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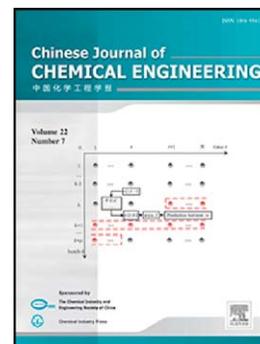
Recent Advances on Mixed Matrix Membranes for CO_2 Separation[*]

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Abstract Recent advances on mixed matrix membrane for CO_2 separation is reviewed in this paper. To improve CO_2 separation performance of polymer membranes, mixed matrix membranes (MMMs) are developed. The concept of MMM is illustrated distinctly. Suitable polymer and inorganic or organic fillers for MMMs are summarized. Possible interface morphologies between polymer and filler, and the effect of interface morphologies on gas transport properties of MMMs are summarized. The methods to improve compatibility between polymer and filler are introduced. There are eight methods including silane coupling, Grignard reagents treatment, incorporation of additive, grafting, in situ polymerization, polydopamine coating, particle fusion approach and polymer functionalization. To achieve higher productivity for industrial application, mixed matrix composite membranes are developed. The recent development on hollow fiber and flat mixed matrix composite membrane is reviewed in detail. Last, the future trend of MMM is forecasted.

Keywords CO_2 separation, mixed matrix membrane, material selection, compatibility, composite membrane, future direction

1 INTRODUCTION

The energy-efficient and environmentally friendly CO_2 separation technology is increasingly necessary and has huge market in industrial application including CO_2 capture, CO_2 removal from flue gas, natural gas treatment and hydrogen purification[1-3]. Membrane-based gas separation is considered as the candidate technology. However, polymer membranes are shown to suffer a permeability-selectivity trade-off limitation[4]. Recently, mixed matrix membranes

(MMMs) are developed to overcome the limitation [5-9]. In general, MMMs are fabricated by using two or more different materials of distinct properties. One material (usually a polymer) forms a continuous phase, also known as matrix. Another material forms a dispersed phase, inorganic or organic, which is the so-called filler. The matrix and filler is immiscible and possess different transport properties. There are a larger number of scientific literatures on MMMs for CO_2 separation.

Permeability and selectivity are two important parameters to evaluate membrane performance. For the membranes without a support membrane or a support layer, permeability is officially called as permeability coefficient (P). It can be expressed as follows:

$$P_i = \frac{Q_i l}{\Delta P_i A} \tag{1}$$

where Q_i is the permeation rate of gas species i at standard temperature and pressure (STP), l is thicknesss, ΔP_i is the transmembrane partial pressure difference of gas species i, and A is the effective membrane area. The gas permeability coefficient is customarily expressed in the unit of $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$. However, the permeance (R) is usually applied to assess the permeability for composite membranes and asymmetric membranes. It can be expressed as follows:

$$R_i = \frac{P_i}{l} \tag{2}$$

The gas permeance is customarily expressed in the unit of $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$.

The selectivity reflects the capability of a membrane to separate one gas from gas mixture. The ideal selectivity ($\alpha_{i/j}^*$) is given by the ratio of the two pure gas permeabilities shown in Eq. (3) .

$$\alpha_{i/j}^* = \frac{P_i}{P_j} = \frac{R_i}{R_j} \tag{3}$$

where P_i, R_i, P_i and R_j are the permeability coefficient and permeance of gas species i and j in the membrane, respectively.

For permeation of actual i–j mixtures, the mixed gas selectivity, also called as

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separation factor ($\alpha'_{i/j}$), is calculated by Eq. (4).

$$\alpha'_{i/j} = \frac{y_i / y_j}{x_i / x_j} \tag{4}$$

where y_i and y_j are the molar fraction of gas species i and j in the permeate side, while x_i and x_j are the molar fraction of gas species i and j in the feed side.

2 MATERAIL SELECTION FOR MMM

As typical MMMs, the polymer acts as continuous phase and the filler acts as a dispersed phase. To develop high performance MMMs, correct selection of polymer and filler is very important.

2.1 Selection of Polymer

In general, gas transport through polymeric membranes follows the solution-diffusion mechanism. In such membranes, gas molecules first dissolve in the membranes at the interface of the feed side and the membrane, and then diffuse across the membrane to the permeate side [10]. Permeability is the product of gas solubility and diffusivity. As a result, polymer with specific structure or high affinity for CO_2 molecules can provide high CO_2 permselectivity. However, there are different cases inside facilitated transport polymeric membranes. The facilitation of CO_2 transport is accomplished by the "carrier" inside a facilitated transport membrane, which can reversibly react with CO_2 [10]. It is well-known as facilitated transport mechanism or reactivity selective mechanism. At the feed-side interface of the membrane, CO_2 reacts with the carrier and forms a CO_2-carrier reaction product, which diffuses along its concentration gradient to the permeate side of the membrane. Due to a lower CO_2 partial pressure on the permeate side, CO_2 is released from the CO_2-carrier reaction product to the permeate side, while regenerating the carrier that can then react with another CO_2 molecule on the feed side [10]. Hence, a major part of CO_2 is transported by the carriers inside the membranes in addition to the physical solution-diffusion as other non-reactive gases such as N_2, CH_4 and H_2. As a result, both high CO_2 permeability and selectivity can be obtained for facilitated transport polymeric

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membrane materials.

To achieve CO_2 separation, as a continuous phase in MMMs, the polymer should have not only high CO_2 permeability but also high selectivity. For CO_2/N_2 or CO_2/CH_4 separation, because the kinetic diameter of CO_2 molecule is less than that of N_2 or CH_4 molecule (Table 1), diffusivity selectivity of the polymer is higher than one. For CO_2/H_2 separation, because the kinetic diameter of CO_2 molecule is larger than that of H_2 molecule, diffusivity selectivity of the polymer is less than one. To meet high selectivity for CO_2 separation, the polymer should have high solubility selectivity or reactivity selectivity. Hence, the polymer should contain functional groups which only have high affinity for CO_2 molecules or react with CO_2 molecules. Furthermore, the polymer should have high mechanical strength and good thermal stability. Due to the different sources of CO_2, the content, pressure and temperatures vary widely. The polymer should be selected based on practical application conditions. High performance glassy polymers with robust mechanical strength may be applicable for high pressure conditions such as natural gas purification; Facilitated transport membrane material may be suitable for low pressure flue gas purification, biogas treatment, and hot (>100°C) syngas separation [11]. Besides, because various kinds of impurity gases such as water, O_2, SO_x, NO_x, H_2S, etc. are present as minor components in industrial CO_2 gas feeds, the polymer should have good chemical stability. Finally, the polymer should good processability. To be employed in large scale applications, the polymer should be capable of being formed into thin membranes with separation layers to achieve high CO_2 permeance.

Table 1

Distinctions of gases in size, condensability and reactivity

Gas molecular	Kinetic diameter/nm	Critical temperature/°C	Whether gas molecular reacts with amine or carboxylate groups
CO_2	0.33	31.05	Yes
N_2	0.364	-147.05	No
CH_4	0.38	-82.45	No
H_2	0.289	-239.85	No

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The common polymers include polyethersulfone (PES)[12-15], polycarbonate (PC)[16], poly(vinyl acetate) (PVAc)[17-19], sulfonated poly(ether ether ketone)(SPEEK) [20, 21], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)[22], cellulose acetate (CA)[23, 24], polyimide (PI, such as Matrimid®[25-29]), Polyetherimide (such as Ultem[30]), PIM-1[31-35],poly(ether-block-amide) (Pebax, such as Pebax 1657[36-39], Pebax 2533[40] and Pebax1074[41]) and poly(vinylamine) (PVAm)[42, 43]. The above polymer materials possess different characteristics. PES, PC, SPEEK, PPO,CA, PI, and Ultem are glassy polymers, and have good chemical and thermal stability, permselectivity and processibility. PIM-1 is a new kind of glassy polymer. Due to its special ladder-type structure with contorted sites that prevent polymer chains from rotating and packing efficiently, PIM-1 has high free volumes, which results in superior gas separation performance. Pebax as a copolymer has a soft (rubbery) polymer segment such as polyethylene oxide (PEO) and a hard (glassy) polymer segment such as polyamide (PA). On the one hand, PEO soft segment provides enough adhesion between polymer and filler. On the other hand, PEO soft segment has high affinity for CO_2 molecules. PA hard segment provides the mechanical strength. As the facilitated transport membranes material, PVAm containing amine groups exhibits both high permeability and high selectivity through the reversible reactions between reactive carriers - amine groups and CO_2 molecules.

To sum up, Matrimid® is the best polymer for CO_2/CH_4 separation under high pressure, and PVAm is the best polymer for CO_2/N_2, CO_2/CH_4 and CO_2/H_2 separation under low pressure.

2.2 Selection of filler

To achieve CO_2 separation, as a dispersed phase in MMMs, the filler should have high selectivity. The selected filler must exactly correspond to the shape, size and other property difference of the targeted gas molecules, which facilitates CO_2 transport. Furthermore, the selected filler should have good compatibility with polymer matrix. Suitable combination of filler and polymer is an very important factor for improving

CO_2 selectivity. Besides, the particle size of the filler should be small. To be employed in industrial applications, separation layer thickness of MMMs is only several micrometers, so the particle size of the filler should be as small as possible.

As a dispersed phase in MMMs, inorganic nanomaterials and organic nanomaterials can both be used as fillers. Inorganic nanofillers used in MMMs can be divided into two classes: solid or impermeable (filled) nanofillers and porous or permeable nanofillers. The impermeable nanofillers include silica and TiO_2. The permeable nanofillers include zeolite, carbon molecular sieve, carbon nanotube, montmorillonite, metal-organic framework, graphene oxide and so on. The critical reviews on nanofillers were made[44-48].

In this section, we critically review the recent progress made in nanofillers. The typical size of the fillers range from dozens of nanometers to hundreds of nanometers, and the biggest size of fillers is twenty micrometers. The typical loading of porous inorganic fillers, laminar inorganic fillers and organic fillers ranges from 10wt% to 30wt%, from 1.5wt% to 6wt%, and from 15wt% to 30wt%, respectively. For most of the porous fillers used in MMMs for CO_2 separation, the pore size ranges from 0.34nm to 2.6nm.

For porous filler, the pore size determines CO_2 transport and CO_2 separation mechanism. Generally, CO_2 transport through porous filler follows molecular sieving mechanism and surface diffusion mechanism. When the pore size of the porous filler is roughly the same as kinetic diameter of the permeating gas molecule, gas transport through porous filler follows molecular sieving mechanism [49]. If the pore size of the porous filler is between the diameters of the CO_2 and other gas molecules, only the smaller gas molecule can permeate through the porous filler leading to a more efficient separation. When the pore size of the porous filler increases, if the gas molecule exhibits a strong affinity for the filler surface and adsorption along the pore walls, gas transport through porous filler follows surface diffusion mechanism [49]. Efficient CO_2 separation can take place by this mechanism due to differences in the amount of adsorption of the CO_2 and other gas molecules. When the pore size of the porous filler

is big enough, molecular sieving and surface diffusion mechanisms often coexist. For the laminar inorganic fillers, interlamellar spacing determines CO_2 transport and CO_2 separation mechanism. In general, CO_2 transport through galleries between the neighboring nanosheets follows molecular sieving mechanism.

Effect of the fillers on CO_2 separation performance of MMMs are summarized in Table 2. The fillers not only disturb polymer chain packing and increase free volume, but also facilitate CO_2 transport by itself, which results in improvement of membrane performance. The fillers are reviewed in the section in detail.

