Introducing amphiphatic copolymer into intermediate layer to fabricate ultra-thin Pebax composite membrane for efficient CO₂ capture

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A B S T R A C T

Pebax-based membranes have attracted intensive interest for high separation efficacy of carbon dioxide. For achieving excellent gas permeance, ultrathin membrane thickness is always the pursuit of composite membrane technology, in which controlling the interfacial property of the multi-layer remain a great challenge. Herein, we introduced an amphiphatic copolymer polydimethylsiloxane (PDMS)-block-polyethylene oxide (PEO) (PDMS-b-PEO) into the intermediate layer to tune the interfacial adhesion, enabling fabrication of ultra-thin Pebax composite membrane. It was demonstrated that surface segregation of PEO segments not only suppressed formation of dense SiO₂ layer due to the plasma treatment on PDMS intermediate layer, but also provided extra hydrophilic sites and interfacial compatibility for subsequent Pebax selective layer coating. With the present of PDMS-b-PEO in the intermediate layer, an integrated Pebax selective layer with thickness of ~50 nm was successfully fabricated. The resulting ultra-thin Pebax composite membrane exhibited outstanding performance with CO₂ permeance of 2142 GPU and CO₂/N₂ selectivity of 36. The strategy of using amphiphatic copolymer as intermediate layer enhanced the composite membrane integrity and simplified the plasma pre-treatment, showing great potential in developing highly permeable membrane for efficient CO₂ capture.

1. Introduction

Excessive carbon dioxide emission from flue gas and the fossil fuel combustion have exacerbated some rigorous environmental issues, such as the green-house effect as well as the climate change and glaciers melting [1]. Membrane separation process is regarded as the candidate technology to implement the efficient carbon capture by virtue of low cost, feasible upscaling and energy conservation [2–4]. Polymer-based membranes has attracted intensive research involving different levels of CO₂ selectivity and permeability [5–7]. The separation process of polymer-based membranes follows the solution-diffusion mechanism [8]. The affinity of membrane material towards CO₂ and the free volume for mass transport dominate the separation performance of CO₂/N₂ [9–13].

Pebax and polydimethylsiloxane (PDMS) are the representative rubbery polymer materials for gas separation [14–18]. The polyethylene oxide (PEO) segments endow Pebax with strong affinity to CO₂, whereas the glassy segments of polyamide increase the resistance of mass transport [19]. Alternatively, PDMS with softer main chain containing high free volume fraction exhibits obvious advantage into permeability. Though vigorous researches have been plugged into the development of PDMS membrane and Pebax membrane [20–24], the trade-off relationship between permeability and selectivity still restrains the CO₂ separation performance [25]. In efforts to improve the gas permeance of membrane with intrinsic selectivity, both the ultrathin thickness and the integrity of selective layer are indispensable [26,27]. However, diluted casting solution would inevitably intrude into the nanopores of substrate, inducing the decline of gas permeance and selectivity. To address this issue, polymers with high gas permeance [28,29], 2D materials [14] or inorganic materials [30] were adopted to construct an intermediate layer to form ultra-thin composite membrane. The multilayer structure integrating the superiorities of PDMS and Pebax has been confirmed.

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accessible to fabricate ultrathin Pebax membrane.

The interfacial compatibility between intermediate layer and selective layer is crucial for multilayered membrane. To develop ultra-thin Pebax composite membrane, however, the hydrophilic Pebax casting solution is challenging to be uniformly deposited on the hydrophobic PDMS intermediate layer. Thus, pre-treatment process mainly involving hydrophilic modification of PDMS surface is often adopted to enhance the interfacial adhesion of Pebax selective layer onto the PDMS intermediate layer. Up to now, surface modification strategies were mainly based on applying irradiation with high energy such as plasma and UV to break the robust Si–C bonds and Si–O–Si bonds, and generate abundant hydroxyl groups [31]. There are several limitations for current strategies to accomplish practical application. First, the rearrangement of oligomer induced to rapid recovery of hydrophobicity to the PDMS intermediate layer [32]. Second, the irradiation process required specific atmosphere (e.g., pure oxygen) to provide enough free radicals, which would increase the equipment investment and restrict the scale-up fabrication. It has been rarely reported that air was directly applied as the treatment atmosphere [15,33]. Because the low volume fraction of oxygen in the air is hardly to produce sufficient oxygen plasma, thereby limiting the efficacy of hydrophilic modification. Recently, Jiang et al. [33] developed an air plasma assisted spray coating method to fabricate Pebax thin-film composite membrane. Despite of a significant advance in CO₂/N₂ separation performance, the unevenness of PDMS surface and limited irradiation duration induced interfacial defects and thus achieved relatively low gas selectivity. Meanwhile, SiOₓ domains with high transport resistance were inevitably formed during the plasma treatment on the PDMS intermediate layer, inhibiting the further improvement of gas permeance.

