Pebax/PEG Grafted CNT-hybrid Membranes for Enhanced CO_2/N_2 Separation

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KEYWORDS:

Pebax®; hybrid membranes; carbon nanotubes; poly(ethylene glycol); CO_2 separation

ABSTRACT:

In the present study, the poly(ethylene glycol) (PEG) functionalized carbon nanotubes (CNT-PEG) was embedded into Pebax® 1657 matrix to fabricate hybrid membranes for enhanced CO_2 separation. The resultant membranes were characterized using various techniques. It is found out that grafting PEG onto CNT fibers greatly improves the CNT dispersion; No noticeable aggregation can be found in the hybrid membranes with the CNT-PEG content of up to 20 wt.%. XRD results denote that the presence of CNT-PEG in the Pebax® matrix increases the amorphous phase content, which is beneficial for CO_2 permeation. Gas permeation properties of the resultant hybrid membranes were also investigated. CO_2 permeability first increases then decreases with increasing CNT-PEG content at the dry state. The presence of water vapor further improves the CO_2 permeability. At 100% RH, CO_2 permeability of 369.1 Barrer with CO_2/N_2 selectivity of 110.8 was obtained for a hybrid membrane containing 3 wt.% CNT-PEG, which overcomes the Robeson upper bound. The combination of high permeability and selectivity makes the Pebax/CNT-PEG hybrid membranes promising for industrial CO_2 separation applications.

TOC:

Homogeneous
CNT hybrid membrane

CO_2 fast transport channel
along CNT

PEG grafted CNT
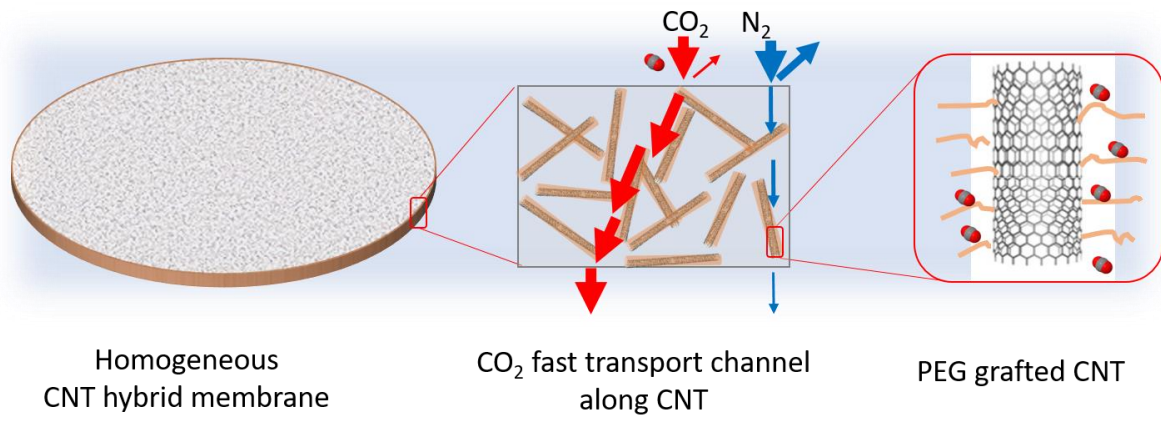
1. Introduction

Gas separation through polymer membranes is commonly accepted to be an effective approach for the separation of gaseous mixtures due to its high separation efficiency, low running costs, and simple operating procedures compared to conventional separation methods.[1] Hence, membrane materials with both high permeability and high selectivity are always desired to make the membrane gas separation process more economically competitive. However, for most of the membrane materials, there exists a trade-off relationship between the permeability and selectivity, known as the 'Robeson upper bound'.[2-3]

In the past decades, both physical and chemical modification methods have been developed to improve membrane separation performances.[4] Chemical modification methods including cross-linking, grafting, and chemical modification of the polymer chain have been used to change the composition or structure of the membranes, thereby improving the gas separation performance. Compared to chemical modification methods, physical modification is relatively simpler. Normally, in a physical modification process, the polymeric phase is blended or mixed with a second material phase, which can be the second polymer phase, porous or non-porous nano-materials (e.g., 0D nanoparticles, 1D nanofibers, 2D nanosheets, and 3D nanoparticles),[5] liquid additives,[6] and salts.[7] The membrane fabricated via physical blending is generally recognized as hybrid membranes. One advantage of the hybrid membrane is the possibility of capturing the desirable attributes of the different components in a single composite. For instance, the polymeric phase offers flexibility and easy processability, and the additives could have superior gas separation performances, better mechanical strength, and/or thermal stability. It is also possible to discover new synergistic properties by combining two or more materials.[8]

An abundant amount of materials have been used as additives in membranes for CO_2 separation.[5, 9] Zeolite, metal-organic-frame works (MOFs), porous organic frameworks (POFs), carbon nanotubes (CNTs), graphene and graphene oxides (GO) are representative materials applied in hybrid membranes.[8] Among them, CNTs has been one of the most intensively studied nanomaterials in hybrid membranes for different gas separation applications.[10]

Various polymeric membrane materials have been employed to mix with CNTs to fabricate hybrid membranes. Ahmad and co-workers used CNT in cellulose acetate matrix; the addition of only 0.1 wt.% CNT into the hybrid membrane significantly enhanced the overall gas separation performances.[11] Ansaloni *et al.* used multi-walled carbon nanotubes (MWNTs) as mechanical reinforcement filler in cross-linked poly(vinyl alcohol) (PVA), and the resultant

membrane showed no change of gas permeability for 444 h (18.5 days) when operated at 1.52 MPa and 380.15 K.[12] Li and co-workers mixed CNT with GO and used them as additives to enhance Matrimid® gas separation properties; With 5 wt.% CNT/GO in Matrimid® matrix, the CO_2 permeability and CO_2/N_2 selectivity were enhanced by 331% and 147%, respectively.[13] In another study, CNT was mixed with Pebax 1657 followed by cross-linking the polymeric matrix with 2,4-toluylene diisocyanate (TDI). Loading of only 2 wt.% of CNT into Pebax matrix resulted in a simultaneous enhancement in both CO_2 permeability and CO_2/N_2 selectivity.[14] Other polymers such as polysulfone have also been as the polymer phase to fabricate hybrid membranes with CNTs.[15] Deng and co-workers mixed CNT into PVA-mimic enzyme nanocomposite membranes;[16] under an optimized condition, a CO_2 permeance of ~ 370 GPU with CO_2/N_2 selectivity of up to 120 was obtained.

Despite the promising results obtained by the studies above, due to their chemically inert properties and inability to be dispersed in typical organic solvents, it is difficult to disperse CNT fibers in polymer matrices homogeneously. In most cases, agglomeration can be found in CNT-based hybrid membranes. Therefore, much effort has been focused on functionalizing and modifying CNTs to improve their dispersion ability.[8] Habibiannejad *et al.* modified CNT fibers with various functional groups or molecules, including –COOH group, Triton X-100, or m-phenylenediamine.[17] After the functionalization, the CNT fibers can be dispersed evenly through the whole polymer matrix without any aggregation. Ismail *et al.* employed chitosan as functionalization agent for CNT fibers;[18] although the functionalized CNT fibers improved both CO_2 permeability and CO_2/CH_4 selectivity, agglomeration of CNT fibers can still be found in the hybrid membranes. Abetz *et al.* functionalized CNT with poly(ethylene glycol)(PEG) 200 and embedded the functionalized CNT into polymers of intrinsic microporosity (PIMs) matrix.[19] Even though the grafted PEG content on the CNT fibers was relatively low (1.77 wt%), it was well documented that PEG functionalized CNT was an effective nanofiller for hybrid membranes to improve CO_2 permeability.