Table 2

Effect of fillers on CO_2 separation performance of MMMs

Type of filler	Filler[①]	Particle size/nm	Pore size/nm	Loading/ wt%	Polymer[②]	Feed gas	Operation conditions	CO_2 Permeability $\times 10^{14}$/mol·m· $m^{-2} \cdot s^{-1} \cdot Pa^{-1}$	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity	Ref.
Inorganic	CSM-18.4	~520±140	1.54	30	Matrimid®	CO_2/N_2 (50:50, v/v)	35 °C, 0.9 MPa	1.32	38.1	-	-	[50]
						CO_2/CH_4(50:50, v/v)		1.30	-	41.9	-	
	CSM-23.3	~520±140	1.48	30	Matrimid®	CO_2/N_2 (50:50, v/v)	35 °C, 0.9 MPa	1.76	37.8	-	-	
						CO_2/CH_4(50:50, v/v)		1.63	-	38	-	
	PRG	-	11.95	~5	Pebax®	Pure gases	30°C, 0.2 MPa	3.99	104	-	-	[39]
	ATP	Length: 500–1500 Width: 30–50	0.66	1.7	Pebax®	Pure gases	35 °C, 1.0 MPa	3.48	84	-	-	[51]
	Cu-BTC-S1	13000	-	10	PPO	Pure gases	30°C	~2.85	~18.5	~23.5	~1.0	[22]
	Cu-BTC-S2	6000	-	10	PPO	Pure gases	30°C	~2.88	~23.5	~28.5	~1.0	
	sod-ZMOF	2000~20000	0.96	5,10,20	Matrimid®	CO_2:CH_4 (50:50	35 °C, 0.4 MPa	0.23-0.46	-	36.6-43.4	-	[52]

Table 2 *(Continued)*

Type of filler	Filler[①]	Particle size/nm	Pore size/nm	Loading/ wt%	Polymer[②]	Feed gas	Operation conditions	CO_2 Permeability $\times 10^{14}$/mol·m· $m^{-2} \cdot s^{-1} \cdot Pa^{-1}$	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity	Ref.
						mol/mol)						
	MIL-53	123.4, 466.8	-	15	Matrimid®	Pure gases	0.3MPa	0.42	-	51.8	-	[27]
	MIL-53	100	0.91	30	PMP	Pure gases	30 °C, 0.8 MPa	12.64	-	-	24.96	[53]
	NH_2-MIL-53	~1000	-	25	Matrimid®	CO_2:CH_4 (50:50, mol/mol)	30 °C, 0.3 MPa	~0.49	-	~35	-	[54]
	MIL-101	<1000	-	10	Matrimid®	Pure gases	35 °C, 1.0 MPa	0.23	52.92	55.77	-	[55]
	S-MIL-101(Cr)	~550	0.5~2.6	40	SPEEK	Pure gas	30 °C, 0.1 MPa, in humidified state	69.14	53	50	-	[21]
						CO_2/N_2 (20:80, v/v)		1.11	40	-	-	
						CO_2/CH_4(30:70, v/v)		1.14	-	39	-	
	NH_2-MIL-101 (Al)	104 ± 28	-	10	P1	Pure gas	35 °C, 0.3 MPa	2.38	-	41.6	-	[56]
					P2			5.03	-	29.6	-	
	MW-NH_2-MIL-101(Al)	~1000	-	8,15,25	PSF	CO_2/CH_4(1:1)	35 °C, 0.3 MPa	~0.18-~0.28	-	~24-~29.0	-	[57]
				8,15	Matrimid®	CO_2/CH_4(1:1)		~0.35,~0.32	-	~35,~36	-	

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Table 2 *(Continued)*

Type of filler	Filler[①]	Particle size/nm	Pore size/nm	Loading/ wt%	Polymer[②]	Feed gas	Operation conditions	CO_2 Permeability $\times10^{14}$/mol·m· $m^{-2}·s^{-1}·Pa^{-1}$	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity	Ref.
	MIL-125	1500-2000	-	15,30	Matrimid®	$CO_2:CH_4$ (50:50, mol/mol)	0.9MPa	0.60,0.90	-	44,37	-	[29]
	NH$_2$-MIL-125	<1500-2000	-	15,30	Matrimid®	$CO_2:CH_4$ (50:50, mol/mol)	0.9MPa	0.57,1.68	-	50,37	-	
	NH$_2$-MIL-125 (Ti)	Length:1000 Width:500	-	10,20,30	PSF	$CO_2:CH_4$ (50:50, mol/mol)	30°C, 0.3 MPa	0.62-1.34	-	28.3-29.2	-	[58]
	UiO-66	60–80	0.6	10	Pebax®	CO_2/N_2 (50:50, v/v)	25°C,0.3 MPa,in humidified stated state	4.68	61.1	-	-	[59]
	UiO-66-NH$_2$	60–80	0.59	10	Pebax®	CO_2/N_2 (50:50, v/v)		4.36	72.2	-	-	
	MOF-74	10000-15000	1.08	10,15,20	PIM-1	Pure gas	25°C, 0.2MPa,	314.90-712.51	21.2-28.7	14.3-19.1	-	[34]
	ZIF-71	-	-	20	UV-PIM	$CO_2:CH_4$ (50:50, mol/mol)	35°C, 0.35MPa	74.51	-	32.8	-	[60]
						$CO_2:CH_4$ (30:70,		63.80	-	32.2	-	

Table 2 *(Continued)*

Type of filler	Filler[①]	Particle size/nm	Pore size/nm	Loading/ wt%	Polymer[②]	Feed gas	Operation conditions	CO_2 Permeability $\times 10^{14}$/mol·m· m^{-2}·s^{-1}·Pa^{-1}	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity	Ref.
						mol/mol)						
	ZIF-8	<80	-	20	6FDA-Durene/DABA (9/1)	CO_2/CH_4 (50:50)	35°C, 0.2MPa	24.39	-	19.61	-	[61]
	ZIF-8	-	-	5,10,15,20,25,30,35	Pebax®	Pure gas	25°C, 0.2MPa	12.23-43.11	29.6-32.3	8.1-9.0	-	[40]
	ZIF-8	100-200		3,5,7,10,15,20,30	6FDA-Durene	Pure gas	25°C, 0.2MPa	53.38-73.21	25.7-17.0	21.9-17.1	-	[62]
	ZIF-8(S)	88	-	30	SEBS	Pure gas	25°C	14.71	10.6	5.2	-	[63]
	ZIF-8(M)	240						15.23	12.0	5.4	-	
	ZIF-8(L)	533						15.59	10.8	5.2	-	
	H_ZIF-8	721±36	-	10,20,30	PVC-g-POEM	Pure gas	35°C	5.70-20.87	-	12.2-11.2	-	[64]

Table 2 *(Continued)*

Type of filler	Filler[①]	Particle size/nm	Pore size/nm	Loading/ wt%	Polymer[②]	Feed gas	Operation conditions	CO_2 Permeability $\times 10^{14}$/mol·m· $m^{-2} \cdot s^{-1} \cdot Pa^{-1}$	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity	Ref.
	ZIF-11	500-5000	-	10-70	Pebax®	Pure gas	20°C, 0.2MPa	6.90-13.50	52.96-29.0	9.50-12.49	8.0-2.5	[65]
	CNTs/GO	-	-	5/5	Matrimid®	Pure gas	30°C, 0.2MPa	1.28	81	84.60	-	[66]
	ZIF-8@GO-6	-	-	6	Pebax®	Pure gas	25°C, 0.1MPa	8.34	47.6	-	-	[67]
Organic	PANI nanosheet	Thickness:40-60	-	17	PVAm	CO_2/N_2 (20:80 v/v)	25°C, 0.11MPa, in humidified stated state	$40.20*l$[③]	120	-	-	[68]
	PANI nanorod	Diameter:50 Length:160	-	17	PVAm	CO_2/N_2 (15:85 v/v)	25°C, 0.11MPa, in humidified stated state	53.67[③]	240	-	-	[69]
	NHs	~250	-	5,10,15,20	Matrimid®	Pure gas	30°C,0.2 MPa,in humidified stated state	4.56-9.31	43-52	52-61	-	[70]
	CANs	400	-	5,10,15,20	Pebax®	Pure gas	25°C,0.2 MPa,in	29.82-67.87	56-85	19-33	-	[71]

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Table 2 *(Continued)*

Type of filler	Filler[1]	Particle size/nm	Pore size/nm	Loading/ wt%	Polymer[2]	Feed gas	Operation conditions	CO_2 Permeability $\times 10^{14}$/mol·m· $m^{-2} \cdot s^{-1} \cdot Pa^{-1}$	CO_2/N_2 Selectivity	CO_2/CH_4 Selectivity	CO_2/H_2 Selectivity	Ref.
				,30			humidified stated state					
	PEGSS	350–420	-	20	Matrimid®	Pure gas	30°C,0.1 MPa	0.28	61.24	50.29	-	[72]
	HCP	55	-	16.67	PIM-1	Pure gas	25°C,0.2 MPa,	334.06	20.27	-	-	[33]

[1]CSM: Carbon–silica nanocomposite materials, PRG: porous reduced graphene oxide, ATP: attapulgite, GO: graphene oxide, PANI: polyaniline, NHs: nanohydrogels, CANs: carboxylic acid nanogels, PEGSS: poly(ethylene glycol)-containing polymeric submicrospheres, HCP: hypercrosslinked polystyrene.

[2] PPO: poly(2,6-dimethyl-1,4-phenylene oxide), PMP: poly(4-methyl-1-pentyne), SPEEK: sulfonated poly(ether ether ketone), P1: sulfur-containing copolyimides (6FDA:DSDA/4MPD:4,40-SDA 1:1), P2: sulfur-containing copolyimides (6FDA/4MPD:4,40-SDA 1:1), PSF: polysulfone, UV-PIM: UV treated PIM, SEBS: polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene, PVC-g-POEM: poly(vinyl chloride)-g-poly(oxyethy-lene methacrylate), PVAm: poly(vinylamine).

[3]Permeability is calculated by permeance multiplied by the separation layer thickness, *l*: the separation layer thickness, μm.

2.2.1 *Carbon–silica nanocomposite materials*

Carbon–silica nanocomposite materials (CSMs) have a tunable porosity and surface chemistry which is controlled by the carbon deposition, the pyrolysis conditions and post-synthetic treatments. The carbon fraction of such nanocomposite fillers increases the affinity for CO_2.

Anjum *et al.* [50] developed MMMs by adding porous CSM fillers to Matrimid® matrix. Owing to the addition of a carbon phase, providing an increased affinity for the CO_2 molecules next to the creation of extra porosity and free volume, the overall separation efficiency of MMMs increased.

2.2.2 *Graphene oxide*

The effective gas separation for graphene oxide (GO) is based on the formation of the molecular sieving galleries between the neighboring nanosheets or possible defects on the nanosheets.

Dong *et al.* blended the partially porous reduced graphene oxide (PRG) nanosheets into Pebax1657 polymer to prepare MMMs[39]. For PRG, the narrow gas flow galleries (average width of 0.34 nm) between the neighboring nanosheets ensured effective molecular sieving of CO_2 against other larger gas molecules, while the mesoscopic pores on the laminate provided rapid gas transport pathways. Hence, The MMMs had substantially improved CO_2 permeability as well as CO_2/N_2 selectivity.

2.2.3 *Attapulgite*

Attapulgite (ATP) is one kind of natural clay with low cost and high availability. In view of its narrow size of the tunnel-like rectangular microspores (0.37nm×0.60nm), ATP is anticipated to distinguish CO_2 (0.33nm) from N_2 (0.364nm).

Xiang *et al.* blended Pebax1657 and ATP nanorods to fabricate MMMs[51]. Both the CO_2 permeability and CO_2/N_2 selectivity of the MMMs increased at low ATP loadings (< 6.3 wt%). Compared with the pristine Pebax membrane, CO_2 permeability and CO_2/N_2 selectivity of the MMMs with 1.7wt% ATP increased by 37.5% and 30%, respectively.

2.2.4 *Metal-organic frameworks*

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Metal-organic frameworks (MOFs) are a large emerging class of hybrid materials with porous crystalline structures, and combine the connectivity of metal centers with the bridging ability of organic ligands. Careful choice of metal and linker allows MOFs to be designed and synthesized with the desired functionalities, pore sizes and pore shapes.

Ge *et al.* [22] developed MMMs by incorporating size-reduced Cu-BTC in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) matrix, and demonstrated that the incorporation of the Cu-BTC led to the improvement of both gas permeability and selectivity. Kılıç *et al.* [52] fabricated Matrimid-*sod*-ZMOF MMMs, and found that with increasing *sod*-ZMOF, both CO_2 permeability and selectivity of the MMMs increased.

