Poly(ether-*block*-amide) Copolymer Membranes in CO$_2$ Separation Applications

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ABSTRACT: Poly(ether-*block*-amide) (PEBA, commercialized as Pebax) copolymer membranes show a highly promising platform for preparing high-performance membranes for CO$_2$ capture from process streams containing CH$_4$ and N$_2$. Pebax combines high CO$_2$ affinity with the desired mechanical strength for polymeric membranes thanks to its flexible polyether segment and hard polyamide block, respectively. Furthermore, researchers have been improving the performance of these membranes by preparing a thin Pebax selective layer on top of porous supports and by incorporating inorganic and organic nanofillers into the Pebax matrix to overcome the permeance-selectivity limit. The chemical and structural characteristics of Pebax membranes according to the different fabrication techniques and parameters are discussed first. Then, the recent developments in terms of both Pebax-based thin film composite and mixed matrix membranes are summarized. Finally, thermal and water stabilities of these membranes are addressed.
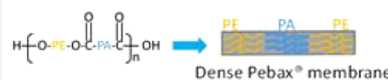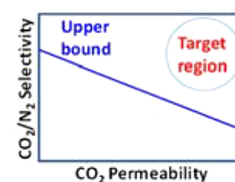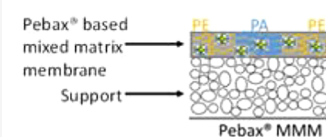
1. INTRODUCTION

Carbon dioxide, which is primarily produced as the main waste-product in combustion processes (e.g., fossil fuel power plant[1] or petrochemical[2]) and other industries (cement[3] and steel[4]), holds a major share in causing dramatic climate changes[5] and its impact can now be seen on the world panorama. An increase in the average surface temperature of the planet, rise in sea level, shrinking ice sheets, the retreat of glaciers, and the increase in the occurrence of extreme weather conditions are some manifestations of this climate change problem.[6] Therefore, it is essential to reduce the CO$_2$ emissions from all combustion sources. In addition, the separation and capture of CO$_2$ from CH$_4$ and N$_2$ gases is essential in natural gas sweetening, biogas upgrading, and compositional flue gas treatment to obtain a high-quality fuel.[5]

Postcombustion, precombustion, and oxyfuel combustion are the three main CO$_2$ capture systems related to different combustion processes. Postcombustion CO$_2$ capture, based on the separation of CO$_2$ from N$_2$, is the simplest and most feasible technology since it can be easily implemented to already existing industrial plants, including not only energy facilities but also intensive CO$_2$ producers such as the steel and cement industries. Currently, many conventional postcombustion separation technologies are applied for the separation of CO$_2$ from different gas mixtures, such as absorption, cryogenic distillation, and adsorption. Among these methods, chemical absorption with amine aqueous solutions is the most

developed process because of its high performance. However, conventional processes, even if commercially established, are cumbersome in terms of toxicity and economy as they require a gas to liquid phase change which increases the energy cost of the separation process significantly.[7−10]

As such, membrane-based gas separation technology, which is a simpler technology and an energy-efficient and environmentally friendly approach, has garnered attention of researchers in the last 2 decades. Unlike the conventional CO$_2$ separation technologies, the membrane process does not require a phase change, thus retains an inherent advantage of high energy efficiency and less operation cost. Moreover, it uses modules to build a compact system and offers good mechanical complexity, process flexibility, and simplicity during the operation and maintenance process.[11,12] Table 1 shows the comparison between different postcombustion carbon capture technologies.

Table 1 clearly indicates that membranes surpass other gas separation technologies in many aspects: such as in operating flexibility, reliability, low energy requirement, and no toxicity

Table 1. Comparison of Postcombustion Carbon Capture Technologies[8,10,13−15]

	gas separation technologies			
technology	absorption[a]	adsorption[a]	cryogenic distillation	membrane
operating flexibility	high	moderate	low	high
reliability	moderate	moderate	limited	100%
response to variation	rapid (5−15 min)	N/A	slow	instantaneous
control requirement	high	high	high	low
energy requirement	4−6 MJ/kgCO$_2$	2−3 MJ/kgCO$_2$	6−10 MJ/kgCO$_2$	0.5−6 MJ/kgCO$_2$
CO$_2$ recovery efficiency	90−98%	80−95%	>95%	80−90%
toxicity	emission of corrosive and harmful solvent	N/A	no solvent need	clean
operating temperature (°C)	50 (A) and 120 (R)	CFCMS 30 (A) and 60 (D)	−56.6 to −100	25 (polymeric) and 350 (ceramic)
operating pressure (atm)	2.24 (A) and 1 (R)	19.7 (A) and 1 (D)	7.4	1
TRL	9	7	7−8	3 (ceramic) and 7 (polymeric)

[a]A, R, D, CFCMS, and TRL represent absorption or adsorption, regeneration, desorption, carbon fiber composite molecular sieve, monoethanolamine, and technology readiness level, respectively.

to name a few. Thus, the objective of this review is to revise the state of the art regarding poly(ether-*block*-amide) (PEBA, commercialized as Pebax) membranes and their derivatives as mixed matrix membranes (MMMs) on the application of carbon dioxide capture, focusing on CO$_2$/CH$_4$ and CO$_2$/N$_2$ separation processes. The effect of various membrane fabrication parameters such as solvent selection, polymer type and concentration, solvent evaporation temperature, and membrane thickness on morphological properties of Pebax membranes are discussed. This serves as a basis for the subsequent discussion of CO$_2$ separation performance of Pebax membranes. Besides, the influence of various nanofillers on the performance of free-standing and supported Pebax MMMs are summarized. PEBA polymeric membranes constitute a recently emerging topic. In fact, Web of Science showed for the combined topic "membrane-polymer-CO$_2$" a cumulative number of 4611 publications until 2020 (482 and 156 in 2020 and 2010, respectively), while PEBA membranes for the same purpose accumulated 247 until 2020 (40 and 6 in 2020 and 2010, respectively).

2. MEMBRANES FOR GAS SEPARATION: A GENERAL OVERVIEW

According to the type of material, membranes can be classified into inorganic or organic (polymeric) films. The inorganic membrane substrates made from metal, metal oxide, ceramic, glass frit, silicate, carbon, zeolitic materials, etc. are in general thermally and chemically stable; however, they are expensive and fragile.[16−18] Organic membranes are those made of polymers and, despite their limited thermal, chemical, and mechanical stabilities, robustness, and relatively high sensitivity to aging and swelling compared to inorganic membranes, they have gained an increasing importance in gas separation applications due to their low capital cost of fabrication, good processability, ability to cope with high pressure-drops, long-term operation under mild conditions, and good scalability. Several kinds of polymers have been used for gas separation including both glassy (polysulfone (PSF), polyethersulfone (PES), polyetherimide (PEI), or polyimide (PI)) and rubbery (poly(dimethyl siloxane) (PDMS) or polyethylene (PE)). Pebax is a combination of both glassy and rubbery polymers and is the focus of this review and will be discussed later.[19]

In the gas separation processes, gas molecules pass through a membrane when a mixture of gases faces the high-pressure side of a membrane, due to the pressure difference between the two

sides. In a nonporous membrane, gas mixtures are fractionated in virtue of the difference in solubility and diffusivity in a polymer as an intrinsic material property (Figure 1). Such
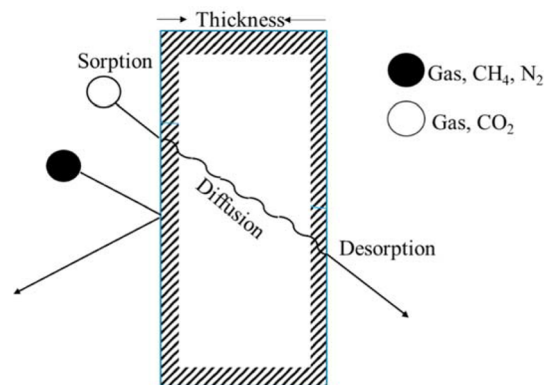

Figure 1. Schematic representation of gas transport mechanism through dense membrane. CO$_2$, N$_2$, and CH$_4$ kinetic diameters are 0.33, 0.364, and 0.38 nm, respectively; this together with the high affinity of PEBA polymer to CO$_2$ means that the CO$_2$ molecule is favored over the others both from the point of view of solubility and diffusivity when dealing with the CO$_2$/N$_2$ and CO$_2$/CH$_4$ mixtures.

transport is described by a solution-diffusion mechanism which is dominant in gas separation applications.[20,21] The relationship of the solubility and diffusion of this model with the parameters (permeability (P_i) and selectivity (α_{ij})) that mark the performance of the membrane on gas separation can be seen in the Supporting Information.

