Membrane-based technologies for biogas separations

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Received 6th March 2009 First published as an Advance Article on the web 6th October 2009 DOI: 10.1039/b817050a

Over the past two decades, membrane processes have gained a lot of attention for the separation of gases. They have been found to be very suitable for wide scale applications owing to their reasonable cost, good selectivity and easily engineered modules. This critical review primarily focuses on the various aspects of membrane processes related to the separation of biogas, more in specific CO_2 and H_2S removal from CH_4 and H_2 streams. Considering the limitations of inorganic materials for membranes, the present review will only focus on work done with polymeric materials. An overview on the performance of commercial membranes and lab-made membranes highlighting the problems associated with their applications will be given first. The development studies carried out to enhance the performance of membranes for gas separation will be discussed in the subsequent section. This review has been broadly divided into three sections (i) performance of commercial polymeric membranes (ii) performance of lab-made polymeric membranes and (iii) performance of mixed matrix membranes (MMMs) for gas separations. It will include structural modifications at polymer level, polymer blending, as well as synthesis of mixed matrix membranes, for which addition of silane-coupling agents and selection of suitable fillers will receive special attention. Apart from an overview of the different membrane materials, the study will also highlight the effects of different operating conditions that eventually decide the performance and longevity of membrane applications in gas separations. The discussion will be largely restricted to the studies carried out on polyimide (PI), cellulose acetate (CA), polysulfone (PSf) and polydimethyl siloxane (PDMS) membranes, as these membrane materials have been most widely used for commercial applications. Finally, the most important strategies that would ensure new commercial applications will be discussed (156 references).

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1. Introduction

Energy is inevitable to global prosperity. Fossil fuels are still the primary source of energy by preference. However, as fossil fuels become scarcer and more expensive, the quest for alternate sources of energy is a requirement of the utmost

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importance. Anaerobic digestion of biological resources—and most interestingly of biological waste—could be a promising alternative energy carrier. In a controlled reaction system, the gaseous mixture thus produced can contain up to 70% of biohydrogen and biomethane, respectively, that can be used for commercial applications.¹Fig. 1 summarizes the different steps involved in the production of biohydrogen and biomethane from organic wastes. The anaerobic digestion process can be broadly classified into hydrolysis, acidogenesis, acetogenesis and methanogenesis, involving a complex set of reactions. Organic substrates can be converted to biogas by a diverse group of microbes using multi-enzyme (cellulases, amylases, lipases, proteases *etc.*) systems.

Biohydrogen generated in fermentation processes (*e.g.* anaerobic fermentation, photo-fermentation, dark fermentation) mainly consists of hydrogen and carbon dioxide. Biomethane on the other hand, generated during anaerobic digestion of biological wastes (*e.g.* kitchen waste, landfill sites, animal



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Fig. 1 Schematic representation of the anaerobic digestion process for biogas generation.

waste), typically consists of 55-60% methane, 38-40% carbon dioxide and smaller amounts of hydrogen sulfide. Also, trace amounts (ppm) of hydrogen, nitrogen, oxygen and volatiles are present.² Biogas typically has a calorific value of $35-44 \text{ kJ g}^{-1}$. comparable to kerosene, petrol, diesel and LPG (butane) and higher than many solid fuels like coal, charcoal wood, etc.³ Biogas could thus be considered as a potential source of environmentally benign, clean and cheap alternative energy. However, commercial use of biogas is restricted near to its site of formation. Indeed, the presence of incombustible and acid gases, like CO₂ and H₂S, not only reduces its calorific value, but their corrosive nature also reduces the possibilities to compress and transport it over longer distances. One of the many trace components includes silicone containing compounds, so-called siloxanes. Commonly occurring siloxanes in biogas are known as volatile methyl siloxanes (VMS) that include cyclic tri-, tetra-, and penta-siloxane, as well as linear di-, tri-, tetra-siloxane.⁴ On combustion, highly undesired silicates and microcrystalline quartz are produced. This leads to engine and turbine wear and fouling in air-pollution control



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Fig. 2 Various possible applications of biogas as future energy carrier.⁵

devices. Purified biogas enriched in H_2 could be used as a feed to fuel cell. Similarly, CH_4 could be used for domestic applications, automobile fuel and power generation. Fig. 2 represents the possible applications of biogas.

2. Current technologies

The current efficiency of existing biogas production processes is limited, as the produced gas streams are too dilute. Obviously, CO_2 is abundantly present in these streams, but also the presence of H₂S, water and volatile organics complicates applications, due to the lowered calorific value and possible corrosion problems during biogas storage and transportation. Storage and transport can take place by compressing the biogas in cylinders—like compressed natural gas (CNG) after removing CO_2 , H₂S and other trace gases. Current technologies to remove CO_2 , H₂S and siloxanes from biogas to reach automobile fuel standards are as follows:

2.1 Removal of CO₂

- (i) Water scrubbing
- (ii) Polyethylene glycol absorption
- (iii) Pressure swing adsorption
- (iv) Cryogenic separation
- (v) Membrane separation

Water scrubbing is used to separate both CO_2 and H_2S from biogas owing to their higher solubility in water than H_2 and CH_4 . Generally, the biogas and water jet are fed to a packed column (typically, high surface area plastic media) in countercurrent.⁶ Polyethylene glycol absorption is similar to the water scrubbing process, but with the water replaced by a better suited solvent (*e.g.* The Lurgi Purisol[®] process and UOP SelexolTM process). Pressure swing adsorption uses materials like activated carbon, carbon molecular sieves *etc.* that are suitable to separate a number of different gaseous compounds from biogas. Cryogenic separation is based on fractional distillation. CO_2 is then separated by condensation either by lowering the temperature or increasing the pressure. Membrane separation processes for CO_2 removal generally provide several advantages over the above-mentioned conventional separation techniques including low capital cost, high energy efficiency, ease of processing, simple process equipment, and relative ease to operate and control. Polymeric membranes, such as UOP SeparexTM cellulose acetate (CA) membranes, have already proven to operate successfully for natural gas upgrading.

2.2 Removal of H₂S

A very important stage of biogas upgrading is its separation from H_2S traces *via* one of the following methods.

- (i) Dry oxidation
- (ii) Liquid phase absorption

The dry oxidation process is used for gas with low sulfur content and for high purity requirements. The process involves oxidation of sulfide into sulfur. This is a simple and low cost process. Liquid phase absorption processes involve absorption of gases in suitable solvents like water or an aqueous amine or sodium hydroxide solution.⁷ The commercial UOP Amine GuardTM FS process exists for selective removal of H₂S. Chemical reactions with quicklime in solid form and slaked lime in liquid form are also used. However, high concentrations of CO₂ in the biogas cause difficulties in removal of H₂S, as CO₂ reacts with quicklime and slaked lime faster than H₂S.⁸

2.3 Removal of siloxanes

The following technologies have been used for the removal of siloxanes from biogas.

- (i) Activated carbon
- (ii) Condensation
- (iii) Synthetic resins
- (iv) Liquid adsorbents
- (v) Membrane separation

Activated carbon has been widely used in the late 80's and 90's for the removal of gases and liquids owing to its strong adsorption properties and large surface area. However, its performance in removing siloxanes from gas streams is inadequate.⁴ Recent work on pressure swing adsorption has resulted in promising results.9 Reducing the temperature of the exhaust gas and letting it condense to a liquid is another method of removing siloxane from biogas. However, only a modest removal can be achieved by this way.¹⁰ Like activated carbon, synthetic resins are an alternative for siloxane removal through adsorption. But the resin regeneration requires microwave heating.¹¹ Liquid adsorbents, like the Selexol solvent, were developed for removal of CO₂, H₂S, mercaptan, BTEX, halogenated hydrocarbons,... from biogas. Among upcoming technological developments, membrane processes have been reported as a potential technology. Polydimethyl siloxane (PDMS) has been identified as a potential membrane material for removal of many siloxanes and other trace volatile compounds.11

Country	Biogas production	CH ₄ enrichment (%)	CO ₂ removal technology	H ₂ S removal technology	
Czech Rep.	Sewage sludge	95	Water scrub.	Water scrub.	
France	Sewage sludge and landfill	96.7	Water scrub.	Water scrub.	
The Netherlands	Landfill, sewage sludge, green waste	88.0	Membranes, CMS, water scrub.	Activated carbon, iron oxide pellets	
New Zealand	_	_	Water scrub.		
Sweden	Sewage sludge, vegetable waste, manure, slaughter house waste, fish waste	97	Water scrub., CMS	Activated carbon, water scrub., iron–chloride dosing	
Switzerland	Biowaste	96	CMS	Activated carbon	
USA	Sewage sludge, landfill	96–98	Membranes, Selexol sol. gscrub., water scrub.	Selexol sol. scrub., water scrub., activated carbon	
Germany	Biowaste	99	ĈMS	CMS	

 Table 1
 Summary of the biogas purification process at various plants in operation⁷

A summary of the various biogas purification processes currently applied in industries⁷ has been enumerated in Table 1.