MIL-53 has open pores of diameter 8.5 Å at room temperature. MIL-53 was added to Matrimid® and poly(4-methyl-1-pentyne) (PMP) for CO_2/CH_4 and CO_2/H_2 separation, respectively [27, 53]. MIL-53 with polar functional groups are selected as fillers. Rodenas *et al.* [54] fabricated MMMs by incorporating NH_2-functionalized MIL-53(Al) in PI.

MIL-101(Cr) exhibits two types of cages: small cages, which possess a free diameter of 2.9 nm and pentagonal windows of 1.2 nm, and larger cages with a free diameter of 3.4 nm and both pentagonal and hexagonal windows, the latter with a 1.45 nm by 1.6 nm free aperture. Naseri *et al.* [55] prepared the Matrimid-MIL-101 MMMs. Compared with the neat Matrimid® membrane, CO_2/CH_4 and CO_2/N_2 ideal selectivities of the MMMs increased. MIL-101 with polar functional groups are selected as fillers. Xin *et al.* [21] modified MIL-101(Cr) by concentrated sulfuric acid and trifluoromethanesulfonic anhydride to prepare sulfonated MIL-101(Cr) [S-MIL-101(Cr)], and then incorporated the S-MIL-101(Cr) into SPEEK to prepare MMMs. The addition of the S-MIL-101(Cr) increased the CO_2/CH_4 and CO_2/N_2 selectivity of the MMMs due to the increased CO_2 solubility. Seoane *et al.* [56] developed MMMs by dispersing amino functionalized MOFs (NH_2-MIL-53(Al) or NH_2-MIL-101(Al)) in sulfur-containing copolyimide. Rodenas *et al.* [57] prepared

MMMs by dispersing NH_2-MIL-53(Al) and NH_2-MIL-101(Al) in polysulfone (PSf) and PI, and found that the incorporation of the MOF fillers had a positive effect on the separation performance.

MIL-125 has a quasi-cubic tetragonal structure in which the octahedral (10.7 Å) and tetrahedral (0.47 nm) cages are accessible through a window of about 0.5–0.7 nm. Guo *et al.* [58] fabricated MMMs by incorporating NH_2-MIL-125 into PSf matrix, and demonstrated that the incorporation of NH_2-MIL-125(Ti) particles could significantly improve the CO_2 permeability, and slightly enhance CO_2/CH_4 separation factor. Anjum *et al.* [29] added MIL-125(Ti) and the amine-functionalized counterpart (NH_2-MIL-125) as fillers to Matrimid® polyimide. The synthesized MMMs had the good adhesion between the fillers and the polymer matrix, and the NH_2-functionalized filler was preferred as it led to higher selectivities and permeabilities.

UiO-66 can exhibit strong affinity for CO_2 molecules owing to the -OH groups coordinated to Zr cluster, and triangular windows possess the size of 0.6 nm. Shen *et al.* [59] embedded CO_2-philic zirconium metal organic framework UiO-66 and UiO-66-NH_2 nanocrystals into Pebax membranes. The hydrogen bonding frameworks between UiO-66-NH_2 and Pebax were enhanced. The as-prepared Pebax-UiO-66-NH_2 MMM with MOFs loading of 10 wt% displayed a CO_2 permeability of 4.36×10^{-14} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and CO_2/N_2 selectivity of 72.

MOFs with hydroxyl groups are selected as fillers. Mg-MOF-74 exhibit exceptionally high CO_2 selective adsorption over CH_4 and 1-D hexagonal channels of 1.1 nm diameter. Tien-Binh *et al.* [34] added a novel filler having hydroxyl functional groups on the surface (Mg-MOF-74) to PIM-1. Under optimized conditions, chemical crosslinking between the hydroxyl groups and the fluoride chain-ends of PIM-1 was facilitated to completely remove interfacial defects. Compared with the neat PIM-1 membrane, CO_2 permeability of the MMMs with 20wt% MOF-74 increased by 3.2 times to 7.12×10^{-12} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$, meanwhile CO_2/CH_4 selectivity was improved to 19.1.

2.2.5 *Zeolite imidazolate frameworks*

Zeolite imidazolate frameworks (ZIFs) are built of tetrahedral metal ions (*e.g.* , Zn, Co) bridged by imidazolates. ZIFs have permanent porosity, and relatively high thermal and chemical stability, which makes them attractive candidates for nanofiller used in MMMs.

ZIF-71 has its rhombic structure with an aperture size of 0.42 nm and a pore cavity of 1.65 nm. Hao *et al.* [60] developed MMMs consisting of a zeolite imidazolate framework-71 (ZIF-71, $Zn(cbIm)_2$) and PIM-1 with and without UV irradiation, and found that the addition of ZIF-71 considerably enhanced the gas permeability without compromising the gas pair selectivities of CO_2/N_2 and CO_2/CH_4, and the UV treated MMM with 20 wt% ZIF-71 had a CO_2 permeability of around 6.38×10^{-13} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and a CO_2/CH_4 selectivity of 32.2 under mixed gas tests.

ZIF-8 has large (1.16 nm) pore cavities that are accessible through small (0.34 nm) pore apertures, which complement the kinetic diameter of CO_2 (0.33 nm), allowing for CO_2 separation via a sieving mechanism. Askari *et al.* [61] fabricated MMMs by directly mixing ZIF-8 suspension into three 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)-based polyimide solution, and the MMM made of 6FDA-Durene/DABA (9/1) and 20 wt% ZIF-8 displayed an impressive CO_2 permeability of 2.44×10^{-13} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and a CO_2/CH_4 selectivity of 19.61 in mixed gas tests. Bushell et al. developed MMMs consisting of PIM-1 and ZIF-8, and found that an increase in ZIF-8 loading led to increases in the permeability as well as in the separation factors, and Data points on several Robeson diagrams were located above the 2008 upper bound. Nafis *et al.* [40] developed MMMs by using ZIF-8 as inorganic filler in PEBAX-2533 polymer matrix. As the inorganic filler content increased, the permeability of all examined gases increased. Nafis *et al.*[62] also added ZIF-8 to 6FDA-durene PI. Chi *et al.* [63] prepared MMMs consisting of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) block copolymers and size-controlled ZIF-8 nanoparticles to investigate the effect of filler particle size on MMM gas separation performance, and found that ZIF-8(M) (240 nm) was the most effective in improving gas permeability and selectivity.

Hwang *et al.* [64] fabricated MMMs by dispersing hollow zeolite imidazole frameworks (H_ZIF-8) filler in poly(vinyl chloride)-g-poly(oxyethy-lene methacrylate) (PVC-g-POEM) graft copolymer matrix. Compared with pure PVC-g-POEM membranes, the MMMs exhibited an 8.9-fold increase in CO_2 permeability with only a small decrease in CO_2/CH_4 selectivity.

ZIF-11 has cages with diameter of 1.46 nm which are connected via apertures with diameter of 0.3 nm. Ehsani *et al.* [65] incorporated ZIF-11 into Pebax® 2533 polymer in the range of 10–70 wt% to fabricate MMMs. Excellent adhesion existed between ZIF-11 and polymer matrix, especially at 30 wt% loading. However, At 50 and 70 wt% ZIF-11 loadings, a few voids were observed throughout the membranes.

2.2.6 *Two-component fillers*

Except for single kinds of inorganic nanoparticle as filler, two kinds of inorganic nanoparticles can be added together as two-component fillers. Li *et al.* [66] perpared MMMs by incorporating carbon nanotubes (CNTs) and GO into a Matrimid® matrix. The extraordinary smooth walls of CNTs acted as a highway to render high permeability, whereas the GO nanosheets acted as a selective barrier to render high selectivity through the hydroxyl and carboxyl groups on GO surface in MMMs. The MMM with 5 wt% of CNTs and 5 wt% of GO displayed the optimum performance with a CO_2 permeability of 1.28×10^{-14} mol·m·m^{-2}·s^{-1}·Pa^{-1}, a CO_2/CH_4 selectivity of 84.60 and a CO_2/N_2 selectivity of 81.00. Furthermore, the composites consisting of two kinds of inorganic nanoparticles can be also used as two-component fillers. Dong *et al.* [67] fabricated MMMs by incorporating ZIF-8@GO composites into Pebax matrix. On one hand, the high-aspect ratio GO nanosheets in polymer matrix increased the length of the tortuous path of gas diffusion, which enhanced the diffusivity selectivity. On the other hand, the inherent high permeability of ZIF-8 with ultra-microporosity could enhance the gas permeability and solubility selectivity of MMMs. The MMM containing 6 wt% ZIF-8@GO exhibited the optimum performance with a CO_2 permeability of 8.34×10^{-14} mol·m·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 selectivity of 47.6.

Compared with inorganic nanofillers, organic nanofillers are emerging fillers.

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Organic nanofillers have advantages such as improved adhesion to polymer matrix. This superiority may be attributed to the organic feature of the filler. In addtion, some organic nanofillers can provide unique properties. For instance, nanohydrogels can absorb and retain extremely high water content, and the incorporation of nanohydrogels in MMMs can increase water uptake of MMMs, which is be beneficial to facilitating CO_2 transport.

Mixed matrix material with organic nanofillers and polymer blends are both important membrane materials for CO_2 separation. Polymer blends can be categorized as miscible and phase-separated blends (immiscible and partially miscible blends) [73]. In miscible blends, both the polymers are dissolved in each other at molecular levels representing a homogeneous single-phase behavior. However, in phase-separated blends both the polymers are not dissolved in each other and are separated by an interface between the two phases [74]. Hence, Mixed matrix material with organic nanofillers should be phase-separated blends. Its performance is strongly dependent on interface morphology, specific volume fraction, and size and shape of the dispersed and continuous phase [74]. In many cases, mixed matrix material with organic nanofillers is beneficial to CO_2 transport in compared with miscible blends. It is mainly attributed to suitable interface morphology between two phase and the specific structure of dispersed phase such as pore size and functional groups.

Organic nanofillers used in the MMMs include polyaniline[68, 69], poly(*N*-isopropylacrylamide) nanohydrogels[70], carboxylic acid nanogels[71], poly(ethylene glycol)-containing polymeric submicrospheres[72], and hypercrosslinked polystyrene[33]. The organic nanofillers are reviewed in the following sections.

2.2.7 *Polyaniline*

The incorporation of polyaniline (PANI) disturbs chain packing, and increases fractional free volume. Moreover, PANI with amine groups can facilitate CO_2 transport through reversible reaction between amine groups and CO_2 molecules, which results in the improvement of membrane performance[68, 69].

2.2.8 *Nanohydrogels*

The addition of nanohydrogels increases the fractional free volume, water uptake and water retention capacity of the MMMs, which is beneficial to improving CO_2 separation performance of polymer membranes

Li *et al.* [70] incorporated poly(N-isopropylacrylamide) nanohydrogels (NHs) into Matrimid® to prepare MMMs. The NHs homogeneously embedded in the Matrimid® matrix acted as water reservoirs to not only provide more water for dissolving CO_2, but also construct interconnected CO_2 transport passageways. The as-prepared Matrimid-NHs-20 membrane exhibited CO_2/CH_4 and CO_2/N_2 selectivities of 61 and 52 with a CO_2 permeability of 9.31×10^{-14} mol·m·m^{-2}·s^{-1}·Pa^{-1}. Li *et al.* [71] added carboxylic acid nanogels (CANs) into Pebax 1657 to fabricate MMMs. The incorporation of CANs simultaneously tailored favorable water environment and increased CO_2 transport sites within the membranes. The Pebax-CANs-30 membrane displayed CO_2/CH_4 and CO_2/N_2 selectivities of 33 and 85 with a CO_2 permeability of 6.79×10^{-13} mol·m·m^{-2}·s^{-1}·Pa^{-1}.