In this work, the challenge of using air plasma pre-treatment and enhancing the interfacial adhesion of ultra-thin Pebax composite membrane was addressed by introducing an amphipathic copolymer, PDMS-b-PEO, into the intermediate layer (Fig. 1). The effect of copolymer on enhancing wettability of the intermediate layer can be activated by plasma treatment and air atmosphere was sufficient to construct a surface with high polarity. The PEO segments of the PDMS-b-PEO copolymer were self-migrated to the surface of intermediate layer, maintaining the hydrophilicity to provide highly enhanced interfacial compatibility with Pebax selective layer. Hence, it is feasible to fabricate integrated Pebax membrane with ultrathin thickness. To enhance the interfacial adhesion properties, the effect of chemical environment and composition on the surface of intermediate layer were comprehensively investigated after air plasma treatment. The fabrication conditions such as plasma treatment duration, copolymer blending amount and Pebax casting solution concentration were optimized to pursue higher CO₂/N₂ separation performance for the ultra-thin Pebax/PDMS-PEO/PAN composite membrane.

2. Experimental

2.1. Materials

Hydroxyl terminated polydimethylsiloxane (PDMS, M<sub>w</sub> = 6000) was supplied by Sigma Aldrich. Polydimethylsiloxane-block-polyethylene oxide (50–55%, M<sub>w</sub> = 5000), abbreviated to PDMS-b-PEO, was purchased from Gelest Inc. Pebax-1657 was bought from Arkema, France. The polyacrylonitrile (PAN) ultrafiltration membrane (molecular weight cut-off: 100 kDa) was utilized as the substrate which was purchased from Shandong Megavision Membrane Technology & Engineering Co., Ltd., China. Dibutyltin dilaurate (DBTDL, ≥95%) was supplied by Shanghai Aladdin Co., Ltd, China. Ethanol, tetraethyl orthosilicate (TEOS), and n-heptane were obtained from Sinopharm Chemical Reagent Co., Ltd, China. The deionized water was homemade. All chemical reagents were used as received without further purification.

2.2. Membrane fabrication

2.2.1. PDMS-PEO/PAN and PDMS/PAN composite membranes

The PDMS casting solution was prepared by mixing 1.03 g hydroxyl terminated PDMS monomer, 0.103 g cross-linking agent TEOS and 0.0103 g catalyst DBTDL in 150 mL n-heptane. The crosslinked network of PDMS was constructed from the condensation reaction between the terminated hydroxyl with the ethoxy of crosslinking agent (TEOS), and n-heptane was utilized as the substrate which was purchased from Shandong Megavision Membrane Technology & Engineering Co., Ltd., China. Dibutyltin dilaurate (DBTDL, ≥95%) was supplied by Shanghai Aladdin Co., Ltd, China. Ethanol, tetraethyl orthosilicate (TEOS), and n-heptane were obtained from Sinopharm Chemical Reagent Co., Ltd, China. The deionized water was homemade. All chemical reagents were used as received without further purification.
solution and the homogenous solution was obtained after sufficient agitation until no obvious flocule was observed. After the viscosity reaching 45 cP, the casting solution was spin-coated on the surface of PAN substrate with low speed of 300 for 9 s, then high speed of 3000 rpm for 40 s. The PDMS-PEO/PAN membranes were obtained after post thermal treatment under 60 °C for 12 h. The fabrication process of PDMS/PAN membrane was consistent with PDMS-PEO/PAN membrane without the introduction of PDMS-b-PEO copolymer.