Table 1 reveals that pressure swing adsorption (on CMS) and water scrubbing are the most commonly used technologies for gas separation. Correspondingly, membrane processes for gas separation have so far received relatively little attention for purification of the typical composition of biogas. However, considering the quantum of peer-reviewed publications and patents over the last few years (for instance, more than 40 patents filed on CO₂ separation through polymeric membranes over the last 8 years) on effectiveness of membrane technology for gas separation, the process seems to produce a clear economic alternative to absorption and adsorption for purification of biogas and enrichment in H₂ and CH₄, respectively. Several thermal and electrochemical routes (e.g. steam reforming of natural gas, coal gasification, water electrolysis,...) are used for the production of pure hydrogen on saleable scale. However, hydrogen generation from biological waste on commercial scale and its purification for further usage is still not in operation.

Presently, there are more than 4500 biogas plants in Europe.¹² Table 2 summarizes the total amount of biomass that would be available by end of 2020 and the amount of energy that could be generated from it in each of these

Table 2 Estimated potential of total energy generation from biogas in EU by 2020^{13}

Countries	Total biomass (million tonnes)	Total energy from biogas/TWh year ⁻¹
Austria	36.1	6.1
Belgium	52.0	8.8
Denmark	52.5	8.9
Finland	18.5	3.1
France	251.9	42.7
Germany	234.6	39.8
Greece	11.4	1.9
Ireland	70.5	11.9
Italy	112.0	19.0
Luxemburg	2.08	0.4
The Netherlands	80.8	13.7
Portugal	22.0	3.7
Spain	108.2	18.3
Sweden	26.3	4.4
United Kingdom	155.4	26.3
Total EU	1234.3	209

15 countries. The countries with the highest biogas production per capita at this moment are UK, Sweden, Denmark and The Netherlands. For example, Denmark has 45, Sweden 18 and Germany more than 200 biogas plants running successfully.¹² The source of biogas includes sewage treatment plants, landfills, cleaning of organic industrial waste streams, and microbial digestion of organic wastes. For instance, it is estimated that today more than 4000 vehicles in Sweden are running on biogas and natural gas.

3. Potential of membrane processes for biogas purification

As partly mentioned already, the presence of sour gases (CO_2 and H₂S) in the biogas (i) reduces the heating value, (ii) increases the quantum of gas transported through pipelines, (iii) increases pipeline corrosion during transportation and distribution, and (iv) emits sulfur dioxide (SO₂) in the atmosphere upon combustion. In order to avoid these complications, the US pipeline specification for distribution and consumption of biogas is $CO_2 < 2 \mod \%$ and $H_2S < 4 ppm.^{14}$ Thus, considerable interest developed in accentuating the energy content and in the so-called sweetening of biogas through the removal of H₂S and CO₂, yielding a marketable energy source. Another important aspect to be considered during biogas commercialization is the presence of volatile organic compounds (VOCs). Membrane separation processes are also gaining importance because their operating costs are almost independent of the VOC concentration in the feed.¹⁵ PDMS membranes have for instance been found to be very effective for the separation of acetate and other VOCs.^{16–19}

The selection of the appropriate process for CO_2 and H_2S removal is a complex issue and requires accurate and sufficient data, in-depth analysis and good technical understanding. A comparative study of the various gas separation processes is summarized in Table 3. The most important criteria were costs, product recovery, purity and ease to operate and handle. Conventionally, biogas purification is achieved through gas absorption in suitable solvents. However, absorption processes are highly energy-intensive and not well-suited for large-scale applications due to the bigger size and weight of the process equipment.²⁰

Process	Main features	Future challenges
Water scrubbing	Simple and widely used technology, removes both CO ₂ and H ₂ S	Fugitive emissions, odor problem, pretreatment required
Adsorption	High purity transportable products	Lower recovery of products
Absorption	Removes both CO_2 and H_2S	High pressure required for solvents, low purity
Cryogenic separation	High recovery, moderate purity, economical at low flows	Complete CO ₂ removal requires freezing temperatures that deter its commercial applications, complex process, long start-up and shut-down, not suitable for gas plants
Membrane	Simple, low capital cost, high energy efficiency, compact, modular and scalable, stable at high pressure, operational at ambient temperature, high product recovery	Membrane plasticization, low contaminant resistance, lower product purity than adsorption

 Table 3 Main features and future challenges of the different biogas separation processes²¹

4. Types of membrane materials used for gas separation

Inorganic, polymeric as well as composite membranes have been studied extensively for gas separation over the last few decades. Table 4 summarizes the most important kinds of materials that have been used for gas separations.

Non-polymeric membranes e.g. alumina, zeolites, carbon etc. generally have better separation properties, as well as higher chemical and thermal stability than polymers, but they are characterized by high cost, poor mechanical properties and difficult processing. Ceramic membranes, porous or dense, are chemically stable and can withstand high temperatures,²² and provide good selectivity and high permeability.^{23,24} They are used in the form of oxide, nitride or carbide by combining a metal with non-metal. For instance, crystalline zeolite membranes such as SAPO-34 and Si-DDR membranes have shown significantly higher selectivities than polymeric membranes for gas separations. These membranes, however, are associated with intracrystalline defects that lead to non-selective transport.²⁵ These defects are a more critical issue in gas separations than in liquid separations, where difficult wetting might prevent liquids to enter small cracks. Pd membranes have undergone more than 5 decades of extensive research, but efforts are still underway to reduce their thickness and make them cost effective.²⁶ Pd alloy membranes have exhibited excellent gas separation performance,²⁷ but still they are an unattractive commercial choice due to their very high cost, sensitivity to various chemicals and inability to work at lower temperatures.28 CMS membranes are quite brittle and are thus difficult to

 Table 4
 Materials used for gas separations²²

Organic polymers	Non-polymeric materials
Polysulfone (PSf), polyethersulfone (PES)	Carbon molecular sieves (CMS)
Cellulose acetate (CA), cellulose triacetate (CTA)	Non-porous carbon
Polyimide (PI), polyetherimide (PEI)	Zeolites and non-zeolitic molecular sieves
Polyaramide (PA)	Ultramicroporous amorphous silica
Polycarbonate (brominated) (PC)	Palladium allovs
Polyphenyleneoxide (PPO)	Mixed conducting perovskites
Polymethylpentene (PMP)	
Polydimethylsiloxane (PDMS)	_
Polyvinyltrimethylsilane (PVTS)	

prepare on industrial scale although they normally have high selectivity and permeability.²⁹ These membranes are currently unavailable on commercial scale due to their high cost and inherent brittleness.³⁰

Membrane technology is attractive for molecular scale separations because of its inherent advantages, such as low cost, high energy efficiency, ease of processing, excellent reliability and small footprint.^{31,32} However, the potential application of membrane technology largely depends on the ability of membrane materials to exhibit high separation performance at practical feed concentrations (biogas feed streams typically contain high pressure CO_2 and impurities like H₂S and H₂O).³³ Polymeric membranes dominate traditional gas separations because they are (i) much cheaper than inorganic membranes, (ii) able to be easily fabricated into commercially viable hollow fibers or flat sheets that can be processed into hollow fiber or spiral wound modules, (iii) in advanced stage of development, (iv) stable at high pressures, and (v) easily scalable.^{34–37}

Many different polymer families have been investigated as gas separation materials such as PC, CA, polyesters, PSf, PI, and polypyrrolones. CA, PSf and PI have been widely used for industrial scale applications. Several companies are currently producing gas separation membranes on commercial scale (e.g. Membrane Technology Research, Air Products, UOP, Air Liquide, Praxair, Cynara, UBE, GKSS Licensees).³⁸ Considering the limitations of inorganic materials for membranes, the present study will only focus on work done with polymeric materials. Polymeric membranes exhibit inverse permeability/selectivity behavior. This was illustrated by Robeson in 1991,³⁹ where an 'upper bound trade-off' curve was plotted between selectivity and permeability of gases (Fig. 3 and 4). Both these figures include H_2 -CO₂ and CO2-CH4 selective polymeric membranes with and without chemical modifications.^{40,41} It shows that glassy and rubbery membranes for H₂-CO₂ are below the previous and currently available trade-off lines. In contrary, notable improvements in CO₂-CH₄ selective membranes have taken place over the last few decades. Most of the membranes with chemical modifications surpassed the trade-off line. A detailed discussion on chemical modifications of membranes is in Section 6. Table 5 summarizes the performance of some of the polymeric membranes widely used for gas separations.²²

The variation in permeability and selectivity clearly indicates that the polymeric membranes with solution-diffusion transport



Fig. 3 Robeson trade-off curve for H_2 -CO₂ selective polymeric membranes.