Pebax® has been reported as promising membrane materials for gas separation, in particular, CO_2 separation. Up to now, different types of Pebax® copolymers have been manufactured by changing PE and PA compositions in the structure.[20] Among them, Pebax® 1657 and Pebax® 2533 are the two representative polymers abundantly studied as CO_2 separation membrane materials. For Pebax® 2533, ethanol (96%) was usually used as the solvent, but the CNT-PEG fibers were found forming precipitation with Pebax® 2533 in the 96% ethanol solution in a very short time; no homogeneous membrane can be obtained. Therefore, Pebax® 1657 was selected

to be the polymer matrix in the hybrid membrane as several solvents could be used to dissolve Pebax® 1657, such as N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), N-methyl-2-pyrrolidone (NMP), formic acid, and mixture of ethanol (EtOH) with water (H_2O). It is critical to determine a suitable solvent for good dispersion of the CNT fibers in the polymer phase to ensure the fabrication of the hybrid membranes. In the present study, EtOH/H_2O (70/30 wt.%) was chosen as the solvent for Pebax 1657 as the dispersion of CNT-PEG is better in EtOH/H_2O mixtures than in other solvents. Moreover, this cheap, simple binary mixture is convenient for large-scale membrane preparation in the future.

Pebax® 1657 is a thermoplastic elastomer consisting of 40 wt % rigid polyamide (PA) and 60 wt % flexible polyether (PE) blocks. The chemical structure of Pebax® 1657 is shown in **Scheme 1**.
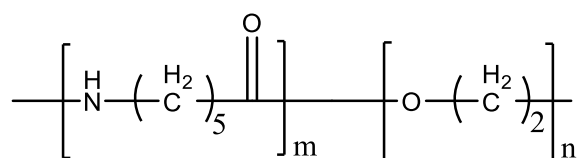
Scheme 1. Chemical structure of Pebax® 1657

Herein, in the present work, hybrid membranes of PEG-functionalized CNT and Pebax®1657 were developed, and the effects of the CNT-PEG in the membrane were investigated. The morphologic, chemical and physical properties of the membrane materials and the as-prepared hybrid membranes were characterized using different techniques such as SEM, TEM, FTIR, TGA, DSC, and water uptake. Gas permeability and selectivity were studied by mixed gas permeation measurements at the dry state and under different relative humidity (RH) conditions.

2. Experimental

2.1. Materials

Pebax® MH1657 (Pebax®1657) was purchased from Arkema Inc., France. Absolute EtOH was ordered from Sigma-Aldrich Chemical Co., Germany. Toluene, dimethylsulfoxide (DMSO) and methylmethacrylate end-capped poly(ethylene glycol) (PEG-MMA) were ordered from Sigma, Taiwan. Multiwalled carbon nanotube (referred to as CNT in the current work) was received from the Carbon Nanotube Co., Ltd., Incheon, Korea. The CNT sample was washed with dimethylsulfoxide (DMSO) before use. PEG-grafted CNTs were prepared following an

optimized procedure; detailed information can be found in a prior work[21] and also in the Supporting Information.

2.2 Membrane preparation

The membranes were prepared by the solution-casting method (procedure shown in **Figure 1**). Pebax® 1657 was dissolved in the ethanol/H_2O (70/30 wt.%) mixture at 80 °C for around 4 hours with a concentration of 4 wt.%. CNT-PEG was dispersed in ethanol/H_2O mixture using an ultrasonication probe for 3 hours with a concentration of 0.5 wt.%. Then the Pebax solution and CNT dispersion were mixed and diluted to a total solid concentration of 0.8 wt.%. The mixture was ultrasonicated for another 3 hours before being poured into a Teflon Petri dish to prepare the self-standing membranes. The Pebax/CNT-PEG blend was kept in a convection oven with temperature controlled to 40 °C. The CNT content (ω_{CNT}, wt%) in each hybrid membrane was calculated from equation (1):

$$\omega_{CNT} = \frac{w_{CNT}}{w_{CNT} + w_{pebax}} \times 100\% \tag{1}$$

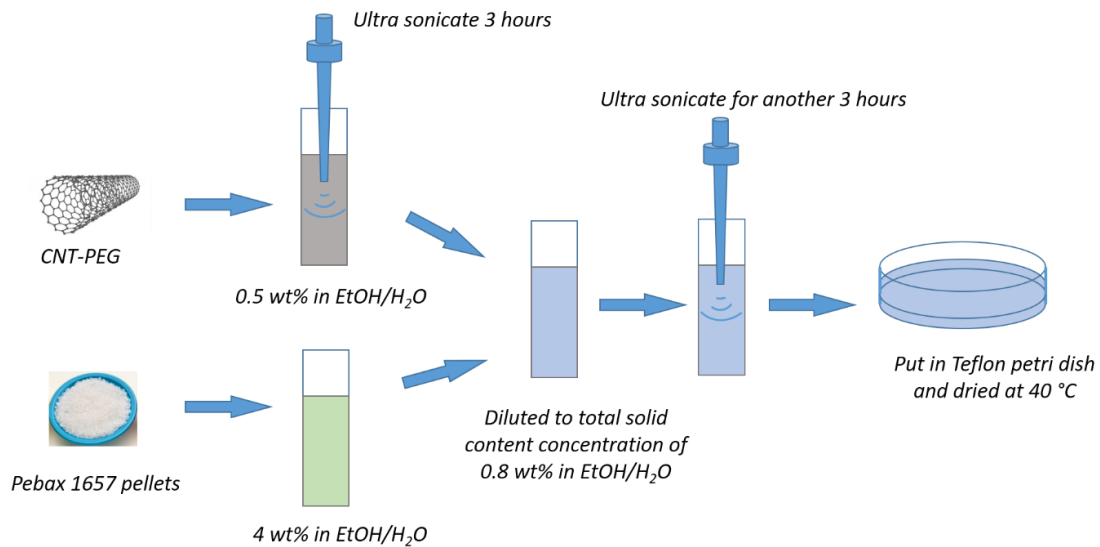where w_{CNT} and w_{Pebax} are the weights of CNT and Pebax, respectively.

Figure 1. Pebax/CNT-PEG membrane fabrication procedure

2.3 Membrane characterization

Various characterization techniques have been used to characterize the resultant Pebax/CNT-PEG membranes.

FTIR spectra of the Pebax/CNT-PEG hybrid membranes were measured using a Nicolet iS-50 FTIR spectrometer equipped with a Specac ATR unit (Golden Gate high-performance single reflection monolithic diamond ATR, Thermo Scientific, USA) within the range between 4000 and 650 cm^{-1}. The result was an average of 16 scans.

Thermogravimetric analysis Instrument (TGA, TG 209F1 Libra, Netzsch, Germany) was used to determine the amount and rate of weight changes as a function of temperature over time. About 10 mg of the sample was heated from R.T to 800 °C with a heating rate of 10 °C/min.

Thermal properties of the Pebax/CNT-PEG hybrid membranes were investigated using differential scanning calorimeter (Netzsch Polyma, Netzsch, Germany). A sample of ~10 mg was used and the heating rate was controlled at 10 °C/min within the whole tested temperature range.

Scanning electron microscope (SEM, TM3030 tabletop microscope, Hitachi High Technologies America, Inc. Japan) was used to investigate the morphology of the CNT-PEG and Pebax/CNT-PEG membranes. To avoid charging of samples, all samples were sputter-coated with conducting gold.

A Bruker D8 A25 DaVinci X-ray Diffractometer was used to carry out the X-ray diffraction measurements (Bruker, Netherlands). The scans were taken in the 2θ range with a step size of 0.045° from 5° to 75°.

Water uptake (Ω, in %) measurement of the membrane was carried out by first placing each dry membrane (of mass m_D) in a desiccator saturated with water vapor and then measuring the humid mass (m_H) when the equilibrium was reached. The water uptake was calculated as:

$$\Omega = \frac{m_H - m_D}{m_D} \times 100\% \qquad (2)$$

Gas-separation performance was tested in the mixed-gas setup as described in our previous work.[22] In brief, a CO_2/N_2 gas mixture (10/90 v/v) was used as the feed gas, whereas pure CH_4 was used as the sweep gas. The feed pressure and sweep pressure were kept at 2.0 bar and 1.05 bar, respectively, for all the experiments. The compositions of permeate and retentate streams were monitored by a gas chromatograph (490 Micro GC, Agilent) during the tests. Each test continued for at least 6 h to ensure the steady state.

