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ABSTRACT

Global warming is considered as a consequence of extensive use of fossil fuels. Post combustion CO_2 capture is an interesting and alternative solution where mixed matrix membranes (MMMs) can be an exciting candidate. This research focuses on the optimization of MMM composition consisting of Pebax® 3533 as the polymer matrix and porous coordination polymer (PCP) MIL-178(Fe) as a filler for gas separation application. MIL-178(Fe) characterized with SEM, TEM and TGA were applied to compare bare polymer and MMM. Optimum composition of the MMM obtained was 5 wt.% MIL-178(Fe) in Pebax® 3533. Average thickness of the optimized dense MMM was 116 ± 8 μm. Such MMM showed CO_2 permeability and CO_2/N_2 selectivity of 312 ± 5 Barrer and 25.0 ± 0.5, respectively, 12% and 25% improved regarding the bare membrane. Additionally, optimum MMM was applied for CO_2/CH_4 separation and successfully compared in terms of improved CO_2 permeability and CO_2/CH_4 selectivity.

1. Introduction

Anthropogenic activities necessitate substantial amount of fossil fuels which produce CO_2 with a 6% increment every year (Dai et al., 2016) causing global warming and unpredictable climatic changes to the environment. Stationary platforms such as power plants, oil refineries, certain industries, etc. release more than 60% of the global CO_2 emission. To mitigate such a drastic effect on the atmosphere, it has been agreed to limit the global temperature rise below 2 °C (Paris conference in 2015 (Xie et al., 2019), confirmed at the Glasgow COP26 in 2021 ("COP26: green technologies could turn the tide," 2021)). Accordingly, control of such mighty gas release at those stationary plants can reduce global warming in a significant extend.

Since 1970s, membrane separation has become an interesting technology to capture CO_2 from its mixtures with non-polar gases (such as CO_2/N_2, CO_2/H_2, CO_2/CH_4 gas mixtures). It is considered an eco-friendly know-how that is expected to replace some of the conventional energy-intensive carbon capture and storage (CCS) technologies such as absorption (solvent based), adsorption (solid adsorbent based), cryogenic processes, etc., since they are characterized by high cost of operation and lack of reusability (Choi et al., 2009; Dai et al., 2016). On the contrary, polymeric membranes feature high thermal and mechanical stability (at the operating condition), easy scaling up and show significantly smaller footprint. Mixed matrix membranes (MMMs) made of integrated base polymeric matrix and a compatible ideally nanosized filler (Zhou et al., 2012) show improved separation performance and good mechanical and thermal properties, which enable them as potential technology for CCS (Hu et al., 2022). Literature on the subject suggests that the existence of polar groups having intensive affinity towards CO_2 in the membrane produces better CCS performance from a CO_2/non-polar gas mixture. Poly(ether-block-amide) (PEBA) copolymers are interesting for CCS application since they consist of both rigid glassy polyamide (PA) segments (e.g. PA6, PA12) and flexile rubbery polyethylene (PE) segments (e.g. PEO, PTMO) which offer high

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permeability for CO_2 without sacrificing mechanical stability and selectivity (Seddigh et al., 2014). Among all Pebax® codes Pebax® 1657 is interesting for CCS application because of its better selectivity, but its affinity to water may restrict its application for CCS under humid conditions (since coal-derived flue gases often contains oxygen, SOx, NOx and other minor components like water vapor) (Merkel et al., 2010). Pebax® 3533 is another interesting block copolymer composed of 75 wt.% of PE (PTMO) and 25 wt.% of PA (PA12). Due to its high solubility in alcoholic solvents (less polar in nature than water), this polymer would be prone to exhibit a long-term stability and durability under humid conditions and it has shown good performance in the separation of CO_2 containing mixtures (Benzaqui et al., 2022; Martínez-Izquierdo et al., 2021).

In literature, different metal organic frameworks (MOFs) and porous coordination polymers (PCPs) have been incorporated in MMMs for CCS application such as ZIF-8, ZIF-94, ZIF-67, ZIF-71, ZIF-300, UiO-66, UiO-67, MIL-53(Al), to name a few (Ehsani and Pakizeh, 2016; Etxeberria--Benavides et al., 2018; Gökpinar et al., 2017; Gong et al., 2017; Japip et al., 2016; Meshkat et al., 2020, 2018; Sánchez-Laínez et al., 2016; Sasikumar et al., 2021; Yuan et al., 2017). Such incorporation of MOFs in polymer matrices results in improvement of thermal and mechanical properties of the membranes (Nasir et al., 2021). Even if such membranes are selective for CO_2 capture from non-polar gases, there are still scopes to study on MMMs concerning new raw materials, application environment, solvent selection, drying conditions, etc. In this sense, MIL-178(Fe) is a recently reported one dimensional Fe (III) based PCP whose combination with Pebax® 3533 led to the processing of an efficient membrane for CO_2 capture (Benzaqui et al., 2022). The authors reported mechanically stable MMMs with about 80% improvement in terms of CO_2/N_2 selectivity (16.0 ± 0.7) compared to bare membrane (9.0 ± 0.7). This is the reason why more detailed investigation and optimization of Pebax® 3533 and new PCP MIL-178(Fe) is interesting, since, for instance, solvent evaporation conditions can alter the gas separation performance (Karamouz et al., 2016). Besides, a proper polymer concentration in the membrane casting solution can significantly improve CCS performance (Martínez-Izquierdo et al., 2019). Moreover, filler loading in the MMM has a direct effect on the gas separation performance (Hasan et al., 2021), as well as the use of ionic liquids (Pardo et al., 2021) or the blending of Pebax® with other polymers (Kheirtalab et al., 2020) can be considered among other improvement options.

