Mixed Matrix Membranes for Carbon Capture and Sequestration: Challenges and Scope

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ABSTRACT: Carbon dioxide (CO_2) is a major greenhouse gas responsible for the increase in global temperature, making carbon capture and sequestration (CCS) crucial for controlling global warming. Traditional CCS methods such as absorption, adsorption, and cryogenic distillation are energy-intensive and expensive. In recent years, researchers have focused on CCS using membranes, specifically solution-diffusion, glassy, and polymeric membranes, due to their favorable properties for CCS applications. However, existing polymeric membranes have limitations in terms of permeability and selectivity trade-off, despite efforts to modify their structure. Mixed matrix membranes (MMMs) offer advantages in terms of energy usage, cost, and operation for CCS, as they can overcome the limitations of polymeric membranes by incorporating inorganic fillers, such as graphene oxide, zeolite, silica, carbon nanotubes, and metal−organic frameworks. MMMs have shown superior gas separation performance compared to polymeric membranes. However, challenges with MMMs include interfacial defects between the polymeric and inorganic phases, as well as agglomeration with increasing filler content, which can decrease selectivity. Additionally, there is a need for renewable and naturally occurring polymeric materials for the industrial-scale production of MMMs for CCS applications, which poses fabrication and reproducibility challenges. Therefore, this research focuses on different methodologies for carbon capture and sequestration techniques, discusses their merits and demerits, and elaborates on the most efficient method. Factors to consider in developing MMMs for gas separation, such as matrix and filler properties, and their synergistic effect are also explained in this Review.
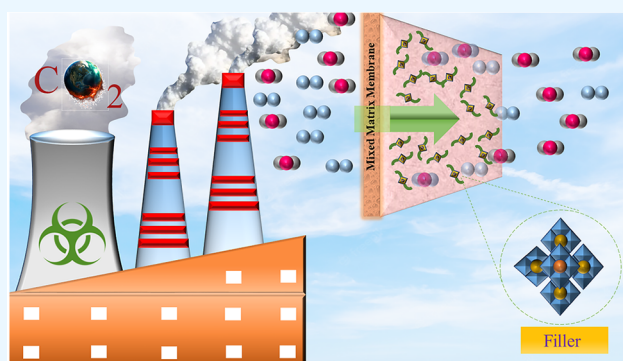
1. INTRODUCTION

Gases such as nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2) are called greenhouse gases (GHGs) because these gases trap infrared radiation and radiate it back to the atmosphere, which leads to an increase in global temperature. Owing to rapid population growth and a sharp rise in energy demand, the GHG concentration in the atmosphere has amplified rapidly.[1,2] The global mean surface temperature (GMST) was 1.0 °C higher compared to that in the preindustrial era (1850−1900) in 2017 due to the increased GHG concentration.[3] The Intergovernmental Panel on Climate Change (IPCC) has reported that GMST will rise to 2.0 °C above that of the preindustrial era by 2035.[4] This rise in the GMST has severely affected our ecosystems, such as the melting of ice, floods in low-level countries, and wildfires. To stabilize the rise of the GMST under 1.5 °C, CO_2 capture, utilization, and sequestration (CCUS) are crucial processes that can be applied on an industrial scale.

To capture the CO_2 gas generated from large point sources, there are mainly four approaches available: precombustion capture, postcombustion capture, chemical-looping combustion, and oxycombustion. Oxycombustion and precombustion capture cannot be retrofitted into the existing power plants, so these two can be utilized for future power plants.[5] Postcombustion technologies include the capture of CO_2 from the exhaust gas of a fossil-fuel-fired power plant.[6] This can be considered a preferable option, as this technology can be installed as an add-on in existing power plants, which use air for fuel combustion. There are several postcombustion CO_2 capture technologies available, which include membrane separation, adsorption, absorption, and cryogenic separation.[7] Absorption is the most effective technology widely used to remove CO_2 from synthesis and natural gas.[5] The disadvan-

Table 1. Advantages and Disadvantages of Different Kinds of CO₂ Capture Processes

CO_2 capture process	advantages	disadvantages
precombustion	the high partial pressure of CO_2 because of CO_2-rich effluent leads to a high driving force for separation. thus, this process requires a lower compression cost.	not compatible with old plants. high cost of equipment.
postcombustion	it can be retrofitted with the existing power plants.	low concentration of CO_2 in the effluent and at atmospheric pressure causes a low partial pressure of CO_2. difficult and expensive to separate.
oxycombustion	concentrated CO_2 in the effluent and this process cannot be retrofitted.	incompatible with the current power plant configurations. the requirements for a cryogenic O_2 generator and O_2 removal from the pipeline make it expensive.
chemical-looping combustion	highly concentrated CO_2 in the effluent stream.	side chemical reactions may take place during the reaction. coke formation may take place, which decreases the efficiency of chemical-looping combustion.

tages associated with absorption are huge costs and high energy consumption. Adsorption technologies suffer from high regeneration costs and batch operation. In cryogenic separation, the acid gas is frozen to separate the CO_2 in liquid form. The major disadvantage of this technology is the requirement of enormous power to operate the refrigeration unit. Membrane separation is currently a rapidly developing technology for CO_2 capture. It offers many advantages over other traditional technologies, such as ease of operation, flexibility, versatility, environmental friendliness, low energy demand, continuous operation, less maintenance costs, and lower space requirements, among others.[8]

The advantages and disadvantages associated with all the above-mentioned CO_2 capture processes are listed in Table 1.

Membrane separation of gases developed from a technical curiosity in the 1960s to the beginning of industrialization in the 1970s, followed by strong research efforts in the 1980s and commercialization.[9] The ability to produce ultrathin permselective membranes (on the order of 100 nm) through advancements in the asymmetric membrane was likely the key to this achievement. Another essential component of this research was finding materials that increased the target gas permeability (P) while maintaining its selectivity.[10] Membranes are mainly characterized based on materials used for fabrication such as polymeric, inorganic, and mixed matrix membranes, whose pros and cons are tabulated in Table 2. Polymeric membranes, being highly popular, suffer from a trade-off between selectivity and permeability, whereas inorganic membranes go through an expensive and compli-

cated fabrication process. High permeability and selectivity are characteristic features of an ideal membrane for the maximization of its performance at low production cost. However, for membranes the trade-off effect, first introduced by Robeson, comes into the picture, i.e., high selectivity comes with an expense of low permeability and vice versa. The selectivity of a membrane is also deteriorated by an excessive increase in fractional free volume (FFV) caused by plasticization. In addition, the aging effect in the case of the glassy polymeric membranes reduces the gas permeability with the reduction in the FFV. It has been evident since the year 1990 that there is another way to improve the gas separation performance of membrane materials. The method, which is currently extremely popular, is called "mixed matrix membranes" (MMM).[11] It involves incorporating tiny inorganic or organic−inorganic fillers into polymeric matrices, particularly with particle sizes between 10 and 100 nm.[12] Such an approach frequently led to the enhancement of either permeability or selectivity (or frequently both). In MMMs, the addition of porous nanofillers results in an increase in permeability while maintaining the selectivity. In contrast, the selectivity of the membrane can be altered if modifications made to fillers are specific to various penetrants. These changes are often brought up by altering the diffusion coefficients and solubility coefficients.[13−19]

As the MMM is a selective barrier, one component from a mixture can pass through it more readily than other components. The separation performance of the MMM is judged in two terms, the selectivity and permeability of gases. The formulas for the evaluation of permeability (P) and selectivity (α_{ij}) are given below:

$$P_i = \frac{\text{volume of gas} \times \text{thickness of membrane}}{\text{area of membrane} \times \text{time} \times \text{pressure difference across the membrane}} \quad (1)$$

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

where P_i is the permeability of the i gas, P_j is the permeability of the j gas, and α_{ij} is the selectivity of the i gas from the mixture of binary gases i and j.

When examining the suitability of membranes for mixed gas separation, permeance is a crucial factor. It describes the way that gas moves through the membrane. It is defined as the ratio of gas permeability to the effective thickness of the membrane and can be expressed as

$$p_i = \frac{P_i}{\text{effective thickness of membrane}} \quad (3)$$

Table 2. Comparison of the Advantages and Disadvantages of All Three Types of Membranes

membranes	advantages	disadvantages
polymeric membranes	easy to synthesize and fabricate	low thermal and chemical stability
	low cost	pore size not tunable
	easy upscaling and modulation	trade-off between permeability and selectivity
inorganic membranes	better thermal, chemical, and mechanical stability	expensive
	tunable pore size	brittle
	can operate at high temperatures and pressures	
mixed matrix membranes	mechanically and thermally stable	becomes brittle with a high amount of fillers
	less plasticization	interfacial defects
	surpass the trade-off between permeability and selectivity	

where p_i is the permeance of the i gas. The unit of permeability is Barrer, and the unit of permeance is the gas permeation unit (GPU). Since selectivity is the ratio of permeability, it is unitless.

$$1 \text{ barrer} = 10^{-10}[cm^3(STP)cm]/[cm^2 \text{ s cmHg}]$$

$$1 GPU = 10^{-6}[cm^3(STP)]/[cm^2 \text{ s cmHg}]$$

In some of the research articles, enhanced separation performance (selectivity and permeability) after including fillers in the polymer matrix has been evaluated as the ratio of the performance by the mixed matrix membrane (MMM) to the performance by the polymeric membrane itself.

$$\text{permeability factor (PF)} = \frac{P(MMM)}{P(\text{polymeric membrane})} \quad (4)$$

The current work primarily focuses on the recent scientific and technological advances for the development of high-performance MMMs for gas separation applications. First the basics of transport mechanism will be discussed to understand the various possible ways molecules pass through the membrane. Afterward, a brief description of membrane types is given to understand the need for MMMs, followed by the introduction of the overview of the state-of-the-art in MMMs utilizing various kinds of fillers. The reported MMM morphologies, chemical properties, and thermal characteristics are summarized and discussed. Taking into consideration the status, applicability, and future theoretical research in estimating the gas separation performance of MMMs, the Conclusions and Future Directions section summarizes the challenges and future perspectives for the development of high-performance MMMs.