Moreover, membranes can be further grouped into symmetric (dense) and asymmetric structures (Figure 2). Symmetric membranes are made of several to tens of micrometers thick, dense, homogeneous structures with identical physical and chemical characteristics throughout their thickness. Asymmetric membranes have a distinct, thin, dense, selective skin supported by a thick porous support layer, thus exhibiting partially different chemical or physical structure in the surface and inner layers.[22] Although dense homogeneous symmetric membranes are used to investigate the performance of polymer materials, their relatively large thickness leads to lower gas fluxes compared to asymmetric membrane structures.[23]
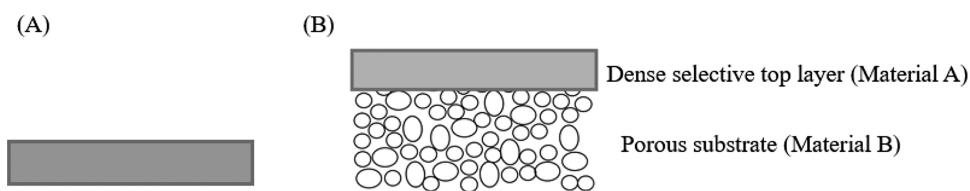
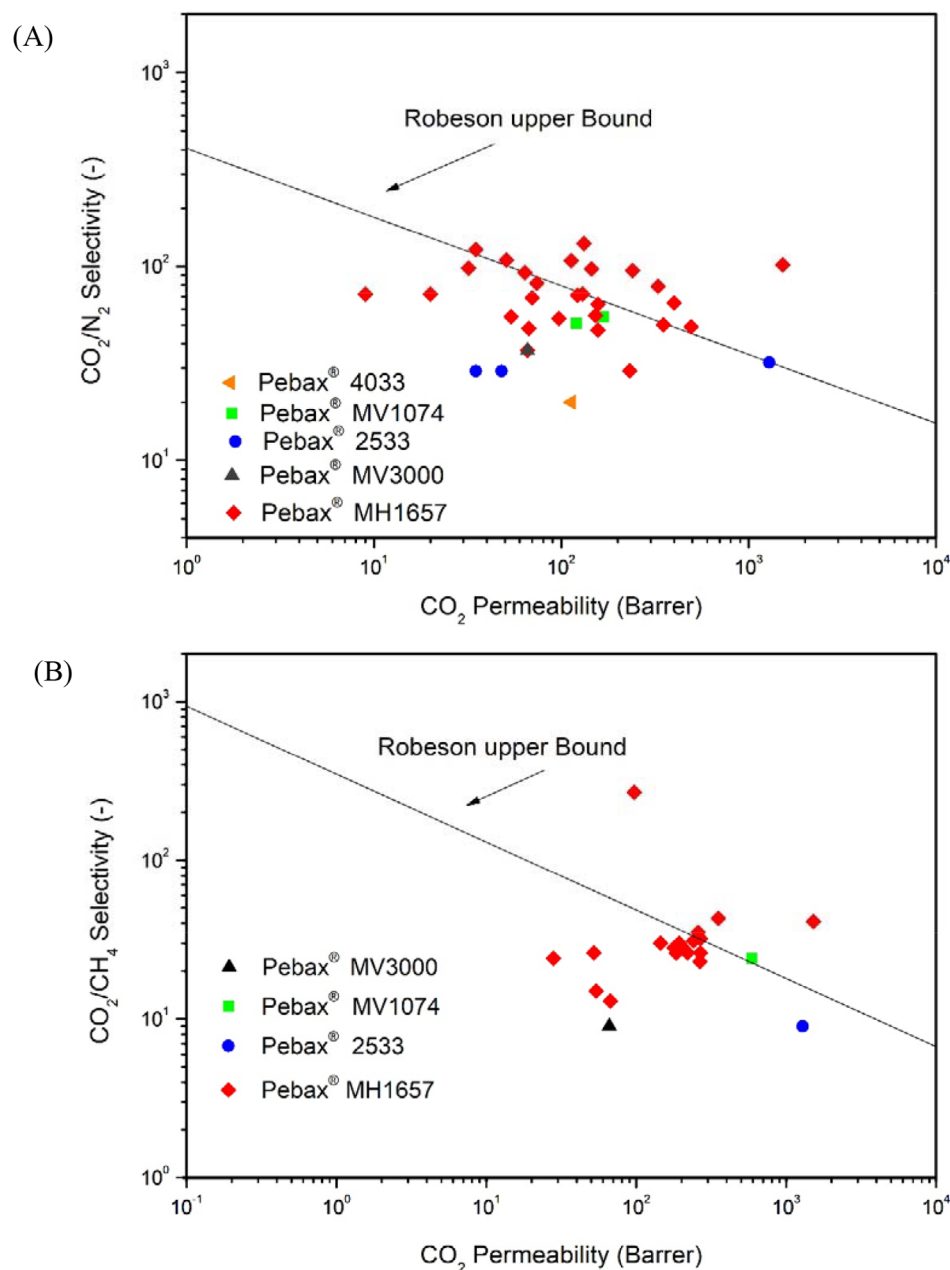**Figure 2.** Symmetric dense membrane (A) and asymmetric composite membrane (B).

Figure 3. Robeson upper bound plots for CO_2/N_2 (A) and CO_2/CH_4 (B) separation. See Tables 4−8 for additional details.

Even though membrane separation is in general a very attractive technology, it shows some limitations for the gas separation application. It has to be considered that an efficient CO_2 separation process needs polymers with high permeability to reduce the membrane area, excellent selectivity toward CO_2, and good stability and longer service time when exposed to a harsh environment. Unfortunately, the inherent trade-off between permeability and selectivity demonstrated by Robeson in 1991 and 2008 remains to be the biggest challenge in the development of polymeric membranes. Polymers with high permeability will exhibit low selectivity and vice versa.[24−26]

The Robeson upper bound (Figure 3) represents the most favorable combinations of permeability and selectivity values of Pebax membranes reported in the literature for CO_2/N_2 and

CO_2/CH_4 separations. Higher permeability leads to higher productivity and lowers capital cost due to minimum membrane area, whereas higher selectivity affords more efficient separations in a lesser number of stages, higher purity of end product, and lower power costs. Membranes that display high selectivity combined with a high permeability would lead to the most economical gas separation process. Numerous attempts have been made to overcome the undesirable trade-off relationship between permeability and selectivity, specifically in CO_2/CH_4 and CO_2/N_2 separations. One approach to beat this problem is to combine the flexibility of polymers such as poly(ethylene oxide) (PEO) with the mechanical stability of hard or crystalline polymers like polyamide (PA), polyimides (PI), and polystyrene (PS).[27] Among the many polymers studied, polyether block amide (PEBA) copolymers are considered some of the most promising materials.

3. PEBA-BASED MEMBRANES AS A CO_2 CAPTURE TECHNOLOGY

Polyether block amides commercialized under the trademark of Pebax are a series of novel thermoplastic elastomers comprised of rigid polyamide blocks (PA) and flexible polyether (PE) segments which are glassy and rubbery at room temperature, respectively.[28] The basic chemical formula of Pebax copolymers is depicted in Figure 4. Various grades of
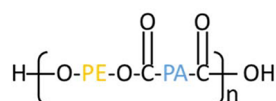
Figure 4. General chemical structure of Pebax copolymers.

Pebax copolymers are available in the marketplace, and they commonly possess high mechanical strength and good chemical stability. Table 2 shows the physical properties of several grades of Pebax copolymers applied as gas separation membranes.

Table 2. Physical Properties of Selected Pebax Copolymers Applied as Gas Separation Membranes for CO_2 Capture

Pebax grade	PE[a]	PA	PE:PA (wt %)	density (g/cm³)	melting point (°C)	ref
Pebax 2533	PTMO	PA12	80:20	1.01	134	29
Pebax 3533	PTMO	PA12	70:30	1.01	144	30
Pebax 4033	PTMO	PA12	53:47	1.01	160	29
Pebax 5533	PTMO	PA12	38:62	1.01	159	29
Pebax 6333	PTMO	PA12	24:76	1.01	169	31
Pebax 7033	PTMO	PA12	25:75	1.01	172	18,32
Pebax MH1657	PEO	PA6	60:40	1.14	204	33
Pebax MV1074	PEO	PA12	55:45	1.09	158	29
Pebax MV1041	PTMO	PA12	75:25	1.04	170	34,35

[a]PEO, poly(ethylene oxide) and PTMO, polytetramethylene oxide.

In this microbiphasic structure, the relative proportion of these alternating immiscible components and the interactions between them determine the properties of a given Pebax grade and offer interesting characteristics of end-use performance features. Besides, the PE phase of Pebax could be composed of either poly(ethylene oxide) (PEO) or polytetramethylene oxide (PTMO). Similarly, the PA phase can be comprised of 5 methyl units (PA6) or 11 methyl units (PA12). The chemical structures of PEO, PTMO, PA6, and PA12 are depicted in Figure 5.
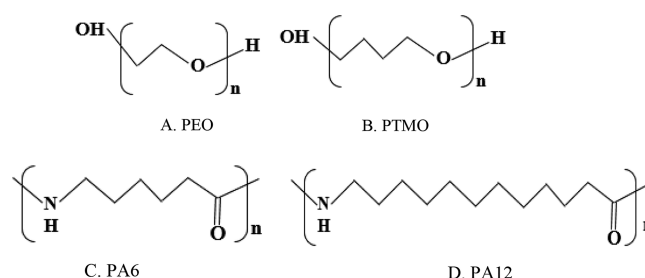
Figure 5. Poly(ethylene oxide), PEO (A); polytetramethylene oxide, PTMO (B); polyamide 6, PA6 (C); and polyamide 12, PA12 (D).

Recently, Pebax block copolymers have emerged as a potentially interesting material for CO_2 separation membranes. In fact, the special chemical composition of these polymers provides a relatively high CO_2 permselectivity in $CO_2/$nonpolar gas separations (e.g., CO_2/CH_4 or CO_2/N_2). The polar polyether block of Pebax, soft segment, has a strong affinity to CO_2 due to dipole−quadrupole interaction (related to properties of the permeating molecules such as critical temperature and kinetic diameters), whereas the polyamide hard segment mainly provides good mechanical strength to the material.[36,37] CO_2 possess the smallest kinetic diameter (0.33 nm) compared to N_2 (0.364 nm) and CH_4 (0.38 nm). Similarly, the gases retain critical temperatures of 304, 190, and 126 K for CO_2, CH_4, and N_2, respectively.