The permeability(P_i, in Barrer, $1 Barrer = 10^{-10} \frac{cm^3_{STP} \Box cm}{cm^2 \Box s \Box cmHg}$) of the ith penetrant species was

measured by equation (3):

$$P_{m,i} = \frac{N_{perm} \Box (1 - y_{H2O}) \Box y_i \Box l}{A \Box (\langle p_{i,feed}, p_{i,ret} \rangle - p_{i,perm})} \tag{3}$$

where N_{perm} is the total permeate flow measured with a bubble flow meter, y_{H_2O} is the molar fraction of water in the permeate flow (calculated according to the RH value and the vapor pressure at the given temperature), and y_i is the molar fraction of the species of interest in the permeate stream. l and A denote the membrane thickness and membrane area, respectively, and $p_{i,feed}$, $p_{i,ret}$, and $p_{i,perm}$ identify the partial pressures of the ith species in the feed, retentate, and permeate, respectively. The separation factor ($\alpha_{i/j} = \frac{y_i/x_i}{y_j/x_j}$) was applied for mixed-gas permeation tests in the current study. All the gas permeation test were carried out with, at least, two samples with deviation lower than 10 %, thus the error bars were not presented in the figures in this work.

3. Results and discussion

3.1 CNT-PEG preparation and characterization

The raw CNT and CNT-PEG were characterized using different techniques including XPS, TGA, Raman, TEM, and FTIR. Raman spectra and TEM micrographs of the raw CNT and CNT-PEG can be found in **Figure 2** while other characterization results are presented in the Supporting Information in **Figures S1** to **S3**.
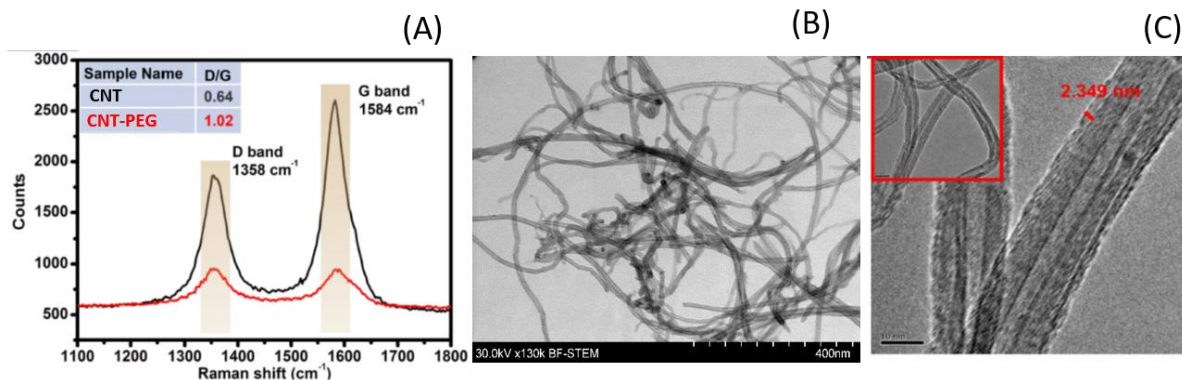
Figure 2. Raman spectra (A) and TEM micrographs of the CNT-PEG (B) and (C).

From the Raman spectra results (**Figure 2 (A)**), the CNT-PEG shows an increase in the peak intensity ratio of D band over G band (D/G) from 0.64 to 1.02. The increased D/G value indicates that the chemical reaction happens at the sp^2 hybrid carbon of CNT to form sp^3 hybrid carbon.

TEM was employed to study the morphology of the prepared CNT-PEG. **Figure 2 (B)** clearly shows that even though ultrasonic probe has been used to disperse the CNT-PEG in $EtOH/H_2O$ mixture, the CNT-PEG is mainly in the state of agglomeration, similar to literature results. It is worth mentioning that even though the CNT-PEG was dispersed in a rather low concentration in the $EtOH/H_2O$ mixture (e.g., 0.1 wt.%), flocculation was found in the dispersion short after the sonication, but it is still better than other solvents such as NMP and DMF. Conversely, adding Pebax into the CNT-PEG dispersion effectively improves the dispersion stability probably because the Pebax polymer chain works as a stabilizer for the CNT-PEG fibers in the solution; no flocculation could be observed in the Pebax/CNT-PEG solution for 1 day.

The high-resolution TEM results are shown in **Figure 2 (C)**, where the CNT-PEG shows a typical CNT hollow fiber shape. Compared to the neat CNT, CNT-PEG shows an amorphous layer with a thickness of about 2.3 nm covering at the outer surface of layered CNT in high-resolution TEM micrograph, which denotes that the PEG is successfully grafted on the CNT fibers.

3.2 Membrane characterization

The chemical-physical properties of the resultant Pebax/CNT-PEG hybrid membranes have been studied using various techniques. Results are shown in **Figure 3**.
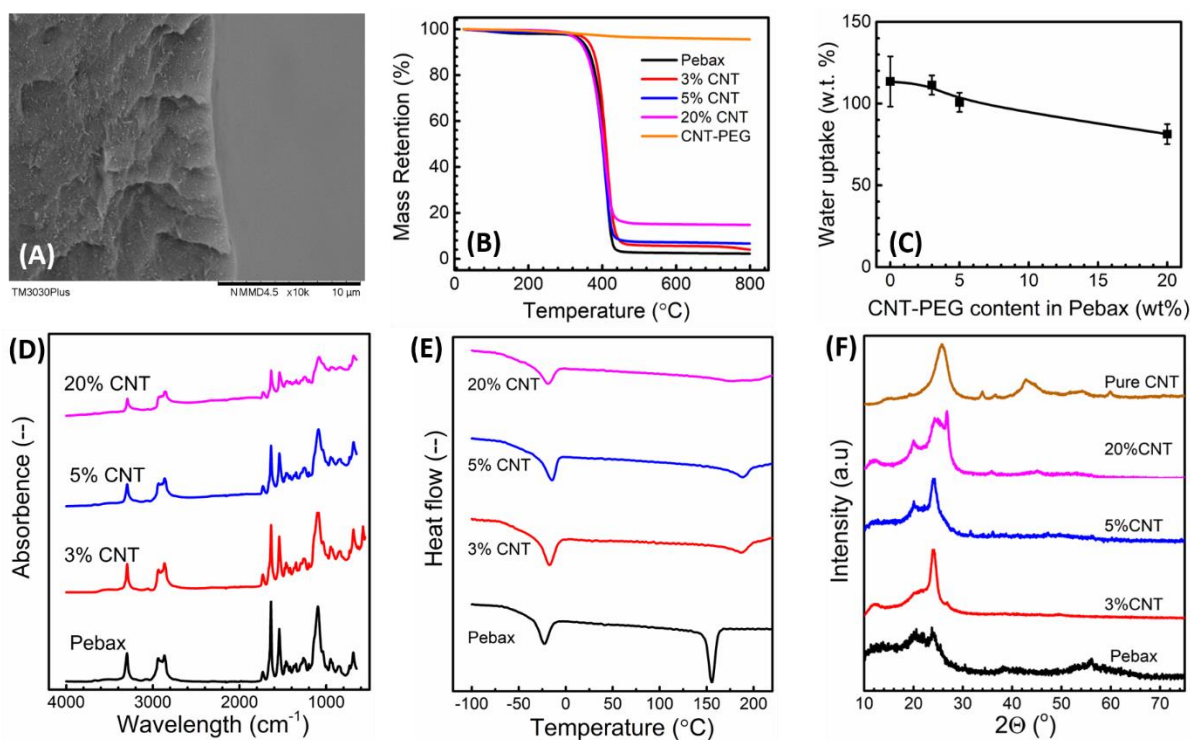
Figure 3. Various characterization results for Pebax/CNT-PEG hybrid membranes. (A) Cross-section SEM image of the Pebax/CNT-PEG hybrid membrane containing 20 wt% CNT-PEG, and (B) TGA, (C) water uptake, (D) FTIR, (E) DSC and (F) XRD results for Pebax/CNT-PEG hybrid membranes of 0 wt.%, 3 wt.%, 5 wt.%, and 20 wt.% CNT-PEG content.

