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Membrane fabricated via a facile non-solvent induced microstructure re-arrangement with superior CO_2 separation performances

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Abstract:

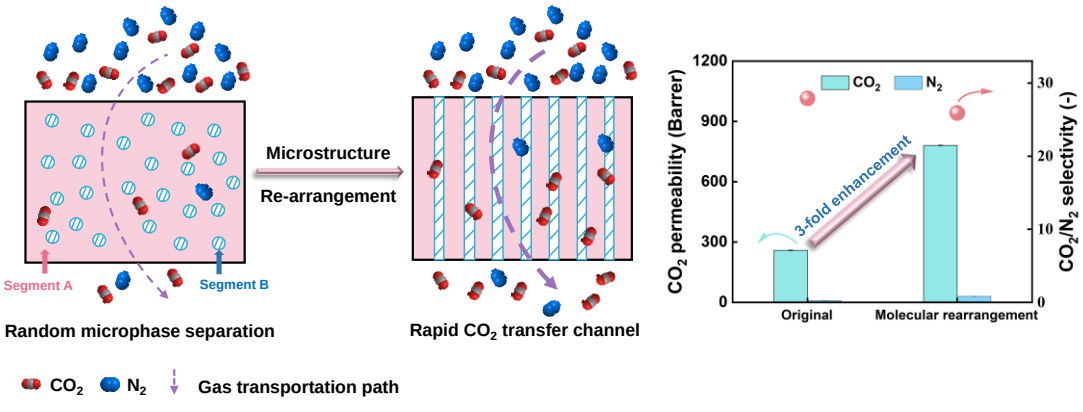
CO_2 capture and storage (CCS) is taken as an immediate solution to mitigate the impactof increasing atmospheric CO_2 on global climate change, and CO_2 separation using high-performance membranes is considered a green and energy-efficient technology in CCS. In this study, we developed a novel non-solvent induced microstructure re-arrangement method to improve CO_2 separation properties of block

copolymer-based membranes, e.g., Pebax 2533. Experiments demonstrate that microstructure re-arrangement in deionized (DI) water significantly enhances gas separation performances of Pebax 2533 and reveal that the CO_2/N_2 selectivity of the treated membranes remains stable with the CO_2 permeability increased by three folds to 782.3 Barrers. These findings suggest that microstructure re-arrangement can be a practical method to improve CO_2 separation performance of block copolymer-based membrane materials, enabling a broad application in developing gas separation membranes.

Highlights:

* Non-solvent induced microstructure re-arrangement of block copolymers is studied;
* Microstructure re-arranged Pebax 2533 membranes show greatly improved CO_2 separation performance;
* Simple treatment of Pebax 2533 membrane by DI water enables an increase of CO_2 permeability by three folds;
* The effects of re-arrangement conditions were studied to optimize the membrane microstructure.
* The rearranged membrane demonstrated good long-term stability after 300 days storage
.

Graphic abstract:


Microstructure
Re-arrangement
Segment A
Segment B
Random microphase separation
Rapid CO2 transfer channel
CO2
N2
Gas transportation path
CO2 permeability (Barrer)
CO2/N2 selectivity (-)
3-fold enhancement
Original
Molecular rearrangement

1. Introduction

It is well-known that carbon dioxide (CO_2) emissions are the main cause of global climate anomalies [1]. Therefore, to alleviate the global climate change caused by excessive CO_2 emissions, the development of advanced CO_2 capture technology has become the focus of scientists [2, 3]. CO_2 capture and storage (CCS) is widely accepted as an effective, immediate solution to mitigate CO_2 emission while keeping the usage of fossil fuels [4]. Among the various CO_2 capture technologies (e.g., absorption, adsorption, membrane separation, and chemical looping), membrane separation is considered an emerging technology with enormous potential to improve its process efficiencies [5], with the advantages of small footprint, energy saving, and linear scaling up [6]. Up to now, numerous types of membrane materials have been developed for CO_2 capture, including polymeric membranes [7], mixed matrix membranes(MMMs) [8], and inorganic membranes (e.g., carbon molecule sieve (CMS) membranes [9], metal organic framework (MOF) membranes [10] and 2D materials based membranes [11]). The polymeric membrane is currently the most intensively studied and used CO_2 separation membrane materials due to its excellent processability, relatively low price, and moderate CO_2 separation performances [12]. However, most polymeric membranes suffer from the permeability-selectivity trade-off and the CO_2 separation performances below the famous Robeson upper bound [13]. There is an urgent need to develop membrane materials with high CO_2 separation performance and good long-term stability to further enhance the competitiveness of membrane-based CO_2 separation processes.

Block copolymer is a special type of polymer consisting of a series of alternating flexible and crystalline hard segments that integrate the excellent properties of different segments [14]. In the case of block copolymer based membranes, the soft chain segment is the permeable phase of gas, while the hard chains provide mechanical stability to the material [15]. The combination of the two chain segments can effectively balance the

gas separation performance and mechanical properties and has a wide range of applications in the field of gas separation and water separation [16, 17]. On the other hand, due to the incompatibility of each chain segment, the block copolymer will undergo microphase separation during membrane preparation, forming different microscopic configurations, which, in turn, produce different transport characteristics [18].

In our previous work, attempts have been made to add ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) into the sulfonated pentablock copolymer Nexar (commercialized as Nexar®) to prepare a series of hybrid membranes for CO_2/N_2 separation [19]. Small-angle X-ray scattering (SAXS) results clearly show that the microstructure of the hybrid membranes has changed with the presence of IL, and the CO_2 separation performances thus changed accordingly. In another study, ILs and polyethylene glycols (PEGs) were added into Nafion® as additives to make hybrid membranes [20], where the ILs and PEGs not only worked as plasticizers of the polymeric chains but also tuned the microstructure of the Nafion® matrix, with significant changes of the morphology (observed by transmission electron microscope (TEM) and SAXS). In addition, the CO_2 permeation performances were enhanced for over 2 orders of magnitudes.

On the other hand, as typical block copolymers, poly (ethylene oxide) (PEO)-based membranes have been widely used in CO_2 separations [21, 22]. Among these polymers, Pebax is a representative commercial polyether-polyamide block copolymer thermoplastic elastomer, with flexible PEO segment and rigid polyamide (PA) blocks [23]. Due to its good mechanical properties, processing possibilities, and moderate CO_2 separation performances, Pebax has been intensively studied for different CO_2 separation applications. Researchers found that using different solvents to prepare Pebax membranes will lead to significantly different CO_2 separation performances [24, 25], but the detailed characterization and in-depth analysis of the microstructure are missing. In addition, reports about employing proper solvents-non solvents

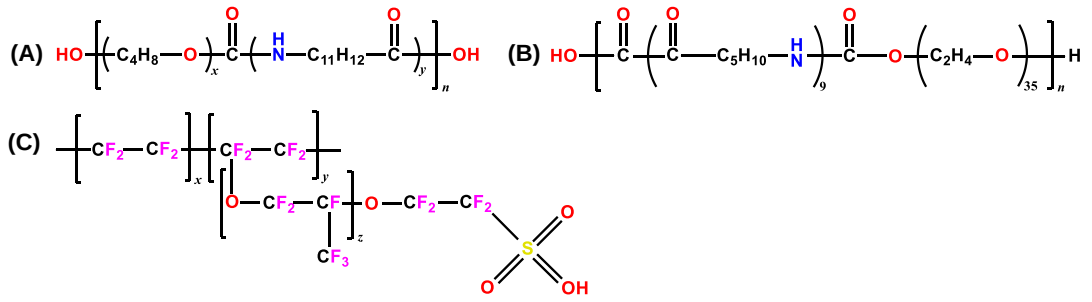
combination to optimize the microstructure and improve the membranes separation performances were intensively studied for liquid separation [26-28], but it can be rarely seen in gas separation applications.