2.2.9 *Poly(ethylene glycol)-containing polymeric submicrospheres*

Wang *et al.* [72] incorporated poly(ethylene glycol) (PEG)-containing polymeric submicrospheres (PEGSS) into PI to prepare MMMs. The favorable affinity between PEGSS and CO_2 greatly increased CO_2 solubility, which led to an increase in CO_2 permeability. Compared with those of pristine PI membrane, CO_2 permeability and CO_2/N_2 selectivity of the PI–PEGSS(20) membrane with 20 wt% PEGSS increased by 35% and 104%, respectively.

2.2.10 *Hypercrosslinked polystyrene*

Mitra *et al.* [33] added hypercrosslinked polystyrene (HCP) into PIM-1 to fabricate MMMs. Because the nanosized HCP possessed rigid nanoporous structure, the addition of the HCP not only led to higher permeability but also to a significant arrest in polymer aging and permeability loss.

To sum up, in view of selectivity, compatibility and particle size, PANI is the best filler for CO_2/N_2 separation, NHs is the best filler for CO_2/CH_4 separation, and MIL-53

is the best filler for CO_2/H_2 separation .

3 INTERFACE MORPHOLOGIES

Interface morphology is a determinant factor for the overall transport property. Figure 1 displays a schematic diagram of various nanoscale structures at the polymer/filler interface[5]. Case 1 shows an ideal morphology. Case 2 represents the detachment of polymer chains from the filler surface, causing the interface voids. Case 3 displays that the polymer chains in direct contact with the filler surface can be rigidified compared to the bulk polymer chains. Case 4 indicates a situation in which the surface pores of the filler has been partially sealed by the rigidified polymer chains.

When there is a poor compatibility between polymer matrix and filler, Case 2 appears. Due to the less resistantance in interface voids, gas transports through interface voids instead of polymer matrix or filler, which improves gas permability. Meanwhile, change on gas selectivity is dependent on the size of interface voids. Generally, gas selectivity decreases. In other words, as gas molecules take this non-selective and less resistant by-pass instead passing through pores in the filler, membrane performance deteriorates more or less. When there is a very good compatibility between polymer matrix and filler, Case 3 and Case 4 occur. If Case 3 happens, the movement of polymer chain at polymer/filler interface is restrained, which reduces gas adsorportion, and then reduce gas permeation. Hence, gas permeability decrease, but an increase in gas selectivity is not obvious. If Case 4 happens, because pores of the filler are partially sealed, gas permeability declines.
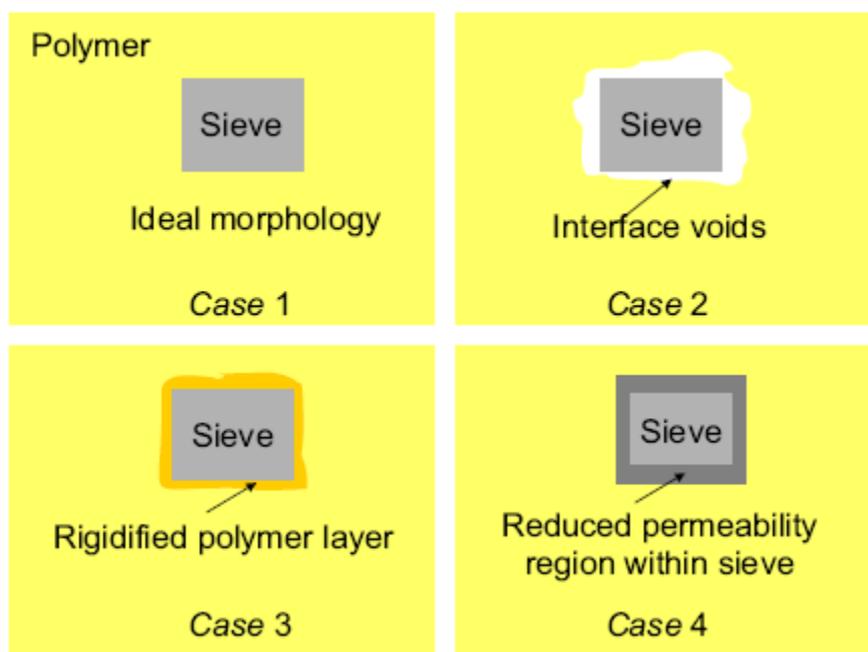
Figure 1 The schematic diagram of various nanoscale morphology of the mixed matrix structure [5]

In order to discuss the structure-property relationship of the MMMs conveniently, interface morphologies can be roughly divided into two classes: there are interface voids and there are no interface voids. Based on this, Wang *et al.*[75] systematically analyzed the relationship between polymer–filler interfaces and gas transport properties of the MMMs with different nanofillers. As shown in Figure 2, considering interface morphology, types of nanofillers and distribution of nanofillers in membrane, ten kinds of possible separation layer structure of MMMs were proposed, and its corresponding gas transport pathway was discussed. Moreover, for each case, the change on gas permeance of the MMMs with increasing feed pressure was analyzed. If the size of interface voids was larger than the mean free path of the gas molecules, and the interconnectivity of interface voids formed interface void channels across the separation layer of the MMM, viscous flow could occur, which led to an increase in gas permeance and a decrease in gas selectivity with increasing feed pressure. Conversely, when viscous flow could not occur for N_2, O_2 or CH_4 transport through nanofillers, an increase in gas permeance of the MMMs with increasing feed pressure demonstrated that there were void channels between polymer phase and nanofiller phase and the size

of interface voids was larger than the mean free path of the gas molecules.
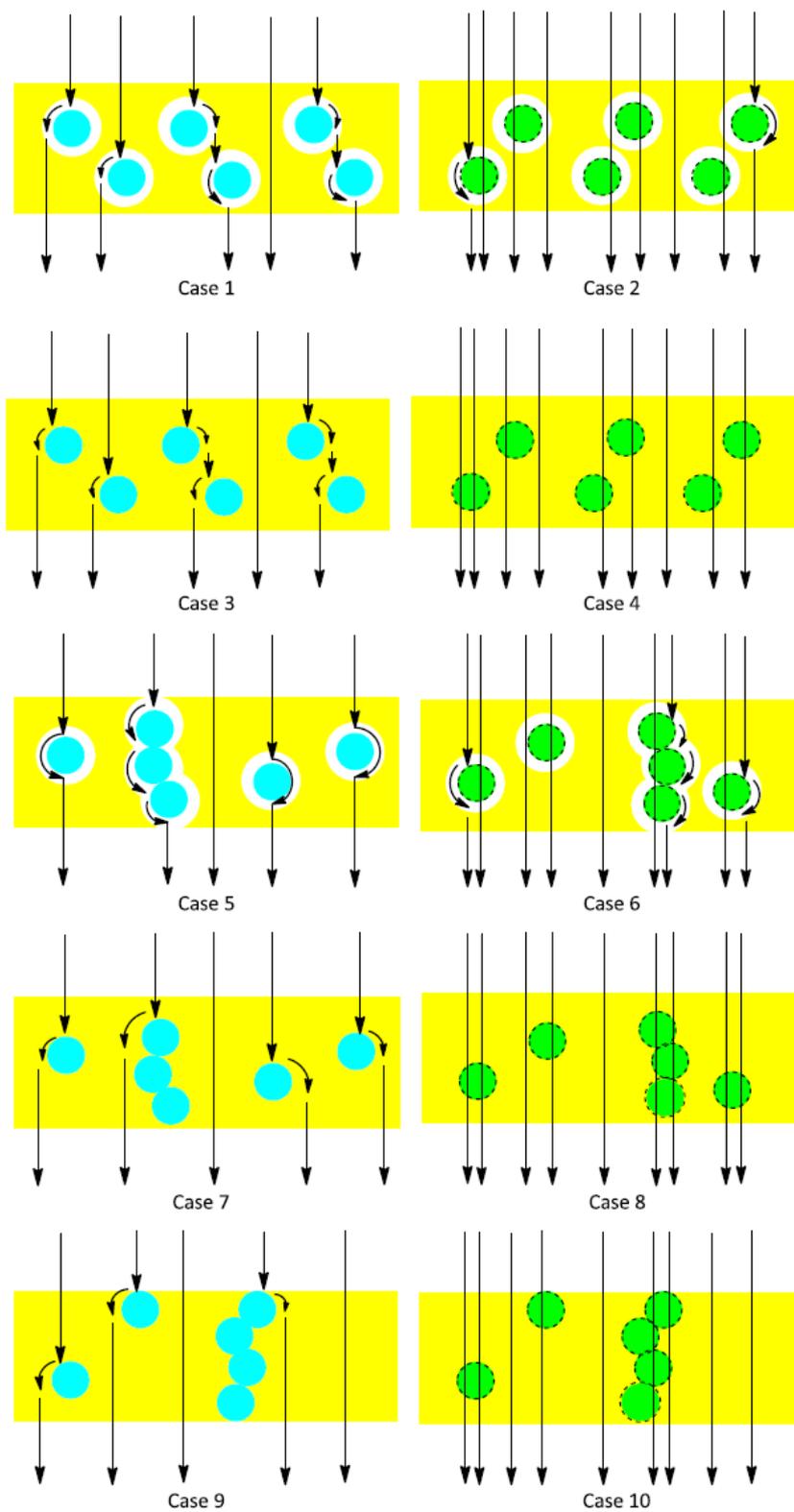
Figure 2 Schematic diagram of separation layer structure of the MMMs and its corresponding

gas transport pathway [75]

4 METHODS TO IMPROVE COMPATIBILITY

Generally, there are a poor compatibility between glassy polymer and filler, which results in a decrease in gas selectivity. To avoid interface void and improve membrane performance, researchers adopts the following eight methods to improve interface compatibility.

4.1 Silane coupling

Organofunctional silanes as the most prominent members of coupling agents can be hydrolyzed to form silanol groups. These silanol groups then react with the hydroxyl groups on surface of inorganic filler during condensation reaction to form stable siloxane bonds. By introducing the silylated inorganic fillers into a polymeric matrix, the dual reactivity of silicone in organosilane serves as bridges between fillers and matrix.

Sanaeepur *et al.* [76] modified micro-sized nanoporous sodium zeolite-Y (NaY) by 3-aminopropyl(diethoxy)methylsilane (APDEMS), and incorporated the silylated particles into a homogeneous CA membrane to achieve better polymer-zeolite adhesion in MMMs. Amooghin *et al.* [77] also modified NaY by APDEMS, and embedded the modified particles into the Matrimid® 5218 matrix to prepare MMMs with defect free polymer/filler interface. Figure 3 shows the grafting reaction between the APDEMS and zeolite surface, and also the proposed possible reaction between silane modified zeolite and Matrimid. As shown in Figure 3, APDEMS reacts with the hydroxyl groups on zeolite surface, the amino group of APDEMS reacts with the imide group of Matrimid and consequently forms the covalent bonding between zeolite and Matrimid, which results in the good interface compatibility between the two phases. Compared with pure Matrimid® membrane, the CO_2 permeability and CO_2/CH_4 selectivity of the MMMs with 15 wt% loading increased by 16% to 3.25×10^{-15} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and by 57% to 57.1, respectively. Laghaei *et al.* [78] modifying the surface of MCM-41