Fig. 4 Robeson trade-off curve for CO_2 -CH₄ selective polymeric membranes.

mechanism are selective to certain gas molecules based on their size, as given in Table 6. Also, the permeability of gases in membranes is largely controlled by the solubility which is mainly governed by the possibility of these gas molecules to condense. Thus, CO_2 and CH_4 , which are among the most condensable gases, are mostly more permeable through elastomeric polymer types. Permeability and selectivity of pure and mixed gases are expressed as

4.1 Pure-gas permeability

$$\mathbf{P} = \frac{Ql}{A\Delta p} = \frac{Q \times 1}{A(p_{\text{feed}} - p_{\text{perm}})} \tag{i}$$

Where, *P* is the pure-gas permeability coefficient, a measure of flux of the membrane. It is expressed in Barrer (10^{-10} cm^3)

(STP) cm cm⁻² s⁻¹ cmHg⁻¹). The permeability is related to the permeate flow rate through the membrane (Q), the area of the membrane (A), the selective layer thickness of the membrane (l) and the driving force for separation, the pressure difference across the membrane (Δp). The p_{feed} and p_{perm} are the feed and permeate pressures, respectively.

4.2 Pure-gas selectivity

The pure-gas selectivity $(\alpha_{a/b})$ of one gas, a, over another gas, b is defined as

$$\alpha_{a/b} = P_a/P_b = \frac{Q_a(p_{\text{feed},b} - p_{\text{perm},b})}{Q_b(p_{\text{feed},a} - p_{\text{perm},a})}$$
(ii)

where P_a and P_b are the permeabilities of gas a and gas b, respectively. Q_a and Q_b are the flow rates of gas a and gas b, respectively. The $p_{\text{feed},a}$ and $p_{\text{perm},a}$ are the feed and permeate pressures of gas a, respectively. The $p_{\text{feed},b}$ and $p_{\text{perm},b}$ are the feed and permeate pressures of gas b, respectively.

4.3 Mixed-gas permeability of each component

$$P_{i} = \frac{Q \times x_{\text{perm,i}} \times 1}{A(p_{\text{feed}} x_{\text{feed,i}} - p_{\text{perm}} x_{\text{perm,i}})}$$
(iii)

where P_i is the mixed-gas permeability coefficient of component i. The $x_{\text{feed},i}$ and $x_{\text{perm},i}$ are the mole fractions of component i in the feed and permeate stream, respectively.

4.4 Mixed-gas selectivity

$$\alpha_{a/b} = \frac{x_{\text{perm,a}}(p_{\text{feed}}x_{\text{feed},b} - p_{\text{perm}}x_{\text{perm,b}})}{x_{\text{perm,b}}(p_{\text{feed}}x_{\text{feed},a} - p_{\text{perm}}x_{\text{perm,a}})}$$
(iv)

where $x_{\text{feed},a}$ and $x_{\text{perm},a}$ are the mole fractions of component a in the feed and permeate stream, respectively. $x_{\text{feed},b}$ and $x_{\text{perm},b}$ are the mole fractions of component b in the feed and permeate stream, respectively.

5. Commercial polymeric membranes

The polymeric membranes used in most commercial applications operate on the solution-diffusion mechanism.⁴³ The selection of the right polymeric membrane material for a given gas separation generally depends on the (i) cost, (ii) selectivity, (iii) permeability, (iv) processability, (v) chemical, mechanical, and thermal stability, (vi) availability of material (vii), glass

 Table 5
 Permeability and selectivity of polymeric membranes for gas separations²²

Polymer	Permeabilit	ty at 30 °C/Barro	er	Selectivity				
	H_2	N_2	O_2	CH_4	CO_2	H ₂ -CO ₂	CO ₂ -CH ₄	$T_{ m g}/^{\circ}{ m C}$
CA	2.63	0.21	0.59	0.21	6.3	0.41	30.0	80
EC	87	8.4	26.5	19	26.5	3.33	1.39	43
PC	_	0.18	1.36	0.13	4.23	_	32.5	150
PDMS	550	250	500	800	2700	0.20	3.38	-123
PI	28.1	0.32	2.13	0.25	10.7	2.63	42.8	317
PMP	125	6.7	27	14.9	84.6	1.49	5.75	30
PPO	113	3.81	16.8	11	75.8	1.49	6.89	210
PSf	14	0.25	1.4	0.25	5.6	2.5	22.4	190

Table 6 Physical properties of gas molecules influence transport $\operatorname{properties}^{42}$

Gas	Kinetic diameter/nm	Condensation temperature/K
CH ₄	0.380	191.05
CO ₂	0.330	304.21
H_2	0.289	33.24
N_2	0.364	126.2
0 ₂	0.346	154.6

transition temperature (T_g), and (viii) critical CO₂ pressure for plasticization.⁴⁴

A CH₄ enrichment of 91-94% at CH₄ feed concentrations of 55-85% together with high permeability of H₂O and H₂S was achieved with a PI-based hollow fiber module (UBE Europa GmbH).⁹ PI presented a higher selectivity than PPO for CO₂-CH₄ (36.0 and 16.4 CO₂-CH₄ selectivity, respectively, Aquilo Gas Separation).⁴⁵ Furthermore, the separation factor of CO₂-CH₄ improved with increased stage cuts (permeate flow rate/feed flow rate). PPO produced a stable permeation rate with time, while the permeability of PI decreased after 3 months of operation. The study of 12 commercial membranes based on caprolactam, PI, polyester, polyethersulfone fluorocarbon (General Electric) dimethyl silicon, silicon polycarbonate, poly-monocholoro-p-xylene, poly-p-xylene (Union Carbide), CA (UOP Separex[™]) and silicone (Dow Corning) for CH₄, CO₂ and H₂S separations at room temperature and low pressures, reported that most of them were poorly permeable to these gases.⁴⁶ CA with CO₂-CH₄ selectivity of 14 outperforms other membranes. Likewise, CA (Cynara) achieved around 41% CO₂ removal from natural gas.⁴⁷ Another comparative study between different commercial gas separation membranes, purchased from ACME Rubber Company (Tempe, AZ) and Degussa (Parsypanny, NJ), reported that the mean transport properties (permeability, diffusivity and solubility) of different gases (CH₄, He, CO₂, N₂ and CH₂O) decreased in the order of PDMS > polyisoprene (PoI) > polyocenamer $(PO) > polyurethane (PU).^{48} A similar study carried out$ with PDMS and poly(1-trimethyl-silyl-1-propyne) (PTMSP) (membranes from MTR) reported that at room temperature both CO₂ and H₂S show higher permeability than H₂ through both membranes. Towards increasing temperature however, H₂ permeability increased linearly through PDMS but decreased abruptly through PTMSP,49 possibly due to the enhanced physical ageing of the PTMSP polymer. PDMS composite membranes and copolymer poly(dimethyl, methylphenyl) siloxane (PMPS) from MTR resulted in high

 Table 7
 Summary of the commercial polymeric membranes

Membrane	Supplier	Separation
PDMS and PMPS	MTR	Hydrocarbon vapor separation
PSf	Air Products	H_2 and air separation
PC	MG Generon (Messer)	Air separation
PI	UBE, MEDAL (Air Liquide)	CO ₂ –CH ₄ , H ₂ –CH ₄ , and air separation
PA	MEDAL (Air Liquide)	H_2 separation
CA, CTA	Cynara (Natco), Separex (UOP)	CO_2 – CH_4 separation

 CO_2 permeability.⁵⁰ In pure gas, CO_2 permeability increased from 2645 to 2792 Barrer for PDMS and from 1450 to 1650 Barrer for PMPS, respectively, as the temperature decreased from 21 °C to -20 °C. In mixed gas (95% CO_2 and 5% N₂) under similar operating conditions, CO_2 permeability for PDMS increased from 2482 to 2619 Barrer and selectivity decreased from 14 to 7, while those of PMPS changed from 1150 to 1000 Barrer and 25 to 12, respectively. This indicates that the presence of N₂ hindered the CO_2 permeability in mixed gas. PMPS was found to be a better CO_2 separation candidate than PDMS owing to the higher polymer rigidity. A list of all the commercial polymeric membranes has been enumerated in Table 7.

6. Developments and problems associated with polymeric membranes

6.1 Improvements in gas transport properties

Membranes exhibiting high CO_2 - CH_4 and H_2 - CO_2 selectivity and CO_2 permeability are suitable for biogas separation. Considerable attempts have been made till date to improve the performance of such membranes. The Robeson's upper boundary curves for both gas pairs have generally been considered as the benchmark towards development.

Chemical transformation of polymers with side chain and backbone modifications, more specifically by introducing bulky functional groups, *e.g.* $-Si(CH_3)_3$, or by replacing flexible bonds with tougher ones, like *e.g.* replacing -SiO-linkages with $-SiCH_2$ -, increased T_g and chain packing density.⁵¹ The CO₂-CH₄ selectivity for silicone polymers (*e.g.* [PDMS (CH₃)₂SiO-]_n) increased by 50–55% with side-chain modification (*e.g.* [(CF₃C₂H₄)CH₃SiO]_n) and 39% with backbone chain modification. Likewise, PI exhibits a conspicuous increase in CO₂-CH₄ selectivity with a hexafluoro substitute carbon $-C(CF_3)_2$ in the backbone chain. The relevant structural modifications are shown in Table 8.

