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Enhancement strategies of poly(ether-block-amide) copolymer membranes for CO₂ separation: A review

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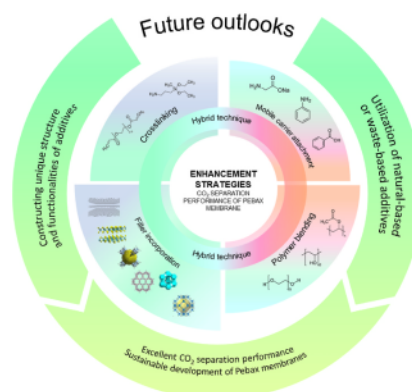
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HIGHLIGHTS

- Enhanced CO₂ separation performance of Pebax was mainly due to the structural alteration.
- Filler incorporation is most common strategy for better Pebax membrane CO₂ separation.
- Perm-selectivity trade-off and mechanical strength reduction should be simultaneously overcome.
- Constructing unique structure and functionalities is viable for future filler materials.
- Utilization of eco-friendly additives materials will support circular economy development.

GRAPHICAL ABSTRACT



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ABSTRACT

Poly(ether-block-amide) (Pebax) membranes have become the preferred CO₂ separation membrane because of their excellent CO₂ affinity and robust mechanical resistance. Nevertheless, their development must be considered to overcome the typical obstacles in polymeric membranes, including the perm-selectivity trade-off, plasticization, and physical aging. This article discusses the recent enhancement strategies as a guideline for designing and developing Pebax membranes. Five strategies were developed in the past few years to improve Pebax gas transport properties, including crosslinking, mobile carrier attachment, polymer blending, filler incorporation, and the hybrid technique. Among them, filler incorporation and the hybrid technique were most favorable for boosting CO₂/N₂ and CO₂/CH₄ separation performance with a trade-off-free profile. On the other hand, modified Pebax membranes must deal with two latent issues, mechanical strength loss, and perm-selectivity off-balance. Therefore, exploring novel materials with unique structures and surface properties will be promising for further research. In addition, seeking eco-friendly additives has become worthwhile for establishing Pebax membrane sustainable development for gas separation.

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Nomenclature

AFFs	Amine-functionalized fillers	MFI	Mobil-type five zeolites
APDEMS	3-Aminopropyl(diethoxy) methyl silane	MIL	Matériaux de l'Institut Lavoisier
APDS	3-(2-aminoethylamino) propyl-dimethoxymethylsilane	MMMs	Mixed matrix membranes
APTES	3-Aminopropyltriethoxysilane	MOFs	Metal-organic frameworks
APTMS	3-Aminopropyltrimethoxysilane	MTER	Melting temperature enhancement ratio
BD	Balance degree	Ni-NS	Ni-MOF nanosheets
BDC	Benzene-1,3,5-tricarboxylate	NOHMs	Nanoparticle organic hybrid materials
BNNS	2D Boron nitride nanosheets	NPC	Nitrogen-doped porous carbons
BTC	Benzene-1,4-dicarboxylic acid	P	Permeability
CA	p-tert-butylcalix4arene	PA	Polyamide
CCNS	2D Carboxyl functionalized carbon nanosheets	PEO	Polyethylene oxide
CHA	Chabazite	PEG	Polyethylene glycol
CNTs	Carbon nanotubes	PEGDA	Poly (ethylene glycol) diacrylate
COFs	Covalent organic frameworks	PER	Permeability enhancement ratio
CrER	Crystallinity enhancement ratio	PGP	Poly (glycidyl methacrylate-g-polypropylene glycol)
CTPP	Covalent triazine piperazine polymer	PPAC	Pineapple peel-activated carbon
CuZnIF	Copper-zinc bimetallic imidazolate	POEM	Poly (oxyethylene methacrylate)
D	Diffusivity	PSINTs	Porous silica nanotubes
DBM	Dibutyl maleate	PQDs	Polymer-like quantum dots
DER	Diffusivity enhancement ratio	PVA	Polyvinyl alcohol
EER	Elongation at break enhancement ratio	PVAc	Polyvinyl acetate
FAU	Faujasites	S	Solubility
FFV	Fractional free volume	SAPO	Silicoaluminophosphate
FS	Fumed silica	SeER	Selectivity enhancement ratio
GPTMS	3-Glycidylpropyltrimethoxysilane	SG	Sodium glycine
GQDs	Graphene-like quantum dots	SoER	Solubility enhancement ratio
GTER	Glass-transition temperature enhancement ratio	STP	Standard temperature and pressure
HNTs	Halloysite nanotubes	TBT	Tributyrin
HS	Hollow spherical	TCP	Tricapronin
MCNs	Microporous carbon nanoparticles	TCPP	Tetra-(4-carboxyphenyl)porphyrin
MCNPs	2D Microporous carbon nanoplates	TPP	Tripropionin
MER	Young's modulus enhancement ratio	TER	Tensile strength enhancement ratio
		ZIF	Zeolitic imidazolate framework

1. Introduction

Chemical mixture separation and purification represent approximately 10–15% of global energy consumption (Sholl and Lively, 2016; Duan et al., 2018; Abdul Hamid et al., 2021). Therefore, an advanced separation technique is necessary to economize membrane costs and diminish gas emissions. Membrane technology is an emerging alternative to the traditional thermally driven process for industrial gas separation. Membrane technology has the advantages of low-energy utilization, operational flexibility-simplicity, excellent mechanical complexity, less space requirement, scale-up applicability, and small carbon footprint (Shah Buddin and Ahmad, 2021; Tengku Hassan et al., 2021; Yong and Zhang, 2021). Consequently, the membrane market value is still expanding and is projected to be \$2.61 billion annually in 2022 (Qian et al., 2020).

Polymers, among membrane materials, have received high interest in industrial-scale applications and academic study, primarily due to their economic, environmental, and engineering feasibility (Bernardo et al., 2009; Vinoba et al., 2017; Ahmad et al., 2019). As a result, several common polymers have been recently studied for gas separation, such as polysulfones, cellulose acetate, aramids, polycarbonates, polyphenyl oxide, and polyimides (Sidhikku Kandath Valappil et al., 2021). However, developing a new class of polymer materials is still expanding to enhance the gas separation properties of existing membrane materials. The emerging polymer materials that should be considered are ether oxygen-rich polymers, polymeric ionic liquids, perfluoro polymers, thermally rearranged polymers, glassy polymers with iptycene as a

building block, other non-reactive polymers, and facilitated transport polymers (Han and Ho, 2021).

Poly(ether-block-amide), under the trade name of Pebax®, is an ether oxygen-rich polymer containing polyamide segments that exhibit a remarkable polar gas perm-selectivity and tuneable thermal and mechanical properties (Clarizia et al., 2018; Maleh and Raisi, 2019; Salehi Maleh and Raisi, 2019; Habibi and Bakhtiari, 2021; Taheri et al., 2021a; Wang et al., 2021b). Pebax is affordable with different grades related to specific segmental compositions, resulting in flexibility for various purposes (Zhu et al., 2020). Pebax has been widely investigated for the separation of polar/nonpolar gas mixtures, like CO₂/CH₄ (Thankamony et al., 2019; Wang et al., 2020b, 2021d; Zhao et al., 2020; Liu et al., 2021; Zhang et al., 2021b), CO₂/N₂ separation (He et al., 2021; Jiang et al., 2021; Wang et al., 2021a, 2021c; Yang et al., 2021b; Zhang et al., 2021a), CO₂/H₂ separation (Fan et al., 2018; Shamsabadi et al., 2020; Wong et al., 2021), H₂S/CH₄ separation (Harrigan et al., 2020; Hayek et al., 2021), CH₄/N₂ separation (Guan et al., 2017), O₂/N₂ separation (Nikpour and Khoshnevisan, 2020), NH₃/N₂ or NH₃/H₂ separation (Yang et al., 2021a), ethylbenzene/N₂ separation (Guo et al., 2021), and even hydrofluorocarbons (HFCs)/hydrofluorolefin (HFO) separation (Pardo et al., 2020, 2021).

While promising, Pebax has typical polymeric membrane limitations regarding perm-selectivity off-balance. Pebax exhibits a relatively high gas permeability but cannot achieve sufficient selectivity in many cases. This is mainly related to the swelling phenomenon during the separation operation due to strongly condensable feed gas on the polymer chain under elevated pressure (Wang et al., 2020b, 2021b; Ebadi et al., 2021;

Hayek et al., 2021; Pardo et al., 2021). These conditions increase the chain mobility and free volume, avoiding selective flow through the membrane. The competitive adsorption effect among the feed gases may significantly reduce the separation factor (Jiang et al., 2021; Kojabad et al., 2021a). In addition, water-driven plasticization could also be considered in the case of Pebax membrane enlargement d-spacing and reduced gas (Shi et al., 2020).

Various additive materials have been investigated to modify the Pebax membrane structural and surface properties to overcome the abovementioned drawbacks for better CO₂ separation performance. This article comprehensively summarized and systematically sorted out the enhancement strategies for Pebax membranes based on various additive materials. A comparative analysis was also conducted to determine the preferable enhancement strategies concerning overall membrane properties. This research is expected to give readers a clear understanding of the research progress and a scientific reference for developing Pebax membranes.

2. Pebax membrane modification fundamental principles

The gas transport process through a Pebax membrane follows the solution-diffusion theory derived from Fick's first law of diffusion. In this model, permeability becomes a critical parameter for evaluating membrane gas transport capacity and can be simply defined as follows

$$P = D \times S \quad (1)$$

where P is the gas permeability expressed in Barrer (1 Barrer = $1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$), D is the diffusivity ($\text{cm}^2 \text{ s}^{-1}$), and S is the solubility ($\text{cm}^3 \text{ (STP) cm Hg}^{-1}$). Diffusivity is a coefficient expressing the gas movement speed through the membrane and is directly related to the membrane's fractional free volume (FFV). Thus, polyamide (PA) as a Pebax crystalline segment is predominantly associated with the diffusivity coefficient because it regulates the intersegmental space for gas penetration. On the other hand, solubility is a parameter associated with the inherent properties of gas molecules and polymers. In this case, polyethylene oxide (PEO) segments will establish Pebax membrane solubility regarding their strong dipole-quadrupole interaction with polar gases like CO₂.

Membrane selectivity (α), on the other hand, is another crucial characteristic of membranes, represented by the permeability ratio of the two gas molecules (i and j) as given by Eq. (2).

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (2)$$

Membrane gas separation performance can be evaluated by considering permeability, selectivity, diffusivity, and solubility coefficients. Therefore, the PER (permeability enhancement ratio), SeER (selectivity enhancement ratio), DER (diffusivity enhancement ratio), and SoER (solubility enhancement ratio) can be considered and calculated using the following equations:

$$PER_{CO_2} = (P_{mod} - P_{neat}) / P_{neat} \quad (3)$$

$$SeER_{CO_2} = (\alpha_{mod} - \alpha_{neat}) / \alpha_{neat} \quad (4)$$

$$DER_{CO_2} = (D_{CO_2,mod} - D_{CO_2,neat}) / D_{CO_2,neat} \quad (5)$$

$$SoER_{CO_2} = (S_{CO_2,mod} - S_{CO_2,neat}) / S_{CO_2,neat} \quad (6)$$

The strategies for improving the Pebax membrane's efficiency involve additives that modify the original matrix's basic structure. Hence, these additives alter the Pebax membrane's thermal stability, physical resistance, and mechanical strength. How these additives modify the membrane structure should be examined. The modified membrane characteristics consist of the glass transition temperature (T_g), melting temperature (T_m), crystallinity (X_c), tensile strength (TS),

Young's modulus (E), and elongation at break ($Z\%$).

$$GTER = (T_{g,mod} - T_{g,neat}) / T_{g,neat} \quad (7)$$

$$MTER1 = (T_{m,PE,mod} - T_{m,PE,neat}) / T_{m,PE,neat} \quad (8)$$

$$MTER2 = (T_{m,PA,mod} - T_{m,PA,neat}) / T_{m,PA,neat} \quad (9)$$

$$CrER1 = (X_{c,PE,mod} - X_{c,PE,neat}) / X_{c,PE,neat} \quad (10)$$

$$CrER2 = (X_{c,PA,mod} - X_{c,PA,neat}) / X_{c,PA,neat} \quad (11)$$

$$TER = (TS_{mod} - TS_{neat}) / TS_{neat} \quad (12)$$

$$MER = (E_{mod} - E_{neat}) / E_{neat} \quad (13)$$

$$EER = (\%Z_{mod} - \%Z_{neat}) / \%Z_{neat} \quad (14)$$

where $GTER$, $MTER1$, $MTER2$, $CrER1$, $CrER2$, TER , MER , and EER represent the glass transition temperature, melting temperature PEO, melting temperature PA, crystallinity PEO, crystallinity PA, tensile strength, Young's modulus, and elongation at break enhancement ratios, respectively. The subscript "mod" corresponds to the modified membrane, while "neat" indicates the pure Pebax membrane. All items are plotted to understand each enhancement strategy's impact on Pebax membrane CO₂ separation.

Balance degree (BD) is another critical parameter for evaluating the direction of each enhancement strategy (permeability-oriented, selectivity-oriented, or synchronous mode). It is expressed as follows

$$BD = 1 - |PER - SeER| \quad (15)$$

The minus value indicates no equality (off-balance) in improving the permeability and selectivity. Synchronous mode is expressed by $0.8 \leq BD \leq 1.0$, corresponding to the perfect equality between permeability and selectivity enhancement.

3. Recent pebax membrane enhancement strategies and their impacts on structural properties and gas separation features

Five approaches have been used to enhance Pebax membrane CO₂ separation performance: crosslinking, mobile carrier attachment, polymer blending, filler incorporation, and hybrid techniques. In terms of hybrid technique, two or three single approaches (crosslinking, mobile carrier attachment, polymer blending, or filler incorporation) are used to assemble Pebax membrane ternary or quaternary modules, as seen in Fig. 1. The application of these approaches generally relies on various related additives' ability to modify the Pebax membrane original properties to boost their gas transport parameters.

3.1. Crosslinking

This technique arranges a network structure using intermolecular bond formation through covalent bonds connecting polymer chains. As a result, the membrane's fractional free volume and chain mobility will decrease, resulting in higher resistance toward aging and plasticization. While promising, crosslinking has rarely been studied using Pebax membranes for gas separation. Sanaeepur et al. (2019b) employed 3-aminopropyl(diethoxy) methyl silane (APDEMS) as a cross-linking agent to prepare novel cross-linked Pebax membranes for CO₂/N₂ gas separation. The results indicated that APDEMS could increase the Pebax 2533 membrane selectivity by either restricting the Pebax 2533 chain mobility to lessen its crystallinity or increasing the CO₂ solubility due to the presence of amine groups. Moreover, CO₂ permeability did not reduce so much because the amino silane agent Si-O links with local mobility. APDEMS 2 wt% achieved the best performance with a 91% increase in ideal CO₂/N₂ selectivity and an 18% slight decrease in CO₂

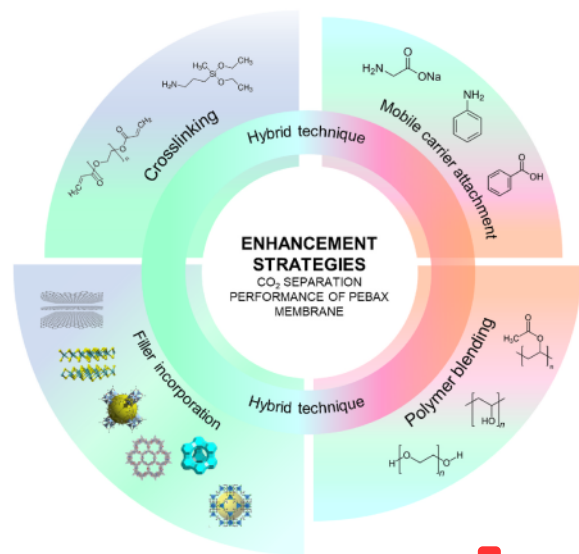


Fig. 1. Recent enhancement approaches on Pebax membrane gas separation performance.

permeability compared to the pure Pebax membrane. Another study was carried out by Taheri et al. (2021a) using poly (ethylene glycol) diacrylate (PEGDA) to crosslink Pebax 1657. It was revealed that introducing PEGDA improved the Pebax 1657 membrane tightness and

crystallinity. Moreover, the T_g value increased by 4% by increasing the PEGDA content. At 6 wt% of PEGDA load, Pebax 1657 exhibited the best performance, surpassing Robeson's upper boundary.