The objective of this article is to understand the impact of polymer-filler composition and drying conditions of MIL-178(Fe)/ Pebax® 3533 MMMs on CCS performance. For this purpose, we focus on the optimization of the MIL-178(Fe) loading and Pebax® 3533 concentration in MMMs for an efficient capture of CO_2 from both CO_2/N_2 and CO_2/CH_4 gas mixtures.

2. Experimental methods

2.1. Materials

Pebax® 3533 (75 wt.% poly (tetramethylene oxide) (PTMO) and 25 wt.% aliphatic polyamide (PA12)) in the form of pellets was kindly provided by Arkema, France. Solvents, 1-propanol (Labbox, 99%) and 1-butanol (Scharlab, 99%) were used as received. MIL-178(Fe) was prepared at RT (room temperature) from anhydrous $FeCl_3$ (Sigma Aldrich, 99%) and 1,2,4-benzene tricarboxylic acid (Sigma Aldrich, 95%) followed the recent reported recipe (Benzaqui et al., 2022). All research grade gases (greater than 99.995% of purity) used for the separation experiment were supplied by Abelló Linde S.A., Spain.

2.2. Membrane fabrication

To fabricate bare membranes, 1-6 wt.% Pebax® 3533 (of total weight of 10 g (polymer + solvent)) was dissolved in 1-propanol/1-butanol (75/25 (v/v)) by stirring under reflux for 1 h. Afterwards, the solution was poured in a Petri dish and dried for 24 h at 40 °C. In case of MMMs, MIL-178(Fe) was dispersed in the dissolved polymer. First, the required amount of filler (3–15 wt.%), which was calculated against the amount of Pebax® 3533 present in the best bare membrane composition, was dispersed in 1.5 mL of 1-propanol/1-butanol (75/25 (v/v)) by repeated sonication and stirring at RT for 1 h. Next, both dispersions (filler suspension and polymer solution) were mixed and maintained under stirring overnight at RT. In the next step, the final dispersion was poured in a Petri dish (5 cm of diameter) and dried in an oven at 40 °C for 24 h. Illustration of the fabrication of membranes is shown in Fig. 1 and identification names of the obtained membranes are given in Table 1.

2.3. Characterization

The morphology of MIL-178(Fe) was investigated with TEM and SEM. TEM samples were prepared by drop-casting a MIL-78(Fe) suspension on a 200-mesh carbon-coated copper TEM grid. TEM images were acquired on a JEOL 2010 TEM microscope operating at 200 kV. Cross-sectional morphologies of Pebax® 3533 bare membrane and their MMM were studied by scanning electron microscopy (SEM) using an Inspect F50 model scanning microscope (FEI) operated at 10 kV. Cross-sections of membranes were prepared by freeze-fracturing after immersion in liquid N_2 and subsequently coated with Pt. The zeta potential of the membrane was measured by an electrokinetic analyzer (SurPass 3, Anton Paar). The membranes were cut in the form of a rectangle (2 cm x 1 cm) and placed inside the SurPass flow cell. Thermogravimetric analysis (TGA) of membranes and MIL-178(Fe) were carried out using a Mettler Toledo TGA/STDA 851e which produces loss of weight as a function of temperature. For TGA analysis, a small piece of membranes or amount of PCP powder (approx. 8 mg) were placed in 70 μL alumina pans that were heated under an air flow (40 mL (STP) min^{-1}) from 35 to 700 °C at a heating rate of 10 °C min^{-1}. Membranes and MIL-178(Fe) particles were also characterized by X-ray diffraction (XRD) using a Panalytical Empyrean equipment with CuK_α radiation ($\lambda = 0.154$ nm), over the range of 5°–40° at a scan rate of 0.03° s^{-1}. SMART L Fungilab rotational viscometer was used to investigate viscosity of the polymer solutions.

2.4. Gas permeation measurement

The experimental set-up used for the separation of the CO_2/N_2 and CO_2/CH_4 mixtures is schematically presented in Fig. 2. A small circle of the membrane was cut and placed in a module consisting of two stainless steel pieces and a 316LSS macroporous disc support (Mott Co.) with a 20 μm nominal pore size. Membranes, 2.12 cm^2 in area, were gripped inside with Viton o-rings. Temperature was controlled at 35 °C by placing the permeation module in an UNE 200 Memmert oven. Gas separation measurements were carried out by feeding the gaseous mixtures of CO_2/N_2 (15/85, both cm^3(STP) min^{-1}) or CO_2/CH_4 (50/50, both cm^3(STP) min^{-1}) at an operating pressure of 3 bar to the feed side, controlled by two mass-flow controllers (Alicat Scientific, MC-100CCM-D). The permeate side of the membrane was swept with 2 cm^3(STP) min^{-1} of He (Alicat Scientific, MC-5CCM-D), at atmospheric pressure (approx. 1 bar). Concentrations of CO_2, N_2 and CH_4 in the permeate stream were analyzed online by an Agilent 3000A micro-gas chromatograph. Permeability was calculated in Barrer (10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1}) once steady state of the exit stream was reached (at ca. 3 h). The separation selectivity was calculated as the ratio of the corresponding permeabilities.