The morphologies of Pebax/CNT-PEG hybrid membranes were investigated by an SEM. **Figure 3(A)** shows the cross-section morphology of the membrane with up to 20 wt% CNT-PEG. SEM images of hybrid membranes with other CNT-PEG content can be found in **Figure S4** in the Supporting Information. It is well known that pristine CNT fibers have a high tendency to form aggregates because of the interactions among pristine CNT fibers (π–π interaction) are stronger than those with the polymer matrix.[23] Therefore, functionalization of CNT fibers with various functional groups (e.g., -NH$_2$, –OH) have been employed to improve the CNT dispersion.[24] It has been reported that functionalizing CNT with PEG molecule could de-bundle the highly entangled fibers, hence improve the CNT dispersion in PIM-1 matrix.[19] However, as the amount of PEG grafted on CNT fibers was relatively low (1.77 wt.%), agglomeration was found at a higher CNT content (e.g., 3 wt.%). In our case, however, no aggregation could be found even at the CNT content of up to 20 wt.%, demonstrating that functionalizing CNT with a higher PEG content (4.12 wt.%) is an effective way of improving the dispersion property of CNT fibers. The grafted PEG onto the CNT fibers could effectively de-bundle the entangled fibers. In addition, it has been proven that low molecule weight PEG

has a good compatibility with Pebax;[25] thus there might be synergistic effect in stabilizing the dispersion of CNT-PEG fibers in the Pebax matrix.

Figure 3(B) shows the TGA curve of the Pebax/CNT-PEG samples with different CNT-PEG content. The CNT-PEG employed in the current study exhibited superior thermal stability. The PEG-grafted CNT sample shows less than 5 % weight loss at 800 °C, which corresponds to the PEG grafted onto the CNT fibers. All the thermal weight loss profiles for those hybrid membrane samples almost show the same trend as the neat Pebax membrane,[26-27] denoting that pyrolysis of the polymer chain dominates in the overall thermal decomposition process.

Water uptake of the Pebax/CNT-PEG membrane was also measured. The results were presented in **Figure 3(C)**. It is worth mentioning that even with the same Pebax 1657, considerable differences in water uptake has been reported from different research groups. For instance, Jiang and coworkers reported a water uptake for Pebax as low as ~5 wt.%,[28-29] while Peinemann and co-workers reported a water uptake of ~35 wt.% with a water activity of 0.9,[30] and the water uptake increased exponentially with increasing water vapor activity; thus the water uptake at 100% relative humidity (RH) could be much higher than 35 wt.%. In another report, water uptake of 40 wt.% was obtained at 95% RH.[31] The differences are probably due to the different test methods and the condition, and the processing of the samples (e.g., size and thickness of samples). In the present study, the neat Pebax presents a water uptake of ~115%, which is in good agreement with the literature value from Ghasemi Estahbanati *et al.* (120 wt.%).[32] It is also found out that the sorption characteristics of the membranes were only moderately affected by the addition of CNT-PEG fibers; adding CNT-PEG into Pebax matrix led to slightly reduced water uptake (up to 20% reduction).

FTIR analysis was further carried out to explore the interaction between CNT-PEG and Pebax polymer (shown in **Figure 3(D)**). FTIR spectrum of the pure CNT-PEG can be found in **Figure S1** in the supporting information. In terms of the pristine Pebax membrane sample, two characteristic absorptive bands at 1657 and 1640 cm^{-1} can be found, which represent the C=O stretching in two types of amide group. The band at 3300 cm^{-1} represents the stretching vibration of N-H.[33] The stretching vibration at 2940 cm^{-1} indicates the presence of aliphatic -C-H. The peaks at 1732 and 1102 cm^{-1} represent –C=O and –C-O- stretching vibrations, respectively.[14] Considering the CNT-PEG sample, the characteristic peak at 1652 cm^{-1} represents the presence of a C=C bond.[14] In the case of Pebax/CNT-PEG membrane samples, the peaks mostly synchronize with the ones in the Pebax membrane. With increasing CNT-

PEG loading, the corresponding Pebax-related peak intensity decreases, which is obviously attributed to a greater extent to the filler loading. No new peak or peak position shift was observed; thus, functional groups of Pebax polymer indulge only in physical interactions with CNT-PEG.

Figure 3(E) shows DSC curves (second cooling cycle) of pristine Pebax membrane and Pebax/CNT-PEG hybrid membranes. It is well-known that Pebax 1657 has two exothermic peaks, one at 7~ 14 °C and the second one at 200~210 °C.[26, 34-36] These two peaks are assigned to the solidification temperatures of the polyether (PE) block and polyamide (PA) block. It has also been reported that the thermal treatment history has a significant effect on the melting temperature of the PE block (T_{mE}) of Pebax.[35] T_m of polyether block can be changed from -5 ~ -20 °C by adjusting the heating protocol.[35] In the present study, a T_m of approximately -18 °C was obtained for the pristine Pebax membrane sample, which is comparable with ref [37] (T_m value of -19.1°C). The relatively lower T_{mE} value for our sample may be attributed to the different heating history for our Pebax samples. It is believed that the CNT-PEG could act as a nucleating agent on the polyether domain, thus reducing the T_{mE} value. It is worth mentioning that, generally, Pebax® 1657 shows a glass transition temperature (T_g) of ~ -50 °C. However, in many other reports, it is also found out that the T_g peak was small and not clearly observable.[26, 37] Incorporating CNT-PEG into Pebax matrix slightly reduced the heat of fusion of the PA block (ΔH_{mA}), indicating that the degree of crystallinity of the hybrid membrane decreases as the content of CNT-PEG increases, which may be attributed to the disruption of the interchain hydrogen bonding in the PA domain.[31]

The crystalline properties of CNT-PEG, pristine Pebax membrane, and Pebax/CNT-PEG hybrid membranes were measured by XRD, and the results are shown in **Figure 3(F)**. Pebax is a semicrystalline polymer that shows narrow diffraction peaks at 12°, 24°, and 54° of 2θ.[14] In terms of CNT-PEG samples, diffraction peaks can be found at 26° and 43° of 2θ which can be attributed to the hexagonal graphite structure (002) and (100), respectively.[33] In the Pebax/CNT-PEG hybrid membranes, the intensity of diffraction peak at 2θ =24° decreases with increase in the CNT-PEG content in the hybrid membrane. This trend indicates that inter-chain hydrogen bonding between PA segments in Pebax is disturbed by the incorporation of CNT-PEG, resulting in higher amorphous region content in Pebax/CNT-PEG hybrid membranes, which is preferable for higher gas permeability.[33] At the same time, the intensity of the characteristic peak of the CNT-PEG at 2θ=26° increases with the CNT-PEG content increase in the hybrid membranes.

Characterization results for membranes of CNT-PEG content of 1 wt.%, 2 wt.%, 7 wt.%, and 10 wt.% can be found in the Supporting Information (S5-S8).

3.3 Mixed gas permeation results

3.3.1 Effect of CNT-PEG content at the dry state

Generally speaking, adding nanofillers into polymeric membranes could affect the gas permeation properties in different ways. In the first case, nanofillers may disturb the polymeric chain packing, thus increasing the free volumes between the polymer chains or creating micro-voids between the polymer/filler interface, which is usually beneficial for gas permeation (e.g., adding solid fumed silica into PIM-1 [38]). In the second case, nanofillers could increase the tortuosity and/or the polymer chain rigidification, which could deteriorate the gas diffusivity and consequently lead to lower gas permeability. [39-40] In the third case, if porous nanofiller is employed in a hybrid membrane, it could improve the overall separation performances of the hybrid membranes due to the intrinsically higher permeability and/or higher selectivity of the chosen porous nanofiller (e.g., mixing MOFs into polymeric matrix [41]). In the fourth case, surfaces of nanofillers can be functionalized with desired functional groups to improve the affinity or reactivity between the nanofiller and the targeted gases to improve the overall separation performances (e.g., mixing functionalized MOF particles into polymers [42-43]).