3.2. Mobile carrier attachment

Using mobile carriers to modify Pebax membranes has a similar effect as crosslinking in the case of tightening polymer chain packing (as shown in Fig. 2). Mobile carriers may also react with a target gas and diffuse along its concentration gradient across the membrane thickness, establishing a facilitated transport mechanism. Meshkat et al. (2019) utilized benzoic acid and isophthalic acid to modify the Pebax membrane 1657 gas permeability. The intense interaction between carboxylic groups and Pebax chains could decrease the flexibility of the resulting membranes, indicated by higher T_g . Regarding CO_2 permeability, isophthalic acid 10 wt% exhibited a higher enhancement ratio ($P_{\text{CO}_2} = 148.3$ Barrer with $\text{PER}_{\text{CO}_2} = 1.26$) than benzoic acid ($P_{\text{CO}_2} = 148.3$ Barrer with $\text{PER}_{\text{CO}_2} = 1.12$). That was related to double carboxylic groups and smaller cavities in its structure, providing selective CO_2 transport. In contrast, benzoic acid was more remarkable in upgrading CO_2/CH_4 selectivity up to 27 ($\text{SeER}_{\text{CO}_2/\text{CH}_4} = 0.57$) and CO_2/N_2 selectivity up to 93 ($\text{SeER}_{\text{CO}_2/\text{N}_2} = 0.81$), indicating a balance between improved CO_2 solubility and higher diffusivity.

Sodium glycine (SG), an amino acid salt, is another type of mobile carrier for improving Pebax membrane gas separation. Zhang et al. (2018a) highlighted two essential roles provided by SG to improve Pebax membrane CO_2 separation. First, SG promotes plenteous amine groups ($-\text{NH}_2$) and carboxylate groups ($-\text{COO}^-$) as carriers for facilitating CO_2 transport. Second, SG enables adsorbing water more easily to create additional CO_2 reactive sites and swell the polymer chain to enrich the diffusional pathway. As a result, Pebax/SG 15 wt% presented

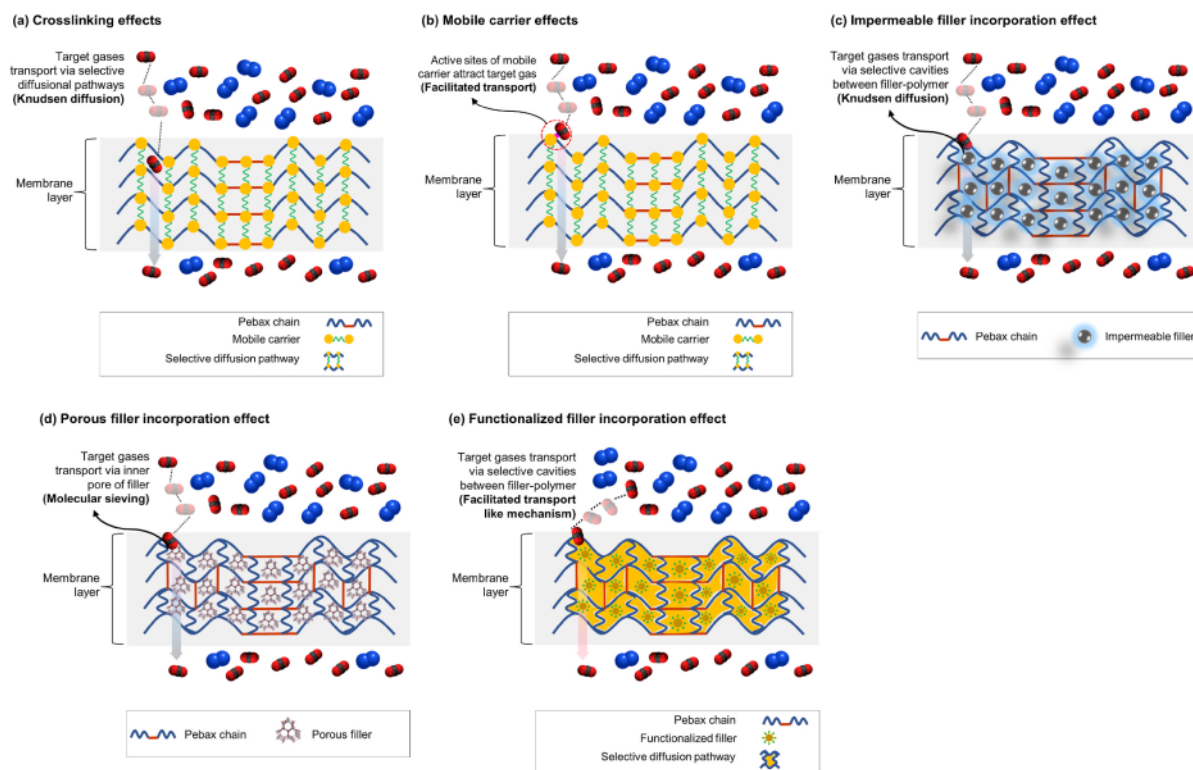


Fig. 2. Schematic diagram illustrating the effect of different modification approaches on Pebax's chain packing and gas transport properties.

the highest 1023 Barrer CO₂ permeability (PER_{CO₂} = 1.24) with CO₂/CH₄ ideal selectivity of 46 (SeER_{CO₂/CH₄} = 0.43) and CO₂/N₂ selectivity of 91 (SeER_{CO₂/N₂} = 0.62).

Semi-mobile carriers like aniline offer a different facilitated transport mechanism called the "hopping-vehicle mechanism" that combines the eminence of fixed and mobile carriers. Kojabad et al. (2021a) found the crystallinity of both PE and PA segments in Pebax membrane reduced with increasing aniline content up to 50 wt%. On the other hand, the aniline high diffusion coefficient was favorable to driving its free motion within the Pebax matrix as well as facilitating CO₂ transport via the hopping-vehicle mechanism. In addition, Pebax/aniline 50 wt% exhibited the highest CO₂ permeability of 151 Barrer (PER = 0.76) and CO₂/N₂ selectivity of 92.5 (SeER = 1.01).

3.3. Polymer blending

This technique exploits a variety of polymers to manipulate the Pebax membrane structural properties and enrich the gas adsorption sites. Pebax originated from rubbery polymers, bulky polymers, and copolymers.

Different low molecular weight polymers like PEG-200, PEG-400, and PEG-550 were reported to enhance Pebax membrane CO₂ separation efficiency. These PEG series are plasticizers to soften the base copolymer molecular structure, promoting a higher CO₂ diffusivity coefficient. Meanwhile, the CO₂ solubility coefficient upgrade may also be obtained, corresponding to a strong interaction between PEG ether-oxygen (EO) units and CO₂. Synchronized improvement in diffusivity-solubility brings remarkable Pebax membrane gas separation performance. Azizi et al. (2017a) reported that PEG-400 could significantly increase Pebax-1074 membrane CO₂ permeability by up to 160%, with little change in CO₂/CH₄ selectivity. Similar Pebax MMMs were also prepared by Azizi et al. (2017b) with identical CO₂ separation improvement. Another PEG series, PEG-200, was then investigated by Azizi et al. (2018) to modify the Pebax-2533 gas permeability for CO₂/CH₄ separation. The CO₂ permeability enhancement was slightly lower at 88%, but CO₂/CH₄ selectivity increased by 26%. In the case of CO₂ permeability enhancement (PER_{CO₂} = 3.88), PEG-550 (30 wt%) became superior to other polymer additives, as seen in Fig. 4. Nadeali et al. (2020) argued this was associated with the PEG-550 ability to alter the host polymer intersegmental structure (GTER = -0.26 and CrER2 = -0.28), causing superior reinforcement in gas separation performance.

Bulky polymers offer a different way to obtain higher gas separation performance. They are mainly in rigid form, which can close polymer chain packing, resulting in a drastic reduction in permeability. It was proved by Taheri et al. (2021b) found that PEG-4000 blending caused a more severe decrease in CO₂ permeability (almost 100%). In contrast, gas selectivity improves significantly due to polar substituents in the PEG backbone. The improvement in CO₂/CH₄ selectivity due to PEG-1000 in Pebax MMMs (SeER = 0.51) was consequently highlighted by Azizi et al. (2017a). Other bulky polymers, like PVA-60000, were also reported to increase CO₂ selectivity. Kheirtalab et al. (2020) argued that the oxygen atoms of hydroxyl groups on PVA could act as electron donors toward the positively charged CO₂ central carbon atom, resulting in better CO₂/CH₄ selectivity (up to 33%) and CO₂/N₂ selectivity (up to 100%). Polyvinyl acetates (PVAc) have been an option with a base structure similar to PVA with additional ester groups. Abdollahi et al. (2017) reported that the Pebax-1657 membrane CO₂/CH₄ selectivity could be enhanced up to 85% with 10 wt% PVAc incorporation. Another study by Shirinia et al. (2020) presented higher CO₂/CH₄ selectivity (114%) and CO₂/N₂ selectivity (118%) Pebax-1657 membrane enhancement levels with 30 wt% PVAc. The gas selectivity enhancement was primarily related to acetate polar groups promoting higher SoER_{CO₂} (0.92), the best of the polymer additives (see Fig. 3).

Copolymers were also used for fabricating a Pebax membrane blend by providing better-aging resistance and higher gas solubility than homopolymers. For example, Abdollahi et al. (2017) utilized VAc/dibutyl

maleate (P(VAc-co-DBM)) copolymer and Pebax to produce a blend membrane with high CO₂ solubility. As a result, the Pebax membrane containing 30 wt% P(VAc-co-DBM) copolymer exhibited CO₂/CH₄ selectivity at 37.5, an increase of 113% from the pure Pebax membrane. Further study by Shirinia et al. (2020) tried to examine the influence of different DBM molar fractions in P(VAc-co-DBM) copolymer on the gas separation properties of its blend membranes. The results implied that the blend membrane containing 30 wt% VD72 copolymer showed the best CO₂ permeability (~161 Barrer with PER_{CO₂} = 1.98), CO₂/CH₄ selectivity (~28 with SeER_{CO₂/CH₄} = 1.57), and CO₂/N₂ selectivity (~40 with SeER_{CO₂/N₂} = 1.55). Poly (glycidyl methacrylate-g-polypropylene glycol)-copoly(oxyethylene methacrylate) (PGP-POEM) is a self-cross-linkable comb copolymer, another class of copolymer that has been investigated in terms of Pebax blend membranes. A study by Kim et al. (2019) revealed the excellent ability of PGP-POEM 40 wt% to enhance the CO₂ permeability of membranes up to 123%.

3.4. Filler incorporation

Filler materials are required to fulfill critical criteria for improving the overall gas separation performance of the resulting membranes, including dispersibility, particle size, and hydrophilicity/hydrophobicity (Kamble et al., 2021). Dispersibility will determine the aggregation and tortuosity degree of particles in Pebax matrices. Non-uniform filler dispersion in the Pebax matrix usually promotes either non-selective voids or high tortuosity that affect the gas separation performance of the membrane. Another factor, particle size, may also relate to agglomeration phenomena. Bigger particle size tends to form a heterogeneous cluster in the Pebax matrix, reducing the interfacial network between two component phases. Weak interfacial interactions may severely reduce the mechanical strength of the membrane, avoiding pressurized operation conditions. Hydrophilicity/hydrophobicity, as the last factor, is necessary to prevent interfacial defect formation and provide a sufficient reactive site for target gases. Different types of materials can be incorporated into Pebax membranes to rearrange their polymer chain packing: (1) impermeable filler; (2) porous filler; (3) functionalized filler; and (4) liquid additive.

3.4.1. Impermeable filler

Metal oxides are among the most widely used nonporous fillers for developing MMMs. For instance, Farashi et al. (2019) utilized γ -Al₂O₃ at different loads to fabricate Pebax-1657 MMMs. Adding γ -Al₂O₃ into the polymer matrix reduced membrane crystallinity and enlarged the d-spacing resulting in more diffusion paths for the target gas. The highest separation efficiency could be obtained at 8 wt% with 159.27 Barrer CO₂ permeability and 24.73 CO₂/CH₄ selectivity. The excellent ability of γ -Al₂O₃ nanoparticles to level-up Pebax-1074 membranes was also proven by Azizi et al. (2017d). γ -Al₂O₃ nanoparticles were superior to other tested fillers due to better particle distribution, effective voids formation, and higher CO₂ affinity.

Silicon dioxide (SiO₂) nanoparticles have become the most popular oxide as a dispersed phase in composite membranes. Aghaei et al. (2018) revealed that adding 10 wt% 7 nm FS nanoparticles into the Pebax matrix could significantly boost CO₂ permeability (67%) and CO₂/CH₄ selectivity (36%) compared to the pristine Pebax membrane. Another study consequently proved this correlation by utilizing FS nanoparticles 40 nm as a dispersed phase for Pebax-1657 (Isanejad and Mohammadi, 2018). As a result, CO₂ permeability and CO₂/CH₄ selectivity were increased up to 38% and 53% by comprising 10 wt% FS-40.

Iron oxide (Fe₂O₃) nanoparticles proposed different features to improve CO₂ separation. Fe₂O₃ was presumed to provide a magnetic channel within the Pebax matrix leading to sufficient paramagnetic CO₂ attraction as well as CH₄ and N₂ repulsion. In Riasat Harami et al. (2019) work, Pebax/Fe₂O₃ 1.5 wt% membranes showed the best performance with 30, 42, and 81% enhancements on CO₂ permeability, CO₂/CH₄ selectivity, and CO₂/N₂ selectivity compared to the neat membrane.

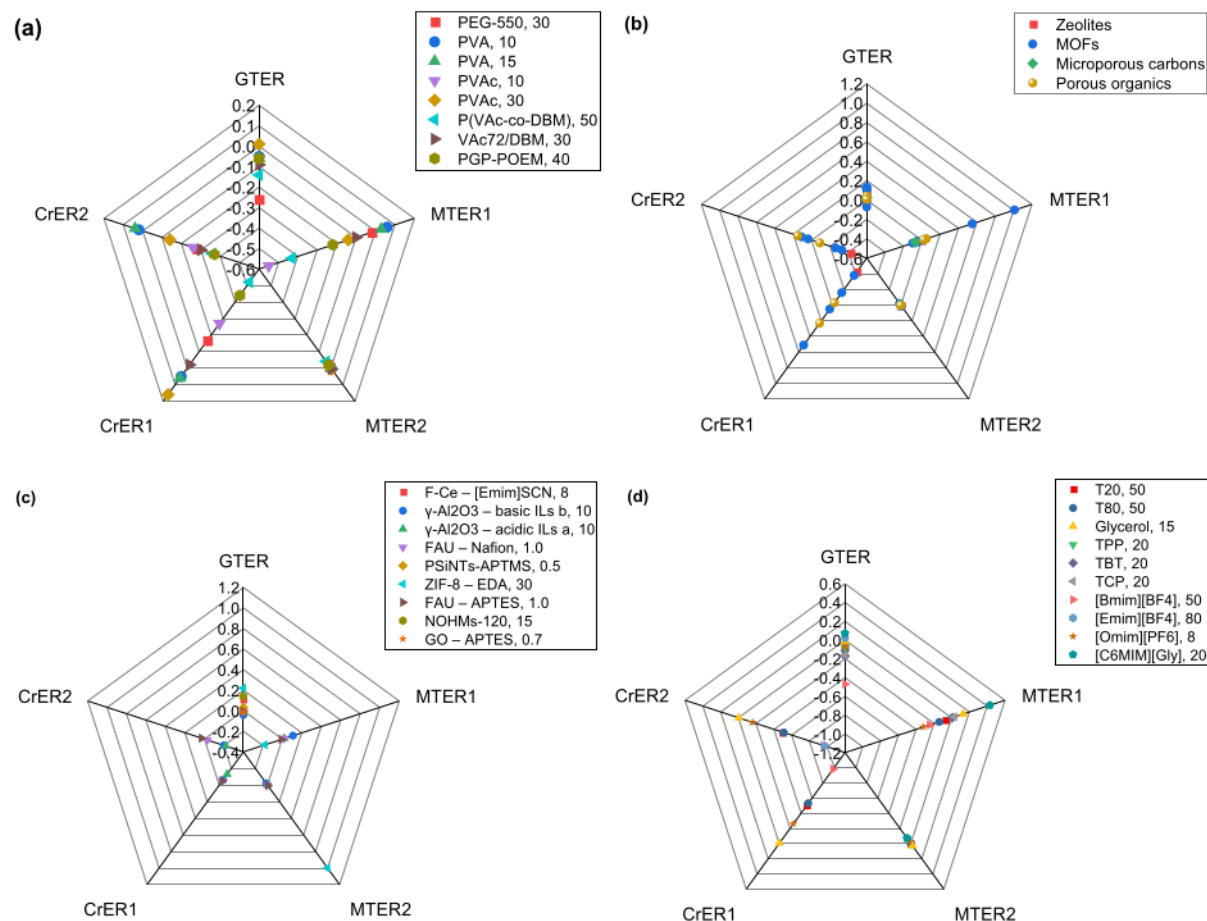


Fig. 3. The influence of different additives on Pebax membrane structural properties: (a) polymer additives, (b) porous fillers, (c) functionalized fillers, and (d) liquid additives. (Data was plotted from Tables S1, S5, S7, S90, and S11).