2.2.2. Pebax/PDMS-PEO/PAN composite membranes

Pebax-1657 polymer particles were dissolved into ethanol (70 wt %)-water mixed solvent under 80 °C for 12 h. Before fabrication of Pebax-1657 composite membrane, plasma treatment was carried out directly in the air atmosphere to improve the surface wettability of PDMS-PEO membrane. The plasma generator device (CTP-2000K) with the effective treatment area of 28.3 cm² was provided from Sunan Plasma Technology Co., Ltd, Nanjing, China. The operation current and voltage were 1 A and 55 V, respectively. The distance between sample and upper electrode was 0.6 cm. The Pebax-1657 casting solution was deposited on the PDMS-PEO surface by blade casting. The Pebax/PDMS-PEO/PAN membranes were obtained after post thermal treatment under 60 °C for 12 h.

2.3. Characterizations

The surface morphology and thickness of each layer were characterized by field emission scanning electron microscope (FE-SEM, S-4800, Hitachi Limited, Japan). The atomic force microscopy (AFM, Bruker Dimension Icon, American, tapping mode) was carried out to obtain the surface roughness. The water contact angle was measured by using a contact angle Drop-Meter (A-100, Haishu Maishi Co., Ltd, Ningbo, China). Attenuated total reflection fluorier transformed infrared spectroscopy (ATR-FTIR, PerkinElmer Spectrum IR, USA) was adopted to analyze the chemical composition of the PDMS-PEO samples surface after plasma treatment. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) was applied to analyze the chemical bonds constitution of PDMS-PEO membrane surface after plasma treatment. The surface charge properties of the membranes were analyzed by the solid surface Zeta potential analyzer (Anton Paar SurPASS 3, Austria) under the values of pH from 3 to 10.

2.4. Gas permeation measurements

The constant volume/variable pressure method was applied to evaluate the pure gas separation performance of PDMS-PEO membranes and Pebax multi-layer membranes. The specific schematic test device was shown in Fig. S2. The permeation test was repeated for at least three times. The operation pressure was controlled to 0.3 MPa and the test temperature was 30 °C. The permeance of component i was obtained by the following equation:

$$ P_i = \frac{\frac{dp}{dT} \times V}{A \times T \times \Delta \rho} $$

where $P_i$ represents the gas permeance (1 GPU = $10^{-6}$ cm³ STP cm⁻² s⁻¹ cmHg⁻¹), $\Delta \rho$ indicates the transmembrane pressure (MPa). $A$ represents the effective membrane area (m²), $T$ is the testing temperature (°C), $\frac{dp}{dT}$ is the slope of the permeate pressure change which was detected by pressure transducer INFICON CDP020D. $V$ is the downstream volume. The gas selectivity ($a_i$) calculation for CO₂/N₂ can be done by bringing the permeance of the composite membrane into Equation (2), where the permeance of fast gas is $P_i$ and $P_j$ represents the permeance of slow gas.

$$ a_i = \frac{P_i}{P_j} $$

For gas mixture (CO₂: N₂, 15 vol%: 85 vol%) testing, the total permeate pressure of the gas mixture was set at 0.3 MPa and the temperature was 30 °C. In addition, gas chromatography (Agilent 8890 GC, USA) was used to detect the gas mixture components. The stage cut was set lower than 1% to eliminate concentration polarization.