Therefore, in this paper, we propose a facile environmentally friendly method to realize the microstructure re-arrangement of Pebax 2533 membranes. By using a proper combination of solvents and non-solvents, the microstructure of the block copolymer-based membranes can be fine-tuned, and random microstructure is re-constructed to be more organized, which promotes the formation of high-speed CO_2 transmission channels and thus improves the membranes' CO_2 separation efficiency. The effects of different microstructure re-arrangement conditions, e.g., non-solvent type, soaking duration, and temperature, on the morphology and separation performance of Pebax membranes were systematically investigated. The gas permeation properties of the obtained membranes were also tested under different conditions.

2. Experimental

2.1 Materials

Commercial Pebax 2533 and Pebax 1657 were ordered from Arkema (France). Alcohol-based Nafion D520 solution was obtained from Ion Power (Munich, Germany). Reagent-grade ethanol was purchased from Jinshan Chemical Test Co., Ltd. (Chengdu, China) and used without further purification. DI water was prepared using a laboratory water purification system (TE-S20). The CO_2 and N_2 gases used in the experiment were purchased from Chengdu Xuyuan Chemical Co., Ltd (Chengdu, China), and were used directly upon receipt. The purity of the single-component gas was 99.999%.



Scheme. 1. Molecular structure of Pebax 2533 (A), Pebax 1657 (B), and Nafion D520 (C).

2.2 Membrane fabrication

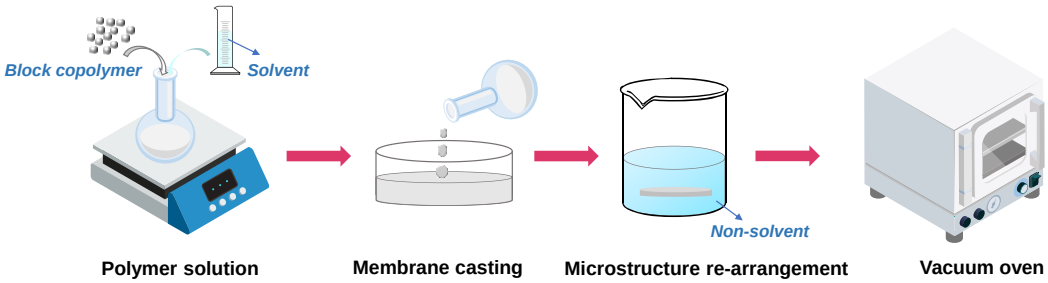
The membranes were prepared by solution casting, as shown in Scheme 2. A certain amount of Pebax 2533 polymer was weighed into a single-mouth flask, and ethanol was added to obtain an 8 *wt.*% polymer membrane solution by reflux stirring at 80 °C for 8 h. The solution was then poured into a Teflon petri dish, and the solvent was volatilized for 24 h at room temperature (RT). The membrane was then removed from the casting petri dish and placed in a vacuum oven, where it was dried at 50 °C for 24 h to remove residual solvents and adsorbed impurity gas on the membrane.

An appropriate amount of Pebax 1657 was added to 70/30 *w/w*% ethanol/water solution and stirred at 80 ^{o}C for 30 min to ensure the Pebax was completely dissolved, and 1.5 *wt.*% Pebax solution was obtained. The solution was then poured into a Teflon petri dish, and the solvent was volatilized for 24 h at RT. The membrane was then removed from the casting petri dish and placed in a vacuum oven, where it was dried at 50 °C for 24 h to remove residual solvents and adsorbed impurity gas on the membrane.

Nafion dispersion was stirred magnetically in a round-bottomed flask for at least 30 minutes. It is then poured into a glass petri dish. To keep the membranes uniform and uncracked, it needs to be heated at 80 ^{o}C for 100-120 minutes, while another petri dish is covered with the first one to reduce the evaporation rate of the solvent. After the solution was evaporated, the resulting membrane was dried at 60 ^{o}C under vacuum for 6 hours before it was used for subsequent tests.

For non-solvent induced microstructure re-arrangement, the membranes were

immersed in corresponding non-solvent for 24 h and then dried under vacuum at 35 °C for 24 h before being used for subsequent analysis. The membrane thicknesses were measured using a Digimatic micrometer (SanLiang, China), and the average of at least 10 measurements over the entire permeating area was recorded.



Scheme. 2. Microstructure re-arrangement membranes fabrication.

2.3 Membrane characterization

Thermogravimetric analysis (TGA) was characterized using a synchronous thermal analyzer (NETZSCH, STA 449, Germany) with a temperature range of 30-800 °C and a heating rate of 10 °C min^{-1}. To prevent premature degradation, high purity N_2 gas (99.999%) was used as scanning and protective gas at a flow rate of 60 mL min^{-1}. The differential scanning calorimeter (DSC) (NETZSCH, 204 F1, Germany) was utilized to determine the basic thermal properties and analyze the glass transition temperature (T_g) of different microstructure re-arrangement membranes. The testing procedure consisted of three steps: first, the membrane was brought up to 150 °C in a high purity N_2 atmosphere (99.999%) to remove moisture and other impurities, then the sample was cooled to -150 °C and then again raised to 150 °C at a heating/cooling rate of 10 °C min^{-1}. The second heating ramp was used to analyze the glass transition temperature of the membrane. Fourier-transform infrared (FTIR) spectroscopy (PerkinElmer, Frontier, USA) was used to qualitatively analyze the chemical bonds of the membranes, with a wavelength range of 4000-650 cm^{-1}. TEM (FEI, Tecnai G2 F20, USA) was used to examine the morphology of the membrane. Membrane samples were stained with a saturated lead acetate aqueous solution and then embedded in epoxy resin for slicing.

The chemical composition of the membranes was analyzed by X-ray photoelectron spectroscopy (XPS) (KRATOS, XSAM 800, UK). The nanostructures of Pebax membranes were also characterized by SAXS (Nanostar U SAXS, Bruker, Germany). The sample was exposed to a 14 keV beam (wavelength, λ=0.154 nm), and the distance between the sample and detector was 2 m with a spot size of 0.5 x 0.5 mm. Azimuth integration of the obtained two-dimensional scattering diagram provided a one-dimensional intensity distribution of the scattering vector q= (4π/λ) sinθ, where λ is the X-ray wavelength and θ is the half angle of scattering. The microstructure of the samples was detected using the X-ray diffractometer (XRD) (Rigaku Ultima IV) with Cu target wide-angle diffraction. The scanning range was 5~75 °, the scanning rate was 10 ° min^{-1}, and the step size was 0.02 °.

The liquid water uptake test was performed at RT and atmospheric pressure. The samples were immersed in DI water for 24 hours. The liquid water uptake was calculated as follows

$$\Omega_{H_2O} = \frac{W_\infty - W_D}{W_D} \times 100 \qquad (1)$$

where W_∞ and W_D represent the weight of dry and water-saturated membranes, respectively. According to the average value of the two samples, the experimental error is less than 5%.

Single gas permeability was tested by constant-volume variable-pressure method [29]. The gas permeability (P) is calculated based on equation (2):

$$P = \frac{Vd}{RTA} \times \frac{l}{(pu - pd)} \times \left[\left(\frac{dp}{dt}\right)_{t\to\infty} - \left(\frac{dp}{dt}\right)_{leak}\right] \qquad (2)$$

where V_d is the permeation volume, R is the universal gas constant, T is the test temperature, A refers to the effective permeation area, l is the thickness of the membrane, and p_u-p_d is the pressure difference across the membrane, $\left(\frac{dp}{dt}\right)_{t\to\infty}$ is the pressure gradient on the downstream side at a steady state, while $\left(\frac{dp}{dt}\right)_{leak}$ is the leakage rate of the permeation rig.