Zinc oxide (ZnO) nanoparticles offered a simultaneous upgrade in permeability and selectivity based on several reports. Azizi et al. (2017c) found 38%, 22%, and 24% enhancements in CO_2 permeability, CO_2/CH_4 , and CO_2/N_2 selectivities when 8 wt% of ZnO loaded into the Pebax-1074 matrix. Jazebizadeh and Khazraei (2017) found that Pebax/ZnO 4 wt% membrane displayed 87 Barrer of CO_2 permeability and 31.8 of CO_2/CH_4 selectivity, increased by 48% and 55% from the pure membranes. In the work of Sheikh et al. (2017), all gas separation factors were doubled by embedding 0.1 wt% of ZnO nanoparticles under a highly pressurized environment because of the synergistic effect between the sufficient gas diffusion pathways and the hydrophilic properties promoting high solubility toward polar gases.

Recent experimental work by Azizi et al. (2023) investigated the impact of incorporating magnesium oxide (MgO) toward the CO_2 permeation features of Pebax membrane. The research outcomes indicated that MgO could reduce crystallinity by disrupting the hydrogen bonding in PA blocks, then enlarge d-spacing and FFV as a proxy for swifter gas transport through the membrane. In addition, nanovoids might also exist in the interfacial network, flourishing diffusional routes for targeted gases. As a result, CO_2 permeability and CO_2/CH_4 selectivity could be improved at 28.81% and 15.95%, respectively, with 8 wt% MgO addition into Pebax membranes.

In general, oxide particles perform in an identical direction to disrupt the Pebax chain packing for establishing selective diffusional gas

pathways for target gases. However, the characteristics of functional groups or metals will determine the distinction between each oxide. For instance, SiO_2 and ZnO rely on their hydrophilicity to provide high solubility for polar gases in Pebax membranes. In other cases, the reactive metals in Al_2O_3 and Fe_2O_3 can assist the CO_2 separation process in Pebax MMMs.

Two-dimensional (2D) metal/metal oxide nanosheets may become another option for improving the Pebax membrane's efficiency. One of the alternatives is molybdenum disulfide (MoS_2), an emerging graphene-like 2D material with a strong affinity toward polar gases like NO_2 and CO_2 (Yue et al., 2013; Zhao et al., 2014). A Pebax membrane comprised of 4.76 wt% MoS_2 exhibited CO_2 permeability of 67.05 Barrer ($\text{PER}_{\text{CO}_2} = 0.46$) and CO_2/N_2 selectivity of 90.61 ($\text{Se}_{\text{ER}_{\text{CO}_2/\text{N}_2}} = 1.02$) (Liu et al., 2019). MXene is another newly developed 2D material for Pebax membranes for higher Pebax membrane separation performances. Guan et al. (2021) reported that by doping 0.5 wt% m-MXene into Pebax-1657 membranes, CO_2 permeability and CO_2/N_2 selectivity could be simultaneously enhanced up to 15% and 68%, respectively. It was related to the O-containing groups on m-MXene and H-bonding with Pebax, enabling a robust molecular sieving effect. In other work, Shi et al. (2021) also found that the Pebax-1657 membrane improved by up to 66% in CO_2 permeability and 16% in CO_2/N_2 selectivity by adding 1 wt% MXene. Zhu et al. (2021) recently gained an outstanding result by incorporating 2D porous bimetal oxide nanosheets, ZnCo_2O_4 , into

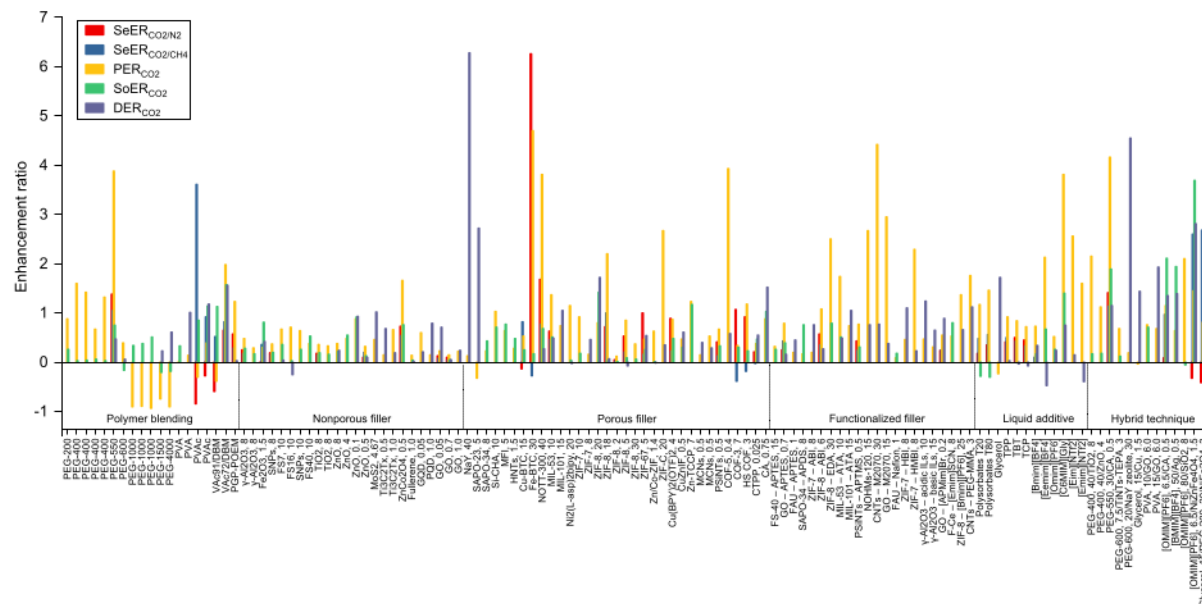


Fig. 4. The influence of different polymer additives on Pebax membrane gas separation performance (Data was plotted from Tables S2, S6, S8, S10, S12, and S14).

Pebax-1657 membranes for CO₂/CH₄ separation. CO₂ permeability and CO₂/CH₄ selectivity reached 139.10 Ba¹ and 15.38 in this work, respectively, increasing 166% and 76% compared to the neat Pebax membrane. Regarding CO₂ permeability enhancement, ZnCo₂O₄ is the most noteworthy impermeable filler for Pebax MMMs, as illustrated in Fig. 4. It was because bimetallic Zn²⁺ and Co²⁺ could generate oxygen vacancies (O^{-δ}) for providing more CO₂ (C^{-δ}) adsorption sites.

In the carbon-based filler case, two novel materials, fullerene and carbon quantum dots, have been recently developed to fabricate Pebax MMMs. Fullerene (C₆₀(OH)₂₄) is a nonporous filler with high water solubility synthesized by surface hydroxylation of fullerene. Wu et al. (2019) revealed a 14% enhancement in CO₂ permeability with minor changes in CO₂/CH₄ and CO₂/N₂ selectivities by incorporating 1 wt% C₆₀(OH)₂₄ particles into Pebax membranes. That was mainly due to polymer chain packing disruption synchronized with polar-quadrupole interaction between abundant hydroxyl groups and CO₂. Carbon quantum dots (QDs) is another novel carbon material for fabricating Pebax MMMs. Shi et al. (2020) developed two types of QDs, polymer-like QDs (PQD) and graphene oxide QDs (GQD), to manipulate the Pebax membrane microphase structures for CO₂ separation. PQD has more functional groups, which are favorable for disrupting Pebax segmental crystalline phase. Otherwise, with fewer functional groups, GQD can effectively enhance Pebax microphase separation.

Graphene oxide (GO) nanosheets can also be admitted as a Pebax membrane impermeable filler material for CO₂/N₂ separation. GO nanosheet interlayer spacing is essential in providing sufficient gas diffusional pathways through the Pebax membrane, resulting in higher gas permeability. Huang et al. (2018) reported an improved CO₂ permeability of 23% and CO₂/N₂ selectivity of 71% when 0.05 wt% GO was incorporated into Pebax membranes. Likewise, Shi et al. (2021) observed a relatively similar enhancement ratio in CO₂ permeability with a lower CO₂/N₂ selectivity enhancement of 24% on Pebax MMMs containing 1 wt% GO. In another study by Zhang et al. (2019), less CO₂ permeability improvement was observed at 15%, with a neglected increase in CO₂/N₂ selectivity.

3.4.2. Porous filler

These materials offer molecular sieving channels in Pebax matrices

for gas separation. In many cases, the incorporation of porous fillers positively impacts the physical and thermal strength of the resultant membrane, as seen in Fig. 3b.

Zeolites are inorganic microporous crystalline materials with beneficial characteristics such as superior surface area, water-insoluble, intensive active metal speciation, high resistance in pressurized conditions, high chemical-thermal stability, and structure-shape variety (Kamble et al., 2021). Zheng et al. (2020) highlighted the prominence of diffusivity rather than the solubility in CO₂ separation through Pebax MMMs containing NaY. It might create micro-sized voids and particle aggregations, creating selective diffusional pathways through MMMs. Pebax membrane containing 40 wt% NaY could increase CO₂/N₂ selectivity by 628%, the highest value compared to other porous fillers, as seen in Fig. 4.

Zhang et al. (2021c) also found selective diffusivity through microvoids in Pebax/SAPO-23 MMMs. At 5 wt% SAPO-23 loading, CO₂ permeability dropped by 13%, whereas CO₂/N₂ selectivity improved considerably by 272% compared to neat Pebax membranes. Other zeolites like SAPO-34, Si-CHA, and MFI were applied to fabricate Pebax MMMs for CO₂/CH₄ separation. Zhao et al. (2021) reported that CO₂ permeability and CO₂/CH₄ selectivity of Pebax membrane was increased by 23% and 43% with 8 wt% SAPO-34 incorporations. SAPO-34 could create micro-cracks on the MMMs surface for selective CO₂/CH₄ separation. This improvement is relatively similar to the halloysite nanotubes (HNTs) effect on the CO₂/CH₄ performance of Pebax membranes (PER = 0.28 and SeER = 0.48). Ebadi et al. (2021) utilized the pore size similarity of Si-CHA zeolite with a CH₄ kinetic diameter to achieve better Pebax membrane CO₂/CH₄ separation. Due to the perfect molecular sieving of Si-CHA in Pebax MMMs, CO₂ permeability and CO₂/CH₄ selectivity can be enhanced by 103% and 71%, respectively.

Two-dimensional (2D) zeolite was further developed as an inorganic filler in Pebax membranes to improve the interfacial connectivity and restrain the agglomeration of highly loaded filler. Zhang et al. (2021b) embedded MFI nanosheets with a thickness of 6 nm, microporous aperture of 0.55 nm, and aspect ratio of 200 into Pebax for preparing MMMs. This zeolite nanosheet was widely known for owning a terrific CO₂ adsorption affinity with a saturation tendency toward CH₄. In addition, its high aspect ratio could enrich nanosheet tortuosity,

promoting high gas selectivity.

MOFs are an emerging class of filler material in MMMs development with a cage-like structure. Khosravi et al. (2017) incorporated copper benzenetri-carboxylate ($\text{Cu}_3\text{BTC}_2/\text{Cu-BTC}$) into Pebax-1657 to modify the CO_2/CH_4 separation performance of Pebax membranes. With 15 wt% CuBTC addition, the CO_2 permeability and CO_2/CH_4 selectivity were risen by 53% and 25%. Higher CO_2 permeability was strongly related to the enhancement in CO_2 solubility at around 82%. Indeed, the coordinatively unsaturated Cu^{2+} sites could interact with a decisive quadrupole moment of CO_2 , leading to more CO_2 sorption than CH_4 . Another study by Dorosti and Alizadehdakheel (2018) found exceptional enhancement in CO_2 permeability (up to 470%) with Fe-BTC incorporation into Pebax-1657. Fe-BTC has a similar topology to Cu-BTC with a larger aperture size. Hence, the CO_2 diffusivity can be dramatically improved at around 600% compared to the neat Pebax membrane. The CO_2 diffusivity and permeability enhancement ratios from Fe-BTC incorporation have become most prominent among porous filler materials for Pebax MMMs, as illustrated in Fig. 4. MIL-53 and MIL-101 are other considerable MOFs synthesized with a similar ligand, benzene-1,4-dicarboxylic acid (BDC). Meshkat et al. (2018) revealed that CO_2 solubility and diffusivity coefficients rose simultaneously, promoting impressive progress in CO_2 selectivity. With a smaller pore aperture, MIL-101 exhibited lower CO_2 permeability enhancement (74%) and a higher increase in CO_2/N_2 selectivity (105%) (Song et al., 2020). Meanwhile, $\text{Ni}_2(\text{L-asp})_2\text{bipy}$ exhibited comparable CO_2 permeability enhancement (115%) with MIL-53 when it was used as a dispersed phase in Pebax MMMs (Fan et al., 2018). Although $\text{Ni}_2(\text{L-asp})_2\text{bipy}$ has a smaller window size than MIL-53, its structure strongly interacts with CO_2 molecules, facilitating their diffusion and thus escalating permeability.

ZIFs have been widely applied as fillers in Pebax MMMs due to their simplicity and less energy requirement in the synthesis process. Azizi and Hojati (2018) reported ZIF-7 10 wt% could magnify CO_2 permeability and Pebax-1074 membrane CO_2/CH_4 selectivity. Selective diffusion could occur through the ZIF-7 flexible pore gate, which was more likely favorable for CO_2 than CH_4 . In another Gao et al. (2020) study, ZIF-7 could also upgrade the Pebax-233 membrane CO_2/N_2 separation ($\text{PER}_{\text{CO}_2} = 0.18$ and $\text{SeER}_{\text{CO}_2/\text{N}_2} = 0.5$ at 8 wt% ZIF-7 loads). ZIF-8 and ZIF-67 can improve Pebax membrane performance with a higher surface area attribute. Xu et al. (2017) observed a PER_{CO_2} of 2.2 (3 times pristine Pebax) with slight increases in CO_2/CH_4 and CO_2/N_2 selectivities by 18 wt% ZIF-8 incorporation into the Pebax-1657 membrane. The positive change in CO_2 permeability was primarily related to the simultaneous upgrade in diffusivity and solubility coefficients. Other studies found this trend despite lower PER_{CO_2} (see Fig. 4). Sutrisna et al. (2017) reported the CO_2 permeability of Pebax MMMs containing 20 wt% ZIF-8 was 80% higher than the pure Pebax membrane, with a drop in CO_2/CH_4 and CO_2/N_2 selectivities. Similarly, Meshkat et al. (2020) found an 85% increment in CO_2 permeability with insignificant changes in CO_2/CH_4 and CO_2/N_2 selectivities by adding 5 wt% ZIF-8 into Pebax-1657 membranes. PER_{CO_2} was even less at 65% when 1.4 wt% Zn/Co ZIF was loaded into Pebax-1657 membranes (Cheng et al., 2020). With a lower ZIF-8 loading at 2 wt%, Zhang et al. (2018b) obtained minor ascension in Pebax-1657 membrane CO_2 permeability and selectivity. This phenomenon also emerged when ZIF-8 was introduced into higher PA content. Atash Jameh et al. (2020) reported that Pebax-1074/ZIF-8 30 wt% had a CO_2 permeability of 134 Barrer, which increased by almost 40% from its pure membranes. ZIF-67 offered a synchronized upgrade for permeability and selectivity. Meshkat et al. (2020) reported a balanced refinement in CO_2 permeability ($\text{PER}_{\text{CO}_2} = \sim 0.5$) and CO_2/CH_4 selectivity ($\text{SeER}_{\text{CO}_2/\text{CH}_4} = \sim 0.55$) of Pebax MMMs containing 5 wt% ZIF-67. That was strongly associated with its effective pore aperture and large pore gates, promoting a superior advance in CO_2 diffusivity ($\text{DER}_{\text{CO}_2} = 1.00$). Kardani et al. (2020) also observed this refinement by utilizing mesoporous copper-zinc bimetallic imidazolate (CuZnIF) as a dispersed phase for the Pebax-1657 matrix, bringing out

PER_{CO_2} of almost 0.5 and $\text{SeER}_{\text{CO}_2/\text{N}_2}$ of 0.61. Instead of a larger pore diameter, the improved perm-selectivity was also related to the CuZnIF CO_2 -philic characteristic.