2. TRANSPORT MECHANISM OF GAS IN MEMBRANES

2.1. Solution-Diffusion Mechanism. The solution-diffusion mechanism (SDM) assumes no voids in the membrane and no particular reactions between CO_2 and functional groups of membrane materials. The domination of SDM has been seen frequently in nonporous polymeric membranes. According to SDM, there are three steps involved during the transport of gas molecules across the membranes: at first, the gases are adsorbed in the membrane on the feed side, then diffuse across the membrane due to the driving force and finally escape from the membrane on the sweep side (Figure 1). Separation occurs due to the difference in the solubilities and diffusivities of the gases. Permeability is expressed in terms of the diffusion coefficient (D) and the solubility coefficient (S) as given below:

$$P = D \times S \quad (5)$$

As mentioned in eq 2, selectivity is the ratio of individual gas permeability; therefore, permeability and selectivity are related to the diffusion and solubility coefficients. The affinity and condensability of gas molecules in the membrane govern the solubility coefficient. For the gas to have a higher solubility coefficient, it should have a higher critical temperature. The diffusion coefficient of the membrane is dependent on the kinetic diameter of the gases, the polymer chain spacing, and the random motion of the chain segment in the membrane. The diffusivity coefficient increases with the decreasing kinetic diameter and increasing chain spacing and random motion of
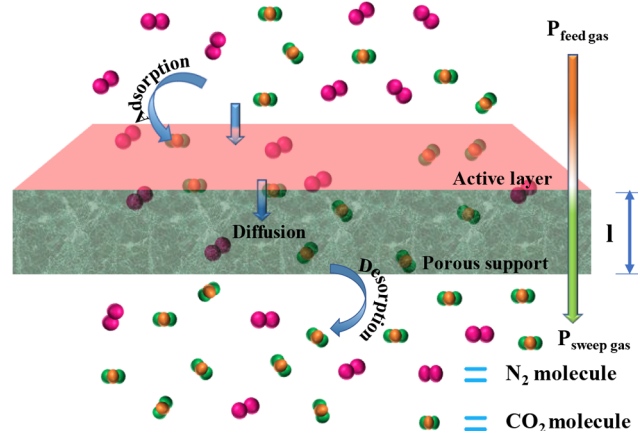

Figure 1. Solution-diffusion transport mechanism of gas separation.

the chain segment in the membrane. Considering CO_2, CH_4, N_2, and H_2, CO_2 possesses the highest critical temperature (304.2 K) among all four gases, which helps CO_2 to dissolve in the membrane. Additionally, CH_4 and N_2 have larger kinetic diameters than CO_2, which help in the faster transport of CO_2 across membranes. H_2 has faster transport than CO_2 in the membrane due to its smaller kinetic diameter compared to CO_2. Between CO_2 and H_2, CO_2 has higher solubility and H_2 has higher diffusivity, thus making it difficult to get high CO_2/H_2 selectivity considering only solution-diffusion.

2.2. Molecular Sieving Mechanism. The porous structure of inorganic fillers considerably aids the separation of the gases according to the molecular sieving mechanism. When the diameter of the pores is between the kinetic diameters of the gases in the gaseous mixture to be separated, the gases with a kinetic diameter smaller than the pore size are transported across the MMMs while the gases with a greater kinetic diameter than pore size get blocked (Figure 2). As the
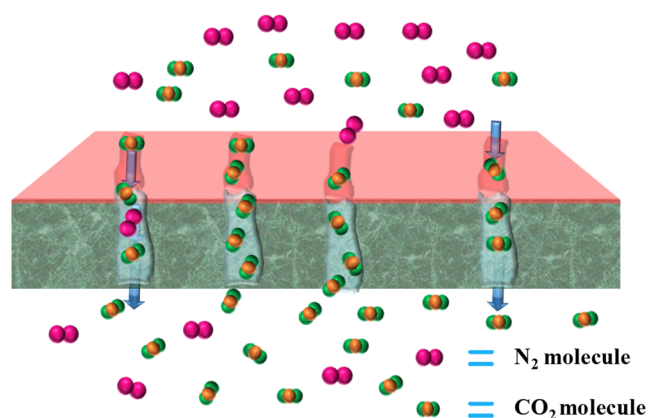

Figure 2. Molecular sieving transport mechanism of gas separation.

kinetic diameters of CO_2 and other gases vary very little, the pore diameter should be precisely controlled as per the requirement. Microporous materials like porous graphene oxide, metal−organic frameworks (MOFs), covalent−organic frameworks (COFs), and carbon molecular sieves (CMS) with pore sizes on a molecular scale and fine pore size distributions can be used to get higher selectivity for the separation of gases as filler in the MMMs.

2.3. Facilitated Transport Mechanism. This mechanism is inspired by biological membranes, where active and passive transport take place. The facilitated transport membrane has specific interactions between CO_2 and the amine groups. The reversible chemical reaction between CO_2 and a few functional groups helps to enhance the passage of CO_2 from upstream to downstream across the membrane (Figure 3). The most
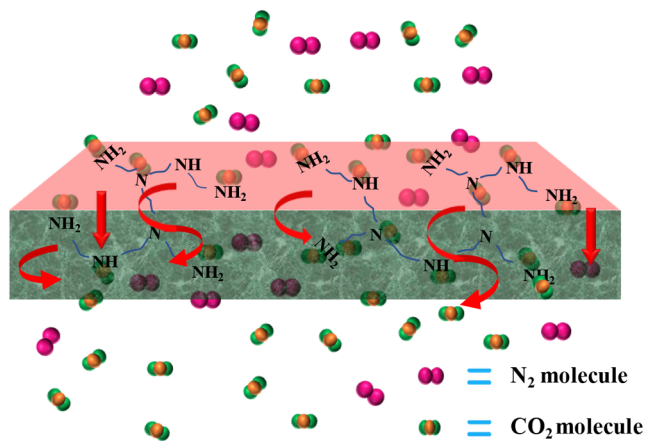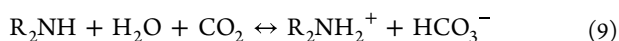

**Figure 3.** Facilitated transport mechanism of gas separation.

common functional groups that acts as carriers for CO_2 separation are the amine groups.[20,21] CO_2 reactions with primary, secondary, and tertiary amines are depicted as follows:

$$2RNH_2 + CO_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (6)$$

$$RNH_2 + H_2O + CO_2 \leftrightarrow RNH_3^+ + HCO_3^- \qquad (7)$$

$$2R_2NH + CO_2 \leftrightarrow R_2NCOO^- + R_2NH_2^+ \qquad (8)$$

$$R_2NH + H_2O + CO_2 \leftrightarrow R_2NH_2^+ + HCO_3^- \qquad (9)$$

$$R_3N + H_2O + CO_2 \leftrightarrow R_3NH^+ + HCO_3^- \qquad (10)$$

It can be seen from the equations mentioned above that CO_2 reacts with primary and secondary amines in either the presence or absence of H_2O. In contrast, a tertiary amine only reacts with CO_2 in the presence of water. In primary and secondary amines, 0.5 mol CO_2 reacts with 1 mol amine to form the stable carbamate ion without water. The amount of CO_2 reacting with primary and secondary amines increases from 0.5 to 1 mol for each mole of amine with water, leading to the increase in the reaction rate. The tertiary amine is a weak

basic catalyst for the hydration reaction of CO_2 in the presence of water, resulting in bicarbonate formation.

Basic groups other than amine that act as CO_2 carriers are PO_4^{3-}, F^-, CO_3^{2-}, and $-COO^-$. The reaction between CO_2 and the carboxyl group is given as follows:

$$RCOO^- + H_2O + CO_2 \leftrightarrow RCOOH + HCO_3^- \qquad (11)$$
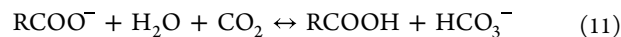
where R denotes the alkyl group.

As explained above, the presence of amine functional groups is very crucial to facilitate the transport of CO_2 across the membrane. To achieve facilitated transport effects, there are various methods available to modify the fillers of MMMs, such as blending, grafting, conjugation, post-synthetic modifications, and the use of ligands that contain amine functional groups in their molecules during MOF, COF, and POF synthesis.

3. MEMBRANES USED FOR CO$_2$ SEPARATION

In recent times, a slow and steady increase in the usage of membranes in separation procedures has taken place. It is anticipated in the current situation where, notwithstanding the unpredictability of energy costs, membrane GS is contemplated for minimizing the ecological footprint and energy requirement costs of industrial operations. In this section, a detailed description is provided for membranes that can be categorized as inorganic, polymeric, and mixed matrix membranes; their morphological features are shown in Figure 4.