Bromination of PI doubled CO₂ permeability, while maintaining similar CO₂-CH₄ selectivity. Suppression of inter-chain packing by addition of the bulky bromine groups and structural modifications through substitution of hydrogen atom by bromine atom in the backbone chain of PI thereby enhanced membrane permeation.⁵² CO₂-CH₄ and H₂-CO₂ selectivity of a 2,2'-bis (3,4'dicarboxyphenyl) hexafluoropropane dianhvdride (6FDA)-2.4.6-trimethyl-1.3-phenylenediamine (TMPDA)-1,3-phenylenediamine (m-PDA) PI-membrane increased by 1.6 and 1.4 times, respectively, with increasing *m*-PDA content in 6FDA-TMPDA (from 1/3 to 3/1).⁵³ 6FDA-based PI-membranes with polar hydroxyl and carbonyl groups (2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BAPAF), 2,4-diaminophenol dihydrochloride (DAP), 3,5-diaminobenzoic acid (6FDA-BAPAF, 6FDA-DAP, 6FDA-DABA)) in the chain increased CO₂ permeability and CO_2-N_2 and CO_2-CH_4 selectivities⁵⁴ compared to other studies on 6FDA-based PI membranes.^{55–58}

Crosslinking of 6FDA-based copolyimides with ethylene glycol improved CO_2 -CH₄ selectivity.⁵⁹ Similarly, crosslinking of PI membranes with *p*-xylenediamine improved mixed gas selectivity of CO_2 -CH₄ than pure gases.⁶⁰ Likewise,



Table 8 Molecular structure of the chemical compounds used to reduce plasticization in PI, CA and PSf membranes

Table 8 (continued)



crosslinking of a 6FDA-durene PI-membrane increased the CO₂-CH₄ and H₂-CO₂ selectivity up to 30 and 4, respectively, compared to 13 and 1.3 for the original 6FDA-durene PI.⁶¹ Amidation with N,N-dimethylaminoethyleneamine (DMEA) of 6FDA-durene/m-PDA (50 : 50) increased CO₂-CH₄ selectivity from 12 for 6FDA-durene up to 35.62 Crosslinking of propane-1,3-diamine (PDiA)-based PI-membranes with diamines has allowed us to surpass the trade-off line for H₂-CO₂, by realizing an ideal and mixed gas selectivity of 101 and 42, respectively.⁶³ The difference is because the slower CO₂ molecule obstructs the faster H₂ molecule from penetrating through membrane. 6FDA-ODA/NDA copolyimide (4,4'-diphenylene oxide/1,5-naphthalene-2,2'-bis(3,4-dicarboxylphenyl)hexafluoropropanediimide) membrane with PDiA (1,3-diaminopropane) showed 96% increased H₂-CO₂ selectivity after PDiA modifications.64

Similar variations like with PI-membrane in gas permeability and selectivity related to changes in the polymer free volume upon chemical modification of the polymer chains have also been observed for PSf-membranes. Substitution of $-C(CF_3)_{2^{-1}}$ for $-C(CH_3)_{2^{-1}}$ in PSf increased the CO₂ permeability while maintaining constant CO₂-CH₄ selectivity.⁶⁵ The substitution of hydrogen atoms by the larger fluoride atoms opens up the polymer packing and increases the free volume, eventually leading to an increased permeability. In chemically modified PSf, CO₂ permeability in TMSPSf (bisphenol-A trimethylsilylated polysulfone) bisphenol-A trimethylsilylated (TMS) PSf and bromobisphenol-A trimethylsilylated polysulfone (BTMSPSf) was higher than that of PSf membrane.⁶⁶ The replacement of phenylene hydrogens in the PSf with trimethylsilyl groups increased the inter-chain distance and decreased chain stiffness, resulting in higher fractional free volume (FFV). Similarly, CA-membranes showed increased CO₂ permeability with incorporation of silyl groups.⁶⁷

6.2 Plasticization

The above-mentioned membranes have lots of potential for application in industries for biogas separations. Glassy polymers are mostly preferred as membrane material due to their higher gas selectivity. However, glassy polymers are often associated with problems like densification, ageing or plasticization. Plasticization occurs due to dissolution of gas molecules into micro-voids inside the polymer matrix that are intrinsically smaller than the gas molecule diameter. This 'molecular mismatch' indicates that the polymer matrix swells to accommodate the gas molecules, resulting in permanent damage to the matrix.⁶⁸ Consequently, plasticization leads to

larger inter-chain spacing in the polymer, and drastic increase in gas diffusion. This goes together with a reduced performance of the membranes, as the selectivity largely decreases.

For a CO₂–CH₄ binary mixture for instance, increased feed pressures and CO₂ concentrations (10–45 mol%) lowered the CO₂–CH₄ selectivity for CA membranes by a factor of 1.5–1.2 between 10 and 50 bar.⁶⁹ In a similar study, the ideal selectivity of CO₂ over CH₄ was 3–5 times higher than the selectivity of the mixed gases for CA membranes at feed CO₂ concentrations higher than 50% and pressure up to 54 bar.⁷⁰ This is attributed to swelling or/and plasticization effects of CO₂, since CO₂ is much more soluble in CA than CH₄. However, it was proved that CA membranes can still be used to remove both CO₂ and H₂S and reach the US pipeline specification for the sour gases, if the feed gas contains less than 15% CO₂ and 250 ppm H₂S, and no water vapor.⁷¹

Likewise, varying the CO₂ feed concentration from 0 to 20 mol%, three PI membranes (Matrimid[®], P84[®] and Kapton[®]) showed different permeabilities and CO₂–CH₄ selectivities for pure gas and binary gas mixture. Mixed gas selectivity for Matrimid membranes was 76% lower than the ideal selectivity and 40% lower for the other two PIs.⁷² It was ascribed to coupling effects between CO₂ and CH₄ and plasticization at higher CO₂ concentration, both resulting in loss of selectivity. As plasticization and the following selectivity loss are highly undesired, many different attempts have been made to overcome the chances of plasticization of glassy polymers.

6.3 Preventing plasticization

6.3.1 Membrane heat treatment. Heat treatment of the membrane before use reduces CO_2 plasticization in glassy membranes. It is inferred that heating near to the glass transition temperature (T_g) disrupts the chain rigidity and allows a better chain packing, thereby attenuating the CO_2 permeability with increasing feed pressure.⁷³ For instance, PSf membranes treated at 140 °C showed enhanced stability against CO_2 plasticization. Similar effects were realized for PI-membranes after treatment at 350 °C.⁷⁴Table 9 summarizes the various studies carried out against plasticization using heat treatment process.

6.3.2 Chemical modifications. Introducing crosslinkable structures in the polymer backbone reduces the chances of plasticization in polymeric membranes. Crosslinking prevents the material from swelling in the presence of plasticizing agents and promotes chemical and thermal stability.⁷⁹ It thus not only provides good chemical resistance and antiplasticization, but also better long-term performance stability. *p*-Xylenediamine crosslinked 6FDA-(2,6-diamino toluene) (DAT) PI-membranes resulted in reduced CO₂ plasticization and increased CO₂–CH₄ selectivity.⁸⁰ 1,3-Propanediol (PDL) crosslinked PI-membranes showed a greatly suppressed CO₂ plasticization as well.⁸¹

The hydrogen bonding between COOH groups in 6FDA-*m*-PDA–DABA (9 : 1) reduced CO₂ plasticization up to 14 bar. Chemical crosslinking with ethylene glycol further improved the stability up to 35 bar. Moreover, a 10% degree of cross-linking increased CO₂–CH₄ selectivity by 20%, compared to a reference PI. The increased free volume between the polymer

 $\label{eq:Table 9} \begin{array}{ll} \mbox{Summary of various heat treatment conditions for different} \\ \mbox{membranes} \end{array}$

Membrane	Operating conditions	References
Polyimide 6FDA-m-DDS	150, 222, 250 °C	75
Matrimid [®]	350 °C for 15 min	74
Matrimid [®]	150, 250, 300, 350 °C	76
	for 2–5 min	
6FDA-2,6 DAT	150-320 °C for 10 min	77
PSf	100, 120, 140, 160,	73
	180 °C for 10-50 min	
PSf	70 °C for 5 min	78

chains, caused by the crosslinking agent, was said to improve this selectivity.79 6FDA-diaminomesitylene (DAM) with DABA units in the chain (2:1) and crosslinked with butylene glycol (BG) proved an optimal combination to mitigate CO₂ plasticization and physical ageing (up to 2 months) of a CO₂-CH₄ stream operated at 35 °C.⁸² In another example, 6FDA-DABA-based PI crosslinked with ethylene glycol and aluminium acetylacetonate improved CO₂-CH₄ (50 : 50) selectivity at 35 °C without any CO₂ plasticization till 58 bar. This indicates that the covalent linkage between the carboxylic acid groups in DABA and the crosslinkers suppresses CO₂ plasticization.⁸³ Likewise, 6FDA-based copoly(4,4-diphenylene oxide/1,5-naphthalene-2,2-bis(3,4-dicarboxylphenyl) hexafluoropropane diimide) (6FDA-ODA/ NDA) (50 : 50) crosslinked with p-xylenediamine showed CO2-CH4 selectivity of 36 and CO2 plasticization upto 40 bar.⁸⁴ Torlon[®] (a polyimide–amide polymer) is highly resistant to CO₂ plasticization, because of inter and intra-chain hydrogen bonding between N-H and C=O groups. It is resistant to 82 bar (much higher than Ultem[®], 6FDA-DAM : DABA 2 : 1 and similar to Matrimid[®]) with CO₂-CH₄ selectivity of 40.85