The CO_2 separation efficiency of pristine Pebax membranes and the effect of various parameters such as chemical structure, thickness, crystallinity, and thermal stability on the membrane performance have been studied in different reports.[38−41] Additionally, many already published studies have aimed at improving the properties of Pebax copolymers for gas separation, specifically in pre- and postcombustion processes. Membranes based on chemically modified or cross-linked polymers and nanocomposite membranes with organic or inorganic dispersed fillers are the outcomes of such studies.[42−46]

3.1. Properties and Fabrication of Pebax Membranes. Generally, the fabrication of Pebax membranes starts by dissolving a known amount of Pebax pellets in a selected solvent at a certain temperature for a specified time.[47] The mixture is kept under continuous stirring and reflux until it dissolves completely. Next, the membrane is usually prepared either by casting with a casting knife or by pouring the solution onto a Petri dish followed by a controlled drying to remove the solvent.[41] The film can further be subjected to vacuum drying for conditioning before permeation testing to remove any remaining solvent.[48]

As it can be observed from the fabrication process (Figure 6), several parameters such as polymer casting concentration, Pebax grade, the solvent used, or the solvent evaporation
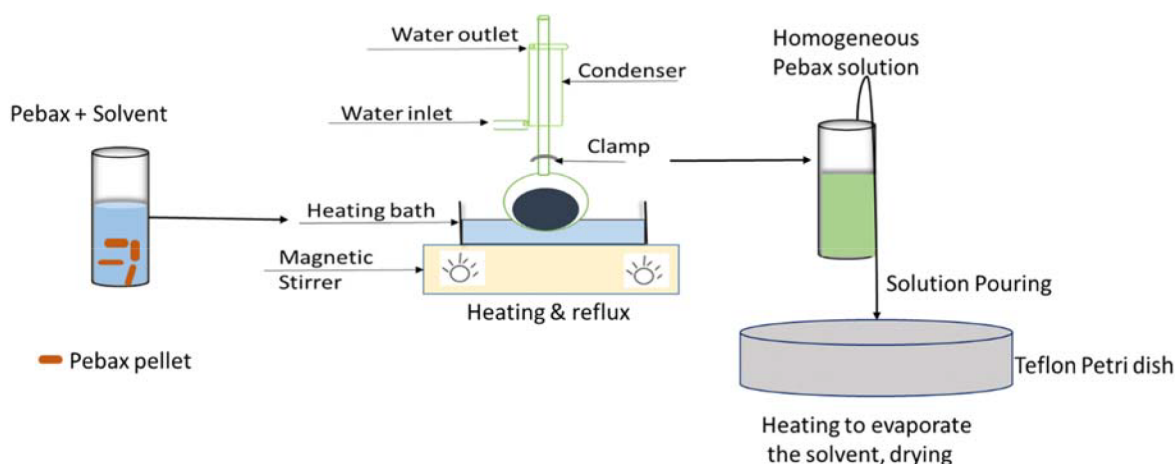
Figure 6. Fabrication of Pebax based membrane.

Table 3. Effect of Fabrication Conditions on Thermal and Crystallinity Properties of Pebax Membranes

Pebax grade	solvent used	Pebax concn (wt %)	evaporation temp (°C)	thickness (μm)	T_mPEO (°C)	T_mPA (°C)	crystallinity (%)	ref
Pebax MH1657	EtOH/H$_2$O	1	25	40	31	205	N/A	39
Pebax MH1657	EtOH/H$_2$O	3	25	40	33	204	N/A	39
Pebax MH1657	EtOH/H$_2$O	5	25	40	31	204	N/A	39
Pebax MH1657	EtOH/H$_2$O	6	70	N/A	N/A	N/A	40	47
Pebax MH1657	DMF	6	70	N/A	N/A	N/A	62	47
Pebax MH1657	NMP	6	70	N/A	N/A	N/A	65	47
Pebax MH1657	formic acid	6	70	N/A	N/A	N/A	42	47
Pebax MH1657	DMAc	6	70	N/A	N/A	N/A	70	47
Pebax MH1657	propanol/water	3	35	28 ± 0.5	11	206	44	41
Pebax MH1657	propanol/water	6	35	98 ± 0.5	13	206	36	41
Pebax MV1074	propanol/water	1	35	55 ± 0.5	8	155	33	41
Pebax MV1074	propanol/water	3	35	19 ± 0.5	6	152	42	41

temperature, to name a few, dictate the final microstructural and thermal characteristics of the film.

The first and probably the most crucial parameter that affects the fabrication and final behavior of Pebax membranes is the selection of a suitable solvent to dissolve the Pebax pellets. First requirement of the proper solvent is the ability to completely dissolve the selected Pebax grade. As shown below, the solvents or mixtures of them are generally polar, from the water/ethanol mixture applied to the most studied Pebax MH1657 to mixtures of alcohols or pure alcohols (e.g., *n*-butanol for Pebax 4033 with a less polar structure due longer PA12 segment instead of PA6 in Pebax MH1657) for others. Isanejad et al.[47] researched the effects of various casting solvents used on the morphology and structure of Pebax MH1657 membranes prepared. The authors reported the formation of defect-free dense films with distinct crystallinity according to the boiling point and Hansen solubility parameters (i.e., according to contributions from dispersion forces (D), polar interactions (P), and hydrogen bonding forces (H)) of the solvent used (DMAc, DMF, NMP, formic acid, and H$_2$O/EtOH). Membranes fabricated with dimethylacetamide (DMAc), dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) generally produced a crystalline structure dominated by the hard phase, whereas the structure of the films synthesized with formic acid and H$_2$O/EtOH mixture were mainly amorphous. Moreover, the polymer fractional free volume and *d*-spacing parameter increased with increasing solvent molar volume due to the transient template effect for all of the membranes, except for that fabricated with

DMAc. This phenomenon ascribes to the high boiling point and lowest solubility parameter difference between DMAc and Pebax MH1657. In another study, Karamouz et al.[40] reported a similar impact of solvent evaporation rate on the microstructure of Pebax MV1074. In this case, Pebax MV1074 membranes were prepared by dissolving the polymer in DMF at a 3 wt % casting solution concentration and changing the drying temperature, i.e., 60, 80, and 100 °C. The authors found that membranes fabricated at 100 °C demonstrated the presence of nonselective microvoids due to the rapid solvent evaporation.

To sum up, the selection of an appropriate solvent depends on the chemical composition and polarity of the Pebax segments. For instance, several solvents such as DMAc, DMF, NMP, formic acid, and water/ethanol mixture can evenly dissolve Pebax MH1657. Nevertheless, only a few solvents (formic acid and water/ethanol mixture) are able to form proper solution that avoids gelation at room temperature or beyond a certain concentration. This is ascribed to the existence of a more polar PA6 group in Pebax MH1657. However, due to the high cost and toxicity of formic acid, the water/ethanol mixture is the most commonly used solvent for preparing Pebax MH1657 solutions.[48] On the other hand, Pebax MV1074, which contains long PA12, is better dissolved in a single organic solvent such as DMF, NMP, or 1-butanol, since it has been found that Pebax MV1074 prepared with 1-propanol/water mixture exhibited a gelation effect at a polymer concentration higher than 1 wt % in the casting solution.[41] Moreover, Pebax 2533 that possess relatively less polar PA12

Table 4. CO_2/N_2 Separation Performance of Dense Pebax Membranes

Pebax grade	solvent	pressure (bar)	temperature (°C)	thickness (μm)	permeability CO_2(Barrer)	selectivity CO_2/N_2	ref
Pebax 4033	*n*-butanol	10	35	30	113	20	53
Pebax MH1657	*n*-butanol	10	35	30	66	56	53
Pebax MV1074	*n*-butanol	10	35	95	120	51	53
Pebax MV1074	1-propanol/water	13.8	35	53	168	55	41
Pebax MH1657	ethanol/water	13.8	35	98	147	89	41
Pebax MH1657	1-propanol/1-butanol	3	25	N/A	122	71	38
Pebax MH1657	1-propanol/1-butanol	3	45	N/A	157	47	38
Pebax MH1657	1-propanol/1-butanol	3	65	N/A	232	29	38
Pebax MH1657	DMF	10	30	110	67	48	33
PU/Pebax MH1657	DMF	10	30	110	54	55	33
Pebax MV3000	DMF	10	30	110	66	37	33

and PTMO segments can be easily dissolved in 1-butanol, ethanol, and ethanol/water 90/10.[48] Table 3 shows the influence that solvents and drying temperatures have on the crystallinity of different Pebax grades.

Other variables that affect the membrane performance are the polymer type, polymer concentration, and the ratio of PEO to PA in the polymeric matrix. Wang et al.[41] investigated the influence of these parameters on the architecture of Pebax MH1657 and Pebax MV1074 dense films prepared by the sol−gel method. During the fabrication process, top layers of the films prepared with a 6 wt % Pebax MH1657 concentration experienced faster sol-to-gel transition than those with lower Pebax MH1657 concentration in the casting solution at the same temperature. Compared to Pebax MH1657, Pebax MV1074 achieved a quicker sol−gel process due to its relatively longer PA12 chain. Rapid sol−gel transition encourages random chain packing in the bulk film and, thus, a less regular microstructure and higher gas permeability.

Recently, Martinez-Izquierdo et al.[39] studied the influence of the casting solution concentration (1, 3, and 5 wt % polymer in solution) on the morphology and thermal properties of Pebax MH1657 membranes. X-ray diffraction analysis proved the formation of a semicrystalline structure due to the presence of PA and PEO phases. An increase in crystallinity was observed with an increment in the amount of solvent in the casting solution. Similar to the previous work by Wang et al.,[41] this behavior was associated with the evaporation rate, as a greater amount of solvent was translated into longer evaporation time, which aided in the arrangement of the polymer thus obtaining a better-structured membrane. As a result of the trade-off between crystallinity and CO_2/N_2 separation properties, the membrane fabricated with 3 wt % polymer concentration was selected as the most appropriate for this application. Finally, the study confirmed the direct impact of crystallinity on improving thermal degradation.

Generally, it can be deduced that the following parameters lead to the formation of a more regularly structured film: (1) higher solvent concentration in the casting solution, (2) slow evaporation rate, (3) low solubility parameter difference between solvent and polymer, and (4) short PA length in the polymer. Therefore, the selection of a proper solvent, drying temperature, and composition of the casting solution are vitally important as far as gas separation performance of polymeric membranes relies on crystallinity, polymer morphology, and chemical microstructure of the film, all favoring the formation of a homogeneous dense PEBA membrane. Although it is hard to single out a specific parameter as the most crucial one, the solvent selection seems to have a

dominant impact on the fabrication of Pebax membranes. This is because the solvent property can dictate the solvent evaporation temperature, gelation, and viscosity of the solution, and thus, the final microstructure of the prepared film. Furthermore, due to the trade-off between crystallinity and gas permeability, a compromise seems inevitable between the above-mentioned parameters to achieve a good separation performance.

