Enhancement strategies of poly(ether-block-amide) copolymer membranes for CO_2 separation: A review

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HIGHLIGHTS

- Enhanced CO_2 separation performance of Pebax was mainly due to the structural alteration.
- Filler incorporation is most common strategy for better Pebax membrane CO_2 separation.
- Perm-selectivity trade-off and mechanical strength reduction should be simultaneously overcame.
- Constructing unique structure and functionalities is viable for future filler materials.
- Utilization of eco-fiendly additives materials will support circular economy development.

GRAPHICAL ABSTRACT
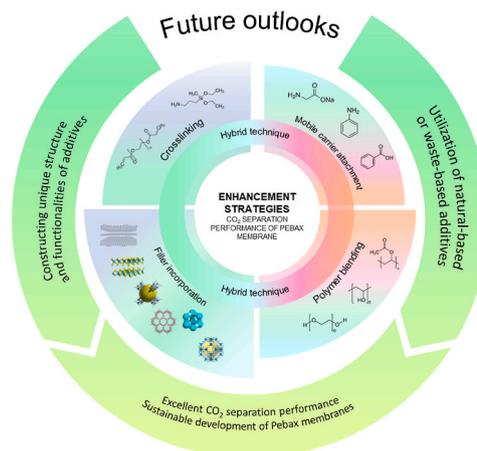
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ABSTRACT

Poly(ether-block-amide) (Pebax) membranes have become the preferred CO_2 separation membrane because of their excellent CO_2 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 CO_2/N_2 and CO_2/CH_4 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.

Nomenclature

AFFs	Amine-functionalized fillers
APDEMS	3-Aminopropyl(diethoxy) methyl silane
APDS	3-(2-aminoethylamino) propyl-dimethoxymethylsilane
APTES	3-Aminopropyltriethoxysilane
APTMS	3-Aminopropyltrimethoxysilane
BD	Balance degree
BDC	Benzene-1,3,5-tricarboxylate
BNNS	2D Boron nitride nanosheets
BTC	Benzene-1,4-dicarboxylic acid
CA	p-tert-butylcalix4arene
CCNS	2D Carboxyl functionalized carbon nanosheets
CHA	Chabazite
CNTs	Carbon nanotubes
COFs	Covalent organic frameworks
CrER	Crystallinity enhancement ratio
CTPP	Covalent triazine piperazine polymer
CuZnIF	Copper-zinc bimetallic imidazolate
D	Diffusivity
DBM	Dibutyl maleate
DER	Diffusivity enhancement ratio
EER	Elongation at break enhancement ratio
FAU	Faujasites
FFV	Fractional free volume
FS	Fumed silica
GPTMS	3-Glycidyloxypropyltrimethoxysilane
GQDs	Graphene-like quantum dots
GTER	Glass-transition temperature enhancement ratio
HNTs	Halloysite nanotubes
HS	Hollow spherical
MCNs	Microporous carbon nanoparticles
MCNPs	2D Microporous carbon nanoplates
MER	Young's modulus enhancement ratio
MFI	Mobil-type five zeolites
MIL	Matériaux de l'Institut Lavoisier
MMMs	Mixed matrix membranes
MOFs	Metal-organic frameworks
MTER	Melting temperature enhancement ratio
Ni-NS	Ni-MOF nanosheets
NOHMs	Nanoparticle organic hybrid materials
NPC	Nitrogen-doped porous carbons
P	Permeability
PA	Polyamide
PEO	Polyethylene oxide
PEG	Polyethylene glycol
PEGDA	Poly (ethylene glycol) diacrylate
PER	Permeability enhancement ratio
PGP	Poly (glycidyl methacrylate-g-polypropylene glycol)
PPAC	Pineapple peel-activated carbon
POEM	Poly (oxyethylene methacrylate)
PSiNTs	Porous silica nanotubes
PQDs	Polymer-like quantum dots
PVA	Polyvinyl alcohol
PVAc	Polyvinyl acetate
S	Solubility
SAPO	Silicoaluminophosphate
SeER	Selectivity enhancement ratio
SG	Sodium glycine
SoER	Solubility enhancement ratio
STP	Standard temperature and pressure
TBT	Tributyrin
TCP	Tricapronin
TCPP	Tetra-(4-carboxyphenyl)porphyrin
TPP	Tripropionin
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 CO_2/CH_4 (Thankamony et al., 2019; Wang et al., 2020b, 2021d; Zhao et al., 2020; Liu et al., 2021; Zhang et al., 2021b), CO_2/N_2 separation (He et al., 2021; Jiang et al., 2021; Wang et al., 2021a, 2021c; Yang et al., 2021b; Zhang et al., 2021a), CO_2/H_2 separation (Fan et al., 2018; Shamsabadi et al., 2020; Wong et al., 2021), H_2S/CH_4 separation (Harrigan et al., 2020; Hayek et al., 2021), CH_4/N_2 separation (Guan et al., 2017), O_2/N_2 separation (Nikpour and Khoshnevisan, 2020), NH_3/N_2 or NH_3/H_2 separation (Yang et al., 2021a), ethylbenzene/N_2 separation (Guo et al., 2021), and even hydrofluorocarbons (HFCs)/hydroflurolefin (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 CO_2 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

$$P = D \times S \tag{1}$$

where P is the gas permeability expressed in Barrer (1 Barrer = 1 × 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}), D is the diffusivity (cm^2 s^{-1}), and S is the solubility (cm^3 (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 CO_2.