Two-dimensional (2D) MOFs could enhance perm-selectivity due to the selective multilayer separation channel arrangement within Pebax matrices. The roles of some novel 2D MOFs to facilitate CO_2 transport in Pebax membranes have recently been investigated. For example, Li et al. (2019) synthesized Zn-tetra-(4-carboxyphenyl)porphyrin (Zn-TCCP) to fabricate Pebax-1657 MMMs for efficient CO_2 separation. As a result, a simultaneous improvement in CO_2 permeability (123%) and CO_2/CH_4 selectivity (117%) was observed by adding 7 wt% Zn-TCCP into Pebax matrices. The Zn-TCCP microporous structure could shorten the diffusional gas pathways and provide fast transport channels to increase CO_2 permeability. At the same time, the Zn-TCCP multilayer horizontal arrangement was sufficiently tortuous for larger gas molecules like CH_4 , resulting in higher CO_2/CH_4 selectivity. Similarly, incorporating 10 wt% zeolitic imidazolate framework ctid (ZIF-C, MW = 85–124) into Pebax could significantly increase CO_2 permeability ($\sim 100\%$) with a slight enhancement in CO_2/N_2 selectivity of 34% at dry state (Deng et al., 2020). The layered Ni-MOF nanosheets (Ni-NS) were recently investigated by Zhu et al. (2023) as fillers to fabricate high-performance Pebax MMMs for CO_2 separation. Ni-NS with defective structure showed an ability to accelerate CO_2 separation through Pebax MMMs relying on enlarged pore size and enriched adsorption sites. Ni-NS 8 wt%, in particular, provided the most significant impact on CO_2 permeability ($\text{PER} = 1.15$) and CO_2/CH_4 selectivity ($\text{SeER} = 0.18$). In another study by Feng et al. (2023), a 2D Zr-hydroxamate MOF, SUM-9, was successfully embedded into Pebax 2533 membranes CO_2/N_2 separation. It has a honeycomb topology of 2D layers and hexagonal 1D channels to intensify gas permeation in Pebax membranes. With only 1 wt% loading, SUM-9 could tremendously improve CO_2 permeability ($\text{PER} = 1.30$) and CO_2/CH_4 selectivity ($\text{SeER} = 0.11$) of Pebax 2533 membranes at 6 bar operation.

Microporous carbon nanoparticles (MCNs) can be another reasonable choice for intensifying the host polymeric membrane gas transport channels. Wang et al. (2021b) revealed the ability of carbonized microporous nanospheres to improve the Pebax membrane's CO_2/N_2 separation properties. At 0.5 wt% load, the Pebax MMMs demonstrated the best CO_2/N_2 separation performance with a SeER of almost 0.4. This excellent advancement corresponded to a low-resistance transport pathway and high nitrogen content. Another study by Yang et al. (2021b) tried to construct low-resistance, high-selectivity transport multi-channels in Pebax membranes by incorporating 2D microporous carbon nanoplates (MCNPs). Although the addition of MCNPs could reduce polymer chain mobility with a high tendency for lower gas diffusion, higher CO_2/N_2 selectivity was still achieved because of the large nanoplate aspect ratio.

Porous fillers for Pebax MMMs could also be originated from organic materials. Porous silica nanotubes (PSiNTs) can provide rapid gas transport channels and intensify gas diffusion through MMMs, relying on plenteous micropores in their morphological structure (Yang et al., 2019). Thus, the CO_2 diffusivity of Pebax membranes could be improved by around 41% with the PSiNTs incorporation (0.5 wt%), resulting in significant upgrades in CO_2 permeability (67%) and CO_2/CH_4 selectivity (33%).

Meanwhile, covalent organic frameworks (COFs) have a similar effect to MOFs in modifying the gas transport channels within Pebax membranes. For instance, COF-5, a two-dimensional (2D) COF with high rigidity and porosity, probably made a sponge-like Pebax structure with low resistance toward gas molecules, improving gas permeability. It was proven by a report by Duan et al. (2019) that found an excellent CO_2 permeability of 493 Barrer ($\text{PER}_{\text{CO}_2} = 3.93$) with a CO_2/N_2 selectivity of 49.3 ($\text{SeER}_{\text{CO}_2/\text{N}_2} = 0.58$). On the other hand, COF-300, a three-dimensional (3D) COF, exhibited fewer enhancements in the CO_2 permeability enhancement (34%) and CO_2/CH_4 selectivity (30%) of Pebax membranes at 7 wt% filler load under dry-state testing (Zhao

et al., 2020). These refinements were quite similar to the results provided by a covalent triazine piperazine polymer (CTPP), a covalent organic polymer with an amorphous structure with 3D dendrimer-like micropores. Thankamony et al. (2019) revealed significant improvements in all gas separation factors at 0.025 wt% CTPP content. Recent work by Liu et al. (2021) utilized hollow spherical (HS) COF with sufficient mass transport resistance for manipulating the Pebax membrane gas transport channels. As a result, CO₂ permeability and CO₂/CH₄ selectivity were increased by 118% and 23%, respectively. However, the mentioned porous organics could still not significantly upgrade gas selectivity due to insufficient gas solubility. For this reason, p-tert-butylcalix 4 arene (CA), a macrocycle-particles with a basket-like porous structure and large CO₂-philic polyhydroxy groups, were utilized by Nadeali et al. (2019) as a filler for fabricating Pebax MMMs. The result indicated a simultaneous upgrade in CO₂ permeability, CO₂/CH₄, and CO₂/N₂ selectivities at 0.75 wt% filler loading.

3.4.3. Functionalized filler

Appropriate filler materials could effectively enhance Pebax membrane gas diffusivity by creating an additional gas transport mechanism, either Knudsen diffusion or molecular sieving, instead of solution-diffusion. However, gas solubility improvement was restricted in many cases due to the absence of enormous selective reactive sites within the resultant membranes. The incompatibility of some filler materials may also create interfacial defects between the polymer matrix and filler, leading to a severe decline in selectivity. In these regards, filler materials should be functionalized to prevent non-selective cavities formation and intensify reactive sorption areas toward a gas target.

Amines-functionalized fillers (AFFs) have become more pronounced, indicating their compatibility with the Pebax structure. In particular, amines in the filler surface exhibit a strong interaction with functional groups (C=O) in Pebax polyamide domains to rearrange the pore distribution and rigidify the network, resulting in higher gas selectivity (Shah Buddin and Ahmad, 2021). The attached amines are also advantageous for improving the gas permeability of Pebax MMMs regarding their high affinity toward condensable gases.

3-Aminopropyltriethoxysilane (APTES) has been currently used to functionalize nonporous fillers like fumed silica (FS-40) and graphene oxide (GO) nanosheets. Isanejad and Mohammadi (2018) observed a simultaneous upgrade in the CO₂ permeability (PER = 0.32) and CO₂/CH₄ selectivity (SeER = 0.26) at a 15 wt% loading rate of FS-40/APTES. With a larger functionalization area in GO nanosheets, the influence of APTES becomes even more significant in escalating Pebax membrane CO₂ permeability (PER = 0.79) and CO₂/CH₄ selectivity (SeER = 0.39) at 0.7 wt% filler load (Zhang et al., 2019). In another work, Wang et al. (2019) covalently grafted polyether amine (M2070) with either carbon nanotubes (CNTs) or graphene oxide (GO) to prepare their nanofluids. CNTs nanofluids could significantly improve Pebax membrane CO₂ permeability and CO₂/N₂ selectivity at 442% and 77%. It was better than GO nanofluids and has become the best-functionalized filler in CO₂ permeability upgrade compared to others (see Fig. 4). Another study by Wang et al. (2020a) prepared liquid-like nanoparticle organic hybrid materials (NOHMs) to develop Pebax MMMs for CO₂/N₂ separation. NOHMs were synthesized by tethering silica core and polyether amine M2070 canopy using silane coupling agent 3-glycidyl oxy propyl trimethoxy silane (KH560) as corona via a covalent bond. The Pebax membrane CO₂/N₂ separation performance was polished (PER_{CO₂} = 2.76 and SeER_{CO₂/N₂} = 0.76) by incorporating 15 wt% of NOHMs.

Porous fillers with a higher surface area could create more reactive adsorption sites and significant gas selectivity refinement. Mosadegh et al. (2020) functionalized zeolite faujasites (FAU) with APTES via a wet impregnation method and incorporated them into Pebax matrices. As a result, the resulting Pebax MMMs exhibited a CO₂/N₂ selectivity increase (SeER = 0.45). Another amino silane, 3-(2-aminoethylamino) propyl-dimethoxymethylsilane (APDS), was utilized by Zhao et al.

(2021) to modify SAPO-34 as a filler for Pebax membranes. By introducing 8 wt% SAPO-34/APDS into Pebax, CO₂/CH₄ selectivity was remarkably improved by 76%. Meanwhile, porous organosilicon nanotubes (PSiNTs)-modified 3-aminopropyl trimethoxysilane (APTMS) offered a reverse effect. The upgrade in CO₂ permeability was more pronounced than that of CO₂/CH₄ selectivity because of the increased CO₂ solubility coefficients (SoER = 0.24) in the membrane with the presence of amine groups in PSiNTs-APTMS. APTES had no intention to block the micropores in the PSiNTs structure; it established interfacial interactions with Pebax matrices as well as attracted more CO₂.

Amine functionalization was executed simultaneously during the synthesis process using metal linkers containing amine groups for some MOF series. Gao et al. (2020) employed 2-aminobenzimidazole as a metal linker to synthesize ZIF-7-NH₂ for fabricating Pebax MMMs. Utilizing ZIF-7-NH₂ could increase CO₂ permeability and decrease N₂ permeability simultaneously, indicating a selective CO₂/N₂ separation. Hence, with the presence of 8 wt% ZIF-7-NH₂, the CO₂/N₂ selectivity of the Pebax membrane rose 76% from that of the neat membrane. Ding et al. (2020) also used this metal linker to modify ZIF-8 as a filler for Pebax membranes. At 6 wt% ZIF-8-NH₂ load, the best Pebax MMM performance was achieved with CO₂ permeability of 163.8 (PER = 1.08) and CO₂/N₂ selectivity of 62 (SeER = 0.27), respectively. The predominant enhancement in CO₂ permeability indicated that the FFV enlargement effect was more potent than promoting CO₂ affinity by amino groups. Another amine-based metal linker, 2-aminoterephthalic acid, was also used to prepare MIL-53-NH₂ and MIL-101-NH₂. They both faced a similar problem regarding a significant decline in gas selectivity at higher loading. Meshkat et al. (2018) reported that Pebax's ideal selectivities (CO₂/CH₄, CO₂/N₂, CO₂/H₂) comprising MIL-53-NH₂ were not much better than Pebax/MIL-53 at the same filler load. Although the attached amine groups on the MIL-53 surface could adsorb more CO₂, the interfacial defect within Pebax matrices was not wholly avoidable. Likewise, non-selective pores and voids were observed in Pebax containing 15 wt% MIL-101-NH₂, causing a drastic CO₂/N₂ selectivity. In contrast, ethylenediamine (ED)-based ZIF-8 could offer ideal upgrades in CO₂ permeability (PER = 2.51) and CO₂/CH₄ selectivity (SeER = 0.79) of Pebax MMMs (Atash Jameh et al., 2020). This refinement was attributed to the intensified CO₂ transport by enormous CO₂ reactive sites and excellent ED interfacial interaction with Pebax matrices.

Other functional groups, such as -SO₃, -OH, -CH₃OH, and ether-oxygen, are also reported to modify filler materials in Pebax MMMs. Mosadegh et al. (2020) functionalized zeolites FAU using Nafion to improve the CO₂/CH₄ separation features of Pebax membranes. Pebax MMMs comprised of 1 wt% Nafion showed the best CO₂/CH₄ selectivity of 31 (SeER = ~0.20). This improvement is due to the -SO₃H groups with high reactivity toward more quadrupole gases (CO₂ and N₂) than nonpolar gases like CH₄. On the other hand, Gao et al. (2020) prepared ZIF-7-OH and ZIF-7-CH₂OH using 2-hydroxy benzimidazole and 2-hydroxymethyl benzimidazole, respectively. ZIF-7-OH was salient for obtaining a higher CO₂/N₂ selectivity regarding its ability to rigidify the Pebax chains and establish a particular CO₂ sorption site. Otherwise, ZIF-7-CH₂OH had a larger particle size with a strong tendency to form non-selective cavities, leading to higher CO₂ permeability and lower CO₂/N₂ selectivity. Polyethylene glycol has been reported to functionalized carbon nanotubes (CNTs) with ethylene oxide groups for improving Pebax membrane CO₂ separation performance. Dai et al. (2019) mentioned that PEG could create CO₂-philic channels within CNT, establishing selective CO₂ transport. Three wt. % CNT-PEG content in Pebax MMMs produced the optimum CO₂ permeability (PER = ~1.80) and CO₂/N₂ selectivity (SeER = ~1.10) values under dry testing conditions.

Functionalizing filler with ionic liquids (ILs) was also valuable in avoiding non-selective voids formation and intensified reactive sorption sites. Several IL-functionalized fillers have been reported in Pebax MMMs fabrication. For instance, γ-Al₂O₃ was functionalized with two

types of acidic (2-hydroxyethyl ammonium sulfate) and basic (1-(4-aminobutyl)-3-methylimidazolium chloride) ionic liquids for preparing Pebax MMMs in CO₂/N₂ separation (Kojabad et al., 2021b). As a result, both ILs could restrict the γ -Al₂O₃ aggregation within Pebax matrices via electrostatic and steric forces. Acidic IL, however, exhibited a better impact on preventing γ -Al₂O₃ sedimentation than the basic IL. When γ -Al₂O₃ particles are well dispersed, the formation of interfacial defects is restricted. Furthermore, it synergistically collided with the Lewis base-Lewis acid interaction between the S=O groups of acidic IL and the carbon atoms of CO₂, promoting higher CO₂ permeability (PER = 0.47) and CO₂/N₂ selectivity (SeER = 1.24). An identical effect was found when APMimBr and EmimSCN were utilized to functionalize GO nanosheets (Huang et al., 2018) and F-Ce nanosheets (Xin et al., 2020), respectively. Another study by Guo et al. (2020) revealed that BmimPF₆-functionalized ZIF-8 (IL@ZIF-8) could simultaneously accelerate CO₂ permeability and CO₂/N₂ selectivity enhancement in Pebax membranes. Notably, the MMM containing 25 wt% IL@ZIF-8 showed the best gas separation performances with 117 Barrer (PER = 1.37) of CO₂ permeability and 84.5 (SeER = 0.66) of CO₂/N₂ selectivity. Porous IL@ZIF-8 produced facile transport pathways and interphase compatibility, enabling selective moieties at this filler load rate.

3.4.4. Liquid additives

Polysorbate 20 (T20) and polysorbate 80 (T80), non-ionic surfactants with a backbone similar to PEG, also become an alternative for higher Pebax membrane performance. T20 and T80 are derived by sorbitan ethoxylation with lauric acid and oleic acid, respectively. The ability of T20 and T80 as polymer additives for Pebax membranes was reported by Simari et al. (2020). Both T20 and T80 could improve CO₂ diffusion and solubility in the Pebax membrane resulting in a permeability gain of about 120% and 150%. In addition, longer alkyl chains in the T80 backbone created more reactive sites toward polar gas.

Another ester-based polymer additive, triglycerides, has also been applied to prepare a Pebax blend membrane. Three types of triglycerides with different alkyl chain lengths: tripropionin (TP), tributyrin (TBT), and triacprinin (TCP), were successfully studied to enhance the gas separation efficiency of the Pebax-2533 membranes (Wu et al., 2021). The results revealed that Pebax/TBT and Pebax/TCP blend membranes displayed higher flexibility (indicated by lower T_g, see Fig. 3d) than Pebax/TPP blend membranes, promoting a higher gas diffusion coefficient. On the other hand, the CO₂ solubility coefficients in blend membranes insignificantly decreased with increasing triglyceride alkyl chain length. In particular, the concentration of the ester group and its polarity toward CO₂ in blend membranes diminished with a flourishing triglyceride alkyl chain, leading to a lower solubility coefficient. As a result, Pebax/TPP blend membranes exhibited higher solubility than those of Pebax/TBT and Pebax/TCP blend membranes. Glycerol, a low molecular weight polyol, could also be considered a polymer additive for Pebax. Sanaeepur et al. (2019a) found that 15 wt% glycerol could significantly increase CO₂/N₂ selectivity by 172% of pure Pebax membrane despite a 23% drop in CO₂ permeability.