In the present work, hybrid membranes were fabricated with different loadings of CNT-PEG to investigate the effects of adding CNT-PEG into Pebax matrix. The gas separation performances of the Pebax/CNT-PEG hybrid membranes were investigated at the dry state, and the results are shown in **Figure 4**. As can be seen, both CO_2 permeability and CO_2/N_2 selectivity first increase then decrease with increasing CNT-PEG content; similar trend has been reported in many literatures.[19, 34] The neat Pebax membrane shows a CO_2 permeability of 90.7 Barrer with a CO_2/N_2 selectivity of 37.0, which is comparable with other reports using Pebax 1657 as CO_2 separation membranes.[44-45] With the presence of the CNT-PEG fiber in the hybrid membranes, CO_2 permeability increases and reaches the highest value (250.6 Barrer) at 3 wt.% CNT-PEG content, where the CO_2/N_2 selectivity of 78.4 is also the highest in this work. It is commonly accepted that adding CNT fibers into different polymeric matrices significantly enhance CO_2 diffusivity. At a low CNT-PEG content, the CNT-PEG fibers may interrupt the packing of polymer chains, leading to a lower gas diffusion resistance. When the CNT-PEG content increases (e.g., 3 or 5 wt.%),[19] more CNT-PEG fibers could make loosely "connect" or

connect gas paths along the fiber surface rich in PEG, forming CO_2-philic channels, where CO_2 transport could be selectively enhanced along the CO_2-philic channels but N_2 cannot, resulting in a higher CO_2/N_2 selectivity. However, further increasing the CNT-PEG content in the membrane matrix will increase the portion of the impermeable regions occupied by CNT fibers, which will block or impede gas transport and significantly reduce CO_2 permeability. Increasing the amount of CNT-PEG over the optimal amount may also increase the chance of CNT fiber aggregation and hence, the formation of pinholes or other defects, which deteriorate the selectivity.
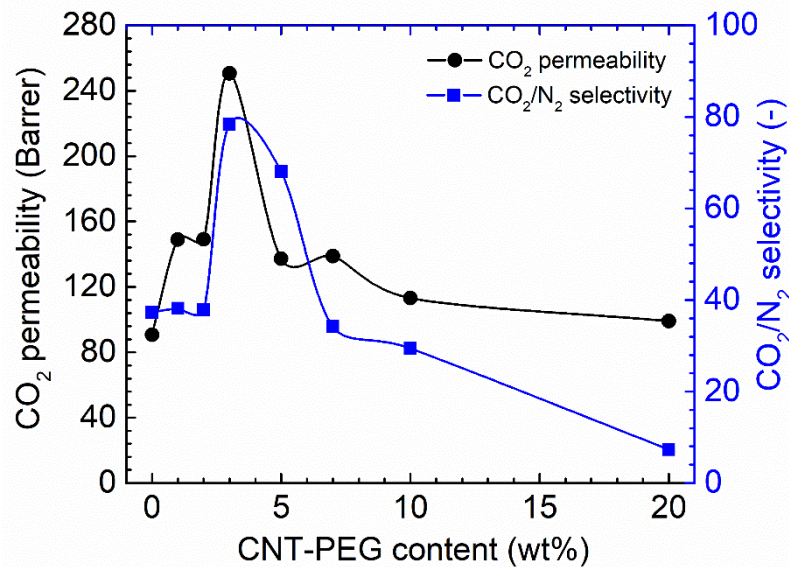

Figure 4. Gas permeation of Pebax/CNT-PEG hybrid membrane of different CNT-PEG content at the dry state.

3.3.2 Effect of relative humidity

The CO_2/N_2 separation performances of the Pebax/CNT-PEG membranes were investigated under different RH conditions. The results are shown in **Figure 5**.
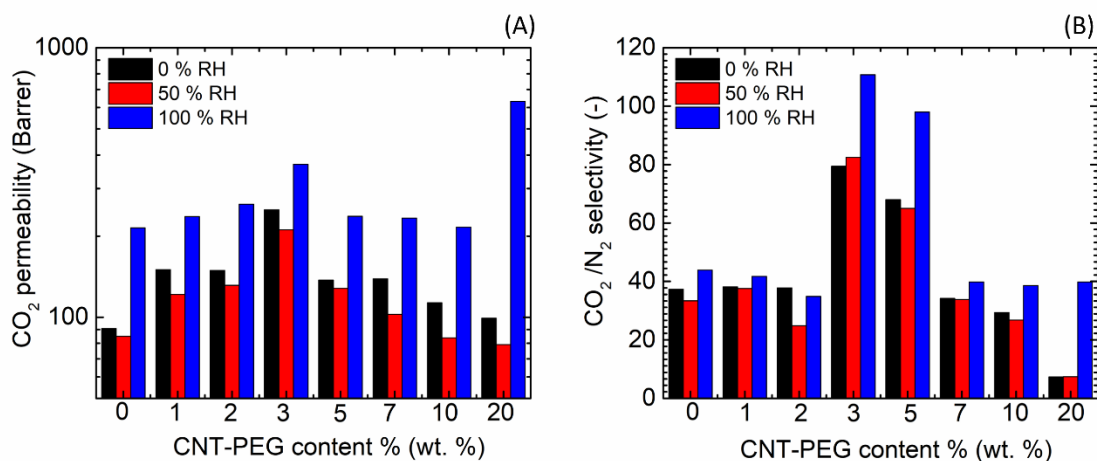
Figure 5. CO$_2$ separation performance of Pebax/CNT-PEG membrane under different RH conditions

It is well-known that the degree of swelling in a membrane has a dramatic effect on its overall gas separation performances. As expected, from **Figure 5(A)** it can be seen that increasing the RH value in the feed stream effectively improves the gas permeability for all the Pebax/CNT-PEG hybrid membranes. In addition, the trend almost follows that of the gas permeability at dry state except for the membrane with 20 wt.% CNT-PEG. In the case of the neat Pebax membrane, increasing RH value from 0 to 100% results in a 2.4× times enhancement in CO$_2$ permeability, from 90.7 Barrer to 214.5 Barrer. For the hybrid membrane containing 3 wt.% CNT-PEG, a CO$_2$ permeability of up to 369.1 Barrer has been obtained at 100% RH with the CO$_2$/N$_2$ selectivity of around 110.8. Further increasing CNT-PEG content between 5 wt.% to 20 wt.% results in a decrement in CO$_2$ permeability at the dry state. However, at the humid state, the CO$_2$ permeability of the membrane with 20 wt.% CNT-PEG increases to 632.1 Barrer, 6.4× times higher than that of the same membrane at the dry state. The improved CO$_2$ permeation at the humid state is believed mainly resulted from the formation of water clusters within the PEG-rich path along the interface between the CNT fibers and the Pebax matrix due to the high hydrophilicity of PEG, and the consequently much increased CO$_2$ diffusion rate. The CO$_2$ solubility should also increase due the presence of the CO$_2$-philic PEG along the CNT fibers (the CO$_2$-philic channels).

It is worth mentioning that except for the neat Pebax membrane, all hybrid membranes of different CNT-PEG contents show the lowest CO$_2$ permeability at 50% RH, which are only slightly lower than that of the same membranes at the dry state. This common trend may be attributed to the competitive transport of water vapor with CO$_2$ when the RH is low, so water

vapor is present in the feed stream but not enough to swell the polymer matrix and/or the interface between CNT-PEG and polymer.

Figure 5(B) presents the CO_2/N_2 selectivity results of the Pebax/CNT-PEG membranes obtained at different RH. For almost all the tested membranes, a slight decrease can be found at 50% RH, which is related to the lower CO_2 permeability obtained at 50 %RH. Further increase in the RH to 100% results in much higher selectivity compared to the dry state, following the trend of CO_2/N_2 selectivity at the dry state; the highest CO_2/N_2 selectivity was obtained from membranes containing 3 wt.% and 5 wt.% CNT-PEG, of 110.8 and 98.0, respectively. A possible explanation can be that the CNT-PEG fibers in the Pebax matric have a higher chance to form CO_2-philic channels,[19] which could selectively promote CO_2 transport and increase the CO_2/N_2 selectivity. However, at a higher CNT-PEG content (e.g., >5%), a large number of aggregations or defects may be created and deteriorates the selectivity of the hybrid membranes.