The corresponding gas ideal selectivity (α) is expressed by the ratio of permeability of

different gas components:

$$\alpha_{ij} = \frac{Pi}{Pj} \quad (3)$$

where P_i and P_j correspond to the permeability of two different gaseous species i and j. and the gas permeability unit used here is the Barrer. 1 Barrer=10^{-10}(cm^3(STP) cm/(cm^2 s cmHg). For each membrane, the final result is reported as the average of the three measurements.

3. Results and discussion

3.1 Miscibility and compatibility study

To determine the optimal solvent and non-solvent for Pebax 2533, we used the Hansen solubility parameter (HSP) to screen common solvents [30]. The HSP method utilizes the difference in solubility parameters between the material and the solvent to determine the solubility of the solvent to the material, and it is often used for the preliminary screening of polymer solvents. Hansen extended the solubility theory to three dimensions, and HSPs are composed of dispersion force (δ_D), polarity force (δ_P), and hydrogen bonding force (δ_H).

To calculate whether a polymer is compatible with the solvent, we can determine the solubility parameter difference between the polymer and the solvent using Equation 4:

$$\Delta\delta = \sqrt{(\delta_{D,i} - \delta_{D,p})^2 + (\delta_{P,i} - \delta_{P,p})^2 + (\delta_{H,i} - \delta_{H,p})^2} \quad (4)$$

In the formula:

Δδ—Solubility parameter difference, $MPa^{0.5}$;

δ_D—Dispersion action solubility parameter, $MPa^{0.5}$;

δ_P—The solubility parameter of polar action, $MPa^{0.5}$;

δ_H—Hydrogen bonding solubility parameter, $MPa^{0.5}$;

Subscripts i and p denote solvent and polymer, respectively.

The three-dimensional solubility parameters of materials can be simulated by Hspip

232 software [31]. HSP solubility parameters of Pebax 2533 and commonly used solvents
233 for Pebax 2533 are shown in **Table 1**.

234 **Table. 1.** Solubility Parameters of solvents/non-solvents for Pebax 2533

Material	Solubility parameter ($MPa^{0.5}$)				
	δ_D [a]	δ_P [a]	δ_H [a]	δ_t [b]	$\Delta\delta$
Pebax 2533	17.6 [c]	7.6 [c]	6.8 [c]	20.3	—
Pebax 1657	18.8	5.4	11.2	22.5	—
Ethanol/water mixture	15.7	11.0	26.3	32.5	—
Ethanol	15.8	8.8	19.4	26.5	12.8
Water	15.5	16	42.3	47.8	36.5
Dimethyl sulfoxide	18.4	16.4	10.2	26.7	9.5
Methanol	15.1	12.3	22.3	29.6	16.4
N, N-Dimethylformamide	17.4	13.7	11.3	24.9	7.6
Tetrahydrofuran	16.8	5.7	8.0	19.4	2.4
N-Methylpyrrolidone	18.0	12.3	7.2	23.0	4.7
Acetic acid	14.5	8.0	13.5	21.4	7.4
Acetaldehyde	14.7	12.5	7.9	20.9	5.8
Acetone	15.5	10.4	7.0	19.9	3.5
Cyclohexane	16.8	0	0.2	16.8	10.1

235 [a] as calculated by HSPiP software.

236 [b] δ_t, total cohesion (solubility) parameter: $\delta_t^2=\delta_D^2+\delta_P^2+\delta_H^2$.

237 [c] The solubility parameters of Pebax 2533 were calculated from the group constants of
238 the polymer structural units [32]

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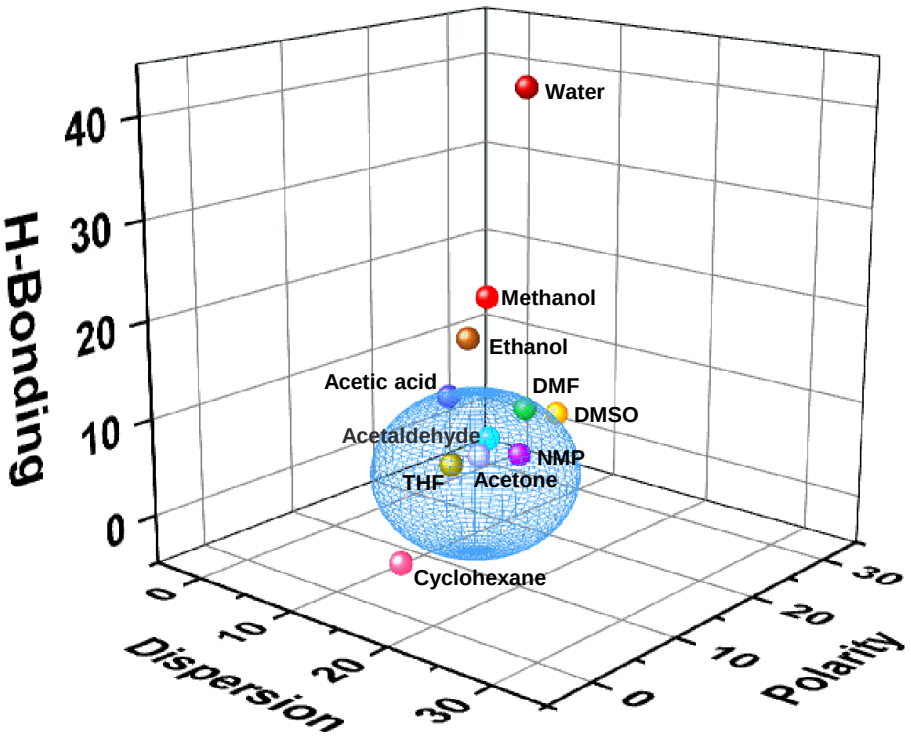


Figure. 1. Plot of solubility parameter for various solvents/non-solvents of Pebax 2533

According to the definition of HSPs, a solvent with Δδ less than 10 is considered a suitable solvent for a polymer compared to a polymer [24, 33]. **Figure 1** plots the solubility parameters of each solvent in **Table 1**, with the sphere representing the HSPs sphere of Pebax 2533 with a radius of 10. The solvent capable of dissolving Pebax 2533 could be located within the sphere area, such as N, N-Dimethylformamide(DMF), Tetrahydrofuran (THF), and N-Methylpyrrolidone (NMP), which have been applied as the solvent for Pebax 2533 to prepare membranes for gas separation [34, 35]. Surprisingly, even though ethanol/water are not considered a 'good' solvent as indicated in the HSPs systems, they have been widely used as solvents for Pebax to prepare gas separation membranes [36-38] due to their low toxicity and good environmental friendly. A large number of literature have shown that membrane materials prepared with ethanol and ethanol/water as solvents have higher separation performance [39-41], possibly due to unexpected micro-structures. Furthermore, the solubility parameter method can also help us to quickly determine the non-solvent that can be used for microstructure re-arrangement. In the current study, ethanol/water was

used as solvents for Pebax 1657, while the mixture of alcohols was used as solvents for the Nafion.

3.2 Effect of non-solvents

To investigate the effect of non-solvent induced microstructure re-arrangement, methanol, dimethyl sulfoxide (DMSO), and water was employed as non-solvent, and the gas permeability of the re-arranged membranes was tested and presented in **Figure 2**. Compared to the neat Pebax 2533 membrane, treating the membrane with non-solvent at RT for 24 hours leads to rather different gas separation performances: the CO_2 permeability was greatly improved with only a slight reduction in CO_2/N_2 selectivity (**Figure 2B**). In addition, among these 3 non-solvents, the water-treated membrane resulted in the highest CO_2 permeability (782.3 Barrer), which is 3 times the value of the neat membrane (258.5 Barrer), while the CO_2/N_2 selectivity was only slightly reduced from 27.9 to 25.9. Therefore, water was employed as the non-solvent to induce potential micro-phase separation in Pebax 1657 and Nafion D520 membranes. The water-induced micro-phase separation resulted in quite different results for Pebax 1657 and Nafion D520 (As shown in **Figure 2C** and **Figure 2D**). It is found that water has significantly enhanced CO_2 permeability for Pebax 2533 membrane, while it is more effective in promoting CO_2/N_2 selectivity for the Nafion D520 membrane. On the other hand, for Pebax 1657, the water-induced micro-phase separation only leads to slightly improved CO_2 permeability and CO_2/N_2 selectivity. In addition, data for Pebax 2533 and Pebax 1657 were obtained using single-gas permeation tests under dry conditions, while data for Nafion D520 were obtained using mixed-gas tests at 100% RH.