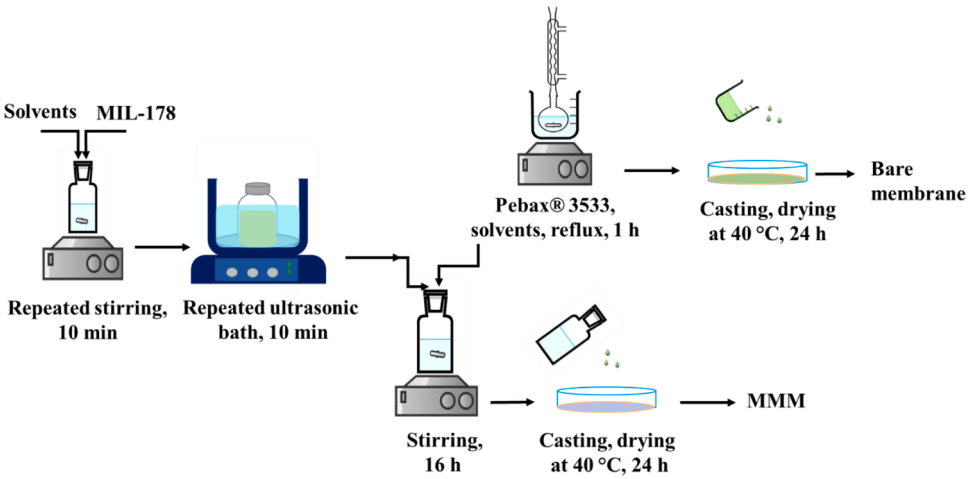

Fig. 1. Sketch of fabrication of bare polymeric membrane and MMM.

Table 1
Membranes fabricated for this study.

Name	Membrane type	Description	Thickness (μm)
M1	Bare polymer	1 wt.% of Pebax® 3533	38 ± 2
M2	Bare polymer	2 wt.% of Pebax® 3533	55 ± 4
M3	Bare polymer	3 wt.% of Pebax® 3533	75 ± 5
M4	Bare polymer	4 wt.% of Pebax® 3533	88 ± 4
M5	Bare polymer	5 wt.% of Pebax® 3533	110 ± 5
M6	Bare polymer	6 wt.% of Pebax® 3533	128 ± 6
M5.3	MMM	5 wt.% of Pebax® 3533 + 3 wt.% MIL-178(Fe)	114 ± 3
M5.5	MMM	5 wt.% of Pebax® 3533 + 5 wt.% MIL-178(Fe)	116 ± 8
M5.10	MMM	5 wt.% of Pebax® 3533 + 10 wt.% MIL-178(Fe)	119 ± 4
M5.15	MMM	5 wt.% of Pebax® 3533 + 15 wt.% MIL-178(Fe)	123 ± 6

3. Result and discussion

3.1. Characterization

Surface and cross section SEM images of bare polymeric membranes in Fig. 3A and 3D reveal the fabrication of defect free membranes. Similarly, cross section SEM images of MMMs consisting of MIL-178(Fe) within polymer matrix are represented in Fig. 3B and 3E, correspondingly. These images show the presence of MIL-178(Fe) particles in the matrix and proper filler-polymer interaction. SEM and TEM images of MIL-178(Fe) (Fig. 3C and 3F) show fusiform morphology of the particles with an aspect ratio of around 4. Additionally, SEM cross-section images of the MMMs (M5.5, M5.10, M5.15) are provided as supporting information (Fig. S1). These images suggest that the agglomeration tendency of fillers in the membranes intensified with the increase of the filler dose. Moreover, zeta potential measurements of the membranes were performed (shown in Fig. S2), revealing a change of the surface charge as a function of pH. At lower pH values, 3% and 5% filler loading MMMs (M5.3 and M5.5) showed lower (higher in absolute value) zeta potential than the bare membrane (M5). In case of higher filler loadings (10% for M5.10 and 15% for M5.15), the zeta potential does not show a clear tendency approaching in some cases the values of the bare polymer. Such changes suggest an agglomeration tendency of the filler at high loadings. This reduces the surface charge of the membrane and in consequence the zeta potential would tend to approach the value of the bare polymer. Powder X-ray diffraction (PXRD) pattern of MIL-178(Fe) (Fig. 4A) is fully consistent with that previously reported by Benzaqui et al. (Benzaqui et al., 2022). PXRD patterns of bare membrane and MMM show the concomitant presence of diffraction peaks of both the Pebax® 3533 and MIL-178(Fe) (Fig. 4A). This is consistent with the preservation of the crystallinity of the PCP once combined with the polymer. TGA of MIL-178(Fe) shows an early weight loss (4% of the total weight) bellow 100 °C due to the removal of moisture (Fig. 4B). Rapid degradation is observed after 350 °C due to the

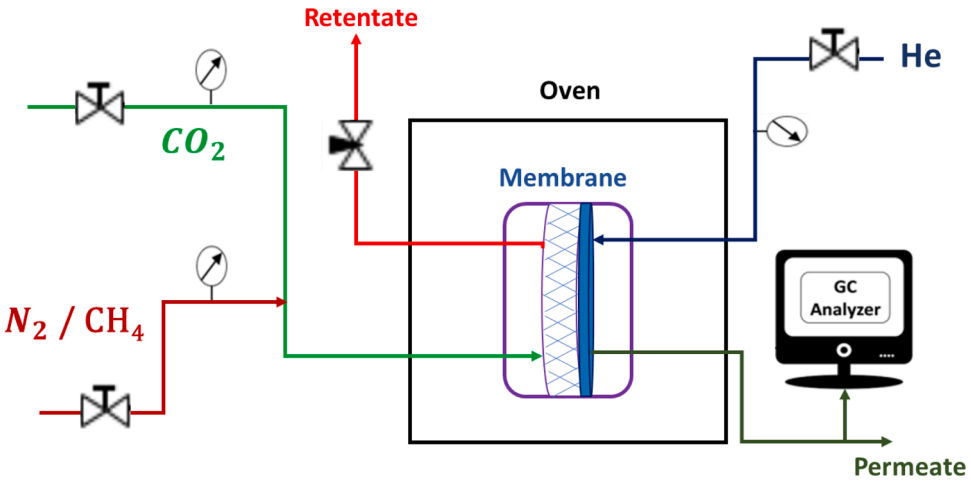

Fig. 2. Gas permeation experimental system operating at 35 °C.