3.2. CO_2/N_2 Separation. Due to the relatively low concentration of CO_2 (typically 10−18 mol % in the flue gas from power plants, ~30 mol % in cement[49] and steel[50] facilities) to be treated, a membrane system with a high processing capacity and a sufficiently high permselectivity for CO_2/N_2 is required to compete with other separation techniques.[51] Ethylene oxide units have been reported to interact with CO_2 which results in high solubility selectivity.[52] As such, phase-separated block copolymer Pebax membranes have been widely considered for this application.[38,39,41,53] As mentioned before, these membranes usually possess high CO_2/nonpolar selectivity (e.g., CO_2/H_2 or CO_2/N_2) coupled with intrinsically higher CO_2 permeability due to the presence of polar ether oxygen atoms in the soft segment (PEO or PTMO) that result in good CO_2 affinity.

Bondar et al.[53] studied the CO_2/N_2 separation performance of several grades of Pebax copolymers (Pebax 2533, 4033, MV1074, and MH1657) at 35 °C of permeation temperature. During the study, high values of CO_2/N_2 selectivity (56) coupled with high CO_2 permeability coefficient (220 Barrer) were obtained for Pebax MH1657. Permeability properties were strongly dependent on the quantity and polarity of the PE component within the block copolymer. In copolymers with an equivalent chemical nature, gas permeability was increased as the percentage of polyether increased (i.e., from Pebax 4033 to Pebax 2533). Conversely, increasing the polarity of the polymer matrix by switching either or both of the segments to PEO or PA6 while maintaining the same concentration of both groups caused a decrease in the solubility of N_2, while carbon dioxide solubility remained unaffected. Therefore, higher CO_2/N_2 selectivity was obtained. This is often attributed to the increased cohesive energy density that hampers the diffusion and permeability of nonpolar gases such as N_2 and H_2. Kim et al.[38] confirmed this fact using different membranes made by solution-casting from four grades of Pebax (Pebax 2533, 3533, and 4033 and MH1657). A maximum CO_2 permeability of 142 Barrer was obtained using Pebax 2533 and dropped down to 110 Barrer for Pebax 4033 when the PA content increased from 20 to 47% (see Table 2).

Table 5. CO_2/CH_4 Separation Performance of Dense Pebax Membranes

Pebax grade	solvent	pressure (bar)	temperature (°C)	thickness (μm)	permeability CO_2(Barrer)	selectivity CO_2/CH_4	ref
Pebax MV1074	DMF	7	30	60	591	24	40
Pebax MV3000	DMF	10	30	110	66	8.6	33
Pebax MH1657	DMF	10	30	110	67	13	33
PU/Pebax MH1657	DMF	10	30	110	54	15	33
Pebax MH1657	ethanol/water	2	20	60	179	28	54
Pebax MH1657	ethanol/water	7	20	60	185	26	54
Pebax MH1657	ethanol/water	10	20	60	194	30	54
Pebax MH1657	ethanol/water	12	20	60	241	31	54
Pebax MH1657	ethanol/water	15	20	60	226	23	54

In a gas permeation experiment carried out by Wang et al.[41] membranes based on Pebax MH1657 displayed a higher CO_2/N_2 selectivity (89) than those composed of Pebax MV1074 (84) at the same conditions due to the microstructural feature of the dense films, discussed in the section of Pebax properties. Overall, the separation performance of Pebax based membranes mainly depends on the percentage and type of rigid and flexible segments in the block copolymer. Table 4 shows the CO_2/N_2 separation performance of some dense Pebax membranes found in the literature.

In another study, Mozaffari et al.[33] separated CO_2 from a mixture of CO_2/N_2 at 30 °C and 10 bar using dense membranes based on a polyurethane/poly(ether-*block*-amide) (PU/PEBAX MH1657) blend. A substantial improvement in CO_2/N_2 selectivity ascribed to the increase in polarity of the blend matrix, and a subsequent decrease in the interaction with and permeation of nonpolar molecules was observed with the increase in Pebax MH1657 percentage in the polymer blend structure. Another reason for the decrease in gas permeability of membranes was the higher crystallinity of Pebax and less phase separation between its soft and hard segments.

Furthermore, as it can be seen from Table 4, the separation performance of Pebax membranes is also affected by the operating temperature (in the 30−65 °C range). A rise in permeation temperature leads to a significant decrease in CO_2/N_2 selectivity, mainly ascribed to the decrease in solubility selectivity while the diffusivity selectivity does not change much.[38]

3.3. CO_2/CH_4 Separation. Some membrane researchers have also attempted to utilize Pebax based membranes for the separation of CO_2 from CH_4. Karamouz et al.[40] prepared Pebax MV1074 membranes by the solvent the evaporation technique with DMF as the solvent and investigated the influence of solvent evaporation temperature in the CO_2/CH_4 separation performance. Single gas permeation experiments indicated that CO_2 permeability and CO_2/CH_4 ideal selectivity increased with the feed pressure and decreased with temperature, due to the high solubility and plasticizing effect of CO_2 at higher pressures. However, a considerable decrease in selectivity was observed with operating temperature increment. Membranes fabricated at 80 °C demonstrated the best performance with a maximum CO_2/CH_4 selectivity of 24 and a CO_2 permeability of 591 Barrer at 7 bar and 30 °C. Table 5 shows the CO_2/CH_4 separation performance of selected dense Pebax membranes found in the literature.

Mozaffari et al.[33] studied the CO_2/CH_4 separation performance of (PU/PEBA) (0−80 wt % Pebax MH1657) blend dense membranes synthesized by thermal phase inversion. The high weight percent (80 wt %) of Pebax MH1657 in the blend solution leads to a more crystalline structure which diminishes the gas permeability of the membrane (see Table 5). On the contrary, selectivity tends to increase with the rise in crystallinity due to the relatively minor decrease in CO_2 permeability. Again, an increment in the amount of Pebax introduces more polarity to the membrane structure and consequently reduces the permeation of nonpolar molecules. Chemical characteristics and thermal properties of the casting solvent exerted a strong influence on the free volume, chain packing, and crystallinity of the film structure, greatly affecting the CO_2/CH_4 separation performance of Pebax MH1657.[47]

An interesting approach is to blend Pebax with ionic liquids (IL) that can facilitate the CO_2 transport. To prepare gel membranes, Bernardo et al.[55] blended a room temperature ionic liquid $[BMIM][CF_3SO_3]$ using percentages of 0−80 wt % with different Pebax grades. In general, the results of these authors showed that Pebax 2533 was not significantly affected, while in the case of Pebax MH1657 the CO_2 permeability increased at the cost of a certain decrease in selectivity. Following the previous work with Pebax MH1657, Estahbanati et al.[56] used $[BMIM][BF_4]$ ionic liquid. In the blended membrane containing 50 wt % IL, the authors obtained a CO_2 permeability of 190 Barrer (100 Barrer pure polymer), CO_2/CH_4 ideal selectivity of 24 (21 pure polymer), and CO_2/N_2 ideal selectivity of 106 (79 pure polymer).

In summary, the solvent evaporation temperature highly affects the CO_2/CH_4 separation performance of Pebax membranes. This is because a higher evaporation temperature creates irregular microstructures and thus lowers the separation selectivity. Therefore, as mentioned in previous sections, the selection of an appropriate solvent and a controlled (slow) evaporation process are necessary to achieve a good separation performance. Moreover, CO_2/CH_4 separation performance of Pebax membranes can be enhanced by blending Pebax copolymers with other polymers such as PU. Through blending, the microstructural behavior of Pebax copolymers can be modified due to the interaction between the two polymers.

4. PEBA-BASED COMPOSITE MEMBRANES FOR CO_2 CAPTURE

Improvements in polar/nonpolar gas selectivity of dense Pebax membranes by tailoring the segment ratio of PA over PE confirmed the potential of Pebax as one of the best materials for gas separation applications. However, the low permeance of its pristine dense film prevents it from being an economically attractive membrane material at the industrial-scale. This variable is not only related to the membrane permeability but to its thickness as well. A practical membrane with high permeance (P_i/l, see the definition in the Supporting Information) without compromising the selectivity can only

be fabricated by making the selective polymer layer as thin as possible (i.e., in the tens to few hundreds of nanometers scale). The typical structure of a multilayer composite membrane can be seen in Figure 7.
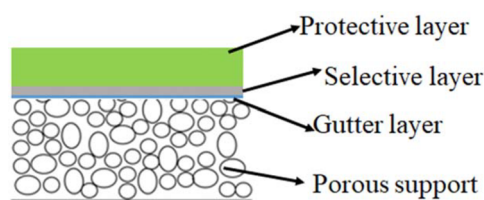

Figure 7. Typical structure of a multilayer composite membrane.

Figure 8. Dip coating (A), spin coating (B), and solution casting (C) techniques.

A thin-film composite (TFC) membrane which entails the coating of a defect-free thin selective layer onto a highly permeable porous substrate with sufficient mechanical strength (provided by a highly permeable support) may help in achieving the goal of high selectivity and permeance at the same time.[48]

A typical TFC is composed of (i) a porous layer that serves as a mechanical support introducing a minimum limit to the mass transfer thanks to its pores, (ii) a very thin selective layer, for the selective separation of a gas mixture, and (iii) a protective layer that is added in order to control the membrane performance by avoiding any possible cracks or defects on the selective layer surface (again without adding any transport resistance). Moreover, recently, a very common procedure is to add a gutter layer in between the porous support and the selective layer to prevent the penetration of the coating solution into the pores of the support.[57−59] Pore filling prompts an increase in the thickness of the selective layer and hence a decline in membrane permeance.[58] Highly gas permeable polydimethylsiloxane (PDMS) and poly(1-(trime-thylsilyl)-1-propyne) (PTMSP) coatings are the most commonly used gutter layers in a TFC membrane fabrication. The ideal gutter layer material should be characterized by a high permeability to gas, thus providing the perfect interface to decrease the TFC thickness down to 2−20 nm,[60] as recently achieved with Pebax MH1657 coated on oxygen plasma treated PDMS.[61] Moreover, support and selective top layers can be separately optimized to achieve a high performing composite membrane.

There are a variety of methods used for the TFC preparation. Different coating techniques such as dip-coating, spin coating, solution-casting, and interfacial polymerization are used to fabricate high-performance, ultrathin, and defect-free layers on top of a porous support.[59] Figure 8 presents a schematic illustration of some of the coating techniques.