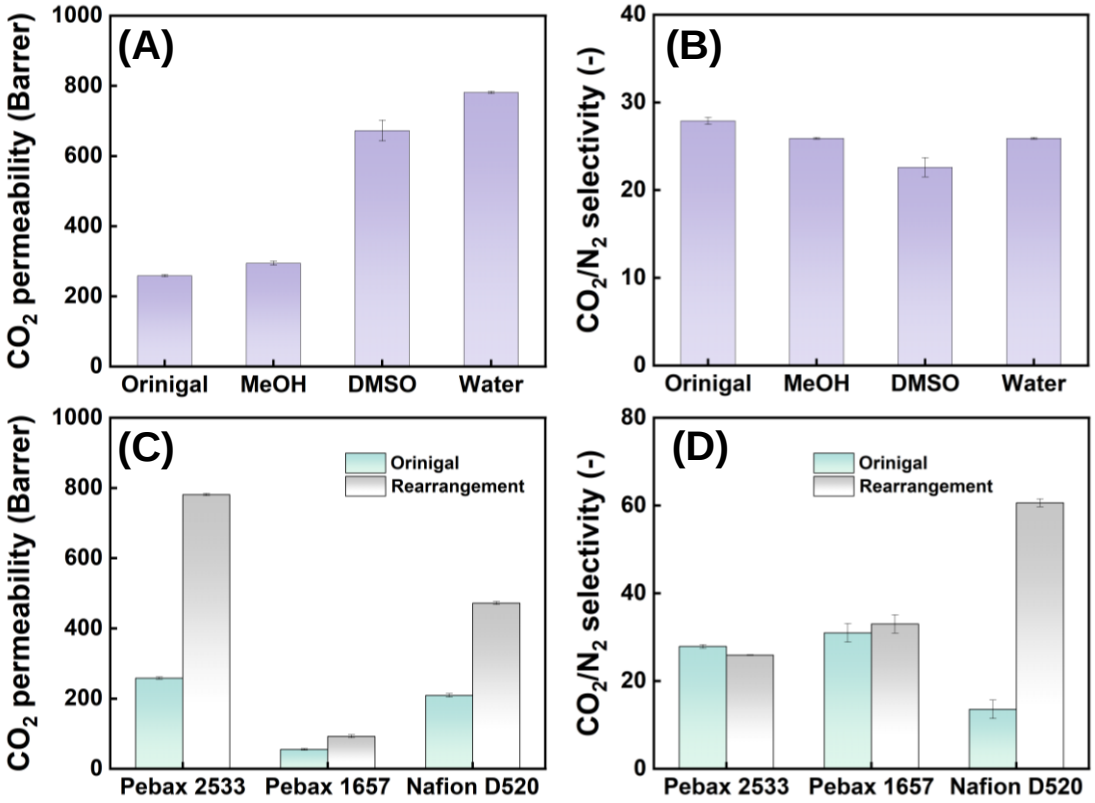


Figure. 2. Effect of non-solvent induced micro-phase separation on gas permeation. CO_2 permeability (A) and CO_2/N_2 selectivity (B) of Pebax 2533 membranes with different non-solvents; CO_2 permeability (C) and CO_2/N_2 selectivity (D) of Pebax 2533, Pebax 1657, and Nafion D520. Gas permeation was tested with a feed pressure of 2 bar at 25 °C.

3.3 Effect of microstructure re-arrange time

The Pebax 2533 was further studied by changing the water treatment duration length. The obtained membranes were thoroughly characterized using various technics, and the results are presented in **Figure 3**.

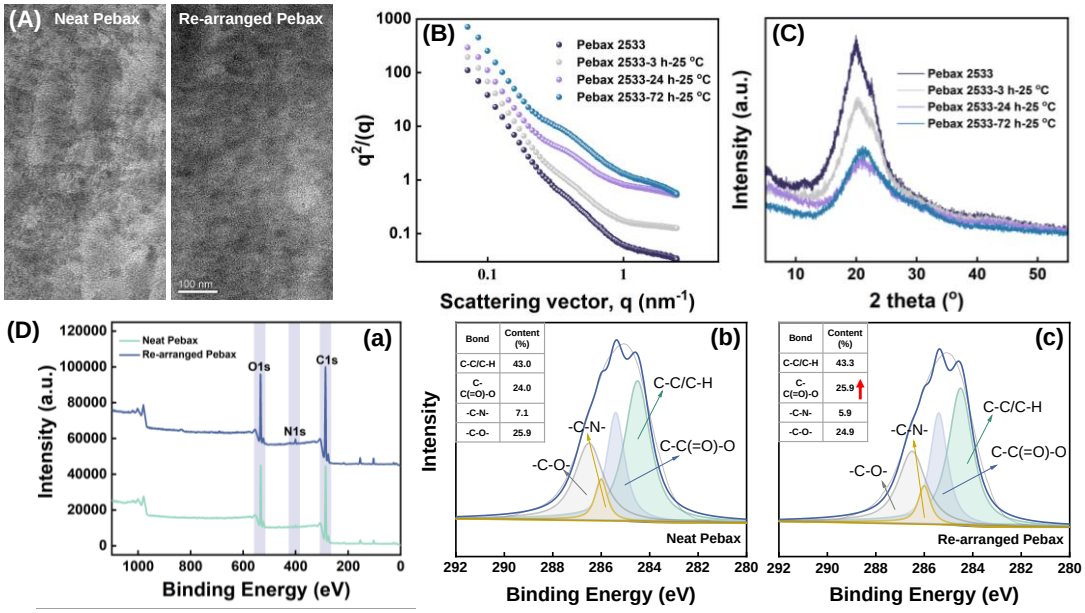


Figure. 3. Chemical-physical characterization of Pebax 2533 before and after water induced micro-phase separation. TEM image of neat Pebax 2533 and Pebax 2533 soaked in water for 24 hours (A); SAXS (B) and XRD results (C) of Pebax 2533 treated with water for different duration time; XPS spectra of neat Pebax 2533 and Pebax 2533 soaked in water for 24 hours (D) (a: complete survey spectrum, b, c: C 1s spectrum).

The mechanism of gas transport within Pebax 2533 is largely determined by the micro-structures before and after re-arrangement. In this study, TEM was used to acquire real-space images of the Pebax 2533 membranes before and after re-arrangement in DI water. Prior to observation, selective staining was performed with saturated lead acetate, so that the PEO region appears electron-opaque (dark), the results of this analysis are presented for comparison in **Figure 3A**. As previously expected in TEM studies of Pebax 2533 [42], the nanostructure is generally irregular, apparently composed of co-continuous hydrophilic (PEO, dark) and hydrophobic (PA, light) features. In contrast, after the microstructure re-arrangement in DI water, Pebax 2533 membrane swelled to form a nanoscale hydrophilic region, resulting in a more homogeneous and connected structure of the hydrophilic network in the membrane, which may lead to rather different CO_2 transport properties. it may also be the result of non-solvent water-induced enhancement of molecular mobility, which contributes to improved spatial

separation of highly incompatible hydrophilic and hydrophobic regions.