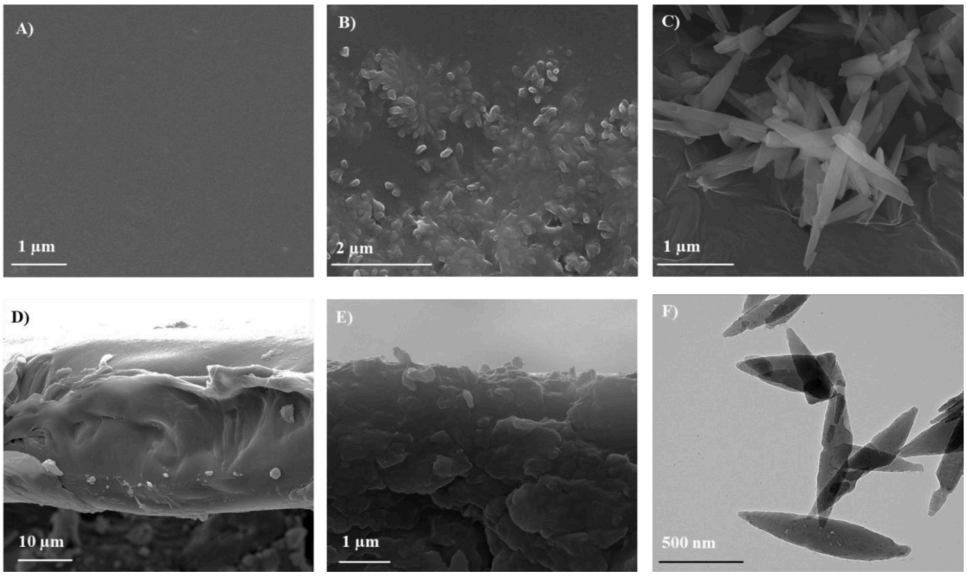

Fig. 3. SEM images of: (A) top surface of bare membrane (M5), (B) top surface of MMM (M5.5), (C) SEM image of MIL-178(Fe), (D) cross-section image of bare membrane (M5), (E) cross-section image of MMM (M5.5), and (F) TEM image of MIL-178(Fe).

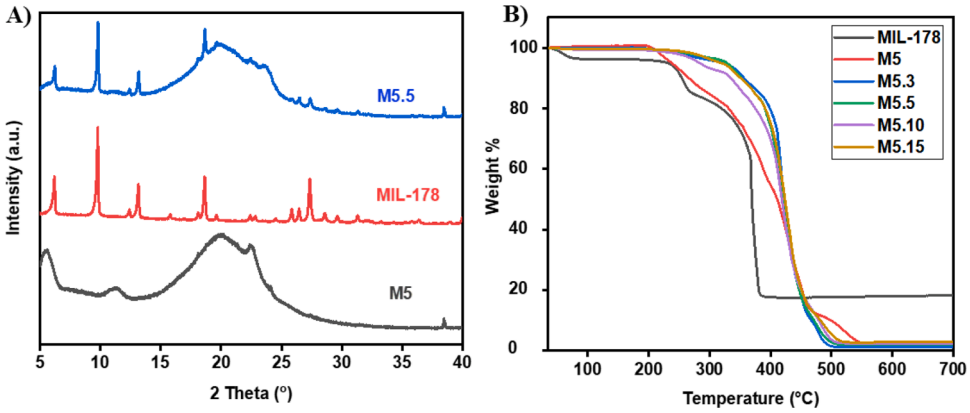

Fig. 4. (A) XRD diffractograms of bare polymer membrane, MIL-178(Fe) and MMM M5.5. (B) TGA of MIL-178(Fe), bare polymer membrane and MMMs.

thermal decomposition of MIL-178(Fe) which results in a ca. 18 wt.% residue of the initial weight which corresponds to the oxidation of the iron of the MOF structure to Fe_2O_3, as previously shown (Benzaqui et al., 2022). Bare polymeric membranes (M5) are found stable up to 220 °C, then they undergo thermal degradation (Fig. 4B). However, the thermal stability of the polymer matrix is improved upon the incorporation of MIL-178(Fe) since the TGA curves of MMMs (M5.3, M5.5, M5.10 and M5.15) clearly show their early stage stability beyond 300°C. Additionally, the increase of fillers content in the membranes augments the quantity of residues, M5.5 and M5.15 producing residues of 2 wt.% and 3 wt.%, respectively).

3.2. Gas permeation measurements

Gas permeation experiments were performed for two different gas mixtures (CO_2/N_2 and CO_2/CH_4) at the prescribed experimental conditions. Detailed interpretation of the acquired data is discussed in the subsequent sections.