Using ionic liquids (ILs) to modify Pebax membranes has a similar effect as introducing plasticizers. Some ILs have been reported as ones considered for modifying Pebax membrane gas perm-selectivity. 1-Butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) ionic liquid was used by Ghasemi Estahbanati et al. (2017b) to modify Pebax CO₂ perm-selectivity. Doping BmimBF₄ could remarkably reduce crystallinity (~100%), then increase the flexibility (~50%) with larger FFV, leading to higher gas diffusion (up to 60% for CO₂). A slight increase in CO₂ solubility at around 10%, with 50 wt% IL addition. Improvement in the diffusivity-solubility promoted a notable CO₂ permeability of 190 Barrer, which increased by 73% compared to the neat Pebax membrane. Similar effects were also presented by other ionic liquids like 1-ethyl-3-methylimidazolium tetrafluoroborate (EmimBF₄), 3-methyl-1-octyl imidazolium hexafluorophosphate (OmimPF₆), and 1-alkyl-3-methylimidazolium glycine (C₆mimGly) for improving CO₂ permeability.

With 80 wt% of EmimBF₄ blend, CO₂ permeability and CO₂/CH₄ selectivity were 270.1 Barrer (PER = 213%) and 27.3 (SeER = 64%), respectively. Meanwhile, 1-alkyl-3-methylimidazolium glycine (C₆mimGly) exhibited the most significant CO₂ permeability enhancement than other ILs, comparable with PEG-550. Li et al. (2020) referred to the ability of the Gly⁻¹ anion and C₆mim⁺ cation to present a favorable radius (0.338 nm) for selective CO₂ diffusion. Plenteous amounts of amino and carboxyl groups in the Gly⁻¹ anion could be CO₂ carriers, facilitating highly efficient CO₂ transport.

3.5. Hybrid technique

Hybrid techniques refer to a method that combines two or three single modification approaches (crosslinking, mobile carrier attachment, polymer blending, or filler incorporation) to fabricate ternary or quaternary Pebax MMMs. In many cases, polymer additives and filler materials were incorporated simultaneously into Pebax for manufacturing ternary MMMs. These two materials are expected to establish facilitated transport, Knudsen diffusion, and molecular sieving aside from solution diffusion as an original gas transport mechanism in Pebax.

Several ternary Pebax MMMs have been developed in recent years. For example, Azizi et al. (2017b) incorporated TiO₂ nanoparticles into Pebax-1074/PEG-400 blend membranes to fabricate ternary MMMs for CO₂/CH₄ separation. Pebax-1074/PEG-400 (40 wt%)/TiO₂ (8 wt%) had the best CO₂ permeability, 204.46 Barrer (PER = 2.15), attributing to polymer chain disruption by TiO₂ nanoparticles and intensified chain mobility by PEG-400. Likewise, Jazebizadeh and Khazraei (2017) found a similar improvement trend in Pebax-1657/PEG-400 (40 wt%)/ZnO (4 wt%) MMMs with PER_{CO₂} of 1.12. A slight upgrade in CO₂/CH₄ selectivity might exist, mainly due to the low interfacial compatibility of nonporous fillers with polymer matrices (Noroozi and Bakhtiari, 2019). Nadeali et al. (2020) employed a basket-like porous organic with enomous -OH groups, p-tert-butylcalix4arene (CA), as a filler for Pebax-1657/PEG-550 blend membranes. The performance of this ternary Pebax MMM stood out, with PER_{CO₂} of 4.16, SeER_{CO₂/CH₄} of 1.89, and SeER_{CO₂/N₂} of 1.15. The enhancement of CO₂ permeability in these ternary Pebax MMMs even becomes the best compared to other mentioned studies, as seen in Fig. 4.

Another work by Zhang et al. (2021a) found a terrific upgrade in CO₂/N₂ selectivity (SeER = 4.55) with a slight CO₂ permeability increase by incorporating 30 wt% NaY zeolites into Pebax-1074/PEG-600 blend membranes. NaY zeolite had a preferential affinity for CO₂ and molecular sieving effect leading to enhanced selective adsorption. A similar refinement was also observed by Sanaeepur et al. (2019a) in Pebax-1657/Cerol (15 wt%)/Cu (1.5 wt%). Kheirtalab et al. (2020) notified that Pebax/PVA (15 wt%)/GO (6 wt%) was preferable for CO₂/N₂ separation (PER = 0.76 and SeER = 0.71), whereas Pebax/PVA (10 wt%)/GO (6 wt%) signified a strong tendency for CO₂/CH₄ separation (PER = 0.68 and SeER = 1.93). Incorporating GO (6 wt%) could create extra intermolecular spaces and embed CO₂-philic carboxyl groups within Pebax membranes.

Another ternary mixture can be prepared by combining ionic liquids, filler materials, and Pebax. Nadeali et al. (2020) utilized the shape and interfacial compatibility of p-tert-butylcalix4arene (CA) and the high viscosity of OMIMPF₆ to achieve higher CO₂/CH₄ selectivity (SeER = 2.11) and CO₂/N₂ selectivity (SeER = 1.35). The CO₂-philic characteristics of PF₆⁻ anion and supramolecular complex of CA were useful for achieving higher CO₂ permeability (PER = 1.15). Silver (Ag) nanoparticles also displayed this trend, and nickel-zinc iron oxide (NiZn-Fe₄O₄) nanoparticles were introduced into Pebax-1657/BmimBF₄ and Pebax-1657/OMIMPF₆, respectively. Notably, Pebax-1657/BmimBF₄ (50 wt%)/Ag (0.5 wt%) exhibited PER_{CO₂} of 0.61, SeER_{CO₂/CH₄} of 1.94, and SeER_{CO₂/N₂} of 1.39 (Ghasemi Estahbanati et al., 2017a). On the other hand, Pebax-1657/OMIMPF₆ (6.5 wt%)/NiZnFe₄O₄ (1.5 wt%) was superior, with PER-CO₂ of 1.45, SeER-CO₂/CH₄ of 3.69, and

SeER- CO_2/N_2 of 2.81 (Kalandari et al., 2020). Interfacial incompatibility of filler tends to form non-selective voids, facilitating more intense diffusion for all gas molecules. It was proven by Mahdavi et al. (2017) as SiO_2 nanoparticles were embedded into Pebax-1657/OMIMPF₆. The CO_2 permeability increased dramatically (PER = 2.10), but the CO_2/CH_4 selectivity upgrade was arduous.

Hybrid techniques may also exist in the form of quaternary Pebax MMMs. For instance, Pebax-1657/glycerol/PI-200/ NiFe_2O_4 quaternary MMMs were prepared by Miri et al. (2020) to improve the CO_2/CH_4 and CO_2/N_2 separation properties of Pebax membranes. As a result, an extraordinary improvement in CO_2/N_2 selectivity (SeER = 5.68) was found in Pebax-1657/glycerol (15 wt%)/PEG-200 (20 wt%)/ NiFe_2O_4 quaternary MMM. The massive impact on gas selectivity was related to the ability of NiFe_2O_4 to make tortuous diffusional pathways for more giant molecular gases. Meanwhile, CO_2 solubility increase might promote CO_2 permeability upgrade regarding the dipole-quadrupole interactions between the hydroxyl groups of each component and the complex formation between CO_2 and nanoparticle transition metal ions.

4. Comparative analysis of different enhancement strategies for pebax membranes

4.1. Trade-off extermination and balance degree analysis

Robeson's upper bound benchmarking is typically used to examine the Pebax membrane enhancement level in CO_2/CH_4 and CO_2/N_2 separation performance. Fig. 5 represent modified Pebax membranes' CO_2/CH_4 and CO_2/N_2 separation benchmarks.

The CO_2/N_2 separation is relatively more benign for all enhancement approaches than its CO_2/CH_4 separation. Because N_2 gas has less condensability and solubility than CH_4 and CO_2 , enhancing CO_2/N_2 separation in Pebax is more practical, either by tuning the intermolecular space or embedding active polar sites within it the membrane structure. There are 35 modified Pebax membranes with different enhancement strategies beyond Robeson's upper bound 2008 CO_2/N_2 separation (see Table S15). In particular, almost 66% of them are dominated by Pebax membranes with a filler incorporation approach, with porous filler and functionalized filler as the top two preferable options. On the other hand, hybrid techniques with ternary mixture offer a similar proportion of functionalized filler incorporation (up to 23%).

Meanwhile, the enhancement strategies for the CO_2/CH_4 separation performance of Pebax membranes should be more intricate, primarily for providing high selective separation channels due to the competition effect between CO_2 and CH_4 . Therefore, fewer Pebax membranes with distinct modification approaches surpassed Robeson's upper bound 2008 CO_2/CH_4 separation (see Table S16). Nevertheless, Pebax membranes with a filler incorporation approach were still prominent, with porous filler addition as the most tempting strategy to enhance CO_2/CH_4 separation capacity. In addition, the hybrid technique cannot be neglected as a considerable enhancement strategy with an identical proportion to the porous filler addition approach.

BD analysis is further carried out to understand the tendency of each approach to improving the CO_2 separation performance of Pebax membranes. Three directions can be generally considered to describe the propensity of an enhancement strategy: (1) permeability-oriented, (2) selectivity-oriented, and (3) synchronous mode. Fig. 6a and b and Fig. S1 illustrate the Pebax membrane improvement profile with CO_2/N_2 and CO_2/CH_4 trade-off extermination. As seen, permeability-oriented is a relatively eminent tendency to exceed trade-off issues in CO_2/N_2 (up to 50%) and CO_2/CH_4 (up to 45%) separation in Pebax membranes. It covers almost all enhancement strategies, including mobile carrier attachment, polymer blending, and filler incorporation, by providing suitable diffusional pathways for CO_2 .

On the other hand, the selectivity-oriented has a slightly lower proportion in surpassing the trade-off benchmark line in CO_2/N_2 (40%) and CO_2/CH_4 (up to 36%). Hybrid techniques dominate this way,

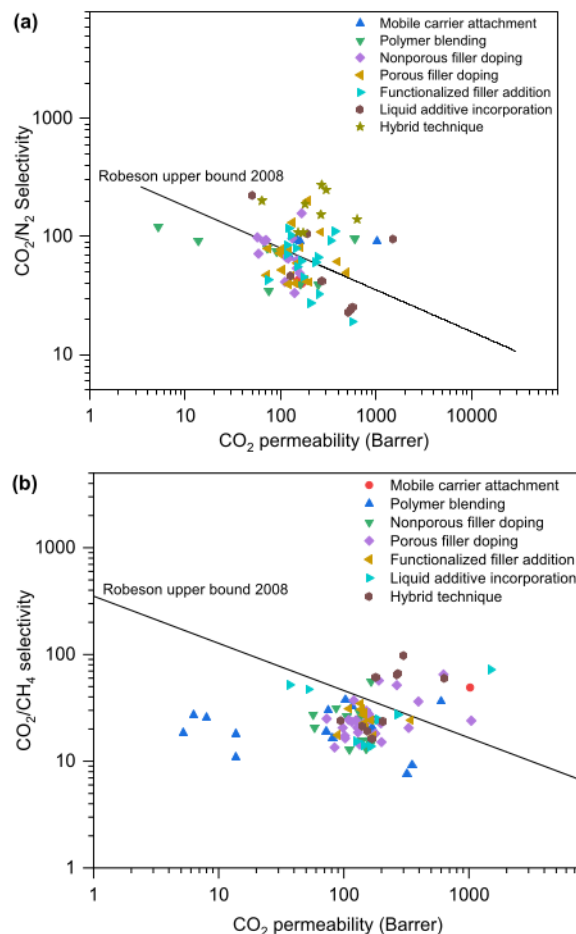


Fig. 5. Various modified Pebax membrane CO_2/N_2 (a) and CO_2/CH_4 (b) separation performance benchmarks.

providing excellent CO_2 solubility to increase the gas selectivities (CO_2/N_2 and CO_2/CH_4) of Pebax membranes. In the case of CO_2/N_2 separation, however, some filler incorporation strategies are involved, especially using novel two-dimensional (2D) or uniquely structured fillers like MXene, MoS_2 , and CA to create high tortuosity in gas diffusional pathways.

Synchronous mode is recently less eminent in surpassing trade-off problems (12% in CO_2/N_2 and 22% in CO_2/CH_4). It is primarily due to the difficulty of fitting the properties of additive materials to establish high permeability and selectivity. Although arduous, some filler incorporation strategies are reliable for synchronous mode by employing filler materials with unique chemical and structural properties such as Fe_2O_3 nanoparticles, copper zinc bimetallic imidazolite framework (CuZnIF) particles, ZIF-67, Zn-tetra-(4-carboxy phenyl) porphyrin (Zn-TCPP), and p-tert-butylcalix4arene (CA). The latter filler even can be used to prepare a ternary mixture Pebax-1657/OMIMPF₆ (6.5 wt%)/CA (0.5 wt%) with balanced CO_2 permeability and CO_2/N_2 selectivity (BD = 0.8).

4.2. Modified pebax membrane mechanical properties with trade-off extermination

The membrane's mechanical properties must be considered

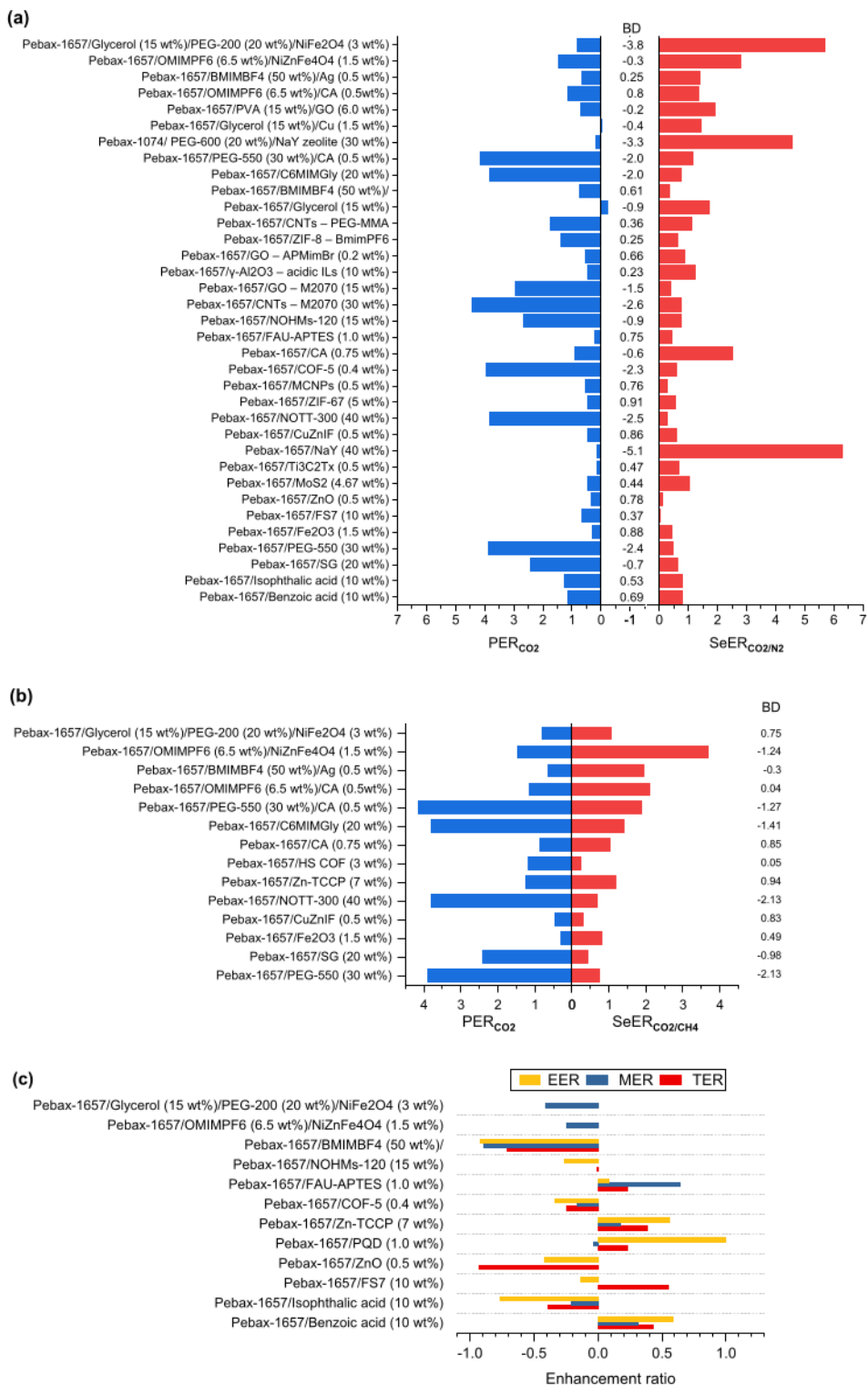


Fig. 6. CO₂/N₂ (a), CO₂/CH₄ (b) separation improvements, and mechanical resistance alteration (c) profiles of “trade-off free” Pebax membranes at different enhancement properties.

regardless of their trade-off-free profile. These properties express resistance to physical defects or harsh operating conditions. In the case of modified Pebax membranes, this is associated with the compatibility of additive materials with the polymer matrix, thereby affecting the separation performance. In addition, the interference of additives components toward the substantial intersegmental parts in Pebax may also become a critical factor in altering the mechanical properties of the resulting membranes. Fig. 6c illustrates the mechanical resistance alteration of several trade-off-free Pebax membranes.