3.1. Inorganic Membranes. In recent years, inorganic membrane development has advanced pretty quickly at laboratory scale.[10] The permselectivity of the porous inorganic membranes is influenced by many factors, which include the microstructures of the membrane and the support composite, the porosity, the tortuosity, and the affinity of the permeating species. Membranes constructed of inorganic materials like zeolites, metals, and ceramics function better and are more thermally and chemically stable.[22] Sharma et al. fabricated an amino-silicate membrane integrated on a cost-effective macroporous industrial alumina-based ceramic support. The synthesized ceramic membrane displayed a CO_2 permeance of 46.44 GPU with a CO_2/N_2 selectivity of 12.5 at 80 °C.[23] However, owing to the challenges of the mass-production of defect free inorganic membranes, polymeric membranes and mixed matrix membranes predominate in commercial uses.[24]

3.2. Polymeric Membranes. The nonporous polymeric membrane gas separation ideas were developed before any other membrane separation techniques. According to research by Mitchell et al., even in the absence of pores, mass transfer in polymeric and liquid films is possible.[25] Graham studied the permeability of several gases through various membranes, such
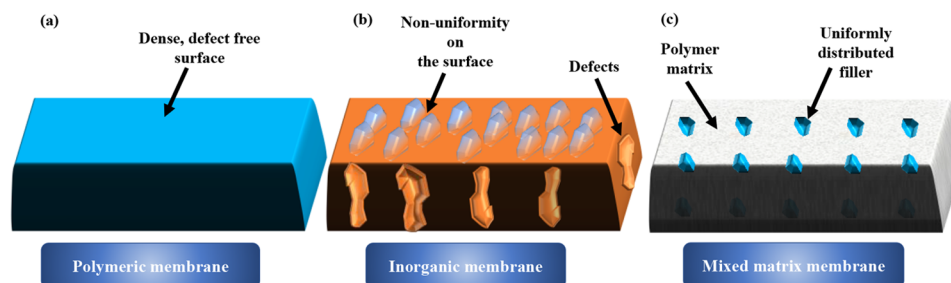

Figure 4. Morphological feature of (a) a polymeric membrane (dense and defect-free), (b) inorganic membranes (defective and porous), and (c) mixed matrix membranes (uniform distribution of fillers into the polymer matrix).
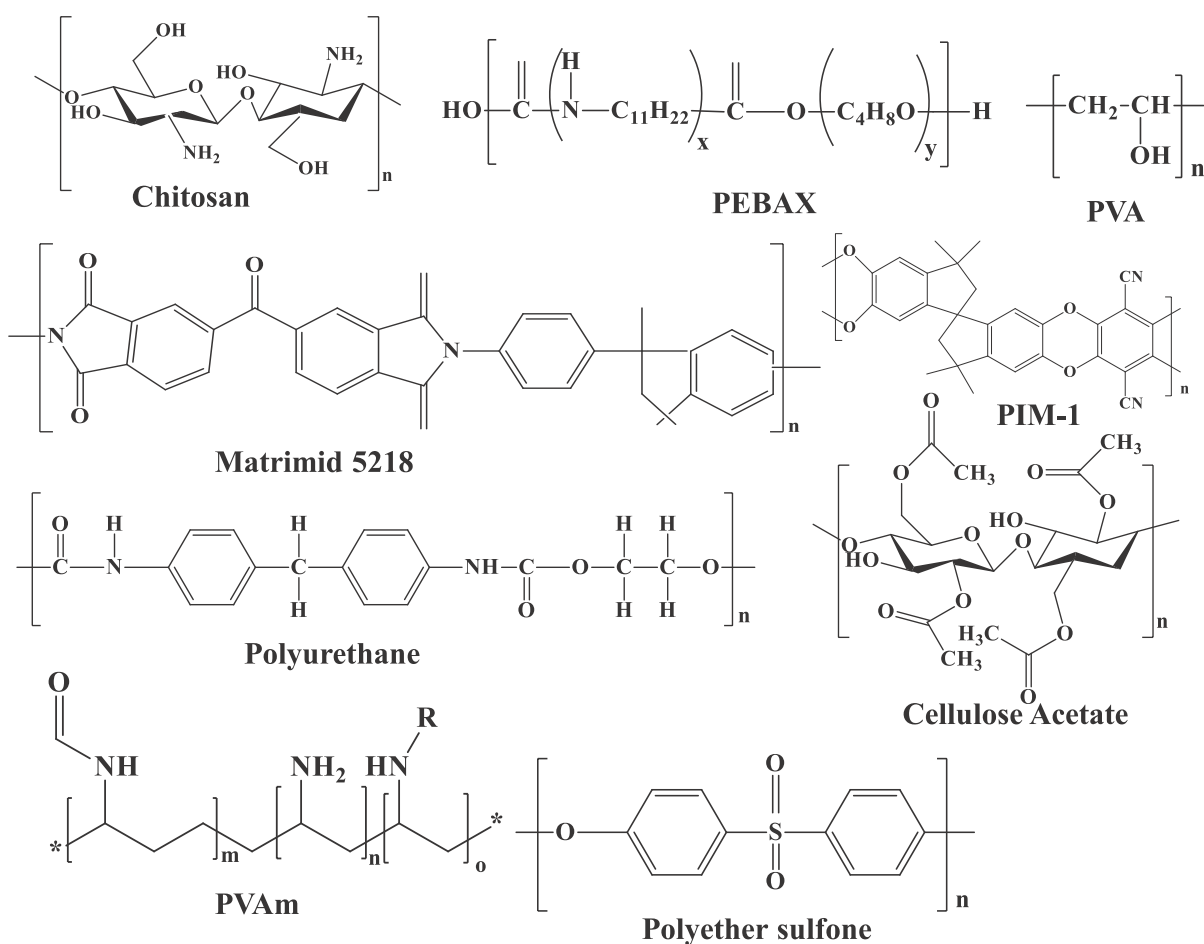
Figure 5. Chemical structures of some commonly used polymers in gas separation applications.

as films made of natural rubber, and observed that carbon dioxide showed the greatest penetration rate among all the measured gases and had the highest solubility in membrane materials.[26]

It was widely believed until the 1970s that glassy polymeric membranes had poor permeability but potentially strong permselectivity. This theory was invalidated after the discovery of poly(vinyl-trimethyl silane) (PVTMS) and, more notably, poly(trimethylsilylpropyne) (PTMSP).[27] The design of these polymeric matrix membranes, which incorporate significant $Si(CH_3)_3$ and have great permeability coefficients, such as that obtained for PTMSP compared to all previously known polymers (primarily polyacetylenes), greatly influences the performance of gas separation and motivates the search for more advanced materials with high permselectivity.

So far, a variety of polymers like chitosan, PVAm, carboxymethyl chitosan, matrimid, PEBAX, PVAm, PVA, polysulfone, and polyurethane, among others (as shown in Figure 5 and Table 3) have been employed commercially or at laboratory scale for CO_2 capture. However, the counter connection between permeability and selectivity places limitations on polymeric membranes despite the fact that they are less expensive and easier to construct than inorganic membranes.[9,28] In a permeability against selectivity plot, polymeric membranes frequently straddle the Robeson upper bound limit. Another significant issue with membrane-based CO_2/N_2 separation is CO_2-induced plasticization.[29] Different penetrants dissolve into the polymer matrix to cause plasticization, which destroys the structure of the polymer. Swelling of the membrane is yet another critical problem for the separation of CO_2/N_2. It is the most crucial parameter that must be considered while deciding on the kind of membrane material.[29] When the polymer dissolves in the specified solvent or as a result of feed moisture, swelling happens. Owing to these and many other drawbacks associated with conventional membranes, researchers' attention has been diverted toward the mixed-matrix membranes (MMMs), the design of which is one of the promising approaches to improve the performance of conventional polymeric and inorganic membranes.[30,31]

3.3. Mixed Matrix Membranes. Since the groundbreaking assessment by Okumus et al.[32] on the possibilities of MMMs, a number of important review papers have been released. These materials classify MMMs in three categories as liquid−polymer, solid−polymer, and solid−liquid polymer MMMs. The fabrication of solid-polymer MMMs has drawn interest in recent years.[33] Solid fillers incorporating polymer matrix MMMs can be traditional (such as carbon molecular sieves (CMSs), silicas, and zeolites) or novel (such as carbon nanotubes (CNTs), metal−organic frameworks (MOFs), graphene oxides (GO), spherical materials, layered materials, or delaminated materials). The structures of some of these materials are shown in Figure 6. The membranes composed of pure MOFs for gas separation include IRMOF-1, MIL-100 (Fe), ZIF-22, UIO-66 (Zr), Cu-(hfipbb)(H₂hfipbb)₀.₅, MOF-5, ZIF-8, IRMOF-3, HKUST-1, MMOF, ZIF-7, ZIF-8, ZIF-90, and $Co_3(HCOO)_6$, among others.[10] Due to the sheer