3.2.1. CO_2/N_2 permeation measurement

We previously demonstrated that a MMM with 6/94 wt.% of Pebax® 3533/solvent in the casting solution (3 g total weight basis and drying condition at RT) and 10/90 wt.% MIL-178(Fe)/polymer produced maximum CO_2/N_2 selectivity, whereas a 15 wt.% MIL-178(Fe) loading showed best CO_2 permeability, although the polymer concentration was not optimized (Benzaqui et al., 2022). Since Lidia-Martinez et al. reported the effect of polymer concentration in bare membrane on CCS performance (Martínez-Izquierdo et al., 2019), this work focuses, firstly, on the optimization of the polymer matrix concentration and, secondly, on the optimization of the filler content to obtain membranes with better gas separation performance. In consequence, a set of bare membranes prepared at different polymer concentrations was investigated for gas separation (see Table 1), while their performances are shown in Fig. 5A. In the current study, the total weight basis (of material to cast the membranes) has been changed from 3 g to 10 g, consequently the polymer content increased more than three times, resulting in thicker membranes that are expected to contain a low amount of defects. Besides, membranes prepared from low polymer concentrations (e.g. 1 wt.%) are thinner (see Table 1) due to the fact that the amount of casting solution is always the same, limited by the Petri dish volume. In any event, this higher amount of casting solution allows to enhance the separation performance of the bare polymer membrane, as shown below. In these conditions, the permeation analysis with such membranes revealed that the bare membrane corresponding to 5 wt.% of polymer composition (named as M5) produces better performance in terms of both CO_2 permeability and CO_2/N_2 selectivity which are 277

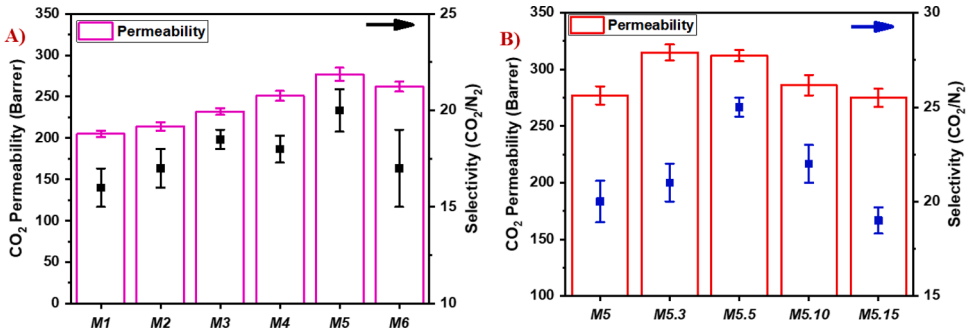

Fig. 5. Separation of the 15/85 CO_2/N_2 mixture at 35 °C: (A) optimization of polymer concentration, (B) optimization of MMMs.

Barrer and 20, respectively. Though an increasing trend of permeability and selectivity was observed for bare membranes having polymer content from 1 wt.% to up to 5 wt.% (CO_2 permeability augments from 205 ± 4 Barrer to 277 ± 8 Barrer and CO_2/N_2 selectivity from 16.0 ± 1.0 to 20.0 ± 1.0), beyond this, both parameters showed a significant downturn to 262 ± 6 Barrer and 17.0 ± 2.0 (for M6). However, in the previous work, the permeation performance of a 6 wt.% Pebax® 3533 bare membrane (on 3 g total wt. basis and dried at RT) corresponded to a CO_2 permeability of 83 ± 6 Barrer and a CO_2/N_2 selectivity of 9.0 ± 0.7 (Benzaqui et al., 2022). Pebax® 3533 polymer is more suitable than other Pebax codes due to its high content in PE with high affinity for CO_2 (e.g. PE/PA ratio is 75/25 and 55/45 Pebax® 3533 and 4533, respectively). This would improve the membrane performance in terms of both CO_2 permeability and CO_2/N_2 selectivity, since increasing the PE content significantly improves the affinity for CO_2 due to the interaction of polar ethylene oxide units with the high quadrupole moment of the highly polarizable CO_2 molecule (Kline et al., 2017). In contrast, the 10% MIL-178(Fe) and 15 wt.% MIL-178(Fe) based MMMs produced CO_2 permeabilities of 165 ± 4 Barrer and 210 ± 15 Barrer and CO_2/N_2 selectivities of 16.0 ± 0.7 and 14.0± 0.7, respectively (Benzaqui et al., 2022). Another empirical difference was related to the membrane drying temperature, this being RT in previous work (Benzaqui et al., 2022). With all these modifications (see Table 2), M5 having a higher polymer loading and improved drying condition at 40 °C in the oven for 24 h allowed the achievement of a better CCS performance. Additionally, the viscosity of the polymer solution of the bare membranes (M3 to M6) was measured at 25 °C (Fig. 6). The sharp rise of polymer viscosity from membrane samples M5 to M6 suggests that a higher homogeneity in the filler distribution could be achieved in the MMMs with the 5 wt.% polymer concentration. This is in agreement with what was observed by Martinez-Izquierdo, who also found that when there was a sudden increase in viscosity with the Pebax® 1657 solution concentration the CO_2 separation properties of the membrane were markedly worsened in terms of permeation and selectivity due to changes in the crystallinity extend of the polymer (Martínez-Izquierdo et al., 2019). Consequently, 5 wt.% polymer content (M5) can be considered as the optimum composition and was selected for subsequent MMMs fabrication.

Accordingly, in order to optimize the filler concentration, a set of MMMs were prepared by dispersing MIL-178(Fe) in 5 wt.% Pebax® 3533 (which are named in Table 1). These membranes were analyzed to reveal their gas separation performance as shown in Fig. 5B. Such

Table 2
Main changes in the membrane preparation conditions for optimum Pebax® 3533 membranes in this work and in previous report (Benzaqui et al., 2022).

