

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

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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 (Ultem®1000) matrix to fabricate MMMs for CO₂ capture. The PMC exhibits a preferential hollow structure within the Ultem 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 CO₂ enhances the CO₂ solubility selectivity. Such integration of physical and chemical microenvironments in the as-designed PEG microcapsule affords highly enhanced CO₂ separation performance. Compared to pristine Ultem®1000, the membrane with 2.5 wt% PMC loading exhibits 310% increment in CO₂ permeability and 22% increment in CO₂/N₂ selectivity, which shows the promising prospects of designing PEG-containing microcapsules as the filler of MMMs for CO₂ capture.

Keywords Mixed matrix membranes (MMMs); Poly(ethylene glycol) microcapsules (PMC); Polyetherimide (Ultem®1000); CO₂ 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 CO₂ from diverse gas mixtures has become an urgent demand, especially in the cases of post-combustion capture, natural gas sweetening, and precombustion capture.^[1–3] Membrane technologies have shown unique superiority in the field of CO₂ capture over traditional processes on account of high efficiency, low energy consumption and easy operation.^[3] Nevertheless, membrane materials with high gas separation performance, mechanical property and long-term stability are highly required to ensure practical application.^[4] 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.^[5–8] However, most of these glassy polymers, especially those with abundant availability, suffer from their low intrinsic gas permeability.^[9]

In the past decades, various strategies have been proposed to improve the permeability of glassy polymers. (i) Introdu-

cing 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).^[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.^[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 CO₂ permeability and CO₂/N₂ selectivity for a representative membrane of MAPDA/PIM-1 with 15 wt% MAPDA.^[17] High porosity and molecular affinity make the predominant contribution to the enhancements of CO₂ permeability and CO₂/N₂ selectivity. Sudeeha *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 CO₂ permeability of 16.57 Barrer and ideal selectivity of 42.6 and 45.6 for CO₂/CH₄ and

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CO₂/N₂, respectively.^[18] 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 submicrospheres (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 amphiphilic poly(vinyl chloride)-*g*-poly(oxyethylene methacrylate) (PVC-*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 PVC-*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 interface 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 polysulfone 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 polyimide 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/PI 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.^[27–30] 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, *M_n* 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-(Methacryloxy)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, *M_n* 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 (*T_g*) 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 Kα 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 (α_{ij}) was calculated by the following equation:

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (1)$$

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 determ-

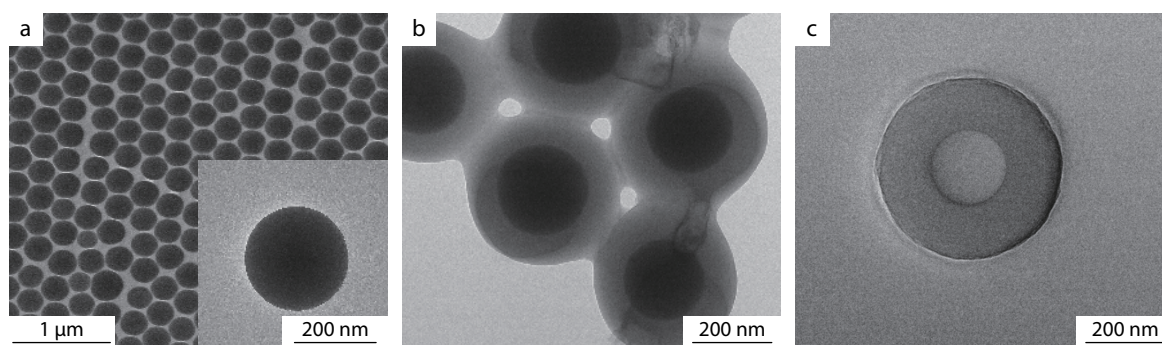


Fig. 1 TEM images of the prepared different particles: (a) SiO₂-MPS, (b) PEGSS and (c) PMC.