The rate of CO_2 transport in Pebax 2533 membranes depends on the size, shape, and connectivity of the hydrophilic region. TEM provides valuable spatial information about these morphological features, while SAXS provides a more sensitive way to distinguish the morphology of the membranes prepared in this study. **Figure 3B** displays the SAXS profiles collected from membranes derived from Pebax 2533 before and after re-arrangement (consistent with TEM images provided in **Figure 3A**). The profile for Pebax 2533 displays a weak peak near the q = 0.4 nm^{-1}, which corresponds to a characteristic spacing (d) of ~15.7 nm according to Bragg's law ($d = 2\pi/q^*$, where q* represents the scattering vector of interest). This characteristic interval is attributed to the hydrophilic region, consistent with the results of Wilkes et al. [43]. After the introduction of DI water, with the extension of water treatment time, the peak broadened significantly and shifted to a lower q, so the corresponding spacing increases slightly to 17.0 nm, which may contribute positively to the gas permeability.

In prior studies [44, 45], TEM combined with SAXS was also used to analyze the microstructures of polymers before and after re-arrangement. For sulfonated block copolymer (Nexar), the introduction of ionic liquids (non-solvent) resulted in profound morphological restructuring, changing from sheet to layered structure. Further introduction of water vapor leads to swelling of the nanostructures, and this microstructure transformation significantly improved CO_2 permeability . For Nafion, another random polymer, the introduction of ionic liquids and water vapor also caused nanostructures change and consequently improvement in CO2 separation performances . XRD is another powerful tool widely used to characterize the Pebax 2533 membranes [36, 47]. In our study, a strong crystallization peak at 20.4° was found for the neat Pebax 2533 membranes and the membrane after water treatment, which is attributed to the crystalline region of PA and is consistent with previous reports in the literature [48] (**Figure 3C**). As expected, soaking the membrane in DI water reduced the peak intensity in the crystalline region of the Pebax 2533 matrix. Thus, crystallinity

decreased with increasing water treatment duration time. This phenomenon is mainly due to the breaking of hydrogen bonds between the PA segments of Pebax 2533, leading to a decrease in the binding energy within the microstructure re-arrangement membrane [49]. As a lower membrane crystallinity degree normally leads to higher CO_2 permeability, it is expected that the water-treated Pebax membranes will result in high gas permeability.

To further explicate the elemental compositions of the original and rearrangement membranes, XPS analysis was performed and the results are shown in **Figure 3D (a)**. As can be seen in **Figure 3D a**, both membranes presented three peaks at 533.2 (O 1s), 400.6 (N 1s), and 286.2 eV (C 1s), the position of the spectral peak remains unchanged after rearrangement. It can be concluded that the rearrangement by water at 25 ^{o}C does not affect the chemical structure of the Pebax membranes. **Figure. 3D (b) and (c)** show the C 1s XPS spectra of the original and rearranged membranes. The typical peaks of C-C/C-H (284.5 eV), C-C(=O)-O (285.4 eV), -C-N- (286.0 eV), and -C-O- (286.5 eV) were observed for both membranes. It is noted that the content of each bond is almost unchanged after re-arrangement, suggesting the re-arrangement is mainly a physical procedure.

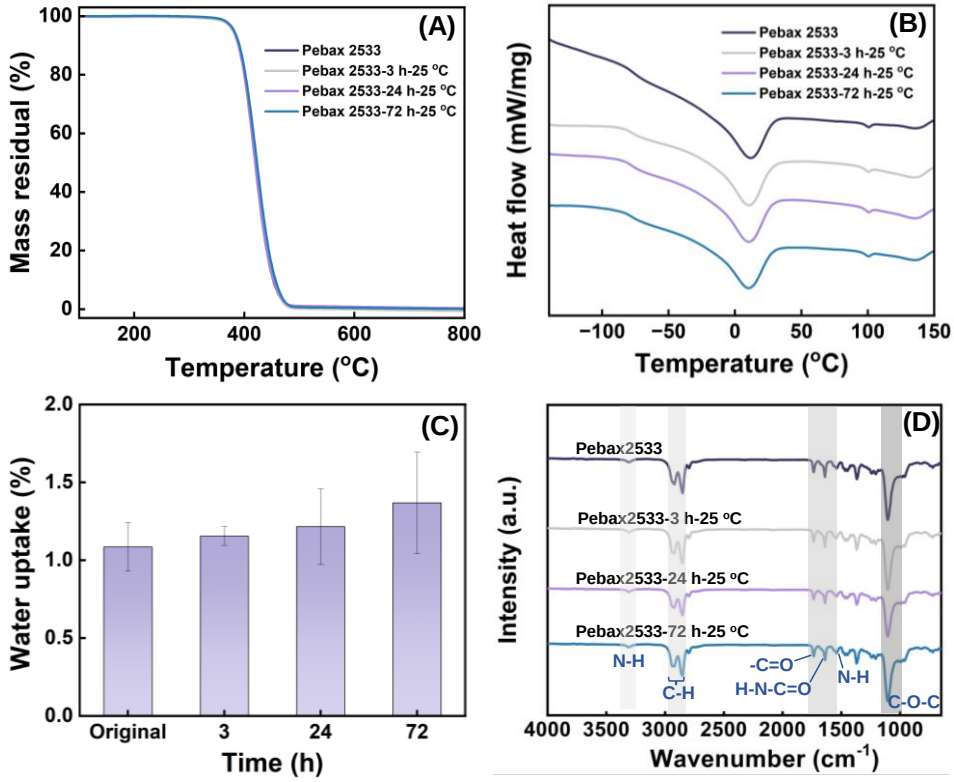


Figure. 4. Thermal stability (A), DSC (B), water uptake (C), and FTIR spectrum (D) of Pebax 2533 membranes treated with water for different duration times.

Other than the morphology of the membranes, their thermal properties were also thoroughly investigated. As expected, the water treatment is mainly a physical procedure that does not lead to any chemical change in the membrane materials. Thus, the thermal stability of the Pebax 2533 before and after water treatment was almost the same (**Figure 4A**); increasing water soaking time leads to no change in the thermal stability of Pebax 2533 membranes. In addition, the thermal decomposition temperature of all membrane materials is above 350 °C, indicating that they can meet the separation requirements under high-temperature conditions [50].

On the other hand, DSC test was also carried out for the Pebax 2533 membranes. The second heating cycle results were analyzed to eliminate surface and internal moisture and impurities. It is well-known that Pebax 2533 is a partially crystalline block copolymer consisting of an amorphous PEO phase and a crystalline PA phase [51]. Prior to was induced microstructure re-arrangement, Pebax 2533 exhibited two melting

point peaks (T_m) at 11.36 °C (PEO segment) and 100.76 °C (PA segment), respectively, indicating the presence of phase separation in the Pebax 2533 membrane, which is consistent with literature reports [52]. As shown in **Figure 4B**, the T_g of Pebax 2533 prior to microstructure re-arrangement was -76.35 °C. After the water treatment, the T_g of the membrane was reduced to -78.65 °C (shown in **Table 2**), at the same time, T_m was also found to decrease slightly, denoting a lower crystallinity degree, these results are in good agreement with the XRD results. The reduced crystallinity degree will result in increased chain segment mobility, and is favorable for gas permeability of Pebax 2533 membranes.

Table. 2. T_g and T_{m1} of PEO segments and T_{m2} of PA of Pebax 2533 membrane before and after microstructure re-arrangement

Membrane	**T_g (°C)**	**$T_{m1\ PEO}$ (°C)**	**$T_{m2\ PA}$ (°C)**
Pebax 2533	-76.35	11.36	100.76
Pebax 2533-3 h-25 °C	-78.65	10.56	100.56
Pebax 2533-24 h-25 °C	-78.45	10.46	100.86
Pebax 2533-72 h-25 °C	-78.26	10.06	100.56

The chemical structure of the Pebax 2533 membranes was characterized using FTIR (**Figure 4D**). The detailed peak assignments of Pebax 2533 are also listed in **Table 3,** which is consistent with data previously reported in the literature [53-55]. From the FTIR results, there was no new peak or peak shift in the Pebax 2533 membrane before and after water treatment, indicating no chemical interaction between the non-solvent water used in this study and Pebax 2533.