6.3.3 Polymer blending. In this context, polymer blending involves mixing a polymer with high plasticization tendency with one that is hardly affected by the sorbed molecules. It can reduce the price of the membrane and increase its processability.⁸⁶ Blend membranes can be considerably more resistant to plasticization than the pure polymers, e.g. a PSf-PI blend compared with pure PI.87 Even blends of 2 different PIs (Matrimid[®]-P84[®] in a 60 : 40 w/w ratio) showed a better CO₂-CH₄ permeability and selectivity than the homopolymers or a Matrimid[®] blend with PSf (50 : 50)⁸⁶ (Fig. 5). Furthermore. Matrimid[®]–P84[®] blends maintained selectivity greater than 35 even under increasing pressure. However, this phenomenon was only valid at CO₂ feed concentrations below 80 mol[%].⁸⁸ For Matrimid[®]–PSf blend membranes with PI contents between 20 and 50 wt%, the critical CO₂ pressure of plasticization was 30–35 bar compared to 18 bar for PI.⁸⁹ The blend also offered improved thermal stability and chemical resistance. Matrimid[®] and PBI (25:75) blends showed high CO₂-CH₄ and H₂-CO₂ selectivities.⁹⁰ This polymer blend crosslinked with *p*-xylenedichloride and *p*-xylenediamine increased H₂-CO₂ selectivity by 28% and 64%, respectively. PSf and PC blends increased permeability of H₂ by 2 times and CO₂ by 4 times. The increased permeability largely corroborates to increased free volume between polymer chains, since chain packing is more difficult between non-similar polymers.⁹¹



Fig. 5 CO_2 -CH₄ selectivity for Matrimid[®](M)–P84 (60%/40%) and Matrimid[®](M)–PSf (50%/50%) blend polymers at variable pressure and at 35 °C (taken from ref. 86).

7. Mixed matrix membranes (MMMs)

7.1 General

MMMs formed by dispersing inorganic filler in a polymer matrix offer a viable approach towards combining the low cost and ease of processing of polymeric membranes with the high selectivity and permeability of inorganic membranes.^{40,92} Polymer-inorganic nanocomposites can either have their polymer and inorganic phases interlinked by covalent bonds, by van der Waals force or via hydrogen bonds.93 Significant studies for improving the performance of polymeric gas separation membranes using the MMM approach have been reported over the last two decades. The Robeson upper bound trade-off curve between gas permeability and selectivity is still considered as a reference frame for the improvement of membranes. Correspondingly, there are several molecular sieving materials such as zeolites, carbon molecular sieves (CMS), carbon nanotubes (CNTs), metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) that offer attractive gas transport properties. Therefore, researchers tried to amalgamate the molecular sieving materials into the polymer matrix to prepare MMMs. The aim was to achieve better permeability and/or selectivity and to overcome the limitations of the 'upper bound trade-off line' that exist for solutiondiffusion type of transport in pure polymeric membranes.

7.2 Filler properties and applicability

Zeolites are the pioneer members of the molecular sieve family used for the preparation of MMMs. Zeolites are crystalline aluminosilicates consisting of AlO₄ and SiO₄ tetrahedra that are connected to form a network of channels and cavities (Fig. 6). The pore aperture size usually varies in the range of molecular dimensions between 0.3 and 1.0 nm. Substitution of Si atoms by Al atoms in the crystal structure results in excess negative charge, compensated by monovalent or divalent cations (K⁺, Na⁺, Ca⁺²), rendering the structure more polar, the higher the Al-content. As a result, polar species (*e.g.* water, ammonia, carbon dioxide, nitrogen and aromatic hydrocarbons) are strongly adsorbed by these zeolites. Hydrophilic zeolites, (*e.g.*, NaX, NaY, 5A, 13X) with high Al content in their frameworks, are highly selective towards polar compounds, like H_2S and CO_2 .⁹⁴ Properties of zeolites that have been commonly used in MMMs are described in Table 10.

CMS are another important type of adsorbent that have found application in gas separations.⁹⁶ CMSs are prepared from carbon containing chemical compounds and polymers. These materials have high surface area to volume ratios, relatively uniform size and small pores. CNTs are long cylinders of covalently bonded carbon atoms. The cylinder may have one end closed or both ends free. It possesses high flexibility and low mass density.⁹⁷ There are two types of CNTs: single wall carbon nanotubes (SWNTs) and multi wall carbon nanotubes (MWNTs). SWNTs adsorb nearly twice the volumes of CO₂ compared to activated carbon over a wide temperature range of 0–200 °C.⁹⁸ CO₂ adsorption takes place on both the external and internal surface areas of the nanotubes.⁹⁹

MOFs are a new family of nanoporous crystalline compounds formed by self-assembly of transition metal ions or clusters that are linked by bridging organic ligands through strong bonds. They possess many attractive properties like adjustable chemical functionality, pore shape and connectivity, high thermal stability, low density, ordered structure, high porosity, and tunable pore structure.¹⁰⁰⁻¹⁰³ CO₂ storage in some MOFs is remarkably higher compared to zeolites and other carbonaceous materials.¹⁰⁴ For instance, IRMOF-10, IRMOF-14 and MOF-177 have 3-5 times higher CO2 adsorption capacity than zeolite 13X and MAXSORB (activated carbon) at 35 bar and room temperature.¹⁰⁵ CO₂ uptake capacity of MOFs changes distinctly from one MOF to another and strongly depends on operating pressure and temperature.¹⁰⁴ For instance, at low pressure, MOF-5, a simple cubic framework, is weakly selective for CO₂ over CH₄ (1 at 10-20 bar). But with increasing pressure, MOF-5 becomes strongly CO₂ selective (5 at 60–100 bar).¹⁰³ Cu-BTC has been reported to be



Fig. 6 Chemical structure of (a) A and (b) faujasite (X and Y) type zeolites.

Table 10 Characteristics of zeolites used in MMMs⁹⁵

Zeolite	Pore size/nm	Si/Al	Cation	Pore volume/cm ³ g^{-1}
3A	0.29	1	K^+	0.197
4A	0.4	1	Na ⁺	0.2
5A	0.4-0.5	1	Ca ⁺²	0.28
13X	0.74	1.2	Na ⁺	0.36
KY	0.74	2.6	\mathbf{K}^+	0.47
Silicalite 1	0.53-0.56	> 500	_	0.18
SSZ-13	0.38	11.8	NH_4	—

very promising for gas separation and purification in industrial applications.¹⁰⁶ MOF-508b with paddle-wheel framework showed high separation of CO₂, CH₄ and N₂ binary and ternary mixtures between 50 °C and 30 °C, but hardly any separation at higher temperatures.¹⁰⁷ Adsorption of CH₄ for MOF-5 and ZIF-8 at low temperature is higher than for H₂.¹⁰⁸

COFs synthesized from light elements (H, B, C, N and O) are a new class of organic frameworks for gas separation and catalytic applications.^{109,110} These materials have rigid structures. high thermal stabilities (up to 600 °C) and low densities. For instance, COF-105 and COF-108 have a much lower density than the highly porous MOFs like MOF-177. They exhibit permanent porosity with specific surface areas exceeding those of zeolites and porous silicates.¹¹¹ COFs appear as 3D, 2D or 1D structure. CO₂ storage in different COFs with 3D (COF-102, COF-103, COF-105 and COF-108), 2D (COF-6, COF-8, COF-10) and 1D (COF-NT) structures has been investigated using atomic simulations.¹¹² The study reported larger free volume, porosity and surface area of 3D COFs than of 2D and 1D COFs. COF-105 and COF-108 showed a very high CO₂ storage capacity, even greater than that of MOF-177. COF-102 and COF-103 showed high adsorption at low pressures owing to compact atomic packing. COF-NT has a similar adsorption to that of CNTs. The study concluded that factors like framework density, free volume, porosity, and surface area are the determining factors in adsorption of CO₂.