3. Results and discussion

3.1. Hydrophilic modification of intermediate layer surface

The selective layer, Pebax, contains hydrophilic polyethylene oxide segments, inhibiting its uniform deposition and adhesion on the hydrophobic surface of PDMS intermediate layer. Hence, hydrophilic modification was performed to the PDMS surface. Generally, physical methods such as UV irradiation and plasma can provide enough energy to break the robust Si–O and Si–C bonds, further forming hydroxyl to improve the water wettability [34–37]. During this process, pure oxygen atmosphere was often required to improve the generation efficiency of hydroxyl. The process complexity triggers the demand of directly utilizing air atmosphere. However, the water contact angle (WCA) of PDMS surface decreased from 110° to 80° (Fig. 2a) after long air plasma treatment (20 s) indicating the low efficiency. To achieve the hydrophilic modification in air atmosphere, PDMS-b-PEO copolymer was adopted to provide extra hydrophilic sites on the surface of intermediate layer. The existence of PDMS segments in this copolymer not only enhanced the compatibility between the hydrophilic PEO segments with PDMS matrix, but also improved the dispersion of PEO segments in n-heptane. It was interesting to note that the WCA of PDMS-PEO membrane (mPDMS: mPDMS-PEO = 1:1.5) decreased from 100° to 58° within 45 s even without the plasma treatment (Fig. 2b). It may ascribe to the migration behavior of PEO segments. This process more likely involved the area near to the surface rather than the deeper polymer matrix. Hence, the migration rate of polymer segments was faster than expected, while it still could not reach the requirement of high continuity of casting solution during the membrane fabrication process. In view of this characteristic, plasma treatment was necessary to enhance the migration behavior of PEO segments.

The WCA of PDMS-PEO surface (Fig. 2c) decreased to 79° after only 4 s and reached to 16° within 10 s. In addition, at the same plasma treatment duration, the WCA decreased obviously with the increment of the copolymer amount. As shown in Fig. 2d, the hydrophobicity of the PDMS surface gradually restore to initial state within 5 min as a result of the migration of PDMS oligomers and the reorientation of polar groups [36]. It was worthy to note that all PDMS-PEO membranes could keep hydrophilic during 3 h (WCA < 90°) and the stabilized WCA was obviously lower than the initial value. Hence, the introduction of PDMS-b-PEO copolymer ensured enough time to deposited Pebax solution on PDMS intermediate layer surface. Jiang et al. [38] also reported similar phenomenon where the WCA of pristine PDMS surface was reduced to 49.3° after 10 s air plasma treatment, nearly twice lower than our result (102’, 10 s). It may attribute to the difference of molecular weight of PDMS and operation voltage of plasma. Nevertheless, our PDMS-PEO membranes-4 s exhibited lower WCA than PDMS membranes-5s reported by Jiang et al. These results indicated that the introduction of PDMS-b-PEO played a critical role in the enhancement of surface hydrophilicity of intermediate layer.

We further investigated the deposition behavior of Pebax casting solution on different kinds of intermediate layer. As shown in Fig. 3a, Pebax solution aggregated as dispersed droplets on the pristine PDMS surface (without introduction of PDMS-b-PEO copolymer), confirming the poor adhesion capacity of hydrophobic PDMS. Moreover, no obvious characteristic peaks of Pebax were observed from the sample of Pebax/PDMS/PAN. In comparison, the Pebax casting solution was well deposited on the surface of PDMS-PEO intermediate layer (Fig. 3b), as verified by the appearance of N–H stretching vibration peak at 3298 cm⁻¹ and C=O stretching vibration peak at 1640 cm⁻¹ [38] (Fig. 3c).
The existence of Si–CH₃ adsorption peak indicated that the thickness of Pebax layer was thin enough to allow the penetration of infrared ray. However, it was difficult to distinguish the difference of chemical bonding on PDMS-PEO membrane surface after short-time air plasma activation. We have measured the surface zeta potentials of PDMS-PEO membranes without air plasma treatment and 4 s air plasma treatment. The result of Fig. S3 exhibited PDMS-PEO membrane after 4 s air plasma treatment possessed −40 mV at around pH 7.0, which was more negative than the samples without air plasma treatment (−24 mV). This result indicated that negative groups were generated after plasma activation.
treatment and provided higher hydrophilicity.