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 CO₂ 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 SiO₂-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 SiO₂, SiO₂-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 vibrati-

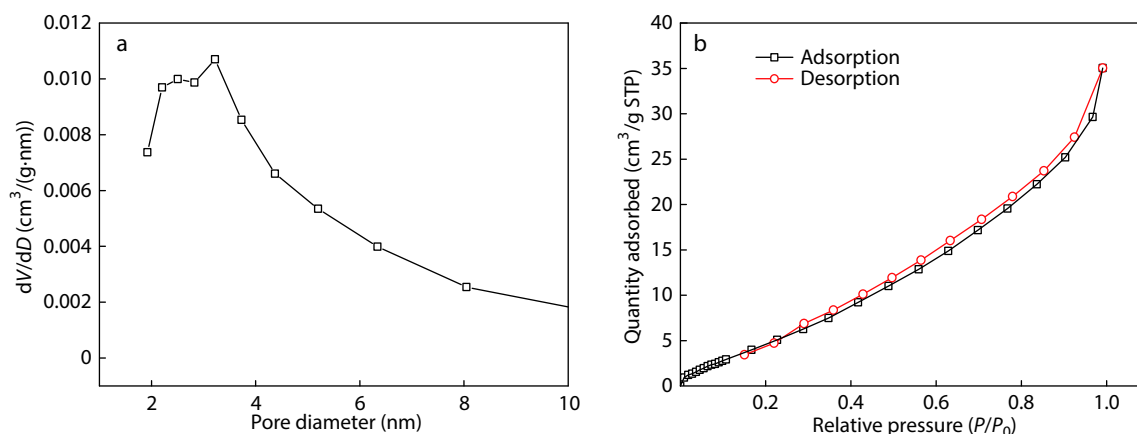


Fig. 2 (a) Pore size distribution curves of PMC; (b) N₂ sorption isotherms of the prepared PMC (square symbol: adsorption; circular symbol: desorption).