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).

$$\alpha_{ij} = \frac{P_i}{P_j} \tag{2}$$

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:

$$PER_{CO2} = (P_{mod} - P_{neat}) / P_{neat} \tag{3}$$

$$SeER_{CO2} = (\alpha_{mod} - \alpha_{neat}) / \alpha_{neat} \tag{4}$$

$$DER_{CO2} = (D_{CO_2,mod} - D_{CO_2,neat}) / D_{CO_2,neat} \tag{5}$$

$$SoER_{CO2} = (S_{CO_2,mod} - S_{CO_2,neat}) / S_{CO_2,neat} \tag{6}$$

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%).

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

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

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

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

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

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

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

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

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 CO_2 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

$$BD = 1 - |PER - SeER| \tag{15}$$

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 CO_2 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 CO_2/N_2 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 CO_2 solubility due to the presence of amine groups. Moreover, CO_2 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 CO_2/N_2 selectivity and an 18% slight decrease in CO_2
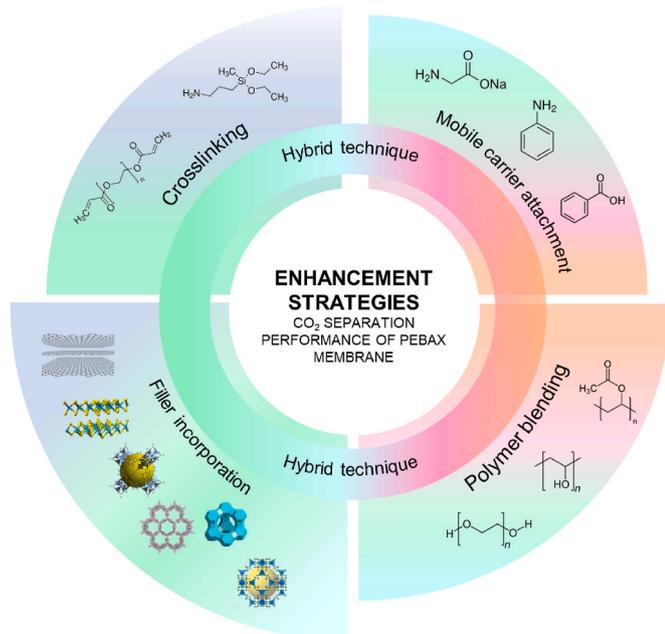
Fig. 1. Recent enhancement approaches on Pebax membrane gas separation performance.

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 ($P_{CO2} = 148.3$ Barrer with $PER_{CO2} = 1.26$) than benzoic acid ($P_{CO2} = 148.3$ Barrer with $PER_{CO2} = 1.12$). 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 ($SeER_{CO2/CH4} = 0.57$) and CO_2/N_2 selectivity up to 93 ($SeER_{CO2/N2} = 0.81$), 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 ($-NH_2$) and carboxylate groups ($-COO^-$) 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
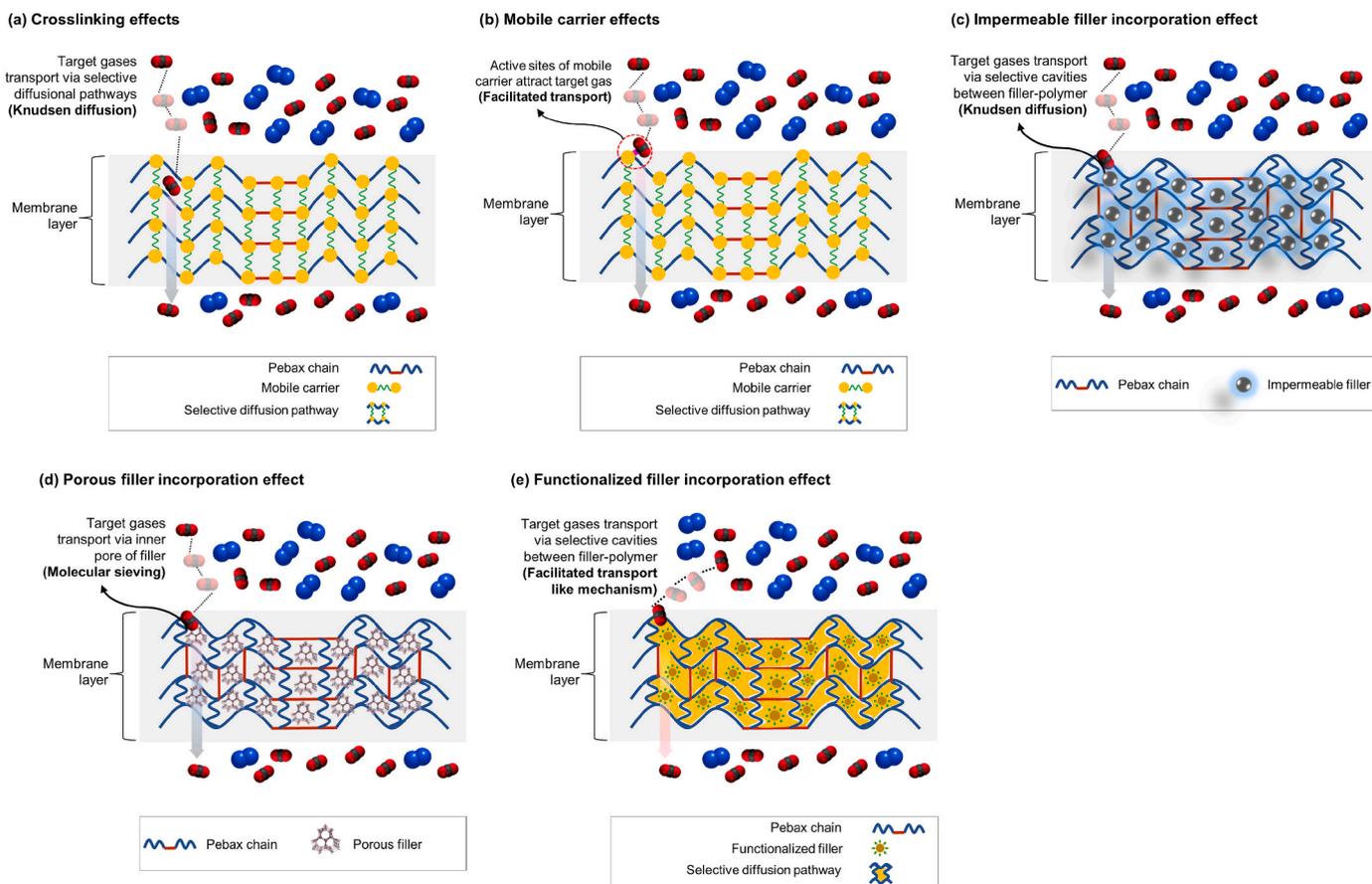
Fig. 2. Schematic diagram illustrating the effect of different modification approaches on Pebax's chain packing and gas transport properties.