by 3-aminopropyltrimethoxysilane (APTMS) and trimethylchlorosilane (TMCS). The APTMS-modified MCM-41 with polar N-H groups and long side chains had a good compatibility with PES matrix, which facilitated the preparation of defect free membranes with gas separation performance by 250% and 40% increment in CO_2 permeability and CO_2/CH_4 selectivity, respectively. However, the TMCS did not interact with the PES as strong as APTMS. Dong *et al.* [79] developed novel MMMs by establishing montmorillonite (MMT) functionalized with PEG and aminosilane coupling agents in a Pebax membrane. There were no evident interfacial voids in all MMMs, and the prepared MMM with 40 wt % of MMT-HD702-PEG5000 displayed a CO_2 permeability of 1.50×10^{-13} mol·m·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 selectivity of 70.73.
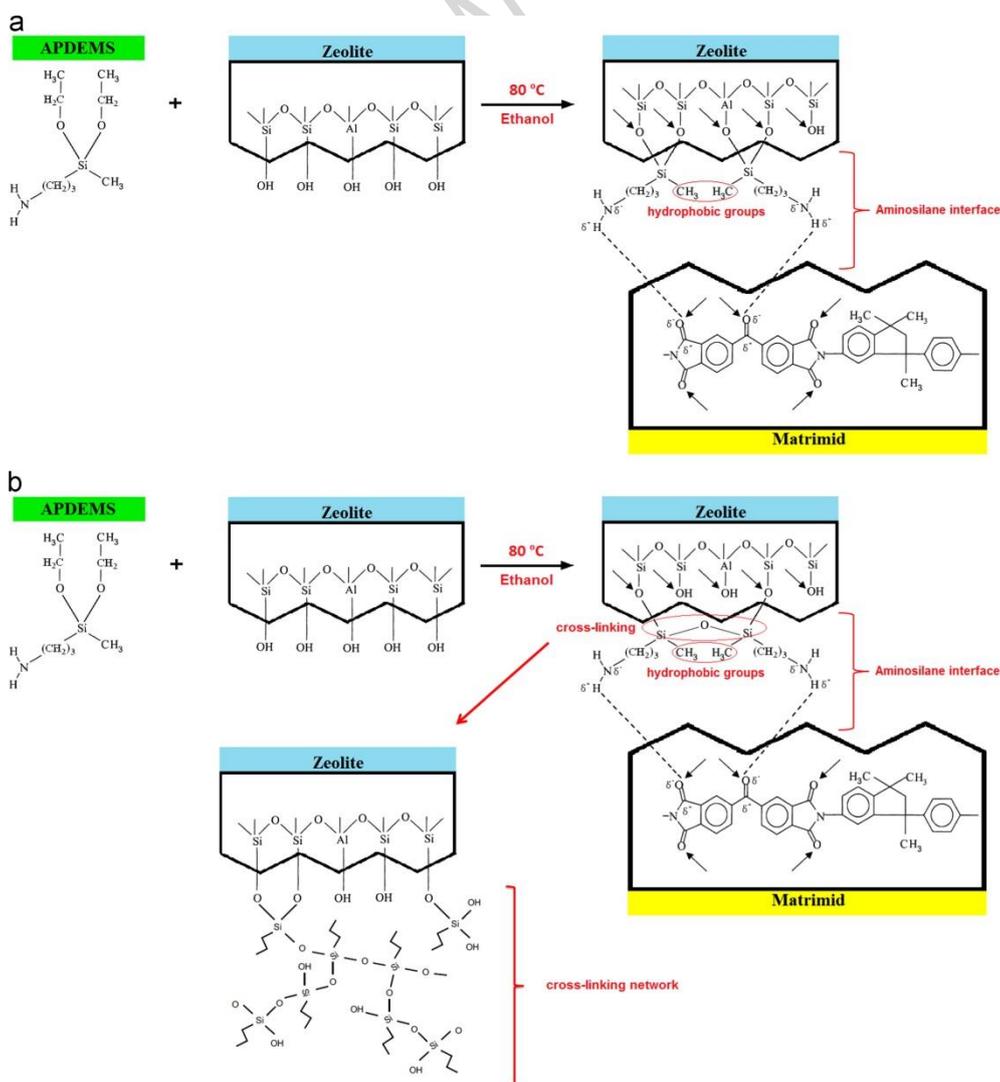
Figure 3 The grafting reaction between APDEMS and zeolite surface, and also the reaction

between Matrimid and the surface modified zeolite [77]

4.2 Grignard reagents treatment

The Grignard treatment method can modify the filler surface, reduce the solvent-filler interaction, and recuperate the interfacial adhesion between filler and polymer. The Grignard treatment involves growing $Mg(OH)_2$ whiskers on the filler surface, and consists of two steps: (i) a crystal seeding step and (ii) the crystal growth step. The Grignard treatment method creates roughened surface morphologies composed of whisker- and platelet-shaped nanocrystals, and the highly roughened filler surfaces are thought to promote adhesion at the polymer particle interface via thermodynamically-induced adsorption and physical entanglement of polymer chains in the whisker structures by minimizing the entropy penalty [46].

Zornoza *et al.* [80] prepared MMMs by adding ordered mesoporous silica MCM-41 spheres (MSSs), Grignard surface functionalized MSSs (Mg-MSSs) and hollow zeolite spheres into 6FDA-DAM polymer matrix. Because the polymer chain tends to be adsorbed onto the heterogenous surface compared with the flat surface, once embedded in the 6FDA-DAM polymer matrix, Mg-MSSs external whisker-like structure promoted interfacial filler-polymer contact, which resulted in excellent adhesion between filler and polymer as shown in Figure 4.The 6FDA-DAM-Mg-MSS MMM had the best performance with CO_2/N_2 and CO_2/CH_4 separation selectivities of 24.4 (4.07×10^{-13} mol·m·m^{-2}·s^{-1}·Pa^{-1} of CO_2), and 31.5 (4.17×10^{-13} mol·m·m^{-2}·s^{-1}·Pa^{-1} of CO_2), respectively.
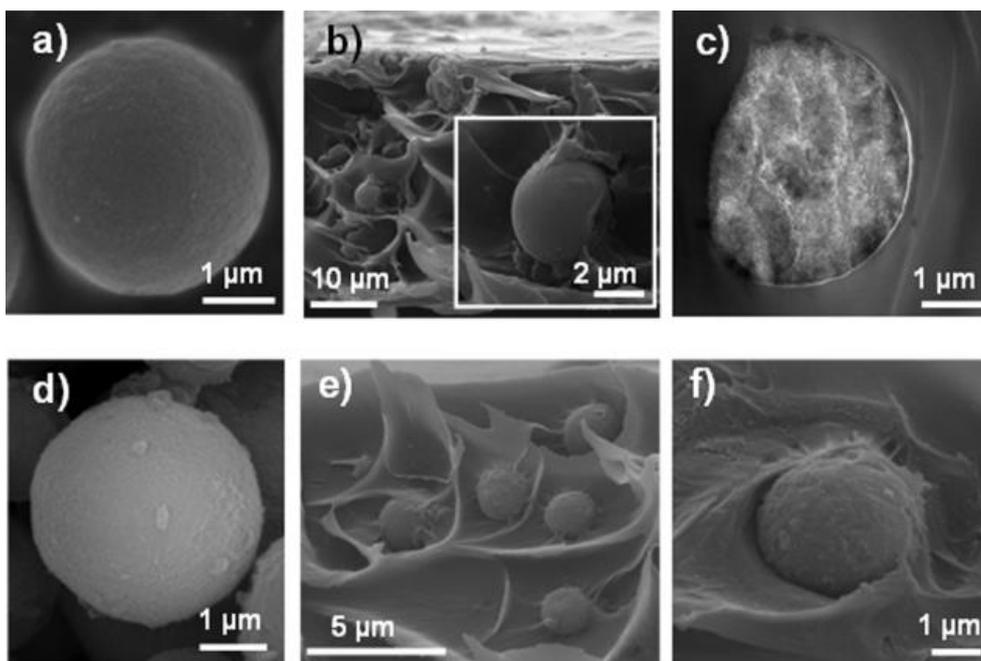
Figure 4 SEM images based of: (a–c) MSSs [(a) individual particle, (b) 8 wt % MSS/6FDA:DAM MMM, and (c) TEM image of an embedded particle], and (d–f) Mg-MSSs [(d) individual particle, (e) 8 wt % Mg-MSS/6FDA-DAM MMM, and (f) inset of (e)] [80]

4.3 Incorporation of additive

Expect polymer and inorganic filler, the addition of the third component as additive can improve compatility between filler and polymer matrix. Such additives include PEG , ionic liquid (IL), polyethylenimine (PEI).

PEG as a low molecular weight CO_2 selective agent can eliminate interfacial voids between the polymer chains and zeolite surface. Loloei *et al.* [81] investigated the effect of low molecular weight PEG 200 on the gas separation properties of Matrimid®5218-ZSM-5 MMM, and demonstrated that there is a good compatibility between ZSM-5 and polymers.

Free ILs act like lubricants between the fillers and the polymer matrices, leading to good compatibility in the three-component MMMs and high CO_2 permeability of the MMMs. Hudiono *et al.* [82, 83] demonstrated that ILs could behave like a wetting agent in polymer-zeolite MMMs and improve the compatibility between polymer and zeolite. Hao *et al.* [84] fabricated poly(ionic liquid)-IL-ZIF-8 MMMs and

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demonstrated that the addition of ZIF-8 considerably improved gas permeability without compromising CO_2/N_2 and CO_2/CH_4 selectivities, indicating the absence of defects in the MMMs. Casado-Coterillo *et al.* [85] incorporated nanometer-sized ZIF-8 or HKUST-1 particles into the mixture of [emim][Ac] IL and chitosan (Cs) to fabricate MMMs and the Cs-IL-ZIF-8 MMMs had a maximum CO_2 permeability of over 1.68×10^{-12} mol·m·m^{-2}·s^{-1}·Pa^{-1}.

Confined ILs can not only improve compatibility between the fillers and the polymer matrices, but also improve the CO_2 selectivity of the resulting MMMs further. Li *et al.*[86] incorporated a room temperature ionic liquid (IL) [bmim][Tf2N] into ZIF-8 cages, and then added the IL-incorporated ZIF-8 (IL@ZIF-8) into Pebax to prepare the Pebax-IL@ZIF-8 MMMs with toughened MOF-polymer interface. A mechanism of the formation of filler-polymer interfaces was proposed in Figure 5. At the beginning of the membrane preparation, the PA blocks would assemble preferentially around the hydrophobic sites of IL@ZIF-8 particles owing to their hydrophobic-hydrophobic interaction. As the membrane had become nearly solidified, the solvent diffused out of the ZIF-8 framework and dragged the IL to the interfaces between fillers and polymers. Because the bulkier IL clusters have good compatibility with the polymer, the bulkier IL clusters embedded in the apertures of ZIF-8 could act as cross-linking agents between the two phases. Due to a stiffer interphase between the filler and the polymer and a reduction in the effective aperture size of ZIF-8, the Pebax-IL@ZIF-8 membranes displayed improved molecular sieving properties. Compared with pure Pebax membrane, CO_2 permeability, CO_2/N_2 selectivity and CO_2/CH_4 selectivity of the MMM with 15 wt% IL@ZIF-8 increased by 45%, 74% and 92%, respectively.

PE block   PA block   [bmim][Tf₂N]   Methanol
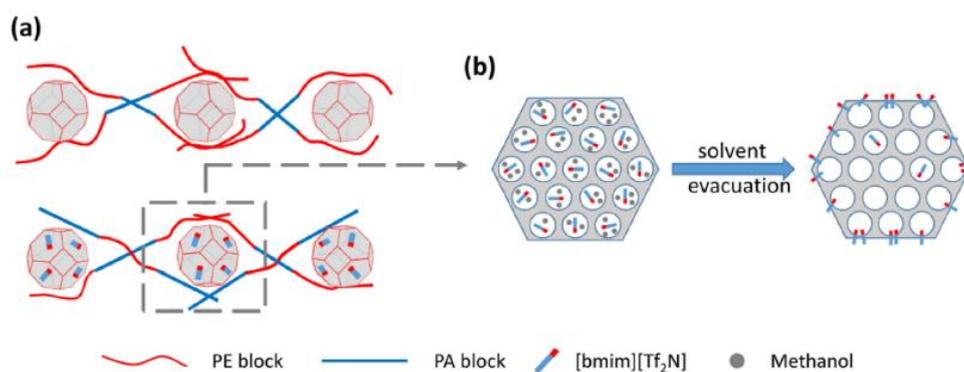
Figure 5 Hypothetical mechanism of the toughening of filler-polymer interface: (a) the preferential adsorption of PA block on IL@ZIF-8 and (b) the aggregation of [bmim][Tf2N] at the filler-polymer interface [86]

MIL-101(Cr) with a particles size of ~550 nm was chemically decorated with polyethylenimine (PEI) rich in amine groups via a facile vacuum-assisted method, and the obtained PEI@MIL-101(Cr) was then incorporated into SPEEK to fabricate SPEEK-PEI@MIL-101(Cr) membranes[87]. Owing to the electrostatic interaction and hydrogen bond between sulfonic acid group and PEI, the PEI both in the pore channels and on the surface of MIL-101(Cr) improved the filler−polymer interface compatibility, and simultaneously rendered abundant amine carriers to facilitate the transport of CO_2 through reversible reaction. The SPEEK-PEI@MIL-101(Cr) membrane with 40 wt% PEI@MIL-101(Cr) displayed the highest ideal selectivities for CO_2/CH_4 and CO_2/N_2 were 71.8 and 80.0, respectively, with a CO_2 permeability of 8.34×10^{-13} $mol\cdot m\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$ at 0.1MPa and 25°C, which surpassed the Robeson's upper bound revised in 2008.