The additive material's ability to create good interfacial adhesion toward the polymer matrix may positively impact the mechanical properties. For instance, Pebax-1657/FAU-APTES (1.0 wt%) exhibited higher Young's modulus (MER = 0.64) and tensile strength (TER = 0.23) compared to pure Pebax membranes. In this study, Mosadegh et al. (2020) explained that FAU-APTES had a high crosslink degree with the Pebax matrix to increase the crystallinity of PA segments resulting in higher mechanical resistance. Polymer-like QDs (PQD) offer a similar effect, showing their strong interaction with Pebax to generate adequate improvements in tensile strength (TER = 0.23) and elongation at break (EER = 1.00) (Shi et al., 2020). Pebax/Zn-TCPP nanosheets (7 wt%) membrane was another one showcasing a high increase in tensile strength and Young's modulus due to the filler's high aspect ratio, leading to high interfacial interaction with the membrane matrix (Li et al., 2019). Instead of filler materials, a mobile carrier like benzoic acid may interact strongly with the Pebax amide groups, making the structure stiffer for a higher Young's modulus (MER = 0.43) (Meshkat et al., 2019).

Trade-off extermination sometimes is not adjacent to mechanical strength improvement in the modified Pebax membrane. Regardless of the higher permeability and selectivity, the mechanical properties weaken once the original Pebax structure loosens due to hydrogen bonding disruption on the polyamide segment. Several reports revealed this occurrence, as depicted in Fig. 6c. For instance, Pebax-1657/ZnO (0.5 wt%) exposed a sharp reduction in tensile strength (TER = -0.93) and elongation at break (EER = -0.42) compared to its pure membrane (Amirkhani et al., 2020). ZnO nanoparticles could reduce the crystallinity, and soften the membrane structure, resulting in a lower mechanical strength. Similarly, NiFe₂O₄ nanoparticles were also reported by Kalantari et al. (2020) and Miri et al. (2020) to reduce the crystallinity of Pebax membranes, then weakening Young's modulus. COF-5 (0.4 wt%) was another filler, decreasing tensile strength (TER = -0.24), Young's modulus (MER = -0.16), and elongation at break (EER = -0.33) of Pebax membranes with a similar reason, reported by Duan et al. (2019). A severe reduction of all mechanical strength parameters was even found in Pebax-1657/BMIMBF₄ (50 wt%) with TER of -0.71, MER of -0.89, and EER of -0.92 compared to its neat membrane (Ghasemi Estabhanati et al., 2017b). A substantial drop in mechanical strength was also revealed by isophthalic acid attachment due to the disturbance of physical crosslinking between the polyether and polyamide blocks. Meshkat et al. (2019) reported that adding isophthalic acid 10 wt% to Pebax could decrease its tensile strength (TER = -0.39), Young's modulus (MER = -0.21), and elongation at break (EER = -0.76).

5. Future outlooks

Pebax membranes with balanced gas permeability and selectivity were rarely found in recent years. Predominant enhancement in permeability often leaves a problem associated with the excessive interfacial gap between additive materials and polymer matrix, weakening the interconnectivity of two segmental Pebax parts. Meanwhile, selectivity-oriented tends to enrich the Pebax soft channels for obtaining higher gas affinity. But, again, the reduction in mechanical resistance becomes inevitable due to crystallinity loss.

Nevertheless, filler incorporation strategies are still fascinating to level up the Pebax membrane gas separation performance. Recent

experimental works have been reported to improve the gas separation performance with good mechanical resistance by relying on the unique filler structure with advantageous functional groups. Seeking inexpensive and eco-friendly additive materials may become a worthy effort to support the sustainable development of Pebax membranes.

5.1. Exploring newly emerging additive materials

Constructing filler material structures has attracted much attention in the past few years to establish MMMs with good structural stability. As a result, various newly-type fillers have been recently developed from existing material families. Wang et al. (2022) developed a highly compatible filler for Pebax by synthesizing novel nitrogen-doped porous carbons (NPC) through a hydrothermal reaction and alkali activation. Nitrogen-containing groups in NPC could provide high CO₂ affinity, and its micropore structure took a role in CO₂ diffusional transport. Although Pebax/NPC 0.5 wt% only approached Robeson's upper bound, significant improvements in CO₂ permeability and CO₂/N₂ selectivity were found.

Employing novel MOF materials with a unique porous structure like BIT-72, MOF-801, and UTSA-16 (Zn) is also tempting for improving Pebax membrane quality. BIT-72 is an aluminum metal-organic framework (Al-MOF) prepared by the reaction between AlCl₃·6H₂O and 2-hydroxy-1,4-benzendicarboxylic acid. Li et al. (2018) found that an extensive surface area profile collided with the polar inner surface environment in BIT-72 became a proxy for obtaining high CO₂ sorption capacity. MOF-81 is a new class of CO₂-philic zirconium-based MOF with a similar framework topology to UiO-66. Chen et al. (2020) revealed that the uniform dispersion of MOF-801 in the polymer matrix could create a channel for the rapid and selective transport of CO₂, promoting higher CO₂ permeability and CO₂/N₂ ideal selectivity with excellent anti-aging performance and long-term working stability. UTSA-16 (Zn) is another exciting novel MOF prepared by replacing cobalt in UTSA-16 (Co) with zinc through microwave irradiation. Gaikwad et al. (2020) claimed that UTSA-16 (Zn) could be promising for CO₂ capture due to its lower production cost, high stability, superior CO₂ adsorption capacity, and selectivity.

Novel two-dimensional (2D) filler materials have been recently developed to fabricate mixed matrix membranes (MMMs) and are probably suitable for Pebax membranes. Ameen et al. (2021) utilized 2D boron nitride nanosheets (BNNS) to overcome the physical aging issue in the polymer of intrinsic microporosity (PIM) membranes for CO₂/CH₄ separation. Tungsten disulfide (WS₂), a graphene-like two-dimensional material, is another 2D material developed by Geng et al. (2018) for the first time in Pebax MMMs. This membrane showcased substantial long-term stability with superior gas selectivity surpassing Robeson's upper boundary. In addition, 2D MOFs (Zn₂(bim)₄) nanosheets are probably suitable for modifying the Pebax membrane due to their excellent molecule sieve ability and chemical stability. (Zn₂(bim)₄) nanosheets were recently used by Ma et al. (2022) to increase the PIM-PMDA-OH membrane microstructure free volume. The results showed that the obtained MMMs had a good CO₂/CH₄ separation performance.

Several following composites fillers have been developed and are reasonably promising for further investigations. Liu et al. (2022b) synthesized the core-shell structured fillers through ZIF-8 on ZIF-L(Co) surface (ZIF-L(Co)@ZIF-8) heteroepitaxial growth, then embedded into Pebax membranes for CO₂/CH₄ separation. The fabricated MMMs displayed superb CO₂/CH₄ separation performance due mainly to core-shell structured fillers in adsorption and molecular sieving. Another study by Zheng et al. (2022) developed 3D hollow CoNi-LDH nanocages to build up low-resistance and CO₂-philic transport pathways in Pebax MMMs. The synchronous effect of abundant hydroxyl groups and stacking tortuosity could remarkably enhance Pebax membrane performances. CuBDC-ns@MoS₂ is a 2D nanocomposite prepared by growing CuBDC-ns on multi-layered MoS₂ via a bottom-up synthesis

strategy. Li *et al.* (2022a) embedded CuBDC-ns@MoS₂ into Pebax membranes to improve their CO₂/CH₄ separation performance, relying on lamellar morphology, narrow pore aperture, and the coordination of complex-unsaturated metal sites. Another work by Guo *et al.* (2022) combined g-C₃N₄ 2D nanosheets with ZIF-90 to construct ZIF-90@C₃N₄ (ZCN), then used it as a filler in Pebax MMMs. The ZCN reported owning a strong screening effect in MMMs leads to a better CO₂/N₂ separation performance. A recent composite filler for Pebax membranes, C-ZIF, was developed by Cheng *et al.* (2023), made by growing carbon nanotubes (CNTs) on carbonized ZIF-L (Zn@Co). The unique structure of C-ZIF brought beneficial abilities to improve the CO₂ diffusivity of Pebax membranes by bothering their chain packing. C-ZIF could also transform saturated Me-N₄ (metal coordinated with quadruple nitrogen) to unsaturated Me-N₂ (metal coordinated with double nitrogen) and imidazole-N to pyridine-N, enriching CO₂ adsorption sites. As a result, CO₂ permeability and CO₂/N₂ selectivity of Pebax membrane were significantly improved at 62.1% and 31.5% with 10 wt% addition of C-ZIF (carbonized at 700 °C).

Polymer additives were also sustainably developed to provide more extraordinary impacts on the gas separation performance of Pebax membranes. For instance, Li *et al.* (2023) proposed integrating the advantages of a semi-interpenetrating polymer network and nanohybrid, providing a high PEO ratio and mechanically robust membrane structure. Thus, poly (ethylene glycol) diamines-3-glycidyloxypropyltrimethoxysilane (PEGDA-GPTMS) was utilized as a filler for fabricating Pebax MMMs for CO₂/N₂ separation. The silane networks comprising low molecular weight PEO (as frameworks) and silica nanoparticles (as nodes) were fabricated via a ring-opening addition reaction. At the same time, silica nanoparticles were in situ formed and homogeneously dispersed within the membrane. As a result, due to the high CO₂ affinity of enormous PEO units and decreased crystallinity of the membrane, better CO₂ separation performance of Pebax membranes could be achieved (2.3 times higher CO₂ permeability and 1.3 times higher CO₂/N₂ selectivity).

5.2. Encouraging the use of eco-friendly additive materials

Biopolymers and natural-based fillers have recently been investigated to upgrade Pebax membrane quality. For example, Prasad *et al.* (2019) used sericin (SC), a natural polymer produced during silk fibroin (SF) degumming, to fabricate a facilitated transport membrane with chitosan (CS) as a blended polymer and Na₂CO₃ as a mobile carrier for CO₂/N₂ separation. This combination could generate superior CO₂/N₂ separation performance exceeding the Robeson upper bound. Salestan *et al.* (2021) utilized biopolymers: sodium alginate (NaAlg), and carboxymethylcellulose (CMC), in Pebax blend membranes. The carboxyl and hydroxyl groups in NaAlg and CMC were crucial to leveling CO₂ permeability and CO₂/CH₄ selectivity. Another work by Ghazali *et al.* (2021) utilized nano pineapple peel-activated carbon (nano-PPAC) as a low-cost filler to fabricate Pebax 1657 nanocomposite membrane for CO₂/CH₄ separation. The nano-PPAC was found in good compatibility with the Pebax matrix. Embedding the right amount of nano-PPAC into Pebax membranes could boost their commercial viability and potential for further investigation. Biomass-derived 2D carboxyl functionalized carbon nanosheets (CCNS) are another natural-based filler option. Khan *et al.* (2020) synthesized CCNS from pyrolysis of the rain/monkey pod tree (*Samanea saman*) leaves and blended them into polyetherimide (PEI) to prepare MMMs for CO₂/CH₄ separation. Hydrogen bonding between the PEI and -COOH groups might induce a robust interfacial interaction within the polymer matrix, resulting in selective CO₂ transport.

6. Conclusions

The enhancement strategies for improving CO₂ separation performance can be classified based on the type and characteristics of additive

materials, including crosslinking, mobile carrier attachment, polymer blending, filler incorporation, and hybrid technique. The gas separation performance improvement is strongly associated with structural changes in Pebax to provide enormous diffusional pathways and create a polar environment for targeted gases. The structural changes were primarily associated with Pebax chain disruption, significantly reducing crystallinity and magnifying intersegmental distance (d-spacing) and free fractional volume (FFV). Additional diffusion mechanisms evidenced enormous diffusional pathways: Knudsen diffusion (crosslinking, polymer blending, and impermeable filler incorporation) or molecular sieving (porous filler incorporation). Meanwhile, polar environments by CO₂-philic functional groups could enable a facilitated transport mechanism for CO₂, mainly by using mobile carrier attachment, functionalized filler incorporation, or even a hybrid technique.

Among the enhancement strategies, filler incorporation and hybrid technique become the top two strategies to generate high Pebax CO₂ separation performance with the trade-off-free profile. In addition, a severe reduction in mechanical properties can be fixed by employing filler materials with layered or heterogeneous structures as well as high-affinity surface properties. Further studies primarily focus on utilizing newly emerging additive materials, encouraging eco-friendly enhancement strategy, permeability-selectivity balancing, and mechanical strength stabilizing.

Credit author statement

Wahyu Kamal Setiawan: Conceptualization; Methodology; Formal analysis; Writing - original draft; Writing - review & editing. Kung-Yuh Chiang: Conceptualization; Methodology; Technically supporting; Reviewing and revising; Supervising.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interest: Kung-Yuh Chiang reports financial support was provided by Taiwan Ministry of Science and Technology, (MOST).

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

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References

- Abdollahi, M., Khoshbin, M., Biazar, H., Khanbabaee, G., 2017. Preparation, morphology and gas permeation properties of carbon dioxide-selective vinyl acetate-based Polymer/Poly(ethylene oxide-b-amide 6) blend membranes. *Polymer* 121, 274–285.
- Abdul Hamid, M.R., Shean Yaw, T.C., Mohd Tohir, M.Z., Wan Abdul Karim Ghani, W.A., Sutrisna, P.D., Jeong, H.-K., 2021. Zeolitic imidazolate framework membranes for gas separations: current state-of-the-art, challenges, and opportunities. *J. Ind. Eng. Chem.* 98, 17–41.
- Aghaei, Z., Naji, L., Hadadi Asl, V., Khanbabaee, G., Dezhgah, F., 2018. The influence of fumed silica content and particle size in poly (amide 6-b-ethylene oxide) mixed matrix membranes for gas separation. *Sep. Purif. Technol.* 199, 47–56.
- Ahmad, J., Rehman, W.U., Deshmukh, K., Basha, S.K., Ahamed, B., Chidambaram, K., 2019. Recent advances in poly (amide-b-ethylene) based membranes for carbon dioxide (CO₂) capture: a review. *Polymer-Plastics Technology and Materials* 58, 366–383.