Table 3. Separation Performance of Various Types of Mixed Matrix Membranes

polymer	filler	testing conditions	P_{CO_2}	S_{CO_2/N_2}	ref
chitosan	Lys-c-GO	0.2 MPa, 85 °C	220[a]	84.5	58
chitosan	graphene	0.2 MPa, 90 °C	159[a]	93	59
carboxymethyl chitosan	CNTs	0.2 MPa, 90 °C	86[a]	45	60
PVA	PG/ZIF-8	0.25 MPa, 95 °C	344[a]	370	19
PVA	PEG/silica	0.25 MPa, 100 °C	400[a]	210	61
Pebax	GO	0.7 MPa, 35 °C	108[a]	48.5	62
Pebax	MWNTs	1 MPa, 25 °C	262[a]	58.5	63
Pebax	PRG	0.2 MPa, 30 °C	119[a]	104	64
Pebax	ZIF-90@C3N4	0.2 MPa, 25 °C	110.5[a]	84.4	65
Pebax	ZIF-7	0.275 MPa, 20 °C	111[a]	97	66
Pebax	ZIF-8@GO	0.3 MPa, 25 °C	136.2[a]	77.9	67
Pebax	[EMIM][OAc]/CuBTC	0.1 MPa, 35 °C	135[a]	32	68
cellulose acetate	MWCNTs	3 MPa, 25 °C	741.67[b]	40.17	69
Matrimid	CNTs/GO	0.2 MPa, 30 °C	38.07[a]	81	70
polyimide, ODPA-TMPDA	SAPO-34-filled CMSMs	0.02 MPa, 35 °C	2280[a]	13.4	71
matrimid	MIL-101	1 MPa, 35 °C	6.95[a]	52.92	72
PVAm/chitosan	HPEI-GO	0.1 MPa, 25 °C	126[a]	107	73
Pebax	COF-5	0.1 MPa, 30 °C	490[a]	49.3	74
polyurethane	UiO-66 (Zr)	0.4 MPa, T_{amb}	75.2[a]	34.2	75
polyurethane	MIL-101 (Cr)	0.4 MPa, T_{amb}	83.1[a]	42.4	75
PIM-1	UiO-66 (Zr)	0.1 MPa, 25 °C	5000[a]	28	76
matrimid	MIL-101 (Cr)	1 MPa, 35 °C	6.95[a]	52	72
cellulose acetate	NH$_2$-MIL-53(Al)	0.3 MPa, 25 °C	52.6[a]	23.4	77
matrimid	Azo-UiO-66	0.4 MPa, 37 °C	13[a]	40	78
polysulfone	Silica	0.17 MPa, 27 °C	14.2[b]	15.6	79
polysulfone	GO	0.5 MPa, 25 °C	74.47[b]	44.4	80
polyurethane	ZnO	1.2 MPa, 30 °C	80.7[a]	57	81
carboxymethyl chitosan	hydrotalcite (HT)	0.2 MPa, 90 °C	90[a]	13	82
carboxymethyl chitosan	HT/poly(amidoamine) dendrime	0.2 MPa, 90 °C	123[a]	67	83
chitosan/[emim][Ac]	ZIF-8	0.5 MPa, 25 °C	5413[a]	11.5	49
chitosan/[emim][Ac]	HKUST-1	0.5 MPa, 25 °C	4754[a]	19.3	49
chitosan	arginine salt	0.15 MPa, 110 °C	1500[a]	852	84
chitosan/polyvinyl amine	hyperbranched polyethylenimine−graphene oxide	0.1 MPa, 25 °C	81[a]	107	73
poly(N-vinyl formamide-co-vinylamine)	multiwalled carbon nanotubes	0.1 MPa, 57 °C	1451[b]	165	85
poly(vinylamine)	zeolite Y	0.25 MPa, 57 °C	1100[b]	200	86
carbon molecular sieve membrane (CMSMs)	Zeolite	0.1 MPa, 35 °C	2615[a]	31.7	71
cellulose acetate	Zeolite Y	0.4 MPa, 25 °C	3.28[a]	29.2	87
polyethersulfone-g-polyethylene glycol (PES-g-PEG)	PMFI Zeolite	0.1 MPa, 35 °C	66.9[a]	9.6	35
cellulose acetate	NaY Zeolite	0.7 MPa, 25 °C	1.52[a]	15.6	88
cellulose acetate	NaY-sm Zeolite	0.4 MPa, 25 °C	4.04[a]	26.2	44
Pebax	ZIF-8@CNT	0.5 MPa, 35 °C	225.5[a]	49.1	89

[a]Barrer. [b]GPU.

improvement in gas separation performance after the incorporation of fillers in the polymer matrix, there is considerable interest in discussing various fillers and their behavior in the membranes toward CO_2 capture as alternatives.

3.3.1. Zeolite. Zeolites are crystalline aluminosilicates having molecular-sized pores and gaps. On a molecular level, zeolite crystals are porous materials.[34] They have a consistent network of pores and channels (between 3 and 15 Å), which form a nanoscale labyrinth that might potentially store water or other guest molecules. These molecular sieving capabilities caused zeolites to be employed as fillers in mixed matrix membranes for CO_2 capture applications. Many researchers have shown the well-documented study of zeolite as a conventional inorganic filler in MMMs. The ability of zeolite-filled MMM to transport gas is significantly influenced by the intrinsic properties of the zeolite particles and the dense polymer phase. The anticipated enhancement happens when dispersed zeolite

particles are incorporated into the dense polymer matrix. Yu et al. prepared a membrane using a polyether sulfone-grafted polyethylene glycol (PES-g-PEG) comb-like copolymer as matrix and malleable MFI zeolite as inorganic filler.[35] At 35 °C, the MMM has a CO_2 permeability and selectivity of 66.9 Barrer and 9.6, respectively. The enhancement in performance is achieved due to the interaction between the filler and the polymer matrix, which is supposed to have disrupted the packing of the polymer chains, enlarged the void, and facilitated gas diffusion. It is also believed that the filler's mesoporous structure reduced the resistance to gas flow. Likewise, a large number of other studies have been conducted and published; Table 3 summarizes their results.

3.3.2. Graphene. A graphene-based material, graphene oxide, was created in 1840, but it was not until 2004 that it gained popularity. Similar to graphite, GO has layers and numerous functional groups, such as lactol, carbonyl,
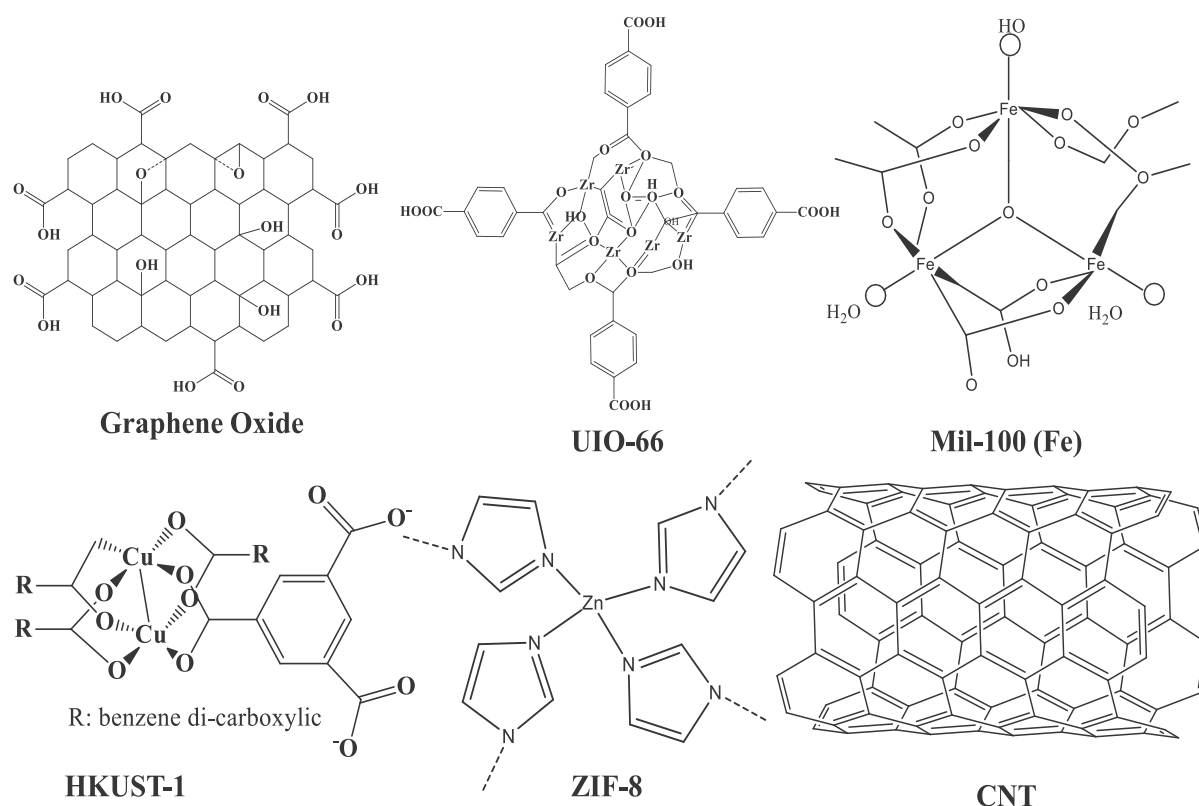
Figure 6. Chemical structures of a few commonly used fillers in gas separation applications.

carboxylic acid, and epoxy groups, that are covalently attached to its basal plane and edges. A complicated, inhomogeneous system made up of a hybrid sp^2/sp^3 system is generated as a result of the interlayer distance expansion.[36−38] This also explains why graphene oxide has tunable optical, chemical, and electrical properties. Graphene oxide and graphene oxide-based hybrid materials are frequently used for CO_2 capture. It has been shown that graphene and GO significantly increase CO_2 transport through their frictionless nanochannels while blocking N_2 or CH_4 to produce high permeance and selectivity. Katare et al. synthesized graphene oxide nanosheets and utilized them as fillers in a chitosan matrix. The group conducted the postsynthetic modification (PSM) of GO sheets by conjugating them with lysine amino acid and then incorporating them into CS. The CO_2/N_2 gas permeation test revealed a significant enhancement in the separation performance of synthesized MMM when compared to that of neat CS. The presence of GO nanosheets increased the surface roughness of the membrane and consequently aided the active survey area available for molecules to travel across the membranes.[39] Prasad et al. incorporated graphene nanoparticles (GNPs) as fillers and silk fibroin (SF) mobile carriers into the CS matrix and observed a significant improvement in gas separation performance compared to that of neat CS, as the CO_2 permeance increased from 12 to 159 GPU and the CO_2/N_2 selectivity increased from 54 to 93. The cooperative effect of the carrier amines from SF supporting the facilitated transportation and the assistance of GNP in the solution-diffusion mechanism boosted the performance factors of the CS/SF/GNP MMM.[40] Lee et al. engineered the surface of GO sheets via grafting with polyethylene glycol (PEG) and embedding with a poly(oxyethylene methacrylate) (POEM) monomer, and the solution was then casted onto a porous

polysulfone (PSf) support along with a poly(trimethylsilyl)-propyene (PTMSP) gutter layer. The highest CO_2 permeance of 3169 GPU and CO_2/N_2 selectivity of 37.4 were achieved in the synthesized MMMs. A selective CO_2 pathway was provided by the interlayer spacing between GO layers as obtained from the optimization of the Lewis acid−base interaction. Upon the construction of a very thin selective layer on the PSf support, an exclusive CO_2 separation performance was achieved.[41]

3.3.3. Carbon Nanotubes (CNTs). Carbon nanotubes (CNT), often known as Bucky tubes, are a family of nanomaterials that were first discovered in 1991. They are constructed of carbon atoms arranged in a two-dimensional (2D) hexagonal lattice.[42,43] CNTs are 1D nanomaterials with excellent mechanical and thermal capabilities. They can be divided into two broad categories: single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). SWCNTs are cylindrical sheets of rolled graphite with a maximum diameter of 1.5 nm. MWCNTs have a high surface area with interstitial channels and are made up of two or more concentrically manufactured cylinders separated by 0.35 nm, which is equivalent to the basal plane spacing.[44] The ability of CNT fillers to capture and transport CO_2 has led to an increase in their use in the membranes for gas separation. Thus, the incorporation of CNT in polymeric membranes has attracted interest as a result of the development of novel gas-separation membrane technologies: MMMs. Borgohain et al. synthesized a mixed matrix membrane with a different loading of MWCNTs into carboxymethyl chitosan (CMC) and utilized it for a CO_2/N_2 gas separation application.[45] The fabricated MMM displayed a CO_2 permeance of 43 GPU and a CO_2/N_2 selectivity of 45. It has been discovered that adding wrapped CNT to CMC produces thermally stable MMM, which

considerably boosted the CO_2/N_2 selectivity. Similarly, many other researchers have also utilized CNT for CO_2 capture, and their findings are summarized in Table 3.