the highest 1023 Barrer CO_2 permeability (PER_{CO2} = 1.24) with CO_2/CH_4 ideal selectivity of 46 ($SeER_{CO2/CH4}$ = 0.43) and CO_2/N_2 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 CO_2 transport via the hopping-vehicle mechanism. In addition, Pebax/aniline 50 wt% exhibited the highest CO_2 permeability of 151 Barrer (PER = 0.76) and CO_2/N_2 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 CO_2 separation efficiency. These PEG series are plasticizers to soften the base copolymer molecular structure, promoting a higher CO_2 diffusivity coefficient. Meanwhile, the CO_2 solubility coefficient upgrade may also be obtained, corresponding to a strong interaction between PEG ether-oxygen (EO) units and CO_2. 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 CO_2 permeability by up to 160%, with little change in CO_2/CH_4 selectivity. Similar Pebax MMMs were also prepared by Azizi et al. (2017b) with identical CO_2 separation improvement. Another PEG series, PEG-200, was then investigated by Azizi et al. (2018) to modify the Pebax-2533 gas permeability for CO_2/CH_4 separation. The CO_2 permeability enhancement was slightly lower at 88%, but CO_2/CH_4 selectivity increased by 26%. In the case of CO_2 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 CO_2 permeability (almost 100%). In contrast, gas selectivity improves significantly due to polar substituents in the PEG backbone. The improvement in CO_2/CH_4 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 CO_2 selectivity. Kheirtalab et al. (2020) argued that the oxygen atoms of hydroxyl groups on PVA could act as electron donors toward the positively charged CO_2 central carbon atom, resulting in better CO_2/CH_4 selectivity (up to 33%) and CO_2/N_2 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 CO_2/CH_4 selectivity could be enhanced up to 85% with 10 wt% PVAc incorporation. Another study by Shirinia et al. (2020) presented higher CO_2/CH_4 selectivity (114%) and CO_2/N_2 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 CO_2 solubility. As a result, the Pebax membrane containing 30 wt% P(VAc-co-DBM) copolymer exhibited CO_2/CH_4 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 CO_2 permeability (~161 Barrer with PER_{CO2} = 1.98), CO_2/CH_4 selectivity (~28 with $SeER_{CO2/CH4}$ = 1.57), and CO_2/N_2 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 CO_2 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-Al_2O_3 at different loads to fabricate Pebax-1657 MMMs. Adding γ-Al_2O_3 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 CO_2 permeability and 24.73 CO_2/CH_4 selectivity. The excellent ability of γ-Al_2O_3 nanoparticles to level-up Pebax-1074 membranes was also proven by Azizi et al. (2017d). γ-Al_2O_3 nanoparticles were superior to other tested fillers due to better particle distribution, effective voids formation, and higher CO_2 affinity.

Silicon dioxide (SiO_2) 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 CO_2 permeability (67%) and CO_2/CH_4 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, CO_2 permeability and CO_2/CH_4 selectivity were increased up to 38% and 53% by comprising 10 wt% FS-40.