According to the technique used, it is important to take into account that the solvent to be used should not affect the porous support; in this sense, the use of water/ethanol mixtures instead of other organic solvents is of interest since most of the common supports resist this mixture. Apart from these methods, a recent work by Sánchez-Laínez at al.[55] considers the phase inversion method as a route to coat Pebax selective layers on top of an asymmetric support. This method consists of the preparation of an emulsion of Pebax MV1041 in water and its subsequent coating on a PSF support by drop casting. With this procedure, the authors were able to obtain a similar gas separation performance when compared to the conventional solvent-evaporation technique (with CO_2 per-
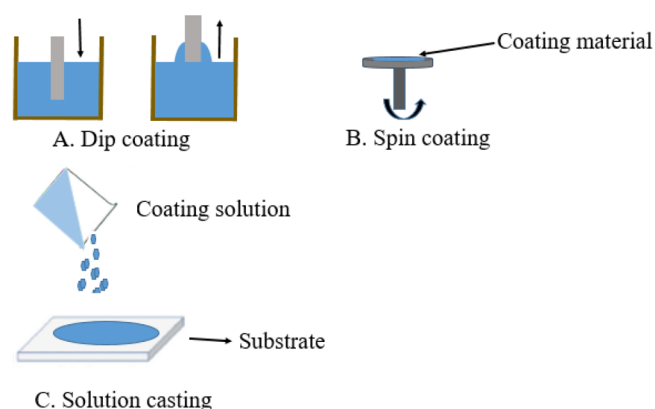
meabilities between 25 and 35 Barrer and a CO_2/N_2 selectivity of 21) but with the advantage of being a greener method, as the formation of toxic DMAc vapors is avoided during membrane preparation.

Pebax copolymers have gained a good reputation as suitable coating materials to prepare a selective top layer for fabricating composite membranes. So far, only a handful of polymeric micro and ultrafiltration membranes, such as PSF, PEI (poly(ether imide)), PVDF (polyvinylidene fluoride), or PAN (polyacrylonitrile), have been reported as porous supports to prepare membranes in the form of thin-film composites. CO_2/N_2 and CO_2/CH_4 separation performances of selected composite membranes based on Pebax as a selective layer are described in the next two sections.

4.1. CO_2/N_2 Separation. Ren et al.[62] prepared a multilayer PEI/PDMS/Pebax MH1657/PDMS composite membrane for high-performance CO_2 separation. The PDMS gutter and protective layers (i.e., PDMS was applied for the two purposes just mentioned) were introduced to prevent the pore penetration of Pebax MH1657 solution into the PEI support membrane and to seal the defects of the Pebax MH1657 selective layer, respectively, thus, enhancing the permeance and selectivity for CO_2 separation. With the PEI/PDMS/Pebax MH1657 membrane that was fabricated without coating of a selective layer with PDMS, a CO_2 permeance of 172 GPU and a CO_2/N_2 selectivity of 47 were achieved at 25 °C and 5 atm. Coating with a PDMS protective layer enhanced the CO_2/N_2 selectivity (64) while reducing the CO_2 permeance down to 157 GPU. The reduction in CO_2 permeance was attributed to the increase in the membrane total thickness due to a coating with a protective layer. The CO_2 induced plasticization effect was highly pronounced during the separation process. As a result, for CO_2/N_2 gas mixture separation, high permeate pressure is always required to obtain a high CO_2 concentration for flue gas.

Besides, Wang et al.[58] separately modified the selective and gutter layers to significantly improve the performance of the Pebax MH1657/amino-PDMS/PAN composite membrane. Multilayer composite membrane with cross-linked amino-PDMS silicone rubber gutter layer exhibited a CO_2 permeance of 350 GPU and a CO_2/N_2 selectivity over 50. The selective Pebax MH1657 coating solution was blended with poly-ethylene glycol-dimethyl ether (PEG-DME) to further improve the performance of the composite membrane. CO_2 permeance of the final Pebax-PEG-DME/amino-PDMS/PAN composite membrane reached 400 GPU with CO_2/N_2 selectivity over 65.

Table 6. CO_2/N_2 Separation Performance of Different Pebax Composite Membranes Prepared over Different Substrates[38,47]

Pebax grade	support	temperature (°C)	pressure (bar)	thickness (μm)	permeance CO_2(GPU)	selectivity CO_2/N_2	ref
Pebax MH1657	PAN (PDMS gutter layer)	20	5	<1	350	50	58
Pebax MH1657	PAN (PDMS gutter layer)	20	5	<1	400	65	58
Pebax MH1657	PAN (PDMS gutter layer)	25	2	0.002−0.02	1200−3500	72−23	61
Pebax MH1657	PEI (PDMS gutter and protective layer)	25	5	0.5	157	64	62
Pebax 2533	PEI	23	7.9	N/A	48	29	51
Pebax 2533	PSF	25	3.5	N/A	35	29	64
Pebax 3533	PSF	35	3	0.7	127	21	65

Table 7. CO_2/CH_4 Separation Performance of Different Pebax Composite Membranes Prepared over Different Substrates

Pebax grade	support	temperature (°C)	pressure (bar)	thickness (μm)	permeance CO_2(GPU)	selectivity CO_2/CH_4	ref
Pebax MH1657	PVC	20	5	20	10	28	54
Pebax MH1657	PVC	20	7	20	11	26	54
Pebax MH1657	PVC	20	10	20	13	35	54
Pebax MH1657	PVC	20	12	20	14	32	54
Pebax MH1657	PVC	20	15	20	14	26	54
Pebax MH1657	PES	25	4	0.5	28	24	69
Pebax MH1657	PEI	25	4	0.52	52	26	69

Moreover, a Pebax MH1657 layer with 2−20 nm thickness prepared on an oxygen plasma activated PDMS surface was transferred to a PAN support yielding CO_2 permeances between 1200 and 3500 GPU with respective CO_2/N_2 selectivities between 72 and 23.[61] Table 6 presents the CO_2/N_2 separation performance of different Pebax based composite membranes along with the type of support used.

Besides, Pebax membranes have been accommodated into hollow fiber modules to intensify the performance due to their advantages such as high membrane surface to module volume ratio. Liu et al.[51] coated a thin layer of Pebax 2533 onto the external part of a microporous poly(ether imide) (PEI) hollow fiber substrate, and the membrane performance for CO_2/N_2 separation was assessed using a simulated flue gas. The best separation performance of 48 GPU of CO_2 permeance accompanied by a CO_2/N_2 selectivity of 26 was obtained using a counter-current flow configuration. Chen et al.[63] fabricated a Pebax MH1657 layer using PDMS as a gutter layer onto the external surface of a PAN hollow fiber membrane. The authors found that the selection of the proper type of a gutter layer is the key since, for instance, a PTMSP gutter layer underwent significant aging. In a CO_2/N_2 mixture (50/50), the authors found a CO_2 permeance of 350 GPU with a CO_2/N_2 selectivity of 38.

These results demonstrate the benefit of reducing the selective layer thickness to achieve a higher membrane permeance (for definitions of permeance and permeability see the Supporting Information). Besides, both the top selective film and support layer could be distinctly amended to achieve higher separation performance. It is interesting to note, upon comparison of Tables 4 and 6, that even though the Pebax selective coating was reduced to ∼1 μm, the intrinsic selectivity observed with the dense membranes was approximately issued with the supported membranes. To sum up, reducing the membrane thickness plays a key role in improving the economics of the gas separation process through an increase of permeance while maintaining a high level of separation selectivity.

4.2. CO_2/CH_4 Separation. Sridhar et al.[66] prepared Pebax MH1657-based TFC membranes on PVDF ultraporous substrate by solution casting and solvent evaporation methods.

The fabricated membranes were cross-linked with toluene diisocyanate (TDI) in hexane to only moderately improve the CO_2/CH_4 separation performance. The permeance of the Pebax MH1657 composite membranes decreased from 3.7 GPU to 0.12 GPU, and the CO_2/CH_4 selectivity increased from 21.2 to 52.4 due to the tighter chain compaction after cross-linking. Pore filling and a subsequent increase in the selective layer thickness were observed. Khalilinejad et al.[67] also prepared a three-layer thin-film composite membrane of Pebax MH1657 on PVC ultrafiltration membrane support and reported that the CO_2 permeance of the thin film composite membrane increased by 16.7% as compared to the pristine Pebax MH1657. This is attributed to the high solubility and plasticizing effect that CO_2 encountered at higher pressures, whereas the selectivity remained almost unchanged.

In another work, Ahmadpour et al.[68] investigated the effect of the trans-membrane pressure (5−15 bar) and temperature range (20−50 °C) on the CO_2/CH_4 separation performance of Pebax MH1657 composite membranes prepared by coating over ultraporous PVC substrate. During single gas permeation, the composite membranes demonstrated a dramatic improvement in permeability for both CO_2 and CH_4 gases with a rise in temperature from 20 to 50 °C due to an increase in the thermal motion of the polymer chains. However, the temperature dependency on the selectivity of the membrane tended to decrease, ascribed to the dominant increase in CH_4 permeability. Similarly, CO_2 permeability raised with an enhancement of the trans-membrane pressure difference due to the plasticization effect at a pressure higher than 10 bar, which could be likely caused by the increased solubility of CO_2 in the membrane.

The influence of different support layers on CO_2/CH_4 permeation properties of Pebax MH1657 composite membranes was also investigated. The PEI supported composite membrane exhibited higher permeance than the one with PES support, thanks to its higher porosity/thickness ratio.[69] In another study, Pebax MH1657/P84 TFC showed higher enhancement in the CO_2/CH_4 selectivity than Pebax MH1657/PTMSP membranes due to the better synergistic compatibility between Pebax MH1657 and P84 polymers.[70] Table 7 shows the CO_2/CH_4 separation efficiency of selected
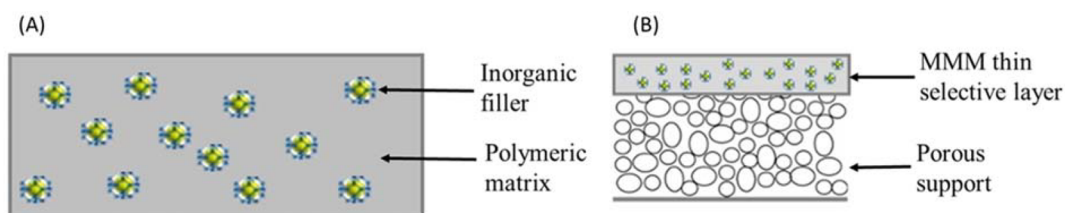
Figure 9. Schematic representation of mixed matrix membrane with metal−organic frameworks (MOFs) as a filler (A) and thin film nanocomposite (TFN) membrane (B).