3.3.4. Metal−Organic Frameworks (MOFs). Metal−organic frameworks (MOFs), a unique class of crystalline porous materials, are gaining increasing attention in the field of gas storage and separation. According to reports, MOFs can be modified before and after synthesis to achieve a strong affinity for CO_2. They also offer the advantages of a tiny aperture size and tunable physical and chemical properties. Moreover, the high porosity of MOFs hastens the movement of gases through the membrane layer.[46] The resulting MMM makes use of the superior qualities of both the polymer and the MOFs, and the chemical bonds created between the polymer chains and the MOFs boost the separation efficiency.[47] Over time, MOFs have drawn increased attention as a result of these characteristics. Basu et al.[48] produced PDMS membranes with a variety of fillers, including MIL-53(Al), MIL-47(V), HKUST-1, and ZIF-8. To separate CO_2 from diverse gas mixtures, Basu et al. also fabricated analogous MMMs by encapsulating the MIL-53(Al), ZIF-8, and HKUST-1 in matrimid. They demonstrated that, when compared to ZIF-8, the HKUST-1 and MIL-53(Al) had improved selectivity with a 0−30 wt % loading. Moreover, they asserted that this outcome was caused by the potent CO_2 interactions between HKUST-1's unsaturated metal sites and its breathing behavior while interacting with MIL-53-(Alhydroxyl) groups.

Coterillo et al.[49] proposed a ternary system by incorporating ZIF-8 in a membrane made of chitosan and [Emim][Ac] and suggested a fascinating method for improving the interface morphology. They claimed that the existence of the ionic liquid at the interface boosted the chitosan−ZIF-8 phase adhesion, which led to the greatest CO_2/N_2 separation performance at low ZIF-8 loading (5 wt %). Hybrid membranes with amine-functionalized UiO-66−NH$_2$ and 5 to 20 wt % pure UiO-66 have been developed. These membranes have a size range from 60 to 80 nm on average. The amount of inorganic phase enhanced the CO_2 permeability for both types of nanoparticles in a proportional manner, achieving an improvement of about 2.5× over the value of the pristine membrane (Table 3). These findings revealed that the exceptional affinity of UIO-66 for CO_2 was caused by an −OH coordinated bond related to the Zr cluster. The CO_2/N_2 selectivity, which showed a peak between 7.5 and 10 wt % loadings, showed a different trend. Compared to the pristine MOF, the UiO-66−NH$_2$ has a higher affinity, as the polymer matrix allowed for a greater selectivity enhancement (88% vs 42%). Interestingly, mixed matrix membranes made with UiO-66-NH$_2$ continued to perform consistently even when humidity was present. In a recent study, Lei et al.[50] reported high-performance CO_2 adsorption by a Ni-based metal−organic framework (MOF-74(Ni)). The high capture is associated with the abundantly available adsorption site and narrow micropore channels. These MOFs provide high CO_2 selectivity (CO_2/N_2= 49), high capture efficiency, and well-tuned isosteric heat of CO_2 adsorption. Guo et al.[51] reported the synergetic effect of adsorption and diffusion for separating CO_2/CH_4 using a ZIF-8-based mixed matrix membrane. The selective adsorption and molecular sieving properties of ZIF-8 nanoparticle fillers improve membrane separation performance. Many research studies have been conducted on the flat sheet mixed matrix membrane rather than thin-film hollow fiber mixed matrix membranes because the incorporation of

fillers on the flat sheet membrane significantly improved the gas separation performance. However, hollow fiber membranes have a potential future in various gas separation processes because of their benefits, such as their self-supporting structure, high packing density, better separation factor, mechanical strength, and thermal and chemical resistivity.[52−55]

Li et al.[56] investigated the formation of the selective layer containing a MOF-based hollow fiber membrane support and its gas separation performance. Amine-functionalized UiO-66 nanoparticles were incorporated into the Pebax 2533 thin selective layer on the polypropylene (PP) hollow fiber supports by a dip coating process. The selectivity (CO_2/N_2) and permeance of the CO_2 of the hollow fiber mixed matrix membrane containing 10 wt % UiO-66 were reported to be 37 and 26 GPU, respectively. The hollow fiber configuration gives exceptional mass transfer properties due to its high surface area and selectivity. Therefore, these configurations are more significant for industrial gas separation applications. Hollow fiber mixed matrix membranes (filler incorporated) with thin selective layers are recommended, as the thickness of the membrane is important for the separation of gas.[57]

3.4. Selection Criteria for Fillers and the Polymer Matrix for MMM Fabrication. MMMs require the homogeneous dispersion of inorganic fillers at the nanoscale level in a polymer matrix to incorporate both the advantageous properties of the polymer and filler materials. Their success relies heavily on the polymer matrix, the inorganic filler, and the interaction between the two phases.[90] The choice of fillers, which affects the gas separation wellness of a membrane, poses the most challenges during the development of MMMs. In case of a defect-free MMM, the minimum separation performance is determined by the polymer phase, while the upgradation of membrane permeability and selectivity is determined by the filler.

The following considerations should be taken into account while choosing proper fillers for MMM:

1. Porous materials, such as MOFs or zeolites, can typically be utilized as nanofillers because they act as molecular sieves and boost selectivity due to their carefully designed architectures.

2. To improve the target gas solubility and selectivity in the MMM, the desired gases, such as CO_2, are made to interact with the filler's surface functionality, such as −NH$_2$.

3. The development of high-performance MMMs depends on the compatibility of the filler phase and the polymeric matrix.

4. The use of MOFs with organic linkers equivalent to the functional groups of polymer chains is appropriate to satisfy the screening requirements for MOFs as MMM fillers.

5. MOFs with amino groups or surfaces containing ammonia are widely used to improve the contact between the filler and the polymer.

6. Hydrogen bonds can be created between the functional groups and polymer chains in MOFs with surface functionalization to improve the compatibility and interactions between the filler and the polymer.

7. By combining two distinct fillers in one polymer, the capacity to separate gases can be enhanced.

The following considerations should be taken into account while choosing a polymer for efficient MMM:

1. The foremost criteria is the film-forming ability; the selected polymeric material should have properties of forming a free-standing stable and rigid film/membrane.

2. Flexibility of the particular polymer during the solvent removal process is the main concern. The glass transition temperature (T_g) is a factor that can be indirectly related to the flexibility of polymeric materials, i.e., the lower the T_g, the more flexible the material. Hence, the matrix's T_g should be considered while selecting of polymer material for the matrix.[91]

3. In order to prevent the blockage of the accessible travel path for gas molecules, the polymer must not pierce the pores of the fillers, which will impair the separation performance.

4. The polymer and filler particles need to get along for the transportation of gas across the polymer. A noticeable improvement in the gas separation performance is achieved when the permeabilities of the faster-permeating component through the polymer and the filler are substantially comparable.

5. Another factor that influences the selection of materials is the polymers' processing capabilities after the addition of filler particles.

6. Another important factor in the development of flawless membranes is the particle dispersion inside the matrix. Polymers should have the ability to embed the filler particles into their matrixes. So far various MMMs have been created using zeolites, MOFs, CNTs, GO, activated carbon, CMS, metal oxides, and other filler particles.

7. The polymer should be mechanically, thermally, and chemically stable to withstand harsh environmental conditions in applications such as flue gas separation.

8. For the mixed matrix approach to be fully effective, the parameters of the polymer matrix should be close to the "upper bound" on the Robeson plot.

3.5. Major Challenges in Mixed Matrix Membranes. Despite the clear benefits that MMMs offer and the vast area of additional research, numerous issues still need to be resolved. There is no precise technique for the fabrication of nonporous membranes or composite membranes based on MMMs. Thus, there is uncertainty about making membranes with uniform nanoparticle distribution with as low of agglomeration as possible. According to conventional thinking, it is challenging to get a better affinity between fillers and the polymer matrix without adequate functionalization. Furthermore, because the additive-free volume is formed at the interface between nanoparticles and the matrix, imperfect compatibility may harm the achievement of greater permeability and diffusivity enhancements. Poor adhesion causes interface problems such as voids, a rigidified polymer, and pore blockage. Moreover, excess inorganic filler dispersion results in its aggregation in the polymer matrix and degrades the properties of the membrane when dealing with high loading compositions of inorganic filler. Moreover, if the polymer matrix is loaded with more inorganic fillers and/or incorrect particle sizes, it leads to pinholes and voids that degrade separation properties of the membrane. There have been no proposed methods for determining the surface energy of the injected nanoparticles beforehand to determine the variety of nanoparticle and polymer matrix combinations. Polymers used as matrices in fabricated MMMs must logically have appropriate permeability and permselectivity even in their raw state. As a result, the introduction of nanoparticles boosts the separation performance even further. Nevertheless, overcoming the Robeson upper bound curve remains a significant challenge. The separation factors and permeability coefficients must be at specific optimized values in practice. Therefore, picking random combinations of polymers and nanoparticles is not advisable. It is necessary to consider the requirements of future industrial applications.