	Previous	*This work*
Polymer + solvent amount	3 g	10 g
Polymer concentration	6 wt.%	5 wt.%
Polymer solution viscosity at 50 r.p.m. and RT	169 mPa·s	72 mPa·s
Drying temperature	RT	40 °C
Membrane thickness	43 μm	110 μm

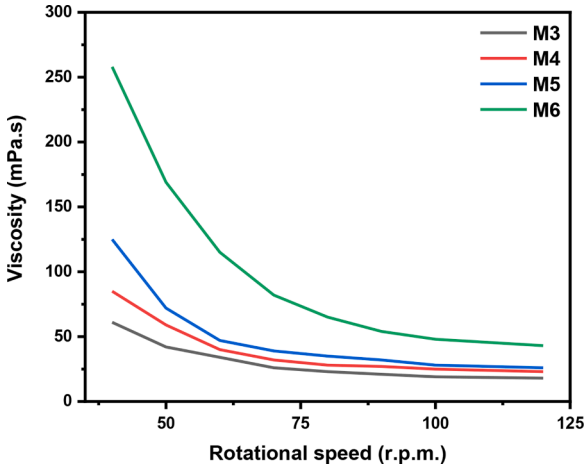

Fig. 6. Effect of polymer concentration on the viscosity of the polymer solution at RT.

MMMs produced improved separation in terms of CO_2 permeability for MMMs M5.3, M5.5 and M5.10 compositions compared to the bare membrane (M5). However, membranes M5.3 and M5.5 showed similar CO_2 permeability (14% and 12% overperformed compared to the bare membrane, respectively) considering both permeability and selectivity, MMM M5.5 outperformed (CO_2 permeability improved by 12% and CO_2/N_2 selectivity enhanced by 25%) the bare membrane (M5). Moreover, 10 and 15 wt.% MIL-178(Fe) based MMMs show a decrease of both permeability and selectivity (with values even smaller than those of the bare membrane M5). Considering both CO_2 permeability and CO_2/N_2 selectivity, M5.5 is the best performing membrane containing MIL-178 (Fe) filler and Pebax® 3533 matrix. Membranes with their CO_2/N_2 separation performance and thicknesses are shortlisted in Table 3. In addition, an aging test of the best MMM (M5.5) was performed over 35 days where both the CO_2 permeability (decreasing from 308 to 249 Barrer) and CO_2/N_2 selectivity (decreasing from 25 to 17) deteriorated over time as shown in Table S1. In general, the membrane was removed from the membrane module every time it was tested. The loss of performance can be due to both the stabilization of the membrane components and the adsorption of some impurity (including moisture) not removable after applying the cleaning treatment (drying at 40 °C for 2 h). In any event, the membrane was stabilized at ca. 250 Barrer of CO_2 permeability and a CO_2/N_2 selectivity of 17 upon 35 days of accumulated testing.

Concerning the role of PCP MIL-178(Fe) in the MMM improved separation ability, it has been demonstrated that its structure with narrow pore channels (pore diameter < 0.45 nm) and decorated with polar groups (μ_2-OH and –CO_2H functionalities) favors the selective adsorption of CO_2 and in turn the CO_2 separation ability of the MMMs containing it (Benzaqui et al., 2022). Moreover, time lag experiments

Table 3
Separation of the 15/85 CO_2/N_2 and 50/50 CO_2/CH_4 mixtures at 35 °C of bare membranes and MMMs.

CO_2/N_2 separation			
Membranes	**Thickness (μm)**	**Permeability CO_2 (Barrer)**	**Selectivity CO_2/N_2**
M1	38 ± 2	205 ± 4	16.0 ± 1.0
M2	55 ± 4	214 ± 5	17.0 ± 1.0
M3	75 ± 5	232 ± 4	18.5 ± 0.5
M4	88 ± 4	251 ± 6	18.0 ± 0.7
M5	110 ± 5	277 ± 8	20.0 ± 1.1
M6	128 ± 6	262 ± 6	17.0 ± 2.0
M5.3	114 ± 3	315 ± 7	21.0 ± 1.0
M5.5	116 ± 8	312 ± 5	25.0 ± 0.5
M5.10	119 ± 4	286 ± 9	22.0 ± 1.0
M5.15	123 ± 6	275 ± 8	19.0 ± 0.7
CO_2/CH_4 separation			
Membranes	**Thickness (μm)**	**Permeability CO_2 (Barrer)**	**Selectivity CO_2/CH_4**
M5	110 ± 5	259 ± 4	4.6 ± 0.8
M5.5	116 ± 8	295 ± 7	8.7 ± 1.3

depicted an important increase of the CO_2 solubility of the Pebax® 3533 polymer based MMM when incorporating MIL-178(Fe) (Benzaqui et al., 2022). This compensates the loss of CO_2 diffusivity observed giving rise to the increase of separation performance already discussed.

3.2.2. CO_2/CH_4 gas permeation measurement

MMM with the optimum concentration of MIL-178(Fe) (5 wt.%) and Pebax® 3533 was investigated for CO_2/CH_4 separation. The MMM (M5.5) was efficient and outperformed the bare membrane (M5) (Table 3 and Fig. S3). This MMM was found to improve the CO_2 permeability and CO_2/CH_4 selectivity by 14% and 89%, respectively, in comparison to the bare membrane (M5). CO_2 permeability and CO_2/CH_4 selectivity of the bare membrane were 259 ± 4 Barrer and 4.6 ± 0.8, respectively, whereas, for MMM both parameters were 295 ± 7 Barrer and 8.7 ± 1.3, respectively. Even if CH_4 (kinetic diameter of 0.38 nm) is a larger molecule than N_2 (0.364 nm) and CO_2 (0.33 nm), which would penalize its diffusivity through the membrane (particularly when filled it with the narrow pore material MIL-178(Fe)), the expected larger CH_4 membrane solubility (probably increased in the MMM by the PCP) due to its easy condensability reduces the separation selectivity of CO_2/CH_4 as compared to that of CO_2/N_2.