As aforementioned, the results of ATR-FTIR were insufficient to reflect the change of chemical bonding. For further explanation, we applied XPS technique to analyze the chemical bonding of the intermediate layer. As shown in Fig. 4a, the C 1s spectrum of PDMS-based samples exhibited four peaks at the binding energy of 288.6, 286.5, 284.8, 284.6 eV, corresponding to C–O, C–O–C, C–Si and C–C, respectively. Among these chemical bonds, the content of ether bond could reflect the enrichment degree of PEO segments on the surface of intermediate layer. Taking pure PDMS as reference, partial PEO segments could expose to the surface without plasma treatment and content of C–O–C increased from 10.2% to 22.6% with extending the air plasma treatment duration to 4 s. It demonstrated that more PEO segments migrated from the bulk to surface of intermediate layer, exposing abundant hydrophilic sites. The result was consistent with the water contact angle test. The existence of C–O bond indicated a partial decomposition of PEO segments. The content of ether bonds decayed to 10.1% when the plasma treatment duration reached to 20 s. On the other hand, longer pre-treatment duration could generate more hydroxyl in the result of lower WCA value. Fig. 4b compared the Si 2p XPS spectra of the pristine PDMS (without plasma treatment) with PDMS-PEO intermediate layers (after 20 s air plasma). The PDMS sample exhibited single characteristic peak at 102.1 eV, corresponding to the silicone atom bonded to two oxygen atoms. After plasma treatment, the Si 2p peak of PDMS-PEO sample shifted to higher bonding energy area and the complex components could be resolved into three parts: Si–O at 102.1 eV, Si–O–Si at 102.8 eV and Si–O at 103.4 eV [39]. The appearance of Si–O peak suggests the formation of SiO2 after plasma treatment on PDMS.

The migration and rearrangement of polymer segments are driven by the thermal motions and surface polarity. It was reported that the fluorinated chains spontaneously migrated to membrane surface and decline the surface energy [40,41]. Similarly, in this work, PEO segments exhibiting higher polarity and hydrophilicity tended to form cluster and self-entanglement in the hydrophobic environment, further resulting coverage by PDMS segments (Fig. 4c). During air plasma treatment, the produced hydroxyl groups increased surface polarity. Meanwhile it prompted the migration motions of PEO segments to membrane surface and gathering, finally induced the optimization of hydrophilicity. Moreover, the line structure and lower molecular weight of PDMS-b-PEO copolymer exhibited higher mobility. In contrast, the movement of PDMS segments were confined by crosslinking network.

The CO2 permeance of PDMS intermediate layer fabricated by different PDMS-b-PEO blending amount were presented in Fig. 5a. When the mass ratio of PDMS to PDMS-b-PEO reached 1:0.5, the enhancement of CO2 permeance from 11174 GPU (pure membrane) to 13030 GPU was owing to the affinity of PEO segments to CO2 molecules. Moreover, the small amount of PEO segments didn’t make inhibition effect on the

Fig. 4. (a) C1s XPS spectra of PDMS samples after different plasma treatment duration (from 0 s to 20 s). (b) The Si 2p XPS spectra of PDMS/PAN membrane and PDMS-PEO/PAN membrane. (c) Schematic of the migration behavior of PEO segments from polymer matrix to the surface after plasma treatment.
polymer stacking structure and gas permeability. By increasing the content of PDMS-\textit{b}-PEO, the CO$_2$ permeance exhibited continuous downward trend and the decline rate of PDMS-PEO/PAN membrane reached 25.8% compared to the pure PDMS/PAN membranes. We further test the intrinsic gas transport properties of PDMS and PDMS-PEO homogenous membranes to exclude the effect of substrates. The result showed that the decline rate between PDMS and PDMS-PEO membranes achieved 30.2% which was higher than the composite membranes (Fig. S7). In view of the selective thickness of all composite membranes possessing similar thickness (around 200 nm), the minor difference of decline rate between composite membranes and homogenous membranes indicated that the decline of CO$_2$ permeance was mainly originated from the nature of PDMS-\textit{b}-PEO. The crystallization behavior of PEO segments and the suppression of chains mobility induced the obvious decline of CO$_2$ permeance \cite{42,43}, although the CO$_2$/N$_2$ selectivity increased from 10.5 to 15.8 (Fig. 5b). Moreover, the main reasons for not directly adopting PDMS-\textit{b}-PEO as the intermediate layer not only included the crystallization behavior, but also the difficulty of customizing the high molecular weight and active groups to construct the stable cross-linked network.