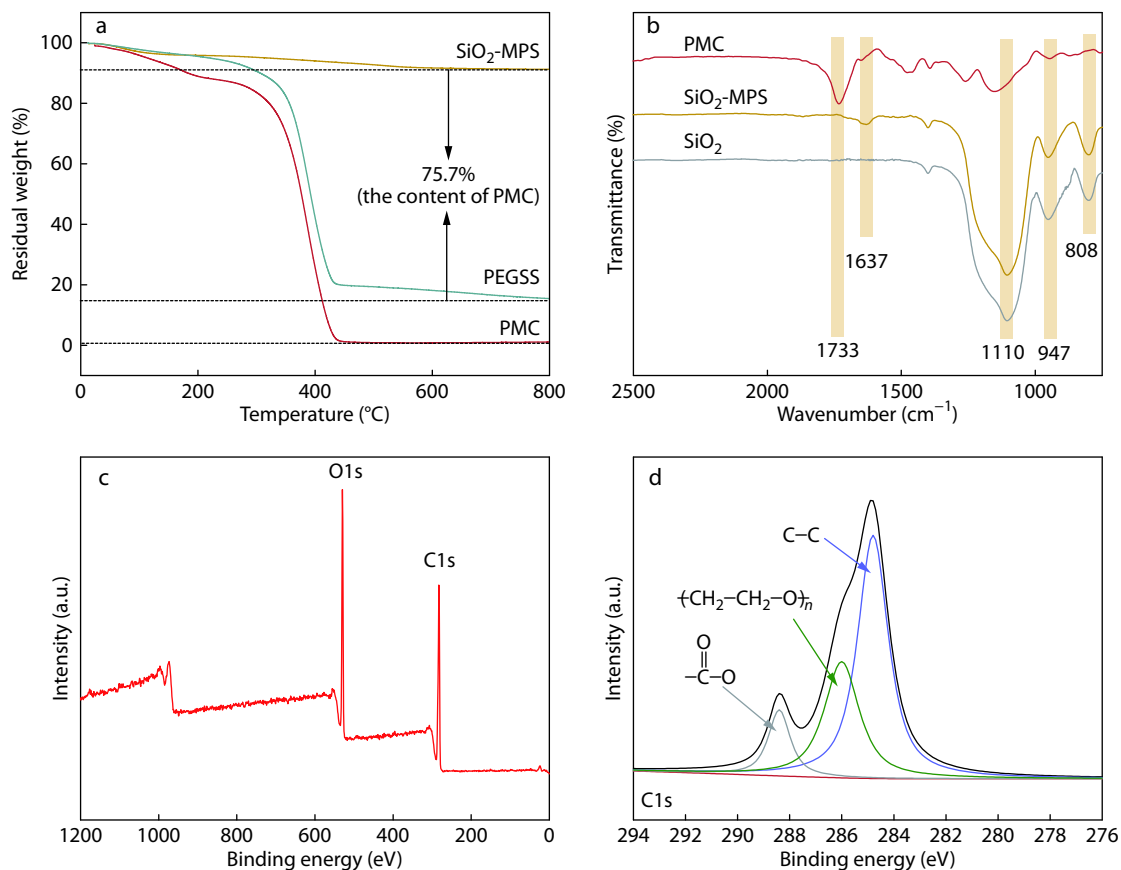


Fig. 3 (a) TGA curves of nanoparticles; (b) FTIR spectra of SiO₂, SiO₂-MPS and PMC; (c) XPS spectra of PMC; (d) C1s spectra of PMC.

ons) and the band at about 1733 cm^{-1} ($\text{C}=\text{O}$ stretching vibrations) represent the presence of MAA.^[26] The band at about 1637 cm^{-1} ($\text{C}=\text{C}$ stretching vibrations) indicates the presence of MPS. The absorption band at 947 cm^{-1} is assigned to the stretching vibration of $\text{Si}-\text{OH}$. The stretching vibration bands at 1110 and 808 cm^{-1} correspond to the asymmetric stretching vibration and symmetric stretching vibration of $\text{Si}-\text{O}-\text{Si}$. 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 $-\text{O}-\text{CH}_2-\text{CH}_2-$ while those of C1s at 288, 286 and 284.8 eV correspond to ester base, ether oxygen group from PEGMA and $\text{C}-\text{C}$, 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 neat 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-

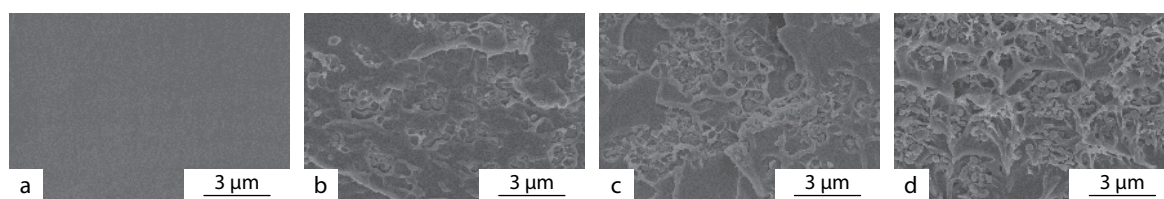


Fig. 4 Cross-section images of membranes: (a) Ultem, (b) Ultem-PMC-1.25, (c) Ultem-PMC-2.5, (d) Ultem-PMC-5.