Finally Fig. S4 shows the comparison of the MMM performance with the corresponding upper bounds for the two studied mixtures (Robeson, 2008).

4. Conclusions

Porous coordination polymer MIL-178(Fe) was incorporated in Pebax® 3533 matrix after the optimization of the polymer concentration to achieve an efficient CO_2/N_2 separation. Due to the good MIL-178(Fe)-polymer compatibility, defect free MMMs with good filler distribution were obtained as confirmed by SEM and zeta potential analyses. An optimized bare polymer membrane (5 wt.% of Pebax® 3533) was prepared by finely tuning different parameters such as the polymer solution viscosity, membrane thickness and drying conditions. This gave rise to an efficient gas separation performance with CO_2 permeability and CO_2/N_2 selectivity of 277 ± 8 Barrer and 20.0 ± 1.1, respectively. These conditions for the preparation of the bare membranes constituted the starting point for the preparation of MMMs. In consequence, the optimum loading of filler was obtained at 5 wt.% in the best matrix composition. This MMM outperformed the bare membrane in terms of both CO_2 permeability (312 ± 5 Barrer) and CO_2/N_2 selectivity (25.0 ± 0.5) by 12% and 25%, respectively. Interestingly, MIL-178(Fe) improved the separation performance of the MMM due to its chemical composition (with CO_2-philic groups) and narrow microporosity (pore diameter < 0.45 nm) which increases the CO_2 solubility of the Pebax® 3533 polymer based MMM, compensating the loss of CO_2 diffusivity. Additionally, the optimized MMM was applied for CO_2/CH_4 separation and compared with the bare polymer membrane where MMM was also found efficient to improve the CO_2 permeability and CO_2/CH_4 selectivity (lower than that corresponding to the CO_2/N_2 mixture because of the CH_4 large condensability as compared to that of N_2) by 14% and 89%, respectively.

CRediT authorship contribution statement

Md Rafiul Hasan: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Heng Zhao:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Nathalie Steunou:** Conceptualization, Writing – original draft, Writing – review & editing. **Christian Serre:** Conceptualization, Writing – original draft, Writing – review & editing. **Magdalena Malankowska:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Carlos Téllez:** Conceptualization, Writing – original draft, Writing – review & editing, Funding acquisition, Supervision. **Joaquín Coronas:** Conceptualization, Writing – original draft, Writing – review & editing, Funding acquisition, Supervision.

Declaration of Competing Interest

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

Data Availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ijggc.2022.103791.

References

Benzaqui, M., Wahiduzzaman, M., Zhao, H., Hasan, M.R., Steenhaut, T., Saad, A., Marrot, J., Normand, P., Grenèche, J.M., Heymans, N., de Weireld, G., Tissot, A., Shepard, W., Filinchuk, Y., Hermans, S., Carn, F., Manlankowska, M., Téllez, C., Coronas, J., Maurin, G., Steunou, N., Serre, C., 2022. A robust eco-compatible microporous iron coordination polymer for CO_2 capture. J. Mater. Chem. A Mater. 10, 8535–8545. https://doi.org/10.1039/d1ta10385g.

Choi, W.J., Seo, J.B., Jang, S.Y., Jung, J.H., Oh, K.J., 2009. Removal characteristics of CO_2 using aqueous MEA/AMP solutions in the absorption and regeneration process. J. Environ. Sci. 21, 907–913. https://doi.org/10.1016/S1001-0742(08)62360-8.

COP26: green technologies could turn the tide. Nat. Rev. Mater. 6, 2021, 959. https://doi.org/10.1038/s41578-021-00390-0.

Dai, Z., Noble, R.D., Gin, D.L., Zhang, X., Deng, L., 2016. Combination of ionic liquids with membrane technology: a new approach for CO_2 separation. J. Membr. Sci. 497, 1–20. https://doi.org/10.1016/j.memsci.2015.08.060.

Ehsani, A., Pakizeh, M., 2016. Synthesis, characterization and gas permeation study of ZIF-11/Pebax® 2533 mixed matrix membranes. J. Taiwan Inst. Chem. Eng. 66, 414–423. https://doi.org/10.1016/j.jtice.2016.07.005.

Etxeberria-Benavides, M., David, O., Johnson, T., Łozińska, M.M., Orsi, A., Wright, P.A., Mastel, S., Hillenbrand, R., Kapteijn, F., Gascon, J., 2018. High performance mixed matrix membranes (MMMs) composed of ZIF-94 filler and 6FDA-DAM polymer. J. Membr. Sci. 550, 198–207. https://doi.org/10.1016/j.memsci.2017.12.033.

Gökpinar, S., Diment, T., Janiak, C., 2017. Environmentally benign dry-gel conversions of Zr-based UiO metal-organic frameworks with high yield and the possibility of solvent re-use. Dalton Trans. 46, 9895–9900. https://doi.org/10.1039/c7dt01717k.

Gong, X., Wang, Y., Kuang, T., 2017. ZIF-8-based membranes for carbon dioxide capture and separation. ACS Sustain. Chem. Eng. 5, 11204–11214. https://doi.org/10.1021/acssuschemeng.7b03613.

Hasan, M.R., Paseta, L., Malankowska, M., Téllez, C., Coronas, J., 2021. Synthesis of ZIF-94 from recycled mother liquors: study of the influence of its loading on postcombustion CO_2 capture with Pebax based mixed matrix membranes. Adv. Sustain. Syst. https://doi.org/10.1002/adsu.202100317, 2100317.

Hu, L., Clark, K., Alebrahim, T., Lin, H., 2022. Mixed matrix membranes for post-combustion carbon capture: from materials design to membrane engineering. J. Membr. Sci. https://doi.org/10.1016/j.memsci.2021.120140, 120140.