Iron oxide (Fe_2O_3) nanoparticles proposed different features to improve CO_2 separation. Fe_2O_3 was presumed to provide a magnetic channel within the Pebax matrix leading to sufficient paramagnetic CO_2 attraction as well as CH_4 and N_2 repulsion. In Riasat Harami et al. (2019) work, Pebax/Fe_2O_3 1.5 wt% membranes showed the best performance with 30, 42, and 81% enhancements on CO_2 permeability, CO_2/CH_4 selectivity, and CO_2/N_2 selectivity compared to the neat membrane.
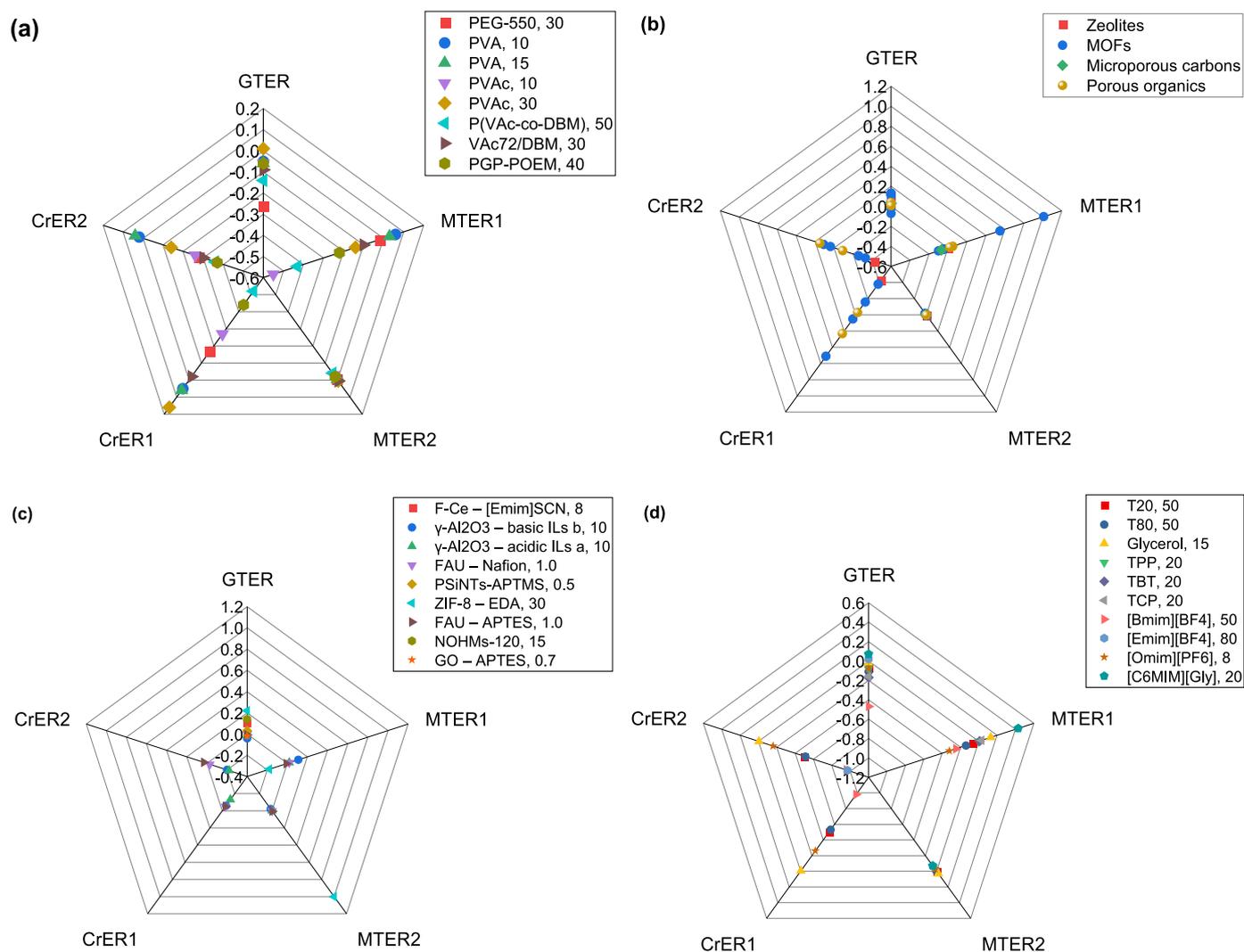
Fig. 3. The influence of different additives on Pebax membrane structural properties: (a)polymer additives, (b)porous fillers, (c) functionalized fillers, and (d) liquid additives. (Data was plotted from Tables S1, S5, S7, S90, and S11).

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 ($PER_{CO2} = 0.46$) and CO_2/N_2 selectivity of 90.61 ($SeER_{CO2/N2} = 1.02$) (Liu et al., 2019). MXne 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 CO_2/CH_4 separation. CO_2 permeability and CO_2/CH_4 selectivity reached 139.10 Barrer and 15.38 in this work, respectively, increasing 166% and 76% compared to the neat Pebax membrane. Regarding CO_2 permeability enhancement, $ZnCo_2O_4$ is the most noteworthy impermeable filler for Pebax MMMs, as illustrated in Fig. 4. It was because bimetallic Zn^{2+} and Co^{2+} could generate oxygen vacancies ($O^{-\delta}$) for providing more CO_2 ($C^{-\delta}$) adsorption sites.