Pebax composite membranes and the type of substrate used. It can be seen from the table that the highest CO_2 permeance (52 GPU) was obtained in the case of Pebax MH1657 on a PEI support mainly due to the very low thickness of the membrane. However, the highest CO_2/CH_4 selectivity (35) was obtained for Pebax MH1657 on a PVC support. In addition, the membrane showed an increase in CO_2 permeance (10−14 GPU) with a pressure (7−14 bar) increase.

In TFC membranes, as seen with dense membranes, attempts have been made to improve the performance of Pebax by blending it with other polymers. Car et al.[71] made a layer of approximately 1−2 μm by blending Pebax MH1657 with different percentages (0−50 wt %) of PEG on a PAN support. Compared to pure Pebax MH1657, the authors observed an increase in CO_2 permeance without substantially affecting the selectivity of CO_2. Another approach, already commented on, to improve the Pebax coating is to blend it with an ionic liquid. In this sense, Fam et al.[72] blended the ionic liquid ([EMIM][BF$_4$]) with Pebax MH1657 on PVDF hollow fibers using PTMSP both as gutter and protective layers. In general, the separation results showed an increase in CO_2 permeance and a slight decrease in CO_2/CH_4 selectivity with ionic liquid loading greater than 10 wt %. The results were explained regarding the interaction between IL and PEO segments that reduces the CO_2 solubility and the crystallinity, affecting both the selectivity and permeance.

On the other hand, a selective layer of Pebax MH1657 has been used as part of a membrane reactor for the separation and transformation of CO_2. For this, the Pebax MH1657 layer has been deposited on a porous poly(ether sulfone)-TiO_2 (PES-TiO_2) that acts as a photocatalytic layer. The Pebax layer separated CO_2 from a mixture of CO_2/CH_4 (molar ratio of 1:4) and the catalytic layer converted CO_2 into methanol.[73]

Good compatibility between the top selective layer and the support holds a key role in producing high performance thin-film composite membranes, i.e., in the ability to translate the separation performance of the dense Pebax membrane to the composite membrane, as it can be inferred from the comparison of Tables 5 and 7. Although composite membranes produce optimized CO_2/CH_4 separation performance, the plasticization effect appears to be a common challenge in gas separation using TFC membranes. A support pore filling problem was avoided by incorporating a gutter layer.

5. MIXED MATRIX MEMBRANES

Another approach to overcome the intrinsic trade-off limit of polymeric membranes is to combine the flexibility of polymers with mechanical strength and separation performance of inorganic, organic, or inorganic−organic solid additives by fabricating a new type of membranes called mixed matrix membranes (MMMs).[74] In MMMs, one or more micro- or

nanosized particles are dispersed in a continuous polymer matrix to conform a film (see Figure 9). In consequence, either or both permeability and selectivity of the membrane can be enhanced through the synergistic combination of the two parts.[70] Nanofillers can be categorized into (i) porous particles that act as a molecular sieve where separation is governed by the size and shape of a filler and (ii) nonporous particles that may simultaneously upsurge the permeability and selectivity by increasing the tortuous path and the fractional free volume (FFV) of the membrane.[75]

There are several reports available in the literature related to CO_2 capture by Pebax-based MMMs prepared with different porous and nonporous fillers including zeolites, pseudozeolites, such as SAPOs, carbon nanotubes, carbon molecular sieves, metal oxides, metal organic frameworks (MOFs), covalent organic frameworks (COFs), graphene oxide (GO), silica, and clays.[76,77] Several aspects, such as the type and physicochemical properties of fillers, filler loading, nature of polymer matrix, filler−matrix interactions, processing methods, etc., influence the performance of the MMMs in the CO_2 separation processes. Particularly, the selection of an appropriate filler along with a suitable polymer matrix is a vital task in the preparation of the MMM.

Rabiee et al.[78] fabricated MMMs using Pebax MV1074 and pseudozeolite SAPO-34 (5−35 wt % loading) to study the permeation of CO_2, N_2, and CH_4 gases. The authors observed that increasing filler loading enhanced CO_2 and N_2 transport values and reduced that of CH_4 due to the molecular sieving effect of the pseudozeolite. Moreover, the authors reported improvements of 70% and 15% in CO_2/CH_4 and CO_2/N_2 selectivities, respectively, with 20 wt % of SAPO-34 loading in the Pebax MV1074 membrane. The performance of the fabricated membrane moved close toward the Robeson upper bound (see Figure 3) for both gas pair separations and showed the possibility of using this membrane in natural gas sweetening and postcombustion carbon capture.

One of the major challenges in the development of MMMs is the nonuniform distribution together with the lack of proper compatibility of the dispersed phase in the continuous phase which gives rise to the formation of defects and cavities at the polymer/filler interface. Surface functionalization of nanofillers can enhance the compatibility between the two phases, thus creating a defect-free selective layer. Ghadimi et al.[79] incorporated a cis-9-octadecenoic acid (OA) modified silica nanoparticle as filler into Pebax MH1657. CO_2/CH_4 and CO_2/N_2 ideal selectivities increased from 18 and 61 to 45 and 137, respectively, at 8 wt % loading compared to the neat membrane under 25 °C and 2 bar operating parameters. Chemical surface modification of SiO_2 nanoparticles with OA efficiently eliminated agglomeration and resulted in excellent dispersion of the SiO_2 nanoparticles in the polymeric matrix. Moreover, increasing the SiO_2 nanoparticle loading led to

Table 8. Separation Performance of Various Pebax MMMs along with the Type of Nanofillers

Pebax grade	filler	support	filler (wt %)	temperature (°C)	pressure (bar)	permeability CO_2(Barrer)	selectivity CO_2/ CH_4	selectivity CO_2/ N_2	ref
Pebax MH1657	zeolite NaA	PES	10	RT	25	97	267	54	83
Pebax MH1657	zeolite NaX	PES	20	25	7	35	N/A	122	84
Pebax MH1657	zeolite NaX	PES	20	25	3	32	N/A	98	84
Pebax MH1657	MWCNT	PES	2	25	10	329	N/A	79	85
Pebax MH1657	ZIF-7	PAN	22	20	N/A	145	30	97	86
Pebax MH1657	nano silica	self-standing	0.3	N/A	N/A	8.9^G	N/A	72	87
Pebax MH1657	nano silica	self-standing	8	25	2	N/A	45	137	79
Pebax MH1657	zeolite NaX	PES	2	25	4	51	N/A	108	82
Pebax MH1657	ZIF-8	PES	2	25	4	113	N/A	107	82
Pebax MH1657	SiO_2	PES	1	25	4	74	N/A	82	82
Pebax MH1657	MoS_2	PSF	0.15	N/A	2	64	N/A	93	88
Pebax MH1657	CuMOF	self-standing	4	25	2	352	43	N/A	89
Pebax MH1657	TpPa-1	PVDF	1	25	3	20.25	N/A	72	90
Pebax MH1657	OCF-5	self-standing	0.4	30	1	493	N/A	49	91
Pebax MH1657	$Ti_3C_2T_x$ MXene	self-standing	60	25	1	70	N/A	69	92
Pebax MH1657	N-FLG	PVDF	4	25	1	240	N/A	95	93
Pebax MH1657	UiO-66	PVDF	10	25	3	130	N/A	72	94
Pebax MH1657	PEI-MCM-41	self-standing	20	25	2	1521	41	102	95
Pebax MH1657	zeolite NaY	self-standing	40	N/A	2.5	132	N/A	131	96
Pebax MH1657	UiO-66	PVDF	50	25	N/A	338^G	N/A	257	97
Pebax MH1657	ZIF-8	PVDF	10	25	3	123	11	28	98
Pebax 2533	ZIF-8	self-standing	35	N/A	N/A	1287	9	32	99
Pebax 3533	GA	self-standing	0.4	55	3	387	32	N/A	80

higher CO_2 permeability through the membrane and lower CH_4 and N_2 permeability values, which was translated into higher CO_2/CH_4 and CO_2/N_2 selectivities surpassing the Robeson upper-bound. In another study, Yousef et al.[80] followed an industrial approach to fabricate graphene (GA)/Pebax 3533 membrane using a solution casting method from GA/PEBA granules that are initially produced using the extrusion method in the presence of paraffin liquid as an adhesive layer between GA and PEBA pellets. The synthesized GA/Pebax 3533 nanocomposite membranes produced a maximum CO_2 permeability of 387 Barrer and CO_2/CH_4 selectivity of 32 at the optimal GA loading of 0.4 wt % at 55 °C.

Moreover, as it was mentioned in section 4 on composite membranes, PDMS and PTMSP can be used to coat a selective layer to seal all the possible cracks and defects in order to optimize and achieve a high-performing MMM.[61]

Pebax thin films loaded with different nanofillers are being used as a selective top layer for preparation of a new type of film: thin film nanocomposite (TFN) membranes. The structure of a TFN membrane is depicted in Figure 9B.

Murali et al.[81] investigated the CO_2/N_2 separation efficiency of Pebax MH1657 MMMs with multiwalled carbon nanotubes (MWCNTs) as a selective layer and ultraporous PES as a substrate. Loadings of 0−5 wt % were incorporated into Pebax MH1657 solutions and sonicated for 2 h to achieve uniform dispersions. At room temperature, the permeabilities of both gases were enhanced with the CO_2 permeation being the highest, thus improving the CO_2/N_2 selectivity from 83 to 162 at 2 wt % MWCNTs loading with increasing feed pressure (1−3 MPa). Moreover, Sanchez-Laínez et al.[70] prepared TFN membranes of Pebax MH1657 modified with MOFs such as ZIF-8, UiO-66, MIL-101(Cr), and ZIF-7/8 core−shell particles on asymmetric porous polyimide P84 supports.