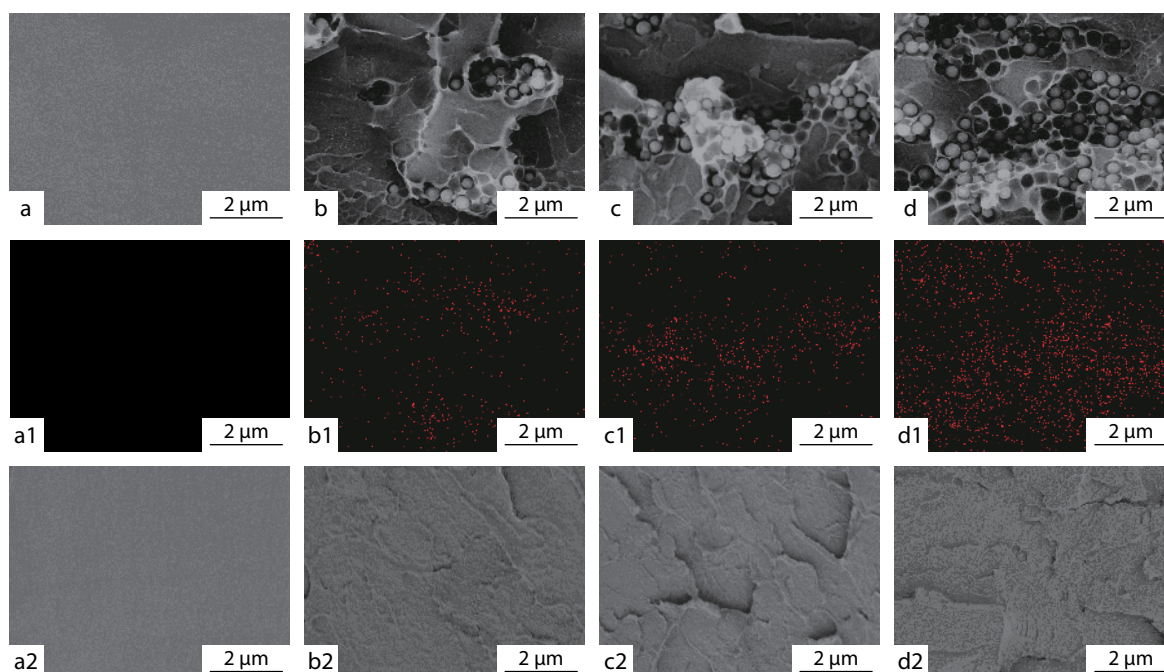


Fig. 5 Cross-section SEM images and elemental mapping of Si in different PEGSS filler loadings: (a, a1) Ultem, (b, b1) Ultem-PEGSS-1.25, (c, c1) Ultem-PEGSS-2.5 and (d, d1) Ultem-PEGSS-5. Cross-section SEM images of the membranes with different PEG contents: (a2) Ultem, (b2) Ultem-PEG-1.25, (c2) Ultem-PEG-2.5 and (d2) Ultem-PEG-5.

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} .^[37] 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 $2\theta=17.5^\circ$, 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 enlarged d -spacing. This phenomenon is likely due to the incorporation of PMC that destroys the initial chain segment stacking, and as a result, the free volume of membranes increases, allowing for higher gas permeability. Sufficient thermal stabilities of the membranes are crucial for long-term operation of MMMs. DSC and TGA were performed to investigate the thermal properties of as-prepared membranes. As seen in Fig. 7(c), with the increase of the filler loading from 0 wt% to 5 wt%, the glass transition temperature of MMMs gradually decreases from 213.6 $^\circ\text{C}$ to 210.5 $^\circ\text{C}$. It indicates that the incorporation of PMC will enhance the motility of the polymer chain, which may be ascribed to the hydrogen bond between PMC and Ultem. To further investigate the thermal properties, TGA was conducted and the results are depicted in Fig. 7(d).

There is a weight loss stage of MMMs before 300 $^\circ\text{C}$, which is attributed to the dehydration by the adsorbed water evaporation. The following weight loss stage (300–500 $^\circ\text{C}$) is caused by the decomposition of polymer. The incorporation of PMC imparts MMMs higher decomposition temperature around 520 $^\circ\text{C}$, while the neat Ultem membrane begins to degrade at a lower temperature around 500 $^\circ\text{C}$. 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 membrane, 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 $^\circ\text{C}$. 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

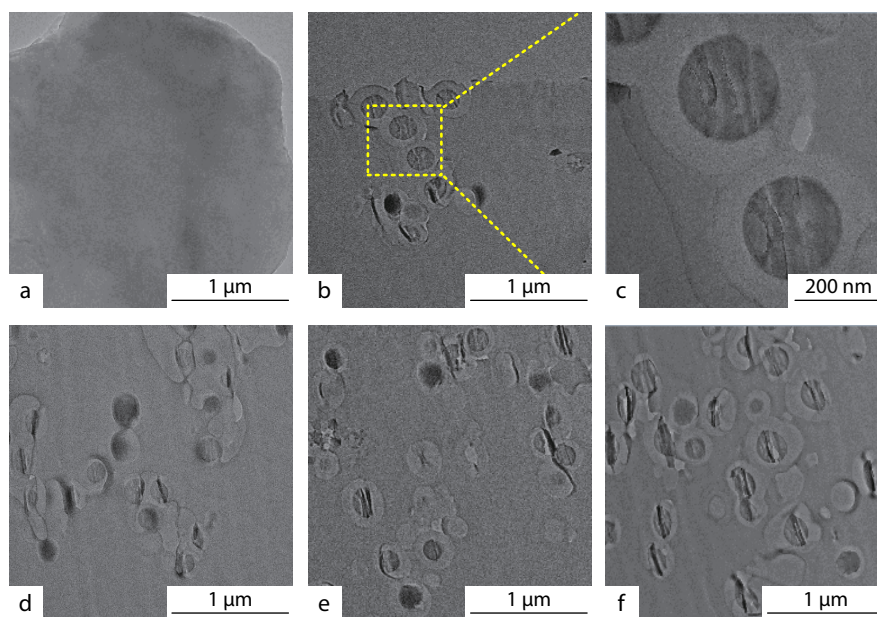


Fig. 6 TEM images of membranes with different PEGSS loadings: (a) Ultem, (b, d) Ultem-PEGSS-1.25, (c) high-resolution TEM image corresponding to the marked zone in (b), (e) Ultem-PEGSS-2.5, (f) Ultem-PEGSS-5.