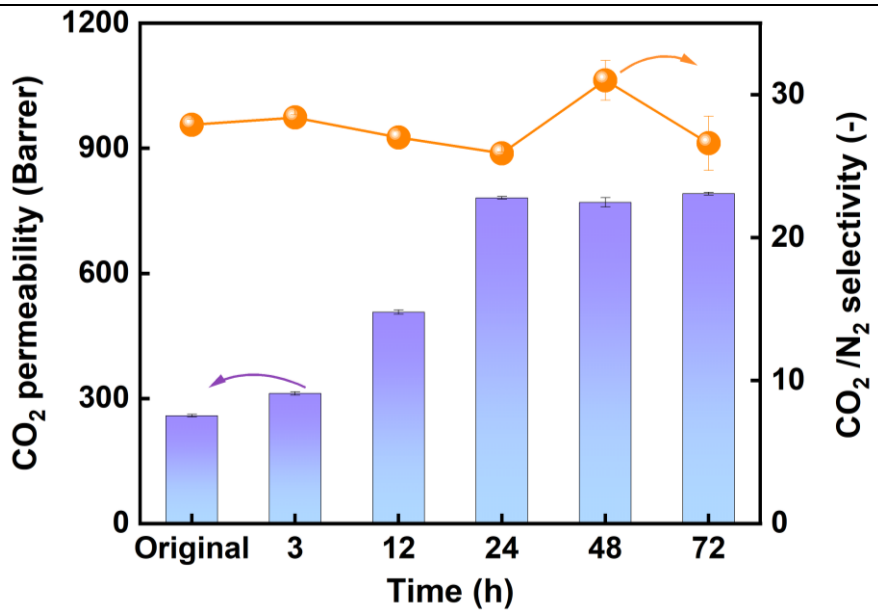
Table. 3. FTIR peak assignments of Pebax 2533

Wavenumber (cm^{-1})	Peak assignment	Ref
1106	stretching of -C-O-C-	[53]
1538	bending of N-H in PA	[53]
1638	stretching of -C=O in H-N-C=O	[54]
1734	stretching of -C=O in PA	[55]
2853	bending of -C-H	[55]

2923	bending of -C-H	[55]
3305	stretching of N-H in PA	[53]

Water uptake can also be an interesting parameter for Pebax 2533 membranes, as the presence of water vapor may have a significant impact on the CO_2 separation properties of Pebax membranes [56]. In the current study, it is found that Pebax 2533 membranes exhibited a slightly higher water uptake after the water treatment (from ~1.1% to ~1.4%, as shown in **Figure 4C**), but the overall water uptake remains in the low region.

The CO_2/N_2 separation performances of the Pebax 2533 treated with water for different duration time were also investigated, and results are presented in **Figure 5**. As indicated in the figure, the Pebax 2533 treated with water will always lead to a higher CO_2 permeability. As the water treatment duration time increased to 24 hours, a CO_2 permeability of 782.3 Barrer was documented, which is 3 times higher than the neat Pebax 2533 membrane (258.5 Barrer). In addition, the water-treated membrane presents a CO_2/N_2 selectivity (25.9) comparable to the neat Pebax 2533 membranes (27.9). The underlying reason for this phenomenon can be that water treatment has resulted in an apparent loosening of chain segments previously partially 'locked' by dipole-dipole interactions, leading to the microstructure change and reduced crystallinity degree, and consequently a higher CO_2 permeability but little change in CO_2/N_2 selectivity. Further increasing the water treatment time gains only slight improvement in CO_2 permeability; thus, 24 hours was selected as the water treatment duration in the further study.



406

407 **Figure. 5.** Gas separation performance of Pebax 2533 membranes with different water treatment

408 duration time, gas permeation test carried out with a feed pressure of 2 bar at 25 ºC.

409 **3.4 Effect of microstructure re-arrangement temperature**

410 It is well-known that membrane casting temperature also plays an important role in the

411 membrane morphology and consequent gas separation properties [57, 58]. Therefore,

412 in the current study, the water bath temperature was also changed to investigate its

413 effect on the membrane's chemical-physical properties.

414 The Pebax membrane was treated with water at different temperatures (5 ºC, 25 ºC, 45

415 ºC, 65 ºC, and 85 ºC) for 24 hours, and the results are presented in **Figure 6**.

416

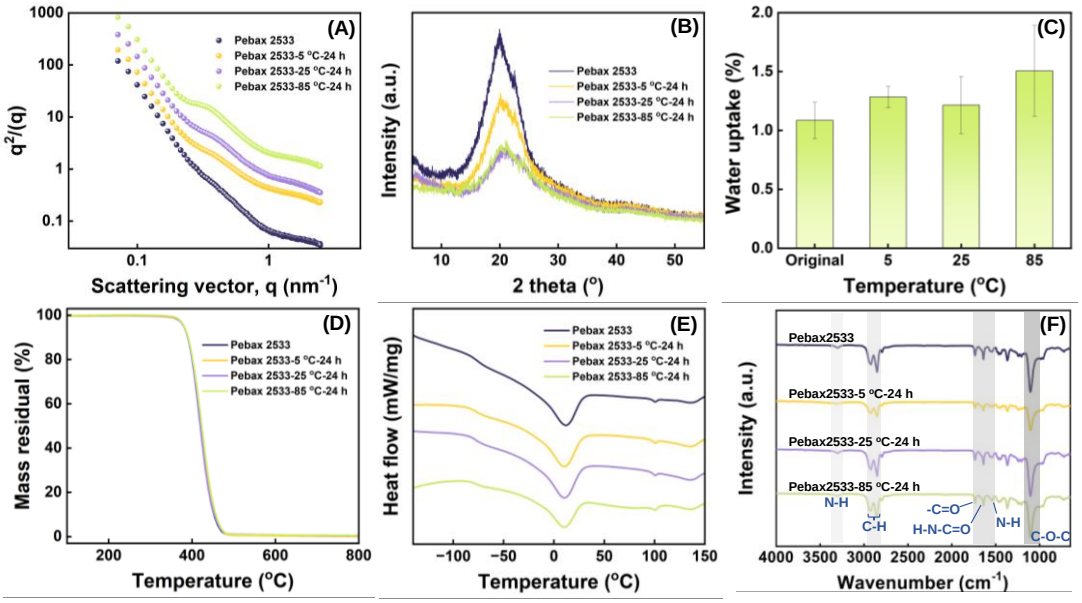


Figure. 6. Chemical-physical characterization of Pebax 2533 before and after water-induced micro-phase separation. SAXS (A), XRD (B), water uptake (C), TGA (D), DSC (E), and FTIR (F) results of Pebax 2533 treated with water at different temperatures for 24 hours.

The SXAS data for the Pebax 2533 membrane obtained with different re-arrangement temperatures are similar to the results obtained from different duration times (**Figure 6A**). As the water treatment temperature increases, the wide first-order interference peak is observed at around q=0.4 nm^{-1}, and it becomes more obverse as the water treatment temperature increases. In addition to the changes associated with peak-recognition ion clusters during treatment, another feature of **Figure 6A** is that the shape of the Pebax 2533 pre-peak scattering profile is quite different from that of the re-arrangement membranes. Although the exact physical significance of these scattered shapes is not fully known at present, it might be related to the differences in the spatial depiction of TEM images discussed in **Figure 3A**.

On the other hand, treating the Pebax 2533 membrane with high temperature also led to a lower crystallinity degree, as indicated by the XRD results shown in **Figure 6B**. In terms of the water uptake, the membrane treated with water at different temperatures presented similar trends compared to the different duration results, with only one exception (5 °C, shown in **Figure 6C**).