7.3 Problems envisaged in MMMs

There are many factors that define MMMs performance¹¹³ (i) Selection of appropriate inorganic fillers and suitable polymer: polymers with low permeability and high selectivity are most suitable for MMMs preparation. (ii) Particle size: smaller particles provide larger interactions between the polymer and the fillers and thereby enhance performance. Their dispersion might be more troublesome. (iii) Particle sedimentation and agglomeration: during the preparation of MMMs, owing to the differences in the physico-chemical properties (among others density and polarity) of the fillers and polymers, filler sedimentation can occur in the MMMs, resulting in inhomogeneous filler and polymer phases. The agglomeration of the fillers results in pinholes that are not reachable by the polymer segments, forming non-selective defects in the MMMs. (iv) Interface morphologies: a poor interaction between the polymer and the inorganic filler that results in interfacial voids. Such non-selective voids allow easy but less selective diffusion of gas molecules. The interfacial interaction between the filler and the matrix has been categorized into three classes based on morphology: (a) 'sieve-in-a-cage morphology', where the non-selective interfacial voids are larger than the penetrating gas molecules. Such voids decrease the selectivity of the MMMs and increase the permeability.^{113,114} (b) 'Leaky interface morphology', where the interface is of molecular scale or sub-molecular scale, resulting in an extra free volume between segments with a small decrease in selectivity and increase in permeability.^{113,115} (c) 'Matrix rigidification morphology', where a reduction in free volume occurs near the sieve surface, resulting in a lower permeability and increased selectivity.113,115

There are still other problems associated with the preparation of MMMs. For instance, poor polymer–filler interactions might occur during the solvent evaporation steps leading to de-wetting of the polymer from the filler surface.¹¹⁶ In addition, the close chain packing in glassy polymers often gets disturbed in the vicinity of the fillers resulting in interfacial voids.¹¹⁷ Other possibilities of interfacial voids are due to repulsive forces between polymer and filler¹¹⁸ and different thermal expansion coefficients for polymer and particle when the membrane is being heated or cooled.¹¹⁹

Some possible solutions to these problems are (i) preparation of highly concentrated polymer solutions in order to increase the viscosity and slow down the particle sedimentation, (ii) rapid membrane preparation will offer the fillers less chance to settle, (iii) a good dispersion of fillers in the polymer matrix can be obtained by matching the polarity of the polymer medium with the particle surface groups, and by controlling film drying conditions. This can be achieved by introducing coupling agents, a kind of compatibilizer between the filler and the polymer matrix, (iv) post-treatment of MMMs (e.g. a zeolite β filled PSf-membrane was soaked in a *p*-xylenediaminemethanol solution before thermal treatment. It resulted in an improved attachment through hydrogen bonding between the polymer matrix and the zeolite surface. A 50% increase in CO₂-CH₄ selectivity followed, as compared to that of the unmodified MMM¹²⁰), (v) development of a priming protocol for preparation of MMMs can also solve adhesion problems. Such typical process involves application of an ultrathin coating of the matrix polymer on the surface of the zeolite particles,¹¹⁸ (vi) the melt extrusion method (e.g. applied to zeolite 13X filled PSf membranes, the dry mixture extruded into thin membrane and heated at 355 °C¹²¹) is another possible way to reduce the occurrence of interfacial voids between polymers and fillers.

7.4 Effects on permeability and selectivity

7.4.1 Zeolites. Zeolite filled rubbery polymers showed significant improvement in the separation of O₂-N₂ and CO_2 -CH₄ compared to the pure polymeric membranes. Silicalite, 13X and KY filled PDMS membranes improved the separation properties of the poorly selective PDMS polymers towards the binary CO₂-CH₄ mixture,¹¹⁴ and also increased CO₂ permeability.¹²² Addition of silicalite to CA increased the CO₂-H₂ selectivity by 85%.¹²³ KY-Matrimid[®] MMMs increased permeability of CO2, but decreased the ideal selectivity of CO₂-CH₄.¹²⁴ Permeability of MMMs (silicalite-PDMS) with different sizes of silicalite showed reduced permeability with decreased particle size, because of increase in the particle surface area and number of interfaces.¹²⁵ When comparing silicalite and NaX filled PDMS, addition of silicalite was found to hinder the movement of the largest molecules, *i.e.* those that could not diffuse through its pores fast enough, such as CH₄. NaX addition to PDMS on the other hand lowered the permeability of all gases. This was explained by the plugging with polymer chains of the pores in NaX, unlike in silicalite-1. Combined with this type of PDMS, the zeolite with the smaller pores thus exhibited better sorption and diffusion properties.126

PSf filled with silica nanoparticles showed an increased permeability and ideal selectivity for CO_2 , CH_4 , O_2 , N_2 and He as referred to in Table 11.¹²⁷ However, the decrease in selectivity for H_2 – CO_2 and CO_2 – CH_4 mixtures with an increase in silica content might be due to poor particle dispersion or agglomeration. PES-4A zeolite modified by Dynasylan Ameo silane-PDMS coated MMMs resulted in defect free membrane and increased CO_2 – CH_4 selectivity by 38% compared to PES membrane. This indicates that undesired non-selective voids in MMMs can be avoided by filler silane surface treatment and PDMS coating.¹²⁸

Often in glassy polymers, the gas permeability increases upon filler addition, as attributed to an increased free volume owing to the lack of chain packing and creation of extra void volume at the interface between polymer and the fillers.¹²⁹ These voids are often created following the poor interfacial compatibility between zeolites and polymer. Sometimes however, these voids do not break down the selectivity. For instance, the incorporation of silicalite in CA, PSf, and PI increased permeability without any change in selectivity. This was ascribed to the formation of interfacial voids due to poor polymer–zeolite adhesion, while leaving an intact membrane skin layer where no fillers perforated.

7.4.2 CMS. The high surface area and well defined pore structure of CMS strongly improved gas separation performance of MMMs by introducing a molecular sieving effect. For instance, CMS in PI and PSf showed increased CO₂ permeability and 40–45% enhancement in CO₂–CH₄ and CO₂–N₂ selectivities.¹³⁰ Likewise, CA with CMS showed increased CO₂–N₂ selectivity. This is attributed to the well defined pore structure of CMS that resulted in a gas separation ruled by size sieving effects.¹³¹ In a similar study, introduction of carbon black in PSf membranes enhanced permeability and selectivity.¹³² However, CMS (Cecalite, W20 and Carbosieve) with PDMS and ethylene–propylene–diene rubber (EPDM) showed no improvement in the separation of CO₂–CH₄, as attributed to the absence of interconnected pores in the applied CMS.¹³³

7.4.3 CNT and MOF. Very recently, incorporation of CNTs and MOFs in polymeric membranes for gas separation has gained attention. Atomic simulations of H_2 and CH_4 in CNTs and zeolites reported faster gas transport rates through CNTs than through zeolites.¹³⁴ This has been attributed to the inherent smoothness of the nanotube pore walls. Furthermore, the study predicted that CNTs could be better suited than inorganic fillers for use in membranes. Acid treated open-ended SWNT in PDMS showed increased gas permeability.¹³⁵ The results were found to agree well with atomic simulation

estimations.¹³⁴ SEM images confirmed a homogeneous dispersion of the fillers in the polymer. At only 2 wt% CNT already, the gas permeability increased most, while at 10 wt% CNT, no significant change in permeability could be observed anymore (Table 12).

COOH functionalized SWNTs incorporated in Matrimid[®] increased permeability in pure gas permeations by 30% without change in selectivity.¹³⁶ In PSf, similar fillers also increased permeability (Table 13).¹³⁷ A good dispersion could only be realized below 10 wt%, with 5 wt% found to be the optimum filler loading. However, the ideal selectivity of the gases decreased for CO2-CH4 but remained almost constant for O₂-N₂ and CH₄-N₂ with increasing SWNT concentrations. SWNT and MWNT addition in brominated poly(2,6-diphenyl-1,4-phenylene oxide) (BPPO) increased CO₂ permeability. The best performance was observed at 5 wt% SWNT and MWNT. Also, addition of CNTs increased the mechanical properties of the BPPO membranes. Similar results were obtained in BPPO for SWNTs that were -COOH functionalized.¹³⁸ A series of benzylamine-modified C60 fullerenes, blended with Matrimid[®], decreased diffusivity and solubility of He, O₂, N₂, CH₄ and CO₂. The reduction in permeability was ascribed to the rigidification of the benzylamine-modified C₆₀ polymer matrix.139

Addition of a MOF (Cu-4,4'-bipyridine-hexafluorosilicate, Cu-BPY-HFS) to Matrimid[®] increased gas permeabilities but decreased ideal CO_2 -CH₄ and H₂-CO₂ selectivities (Table 14).¹⁴⁰ Mixed gas selectivities (Table 15) were still lower, indicating competition between the gas molecules in the mixture for the same active sites, unlike pure gases.

Incorporation of Cu-BTC and Mn(HCOO)₂ in PDMS and PSf showed high adsorption affinity of Cu-BTC for CO₂ and H₂, while Mn(HCOO)₂ showed high adsorption affinity for H₂ only. Higher loadings reduced the gas solubility, but increased the permeability, indicating defective membranes with interfacial voids.¹⁴¹ A 30% MOF-5 loading Matrimid[®] MMMs, without any defects, showed 55% increased CO₂ permeability with 6% increase in CO₂–CH₄ selectivity.¹⁴² This indicates that selection of appropriate MOFs for MMMs is indispensable.