In the carbon-based filler case, two novel materials, fullerenol and carbon quantum dots, have been recently developed to fabricate Pebax MMMs. Fullerenol ($C_{60}(OH)_{24}$) is a nonporous filler with high water solubility synthesized by surface hydroxylation of fullerene. Wu et al. (2019) revealed a 14% enhancement in CO_2 permeability with minor changes in CO_2/CH_4 and CO_2/N_2 selectivities by incorporating 1 wt% $C_{60}(OH)_{24}$ particles into Pebax membranes. That was mainly due to polymer chain packing disruption synchronized with polar-quadrupole interaction between abundant hydroxyl groups and CO_2. 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 CO_2 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 CO_2/N_2 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 CO_2 permeability of 23% and CO_2/N_2 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 CO_2 permeability with a lower CO_2/N_2 selectivity enhancement of 24% on Pebax MMMs containing 1 wt% GO. In another study by Zhang et al. (2019), less CO_2 permeability improvement was observed at 15%, with a neglected increase in CO_2/N_2 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 CO_2 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 CO_2/N_2 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, CO_2 permeability dropped by 13%, whereas CO_2/N_2 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 CO_2/CH_4 separation. Zhao et al. (2021) reported that CO_2 permeability and CO_2/CH_4 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 CO_2/CH_4 separation. This improvement is relatively similar to the halloysite nanotubes (HNTs) effect on the CO_2/CH_4 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 CH_4 kinetic diameter to achieve better Pebax membrane CO_2/CH_4 separation. Due to the perfect molecular sieving of Si-CHA in Pebax MMMs, CO_2 permeability and CO_2/CH_4 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 CO_2 adsorption affinity with a saturation tendency toward CH_4. 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 benzene-1,3,5-tricarboxylate (Cu_3BTC_2/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 Alizadehdakhel (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, $Ni_2(L-asp)_2bipy$ 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 $Ni_2(L-asp)_2bipy$ 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 Hojjati (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 ($PER_{CO2} = 0.18$ and $SeER_{CO2/N2} = 0.5$ 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_{CO2} 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_{CO2} (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_{CO2} 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 (PER_{CO2} = ~0.5) and CO_2/CH_4 selectivity ($SeER_{CO2/CH4}$ = ~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 (DER_{CO2} = 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_{CO2} of almost 0.5 and $SeER_{CO2/N2}$ 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-TCPP) 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 cuboid (ZIF-C, MW = 85–124) into Pebax could significantly increase CO_2 permeability (~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 (PER = 1.15) and CO_2/CH_4 selectivity ($SeER$ = 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 (PER = 1.30) and CO_2/CH_4 selectivity ($SeER$ = 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 (PER_{CO2} = 3.93) with a CO_2/N_2 selectivity of 49.3 ($SeER_{CO2/N2}$ = 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% CTTP 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, CO_2 permeability and CO_2/CH_4 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 CO_2-philic polyhydroxy groups, were utilized by Nadeali et al. (2019) as a filler for fabricating Pebax MMMs. The result indicated a simultaneous upgrade in CO_2 permeability, CO_2/CH_4, and CO_2/N_2 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 CO_2 permeability (PER = 0.32) and CO_2/CH_4 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 CO_2 permeability (PER = 0.79) and CO_2/CH_4 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 CO_2 permeability and CO_2/N_2 selectivity at 442% and 77%. It was better than GO nanofluids and has become the best-functionalized filler in CO_2 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 CO_2/N_2 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 CO_2/N_2 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 CO_2/N_2 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, CO_2/CH_4 selectivity was remarkably improved by 76%. Meanwhile, porous organosilicon nanotubes (PSiNTs)-modified 3-aminopropyl trimethoxysilane (APTMS) offered a reverse effect. The upgrade in CO_2 permeability was more pronounced than that of CO_2/CH_4 selectivity because of the increased CO_2 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 CO_2.

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-NH_2 for fabricating Pebax MMMs. Utilizing ZIF-7-NH_2 could increase CO_2 permeability and decrease N_2 permeability simultaneously, indicating a selective CO_2/N_2 separation. Hence, with the presence of 8 wt% ZIF-7-NH_2, the CO_2/N_2 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-NH_2 load, the best Pebax MMM performance was achieved with CO_2 permeability of 163.8 (PER = 1.08) and CO_2/N_2 selectivity of 62 (SeER = 0.27), respectively. The predominant enhancement in CO_2 permeability indicated that the FFV enlargement effect was more potent than promoting CO_2 affinity by amino groups. Another amine-based metal linker, 2-aminoterephthalic acid, was also used to prepare MIL-53-NH_2 and MIL-101-NH_2. 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 (CO_2/CH_4, CO_2/N_2, CO_2/H_2) comprising MIL-53-NH_2 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 CO_2, 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-NH_2, causing a drastic CO_2/N_2 selectivity. In contrast, ethylenediamine (ED)-based ZIF-8 could offer ideal upgrades in CO_2 permeability (PER = 2.51) and CO_2/CH_4 selectivity (SeER = 0.79) of Pebax MMMs (Atash Jameh et al., 2020). This refinement was attributed to the intensified CO_2 transport by enormous CO_2 reactive sites and excellent ED interfacial interaction with Pebax matrices.

Other functional groups, such as $-SO_3$, $-OH$, $-CH_3OH$, 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 CO_2/CH_4 separation features of Pebax membranes. Pebax MMMs comprised of 1 wt% Nafion showed the best CO_2/CH_4 selectivity of 31 (SeER = ~0.20). This improvement is due to the $-SO_3H$ groups with high reactivity toward more quadrupole gases (CO_2 and N_2) than nonpolar gases like CH_4. On the other hand, Gao et al. (2020) prepared ZIF-7-OH and ZIF-7-CH_2OH using 2-hydroxy benzimidazole and 2-hydroxymethyl benzimidazole, respectively. ZIF-7-OH was salient for obtaining a higher CO_2/N_2 selectivity regarding its ability to rigidify the Pebax chains and establish a particular CO_2 sorption site. Otherwise, ZIF-7-CH_2OH had a larger particle size with a strong tendency to form non-selective cavities, leading to higher CO_2 permeability and lower CO_2/N_2 selectivity. Polyethylene glycol has been reported to functionalized carbon nanotubes (CNTs) with ethylene oxide groups for improving Pebax membrane CO_2 separation performance. Dai et al. (2019) mentioned that PEG could create CO_2-philic channels within CNT, establishing selective CO_2 transport. Three wt. % CNT-PEG content in Pebax MMMs produced the optimum CO_2 permeability (PER = ~1.80) and CO_2/N_2 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-Al_2O_3 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 CO_2/N_2 separation (Kojabad et al., 2021b). As a result, both ILs could restrict the γ-Al_2O_3 aggregation within Pebax matrices via electrostatic and steric forces. Acidic IL, however, exhibited a better impact on preventing γ-Al_2O_3 sedimentation than the basic IL. When γ-Al_2O_3 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 CO_2, promoting higher CO_2 permeability (PER = 0.47) and CO_2/N_2 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 $BmimPF_6$-functionalized ZIF-8 (IL@ZIF-8) could simultaneously accelerate CO_2 permeability and CO_2/N_2 selectivity enhancement in Pebax membranes. Notably, the MMM containing 25 wt% IL8@ZIF-8 showed the best gas separation performances with 117 Barrer (PER = 1.37) of CO_2 permeability and 84.5 (SeER = 0.66) of CO_2/N_2 selectivity. Porous IL8@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 CO_2 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 (TPP), tributyrin (TBT), and tricapronin (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 CO_2 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 CO_2 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 CO_2/N_2 selectivity by 172% of pure Pebax membrane despite a 23% drop in CO_2 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 ($BmimBF_4$) ionic liquid was used by Ghasemi Estahbanati et al. (2017b) to modify Pebax CO_2 perm-selectivity. Doping $BmimBF_4$ could remarkably reduce crystallinity (~100%), then increase the flexibility (~50%) with larger FFV, leading to higher gas diffusion (up to 60% for CO_2). A slight increase in CO_2 solubility at around 10%, with 50 wt% IL addition. Improvement in the diffusivity-solubility promoted a notable CO_2 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 ($EmimBF_4$), 3-methyl-1-octyl imidazolium hexafluorophosphate ($OmimPF_6$), and 1-alkyl-3-methylimidazolium glycine ($C_6mimGly$) for improving CO_2 permeability.