Japip, S., Xiao, Y., Chung, T.S., 2016. Particle-size effects on gas transport properties of 6FDA-durene/ZIF-71 mixed matrix membranes. Ind. Eng. Chem. Res. 55, 9507–9517. https://doi.org/10.1021/acs.iecr.6b02811.

Karamouz, F., Maghsoudi, H., Yegani, R., 2016. Synthesis and characterization of high permeable PEBA membranes for CO_2/CH_4 separation. J. Nat. Gas Sci. Eng. 35, 980–985. https://doi.org/10.1016/j.jngse.2016.09.036.

Kheirtalab, M., Abedini, R., Ghorbani, M., 2020. A novel ternary mixed matrix membrane comprising polyvinyl alcohol (PVA)-modified poly (ether-block-amide) (Pebax®1657)/graphene oxide nanoparticles for CO_2 separation. Process Saf. Environ. 144, 208–224. https://doi.org/10.1016/J.PSEP.2020.07.027.

Kline, G.K., Weidman, J.R., Zhang, Q., Guo, R., 2017. Studies of the synergistic effects of crosslink density and crosslink inhomogeneity on crosslinked PEO membranes for CO_2-selective separations. J. Membr. Sci. 544, 25–34. https://doi.org/10.1016/j.memsci.2017.09.002.

Martínez-Izquierdo, L., Malankowska, M., Sánchez-Laínez, J., Téllez, C., Coronas, J., 2019. Poly(ether-block-amide) copolymer membrane for CO_2/N_2 separation: the influence of the casting solution concentration on its morphology, thermal properties and gas separation performance. R. Soc. Open Sci. 6 https://doi.org/10.1098/rsos.190866.

Martínez-Izquierdo, L., Malankowska, M., Téllez, C., Coronas, J., 2021. Phase inversion method for the preparation of Pebax® 3533 thin film membranes for CO_2/N_2 Separation. J. Environ. Chem. Eng. 9 https://doi.org/10.1016/j.jece.2021.105624.

Merkel, T.C., Lin, H., Wei, X., Baker, R., 2010. Power plant post-combustion carbon dioxide capture: an opportunity for membranes. J. Membr. Sci. 359, 126–139. https://doi.org/10.1016/j.memsci.2009.10.041.

Meshkat, S., Kaliaguine, S., Rodrigue, D., 2020. Comparison between ZIF-67 and ZIF-8 in Pebax® MH-1657 mixed matrix membranes for CO_2 separation. Sep. Purif. Technol. 235, 116150 https://doi.org/10.1016/j.seppur.2019.116150.

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

Nasir, R., Hasan, Md.R., Chowdhury, S., 2021. Synthesis and applications of polymer nanocomposites matrices: a perspective. Handbook of Polymer and Ceramic Nanotechnology. Springer International Publishing, pp. 1–21. https://doi.org/10.1007/978-3-030-10614-0_77-1.

Pardo, F., Zarca, G., Urtiaga, A., 2021. Effect of feed pressure and long-term separation performance of Pebax-ionic liquid membranes for the recovery of difluoromethane (R32) from refrigerant mixture R410A. J. Membr. Sci. 618, 118744 https://doi.org/10.1016/J.MEMSCI.2020.118744.

Robeson, L.M., 2008. The upper bound revisited. J. Membr. Sci. 320, 390–400. https://doi.org/10.1016/j.memsci.2008.04.030.

Sánchez-Laínez, J., Zornoza, B., Friebe, S., Caro, J., Cao, S., Sabetghadam, A., Seoane, B., Gascon, J., Kapteijn, F., Le Guillouzer, C., Clet, G., Daturi, M., Téllez, C., Coronas, J., 2016. Influence of ZIF-8 particle size in the performance of polybenzimidazole mixed matrix membranes for pre-combustion CO_2 capture and its validation through interlaboratory test. J. Membr. Sci. 515, 45–53. https://doi.org/10.1016/j.memsci.2016.05.039.

Sasikumar, B., Bisht, S., Arthanareeswaran, G., Ismail, A.F., Othman, M.H.D., 2021. Performance of polysulfone hollow fiber membranes encompassing ZIF-8, SiO_2/ZIF-8, and amine-modified SiO_2/ZIF-8 nanofillers for CO_2/CH_4 and CO_2/N_2 gas separation. Sep. Purif. Technol. 264 https://doi.org/10.1016/j.seppur.2021.118471.

Seddigh, E., Azizi, M., Sani, E.S., Mohebbi-Kalhori, D., 2014. Investigation of poly(ether-b-amide)/nanosilica membranes for CO_2/CH_4 separation. Chin. J. Polym. Sci. 32, 402–410. https://doi.org/10.1007/s10118-014-1416-y (English Edition).

Xie, K., Fu, Q., Qiao, G.G., Webley, P.A., 2019. Recent progress on fabrication methods of polymeric thin film gas separation membranes for CO_2 capture. J. Membr. Sci. 572, 38–60. https://doi.org/10.1016/j.memsci.2018.10.049.

Yuan, J., Zhu, H., Sun, J., Mao, Y., Liu, G., Jin, W., 2017. Novel ZIF-300 mixed-matrix membranes for efficient CO_2 capture. ACS Appl. Mater. Interfaces 9, 38575–38583. https://doi.org/10.1021/acsami.7b12507.

Zhou, H.C., Long, J.R., Yaghi, O.M., 2012. Introduction to metal-organic frameworks. Chem. Rev. 112, 673–674. https://doi.org/10.1021/cr300014x.