4.4 Grafting

Inorganic naofiller is modified by grafting with low molecular weight polymer containing EO and amine groups. Hydrogen bonding can be easier to form between polymer and modified inorganic nanofiller, which can enhance compatibility.

Li *et al.* [88] prepared MMMs by incorporating polyethyleneglycol- and polyethylenimine-functionalized graphene oxide nano-sheets (PEG−PEI−GO) into a commercial low-cost Pebax matrix. As shown in Figure 6. GO was modified by

grafting with PEI and PEG to fabricate PEG−PEI−GO nanosheets. Hydrogen bonding

could form not only between the amino group of PEI and the ether oxygen group (or

amide group) of Pebax, but also between the ether oxygen group of PEG and amide

group of Pebax. Hence, PEG and PEI on the surface of GO improved the interface

compatibility between the Pebax matrix and GO nanosheets. The MMM with 10 wt %

PEG−PEI−GO showed optimal gas separation performance with a CO_2 permeability of

4.46×10^{-13} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$, a CO_2/CH_4 selectivity of 45, and a CO_2/N_2 selectivity of

120, which surpassed the Robeson's upper bound revised in 2008.
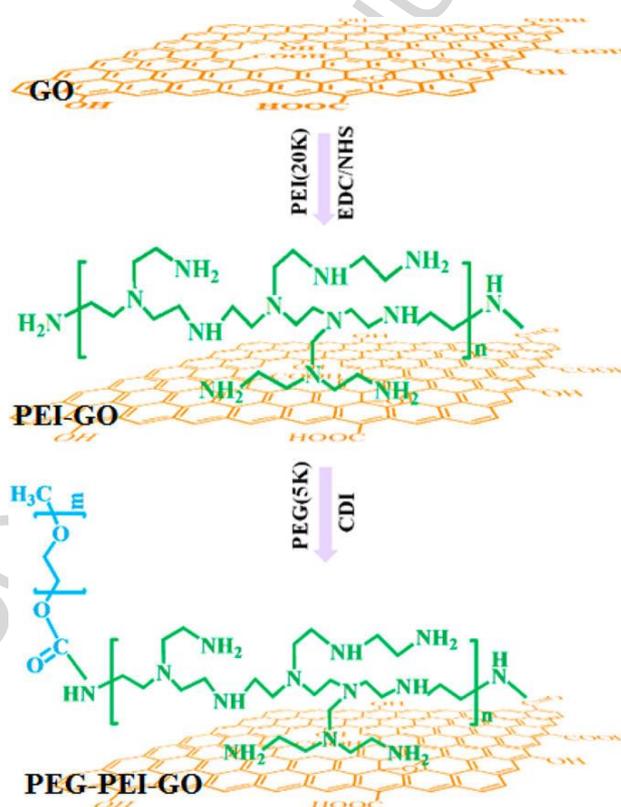
Figure 6 Illustration of the Preparation of PEG−PEI−GO [88]

4.5 In situ polymerization

The added fillers participate in the polymer synthesis, which is called as in situ

polymerization. The chemical bonding can form between polymer and filler by in situ

polymerization, which is beneficial to improving compatibility.

$[Cd_2L(H_2O)]_2 \cdot 5H_2O$ (Cd-6F) synthesized using 6FDA as an organic ligand was

introduced into the 6FDA-ODA polyimide matrix to achieve novel MOF MMMs[89].

As shown in Figure 7, a specific interaction between the uncoordinated $-COO^-$ on the

surface of Cd-6F and the $-NH_2$ groups of the ODA monomer at the terminal of

poly(6FDA-ODA) chains was introduced during the in situ polymerization. Compared

with the pure 6FDA-ODA polyimide membrane, the as-prepared MMM displayed both

higher permeability and selectivity due to the good polymer-MOFs compatibility

resulted from the targeted interfacial interaction. The MMM exhibited a CO_2

permeability of 1.27×10^{-14} mol·m·m^{-2}·s^{-1}·Pa^{-1} with a CO_2/N_2 selectivity of 35.1, and

CO_2/CH_4 selectivity of 44.8.
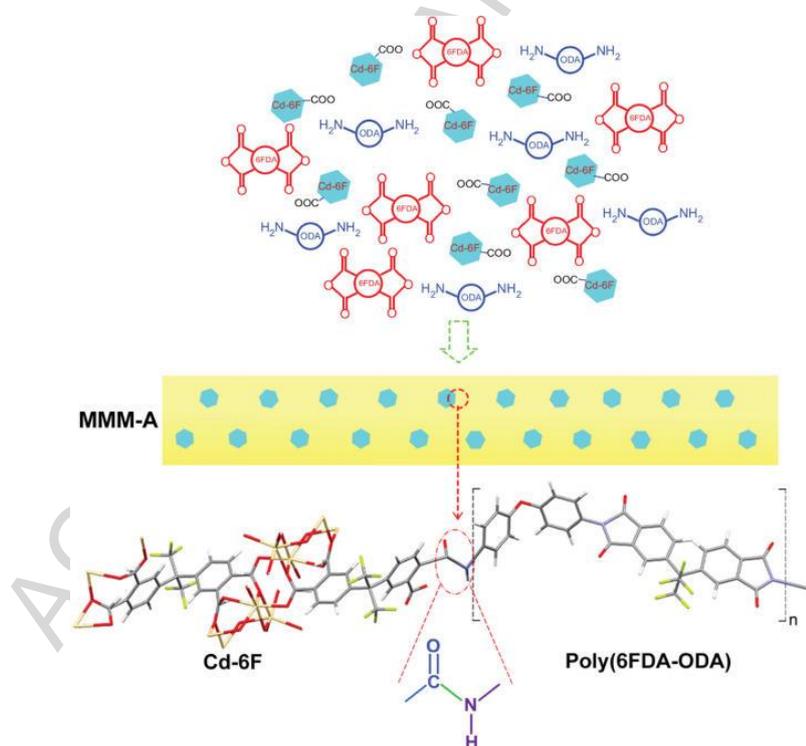
Figure 7 Diagram of designed interaction between Cd-6F and 6FDA-ODA in MMM [89]

4.6 Polydopamine coating

Polydopamine (PD) is a good adhesion agent. PD can conveniently deposit and

further adhere on virtually all types of inorganic and organic supports with controllable

film thickness and durable stability via the oxidative self-polymerization of dopamine

(DOP) in a mildly alkaline environment.

The nanosized ZIF-8 was coated by an ultrathin PD layer, and then incorporated into intrinsically microporous polyimide named TBDA2-6FDA-PI with a Tröger's Base to prepare ZIF-8@PD-PI membrane[90]. The formation of hydrogen bond interaction between the abundant secondary or primary amine groups on PD molecules and the tertiary amine in TB-based PI polymers is beneficial to the improvement of compatibility between the two polymers as schematically shown in Figure 8. For CO_2/N_2 (50/50, v:v) mixed gas, ZIF-8@PD-PI (20%) membrane exhibited a CO_2 permeability of 2.33×10^{-13} mol·m·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 selectivity of 21 at 0.1MPa; For CO_2/CH_4 (50/50, v:v) mixed gas, ZIF-8@PD-PI (20%) membrane exhibited a CO_2 permeability of 2.11×10^{-13} mol·m·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/CH_4 selectivity of 27 at 0.1MPa.
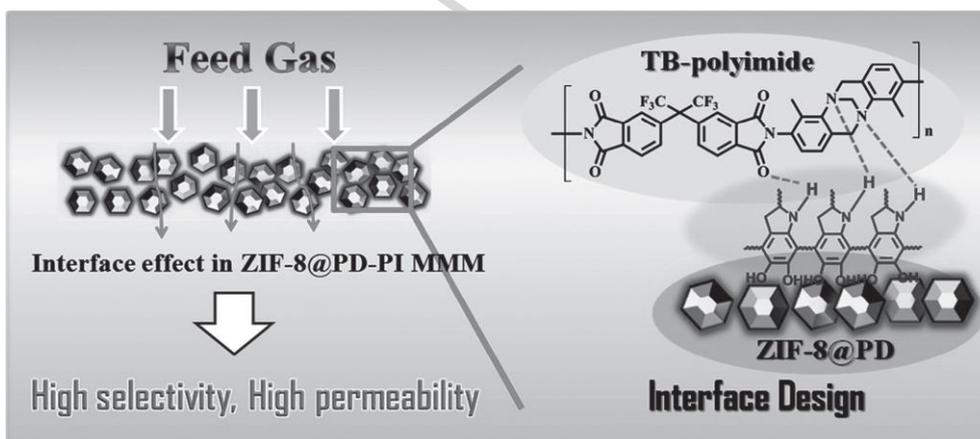

Figure 8 Schematic illustration for interface design of ZIF-8@PD-PI membrane [90]

4.7 Particle fusion approach

Particle fusion method is very versatile, and can enhance compatibility between filler and polymer matrix.

Shahid *et al.* [91] prepared MOF based MMM with better compatibility via a particle fusion approach. Matrimid® polymer particles were first prepared by precipitating a Matrimid® polymer solution in water. The surface of these particles was then modified by the introduction of imidazole groups as shown in Figure 9(a). ZIF-8 nanoparticles were then grown in-situ to this modified polymer particle suspension by

addition of the precursor for ZIF-8 synthesis. The resulted suspension was cast to dryness and annealed in a solvent–vapor environment to induce particle fusion, forming a dense MMM as shown in Figure 9(b). The pendent imidazole units lead to a better compatibility between the polymer phase and the ZIF-8 nanoparticles. The excellent ZIF-8-polymer interfacial adhesion resulted in a significant improvement in both CO_2 permeability and CO_2/CH_4 selectivity. Compared with unfilled Matrimid®, the CO_2 permeability of the MMMs increased by 200% and the CO_2/CH_4 selectivity increased by 65%.
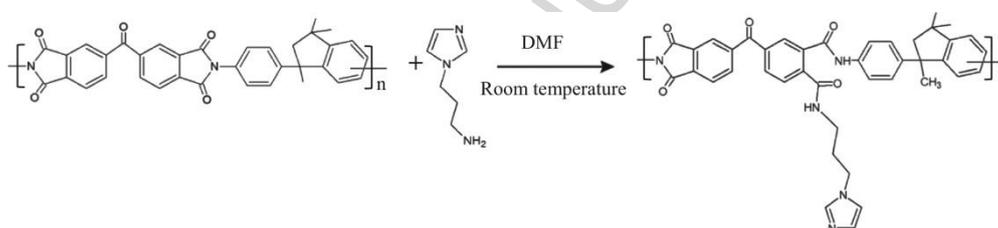
(a)
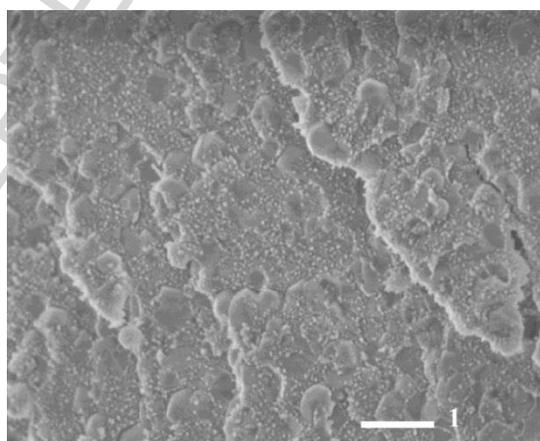
(b)

**Figure 9 Modification process of Matrimid® polymer particles (a) and SEM image of MMM containing 30 wt% ZIF-8 prepared by particle fusion (b) [91]**

4.8 Polymer functionalization

Functionalized polymer is used to improve compatibility, which is called as polymer functionalization. Functionalized polymer can interact with functional groups containing filler, which lead to the enhanced compatibility.