With 80 wt% of $EmimBF_4$ blend, CO_2 permeability and CO_2/CH_4 selectivity were 270.1 Barrer (PER = 213%) and 27.3 (SeER = 64%), respectively. Meanwhile, 1-alkyl-3-methylimidazolium glycine ($C_6mimGly$) exhibited the most significant CO_2 permeability enhancement than other ILs, comparable with PEG-550. Li et al. (2020) referred to the ability of the Gly^{-1} anion and C_6mim^+ cation to present a favorable radius (0.338 nm) for selective CO_2 diffusion. Plenteous amounts of amino and carboxyl groups in the Gly^{-1} anion could be CO_2 carriers, facilitating highly efficient CO_2 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 TiO_2 nanoparticles into Pebax-1074/PEG-400 blend membranes to fabricate ternary MMMs for CO_2/CH_4 separation. Pebax-1074/PEG-400 (40 wt%)/TiO_2 (8 wt%) had the best CO_2 permeability,204.46 Barrer (PER = 2.15), attributing to polymer chain disruption by TiO_2 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 CO_2/CH_4 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 enormous –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 CO_2 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 CO_2/N_2 selectivity (SeER = 4.55) with a slight CO_2 permeability increase by incorporating 30 wt% NaY zeolites into Pebax-1074/PEG-600 blend membranes. NaY zeolite had a preferential affinity for CO_2 and molecular sieving effect leading to enhanced selective adsorption. A similar refinement was also observed by Sanaeepur et al. (2019a) in Pebax-1657/Glycerol (15 wt%)/Cu (1.5 wt%). Kheirtalab et al. (2020) notified that Pebax/PVA (15 wt%)/GO (6 wt%) was preferable for CO_2/N_2 separation (PER = 0.76 and SeER = 0.71), whereas Pebax/PVA (10 wt%)/GO (6 wt%) signified a strong tendency for CO_2/CH_4 separation (PER = 0.68 and SeER = 1.93). Incorporating GO (6 wt%) could create extra intermolecular spaces and embed CO_2-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 $OMIMPF_6$ to achieve higher CO_2/CH_4 selectivity (SeER = 2.11) and CO_2/N_2 selectivity (SeER = 1.35). The CO_2-philic characteristics of PF_6^- anion and supramolecular complex of CA were useful for achieving higher CO_2 permeability (PER = 1.15). Silver (Ag) nanoparticles also displayed this trend, and nickel-zinc iron oxide (NiZn-Fe_4O_4) nanoparticles were introduced into Pebax-1657/$BmimBF_4$ and Pebax-1657/$OMIMPF_6$, respectively. Notably, Pebax-1657/$BmimBF_4$ (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/$OMIMPF_6$ (6.5 wt%)/$NiZnFe_4O_4$ (1.5 wt%) was superior, with PER-CO_2 of 1.45, SeER-CO_2/CH_4 of 3.69, and