Membranes prepared in this way exhibited a notable improvement in CO_2 permeance, especially those embedding UiO-66 which doubled the permeance value of pristine Pebax MH1657 membranes from 6 GPU to 11.5 GPU with a CO_2/CH_4 selectivity value of 55.

Maleh et al.[82] investigated the effects of the type and structure of filler on the microstructure and gas separation performance of Pebax MH1657 based MMM. Three different kinds of membranes were obtained by loading Pebax MH1657 selective layer solutions with nanofillers including zeolite NaX, ZIF-8, and SiO_2 and coating it on a PES support. For TFN membranes loaded with porous nanoparticles (NaX and ZIF-8), the CO_2/N_2 selectivity was enhanced from 62 to 107 and 108, respectively, by increasing both the NaX and ZIF-8 contents up to 2 wt %. Nonetheless, the TFN membrane with SiO_2 as a filler demonstrated lower selectivity (81) due to the nonporous structure of the particles. This is ascribed to the higher cavity size of NaX and ZIF-8 porous fillers than the CO_2 kinetic diameter, superior CO_2 sorption potential, and the stronger interfacial compatibility between porous fillers and polymer chains compared to the SiO_2 nonporous filler. Table 8 represents the published separation results of various Pebax based MMMs along with the nanofillers incorporated and permeation conditions.

Using hollow fibers to improve process intensification, several MMMs based on Pebax have been studied in the literature. Sustrina et al.[98] introduced ZIF-8 inside a Pebax MH1657 layer using a PVDF support, a gutter layer of PTMSP, and a protective layer of their own pure Pebax1657 using dip-coating in all of the procedures. The authors found that ZIF-8 improved compaction/plasticization resistance for the Pebax MH1657 layer and mitigated the aging of the gutter layer. Following the same methodology, Sustrina et al.[97] introduced functionalized UiO-66 and ZIF-7 to the same kind

of membranes, obtaining the best results (CO_2 permeance of 338 GPU and CO_2/N_2 selectivity equal to 57) using 50 wt % of amino UiO-66 as filler, which improved the compatibility and solubility of CO_2.

The use of two-dimensional (2D) materials as fillers for Pebax membranes should be noted as well. Their nanometric dimensions and high aspect ratio make them interesting materials as fillers that provide higher contact area between the filler and the polymer and thus the ability of affecting the performance already with small quantities. In addition to graphene oxide and the clays already mentioned, other 2D fillers used are (i) MoS_2 nanosheets.[88] These materials have been used to prepare a composite mixed matrix membrane with Pebax MH1657 on PSF support using a PDMS gutter layer, where at 0.15 wt % MoS_2 loadings, the CO_2/N_2 ideal selectivity increased up to 93 (44 for the pure polymer); however, permeance decreased due to an increase of the membrane thickness with the filler. (ii) 2D MOF, an example is CuMOF nanosheet (18−26 nm) fabricated by the top-down method and included in a Pebax MH1657 MMM; in this case, the porosity of the MOF provides additional advantages and by using 4 wt % loading of CuMOF, a CO_2 permeability of 352 Barrer and CO_2/CH_4 selectivity of 43 were reached, which exceeded the values of the pure membrane (CO_2 permeability of 183 Barrer and CO_2/CH_4 selectivity 36). The increment in permeability and selectivity are mainly caused by three aspects: (1) the 2D lamellar surface of this MOF provides interlaminar channels for CO_2, which improves diffusivity. (2) The CO_2-philic sites of CuMOF enhance the CO_2 solubility. (3) The good interface compatibility between CuMOF and Pebax results in the increase of selectivity.[89] (iii) 2D COFs, TpPa-1 nanosheet clusters with Pebax (grade is not indicated), were deposited by spin coating on PVDF support to obtain a CO_2 permeance of 7.2 GPU with a CO_2/N_2 selectivity of 72, increasing both in comparison with pure polymer with a filler loading of 1 wt % (see Figure 10).[90]

In other work, 0.4 wt % of COF-5 nanosheets into the Pebax MH1657 matrix improved the CO_2/N_2 ideal selectivity up to 49 (33 pure Pebax MH1657 polymer) with a CO_2 permeability of 493 Barrer.[91] (iv) Transition metal carbides (MXenes); a few layers of $Ti_3C_2T_x$ were incorporated inside the Pebax MH1657 MMM which improved CO_2 separation by the
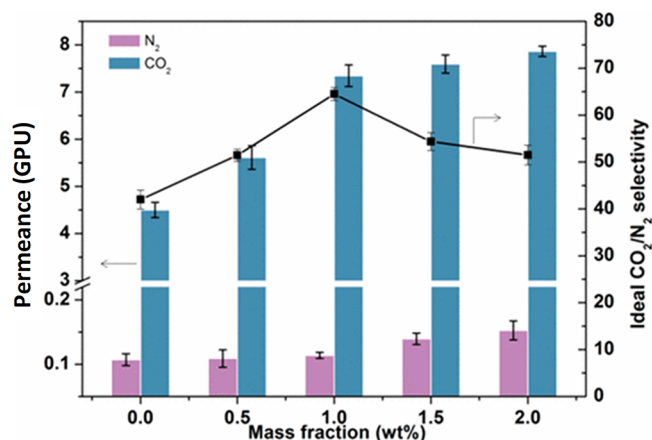

Figure 10. Permeances and CO_2/N_2 ideal selectivities of TpPa-1 nanosheet clusters with Pebax deposited on a PVDF support. Reproduced from ref 90. Copyright 2017, American Chemical Society.

transformation of the filler on a stable solvent-free liquid (MX-fluid) to improve processability, obtaining a CO_2/N_2 ideal selectivity of 69.2 and the CO_2 permeability increased by 178% compared with pure Pebax.[92] (v) N-doped few-layer graphene; N-FLG/Pebax MH1657 MMM was cast onto a PVDF support and provided an optimum CO_2 permeability and CO_2/N_2 ideal selectivity of 240 Barrer and 95, respectively, with the addition of 4 wt % of the filler.[93] The results were explained in terms of the presence of functional groups where the adsorption of CO_2 increased. It should be noted that in this work, molecular simulation successfully predicted the experimental results.

Generally, MMMs show an extraordinary performance for CO_2 separation compared to pristine polymeric membranes and have the potential to overcome the traditional permeability-selectivity trade-off barriers. However, it should be noted that more factors such as ease of processing, long-term operation and lifetime, chemical and thermal stabilities, and operation under realistic composition conditions are dictating the overall success of a MMM. Accordingly, special attention should be given to the selection of suitable nanofillers. Moreover, the permeability of MMMs is a function of pressure and feed composition. However, probably due to the efforts preferentially focused on the creation of new MMMs (e.g., combining a new filler, from the thousands available, with one of the different Pebax grades present in the market), most of these aspects are poorly addressed, not only with Pebax based MMMs but with any types of other materials.

6. WATER AND THERMAL STABILITIES OF PEBAX MEMBRANES

Currently, polymeric membranes are utilized in a wide range of gas stream treatment applications in many industries. However, most of them suffer from poor thermal and chemical resistance. To this end, in some applications, hot gas streams are cooled down solely to accommodate a membrane-based separation process, which afterward are heated back with the corresponding expense of thermal energy. Besides, many hot gas streams in all chemical industries must remain at high temperature during the separation process.[101]

To date, there are no studies explicitly dedicated to the study of the stability of Pebax membranes under different temperatures and/or moisture environments. Nevertheless, some researchers have investigated the thermal properties of Pebax membranes as part of their characterization techniques while developing high-performance gas separation thin films, since gas transport through a dense polymeric membrane is a thermally activated process.[102]

The first important variable is the temperature. As seen in Figure 11a,b, the rise in the operating temperature is usually translated into higher polymer chain mobility, which favors gas permeation through the membrane (higher permeability or permeance) with the corresponding decrease of selectivity. The temperature dependence of penetrant gas permeability through a membrane can be expressed using a modified Arrhenius equation in terms of permeation activation energy (E_p) (eq 1).[39]

$$P = P_0 \exp^{(-E_p/RT)} \tag{1}$$

where P is the gas permeability (Barrer) or the gas permeance (GPU), P_0 is the pre-exponential factor of gas permeability or permeance, respectively, E_p is the permeation activation energy (kJ/mol), R is the ideal gas constant (0.008314 kJ/mol K), and
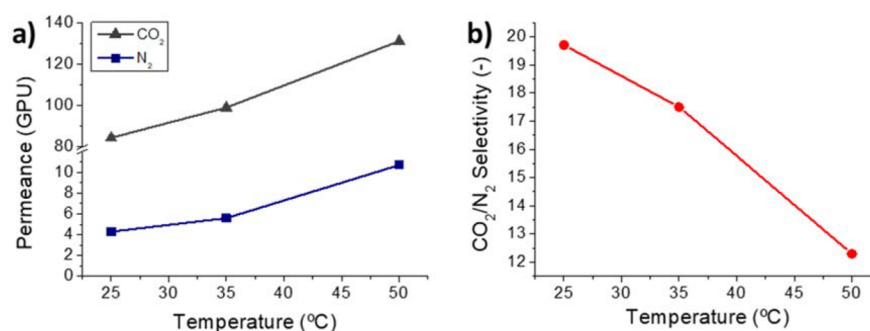
Figure 11. Permeance (a) and CO_2/N_2 selectivity (b) dependence on temperature for Pebax 3533/PSF membranes.[103] Reprinted from L. Martínez-Izquierdo, M. Malankowska, C. Téllez, J. Coronas, Phase inversion method for the preparation of Pebax 3533 thin film membranes for CO_2/N_2 separation. *Journal of Environmental Chemical Engineering*, **2021**, *9*, 105624. Copyright 2021, with permission from Elsevier.

T is the operating temperature (K). As an example, the Arrhenius model applied to the data in Figure 11a,b is depicted in Figure 11c,d. In this figure, the opposite of the slope in the ln P vs $R^{-1}T^{-1}$ (J^{-1} mol) plot is the apparent activation energy of permeation in J mol^{-1}.