4. CONCLUSIONS AND FUTURE DIRECTION

The uses of several membrane types for CCS applications are enumerated in this Review. The significance of mixed matrix membranes over other conventional membranes, namely inorganic and polymeric, for gas separation applications is discussed in this paper. MMMs are a wonderful invention that outperforms the limitation of inorganic and polymeric membranes toward permeability and selectivity. Even though there are many accessible reviews of MMMs, research will continue until new efficient inorganic filler materials are created. Inorganic fillers in MMMs help to achieve higher selectivity and permeability in gas separation applications. Therefore, MMMs comprising various inorganic fillers are found to be a potential research direction for CO_2 separation. The thermal, chemical, and mechanical strength, permeability, and selectivity of the membrane can be tailored by changing both the inorganic and organic phases. More and more studies have been published every year demonstrating exceptional interactions of polymer and filler materials with good gas separation performances. However, industrial engineering research in this field is still in its early stage. This provides many future research and development opportunities to address these engineering challenges. Recent research has mainly been focused on two-dimensional porous materials like MOF, COF, and graphene oxide nanosheets as filler materials in the polymer matrices.

The data of gas separation by various filler-based MMMs revealed that agglomeration in the polymer matrix occurred at higher concentrations of filler in the matrix, resulting in significant deterioration in the gas separation performance. To manage pore size and prevent filler agglomeration, an appropriate amount of fillers in the polymer matrix is crucial. According to research, MMMs can transport gases with exceptional efficiency by increasing the matrix—filler dispersion and employing lower filler concentrations. Therefore, it is essential to develop thin membranes to attain the maximum flux to reduce the cost of separation. Considering sonication and ball milling as the most widely used exfoliation methods, a high-performance homogeneous membrane can be produced with the proper shear forces obtained from sonication or ball milling. For the creation of a thin membrane with excellent performance, the choice of a proper filler—matrix pair is crucial. However, the higher price of filler materials restricts their use on a large scale. In addition, the industrialization of MMMs for CCS applications has necessitated the use of renewable, cost-effective, and naturally occurring polymeric materials. However, the fabrication and reproducibility of thin, defect-free, and biopolymeric MMM instead of a synthetic membrane on a large scale is still challenging.

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Notes

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■ REFERENCES

(1) Ghosal, K.; Freeman, B. D.; Chern, R. T.; Alvarez, J. C.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. Gas Separation Properties of Aromatic Polyamides with Sulfone Groups. *Polymer (Guildf)* **1995**, *36* (4), 793−800.

(2) Feng, S.; Bu, M.; Pang, J.; Fan, W.; Fan, L.; Zhao, H.; Yang, G.; Guo, H.; Kong, G.; Sun, H.; Kang, Z.; Sun, D. Hydrothermal Stable ZIF-67 Nanosheets via Morphology Regulation Strategy to Construct Mixed-Matrix Membrane for Gas Separation. *J. Membr. Sci.* **2020**, *593*, 117404.

(3) Hoegh-Guldberg, O.; Jacob, D.; Taylor, M.; Guillén Bolaños, T.; Bindi, M.; Brown, S.; Camilloni, I. A.; Diedhiou, A.; Djalante, R.; Ebi, K.; Engelbrecht, F.; Guiot, J.; Hijioka, Y.; Mehrotra, S.; Hope, C. W.; Payne, A. J.; Pörtner, H. O.; Seneviratne, S. I.; Thomas, A.; Warren, R.; Zhou, G. The Human Imperative of Stabilizing Global Climate Change at 1.5°C. *Science* **2019**, *365* (6459), No. eaaw6974, DOI: 10.1126/science.aaw6974.

(4) Vinoba, M.; Bhagiyalakshmi, M.; Alqaheem, Y.; Alomair, A. A.; Pérez, A.; Rana, M. S. Recent Progress of Fillers in Mixed Matrix Membranes for CO_2 Separation : A Review. *Sep. Purif. Technol.* **2017**, *188*, 431−450.

(5) Ramasubramanian, K.; Verweij, H.; Winston Ho, W. S. Membrane Processes for Carbon Capture from Coal-Fired Power Plant Flue Gas: A Modeling and Cost Study. *J. Membr. Sci.* **2012**, *421−422*, 299−310.

(6) Hedin, N.; Andersson, L.; Bergström, L.; Yan, J. Adsorbents for the Post-Combustion Capture of CO_2 Using Rapid Temperature Swing or Vacuum Swing Adsorption. *Appl. Energy* **2013**, *104*, 418−433.

(7) Rao, A. B.; Rubin, E. S. A Technical, Economic, and Environmental Assessment of Amine-Based CO_2 Capture Technology for Power Plant Greenhouse Gas Control. *Environ. Sci. Technol.* **2002**, *36* (20), 4467−4475.

(8) Salvi, B. L.; Jindal, S. Recent Developments and Challenges Ahead in Carbon Capture and Sequestration Technologies. *SN Appl. Sci.* **2019**, *1* (8), 885.

(9) Robeson, L. M. Correlation of Separation Factor versus Permeability for Polymeric Membranes. *J. Membr. Sci.* **1991**, *62* (2), 165−185.

(10) Vinoba, M.; Bhagiyalakshmi, M.; Alqaheem, Y.; Alomair, A. A.; Pérez, A.; Rana, M. S. Recent Progress of Fillers in Mixed Matrix Membranes for CO_2 Separation: A Review. *Sep. Purif. Technol.* **2017**, *188*, 431−450.

(11) Chung, T. S.; Jiang, L. Y.; Li, Y.; Kulprathipanja, S. Mixed Matrix Membranes (MMMs) Comprising Organic Polymers with Dispersed Inorganic Fillers for Gas Separation. *Prog. Polym. Sci.* **2007**, *32* (4), 483−507.

(12) Li, S.; Liu, Y.; Wong, D. A.; Yang, J. Recent Advances in Polymer-Inorganic Mixed Matrix Membranes for CO_2 Separation. *Polymers (Basel)* **2021**, *13* (15), 2539.

(13) LU, J.; CHENG, M.; JI, Y.; ZHANG, H. Membrane-Based CO_2 Absorption into Blended Amine Solutions. *J. Fuel Chem. Technol.* **2009**, *37* (6), 740−746.

(14) Li, J.-L.; Chen, B.-H. Review of CO_2 Absorption Using Chemical Solvents in Hollow Fiber Membrane Contactors. *Sep. Purif. Technol.* **2005**, *41* (2), 109−122.

(15) Dehghani Kiadehi, A.; Rahimpour, A.; Jahanshahi, M.; Ghoreyshi, A. A. Novel Carbon Nano-Fibers (CNF)/Polysulfone (PSf) Mixed Matrix Membranes for Gas Separation. *J. Ind. Eng. Chem.* **2015**, *22*, 199−207.

(16) Semsarzadeh, M. A.; Ghalei, B. Preparation, Characterization and Gas Permeation Properties of Polyurethane−Silica/Polyvinyl Alcohol Mixed Matrix Membranes. *J. Membr. Sci.* **2013**, *432*, 115−125.

(17) Widjojo, N.; Li, Y.; Jiang, L.; Chung, T.-S. Recent Progress and Challenges on Mixed Matrix Membranes in Both Material and Configuration Aspects for Gas Separation. In *Advanced Materials for Membrane Preparation*; Guonomenna, M. G., Golemme, G., Eds.; Bentham Science Publisher Ltd.: Sharjah, UAE, 2012; pp 64−82. DOI: 10.2174/978160805308711201010064.

(18) Xin, Q.; Ouyang, J.; Liu, T.; Li, Z.; Li, Z.; Liu, Y.; Wang, S.; Wu, H.; Jiang, Z.; Cao, X. Enhanced Interfacial Interaction and CO_2 Separation Performance of Mixed Matrix Membrane by Incorporating Polyethylenimine-Decorated Metal−Organic Frameworks. *ACS Appl. Mater. Interfaces* **2015**, *7* (2), 1065−1077.

(19) Barooah, M.; Mandal, B. Synthesis, Characterization and CO_2 Separation Performance of Novel PVA/PG/ZIF-8 Mixed Matrix Membrane. *J. Membr. Sci.* **2019**, *572*, 198−209.

(20) Ma, C.; Wang, M.; Wang, Z.; Gao, M.; Wang, J. Recent Progress on Thin Film Composite Membranes for CO_2 separation. *J. CO2 Util.* **2020**, *42* (May), 101296.

(21) Li, S.; Wang, Z.; Yu, X.; Wang, J.; Wang, S. High-Performance Membranes with Multi-Permselectivity for CO_2 Separation. *Adv. Mater.* **2012**, *24* (24), 3196−3200.

(22) Nasir, R.; Mukhtar, H.; Man, Z.; Mohshim, D. F. Material Advancements in Fabrication of Mixed-Matrix Membranes. *Chem. Eng. Technol.* **2013**, *36* (5), 717−727.

(23) Sharma, S. K.; Sanfui, B. K.; Katare, A.; Mandal, B. Fabrication and Performance Evaluation of Industrial Alumina Based Graded Ceramic Substrate for CO_2 Selective Amino Silicate Membrane. *ACS Appl. Mater. Interfaces* **2020**, *12* (36), 40269−40284.

(24) Wong, K. K.; Jawad, Z. A. A Review and Future Prospect of Polymer Blend Mixed Matrix Membrane for CO_2 Separation. *J. Polym. Res.* **2019**, *26* (12), 289.