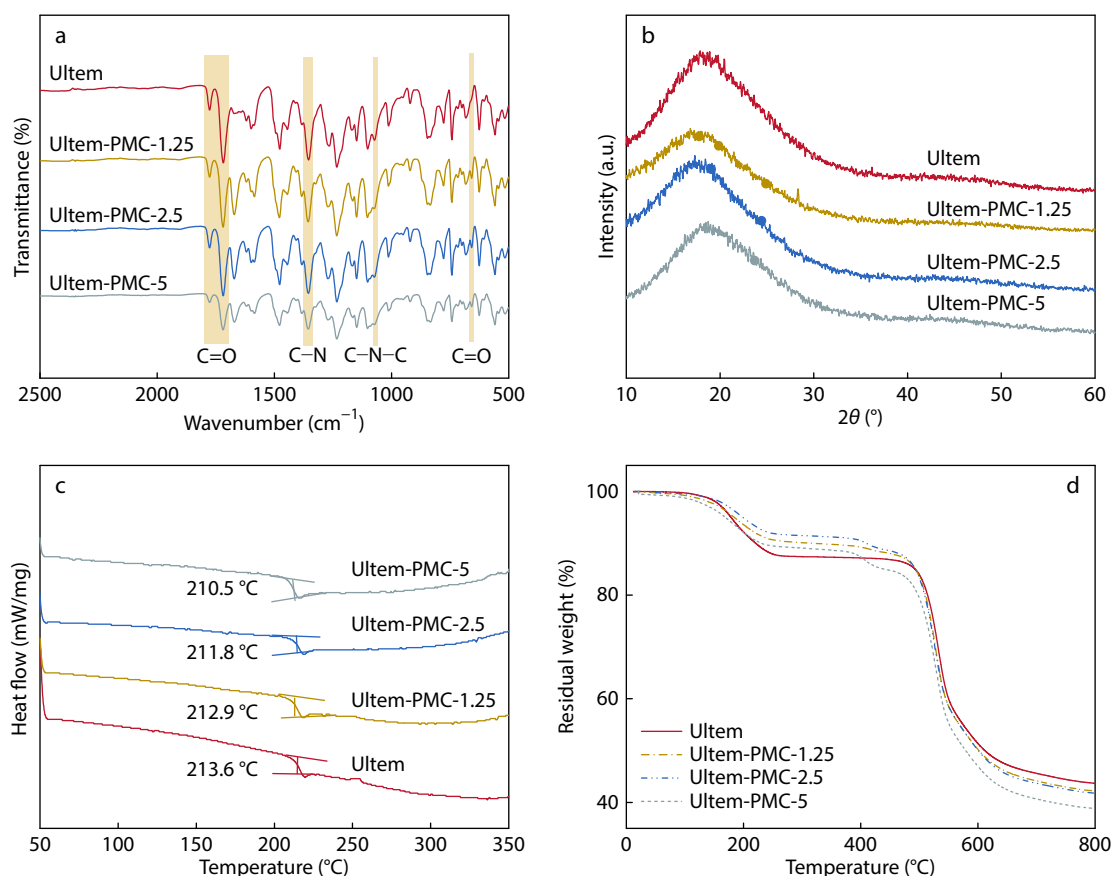


Fig. 7 (a) FTIR spectra of the neat membrane and MMMs at low wavenumber; (b) XRD patterns of the membranes; (c) DSC curves of the membranes with different loadings; (d) TGA curves of the membranes.