Table 12 Gas permeabilities in pure PDMS and CNTs–PDMS MMMs membranes 135

		Permeability/Barrer							
Membrane	CNTs/wt%	He	H_2	CO_2	O ₂	N_2	CH_4		
PDMS	0	59	70	166	32	12	28		
CNT-PDMS	2	67	79	190	36	14	34		
CNT-PDMS	10	68	79	191	40	17	36		

Table 11 Permeability and selectivity of gases in PSf filled with silica nanoparticles¹²⁷

	Permeability/Barrer					Selectivity		
Membrane (Vol.% silica nanoparticles/PSf)	H_2	He	O_2	CO_2	CH_4	H ₂ -CO ₂	CO ₂ -CH ₄	
0/PSf	11.8	11.8	1.4	6.3	0.22	1.87	28.63	
5/PSf	13.8	13.1	1.8	7.7	0.29	1.79	26.55	
10/PSf	15.9	14.9	2.0	9.3	0.38	1.70	24.47	
15/PSf	22.7	20.1	3.4	12.9	0.62	1.75	20.80	

SWNT/wt%	Permeabi	Permeability/Barrer					Ideal selectivity			
	He	CO_2	O_2	N_2	CH_4	He–CH ₄	CO ₂ -CH ₄	$O_2 - N_2$	CH ₄ -N ₂	
0	7.88	3.90	0.84	0.17	0.17	47.50	23.55	5.07	1.00	
5	10.20	5.12	1.16	0.23	0.27	37.51	18.82	5.04	1.17	
10	10.27	5.19	1.23	0.23	0.28	36.43	18.41	5.35	1.21	
15	8.88	4.52	1.11	0.22	0.28	31.66	16.09	5.10	1.27	

Table 13 Gas permeability and selectivity of gases in SWNT-PSf MMMs¹³⁷

Table 14 Permeability and selectivity of pure gases at 35 °C through Cu-BPY-HFS-Matrimid[®] membranes¹⁴⁰

	Permeabilities/Barrer				Selectivity						
	H_2	N_2	O_2	CH_4	CO_2	$H_2\!/N_2$	$O_2 - N_2$	CO ₂ -CH ₄	H ₂ -CH ₄	H ₂ -CO ₂	CH ₄ -N ₂
Matrimid [®]	17.50	0.22	1.46	0.21	7.29	79.55	6.64	34.71	83.33	2.40	0.95
10 wt%	16.91	0.24	1.44	0.24	7.81	71.04	6.04	31.93	69.15	2.17	1.03
20 wt%	16.75	0.31	1.77	0.36	9.88	54.46	5.76	27.62	46.82	1.70	1.16
30 wt%	20.34	0.31	1.98	0.38	10.36	65.23	6.33	27.45	53.89	1.96	1.21
40 wt%	26.74	0.49	3.06	0.59	15.06	54.78	6.27	25.55	45.38	1.78	1.21

Table 15Mixed gas selectivities of 20 wt% Cu-BPY-HFS-Matrimid[®] membranes at 35 °C¹⁴⁰

Selectivity	Mixture/mol%	Matrimid [®]	MOF-Matrimid [®]	Ideal selectivity
CH ₄ –N ₂	94% CH ₄ -6% N ₂	0.88	1.6	1.16
	50% CH ₄ -50% N ₂	0.90	1.7	
CO ₂ -CH ₄	50% CO ₂ -50% CH ₄	36.3	20.5	27.6
2 4	$10\% CO_2 - 90\% CH_4$	35.1	22.5	
H ₂ -CO ₂	50% CO ₂ -50% H ₂	2.56	2.6	1.70
2 2	75% CO ₂ -25% H ₂	2.43	2.4	

7.5 Strategies to enhance filler-polymer compatibility

Attempts were made to enhance the compatibility between the fillers and the polymer by introducing interactive functional groups like silane-coupling agents. Numerous studies on coupling agents with silane groups have been reported to increase the interaction between the fillers and the polymers. The studies were carried out with silanes reacting with the hydroxyl groups on the zeolite surface, and amino groups or other functional groups in the polymer, thereby forming covalent bonds between the two phases.^{118,143–145}

APTES (3-aminopropyl-triethoxysilane)-modified zeolite 3A with aldehyde-modified PSf showed a more than 4 fold increased H2-CO2 selectivity compared to unsilvlated zeolite.¹⁴³ 2,4,6-Triaminopyrimidine (TAP) was also effective as a coupling agent by forming hydrogen bonds between zeolites and PI. It was used in 4A-PI and 13X-PI MMMs to eliminate the interfacial voids. TAP-PI-13X membrane showed lower gas selectivity and higher permeability, while TAP-PI-4A showed lower permeability but higher selectivity for the above gases. This difference was attributed to the larger pore size of 13X in comparison to 4A.¹⁴⁶ Larger pore sizes facilitate movement of the gas molecules and hence increase the permeability. A (3-aminopropyl)-diethoxymethyl silane (APDEMS)-modified zeolite-PES membrane showed a higher selectivity and permeability than unmodified PESmembranes.¹⁴⁷ Similarly, PSf and zeolites 3A, 4A, 5A and 13X modified with dichlorodimethylsilane (DCDMS) or

aminopropyltrimethoxysilane (APTMS) increased gas selectivity and permeability.¹⁴⁸Table 16 shows the structure of the coupling agents discussed above.

Introduction of trimethylsilyl-glucose (TMSG) to two glassy polymers, (PTMSP) and ethyl cellulose (EC), reported a drastic reduction in gas permeability for PTMSP but significant increase for EC.¹⁴⁹ It was interpreted that TMSG occupied the high fractional free volume of PTMSP and thus restricted the transport. In contrast, TMSG acted as a plasticizer in EC, thereby increasing the chain mobility.

Pore blockage by coupling agents is the most important limiting factor for the usefulness of different kinds of compatibilizers, to increase polymer-filler compatibility. Pore blockage reduces the gas permeability. For example, due to zeolite pore blockage by APTES, CO2 permeability decreased in PI-zeolite-APTES MMMs.150 Chemical modification of polymer prior to addition of zeolites and coupling agents greatly reduces the chances of pore blockage.¹⁵¹ Zeolite SSZ-13 (chabazite) was dispersed in a crosslinkable PI (3:2 6FDA-DAM : DABA) with a propyl monoester chain attached to the DABA monomer for reaction with 1,3 propanediol (PDMC polymer). APDEMS was used as a silane-coupling agent to increase the affinity between the filler and the polymer. The results in Table 17 show the resulting increase in CO₂-CH₄ selectivity up to 47 (mixed gas) and CO₂ permeability up to 89 Barrer, thus surpassing the Robeson's trade-off line. The membranes were found to be resistant to CO₂ plasticization up to 30 bar. Thus crosslinked MMMs can

 Table 16
 Molecular structures of the applied coupling agents



overcome the 'upperbound trade-off'polymer limitations and maintain this property even in the presence of aggressive feed gases. Fig. 4 corresponds to industrially relevant permeability and selectivity values for the gas pairs, which could be in reach of MMMs.

CMS, pretreated with polyvinylpyrrolidone (PVP), showed an improved incorporation in PSf. The study showed considerable improvement in selectivity of modified membranes due to reduction of interfacial voids by PVP.¹⁵²

8. Future challenges for gas separation membranes with respect to biogas separations

The present challenges are as follows:

(i) Selection of membrane materials for biogas separation

Certain material characteristics are indicative of a good prospective membrane for biogas applications. For instance, CO_2 has high affinity for ethylene oxide (EO) units, because of the polar ether oxygen. But pure poly(EO) shows low CO_2 permeability owing to high crystallinity. However, random EO and non-EO units in the polymer chain lead to higher CO_2 -H₂

Table 17 Pure gas and mixed gas separation properties forPDMC-SSZ-13 membranes silanated with APDMES151

Types of membranes	$P_{\rm CO_2}/Barrer$	$\alpha_{\rm CO_2-CH_4}$
Crosslinked PDMC, pure gas	57.5 ± 2.9	37.1 ± 0.7
Crosslinked PDMC, mixed gas	57.5 ± 2.9	44.8 ± 0.7
Crosslinked PDMC-SSZ-13,	88.6 ± 4.4	41.9 ± 0.7
mixed matrix silanated, pure gas		
Crosslinked PDMC-SSZ-13,	88.8 ± 4.4	47.0 ± 0.7
mixed matrix silanated, mixed gas		
Maxwell model, crosslinked	67.0 ± 3.4	49.6 ± 0.7
PDMC-SSZ-13, pure gas predictions		
Crosslinked PDMC–SSZ-13, mixed matrix silanated, pure gas Crosslinked PDMC–SSZ-13, mixed matrix silanated, mixed gas Maxwell model, crosslinked PDMC–SSZ-13, pure gas predictions	51.3 ± 2.9 88.6 ± 4.4 88.8 ± 4.4 67.0 ± 3.4	44.8 ± 0.7 41.9 ± 0.7 47.0 ± 0.7 49.6 ± 0.7

and CO_2 – CH_4 separation and reduce CO_2 plasticization.³³ Thus, the amorphous components of polymer matrix encourage dissolution of CO_2 and enhance permeability. It is thus best to select polymers that are not too crystalline. Polar groups in the polymer chain greatly affect CO_2 solubility. For example, poly(methyl methacrylate) (PMMA) has a greater CO_2 solubility than poly(ethylene terephthalate) glycol modified (PETG) owing to the different positioning of the ester group. The CO_2 access to the main chain ester group in PETG is more difficult than in PMMA which has the side chain ester functionality¹⁵³ (Table 9).