Significantly, the CO$_2$ permeance of pure PDMS intermediate layer displayed 42.8% reduction after 4 s air plasma treatment. In contrast, the introduction of PDMS-\textit{b}-PEO effectively relieved the reduction of gas permeance. As shown in Fig. 5a, the decline rate of PDMS-PEO intermediate layer was restricted within 27% after plasma treatment. For further explanation of this phenomenon, we proposed a distribution model of surface structure (Fig. 5c). As aforementioned, the SiO$_x$ layer was inevitably formed after conducting plasma treatment on PDMS, which would increase the gas transport resistance. In case of the migration and rearrangement of polymer chains during the air plasma treatment, more PEO segments exposed to the membrane surface and part of polymer chains may dissociated in the form of carbon dioxide and water. Hence, the dense SiO$_x$ area was replaced by loose area with much lower gas transport resistance, leading to the higher gas permeance. For supplementary, the selectivity of intermediate layer after plasma treatment will be discussed in Fig. 7.

The increment of copolymer blending amount also enriched the hydrophilic site after plasma treatment, further generating higher affinity to Pebax solution. It brought out more Pebax deposited on the intermediate layer surface and higher selective layer thickness. As a result, the CO$_2$ permeance was significantly decreased from 2554 GPU to 312 GPU. The enhancement of selectivity (from 23.6 to 59.6) was ascribed to more completed structure of selective layer (Fig. 5d). By balancing the gas permeance and selectivity, we selected 1:1 as the optimal mass ratio of PDMS to PDMS-\textit{b}-PEO. Compared to the recent reported performance of Pebax TFC membrane (CO$_2$ permeance: 1140 GPU, CO$_2$/N$_2$ selectivity 44), the optimal Pebax/PDMS-PEO/PAN membrane exhibited an obvious advantage in gas permeance (1768 GPU) with equivalent selectivity (43.8). Such major advance can be attributed to the reduction of dense SiO$_x$ area with the introduction of PDMS-\textit{b}-PEO into the intermediate layer (Fig. 5c).

### 3.2. Effect of the air plasma treatment duration

The air plasma treatment duration affects not only the surface wettability, but also the formation of Pebax selective layer. For improving the interfacial adhesion of Pebax layer, longer plasma treatment was required to obtain more hydrophilic surface of the intermediate layer. The surface morphology was also probably changed with the extending the plasma treatment duration. As shown in Fig. 6a–g, the pore structure of substrate occurred collapse gradually by increasing the treatment duration and the intrinsic finger pores of PAN substrate were totally blocked at 20 s. It was hardly to distinguish the boundary between PDMS-PEO intermediate layer and substrate. Meanwhile, large
Fig. 6. The cross-section (a–g) and surface (h–i) SEM images of PDMS-PEO/PAN membranes after different plasma treatment duration (0 s–20 s). (j) AFM images and surface roughness value of PDMS-PEO/PAN membranes after different plasma treatment duration.

Fig. 7. Effect of plasma treatment duration on the separation performance of different membranes. (a) PDMS-PEO/PAN membrane and (b) Pebax/PDMS-PEO/PAN membrane. (m_{PDMS}:m_{PDMS-b-PEO} = 1:1, concentration of Pebax solution: 0.5 wt%, test conditions: pure gas, 30 °C, 0.3 MPa).
defects with tens of micrometers were observed on the surface of PDMS-PEO intermediate layer which was owing to the high energy of air plasma and ultra-thin thickness of intermediate layer (Fig. 6h and i). The AFM images (Fig. 6j) revealed that the extension of plasma treatment duration decreased the surface roughness ($R_a$ value decreased form 15.6 nm–5.1 nm).