Based on the Arrhenius model, the activation energy values of permeability reported in literature for Pebax copolymers ranged from 13.3 to 18.6 kJ mol^{-1} for CO_2 and from 27.2 to 32.0 kJ mol^{-1} for N_2. The higher activation energy of N_2 over CO_2 justifies the reduction of CO_2/N_2 selectivity as a function of temperature, a commonly reported behavior in Pebax copolymer membranes.

Another factor considered is the thermal stability of Pebax membranes. According to the literature, assuming a perfect drying process, Pebax membranes show good thermal stability up to ~350 °C on average. However, they start to lose some weight at 340−380 °C, due to the thermal decomposition of their polymer chains. Pebax membranes experience maximum degradation at a temperature in the range of 400−450 °C.[39,104,105] Besides, another degradation step relating to the combustion of aromatic compounds and residues of degraded chains could follow at a higher temperature range of 460−580 °C.[39,104]

In Pebax MV1074/poly(ethylene glycol) PEG1500 blend membranes, the addition of PEG1500 induces an increase in the melting point of PEO, although the melting point of the PA crystalline phase is slightly reduced, suggesting that the additive PEG1500 acts as a solvent for the block copolymer matrix.[106] The thermal stability of Pebax membranes can be improved by incorporating nanoparticle fillers into the polymer matrix. Compared to the neat Pebax MV1074 film which has a thermal decomposition point at 425 °C, Pebax MV1074/ZnO nanocomposite membrane experienced a maximum thermal degradation at 438 and 442 °C with 4 and 8 wt % loadings of ZnO, respectively.[107]

Interestingly, if we consider Pebax based TFN membranes, higher thermal stability is achieved in a temperature range where the PA segment is in a crystalline state. This is because the crystalline polyamide block provides physical cross-linking between the soft phases, and consequently the nanoparticles are firmly trapped in the amorphous PEO domains of the block copolymer. However, in the absence of physical cross-linking, the nanocomposite triggers reorganization of the domains of the two block copolymers constituting Pebax type polymers and the rejection of nanoparticles from the polyether domains may happen followed by independent crystallization.[108]

The thermal stability of Pebax membranes can be enhanced by following a controlled synthesis procedure. Some of the approaches are (i) adjusting the proportion of hard and soft blocks, (ii) cross-linking the polymer matrix, (iii) creating MMMs, and (iv) increasing the molecular weight of polymers. Nonetheless, significant improvement in thermal stability is made only when the fundamental building blocks of the polymer are modified. In any event, as compared to other polymeric membranes, Pebax containing membranes operate at moderate temperature, the highest testing temperatures reported being 65−70 °C.[38,47]

Another factor that may affect the stability of the membrane operation is the presence of moisture in the feed stream. It is well-known that membrane swelling has a considerable impact on the overall separation efficiency, resulting in high permeability but low selectivity. Thin Pebax MH1657/attapulgite (2 wt % ATP) composite membranes demonstrated stable separation performance for at least 30 h under both dry and humidified conditions.[109] Moreover, the incorporation of ATP improved the CO_2 permeability from 56 to 77 Barrer and the CO_2/N_2 selectivity of from 40 to 52, respectively. In another work,[110] in the presence of 17% of water vapor in the feed gas, Pebax MH1657 membrane showed a 5% decline in CO_2 permeance (867 GPU), whereas CO_2/N_2 selectivity remained unaffected compared to the dry membrane with 912 GPU of CO_2 permeance and CO_2/N_2 selectivity of 30 at 57 °C. Moreover, the incorporation of zeolite Y into this membrane improved the performance of the membrane with an average CO_2 permeance of 940 GPU and a CO_2/N_2 selectivity of 30 at 50 °C for 24 h. The CO_2 induced plasticization effect was observed to strongly impact the membrane performance.[40,54,62] Especially, thin film composite membranes experienced higher plasticization due to the thin selective layer.

Another interesting approach is the use of GO and MXene with the interlayer channels which can rapidly transport CO_2 at the wet state. Under humidification, the higher loading limit of MXene (20 wt %) compared to GO (only 5 wt %) was found to be more effective in improving the separation performance of the membranes. In Pebax-MXene membranes with 10 wt % of filler, a significant enhancement was achieved in terms of both CO_2 permeability (584 Barrer, 218 Barrer pure Pebax polymer) and CO_2/N_2 selectivity (59, 38 pure Pebax polymer).[100] This is because the hydrated interlayer channels of the fillers become CO_2 selective and allow fast transport at the same time. Moreover, the incorporation of MXene enhanced the mechanical stability of the membrane due to

the good interaction between the polar groups at the MXene surface and the Pebax matrix.

7. CONCLUSIONS AND FUTURE DIRECTIONS

Several technologies such as absorption, cryogenic distillation, adsorption, and membrane separation are used for CO_2 capture from different gas mixtures (see Table 1). Among these, membrane-based gas separation has emerged as the most competent one thanks to its less energy-intensive and more affordable approach. Polymeric membranes are dominant in the CO_2 capture process due to their low cost and easy processability. However, the separation performance of polymeric membranes is hampered by the traditional trade-off between permeability and selectivity.

In the search for new membrane materials to overcome this trade-off, Pebax copolymers displayed a promising performance due to their unique chemical composition which contains a hard glassy polyamide segment and a rubbery PEO segment in different proportions depending on the commercial grade. According to the available literature, Pebax MH1657 is the most researched copolymer grade for this application. The intrinsic separation performance of Pebax copolymers has been investigated by following various fabrication techniques such as changing the PA and PEO proportion, solvent, and solvent evaporation temperature. Results found in the literature indicated that proper solvent selection plays a vital role as it impacts the solvent evaporation process, thermal properties, and crystallinity of the resulting membrane and thus the overall economics of the membrane.

Recently, attempts have been made to develop high-performance membranes that could separate CO_2 from nitrogen-rich streams at very high volumetric flow rates and low feed pressure. To do this, researchers attempted to upgrade the Pebax membrane into a composite and/or mixed matrix type. A CO_2 selective, thin Pebax layer coated over different supports improved the permeance and economical cost by lowering the membrane area and thickness. A gutter layer could also be used to avoid pore-filling during TFC membrane preparation.

Several Pebax-based MMMs have demonstrated to exceed the Robeson upper bound limit thanks to the synergetic advantage of this copolymer and inorganic or organic porous fillers. Nonetheless, a wise selection of nanofillers is necessary as it could otherwise hinder the membrane separation performance. Surface modification of nanofillers could be used to improve the adhesion between the two phases. Furthermore, nanoparticle agglomeration can be avoided by casting solution sonication. Interface engineering and surface functionalization combined with the development of hybrid fillers that offer multifunctionality could anticipate higher separation performance of MMMs. Moreover, an interesting approach is to blend Pebax with ionic liquids (IL) that can facilitate the CO_2 transport to prepare, for example, gel membranes. In addition, deepening the understanding of the solubility/diffusion processes not only with experimental work but also with simulation (e.g., molecular simulation) can help in the design and development of MMMs. However, exceeding the Robeson upper bound does not necessarily mean an economically feasible membrane; in fact, a commercially attractive membrane for CO_2 separation should be positioned at the high selectivity and the mid to high permeability regions. An effort must still be made in the stability of the membranes in real working conditions (temperature, pressure, moisture,

etc.) that can differ greatly from the usually binary model mixtures and the real conditions with which the membranes are tested.

The environmental aspect should also be emphasized. Membrane separation, as mentioned, is a more environmentally friendly approach than current separation processes. Nevertheless, in the preparation of membranes, an effort must be made in green chemistry. In that sense, it has already been seen that solvents such as water/ethanol mixtures can be used to replace other organic solvents that are more toxic and harmful to the environment. Moreover, for process intensification, hollow fiber membranes should be further developed as they offer a greater area of membranes per unit volume of equipment than flat-sheet membranes.

It is worth mentioning that Pebax based membranes may find application in other gas separations (e.g., O_2/N_2,[111] CO_2/H_2,[112] CO/CO_2[113]) different from those involving CO_2/N_2 and CO_2/CH_4 mixtures as well as in pervaporation,[114] nanofiltration,[115] reverse osmosis,[116] and membrane distillation,[117] among others. This implies that all the insight gained with this overview may have repercussion on other emerging separation fields for this type of membranes or even other applications of Pebax films such as food packaging and medical devices. In addition, there is a growing interest in technologies that take advantage of CO_2 in applications beyond its capture (carbon capture and utilization, CCU), which enables the CO_2 circular economy. In this sense, the membranes can play a key role as an intermediate process for their recovery and reuse, without ruling out that they may be part of the direct CO_2 reuse process in membrane reactors.

Finally, despite the numerous research efforts dedicated to Pebax based CO_2 capture, many of the studies are conducted at the laboratory scale with only a few square centimeters sized membranes operated for short periods of time and an idealized gas mixture. In consequence, the performance of these membranes in real applications with complex gas mixtures and long-term operation is poorly understood. Therefore, more organized research and development strategies are still needed to exploit the full potential of this technology in large scale applications.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.1c01638.

> Definitions of general terms regarding membrane gas separation (PDF)

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Notes

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Magdalena Malankowska graduated in Chemistry and received her joint Ph.D. (2018) degree in Membrane Engineering from the University of Zaragoza (Spain), University of Twente (The Netherlands), and University Nova de Lisboa (Portugal). Since 2018, she has been working as a Research Associate at the Institute of Nanoscience and Materials of Aragón at the University of Zaragoza. Her research is based on membrane engineering (especially MMMs) for separation processes as well as microfluidics and fluid dynamic modelling.

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Joaquin Coronas graduated in Chemistry and received his Ph.D. in Chemical Engineering from the University of Zaragoza (Spain) in 1995. After research studies at IRCELYON-CNRS, Boulder University, Aveiro University, and Minnesota University and obtaining an Associate Professor position, he became a Full Professor at the University of Zaragoza in 2010. He belongs to the Institute of Nanoscience and Materials of Aragón at the same university. His current research interests include synthesis of silicates, zeolites, and MOFs and their applications in membranes (gas separation, pervaporation, nanofiltration, and osmotic distillation) and encapsulation.

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