3.3.3 Comparison of CNT-based membrane separation performances

CNTs have been widely studied as nanofillers in CO_2 separation membranes. **Figure 6** shows the literature data of several CNT-based hybrid membranes[13-14, 24, 34, 46-52] and the results obtained in this work in comparison with the Robeson upper bound.[2-3] More information on the membranes and the values of the literature data used in **Figure** 6 are listed in **Table 1** with references.
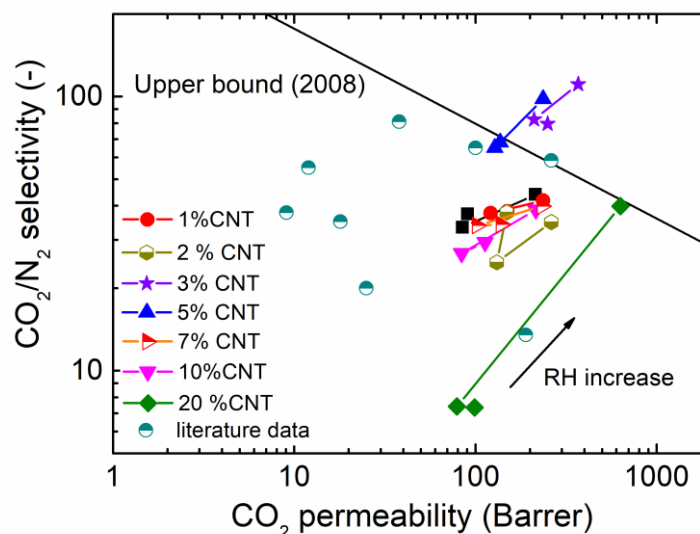
Figure 6. Separation performances of CNT-based membranes for CO_2/N_2 separation. The arrow in black presents the direction of the increasing RH.

As shown in **Figure 6,** with increasing RH, the separation performances of all the hybrid membranes are moving towards the upper bound. In particular, the hybrid membranes containing 3 wt.% and 5 wt.% CNT-PEG exhibit the CO_2/N_2 separation performances cross over the upper bound. On the other hand, the hybrid membrane with 20 wt.% CNT-PEG also shows separation performances close to the upper bound with much improved higher CO_2 permeability. These results demonstrate that adding CNT-PEG into Pebax can be an effective method to enhance CO_2 separation performances. The combination of high CO_2 permeability and high CO_2/N_2 selectivity make the membrane promising for different CO_2 separation applications.

Table 1. Separation performances of CNT-based membranes for CO_2/N_2 separation.

Polymer phase	CO_2 permeability (Barrer)	CO_2/N_2 selectivity (-)	Refs.
Pebax®	100	65	[34]
Matrimid®	38	81	[13]
Pebax®	350	55	[24]
Poly(imide siloxane)	190	13.5	[46]
Pebax®	262.15	58.5	[14]
polyimide	9.06	37.74	[48]
poly(ether sulfone)	4.45	22.1	[49]
polyimide	25	20	[50]
Polycarbonate	12	55	[51]
polysulfone	18	35	[52]

4. Conclusion

In the present study, hybrid membranes of PEG-grafted CNT fibers as nanofillers with Pebax®1657 as the polymeric matrix were fabricated, and enhanced CO_2/N_2 separation performances were documented. The obtained Pebax/CNT-PEG hybrid membranes were characterized using various techniques including TEM, SEM, TGA, FTIR, and XRD. Important conclusions from this work include:

- Grafting PEG onto CNT fibers effectively improves the CNT dispersion property in the membrane casting solution. No obvious aggregation can be found in the resultant hybrid membranes with CNT-PEG content of up to 20 wt.%.

-   From the mixed gas permeation test carried out at both dry and humid states, it is evident that the CNT-PEG plays an important role in gas transport at the dry state. The hybrid membrane of 3 wt.% CNT-PEG content has the highest CO_2 permeability and selectivity at the dry state.

-   The presence of water vapor significantly enhances the gas transport properties of the resultant hybrid membranes. At humid state, the highest CO_2/N_2 selectivity (110.8) with CO_2 permeability of 369.1 Barrer was obtained from the hybrid membrane of 3 wt.% CNT-PEG, while the highest CO_2 permeability (632.1 Barrer) with the CO_2/N_2 selectivity of 39.8 was obtained from the hybrid membrane of 20 wt.% CNT-PEG.

The separation performance of the membrane may be further improved by optimizing the CNT-PEG content, grafting more CO_2-philic molecules on the CNT fiber (e.g., amines), or using other types of CNT with different diameter/length. The good dispersion of the CNT-PEG in the Pebax matrix gives a great potential to fabricate the Pebax/CNT-PEG membrane into thin-film-composite membranes and hollow fiber membranes. Moreover, considering the strong mechanical properties of CNTs, this membrane should be suitable for separation at elevated pressures, such as natural gas treatment; the separation of CO_2/CH_4 gas pairs using the Pebax/CNT-PEG membranes is worth being investigated in the future.

Associated Content

Supporting Information

Supporting Information is available, including information as shown below:

Protocol of PEG-modified MWCNT preparation; ATR-FTIR spectra of CNT and CNT-PEG (**Figure S1**); XPS spectra of CNT and CNT-PEG: (left) wide scans and (right) C_{1s} core-level spectra (**Figure S2**); TGA thermograms of MWCNT, and CNT-PEG and PEG (**Figure S3**); Cross-section SEM images the PeBax membrane and the Pebax/CNT-PEG hybrid membranes with different CNT-PEG content (**Figure S4**); TGA thermograms of Pebax/CNT-PEG hybrid membranes with 1 wt.%, 2 wt.%, 7 wt.%, and 10 wt.% CNT-PEG content (**Figure S5**); DSC curve of Pebax/CNT-PEG hybrid membranes with 1 wt.%, 2 wt.%, 7 wt.%, and 10 wt.% CNT-PEG content **(Figure S6);** FTIR spectra of Pebax/CNT-PEG hybrid membranes with 1 wt.%, 2 wt.%, 7 wt.%, and 10 wt.% CNT-PEG content **(Figure S7);** XRD curve of Pebax/CNT-PEG hybrid membranes with 1 wt.%, 2 wt.%, 7 wt.%, and 10 wt.% CNT-PEG content **(Figure S8).**

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The manuscript was written through the contributions of all authors. All authors have given

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References

(1) Baker, R. W.; Low, B. T. Gas separation membrane materials: A perspective. *Macromolecules* **2014,** *47*, 6999-7013, DOI: doi:10.1021/ma501488s.
(2) Robeson, L. M. The upper bound revisited. *J. Membr. Sci.* **2008,** *320*, 390-400, DOI: https://doi.org/10.1016/j.memsci.2008.04.030.
(3) Robeson, L. M. Correlation of separation factor versus permeability for polymeric membranes. *J. Membr. Sci.* **1991,** *62*, 165-185, DOI: https://doi.org/10.1016/0376-7388(91)80060-J.
(4) Galizia, M.; Chi, W. S.; Smith, Z. P.; Merkel, T. C.; Baker, R. W.; Freeman, B. D. 50th anniversary perspective: Polymers and mixed matrix membranes for gas and vapor separation: A review and prospective opportunities. *Macromolecules* **2017,** *50*, 7809-7843, DOI: DOI: 10.1021/acs.macromol.7b01718.
(5) Ahmadi, M.; Janakiram, S.; Dai, Z.; Ansaloni, L.; Deng, L. Performance of mixed matrix membranes containing porous two-dimensional (2D) and three-dimensional (3D) fillers for CO_2 separation: A review. *Membranes* **2018,** *8* (3), DOI: https://doi.org/10.3390/membranes8030050.

(6) Dai, Z.; Noble, R. D.; Gin, D. L.; Zhang, X.; Deng, L. Combination of ionic liquids with membrane technology: A new approach for CO2 separation. *J. Membr. Sci.* **2016,** *497*, 1-20, DOI: https://doi.org/10.1016/j.memsci.2015.08.060.