SeER-CO_2/N_2 of 2.81 (Kalantari 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/OMIMPF$_6$. 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/PEG-200/NiFe$_2$O$_4$ 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$_2$O$_4$ quaternary MMM. The massive impact on gas selectivity was related to the ability of NiFe$_2$O$_4$ 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 was 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,
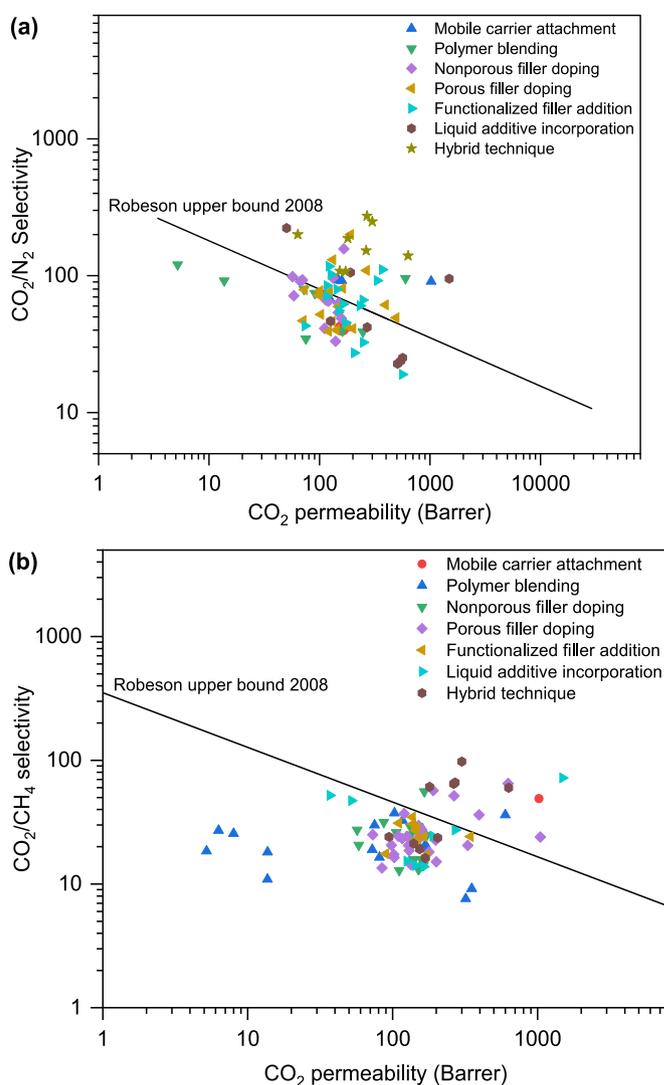
Fig. 5. Various modified Pebax membrane CO_2/N_2 (a) and CO_2/CH_4 (b) separation performance benchmarks.

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$_2$O$_3$ nanoparticles, copper zinc bimetallic imidazolate 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/OMIMPF$_6$ (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
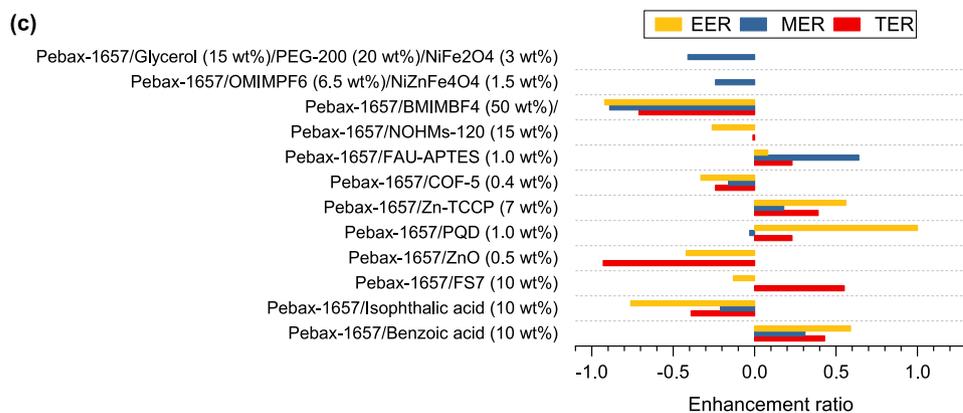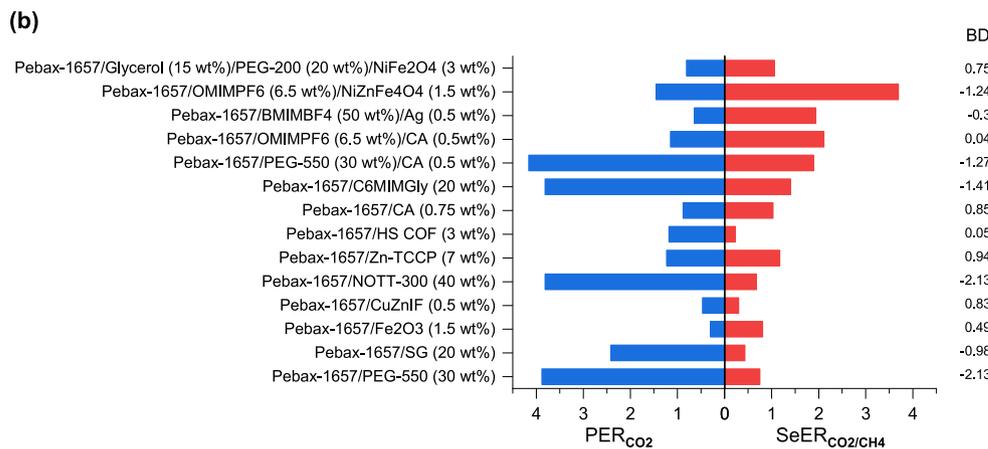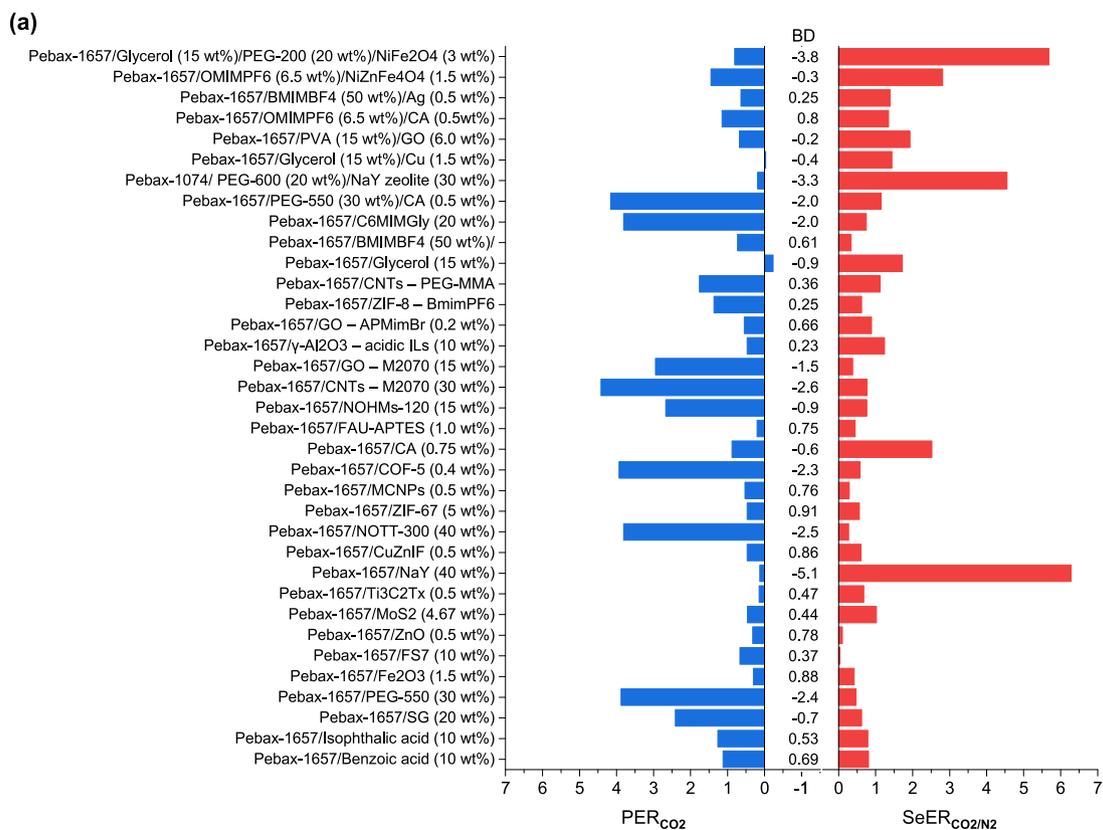
Fig. 6. CO_2/N_2 (a), CO_2/CH_4 (b) separation improvements, and mechanical resistance alteration (c) profiles of "trade-off free" Pebax membranes at different enhancement properties.