During the air plasma treatment, the oxygen radicals can break the Si–CH$_3$ bond, leading to the bonding of silicone ion with oxygen atoms and formation of a silica-like layer [44]. The SiO$_x$ layer possessed high transport resistance and the thickness was positively related to the plasma treatment duration [45]. We also found that with extending the plasma treatment duration to 10 s, the CO$_2$ permeance of PDMS-PEO/PAN membrane decreased from 11538 GPU to 1913 GPU (Fig. 7a). Definitely, the decline of gas permeance was also ascribed to the collapse of substrate pores. According to the literature [39], the high crosslinking structure of SiO$_x$ layer may improve the size-sieving ability and thus increase the gas selectivity, while the CO$_2$/N$_2$ selectivity of PDMS-PEO intermediate layer was decreased from 12.95 to 8.54 in this work. The result of Fig. 6 implied the tiny defect could appear during the plasma treatment process. Furthermore, the Pebax casting solution was deposited on PDMS-PEO intermediate layer with different plasma treatment durations. The variation of CO$_2$ permeance could be divided into two distinct processes (Fig. 7b). The decline from 4 s to 10 s was attributed to the combinatorial effect of larger SiO$_x$ layer thickness and the collapse of substrate pores. It was interesting to find that the CO$_2$ permeance of Pebax-4s was much higher than Pebax-2s in spite of same casting solution concentration. As aforementioned, PDMS-PEO intermediate layer possessed higher roughness after 2 s air plasma treatment. Rougher surface enhanced the interaction with casting blade, inducing more casting solution left and higher thickness of the selective layer. Simultaneously, the growing number of defects combining with thinner Pebax layer thickness caused the decline of CO$_2$/N$_2$ selectivity from 51.4 to 33.3. As a result, 4 s air plasma treatment duration was optimal to obtain relative intact structure and suitable surface roughness of the PDMS-PEO intermediate layer.

3.3. Separation performance of Pebax/PDMS-PEO/PAN composite membranes

After optimizing the fabrication conditions of PDMS-PEO intermediate layer, we investigated the effect of concentration of Pebax casting solution on the separation performance of Pebax/PDMS-PEO/PAN composite membrane. As shown in Fig. 8, the membrane thickness (intermediate layer combined with selective layer) was varied from 156 nm to 994 nm by increasing the Pebax concentration from 0.1 wt% to 1.5 wt%. When the polymer concentration was lower than 0.3 wt%, it was difficult to differentiate the Pebax selective layer and PDMS-PEO intermediate layer under SEM. By using higher concentration of 0.5 wt%, boundary between intermediate layer and selective layer was clearly observed. The thickness of selective layer and intermediate layer was around 50 nm and 200 nm, respectively. The gas separation performance of membranes with multi-layer structure is often described by resistance in series model (Fig. S4). The predictive separation performance could be calculated by the permeability of every layer and their individual thickness. The permeability and ideal selectivity of Pebax and PDMS-PEO ($m_{PDMS}:m_{PDMS-b-PEO} = 1:1$) homogenous membranes were summarized in Fig. S5. Based on the resistance in series model, we found that the calculated values were in basic agreement with experiment values (Fig. 9 and Table S1). The deviation of permeance and selectivity was under 20% and 13%, respectively. In addition, the deviation of
permeance and selectivity both became smallest when the selective layer was the largest. It indicated property of selective layer dominated the overall gas transport. The decline of selectivity from 55.5 to 35.8 could be owing to the lower thickness and the intrinsic property of Pebax. It was worth noting that the experiment value of permeance was slightly higher than the model value. We speculated that the interfacial enhancement promoted the transport of CO$_2$. The two layers were anchored firmly without any interfacial defects observed from Fig. 8c–e. The adhesion between Pebax selective layer and PDMS-PEO intermediate layer can be resulted from two kinds of interactions. First, the hydroxyl created by air plasma interacted with oxygenic functional groups of Pebax to generate the hydrogen-bonding network [31]. Second, the exposure PEO segments of PDMS-PEO membrane exhibited strong affinity to the identical partial of Pebax. It strengthened the physical segments entanglement at the interface of two kinds of polymers.