- Ameen, A.W., Ji, J., Tamaddondar, M., Moshenpour, S., Foster, A.B., Fan, X., Budd, P.M., Mattia, D., Gorgojo, P., 2021. 2D boron nitride nanosheets in PIM-1 membranes for CO₂/CH₄ separation. *J. Membr. Sci.* 636, 119527.
- Amirkhani, F., Harami, H.R., Asghari, M., 2020. CO₂/CH₄ mixed gas separation using poly(ether-b-amide)/ZnO nanocomposite membranes: experimental and molecular dynamics study. *Polym. Test.* 86, 106464, 106464.
- Atash Jameh, A., Mohammadi, T., Bakhtiari, O., 2020. Preparation of PEBAX-1074/modified ZIF-8 nanoparticles mixed matrix membranes for CO₂ removal from natural gas. *Sep. Purif. Technol.* 231, 115900, 115900.
- Azizi, N., Hoojati, M.R., 2018. Using Pebax-1074/ZIF-7 mixed matrix membranes for separation of CO₂ from CH₄. *Petrol. Sci. Technol.* 36, 993–1000.
- Azizi, N., Hoojati, M.R., Zarei, M.M., 2018. Study of CO₂ and CH₄ permeation properties through prepared and characterized blended pebax-2533/PEG-200 membranes. *Silicon* 10, 1461–1467.
- Azizi, N., Jazebizadeh, M.H., Azizi, F., Jahanmahin, O., Parsamehr, P.S., Arzani, M., 2023. Enhancing CO₂ permeation features of PEBAX-based membrane via incorporating MgO nanoparticles in its polymeric matrix. *Mater. Today Commun.* 34, 105460.
- Azizi, N., Mahdavi, H.R., Isanejad, M., Mohammadi, T., 2017a. Effects of low and high molecular mass PEG incorporation into different types of poly(ether-b-amide) copolymers on the permeation properties of CO₂ and CH₄. *J. Polym. Res.* 24, 141, 141.
- Azizi, N., Mohammadi, T., Behbahani, R.M., 2017b. Synthesis of a new nanocomposite membrane (PEBAX-1074/PEG-400/TiO₂) in order to separate CO₂ from CH₄. *J. Nat. Gas Sci. Eng.* 37, 39–51.
- Azizi, N., Mohammadi, T., Behbahani, R.M., 2017c. Synthesis of a PEBAX-1074/ZnO nanocomposite membrane with improved CO₂ separation performance. *J. Energy Chem.* 26, 454–465.
- Azizi, N., Mohammadi, T., Mosayebi Behbahani, R., 2017d. Comparison of permeability performance of PEBAX-1074/TiO₂, PEBAX-1074/SiO₂ and PEBAX-1074/Al₂O₃ nanocomposite membranes for CO₂/CH₄ separation. *Chem. Eng. Res. Des.* 117, 177–189.
- Bernardo, P., Drioli, E., Golemme, G., 2009. Membrane gas separation: a review/state of art. *Ind. Eng. Chem. Res.* 48, 4638–4663.
- Chen, W., Zhang, Z., Hou, L., Yang, C., Shen, H., Yang, K., Wang, Z., 2020. Metal-organic framework MOF-801/PIM-1 mixed-matrix membranes for enhanced CO₂/N₂ separation performance. *Sep. Purif. Technol.* 250, 117198.
- Cheng, J., Wang, Y., Liu, N., Hou, W., Zhou, J., 2020. Enhanced CO₂ selectivity of mixed matrix membranes with carbonized Zn/Co zeolitic imidazolate frameworks. *Appl. Energy* 272, 115179, 115179.
- Cheng, J., Yang, C., Hou, W., Liu, N., Xia, R., Chen, Z., Zhang, H., Liu, J., 2023. Carbon nanotubes grown on ZIF-L(Zn@Co) surface improved CO₂ permeability of mixed matrix membranes. *J. Membr. Sci.* 670, 121356.
- Clarizia, G., Bernardo, P., Gorrasi, G., Zampino, D., Carroccio, S.C., 2018. Influence of the preparation method and photo-oxidation treatment on the thermal and gas transport properties of dense films based on a poly(ether-block-amide) copolymer. *Materials* 11 (Basel, Switzerland).
- Dai, Z., Deng, J., Peng, K.-J., Liu, Y.-L., Deng, L., 2019. Pebax/PEG grafted CNT hybrid Membranes for enhanced CO₂/N₂ separation. *Ind. Eng. Chem. Res.* 58, 12226–12234.
- Deng, J., Dai, Z., Hou, J., Deng, L., 2020. Morphologically tunable MOF nanosheets in mixed matrix membranes for CO₂ separation. *Chem. Mater.* 32, 4174–4184.
- Dorosti, F., Alizadehdakheh, A., 2018. Fabrication and investigation of PEBAX/Fe-BTC, a high permeable and CO₂ selective mixed matrix membrane. *Chem. Eng. Res. Des.* 136, 119–128.
- Duan, J., Pan, Y., Liu, G., Jin, W., 2018. Metal-organic framework adsorbents and membranes for separation applications. *Current Opinion in Chemical Engineering* 20, 122–131.
- Duan, K., Wang, J., Zhang, Y., Liu, J., 2019. Covalent organic frameworks (COFs) functionalized mixed matrix membrane for effective CO₂/N₂ separation. *J. Membr. Sci.* 572, 588–595.
- Ebadi, R., Maghsoudi, H., Babaluo, A.A., 2021. Fabrication and characterization of Pebax-1657 mixed matrix membrane loaded with Si-CHA zeolite for CO₂ separation from CH₄. *J. Nat. Gas Sci. Eng.* 90, 103947, 103947.
- Fan, L., Kang, Z., Shen, Y., Wang, S., Zhao, H., Sun, H., Hu, X., Sun, H., Wang, R., Sun, D., 2018. Mixed matrix membranes based on metal-organic frameworks with tunable pore size for CO₂ separation. *Cryst. Growth Des.* 18, 4365–4371.
- Farashi, Z., Azizi, S., Rezaei-Dasht Arzhandi, M., Noroozi, Z., Azizi, N., 2019. Improving CO₂/CH₄ separation efficiency of Pebax-1657 membrane by adding Al₂O₃ nanoparticles in its matrix. *J. Nat. Gas Sci. Eng.* 72, 103019, 103019.
- Feng, X., Qin, Z., Lai, Q., Zhang, Z., Shao, Z.-W., Tang, W., Wu, W., Dai, Z., Liu, C., 2023. Mixed-matrix membranes based on novel hydroxamate metal-organic frameworks with two-dimensional layers for CO₂/N₂ separation. *Sep. Purif. Technol.* 305, 122476.
- Gaikwad, S., Kim, S.-J., Han, S., 2020. Novel metal-organic framework of UTSA-16 (Zn) synthesized by a microwave method: outstanding performance for CO₂ capture with improved stability to acid gases. *J. Ind. Eng. Chem.* 87, 250–263.
- Gao, J., Mao, H., Jin, H., Chen, C., Feldhoff, A., Li, Y., 2020. Functionalized ZIF-7/ Pebax® 2533 mixed matrix membranes for CO₂/N₂ separation. *Microporous Mesoporous Mater.* 297, 110030, 110030.
- Geng, Z., Song, Q., Zhang, X., Yu, B., Shen, Y., Cong, H., 2018. Mixed matrix membranes composed of WS₂ nanosheets and fluorinated poly(2,6-dimethyl-1,4-phenylene oxide) via Suzuki reaction for improved CO₂ separation. *J. Membr. Sci.* 565, 226–232.
- Ghasemi Estahbanati, E., Omidkhal, M., Ebadi Amooogh, A., 2017a. Interfacial design of ternary mixed matrix membranes containing Pebax 1657/silver-nanopowder/[BMIM][BF₄] for improved CO₂ separation performance. *ACS Appl. Mater. Interfaces* 9, 10094–10105.
- Ghasemi Estahbanati, E., Omidkhal, M., Ebadi Amooogh, A., 2017b. Preparation and characterization of novel Ionic liquid/Pebax membranes for efficient CO₂/light gases separation. *J. Ind. Eng. Chem.* 51, 77–89.
- Ghazali, A.A., Abd Rahman, S., Abu Samah, R., 2021. Preparation and characterisation of pineapple peel waste as nanoadsorbent incorporated into Pebax 1657 nanocomposite membrane for CO₂/CH₄ separation. *Mater. Today: Proc.* 41, 88–95.
- Guan, P., Luo, J., Li, W., Si, Z., 2017. Enhancement of gas permeability for CH₄/N₂ separation membranes by blending SBS to Pebax polymers. *Macromol. Res.* 25, 1007–1014.
- Guan, W., Yang, X., Dong, C., Yan, X., Zheng, W., Xi, Y., Ruan, X., Dai, Y., He, G., 2021. Prestructured MXene fillers with uniform channels to enhance CO₂ selective permeation in mixed matrix membranes. *J. Appl. Polym. Sci.* 138, 49895, 49895.
- Guo, F., Li, D., Ding, R., Gao, J., Ruan, X., Jiang, X., He, G., Xiao, W., 2022. Constructing MOF-doped two-dimensional composite material ZIF-90@C₃N₄ mixed matrix membranes for CO₂/N₂ separation. *Sep. Purif. Technol.* 280, 119803.
- Guo, Z., Liu, Z., Zhang, K., Wang, W., Pang, J., Li, Z., Kang, Z., Zhao, D., 2021. Stable metal-organic frameworks based mixed matrix membranes for Ethylbenzene/N₂ separation. *Chem. Eng. J.* 416, 129193, 129193.
- Guo, Z., Zheng, W., Yan, X., Dai, Y., Ruan, X., Yang, X., Li, X., Zhang, N., He, G., 2020. Ionic liquid tuning nanocage size of MOFs through a two-step adsorption/infiltration strategy for enhanced gas screening of mixed-matrix membranes. *J. Membr. Sci.* 605, 118101, 118101.
- Habibi, R., Bakhtiari, O., 2021. Preparation and characterization of modified halloysite nanotubes—pebax nanocomposite membranes for CO₂/CH₄ separation. *Chem. Eng. Res. Des.* 174, 199–212.
- Han, Y., Ho, W.S.W., 2021. Polymeric membranes for CO₂ separation and capture. *J. Membr. Sci.* 628, 119244, 119244.
- Harrigan, D.J., Yang, J., Sundell, B.J., Lawrence, J.A., O'Brien, J.T., Ostraat, M.L., 2020. Sour gas transport in poly(ether-b-amide) membranes for natural gas separations. *J. Membr. Sci.* 595, 117497, 117497.
- Hayek, A., Shalabi, Y.A., Alsamah, A., 2021. Sour mixed-gas upper bounds of glassy polymeric membranes. *Sep. Purif. Technol.* 277, 119535, 119535.
- He, R., Cong, S., Xu, S., Han, S., Guo, H., Liang, Z., Wang, J., Zhang, Y., 2021. CO₂-philic mixed matrix membranes based on low-molecular-weight polyethylene glycol and porous organic polymers. *J. Membr. Sci.* 624, 119081, 119081.
- Huang, G., Isfahani, A.P., Mughtar, A., Sakurai, K., Shrestha, B.B., Qin, D., Yamaguchi, D., Sivaniah, E., Ghalei, B., 2018. Pebax/ionic liquid modified graphene oxide mixed matrix membranes for enhanced CO₂ capture. *J. Membr. Sci.* 565, 370–379.
- Isanejad, M., Mohammadi, T., 2018. Effect of amine modification on morphology and performance of poly(ether-block-amide)/fumed silica nanocomposite membranes for CO₂/CH₄ separation. *Mater. Chem. Phys.* 205, 303–314.
- Jazebizadeh, M.H., Khazraei, S., 2017. Investigation of methane and carbon dioxide gases permeability through PEBAX/PEG/ZnO nanoparticle mixed matrix membrane. *Silicon* 9, 775–784.
- Jiang, X., Chuah, C.Y., Goh, K., Wang, R., 2021. A facile direct spray-coating of Pebax® 1657: towards large-scale thin-film composite membranes for efficient CO₂/N₂ separation. *J. Membr. Sci.* 638, 119708, 119708.
- Kalantari, S., Omidkhal, M., Ebadi Amooogh, A., Matsuura, T., 2020. Superior interfacial design in ternary mixed matrix membranes to enhance the CO₂ separation performance. *Appl. Mater. Today* 18, 100491, 100491.
- Kamble, A.R., Patel, C.M., Murthy, Z.V.P., 2021. A review on the recent advances in mixed matrix membranes for gas separation processes. *Renew. Sustain. Energy Rev.* 145, 111062, 111062.
- Kardani, R., Asghari, M., Hamedani, N.F., Afsari, M., 2020. Mesoporous copper zinc bimetallic imidazolate MOF as nanofiller to improve gas separation performance of PEBA-based membranes. *J. Ind. Eng. Chem.* 83, 100–110.
- Khan, M.Y., Khan, A., Adewole, J.K., Naim, M., Basha, S.I., Aziz, M.A., 2020. Biomass derived carboxylated carbon nanosheets blended polyetherimide membranes for enhanced CO₂/CH₄ separation. *J. Nat. Gas Sci. Eng.* 75, 103156.
- Kheiralab, 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 CO₂ separation. *Process Saf. Environ. Protect.* 144, 208–224.
- Khosravi, T., Omidkhal, M., Kaliaguine, S., Rodrigue, D., 2017. Amine-functionalized CuBTC/poly(ether-b-amide-6) (Pebax® MH 1657) mixed matrix membranes for CO₂/CH₄ separation. *Can. J. Chem. Eng.* 95, 2024–2033.
- Kim, N.U., Park, B.J., Park, M.S., Park, J.T., Kim, J.H., 2019. Semi-interpenetrating polymer network membranes based on a self-crosslinkable comb copolymer for CO₂ capture. *Chem. Eng. J.* 360, 1468–1476.
- Kojabad, M.E., Babaluo, A., Tavakoli, A., 2021a. A novel semi-mobile carrier facilitated transport membrane containing aniline/poly(ether-block-amide) for CO₂/N₂ separation: molecular simulation and experimental study. *Sep. Purif. Technol.* 266, 118494, 118494.
- Kojabad, M.E., Babaluo, A., Tavakoli, A., Sofla, R.L.M., Kahnamouei, H.G., 2021b. Comparison of acidic and basic ionic liquids effects on dispersion of alumina particles in Pebax composite membranes for CO₂/N₂ separation: experimental study and molecular simulation. *J. Environ. Chem. Eng.* 9, 106116, 106116.
- Li, H., Feng, X., Ma, D., Zhang, M., Zhang, Y., Liu, Y., Zhang, J., Wang, B., 2018. Stable aluminum metal-organic frameworks (Al-MOFs) for balanced CO₂ and water selectivity. *ACS Appl. Mater. Interfaces* 10, 3160–3163.
- Li, X., Ding, S., Zhang, J., Wei, Z., 2020. Optimizing microstructure of polymer composite membranes by tailoring different ionic liquids to accelerate CO₂ transport. *Int. J. Greenh. Gas Control* 101, 103136, 103136.