Tien-Binh *et al.* [92] synthesized hydroxyl-functionalized homo- and co-polyimides 6FDA–(DAM)$_x$–(HAB)$_y$ (with x : y molar ratio of 1 : 0; 2 : 1; 1 : 1; 1 : 2) and two MOFs [MIL-53(Al) and NH$_2$-MIL-53(Al)] to prepare MMMs. A strong interaction exited between the hydroxyl groups in the copolyimides and the amine groups in NH$_2$-MIL-53(Al), which enhanced polymer–filler compatibility. The MMM prepared with 6FDA–DAM–HAB (1 : 1) copolyimide and 10 wt% NH$_2$-MIL-53(Al) displayed a permeability/selectivity behavior approaching the 2008 Robeson's upper bound.

In brief, during modification process by using these methods except Grignard reagents treatment, hydrogen bonding or chemical bonding forms, which leads to the fact that the interactions between polymer matrix and inorganic nanofiller improve interface compatibility.

5 MIXED MATRIX COMPOSITE MEMBRANE

So far, most mixed matrix membranes for CO_2 separation are free-standing membranes without porous membrane as a support layer. The thicknesses of these membranes range from several dozen to several hundred micrometers. However, industrial demands on the membranes of higher productivity motivate researchers to fabricate integrally skinned asymmetric membranes or composite membranes. Hence, mixed matrix asymmetric membranes and mixed matrix composite membranes are developed. The mixed matrix composite membranes are reviewed in the section. A mixed matrix composite membrane consists of a thin separation layer and a support layer, and the thin separation layer known as mixed matrix layer is deposited on the asymmetric support layer. The separation layer is ultrathin, and has only several micrometers at most. when there is a poor compatibility between polymer and filler, interface voids is easier to be formed in the separation layer. For the mixed matrix composite membrane, how to avoid voids is a challenging subject. Recently, mixed matrix composite membranes have attracted the great attention. Most researches have focused on the forms of hollow fiber and flat mixed matrix composite membranes.

5.1 Hollow fiber mixed matrix composite membrane

Ekiner *et al.* [93] reported a patent on the hollow fiber mixed matrix composite membranes in 2003. Later, Chung group does a lot of researches on the hollow fiber mixed matrix composite membranes [94-98]. The outer diameter of these membranes ranges from ~650 to ~1000μm, the inner diameter ranges from ~350 to ~600μm,and the thickness of the dense selective layer ranges from 0.15 to 12μm.

The hollow fiber mixed matrix composite membrane [94-97] are spun by the co-extrusion technique using a dual-layer spinneret as depicted in relative literatures [99]. The flow rates of the bore fluid and both dope solutions are controlled by three pumps. The as-spun hollow fibers are rinsed in the clean water bath for several days to remove the remaining solvent and then carried out solvent exchange without further drying. Finally, these fibers are dried in the air at ambient temperature for use. By lowering the outer layer flow rate (while keeping other spinning conditions constant), the thickness of the outer layer can be reduced [95]. To avoid voids, they attempt several posttreatment methods such as heat treatment and two-step coating, and *p*-xylenediamine/methanol soaking. Jiang *et al.* [96] employed heat treatment and two-step coating processes to bring out the separation properties of zeolite beta imbedded in the polymer matrix for defect-free PES–zeolite beta/P84 hollow fiber membrane. Compared with that of neat PES dense films, the CO_2/CH_4 selectivity of the hollow fiber membranes increased by around 10%–20%. Jiang *et al.* [97] adopted a novel *p*-xylenediamine/methanol soaking method to efficiently remove the PSf–zeolite interface defects of the PSf–zeolite beta/Matrimid® hollow fiber membranes, and found that CO_2/CH_4 ideal selectivities of the PSf–zeolite beta/Matrimid® hollow fiber membranes roughly increased by 50% in comparison with that of the neat PSf/Matrimid® hollow fiber membrane. Hydrogen bonding was proposed as the possible mechanism for the tighter attachment between the PSf matrix and filler (Figure 10). In addition, Chen *et al.* [98] developed novel hollow fiber membranes by surface coating ultrathin layers of a PEG containing hybrid material onto the asymmetric PES hollow fiber substrate. The fabricated membranes exhibited an

impressive CO_2/N_2 selectivity of 50 with the CO_2 permeance of 1.01×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} at 25°C and 0.2 MPa.
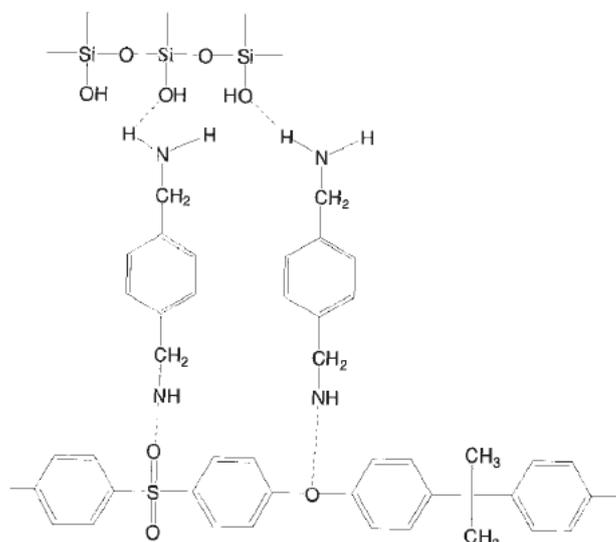

Figure 10 Mechanism of p-xylenediamine priming and possible structure [97]

5.2 Flat mixed matrix composite membrane

Kulprathipanja *et al.* [100] published a patent on mixed matrix membrane for separation of gases in 2004. In the patent, a mixed matrix composite membrane comprised PEG, silicone rubber and activated carbon on a porous support. The membrane perferably also comprised a carbonate such as potassium carbonate. Later, Kulprathipanja *et al.* [101] published another patent. In that patent, a mixed matrix composite membrane comprised a nitrogen containing compound such as amine, silicone rubber and activated carbon on a porous support. The membrane might also comprise a plasticizer such as PEG. Thereafter, a lot of academic papers on flat mixed matrix composite membranes are published.

5.2.1 *Poly(dimethylsiloxane) based mixed matrix composite membrane*

Some researchers select rubbery poly(dimethylsiloxane) (PDMS) as polymer matrix. de Clippel *at al.* [102] developed a defect-free mixed matrix composite membrane by filling a PDMS top layer with porous carbon–silica microspheres (CSM) on a polyimide (PI)/polypropylene (PP) membrane, and The derived MMM displayed a

CO_2 permeance of 2.81×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1}, and a CO_2/H_2 selectivity of 4.7 at 1.0MPa and 25°C. Wang *et al.* [103] also incorporated mesoporous KIT-6 modified by phenyltriethoxysilane (PTES) into PVDF supported PDMS to fabricate PDMS-p-KIT-6/PVDF membranes, but the CO_2/N_2 ideal selectivity of the membrane was too low.

5.2.2 *PIM-1 based mixed matrix composite membrane*

Some researchers choose glassy PIM-1as polymer matrix. Khan *et al.* [104] coated the mixture of PIM-1 and multiwalled carbon nanotubes (MWCNTs) functionalized with PEG on microporous polyacrylonitrile (PAN) membrane to fabricate the PIM-1-f-MWCNT/PAN membrane. The derived MMM with f-MWCNTs loading of 2wt.% reached a high CO_2 permeance of 3.68×10^{-6} mol·m^{-2}·s^{-1}·Pa^{-1}, and a CO_2/N_2 ideal selectivity of 33.5 at 0.2MPa and 27°C.

5.2.3 *EO containing polymer based mixed matrix composite membrane*

Because Pebax 1657 is a commercial candidate polymer material containing EO groups for CO_2 separation, it is also used as polymer matrix. Solid nanoparticles, two-dimensional materials, and three-dimensional porous material are selected as nanofillers, respectively. When solid TiO_2 was chosen as nanofillers, defect-free Pebax 1657-TiO_2/PVC membranes with TiO_2 loading of 3wt% showed the best performance[105]. Shen *et al.* [106] used the mixture of Pebax 1657 and MoS_2 nanosheets as the selective layer, PDMS as the gutter layer, and PSf as a support substrate to prepare the mixed matrix composite membrane. The prepared membrane with 0.15 wt % MoS_2 nanosheets exhibited the best performance with a CO_2 permeance of 5.80×10^{-9} mol·m^{-2}·s^{-1}·Pa^{-1}, and CO_2/N_2 ideal selectivity of 93 at 0.2 MPa and 30°C. Zarshenas *et al.* [107] fabricated mixed matrix membranes by incorporating nano-zeolite NaX into Pebax-1657 as an separation layer on the PES membrane as a support layer. The membrane containing 2wt% zeolite NaX showed a CO_2 permeance of 7.87×10^{-10} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 ideal selectivity of 121.5 at 0.7MPa and 25°C. Li *et al.* [108] deposited the mixuture of Pebax1657 and ZIF-7 on a porous PAN support to prepare Pebax1657-ZIF-7/PAN membranes with polytrimethylsilylpropyne

(PTMSP) gutter layer. The Pebax1657-ZIF-7/PAN membrane with 22wt% ZIF-7 displayed a CO_2 permeance of 4.59×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1}, and CO_2/N_2 ideal selectivity and CO_2/CH_4 ideal selectivity of 97 and 30, respectively at 0.375MPa and 25°C. Jomekian et $al.$ [109] coated Pebax 1657-ZIF-8 on PES layer to fabricate Pebax 1657-ZIF-8/PES membrane. The as-prepared membrane showed a CO_2 permeance of 1.21×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}, and a CO_2/N_2 ideal selectivity of 16.1 at 0.8MPa.

In addtion, PEG is also an important polymer material containing EO groups. Iron dopamine nanoparticles (FeDA NPs) were incorporated into a nanoscale thick PEG matrix on a highly permeable PDMS prelayer spin-coated onto a porous PAN substrate to form mixed matrix composite membranes[110]. The as-prepared membrane displayed excellent gas separation performance with a CO_2 permeance of $\sim4.02 \times 10^{-7}$ mol·m^{-2}·s^{-1}·Pa^{-1} and an enhanced CO_2/N_2 ideal selectivity of over 35 at 0.1MPa and 35°C.

5.2.4 *Facilitated transport based mixed matrix composite membrane*

Facilitated transport based mixed matrix composite membranes have also been investigated. They are roughly reviewed in the lasted two reviews [10, 111]. In this section, they are discussed in detail according to types of polymer matrix.

Our group carry out lots of researches on flat mixed matrix composite membranes, and examined structure-property relationship. Generally, our group choose amine containing polymer as polymer matrix to prepare different flat mixed matrix composite membranes by the addition of different nanofillers. Firstly, our group select the conventional nanomaterials as nanofillers. Yu et $al.$ [112] fabricated the mixed matrix composite membranes by incorporating CO_2-selective adsorptive LUDOX® silica nanoparticles in $situ$ into the tertiary amine containing polyamide membrane formed by interfacial polymerization. The membrane displayed a CO_2 permeance of 1.99×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 selectivity of 85.4 at 0.1MPa. Wang et $al.$ [75] found that surface modification of pristine inorganic nanofillers (MWCNT, SiO_2 and ZSM-5) endowed with amine groups could eliminate or reduce interface voids and improve the interface compatibility between PVAm polymer chains and modified inorganic

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nanofillers.