(25) Mitchell, J. K. On the Penetrativeness of Fluids. *J. Memb. Sci.* **1995**, *100* (1), 11−16.

(26) Graham, T. On the Absorption and Dialytic Separation of Gases by Colloid Septa. *J. Franklin Inst.* **1867**, *83* (1), 39−41.

(27) Bermeshev, M. V.; Syromolotov, A. V.; Gringolts, M. L.; Starannikova, L. E.; Yampolskii, Y. P.; Finkelshtein, E. S. Synthesis of High Molecular Weight Poly[3-{tris(Trimethylsiloxy)Silyl}-tricyclononenes-7] and Their Gas Permeation Properties. *Macromolecules* **2011**, *44* (17), 6637−6640.

(28) Wang, S.; Li, X.; Wu, H.; Tian, Z.; Xin, Q.; He, G.; Peng, D.; Chen, S.; Yin, Y.; Jiang, Z.; Guiver, M. D. Advances in High Permeability Polymer-Based Membrane Materials for CO_2 Separations. *Energy Environ. Sci.* **2016**, *9* (6), 1863−1890.

(29) Suleman, M. S.; Lau, K. K.; Yeong, Y. F. Plasticization and Swelling in Polymeric Membranes in CO_2 Removal from Natural Gas. *Chem. Eng. Technol.* **2016**, *39* (9), 1604−1616.

(30) Dong, G.; Li, H.; Chen, V. Challenges and Opportunities for Mixed-Matrix Membranes for Gas Separation. *J. Mater. Chem. A* **2013**, *1*, 4610−4630.

(31) Kanehashi, S.; Scholes, C. A. Perspective of Mixed Matrix Membranes for Carbon Capture. *Front. Chem. Sci. Eng.* **2020**, *14* (3), 460−469.

(32) Okumus, E.; Gurkan, T.; Yilmaz, L. Development of a Mixed-Matrix Membrane for Pervaporation. *Sep. Sci. Technol* **1994**, *29* (18), 2451−2473.

(33) Pacheco, M. J.; Vences, L. J.; Moreno, H.; Pacheco, J. O.; Valdivia, R.; Hernández, C. Review: Mixed-Matrix Membranes with Cnt for CO_2 Separation Processes. *Membranes* **2021**, *11* (6), No. 457.

(34) Cundy, C. S.; Cox, P. A. The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. *Chem. Rev.* **2003**, *103* (3), 663−702.

(35) Yu, Y.; Zhang, C.; Fan, J.; Liu, D.; Meng, J. A Mixed Matrix Membrane for Enhanced CO_2/N_2 Separation via Aligning Hierarchical Porous Zeolite with a Polyethersulfone Based Comb-like Polymer. *J. Taiwan Inst. Chem. Eng.* **2022**, *132*, 104132.

(36) Singh, M.; Yadav, A.; Kumar, S.; Agarwal, P. Annealing Induced Electrical Conduction and Band Gap Variation in Thermally Reduced Graphene Oxide Films with Different Sp2/Sp3 Fraction. *Appl. Surf. Sci.* **2015**, *326*, 236−242.

(37) Tiwari, S. K.; Mishra, R. K.; Ha, S. K.; Huczko, A. Evolution of Graphene Oxide and Graphene: From Imagination to Industrialization. *ChemNanoMat* **2018**, *4* (7), 598−620.

(38) Chen, D.; Feng, H.; Li, J. Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications. *Chem. Rev.* **2012**, *112* (11), 6027−6053.

(39) Katare, A.; Sharma, S.; Mandal, B. Effects of L-Lysine-Conjugated-Graphene Oxide as a Nanofiller on the CO_2 Separation Performance of Mixed Matrix Chitosan Membrane. *Indian Chem. Eng.* **2022**, 1−12.

(40) Prasad, B.; Mandal, B. Graphene-Incorporated Biopolymeric Mixed-Matrix Membrane for Enhanced CO_2 Separation by Regulating the Support Pore Filling. *ACS Appl. Mater. Interfaces* **2018**, *10* (33), 27810−27820.

(41) Lee, C. S.; Moon, J.; Park, J. T.; Kim, J. H. Engineering CO_2-Philic Pathway via Grafting Poly(Ethylene Glycol) on Graphene Oxide for Mixed Matrix Membranes with High CO_2 Permeance. *Chem. Eng. J.* **2023**, *453*, 139818.

(42) Ismail, A. F.; Goh, P. S.; Sanip, S. M.; Aziz, M. Transport and Separation Properties of Carbon Nanotube-Mixed Matrix Membrane. *Sep. Purif. Technol.* **2009**, *70* (1), 12−26.

(43) Gupta, O.; Roy, S.; Rao, L.; Mitra, S. Graphene Oxide-Carbon Nanotube (GO-CNT) Hybrid Mixed Matrix Membrane for Pervaporative Dehydration of Ethanol. *Membranes (Basel)* **2022**, *12* (12), 1227.

(44) Zhao, P.; Zhang, G.; Yan, H.; Zhao, Y. The Latest Development on Amine Functionalized Solid Adsorbents for Post-Combustion CO_2 Capture: Analysis Review. *Chin. J. Chem. Eng.* **2021**, *35*, 17−43.

(45) Borgohain, R.; Jain, N.; Prasad, B.; Mandal, B.; Su, B. Carboxymethyl Chitosan/Carbon Nanotubes Mixed Matrix Membranes for CO_2 Separation. *React. Funct. Polym.* **2019**, *143*, 104331.

(46) Dechnik, J.; Sumby, C. J.; Janiak, C. Enhancing Mixed-Matrix Membrane Performance with Metal−Organic Framework Additives. *Cryst. Growth Des.* **2017**, *17* (8), 4467−4488.

(47) Shah Buddin, M. M. H.; Ahmad, A. L. A Review on Metal-Organic Frameworks as Filler in Mixed Matrix Membrane: Recent Strategies to Surpass Upper Bound for CO_2 Separation. *J. CO2 Util.* **2021**, *51*, 101616.

(48) Basu, S.; Cano-Odena, A.; Vankelecom, I. F. J. MOF-Containing Mixed-Matrix Membranes for CO_2/CH_4 and CO_2/N_2 Binary Gas Mixture Separations. *Sep. Purif. Technol.* **2011**, *81* (1), 31−40.

(49) Casado-Coterillo, C.; Fernández-Barquín, A.; Zornoza, B.; Téllez, C.; Coronas, J.; Irabien, Á. Synthesis and Characterisation of MOF/Ionic Liquid/Chitosan Mixed Matrix Membranes for CO_2/N_2 Separation. *RSC Adv.* **2015**, *5* (124), 102350−102361.

(50) Lei, L.; Cheng, Y.; Chen, C.; Kosari, M.; Jiang, Z.; He, C. Taming Structure and Modulating Carbon Dioxide (CO_2) Adsorption Isosteric Heat of Nickel-Based Metal Organic Framework (MOF-74(Ni)) for Remarkable CO_2 Capture. *J. Colloid Interface Sci.* **2022**, *612*, 132−145.

(51) Guo, A.; Ban, Y.; Yang, K.; Yang, W. Metal-Organic Framework-Based Mixed Matrix Membranes: Synergetic Effect of Adsorption and Diffusion for CO_2/CH_4 Separation. *J. Membr. Sci.* **2018**, *562*, 76−84.

(52) Li, G.; Kujawski, W.; Válek, R.; Koter, S. A Review - The Development of Hollow Fibre Membranes for Gas Separation Processes. *Int. J. Greenh. Gas Control* **2021**, *104*, 103195.

(53) Li, G.; Kujawski, W.; Knozowska, K.; Kujawa, J. The Effects of PEI Hollow Fiber Substrate Characteristics on PDMS/PEI Hollow Fiber Membranes for CO_2/N_2 Separation. *Membranes (Basel)* **2021**, *11* (1), 56.

(54) Zhu, H.; Jie, X.; Wang, L.; Kang, G.; Liu, D.; Cao, Y. Enhanced Gas Separation Performance of Mixed Matrix Hollow Fiber Membranes Containing Post-Functionalized S-MIL-53. *J. Energy Chem.* **2018**, *27* (3), 781−790.

(55) Widiastuti, N.; Gunawan, T.; Fansuri, H.; Salleh, W. N. W.; Ismail, A. F.; Sazali, N. P84/ZCC Hollow Fiber Mixed Matrix Membrane with PDMS Coating to Enhance Air Separation Performance. *Membranes (Basel)* **2020**, *10* (10), 267.

(56) Li, G.; Kujawski, W.; Knozowska, K.; Kujawa, J. Thin Film Mixed Matrix Hollow Fiber Membrane Fabricated by Incorporation of Amine Functionalized Metal-Organic Framework for CO_2/N_2 Separation. *Materials (Basel)* **2021**, *14* (12), 3366.

(57) Sunder, N.; Fong, Y. Y.; Bustam, M. A.; Suhaimi, N. H. Development of Amine-Functionalized Metal-Organic Frameworks Hollow Fiber Mixed Matrix Membranes for CO_2 and CH_4 Separation: A Review. *Polymers (Basel)* **2022**, *14* (7), 1408.

(58) Katare, A.; Sharma, S.; Mandal, B. Effects of L-Lysine-Conjugated-Graphene Oxide as a Nanofiller on the CO_2 Separation Performance of Mixed Matrix Chitosan Membrane. *Indian Chem. Eng.* **2022**, *0* (0), 1−12.

(59) Prasad, B.; Mandal, B. Graphene-Incorporated Biopolymeric Mixed-Matrix Membrane for Enhanced CO_2 Separation by Regulating the Support Pore Filling. *ACS Appl. Mater. Interfaces* **2018**, *10* (33), 27810−27820.