(7) Ramasubramanian, K.; Ho, W. S. W. Recent developments on membranes for post-combustion carbon capture. *Curr. Opin. Chem. Eng.* **2011,** *1*, 47-54, DOI: https://doi.org/10.1016/j.coche.2011.08.002.

(8) Vinoba, M.; Bhagiyalakshmi, M.; Alqaheem, Y.; Alomair, A. A.; Pérez, A.; Rana, M. S. Recent progress of fillers in mixed matrix membranes for CO_2 separation: A review. *Sep. Purif. Technol.* **2017,** *188*, 431-450, DOI: https://doi.org/10.1016/j.seppur.2017.07.051.

(9) Janakiram, S.; Ahmadi, M.; Dai, Z.; Ansaloni, L.; Deng, L. Performance of nanocomposite membranes containing 0D to 2D nanofillers for CO_2 separation: A review. *Membranes* **2018,** *8*, 24, DOI: https://doi.org/10.3390/membranes8020024.

(10) Ismail, A. F.; Goh, P. S.; Sanip, S. M.; Aziz, M. Transport and separation properties of carbon nanotube-mixed matrix membrane. *Sep. Purif. Technol.* **2009,** *70*, 12-26, DOI: https://doi.org/10.1016/j.seppur.2009.09.002.

(11) Ahmad, A. L.; Jawad, Z. A.; Low, S. C.; Zein, S. H. S. A cellulose acetate/multi-walled carbon nanotube mixed matrix membrane for CO_2/N_2 separation. *J. Membr. Sci.* **2014,** *451*, 55-66, DOI: https://doi.org/10.1016/j.memsci.2013.09.043.

(12) Zhao, Y.; Jung, B. T.; Ansaloni, L.; Ho, W. S. W. Multiwalled carbon nanotube mixed matrix membranes containing amines for high pressure CO_2/H_2 separation. *J. Membr. Sci.* **2014,** *459*, 233-243, DOI: https://doi.org/10.1016/j.memsci.2014.02.022.

(13) Li, X.; Ma, L.; Zhang, H.; Wang, S.; Jiang, Z.; Guo, R.; Wu, H.; Cao, X.; Yang, J.; Wang, B. Synergistic effect of combining carbon nanotubes and graphene oxide in mixed matrix membranes for efficient CO_2 separation. *J. Membr. Sci.* **2015,** *479*, 1-10, DOI: https://doi.org/10.1016/j.memsci.2015.01.014.

(14) Murali, R. S.; Sridhar, S.; Sankarshana, T.; Ravikumar, Y. Gas permeation behavior of Pebax-1657 nanocomposite membrane incorporated with multiwalled carbon nanotubes. *Ind. Eng. Chem. Res.* **2010,** *49*, 6530-6538, DOI: DOI: 10.1021/ie9016495.

(15) Kim, S.; Chen, L.; Johnson, J. K.; Marand, E. Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: Theory and experiment. *J. Membr. Sci.* **2007,** *294*, 147-158, DOI: https://doi.org/10.1016/j.memsci.2007.02.028.

(16) Saeed, M.; Deng, L. Carbon nanotube enhanced PVA-mimic enzyme membrane for post-combustion CO_2 capture. *Int. J. Greenhouse Gas Control* **2016,** *53*, 254-262, DOI: https://doi.org/10.1016/j.ijggc.2016.08.017.

(17) Habibiannejad, S.; Aroujalian, A.; Raisi, A. Pebax-1657 mixed matrix membrane containing surface modified multi-walled carbon nanotubes for gas separation. *RSC Adv.* **2016,** *6*, 79563-79577, DOI: DOI:10.1039/C6RA14141B.

(18) Aroon, M. A.; Ismail, A. F.; Montazer-Rahmati, M. M.; Matsuura, T. Effect of chitosan as a functionalization agent on the performance and separation properties of polyimide/multi-walled carbon nanotubes mixed matrix flat sheet membranes. *J. Membr. Sci.* **2010,** *364*, 309-317, DOI: https://doi.org/10.1016/j.memsci.2010.08.023.

(19) Khan, M. M.; Filiz, V.; Bengtson, G.; Shishatskiy, S.; Rahman, M. M.; Lillepaerg, J.; Abetz, V. Enhanced gas permeability by fabricating mixed matrix membranes of functionalized multiwalled carbon nanotubes and polymers of intrinsic microporosity (PIM). *J. Membr. Sci.* **2013,** *436*, 109-120, DOI: https://doi.org/10.1016/j.memsci.2013.02.032.

(20) Kardani, R.; Asghari, M.; Mohammadi, T.; Afsari, M. Effects of nanofillers on the characteristics and performance of PEBA-based mixed matrix membranes. *Rev. Chem. Eng.* **2018,** *34*, 797-836, DOI: https://doi.org/10.1515/revce-2017-0001.

(21) Chang, C.-M.; Liu, Y.-L. Functionalization of multi-walled carbon nanotubes with non-reactive polymers through an ozone-mediated process for the preparation of a wide range of high performance polymer/carbon nanotube composites. *Carbon* **2010,** *48*, 1289-1297, DOI: https://doi.org/10.1016/j.carbon.2009.12.002.

(22) Dai, Z.; Ansaloni, L.; Ryan, J. J.; Spontak, R. J.; Deng, L. Nafion/IL hybrid membranes with tuned nanostructure for enhanced CO_2 separation: effects of ionic liquid and water vapor. *Green Chem.* **2018,** *20*, 1391-1404, DOI: doi:10.1039/C7GC03727A.

(23) Jeong, W.; Kessler, M. R. Toughness enhancement in ROMP functionalized carbon nanotube/polydicyclopentadiene composites. *Chem. Mater.* **2008,** *20*, 7060-7068, DOI: 10.1021/cm8020947.

(24) Zhao, D.; Ren, J.; Wang, Y.; Qiu, Y.; Li, H.; Hua, K.; Li, X.; Ji, J.; Deng, M. High CO_2 separation performance of Pebax®/CNTs/GTA mixed matrix membranes. *J. Membr. Sci.* **2017,** *521*, 104-113, DOI: https://doi.org/10.1016/j.memsci.2016.08.061.

(25) Car, A.; Stropnik, C.; Yave, W.; Peinemann, K.-V. Pebax®/polyethylene glycol blend thin film composite membranes for CO2 separation: Performance with mixed gases. *Sep. Purif. Technol.* **2008,** *62*, 110-117, DOI: https://doi.org/10.1016/j.seppur.2008.01.001.

(26) Dai, Y.; Ruan, X.; Yan, Z.; Yang, K.; Yu, M.; Li, H.; Zhao, W.; He, G. Imidazole functionalized graphene oxide/PEBAX mixed matrix membranes for efficient CO_2 capture. *Sep. Purif. Technol.* **2016,** *166*, 171-180, DOI: https://doi.org/10.1016/j.seppur.2016.04.038.

(27) Xiang, L.; Pan, Y.; Zeng, G.; Jiang, J.; Chen, J.; Wang, C. Preparation of poly(ether-block-amide)/attapulgite mixed matrix membranes for CO_2/N_2 separation. *J. Membr. Sci.* **2016,** *500*, 66-75, DOI: https://doi.org/10.1016/j.memsci.2015.11.017.

(28) Li, X.; Jiang, Z.; Wu, Y.; Zhang, H.; Cheng, Y.; Guo, R.; Wu, H. High-performance composite membranes incorporated with carboxylic acid nanogels for CO2 separation. *J. Membr. Sci.* **2015,** *495*, 72-80, DOI: https://doi.org/10.1016/j.memsci.2015.07.065.

(29) Li, Y.; Xin, Q.; Wu, H.; Guo, R.; Tian, Z.; Liu, Y.; Wang, S.; He, G.; Pan, F.; Jiang, Z. Efficient CO2 capture by humidified polymer electrolyte membranes with tunable water state. *Energy Environ. Sci.* **2014,** *7*, 1489-1499, DOI: 10.1039/C3EE43163K.