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, $NiFe_2O_4$ 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/$BMIMBF_4$ (50 wt%) with TER of −0.71, MER of −0.89, and EER of −0.92 compared to its neat membrane (Ghasemi Estahbanati 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 CO_2 affinity, and its micropore structure took a role in CO_2 diffusional transport. Although Pebax/NPC 0.5 wt% only approached Robeson's upper bound, significant improvements in CO_2 permeability and CO_2/N_2 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 $AlCl_3 \cdot 6H_2O$ and 2-hydroxy-1,4benzendicarboxylic 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 CO_2 sorption capacity. MOF-81 is a new class of CO_2-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 CO_2, promoting higher CO_2 permeability and CO_2/N_2 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 CO_2 capture due to its lower production cost, high stability, superior CO_2 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 CO_2/CH_4 separation. Tungsten disulfide (WS_2), 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 ($Zn_2(bim)_4$) nanosheets are probably suitable for modifying the Pebax membrane due to their excellent molecule sieve ability and chemical stability. ($Zn_2(bim)_4$) 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 CO_2/CH_4 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 CO_2/CH_4 separation. The fabricated MMMs displayed superb CO_2/CH_4 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 CO_2-philic transport pathways in Pebax MMMs. The synchronous effect of abundant hydroxyl groups and stacking tortuosity could remarkably enhance Pebax membrane performances. CuBDC-ns@MoS_2 is a 2D nanocomposite prepared by growing CuBDC-ns on multi-layered MoS_2 via a bottom-up synthesis

strategy. Liu et al. (2022a) embedded CuBDC-ns@MoS$_2$ into Pebax membranes to improve their CO_2/CH_4 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-C$_3$N$_4$ 2D nanosheets with ZIF-90 to construct ZIF-90@C$_3$N$_4$ (ZCN), then used it as a filler in Pebax MMMs. The ZCN reported owning a strong screening effect in MMMs leads to a better CO_2/N_2 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 CO_2 diffusivity of Pebax membranes by bothering their chain packing. C-ZIF could also transform saturated Me–N$_4$ (metal coordinated with quadruple nitrogen) to unsaturated Me–N$_2$ (metal coordinated with double nitrogen) and imidazole-N to pyridine-N, enriching CO_2 adsorption sites. As a result, CO_2 permeability and CO_2/N_2 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 CO_2/N_2 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 homogenously dispersed within the membrane. As a result, due to the high CO_2 affinity of enormous PEO units and decreased crystallinity of the membrane, better CO_2 separation performance of Pebax membranes could be achieved (2.3 times higher CO_2 permeability and 1.3 times higher CO_2/N_2 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 Na$_2$CO$_3$ as a mobile carrier for CO_2/N_2 separation. This combination could generate superior CO_2/N_2 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 CO_2 permeability and CO_2/CH_4 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 CO_2/CH_4 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 CO_2/CH_4 separation. Hydrogen bonding between the PEI and –COOH groups might induce a robust interfacial interaction within the polymer matrix, resulting in selective CO_2 transport.

6. Conclusions

The enhancement strategies for improving CO_2 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 CO_2-philic functional groups could enable a facilitated transport mechanism for CO_2, 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 CO_2 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

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Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.139478.

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