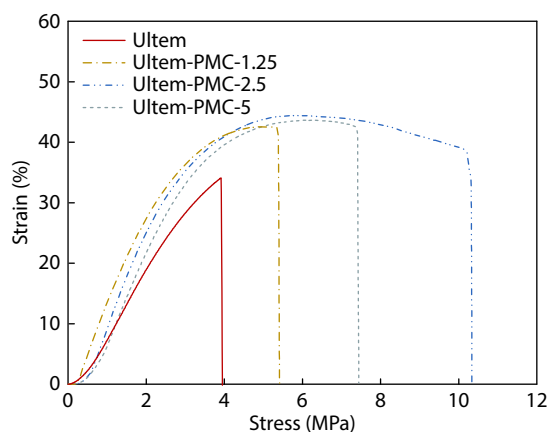


Fig. 8 Stress-strain curves of Ultem control and MMMs.

separation performance exhibits CO₂/N₂ selectivity increment of 22%, CO₂/CH₄ selectivity increment of 9%. The increase of CO₂/N₂ selectivity is more remarkable than CO₂/CH₄. This may be because the critical temperature difference between CO₂ (304.1 K) and N₂ (126.2 K) is larger than that of CO₂ and CH₄ (190.6 K).^[40] 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.^[29,30,41] Firstly, the unique hollow structure of microcapsules and permeable capsule wall provide a fast transfer channel,

Table 1 Gas permeability and selectivity of pristine Ultem and MMMs (tested at 0.4 MPa, 30 °C).

Membrane	P_{CO_2}	P_{CH_4}	P_{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

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 CO₂ molecules enhances the CO₂ 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.^[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-

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

Membrane	$D_{\text{CO}_2}^a$	$D_{\text{CH}_4}^a$	$D_{\text{N}_2}^a$	$S_{\text{CO}_2}^b$	$S_{\text{CH}_4}^b$	$S_{\text{N}_2}^b$	$D_{\text{CO}_2}/D_{\text{N}_2}$	$D_{\text{CO}_2}/D_{\text{CH}_4}$	$S_{\text{CO}_2}/S_{\text{N}_2}$	$S_{\text{CO}_2}/S_{\text{CH}_4}$
Ultem	0.59	0.08	0.18	3.4	0.9	0.40	3.2	7.38	8.4	3.78
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

^a Diffusivity coefficient [cm^2/s] $\times 10^{-8}$; ^b Solubility coefficient [cm^3 (STP)/ cm^3cmHg] $\times 10^{-2}$.

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

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_2 -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

* The values were calculated based upon CO_2 permeance and N_2 permeance of asymmetric hollow fiber membranes; ** Values are reported for CO_2/CH_4 separation.

ity coefficient. Compared with the pristine membrane, all MMMs show increment of gas solubility. This result is ascribed to the disrupted polymer chain packing caused by filler which will create more polar adsorption sites to increase the gas solubility. In addition, the favorable affinity of microcapsule with ether oxygen group towards CO_2 molecules owing to the dipole-quadrupole interactions also strengthens the gas solubility coefficients.^[43] However, the MMMs show a decreasing trend in both solubility and diffusivity coefficients when the filler content increases to 5%. The above phenomenon is largely attributed to the agglomeration of microcapsules in the polymer, which decreases surface area and contact sites for CO_2 molecules. Another important reason may be that the large accumulation density of the microcapsule in a limited area leads to an enhanced transfer resistance, and the increase of the transfer resistance leads to the decrease of the gas diffusion coefficient. Furthermore, such result is not different from the analysis of SEM. From now on, the collaborative reinforcement mechanism of solution-diffusion for the membrane is realized.

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. Concludingly, the incorporation of polymeric capsules in this study provides an efficient approach to enhance the gas separation performance of glassy polyimide membranes.

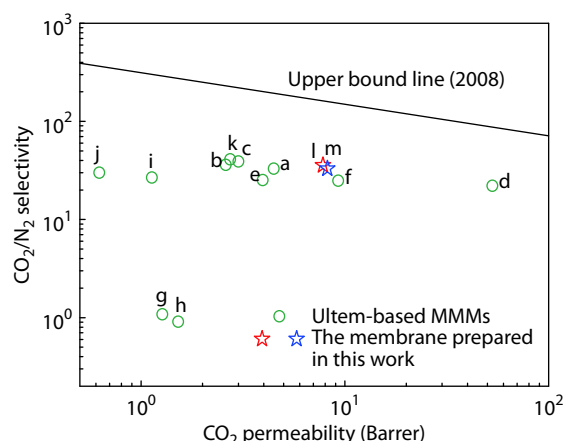


Fig. 9 Comparison of gas transport properties of other Ultem-based MMMs with current work in Robeson upper bound plot. Each data point corresponds to a letter that is consistent with Table 3.

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 interfacial 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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