The mixed gases (CO$_2$:N$_2$ = 15 vol%:85 vol%) were applied to study the effect of operation conditions on the separation performance of Pebax/PDMS-PEO/PAN composite membrane. As shown in Fig. 10a, the increment of temperature provided higher driving force and resulted enhancement of gas performance. The temperature dependence relationship of gas permeance abided the Arrhenius equation $P_i = P_{i,0} \exp\left(-\frac{E_p}{RT}\right)$, where $P_i$ is the partial permeance of component $i$, $P_{i,0}$ is a pre-exponential factor, $E_p$ is the activation energy, $R$ is the gas constant and $T$ is the operation temperature in Kelvin. As shown in Fig. 10b, higher activation energy of N$_2$ indicated the N$_2$ permeance was increased faster than CO$_2$ permeance with increasing temperature. As shown in Fig. 10c, as increasing the operating pressure, the decline of permeance and selectivity was ascribed to the membrane condensation and sorption competition that was often observed in the mixed gas permeation [46–49]. Next, the continuous mixed gas permeation was carried out for 120 h. During the test process, the CO$_2$ permeance and selectivity remained stable at 1339 GPU and 38.5, respectively (Fig. 10d). We further tested the separation performance of PDMS-PEO membranes with different storage time. The result of Fig. S6 displayed that the CO$_2$ permeance still kept stable around 1400 GPU after one year storage. However, the selectivity experienced slight decline from 37.5 to 34.5 which ascribed to the slow aging effect.

Fig. 11 counted the performance comparison of the reported state-of-art membranes for CO$_2$/N$_2$ separation. To satisfy the requirement of economically competitive and energy efficient capture of CO$_2$, the CO$_2$ permeance should exceed 1000 GPU, while the selectivity of CO$_2$/N$_2$ should be higher than 20 (the gray area in Fig. 11) [4,50]. In recent years, researchers continuously reported the work involving the fabrication of ultrathin Pebax membranes. For example, Shigenori Fujikawa [31] deposited Pebax-1657 selective layer on the oxygen plasma-activated surface of PDMS intermediate layer. The pure oxygen atmosphere facilitated the generation of adequate hydroxyl to form high CO$_2$-philic hydrogen bonding network with Pebax-1657 segments. In our work, the enhancement of interfacial adhesion was the combined effect originated from the enrichment of PEO segments on the PDMS intermediate layer surface and the hydroxyl created by air plasma. Moreover, the substitution of oxygen atmosphere by direct air atmosphere simplified the membrane fabrication process. Aside from the pure polymer membrane, novel porous materials and 2D nanosheets were utilized to fabricate mixed matrix membranes and construct channels for

![Fig. 10. Effect of operation conditions on separation performance of Pebax/PDMS-PEO/PAN composite membrane, (a) operation temperature, (b) Arrhenius plot for CO$_2$ and N$_2$, (c) operation pressure and (d) operation time. (membrane fabrication conditions: m$_{PDMS}$:m$_{PDMS-b-PEO}$ = 1:1, air plasma treatment duration: 4 s, the concentration of Pebax casting solution: 0.5 wt%; feed gas: 15 vol% CO$_2$:85 vol% N$_2$, 0.3 MPa).](image-url)
high transport of gas molecules [51]. Our ultra-thin Pebax/PDMS-PEO/PAN composite membranes exhibited superiority of CO$_2$ permeance ($\geq$1700 GPU) with attractive CO$_2$/N$_2$ selectivity ($\geq$35), surpassing the commercial membranes like Polaris and PRISM and locating in the target performance area.

4. Conclusions

In summary, we presented a facile methodology to promote high selective transport of CO$_2$ over N$_2$ through ultrathin Pebax/PDMS-PEO/PAN composite membrane. Specifically, the introduction of amphipathic copolymer PDMS-PEO into the intermediate layer enhanced its surface hydrophilicity after air plasma treatment. The segment rearrangement assisted the exposure of PEO chains, further improving the interfacial adhesion behavior between the intermediate layer and selective layer. After optimization of copolymer blending amount, air plasma treatment duration and Pebax concentration, the as-fabricated Pebax/PDMS-PEO/PAN composite membrane exhibited remarkable enhancement in CO$_2$ permeance, reaching to 2142 GPU with attractive CO$_2$/N$_2$ selectivity of 36. Simultaneously, the robust composite structure endowed membrane with feed pressure resistance and operation stability. We anticipate that our strategy of fabricating intermediate layer by adopting amphipathic copolymer would provide an avenue to address the challenges of scalable fabrication of ultra-thin Pebax-based composite membrane.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2022.121183.

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