- Li, X., Hou, J., Guo, R., Wang, Z., Zhang, J., 2019. Constructing unique cross-sectional structured mixed matrix membranes by incorporating ultrathin microporous nanosheets for efficient CO₂ separation. *ACS Appl. Mater. Interfaces* 11, 24618–24626.
- Liu, N., Cheng, J., Hou, W., Yang, C., Yang, X., Zhou, J., 2022a. Bottom-up synthesis of two-dimensional composite via CuBDC-ns growth on multilayered MoS₂ to boost CO₂ permeability and selectivity in Pebax-based mixed matrix membranes. *Sep. Purif. Technol.* 282, 120007.
- Liu, Y.-C., Chen, C.-Y., Lin, G.-S., Chen, C.-H., Wu, K.C.W., Lin, C.-H., Tung, K.-L., 2019. Characterization and molecular simulation of Pebax-1657-based mixed matrix membranes incorporating MoS₂ nanosheets for carbon dioxide capture enhancement. *J. Membr. Sci.* 582, 358–366.
- Liu, Y., Wu, C., Zhou, Z., Liu, W., Guo, H., Zhang, B., 2022b. Upgrading CO₂/CH₄ separation performances of Pebax-based mixed matrix membranes incorporated with core/shell-structured ZIF-1(Co)/ZIF-8 composite nanosheets. *J. Membr. Sci.* 659, 120787.
- Liu, Y., Wu, H., Wu, S., Song, S., Guo, Z., Ren, Y., Zhao, R., Yang, L., Wu, Y., Jiang, Z., 2021. Multifunctional covalent organic framework (COF)-Based mixed matrix membranes for enhanced CO₂ separation. *J. Membr. Sci.* 618, 118693, 118693.
- Ma, Y., He, X., Tang, S., Xu, S., Qian, Y., Zeng, L., Tang, K., 2022. Enhanced 2-D MOFs nanosheets/PIM-PMDA-OH mixed matrix membrane for efficient CO₂ separation. *J. Environ. Chem. Eng.* 10, 107274.
- Mahdavi, H.R., Azizi, N., Arzani, M., Mohammadi, T., 2017. Improved CO₂/CH₄ separation using a nanocomposite ionic liquid gel membrane. *J. Nat. Gas Sci. Eng.* 46, 275–288.
- Maleh, M.S., Raisi, A., 2019. CO₂-philic moderate selective layer mixed matrix membranes containing surface functionalized NaX towards highly-efficient CO₂ capture. *RSC Adv.* 9, 15542–15553.
- Meshkat, S., Kaliaguine, S., Rodrigue, D., 2018. Mixed matrix membranes based on amine and non-amine MIL-53(Al) in Pebax® MH-1657 for CO₂ separation. *Sep. Purif. Technol.* 200, 177–190.
- Meshkat, S., Kaliaguine, S., Rodrigue, D., 2019. Enhancing CO₂ separation performance of Pebax® MH-1657 with aromatic carboxylic acids. *Sep. Purif. Technol.* 212, 901–912.
- Meshkat, S., Kaliaguine, S., Rodrigue, D., 2020. Comparison between ZIF-67 and ZIF-8 in Pebax® MH-1657 mixed matrix membranes for CO₂ separation. *Sep. Purif. Technol.* 235, 116150, 116150.
- Miri, S., Omidkhah, M., Ebadi Amoghini, A., Matsuura, T., 2020. Membrane-based gas separation accelerated by quaternary mixed matrix membranes. *J. Nat. Gas Sci. Eng.* 84, 103655, 103655.
- Mosadegh, M., Amirkhani, F., Riasat Harami, H., Asghari, M., Pamian, M.J., 2020. Effect of Nafion and APTEOS functionalization on mixed gas separation of PEBA-FAU membranes: experimental study and MD and GCMC simulations. *Sep. Purif. Technol.* 247, 116981, 116981.
- Nadeali, A., Kalantari, S., Yarmohammadi, M., Omidkhah, M., Ebadi Amoghini, A., Zamani Pedram, M., 2020. CO₂ separation properties of a ternary mixed-matrix membrane using ultrasensitive synthesized macrocyclic organic compounds. *ACS Sustain. Chem. Eng.* 8, 12775–12787.
- Nadeali, A., Zamani Pedram, M., Omidkhah, M., Yarmohammadi, M., 2019. Promising performance for efficient CO₂ separation with the p-tert-Butylcalix[4]arene/Pebax-1657 mixed matrix membrane. *ACS Sustain. Chem. Eng.* 7, 19015–19026.
- Nikpour, N., Khoshnevisan, B., 2020. Enhanced selectivity of O₂/N₂ gases in co-casted mixed matrix membranes filled with BaFe₁₂O₁₉ nanoparticles. *Sep. Purif. Technol.* 242, 116815, 116815.
- Noroozi, Z., Bakhtiari, O., 2019. Preparation of amino functionalized titanium oxide nanotubes and their incorporation within Pebax/PEG blended matrix for CO₂/CH₄ separation. *Chem. Eng. Res. Des.* 152, 149–164.
- Pardo, F., Gutiérrez-Hernández, S.V., Zarca, G., Urriaga, A., 2021. Toward the recycling of low-GWP hydrofluorocarbon/hydrofluoroolefin refrigerant mixtures using composite ionic liquid-polymer membranes. *ACS Sustain. Chem. Eng.* 9, 7012–7021.
- Pardo, F., Zarca, G., Urriaga, A., 2020. Separation of refrigerant gas mixtures containing R32, R134a, and R1234yf through poly(ether-block-amide) membranes. *ACS Sustain. Chem. Eng.* 8, 2548–2556.
- Prasad, B., Thakur, R.M., Mandal, B., Su, B., 2019. Enhanced CO₂ separation membrane prepared from waste by-product of silk fibroin. *J. Membr. Sci.* 587, 117170.
- Qian, Q., Asinger, P.A., Lee, M.J., Han, G., Mizrahi Rodriguez, K., Lin, S., Benedetti, F.M., Wu, A.X., Chi, W.S., Smith, Z.P., 2020. MOF-based membranes for gas separations. *Chem. Rev.* 120, 8161–8266.
- Salehi Maleh, M., Raisi, A., 2019. Comparison of porous and nonporous filler effect on performance of poly(ether-block-amide) mixed matrix membranes for gas separation applications. *Chem. Eng. Res. Des.* 147, 545–560.
- Salestan, S.K., Rahimpour, A., Abedini, R., 2021. Experimental and theoretical studies of biopolymers on the efficient CO₂/CH₄ separation of thin-film Pebax®1657 membrane. *Chemical Engineering and Processing - Process Intensification* 163, 108366, 108366.
- Sanaeepur, H., Ahmadi, R., Ebadi Amoghini, A., Ghanbari, D., 2019a. A novel ternary mixed matrix membrane containing glycerol-modified poly(ether-block-amide) (Pebax 1657)/copper nanoparticles for CO₂ separation. *J. Membr. Sci.* 573, 234–246.
- Sanaeepur, H., Mashhadikhan, S., Mardassi, G., Ebadi Amoghini, A., Van der Bruggen, B., Moghadasi, A., 2019b. Amino-silane cross-linked poly(ether-block-amide) PEBAX 2533: characterization and CO₂ separation properties. *Kor. J. Chem. Eng.* 36, 1339–1349.
- Shah Buddin, M.M.H., Ahmad, A.L., 2021. A review on metal-organic frameworks as filler in mixed matrix membrane: recent strategies to surpass upper bound for CO₂ separation. *J. CO₂ Util.* 51, 101616, 101616.
- Shamsabadi, A.A., Isfahani, A.P., Salestan, S.K., Rahimpour, A., Ghalei, B., Sivaniah, E., Soroush, M., 2020. Pushing rubbery polymer membranes to be economic for CO₂ separation: embedment with Ti₃C₂T_x MXene nanosheets. *ACS Appl. Mater. Interfaces* 12, 3984–3992.
- Sheikh, M., Asghari, M., Afsari, M., 2017. Effect of nano zinc oxide on gas permeation through mixed matrix poly (Amide-6-b-Ethylene Oxide)-based membranes. *Int. J. Nano Dimens. (IJND)* 8, 31–39.
- Shi, F., Sun, J., Wang, J., Liu, M., Yan, Z., Zhu, B., Li, Y., Cao, X., 2021. MXene versus graphene oxide: investigation on the effects of 2D nanosheets in mixed matrix membranes for CO₂ separation. *J. Membr. Sci.* 620, 118850, 118850.
- Shi, F., Tian, Q., Wang, J., Wang, Q., Shi, F., Li, Y., Nunes, S.P., 2020. Carbon quantum dot-enabled tuning of the microphase structures of poly(ether-block-amide) membrane for CO₂ separation. *Ind. Eng. Chem. Res.* 59, 14960–14969.
- Shirinia, M., Abdollahi, M., Omidkhah, M., 2020. Simultaneous enhancement of CO₂ permeability and CO₂/CH₄ and CO₂/N₂ selectivity via incorporating dense, rubbery and CO₂-philic vinyl acetate-based copolymers into poly(ethylene oxide-b-amide 6) membranes. *React. Funct. Polym.* 154, 104673, 104673.
- Sholl, D.S., Lively, R.P., 2016. Seven chemical separations to change the world. *Nature* 532, 435–437.
- Sidhikku Kandath Valappil, R., Ghasem, N., Al-Marzouqi, M., 2021. Current and future trends in polymer membrane-based gas separation technology: a comprehensive review. *J. Ind. Eng. Chem.* 98, 103–129.
- Simari, C., Nicotera, I., Perrotta, I.D., Clarizia, G., Bernardo, P., 2020. Microscopic and macroscopic investigation on the gas diffusion in poly(ether-block-amide) membranes doped with polysorbate nonionic surfactants. *Polymer* 209, 122949, 122949.
- Song, C., Li, R., Fan, Z., Liu, Q., Zhang, B., Kitamura, Y., 2020. CO₂/N₂ separation performance of Pebax/MIL-101 and Pebax/NH₂-MIL-101 mixed matrix membranes and intensification via sub-ambient operation. *Sep. Purif. Technol.* 238, 116500, 116500.
- Sutrisna, P.D., Hou, J., Li, H., Zhang, Y., Chen, V., 2017. Improved operational stability of Pebax-based gas separation membranes with ZIF-8: a comparative study of flat sheet and composite hollow fibre membranes. *J. Membr. Sci.* 524, 266–279.
- Taheri, P., Maleh, M.S., Raisi, A., 2021a. Cross-linking of poly(ether-block-amide) by poly(ethylene glycol) diacrylate to prepare plasticizing-resistant CO₂-selective membranes. *J. Environ. Chem. Eng.* 9, 105877, 105877.
- Taheri, P., Raisi, A., Maleh, M.S., 2021b. CO₂-selective poly(ether-block-amide)/polyethylene glycol composite membrane for CO₂ separation from gas mixtures. *Environ. Sci. Pollut. Control Ser.* 28, 38274–38291.
- Tengku Hassan, T.N.A., Jusoh, N., Yeong, Y.F., 2021. Synthesis and characterization of PEBAX 1657 and hierarchical Linde Type-T (h-LTT) zeolite for the fabrication of hybrid membranes. *Mater. Today: Proc.* 47, 1263–1268.
- Thankamony, R.L., Li, X., Das, S.K., Ostwal, M.M., Lai, Z., 2019. Porous covalent triazine piperazine polymer (CTPP)/PEBAX mixed matrix membranes for CO₂/N₂ and CO₂/CH₄ separations. *J. Membr. Sci.* 591, 117348, 117348.
- Vinoba, M., Bhagiyalakshmi, M., Alqaheem, Y., Alomair, A.A., Pérez, A., Rana, M.S., 2017. Recent progress of fillers in mixed matrix membranes for CO₂ separation: a review. *Sep. Purif. Technol.* 188, 431–450.
- Wang, B., Xu, J., Wang, J., Zhao, S., Liu, X., Wang, Z., 2021a. High-performance membrane with angstrom-scale manipulation of gas transport channels via polymeric decorated MOF cavities. *J. Membr. Sci.* 625, 119175, 119175.
- Wang, D., Song, S., Zhang, W., He, Z., Wang, Y., Zheng, Y., Yao, D., Pan, Y., Yang, Z., Meng, Z., Li, Y., 2020a. CO₂ selective separation of Pebax-based mixed matrix membranes (MMMs) accelerated by silica nanoparticle organic hybrid materials (NOHMs). *Sep. Purif. Technol.* 241, 116708, 116708.
- Wang, D., Yao, D., Wang, Y., Wang, F., Xin, Y., Song, S., Zhang, Z., Su, F., Zheng, Y., 2019. Carbon nanotubes and graphene oxide-based solvent-free hybrid nanofluids functionalized mixed-matrix membranes for efficient CO₂/N₂ separation. *Sep. Purif. Technol.* 221, 421–432.
- Wang, H., Zheng, W., Yang, X., Ning, M., Li, X., Xi, Y., Yan, X., Zhang, X., Dai, Y., Liu, H., He, G., 2021b. Pebax-based mixed matrix membranes derived from microporous carbon nanospheres for permeable and selective CO₂ separation. *Sep. Purif. Technol.* 274, 119015, 119015.
- Wang, Q., Dai, Y., Ruan, X., Zheng, W., Yan, X., Li, X., He, G., 2021c. ZIF-8 hollow nanotubes based mixed matrix membranes with high-speed gas transmission channel to promote CO₂/N₂ separation. *J. Membr. Sci.* 630, 119323, 119323.
- Wang, X., Ding, X., Zhao, H., Fu, J., Xin, Q., Zhang, Y., 2020b. Pebax-based mixed matrix membranes containing hollow polypyrrole nanospheres with mesoporous shells for enhanced gas permeation performance. *J. Membr. Sci.* 602, 117968, 117968.
- Wang, Y., Ma, Z., Zhang, X., Li, J., Zhou, Y., Jin, Z., Li, N., 2022. Mixed-matrix membranes consisting of Pebax and novel nitrogen-doped porous carbons for CO₂ separation. *J. Membr. Sci.* 644, 120182.
- Wang, Y., Zhang, N., Wu, H., Ren, Y., Yang, L., Wang, X., Wu, Y., Liu, Y., Zhao, R., Jiang, Z., 2021d. Exfoliation-free layered double hydroxides laminates intercalated with amino acids for enhanced CO₂ separation of mixed matrix membrane. *J. Membr. Sci.* 618, 118691, 118691.
- Wong, K.C., Goh, P.S., Ismail, A.F., 2021. Enhancing hydrogen gas separation performance of thin film composite membrane through facilely blended polyvinyl alcohol and PEBAX. *Int. J. Hydrogen Energy* 46, 19737–19748.
- Wu, Y., Zhao, D., Ren, J., Qiu, Y., Deng, M., 2019. A novel Pebax-C₆₀(OH)₂₄/PAN thin film composite membrane for carbon dioxide capture. *Sep. Purif. Technol.* 215, 480–489.
- Wu, Y., Zhao, D., Ren, J., Qiu, Y., Feng, Y., Deng, M., 2021. Effect of triglyceride on the microstructure and gas permeation performance of Pebax-based blend membranes. *Sep. Purif. Technol.* 256, 117824, 117824.

- Xin, Q., Shao, W., Ma, Q., Ye, X., Huang, Z., Li, B., Wang, S., Li, H., Zhang, Y., 2020. Efficient CO₂ separation of multi-permeable mixed matrix membranes with a unique interfacial structure regulated by mesoporous nanosheets. *ACS Appl. Mater. Interfaces* 12, 48067–48076.
- Xu, L., Xiang, L., Wang, C., Yu, J., Zhang, L., Pan, Y., 2017. Enhanced permeation performance of polyether-polyamide block copolymer membranes through incorporating ZIF-8 nanocrystals. *Chin. J. Chem. Eng.* 25, 882–891.
- Yang, B., Bai, L., Wang, Z., Jiang, H., Zeng, S., Zhang, X., Zhang, X., 2021a. Exploring NH₃ transport properties by tailoring ionic liquids in Pebax-based hybrid membranes. *Ind. Eng. Chem. Res.* 60, 9570–9577.
- Yang, L., Zhang, S., Wu, H., Ye, C., Liang, X., Wang, S., Wu, X., Wu, Y., Ren, Y., Liu, Y., Nasir, N., Jiang, Z., 2019. Porous organosilicon nanotubes in pebax-based mixed-matrix membranes for biogas purification. *J. Membr. Sci.* 573, 301–308.
- Yang, X., Zheng, W., Xi, Y., Guan, W., Yan, X., Ruan, X., Ma, C., Dai, Y., He, G., 2021b. Constructing low-resistance and high-selectivity transport multi-channels in mixed matrix membranes for efficient CO₂ separation. *J. Membr. Sci.* 624, 119046, 119046.
- Yong, W.F., Zhang, H., 2021. Recent advances in polymer blend membranes for gas separation and pervaporation. *Prog. Mater. Sci.* 116, 100713, 100713.
- Yue, Q., Shao, Z., Chang, S., Li, J., 2013. Adsorption of gas molecules on monolayer MoS₂ and effect of applied electric field. *Nanoscale Res. Lett.* 8, 425, 425.
- Zhang, B., Yang, C., Zheng, Y., Wu, Y., Song, C., Liu, Q., Wang, Z., 2021a. Modification of CO₂-selective mixed matrix membranes by a binary composition of poly(ethylene glycol)/NaY zeolite. *J. Membr. Sci.* 627, 119239, 119239.
- Zhang, H., Tian, H., Zhang, J., Guo, R., Li, X., 2018a. Facilitated transport membranes with an amino acid salt for highly efficient CO₂ separation. *Int. J. Greenh. Gas Control* 78, 85–93.
- Zhang, J., Xin, Q., Li, X., Yun, M., Xu, R., Wang, S., Li, Y., Lin, L., Ding, X., Ye, H., Zhang, Y., 2019. Mixed matrix membranes comprising aminosilane-functionalized graphene oxide for enhanced CO₂ separation. *J. Membr. Sci.* 570–571, 343–354.
- Zhang, N., Wu, H., Li, F., Dong, S., Yang, L., Ren, Y., Wu, Y., Wu, X., Jiang, Z., Cao, X., 2018b. Heterostructured filler in mixed matrix membranes to coordinate physical and chemical selectivities for enhanced CO₂ separation. *J. Membr. Sci.* 567, 272–280.
- Zhang, Q., Zhou, M., Liu, X., Zhang, B., 2021b. Pebax/two-dimensional MFI nanosheets mixed-matrix membranes for enhanced CO₂ separation. *J. Membr. Sci.* 636, 119612, 119612.
- Zhao, R., Wu, H., Yang, L., Ren, Y., Liu, Y., Qu, Z., Wu, Y., Cao, L., Chen, Z., Jiang, Z., 2020. Modification of covalent organic frameworks with dual functions ionic liquids for membrane-based biogas upgrading. *J. Membr. Sci.* 600, 117841, 117841.
- Zhao, S., Xue, J., Kang, W., 2014. Gas adsorption on MoS₂ monolayer from first-principles calculations. *Chem. Phys. Lett.* 595–596, 35–42.
- Zhao, X., Liu, W., Liu, X., Zhang, B., 2021. Mixed matrix membranes incorporated with sminosilane-functionalized SAPO-34 for upgrading CO₂/CH₄ separation performances. *Ind. Eng. Chem. Res.* 60, 13927–13937.
- Zheng, W., Yu, J., Hu, Z., Ruan, X., Li, X., Dai, Y., He, G., 2022. 3D hollow CoNi-LDH nanocages based MMMs with low resistance and CO₂-philic transport channel to boost CO₂ capture. *J. Membr. Sci.* 653, 120542.
- Zheng, Y., Wu, Y., Zhang, B., Wang, Z., 2020. Preparation and characterization of CO₂-selective Pebax/NaY mixed matrix membranes. *J. Appl. Polym. Sci.* 137, 48398, 48398.
- Zhu, B., Jiang, X., He, S., Yang, X., Long, J., Zhang, Y., Shao, L., 2020. Rational design of poly(ethylene oxide) based membranes for sustainable CO₂ capture. *J. Mater. Chem.* 8, 24233–24252.
- Zhu, W., Liu, F., Gou, M., Guo, R., Li, X., 2021. Mixed matrix membrane containing metal oxide nanosheets for efficient CO₂ separation. *Green Chemical Engineering* 2, 132–143.
- Zhu, W., Wang, L., Cao, H., Guo, R., Wang, C., 2023. Introducing defect-engineering 2D layered MOF nanosheets into Pebax matrix for CO₂/CH₄ separation. *J. Membr. Sci.* 669, 121305.

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