Considering the thermal properties, the membrane treated at different temperature

conditions also exhibited superior thermal stability precisely the same as the neat Pebax 2533 (**Figure 6D**), while water treatment led to lower T_g, T_m, and consequently lower crystallinity **(Figure 6E**), as confirmed by the XRD results. FTIR results also indicated that there is no chemical reaction between water and Pebax 2533 **(Figure 6F**), as there are no new peaks, and peak position shifting was observed.

The above characterization indicates that the chemical composition and thermal stability of the Pebax 2533 membrane remained consistent before and after the microstructure re-arrangement. The CO_2 separation performances of the Pebax 2533 membrane treated at different temperatures were tested and presented in **Figure 7**. It is clearly shown that the effect of re-arrangement temperature is minimal compared to the duration time, as almost all the re-arranged membranes exhibited a CO_2 permeability close to 800 Barrer and CO_2/N_2 selectivity of ~25, regardless of the rearrangement temperature. Considering the energy cost and process convenience, the optimal rearrangement temperature is set as 25 ^oC.

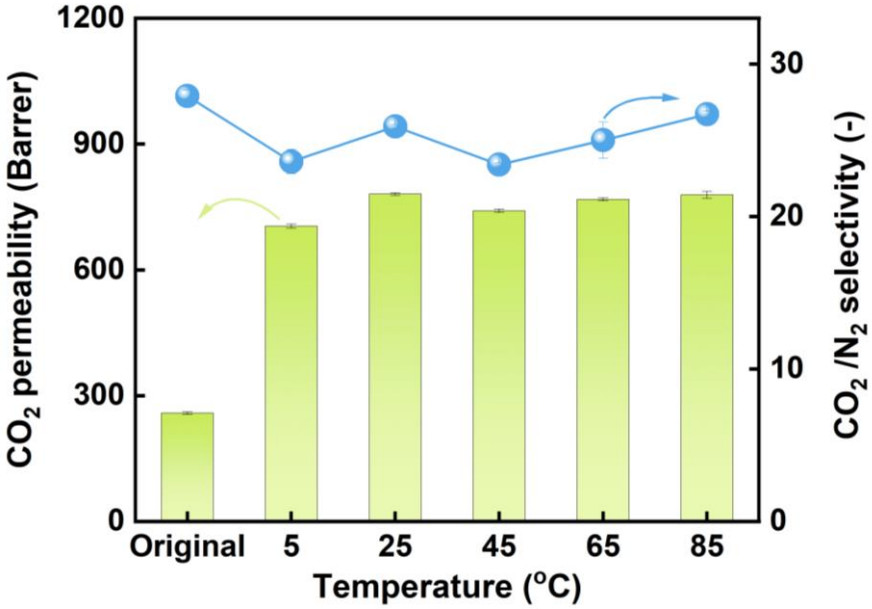


Figure 7. CO_2/N_2 separation performance of Pebax 2533 membranes with different water treatment temperatures, gas permeation test carried out with a feed pressure of 2 bar at 25 ^oC. Pebax 2533 membrane was treated with water for 24 hours

3.5 Gas permeation test conditions and long-term stability

Other than the membrane preparation parameters (e.g., water treatment temperature and soaking duration), it is well-accepted that operation parameters (e.g., testing temperature and feed pressure) also have an important influence on the membrane gas separation performances [59, 60]. Therefore, the effects of feed pressure and temperature were also explored. **Figure 8A** and **Figure 8B** show the CO_2 separation performance of water-treated Pebax 2533 with a feed pressure of 2, 4, and 6 bar. As can be seen from the figure, with the pressure increasing from 2 bar to 6 bar, the CO_2 permeability of the membrane material showed a slowly rising trend, as reported in the literature [61-63], while the CO_2/N_2 selectivity remained stable, indicating the water-treated Pebax 2533 exhibited similar CO_2 separation behavior compared to the neat Pebax 2533 membrane.

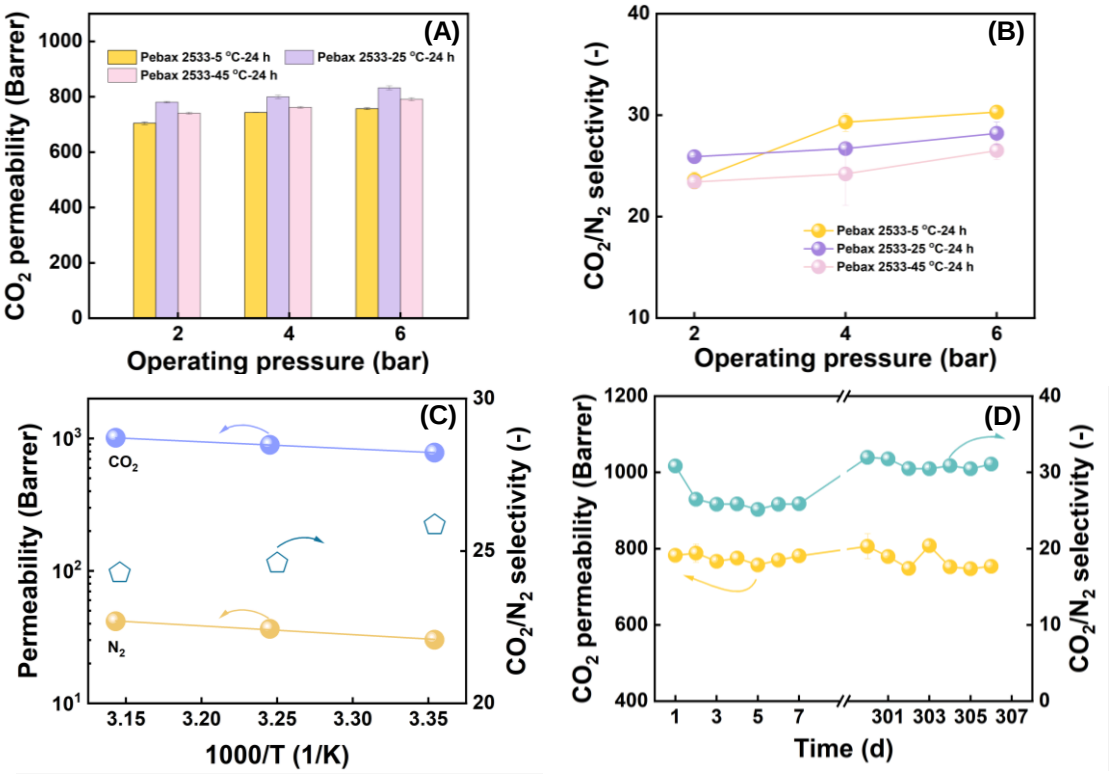


Figure. 8. Effect of feed pressure on Pebax 2533 membrane CO_2 permeability (A) and selectivity (B); effect of feed temperature on Pebax 2533 membrane CO_2 permeability and selectivity (C). Long-term stability of Pebax 2533 membrane tested at a feed pressure of 2 bar at 25 °C (D). The

Pebax membranes were treated in water at 25 °C for 24 hours.

In addition, the effect of test temperature was also investigated in the range of 25 °C to 45 °C. Generally, the increasing testing temperature will result in improved diffusivity and reduced solubility, but the permeability (the product of diffusivity and solubility) will typically increase.

For Pebax 2533 membrane was treated in water at 25 °C for 24 hours, the relationship between temperature and CO_2 gas permeability is shown in **Figure 8C**. As the operating temperature increases from 25 °C to 45 °C, the CO_2 permeability of the membrane material gradually increases from 782.3 Barrer to 1010.2 Barrer. It is well-accepted that for a given polymer, the effect of temperature on gas permeability (P) in a temperature range where there is no obvious thermal conversion can be described by the Arrhenius equation [64]:

$$P = P_0 . exp(-\frac{E_p}{RT}) \qquad (4)$$

Among them, E_p and P_0 are called activation energy and pre-exponential factor, respectively, which are two very important parameters in chemical kinetics. R is the molar gas constant; T is the thermodynamic temperature. In the current study, the Ep values of CO_2 and N_2 were 10.2 and 12.6, respectively, with a correlation coefficient (R^2) always greater than 0.99

Similar to many CO_2-selective membrane materials, increasing testing temperature results in higher CO_2 permeability but with lower CO_2/N_2 selectivity [65]. In the current study, increasing the testing temperature from 25 °C to 45 °C resulted in a negligible reduction of CO_2/N_2 selectivity, which is from 25.9 to 24.3, denoting its superior CO_2 separation performances.