Based on this, silane coupling agents are used to couple polymer with layer nanomerials in order to eliminate or remove interface voids. At the same time, layer nanomerials are beneficial to CO_2 facilitated transport. Liao *et al.* [113] synthesized the polyethyleneimine-based copolymer PEIE with abundant amine groups and moderate hydroxyl groups, chose PEIE as a polymer matrix, chose nanosized hydrotalcite (HT) as a filler, used 3-aminopropyltriethoxysilane (APTES) as a molecular bridge to couple the PEIE and HT , and then coated the PEIE-HT complex on PSf membrane to fabricate the PEIE-HT/PSf membrane. In view of the mobile carriers within the interlayer gap of HT, high-speed CO_2 transport channels were successfully constructed, and the PEIE-HT/PSf membrane exhibited a high CO_2 permeance up to 1.91×10^{-6} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and a CO_2/N_2 selectivity of 268 at 0.11 MPa. To verify high-speed CO_2 transport channels of HT further, Liao *et al* [43] chose PVAm and HT as a polymer matrix and filler, respectively, used 3-Glycidyloxypropyltrimethoxysilane (GLYMO) as a molecular bridge to couple the PVAm and HT , and then prepared the PVAm-HT/PSf membrane. The PVAm-HT/PSf membrane exhibited a high CO_2 permeance of 1.07×10^{-6} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and a CO_2/N_2 selectivity of 296 at 0.11 MPa. To evaluate the effect of arrangement of layer nanomerials on gas permselectivity, Qiao *et al.* [114] immobilized montmorillonite layers bonded and aligned with the chain stretching orientation of polyvinylamineacid onto a porous PSf substrate to fabricate aligned montmorillonite/polysulfone (AMT/PSf) membranes. Owing to aligned interlayer gaps as high-speed CO_2 transport channels, the AMT/PSf membrane achieved a high CO_2 permeance of about 2.68×10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and a high mixed-gas selectivity for CO_2.

Apart from the common nanomaterials and layered nanomaterials, MOF and covalent organic framework (COF) are also used as nanofillers, respectively. On one hand, the addition of MOF and COF disturbs polymer chain packing, and increases free volume, which results in the improvement of CO_2 permeance. On the other hand, CO_2 molecules can transport through the pore of MOF and COF. Zhao *et al.* [42]

incorporated ZIF-8 into a PVAm solution, and coated the PVAm-ZIF-8 mixture on a PSf support membrane to prepare the PVAm-ZIF-8/PSf membrane. Compared with the PVAm/PSf membrane, the CO_2 permeance and CO_2/N_2 selectivity of the PVAm-ZIF-8/PSf membrane with 13.1wt% ZIF-8 increased by about 325% and 65% at 0.15 MPa and 79% and 140% at 2.0 MPa, respectively. However, owing to the nonselective voids between aggregated nanoparticles, CO_2/N_2 selectivity of the PVAm-ZIF-8/PSf membrane with 23.1wt% ZIF-8 decreased to a lower value than that of the PVAm/PSf membrane at a feed pressure of over 1.0 MPa. Cao *et al.* [115] incorporated a highly compatible covalent organic framework COF-LZU1 into PVAm to fabricate the PVAm-COF/PSf membranes. The PVAm-COF/PSf membrane with 10 wt% COF-LZU1 exhibited a CO_2 permeance of 1.33×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/H_2 selectivity of 15 at 0.15 MPa.

In addition, organic nanoparticles are also chosen as nanofillers. Zhao *et al.* [68] coated blend of polyaniline (PANI) nanoparticles and PVAm on PSf membranes to prepare the PVAm-PANI/PSf membranes. At CO_2 partial pressure of 0.02 MPa, the PVAm-PANI/PSf membrane with 17 wt.% PANI nanosheets showed a CO_2 permeance of 4.02×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 selectivity of 120. To prevent the agglomeration of PANI nanomaterials and improve the interface compatibility between PVAm and PANI nanofillers, PANI nanorods modifed by poly(vinylpyrrolidone) (PVP) adsorption layer were incorporated into PVAm matrix to fabricate the PVAm-PANI/PSf membranes[69]. The as-prepared PVAm-PANI/PSf membrane displayed a high CO_2 permeance of 1.03×10^{-6} mol·m^{-2}·s^{-1}·Pa^{-1} and CO_2/N_2 selectivity of 240 at 0.11MPa.

Besides our group, other researchers also use PVAm as polymer matrix. Hägg *et al.* [116] incorporated 1wt% CNTs into the polymer matrix of PVAm and polyvinyl alcohol (PVA), and prepared the PVAm-PVA-CNT/PSf membrane on PSf membrane by dip-coating method for high pressure gas transport measurements. At 1.0 and 1.5MPa, the CO_2 permeance of the PVAm-PVA-CNT/PSf membrane was more than doubled in comparison with counterpart PVAm-PVA/PSf membrane. Shen *et al.* [117] added GO grafted with hyperbranched PEI (HPEI-GO) into the polymer matrix of

PVAm and Cs on a porous PSf support to fabricate PVAm-Cs-HPEI-GO/PSf membrane. For CO_2/N_2 (10:90/v:v) mixed gas, the as-prepared membrane with 2.0 wt % HPEI-GO displayed a CO_2 permeance of 1.21×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 ideal selectivity of 90; The as-prepared membrane with 3.0 wt % HPEI-GO displayed a CO_2 permeance of 1.05×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/N_2 ideal selectivity of 107 at 0.1 MPa and 25 °C.

Ho group incorporates different inorganic nanofillers into PVA matrix containing amine carriers to prepare facilitated transport mixed matrix composite membranes. Xing *et al.* [118] incorporated fumed silica (FS), and the resulting membrane with 22.3wt% FS loading displayed the best performance with a CO_2 permeance of 1.37×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/H_2 selectivity of 87 at 1.52 MPa and 107 °C. Zhao *et al.* [119] incorporated MWCNTs, and the resulting membrane with 2wt% MWCNTs showed a CO_2 permeance of 1.12×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and a CO_2/H_2 selectivity of 43 at 1.52 MPa and 107 °C. The membrane performance was maintained without significant change for 444 hours. To improve affinity with the hydrophilic membrane matrix, Ansaloni *et al.* [120] incorporated amino-functionalized multi-walled carbon nanotubes (AF-MWNTs). The resulting membrane with 2.3wt% AF-MWNTs displayed a CO_2 permeance of 1.11×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1}, a CO_2/N_2 selectivity of 360, a CO_2/CH_4 selectivity of 277, and a CO_2/H_2 selectivity of 56 at 1.5 MPa and 107 °C. Moreover, the resulting membrane demonstrated a good stability.

For flat mixed matrix composite membranes, in addition to material design and selection, technology of membrane formation is very critical for obtaining good separation performance. The flat mixed matrix composite membrane can be mainly fabricated by solution casting method and interfacial polymerization. The solution casting method is simple and cheap. Hence, it is universally used. The mixture solution is cast on substrate (porous support membrane) with a pre-set wet coating thickness by a casting knife, then is dried under certain conditions. After the solvent evaporation, the flat mixed matrix composite membrane are fabricated successfully. To solve the problem of void creation between polymer and filler in conventional solution-casting

methods for the formation of MMMs, casting solutions were prepared as follows [107]. A filler suspension was prepared by adding a specific amount of fillers to solvent and sonicating. Then, a quarter of the polymer solution was added to the filler suspension, stirred and sonicated. This procedure was continued until all of the polymer solution was added to the filler suspension and a homogenous casting solution was obtained.

Compared with solution casting method, interfacial polymerization is rather cockamamie and wastes a great amount of organic solvent. The flat mixed matrix composite membrane were fabricated by interfacial polymerization as follows [112]. The flat sheet support membrane was initially immersed into the aqueous phase for a certain time and then the excess solution was drained from the membrane surface. Subsequently, the impregnated membrane was placed into the organic phase for a certain time at a certain temperature. After that, the resulted composite membrane was rinsed with pure organic solvent and then heat-treated. Furthermore, the composite membrane was washed with deionized water to eliminate excess monomers and byproducts. Finally, the resulted membrane was kept under certain conditions. To solve the problem of void creation between polymer and filler, fillers should be added to the aqueous phase or organic phase in which the fillers can be dispersed uniformly [112].

Generally speaking, compared with hollow fiber mixed matrix composite membrane, flat mixed matrix composite membrane possesses higher CO_2 permeance and higher CO_2/gas selectivity.

6 FUTURE DIRECTION

MMMs are a promising new generation of membranes for CO_2 separation. Compared with polymer membranes, CO_2 permeability and CO_2/gas selectivity of the MMMs both increase by the incorporation of suitable nanofillers. Therefore, in the future, MMMs are still the key research field to improve performance of polymer membranes. Some aspects on MMMs need to be explored further as follows:

(1) Developing new polymers with high permeability and selectivity.

(2) Synthesizing new nanofillers with suitable pore structure and particle size[9,

121], especially organic nanofillers that have interaction with CO_2 molecules.

(3) Investigating the relationship between interface morphology and gas transport properties systematically and qualitatively.

(4) Exploring new methods to improve compatibility between polymer and filler, and enhance gas permselectivity of the MMMs simultaneously.

(5) Developing high performance mixed matrix composite membranes for industrial application.

(6) Large pilot scale testing of membranes based on MMM approach[9].

(7) Employing high performance mixed matrix composite membranes to prepare MMM module for industrial application.

(8) Establishing the membrane separation plant with MMM module, which makes sure that membrane separation plant has advantages such as low cost and less energy consumption.

7 CONCLUSIONS

To improve CO_2 separation performance of polymer membranes, a large number of MMMs have been developed. Generally, MMMs contain two or more different components. Polymer matrix forms a continuous phase, and inorganic or organic fillers act as a dispersed phase. To prepare high performance MMMs for CO_2 separation, correct selection of polymer matrix and filler is essential. The polymer should possess high CO_2 permeability and high CO_2/gas selectivity. Moreover, the polymer should have high mechanical strength, and good thermal stability, chemical stability and processability. Matrimid® is the best polymer for CO_2/CH_4 separation under high pressure, and PVAm is the best polymer for CO_2/N_2, CO_2/CH_4 and CO_2/H_2 separation under low pressure. The filler should have high selectivity, good compatibility with polymer matrix, and small particle size. In the MMMs, the fillers not only disturb polymer chain packing and increase free volume, but also facilitate CO_2 transport by itself. Compared with inorganic fillers, organic fillers are emerging fillers. PANI is the best filler for CO_2/N_2 separation, NHs is the best filler for CO_2/CH_4 separation, and

MIL-53 is the best filler for CO_2/H_2 separation .

Owing to the differences between polymer matrix and filler, there are different interface morphologies between polymer matrix and filler. When there is poor compatibility between polymer matrix and filler, interface voids form. When the size of interface voids was larger than the mean free path of the gas molecules, and the interconnectivity of interface voids formed interface void channels across the MMMs, gas permeability increased and gas selectivity decreased with increasing feed pressure.

To avoid interface voids and improve membrane performance, researchers adopt eight methods including silane coupling, Grignard reagents treatment, incorporation of additive, grafting, in situ polymerization, PD coating, particle fusion approach and polymer functionalization to enhance interface compatibility. In principles, during modification process by using these methods except Grignard reagents treatment, hydrogen bonding or chemical bonding forms, which leads to the fact that the interactions between polymer matrix and inorganic nanofiller improve interface compatibility.

To achieve higher productivity for industrial application, mixed matrix composite membranes are developed. Compared with hollow fiber mixed matrix composite membrane, flat mixed matrix composite membrane possesses higher CO_2 permeance and higher CO_2/gas selectivity.

In the future, further research on MMMs should be focuses on the following aspects. On one hand, researchers should develop new polymer and new filler to prepare high performance lab-scale MMMs, and investigate the effect of interface morphology on gas transport properties. On the other hand, researchers should fabricate large-scale mixed matrix composite membranes with high permselectivity, and then assemble membrane module to built membrane separation plant .

NOMENCLATURE

A membrane area, m^2

l membrane thickness, m

L_c characteristic length of the core region, m

P permeability coefficient, $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$

ΔP transmembrane partial pressure, Pa

Q_e permeation rate, $m^3(STP) \cdot s^{-1}$

R permeance, $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$

x the molar fraction of gas species in the feed side

y the molar fraction of gas species in the permeate side

$\alpha_{i/j}^{*}$ ideal gas selectivity

$\alpha_{i/j}^{/}$ mixed gas selectivity or separation factor

Subscripts

i   gas species

j   gas species

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