(60) Borgohain, R.; Jain, N.; Prasad, B.; Mandal, B.; Su, B. Carboxymethyl Chitosan/Carbon Nanotubes Mixed Matrix Membranes for CO_2 Separation. *React. Funct. Polym.* **2019**, *143* (July), 104331.

(61) Barooah, M.; Mandal, B. Enhanced CO_2 Separation Performance by PVA/PEG/Silica Mixed Matrix Membrane. *J. Appl. Polym. Sci.* **2018**, *135* (28), 46481.

(62) Zhao, D.; Ren, J.; Qiu, Y.; Li, H.; Hua, K.; Li, X.; Deng, M. Effect of Graphene Oxide on the Behavior of Poly(Amide-6-b-Ethylene Oxide)/Graphene Oxide Mixed-Matrix Membranes in the Permeation Process. *J. Appl. Polym. Sci.* **2015**, *132* (41), 42624.

(63) Murali, R. S.; Sridhar, S.; Sankarshana, T.; Ravikumar, Y. V. L. Gas Permeation Behavior of Pebax-1657 Nanocomposite Membrane Incorporated with Multiwalled Carbon Nanotubes. *Ind. Eng. Chem. Res.* **2010**, *49* (14), 6530−6538.

(64) Dong, G.; Hou, J.; Wang, J.; Zhang, Y.; Chen, V.; Liu, J. Enhanced CO_2/N_2 Separation by Porous Reduced Graphene Oxide/Pebax Mixed Matrix Membranes. *J. Membr. Sci.* **2016**, *520*, 860−868.

(65) Guo, F.; Li, D.; Ding, R.; Gao, J.; Ruan, X.; Jiang, X.; He, G.; Xiao, W. Constructing MOF-Doped Two-Dimensional Composite Material ZIF-90@C3N4Mixed Matrix Membranes for CO_2/N_2 Separation. *Sep. Purif. Technol.* **2022**, *280*, 119803.

(66) Li, T.; Pan, Y.; Peinemann, K. V.; Lai, Z. Carbon Dioxide Selective Mixed Matrix Composite Membrane Containing ZIF-7 Nano-Fillers. *J. Membr. Sci.* **2013**, *425−426*, 235−242.

(67) Yang, K.; Dai, Y.; Ruan, X.; Zheng, W.; Yang, X.; Ding, R.; He, G. Stretched ZIF-8@GO Flake-like Fillers via Pre-Zn(II)-Doping Strategy to Enhance CO_2 Permeation in Mixed Matrix Membranes. *J. Membr. Sci.* **2020**, *601*, 117934.

(68) Habib, N.; Durak, O.; Zeeshan, M.; Uzun, A.; Keskin, S. A Novel IL/MOF/Polymer Mixed Matrix Membrane Having Superior CO_2/N_2 Selectivity. *J. Membr. Sci.* **2022**, *658* (March), 120712.

(69) Ahmad, A. L.; Jawad, Z. A.; Low, S. C.; Zein, S. H. S. A Cellulose Acetate/Multi-Walled Carbon Nanotube Mixed Matrix Membrane for CO_2/N_2 Separation. *J. Membr. Sci.* **2014**, *451*, 55−66.

(70) Li, X.; Ma, L.; Zhang, H.; Wang, S.; Jiang, Z.; Guo, R.; Wu, H.; Cao, X. Z.; Yang, J.; Wang, B. Synergistic Effect of Combining Carbon Nanotubes and Graphene Oxide in Mixed Matrix Membranes for Efficient CO_2 Separation. *J. Membr. Sci.* **2015**, *479*, 1−10.

(71) Chuah, C. Y.; Lee, J.; Bao, Y.; Song, J.; Bae, T. H. High-Performance Porous Carbon-Zeolite Mixed-Matrix Membranes for CO_2/N_2 Separation. *J. Membr. Sci.* **2021**, *622*, 119031.

(72) Naseri, M.; Mousavi, S. F.; Mohammadi, T.; Bakhtiari, O. Synthesis and Gas Transport Performance of MIL-101/Matrimid Mixed Matrix Membranes. *J. Ind. Eng. Chem.* **2015**, *29*, 249−256.

(73) Shen, Y.; Wang, H.; Liu, J.; Zhang, Y. Enhanced Performance of a Novel Polyvinyl Amine/Chitosan/Graphene Oxide Mixed Matrix Membrane for CO_2 Capture. *ACS Sustain. Chem. Eng.* **2015**, *3* (8), 1819−1829.

(74) Zhang, Y.; Tong, Y.; Li, X.; Guo, S.; Zhang, H.; Chen, X.; Cai, K.; Cheng, L.; He, W. Pebax Mixed-Matrix Membrane with Highly Dispersed ZIF-8@CNTs to Enhance CO_2/N_2 Separation. *ACS Omega* **2021**, *6*, 18566−18575.

(75) Rodrigues, M. A.; Ribeiro, J. de S.; Costa, E. de S.; de Miranda, J. L.; Ferraz, H. C. Nanostructured Membranes Containing UiO-66 (Zr) and MIL-101 (Cr) for O2/N2 and CO_2/N_2 Separation. *Sep. Purif. Technol.* **2018**, *192*, 491−500.

(76) Khdhayyer, M. R.; Esposito, E.; Fuoco, A.; Monteleone, M.; Giorno, L.; Jansen, J. C.; Attfield, M. P.; Budd, P. M. Mixed Matrix Membranes Based on UiO-66 MOFs in the Polymer of Intrinsic Microporosity PIM-1. *Sep. Purif. Technol.* **2017**, *173*, 304−313.

(77) Mubashir, M.; Yeong, Y. F.; Lau, K. K.; Chew, T. L.; Norwahyu, J. Efficient CO_2/N_2 and CO_2/CH_4 Separation Using NH_2-MIL-53(Al)/Cellulose Acetate (CA) Mixed Matrix Membranes. *Sep. Purif. Technol.* **2018**, *199*, 140−151.

(78) Prasetya, N.; Donose, B. C.; Ladewig, B. P. A New and Highly Robust Light-Responsive Azo-UiO-66 for Highly Selective and Low Energy Post-Combustion CO_2 Capture and Its Application in a Mixed Matrix Membrane for CO_2/N_2 Separation. *J. Mater. Chem. A* **2018**, *6* (34), 16390−16402.

(79) Julian, H.; Sutrisna, D.; Hakim, A. N.; Harsono, H. O.; Hugo, A.; Wenten, I. G. Polymer-Plastics Technology and Materials Nano-Silica/Polysulfone Asymmetric Mixed-Matrix Membranes (MMMs) with High CO_2 Permeance in the Application of CO_2/N_2 Separation. *Polym.-Plast. Technol. Mater.* **2019**, *58* (6), 678−689.

(80) Zahri, K.; Wong, K. C.; Goh, P. S.; Ismail, A. F. Graphene Oxide/Polysulfone Hollow Fiber Mixed Matrix Membranes for Gas Separation. *RSC Adv.* **2016**, *6* (92), 89130−89139.

(81) Soltani, B.; Asghari, M. Membranes Effects of ZnO Nanoparticle on the Gas Separation Performance of Polyurethane Mixed Matrix Membrane. *Membranes* **2017**, *7* (3), No. 43.

(82) Borgohain, R.; Mandal, B. High-Speed CO_2 Transport Channel Containing Carboxymethyl Chitosan/Hydrotalcite Membrane for CO_2 Separation. *J. Appl. Polym. Sci.* **2020**, *137*, 48715.

(83) Borgohain, R.; Mandal, B. Thermally Stable and Moisture Responsive Carboxymethyl Chitosan/Dendrimer/Hydrotalcite Membrane for CO_2 Separation. *J. Membr. Sci.* **2020**, *608* (May), 118214.

(84) El-Azzami, L. A.; Grulke, E. A. Carbon Dioxide Separation from Hydrogen and Nitrogen Facilitated Transport in Arginine Salt-Chitosan Membranes. *J. Membr. Sci.* **2009**, *328* (1−2), 15−22.

(85) Han, Y.; Wu, D.; Ho, W. S. W. Nanotube-Reinforced Facilitated Transport Membrane for CO_2/N_2 Separation with Vacuum Operation. *J. Membr. Sci.* **2018**, *567*, 261−271.

(86) Chen, Y.; Zhao, L.; Wang, B.; Dutta, P.; Ho, W. S. W. Amine-Containing Polymer/Zeolite Y Composite Membranes for CO_2/N_2 Separation Solution-Diffusion. *J. Membr. Sci.* **2016**, *497*, 21−28.

(87) Sanaeepur, H.; Kargari, A.; Nasernejad, B.; Ebadi Amooghin, A.; Omidkhah, M. A Novel CO_2+ Exchanged Zeolite Y/Cellulose Acetate Mixed Matrix Membrane for CO_2/N_2 Separation. *J. Taiwan Inst. Chem. Eng.* **2016**, *60*, 403−413.

(88) Sanaeepur, H.; Nasernejad, B.; Kargari, A. Cellulose Acetate/Nano-Porous Zeolite Mixed Matrix Membrane for CO_2 Separation. *Greenh. Gases Sci. Technol.* **2015**, *5* (3), 291−304.

(89) Zhang, Y.; Tong, Y.; Li, X.; Guo, S.; Zhang, H.; Chen, X.; Cai, K.; Cheng, L.; He, W. Pebax Mixed-Matrix Membrane with Highly Dispersed ZIF-8@CNTs to Enhance CO_2/N_2 Separation. *ACS Omega* **2021**, *6* (29), 18566−18575.

(90) Monsalve-Bravo, G. M.; Bhatia, S. K. Modeling Permeation through Mixed-Matrix Membranes: A Review. *Processes* **2018**, *6* (9), 172.

(91) Mahajan, R.; Burns, R.; Schaeffer, M.; Koros, W. J. Challenges in Forming Successful Mixed Matrix Membranes with Rigid Polymeric Materials. *J. Appl. Polym. Sci.* **2002**, *86* (4), 881−890.