Good long-term stability of membrane material is of critical importance in practical applications. Therefore, the duration stability of the water-treated Pebax 2533 membranes were also tested for 7 days with a feed pressure of 2 bar at 25 °C. As shown in **Figure 8D**, the CO_2 permeability and CO_2/N_2 selectivity of the membrane isquite stable during the 7 days continuous measurement process. In addition, the rearranged

membranes were stored in ambient conditions for about 10 months and it is found the membrane exhibited almost unchanged CO_2 separation performances, reflecting the excellent long-term stability of the re-arranged membranes, which shows great application potential in practical CO_2 separation applications.

3.6 Comparison of gas permeation results

The gas separation performances of the microstructure re-arrangement membranes prepared in this study were compared with literature values, as shown in **Table 6** and **Figure 9**. Notably, for Pebax 2533 membranes, after microstructure re-arrangement in DI water, the CO_2 permeability increased three-fold compared to the original membrane, while the CO_2/N_2 selectivity remained unchanged. In contrast, the microstructure re-arrangement of Nafion membranes seems more effective in promoting CO_2/N_2 permeability. The significantly improved performance in these membranes confirms that microstructure re-arrangement can be used as a technique to optimize CO_2 separation performance of block copolymer membranes, providing a new approach for the preparation of high-performance CO_2 capture membranes.

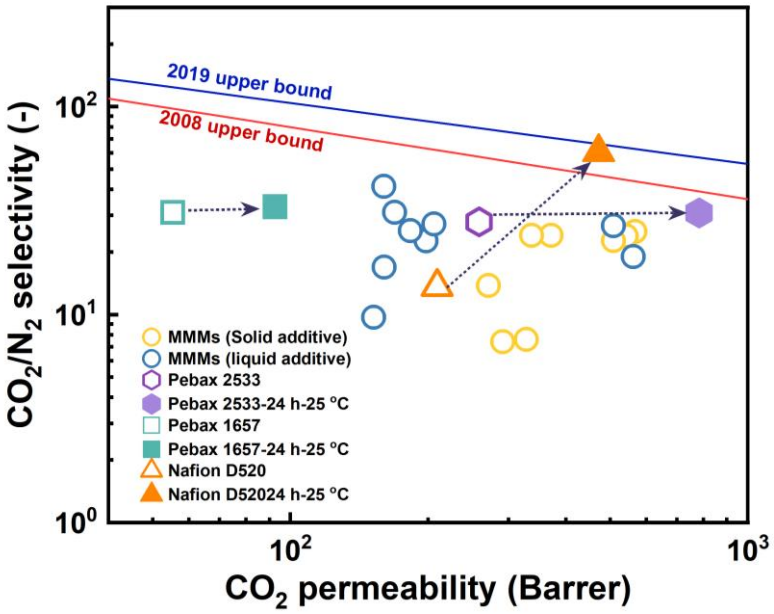


Figure. 9. Robeson plot for the CO_2/N_2 separation performance obtained from single-gas permeation tests of Pebax 2533 membranes before and after microstructure re-arrangement.

Circles are literature data from Table 4

Table. 4. Separation performance of Pebax membranes

Membrane	PCO_2 (Barrer)	$\alpha_{CO_2/N_2}(-)$	Ref.
Pebax 2533+(20 wt.%) PEG 400	291.2	7.4	[55] (1)
Pebax 2533+(40 wt.%) PEG 400	327.8	7.6	[55] (1)
Pebax 2533+(0.02 wt.%) GO	371.4	24.0	[66] (2)
Pebax 2533+(0.1 wt.%) GO	336.8	24.0	[66] (2)
Pebax 2533+(20 wt.%)TPP	566.4	25.1	[67] (3)
Pebax 2533+(21 wt.%)TBT	542.5	23.9	[67] (3)
Pebax 2533+(22 wt.%)TCP	508.4	22.7	[67] (3)
Pebax 2533+(20 wt.%) [TMGH][Im]	271.1	13.8	[68] (4)
Pebax 2533+(15 wt.%) ZIF-8	508.4	22.7	[56] (5)
Pebax 2533+(10 wt.%) PS	152.1	9.7	[69] (6)
Pebax 2533+(10 wt.%) ZIF-Matrimid	160.3	16.9	[69] (6)
Pebax 2533+(3.4 wt.%) ZIF-7	198	22.6	[70] (7)
Pebax 2533+(3.4 wt.%) ZIF-7-NH_2	206	27.3	[70] (7)
Pebax 2533+(3.4 wt.%) ZIF-7-CH_3OH	562.0	19.0	[70] (7)
Pebax 2533+(0.5 wt.%) Apdems	183	25.3	[71] (8)
Pebax 2533+(1.0 wt.%) Apdems	169	31	[71] (8)
Pebax 2533+(2.0 wt.%) Apdems	160	41.3	[71] (8)
Pebax 2533	258.5	27.9	This work (9)
Pebax 2533-24 h-25 ^oC	782.3	30.8	This work (9)
Pebax 1657	55.3	31.0	This work (9)
Pebax 1657-24 h-25 ^oC	92.5	33.0	This work (9)
Nafion D520	209.3	13.6	This work (10)
Nafion D520-24 h-25 ^oC	472.0	60.6	This work (10)

(1) Single-gas permeation test conducted at dry state, with a feed pressure of 4 bar and 25 °C.

(2) Single-gas permeation test conducted at dry state, with a feed pressure of 1 bar and 35 °C.

(3) Single-gas permeation test conducted at dry state, with a feed pressure of 5 bar and 35 °C.

(4) Single-gas permeation test conducted at dry state, with a feed pressure of 4 bar and 25 °C.

(5) Single-gas permeation test conducted at dry state, with a feed pressure of 6 bar and 25 °C.

(6) Single-gas permeation test conducted at dry state, with a feed pressure of 1 bar and 35 °C.

(7) Single-gas permeation test conducted at dry state, with a feed pressure of 4.5 bar and 25 °C.

(8) Single-gas permeation test conducted at dry state, with a feed pressure of 10 bar and ambient temperature.

(9) Single-gas permeation test conducted at dry state, with a feed pressure of 2 bar and 25 °C.

(10) Mixed-gas permeation test conducted at 100% RH, with a feed pressure of 2 bar and ambient temperature.

4. Conclusions

In the current work, a non-solvent induced microstructure re-arrangement process was applied to improve the CO_2 separation performances of block copolymer-based membranes. Different non-solvents were employed to trigger the microstructure transition, among which the DI water performs the best in terms of CO_2 separation performances. The obtained membranes were thoroughly characterized, confirming that the DI water treatment results in more tightly connected ionic microdomains and lower crystallinity degrees of the re-arranged membrane matrix, which are the underlying reasons for the improved CO_2 separation performances. Experiments indicate that the DI water-induced microstructure arrangement is a physical process that does not influence the thermal stability and chemical stability of the Pebax 2533 membranes. The gas permeation test results reveal that the CO_2 permeability of the Pebax 2533 was greatly improved (from 258.5 Barrer to 782.3 Barrer), while the CO_2/N_2 selectivity is almost unchanged. Furthermore, the Pebax 2533 membranes also exhibited promising long-term stability after 300 days storage, denoting its great potential in CO_2 separation applications.

Future work can be carried out to explore the separation performance of the membranes under humid conditions. Developing thin-film-composite membranes using microstructure rearranged membranes can be another option worth trying.

Acknowledgements

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