Interfaces 2018, 10, 43031–43039.
28 Zornoza, B.; Esekhiel, O.; Koros, W. J.; Téllez, C.; Coronas, J. Hollow
silicalite-1 sphere-polymer mixed matrix membranes for gas separation. Sep. Puriﬁ. Technol. 2011, 77, 137–145.

29 Hou, J.; Li, X.; Guo, R.; Zhang, J.; Wang, Z. Mixed matrix membranes with fast and selective transport pathways for efﬁcient CO$_2$ separation. Nanotechnology 2018, 29, 125706.

30 Hwang, S.; Chi, W. S.; Lee, S. J.; Im, S. H.; Kim, J. H.; Kim, J. Hollow ZIF-8 nanoparticles improve the permeability of mixed matrix membranes for CO$_2$/CH$_4$ gas separation. J. Membr. Sci. 2015, 480, 11–19.

31 Ghanem, A. S.; Ba-Shammakh, M.; Usman, M.; Khan, M. F.; Dafallah, H.; Habib, M. A. M.; Al-Maythalony, B. A. High gas perme selectivity in ZIF-302/polyimide self-consistent mixed-matrix membrane. J. Appl. Polymer Sci. 2019, 137, 48513.

32 Aguilar-Lugo, C.; Suárez-García, F.; Hernández, A.; Miguel, J. A.; Lozano, Á. E.; de la Campa, J. G.; Álvarez, C. New materials for gas separation applications: mixed matrix membranes made from linear polyimides and porous polymer networks having lactam groups. Ind. Eng. Chem. Res. 2019, 58, 9585–9595.

33 Zhu, H.; Jie, X.; Wang, L.; Kang, G.; Liu, D.; Cao, Y. Enhanced gas separation performance of mixed matrix hollow ﬁber membranes containing post-functionalized S-MIL-53. J. Energy Chem. 2018, 27, 781–790.

34 Kang, Z.; Peng, Y.; Qian, Y.; Yuan, D.; Addicoat, M. A.; Heine, T.; Hu, Z.; Tee, L.; Guo, Z.; Zhao, D. Mixed matrix membranes (MMMs) comprising exfoliated 2D covalent organic frameworks (COFs) for efﬁcient CO$_2$ separation. Chem. Mater. 2016, 28, 1277–1285.

35 Werner Stober, A. F. Controlled growth of monodisperse silica spheres in the micron size range. J. Colloid Interface Sci. 1968, 26, 62–69.

36 Bai, F.; Yang, X.; Huang, W. Synthesis of narrow or monodisperse poly(divinylbenzene) microspheres by distillation-precipitation polymerization. Macromolecules 2004, 37, 9746–9752.

37 Tin, P. Effects of cross-linking modiﬁcation on gas separation performance of matrimid membranes. J. Membr. Sci. 2003, 225, 77–90.

38 Ahmad, J.; Hägg, M. B. Development of matrimid/zeolite 4A mixed matrix membranes using low boiling point solvent. Sep. Puriﬁ. Technol. 2013, 115, 190–197.

39 Aziz, F.; Ismail, A. F. Preparation and characterization of cross-linked Matrimid® membranes using para-phenylenediamine for O$_2$/N$_2$ separation. Sep. Puriﬁ. Technol. 2010, 73, 421–428.

40 Wang, S. F.; Liu, Y.; Huang, S. X.; Wu, H.; Li, Y. F.; Tian, Z. Z.; Jiang, Z. Y. Pebax-PEG-MWCNT hybrid membranes with enhanced CO$_2$ capture properties. J. Membr. Sci. 2014, 460, 62–70.

41 Vanherck, K.; Aerts, A.; Martens, J. Vankelecom, I. Hollow ﬁller based mixed matrix membranes. Chem. Commun. 2010, 46, 2492–2494.

42 Peng, F. B.; Sun, H. L; Wang, Y. Q.; Liu, J. Q.; Jiang, Z. Y. Hybrid organic-inorganic membrane: solving the tradeoff between permeability and selectivity. Chem. Mater. 2015, 17, 6790–6796.

43 Lin, H.; Freeman, B. D. Materials selection guidelines for membranes that remove CO$_2$ from gas mixtures. J. Mol. Struct. 2005, 739, 57–74.

44 Dai, Y.; Karvan, Sholl, S.; Koros, W. J. Ultem®ZIF-8 mixed matrix hollow ﬁber membranes for CO$_2$/N$_2$ separations. J. Membr. Sci. 2012, 401–402, 76–82.

45 Bae, T. H.; Lee, J. S.; Qiu, W. L.; Koros, W. J.; Jones, C. W.; Nair, S. A high-performance gas-separation membrane containing submicrometer-sized metal-organic framework crystals. Angew. Chem. Int. Ed. 2010, 49, 9863–9866.

46 Mubashir, M.; Yeong, Y. F.; Lau, K. K.; Chew, T. L.; Norwahyu, J. Efﬁcient CO$_2$/$N_2$ and CO$_2$/CH$_4$ separation using NH$_2$-MIL-53(Al)/cellulose acetate (CA) mixed matrix membranes. Sep. Puriﬁ. Technol. 2018, 199, 140–151.

47 Hao, L.; Li, P.; Chung, T. S. PIM-1 as an organic ﬁller to enhance the gas separation performance of Ultem polyetherimide. J. Membr. Sci. 2014, 453, 614–623.

48 Ismail, A. F.; Hashemifard, S. A.; Matsuura, T. Facilitated transport effect of Ag$^+$ ion exchanged halloysite nanotubes on the performance of polyetherimide mixed matrix membrane for gas separation. J. Membr. Sci. 2011, 379, 378–385.

49 Husain, S.; Koros, W. J. Mixed matrix hollow ﬁber membranes made with modiﬁed HSSZ-13 zeolite in polyetherimide polymer matrix for gas separation. J. Membr. Sci. 2007, 288, 195–207.

50 Kooilvand, H.; Sharif, A.; Kashani, M. R.; Karimi, M.; Salooki, M. K.; Semsarzadeh, M. A. Functionalized graphene oxide/polyimide nanocomposites as highly CO$_2$-selective membranes. J. Polym. Res. 2014, 21, 599.