(30) Akhtar, F. H.; Kumar, M.; Peinemann, K.-V. Pebax®1657/Graphene oxide composite membranes for improved water vapor separation. *J. Membr. Sci.* **2017,** *525*, 187-194, DOI: https://doi.org/10.1016/j.memsci.2016.10.045.

(31) Thanakkasaranee, S.; Kim, D.; Seo, J. Preparation and Characterization of Poly(ether-block-amide)/Polyethylene Glycol Composite Films with Temperature-Dependent Permeation. *Polymers* **2018,** *10*, 225.

(32) Ghasemi Estahbanati, E.; Omidkhah, M.; Ebadi Amooghin, A. Preparation and characterization of novel Ionic liquid/Pebax membranes for efficient CO2/light gases separation. *J. Ind. Eng. Chem.* **2017,** *51*, 77-89, DOI: https://doi.org/10.1016/j.jiec.2017.02.017.

(33) Zhao, D.; Ren, J.; Li, H.; Li, X.; Deng, M. Gas separation properties of poly(amide-6-b-ethylene oxide)/amino modified multi-walled carbon nanotubes mixed matrix membranes. *J. Membr. Sci.* **2014,** *467*, 41-47, DOI: https://doi.org/10.1016/j.memsci.2014.05.009.

(34) Yu, B.; Cong, H.; Li, Z.; Tang, J.; Zhao, X. S. Pebax‐1657 nanocomposite membranes incorporated with nanoparticles/colloids/carbon nanotubes for CO_2/N_2 and CO_2/H_2 separation. *J. Appl. Polym. Sci.* **2013,** *130*, 2867-2876, DOI: https://doi.org/10.1002/app.39500.

(35) Rahman, M. M.; Shishatskiy, S.; Abetz, C.; Georgopanos, P.; Neumann, S.; Khan, M. M.; Filiz, V.; Abetz, V. Influence of temperature upon properties of tailor-made PEBAX® MH 1657 nanocomposite membranes for post-combustion CO_2 capture. *J. Membr. Sci.* **2014,** *469*, 344-354, DOI: https://doi.org/10.1016/j.memsci.2014.06.048.

(36) Bernardo, P.; Jansen, J. C.; Bazzarelli, F.; Tasselli, F.; Fuoco, A.; Friess, K.; Izák, P.; Jarmarová, V.; Kačírková, M.; Clarizia, G. Gas transport properties of Pebax®/room temperature ionic liquid gel membranes. *Sep. Purif. Technol.* **2012,** *97*, 73-82, DOI: https://doi.org/10.1016/j.seppur.2012.02.041.

(37) Rahman, M. M.; Filiz, V.; Shishatskiy, S.; Abetz, C.; Neumann, S.; Bolmer, S.; Khan, M. M.; Abetz, V. PEBAX® with PEG functionalized POSS as nanocomposite membranes for CO_2 separation. *J. Membr. Sci.* **2013,** *437*, 286-297, DOI: https://doi.org/10.1016/j.memsci.2013.03.001.

(38) Ahn, J.; Chung, W.-J.; Pinnau, I.; Song, J.; Du, N.; Robertson, G. P.; Guiver, M. D. Gas transport behavior of mixed-matrix membranes composed of silica nanoparticles in a polymer of intrinsic microporosity (PIM-1). *J. Membr. Sci.* **2010**, *346*, 280-287, DOI: https://doi.org/10.1016/j.memsci.2009.09.047.

(39) Li, Y.; Chung, T.-S.; Cao, C.; Kulprathipanja, S. The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite A mixed matrix membranes. *J. Membr. Sci.* **2005**, *260*, 45-55, DOI: https://doi.org/10.1016/j.memsci.2005.03.019.

(40) Li, Y.; Guan, H.-M.; Chung, T.-S.; Kulprathipanja, S. Effects of novel silane modification of zeolite surface on polymer chain rigidification and partial pore blockage in polyethersulfone (PES)–zeolite A mixed matrix membranes. *J. Membr. Sci.* **2006,** *275*, 17-28, DOI: https://doi.org/10.1016/j.memsci.2005.08.015.

(41) Liu, Y.; Liu, G.; Zhang, C.; Qiu, W.; Yi, S.; Chernikova, V.; Chen, Z.; Belmabkhout, Y.; Shekhah, O.; Eddaoudi, M. Enhanced CO_2/CH_4 separation performance of a mixed matrix membrane based on tailored MOF‒polymer formulations. *Adv. Sci.* **2018,** *5* (9), 1800982, DOI: https://doi.org/10.1002/advs.201800982.

(42) Meshkat, S.; Kaliaguine, S.; Rodrigue, D. Mixed matrix membranes based on amine and non-amine MIL-53 (Al) in Pebax® MH-1657 for CO_2 separation. *Sep. Purif. Technol.* **2018,** *200*, 177-190, DOI: https://doi.org/10.1016/j.seppur.2018.02.038.

(43) Xie, K.; Fu, Q.; Webley, P. A.; Qiao, G. G. MOF scaffold for a high performance mixed matrix membrane. *Angew. Chem. Int. Ed.* **2018,** *57*, 8597-8602, DOI: https://doi.org/10.1002/anie.201804162.

(44) Li, T.; Pan, Y.; Peinemann, K.-V.; Lai, Z. Carbon dioxide selective mixed matrix composite membrane containing ZIF-7 nano-fillers. *J. Membr. Sci.* **2013**, *425*, 235-242, DOI: https://doi.org/10.1016/j.memsci.2012.09.006.

(45) Car, A.; Stropnik, C.; Yave, W.; Peinemann, K.-V. PEG modified poly(amide-b-ethylene oxide) membranes for CO_2 separation. *J. Membr. Sci.* **2008,** *307*, 88-95, DOI: https://doi.org/10.1016/j.memsci.2007.09.023.

(46) Kim, S.; Pechar, T. W.; Marand, E. Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation. *Desalination* **2006**, *192*, 330-339, DOI: https://doi.org/10.1016/j.desal.2005.03.098.

(47) Zhang, H.; Guo, R.; Hou, J.; Wei, Z.; Li, X. Mixed-matrix membranes containing carbon nanotubes composite with hydrogel for efficient CO_2 separation. *ACS Appl. Mater. Interfaces* **2016,** *8*, 29044-29051, DOI: doi:10.1021/acsami.6b09786.

(48) Sun, H.; Wang, T.; Xu, Y.; Gao, W.; Li, P.; Niu, Q. J. Fabrication of polyimide and functionalized multi-walled carbon nanotubes mixed matrix membranes by in-situ polymerization for CO_2 separation. *Sep. Purif. Technol.* **2017,** *177*, 327-336, DOI: https://doi.org/10.1016/j.seppur.2017.01.015.

(49) Ge, L.; Zhu, Z.; Li, F.; Liu, S.; Wang, L.; Tang, X.; Rudolph, V. Investigation of gas permeability in carbon nanotube (CNT)–polymer matrix membranes via modifying CNTs with functional groups/metals and controlling modification location. *J. Phys. Chem. C* **2011**, *115*, 6661-6670, DOI: DOI: 10.1021/jp1120965.

(50) Xue, Q.; Pan, X.; Li, X.; Zhang, J.; Guo, Q. Effective enhancement of gas separation performance in mixed matrix membranes using core/shell structured multi-walled carbon nanotube/graphene oxide nanoribbons. *Nanotechnology* **2017**, *28*, 065702, DOI: doi:10.1088/1361-6528/aa510d.

(51) Moghadassi, A. R.; Rajabi, Z.; Hosseini, S. M.; Mohammadi, M. Preparation and characterization of polycarbonate-blend-raw/functionalized multi-walled carbon nano tubes mixed matrix membrane for CO_2 separation. *Sep. Sci. Technol.* **2013,** *48*, 1261-1271, DOI: doi:10.1080/01496395.2012.730597.

(52) Sarfraz, M.; Ba-Shammakh, M. Combined effect of CNTs with ZIF-302 into polysulfone to fabricate MMMs for enhanced CO_2 separation from flue gases. *Arabian J. Sci. Eng.* **2016,** *41*, 2573-2582, DOI: doi:10.1007/s13369-016-2096-4.