(ii) Selection of suitable candidates for polymer blending

Polymer blending is usually done to improve the mechanical, rheological, anti-plasticization and degradative properties of membrane. Polymer blending is effective only when the polymers are well miscible on molecular scale and both possess good mechanical strength. Good candidates for CO_2 -CH₄ separations are *e.g.* PI with PC, PSf, PES, PBI, copolyimide P84...^{86,89,154,155}

(iii) Selection of suitable fillers and synthesis of defect-free MMMs

Addition of fillers (*e.g.* zeolites, CMS, CNTs, MOFs and COFs) to polymer materials can provide high performance gas separation MMMs, on the condition that defects at the filler–polymer interphase can be avoided. This is often really challenging, but proper strategies have been discussed above to tackle this. Moreover, proper matching of the intrinsic permeability and selectivity of the support matrix and the fillers is necessary to allow surpassing the Robeson's trade-off upper boundary curve.

(iv) Selectivity of mixed gases is lower compared to pure gases. This issue is very important for scale-up of polymeric membranes for gas separations. Higher CO_2 -CH₄, H₂-CO₂ and H₂S-CH₄ selectivities are still required for MMMs, maintaining at least equivalent permeability to that of pure membrane under different operating conditions.

9. Possible strategies

Some potential routes to reach better performing gas separation membranes for use in biogas upgrading are discussed in the following section. Based on the extensive research work carried out over the last two decades towards increasing selectivity and permeability through polymeric membranes and reducing plasticization in presence of sour gases, three strategies can be identified: (i) modification of the chemical structure of polymer materials (ii) mixed matrix membranes and (iii) polymer blending.

Chemical modification reduces the chances of plasticization and prevents the polymer material from swelling in the presence of plasticizing gases and increases its thermal stability.^{62,143} It also reduces physical ageing. Such membranes maintain their transport properties under different operating conditions.

Defect-free MMMs are a first alternative to improve membrane transport properties. Proper selection of the desired molecular sieve materials for a particular application and of the compatible polymer is critical. The cost of fabricating high performing MMMs would be close to that of the conventional polymeric membrane fabrication.¹⁵⁶ Introduction of silanecoupling agents to increase the compatibility between the fillers and the polymer is an important way to avoid defects in MMMs. Also, application of appropriate priming protocols to pretreat the filler before addition to the polymer solution has proven to be a good option to realize void-free MMMs. The application of a thin coating of a highly permeable polymer, typically PDMS, on MMMs can drastically reduce the possibility of non-selective voids and improve membrane performance.

Polymer blending can be considered to further optimize membrane properties. It is often difficult to find two compatible polymers suitable for blending, but studies reveal that certain polymer blends respond quite well, *e.g.* blending PSf with an aromatic PI. In addition, this particular polymer blend membrane had an increased permeability with minor change in selectivity.

10. Conclusions

Production of biogas is a mature technology that is well established worldwide, but its commercial utilization is still limited as the gas needs to be purified before on-site use or transportation. Among the various biogas purification processes, membrane technology is a relatively recent technology but very promising. 90% of the total biogas separations discussed in literature are carried out by only 8 or 9 polymer materials. Further research towards better performing membranes, *i.e.* with higher permeability, selectivity and stability (mainly restricted plasticization), is currently underway. This might include specialty polymers for which cost and lifetime can become critical issues.

Inorganic membrane materials have been reported to produce selectivities that are 5–10 fold higher than that of conventional polymeric membranes. However, polymeric membranes have several advantages over inorganic membrane materials making them more economical and thus dominate the membrane gas separation market. Furthermore, their low cost and inter-segmental flexibility make polymeric membranes easy to be fabricated into asymmetric hollow fibers or flat sheets, both commonly used in industrial applications. Many different polymer families have been investigated as gas separation materials such as PC, CA, polyesters, PSf, PI, polypyrolones. PI and CA-based membranes were found to be the most suitable commercial membranes for biogas separation and enrichment.

Polymeric membranes are often still associated with several problems, *e.g.* incapable of maintaining constant permeability and selectivity at different operating conditions and in the presence of contaminants (in particular H₂S, siloxane and other volatile organics for biogas), mainly because of the deleterious effect of plasticization. A significant amount of work to understand and overcome the associated problems with polymeric membranes has been accomplished over the last two decades. The attractiveness of polymeric membranes is evident by increasing numbers of papers in peer-reviewed journals and patents. Selectivity issues of H_2S and CO_2 over H_2 and CH_4 are still important. For instance, membrane materials characterized by a mixed gas CO_2 -CH₄ selectivity of about 20 or more, and a mixed gas H_2S -CH₄ selectivity of 25 or more, would ensure better CO₂ and H_2S removal, and would even target the US pipeline specifications.

The development of more targeted polymers, *i.e.* new crosslinked polymers and polymers with different side chains and backbone modifications, would be a major step forward towards the development of better membrane materials. It would reduce plasticization and improve membrane longevity. Defect-free MMMs, with and without introduction of appropriate coupling agents, would be an added advantage to the above modification and ensure improved selectivity without reduction in permeability. This would eventually improve membrane market value and industrial acceptability.

Abbreviations

6FDA-	2,2'-Bis(3,4-dicarboxyphenyl) hexafluoro- propane dianhydride					
-HAR	3 3'-Hydroxy diaminobenzidine					
- <i>n</i> -PDA	1 4-Phenylenediamine					
-TMPDA	2 4 6-Trimethyl-1 3-phenylenediamine					
-m-PDA	1 3-Phenylenediamine					
-m-DDS	3 3'-Diaminodiphenylsulfone					
-DAT	2 6-Diamino toluene					
-ODA/NDA	4 4-diphenylene oxide/1 5-naphthalene					
APDMES	(3-Aminopropyl)-diethoxymethyl silane					
APTES	3-Aminopropyl-dethoxysilane					
APTMS	A minopropyl-trimethoxysilane					
RAPAF	2 2-Bis(3-amino-4-hydroxynhenyl)-					
DIMIN	2,2-Dis(5-animo-+-nydroxyphenyl)-					
RETX	Benzene ethyl benzene toluene and xylene					
RPP()	Brominated poly(2.6 diphenyl 1.4 phenylene					
biio	oxide)					
RTMSPSF	Bromobisphenol-A trimethylsilylated					
DIMOISI	nolvsulfone					
CA	Cellulose acetate					
CH.	Methane					
CMS	Carbon molecular sieves					
CNG	Compressed natural gas					
CNTs	Carbon nanotubes					
CO	Carbon dioxide					
COFs	Covalent organic frameworks					
CTA	Cellulose tri acetate					
Cu-BPY-HFS	Cu-4 4'-bipyridine-hexafluorosilicate					
CuBTC	Copper(u)-benzene-1 3 5 tricarboxylate					
DABA	3 5-Diaminobenzoic acid					
DAM	Diaminomesitylene					
DAP	2 4-Diaminonhenol dihydrochloride					
DCDMS	Dichlorodimethylsilane					
DMEA	<i>N N</i> -Dimethylaminoethyleneamine					
EC	Ethyl cellulose					
EPDM	Ethylene_propylene_diene_rubber					
FeCl ₂	Ferric chloride					
FFV	Fractional free volume					
IRMOFs	Isoreticular metal–organic framework					
LPG	Liquified petroleum gas					
MMM	Mixed matrix membrane					
Mn(HCOO) ₂	Manganese(II) formate					
MOF	Metal–organic framework					

MWNTs	Multi wall carbon nanotubes
NaOH	Sodium hydroxide
PA	Polyaramide
PBI	Polybenzimidazole
PC	Polycarbonate
PDiA	Propane-1,3-diamine
PDL	1,3 Propanediol
PDMS	Polydimethyl siloxane
PEG	Poly(ethylene glycol)
PES	Polyethersulfone
PEI	Polyetherimide
PETG	Poly(ethylene terephthalate) glycol
PI	Polyimide
PMMA	Polymethyl methacrylate
PMP	Polymethylpentene
PMPS	Poly (dimethyl, methylphenyl siloxane)
PO	Polyocenamer
PoI	Polyisoprene
PPG	Poly(propylene glycol)
PPGDA	Poly(propylene glycol) diamine
PPO	Polyphenyleneoxide
PSf	Polysulfone
PTMSP	Poly(1-trimethyl-silyl-1-propyne)
PU	Polyurethane
PVP	Polyvinylpyrrolidone
PVTS	Polyvinyltrimethylsilane
SAPOs	Silico aluminophosphates
SEM	Scanning electron microscope
Si-DDR	Decadode casil 3R
SWNTs	Single wall carbon nanotubes
TAP	2,4,6-Triaminopyrimidine
$T_{\rm g}$	Glass-rubber transition temperature
TMPSF	Bisphenol-A trimethylsilylated polysulfone
TMSG	Trimethylsilyl-glucose
VMS	Volatile methyl siloxanes
VOC	Volatile organic compound
ZIF 8	Zeolitic imidazolate
ZnBDC	Zn (BDC = 1,4-benzenedicarboxylate,
	4,4'-bipyridine)

Acknowledgements

S.B. and A.L.K. acknowledge the MIP-project (Milieu- & Energietechnologie—Innovatieplatform, Berchem, Belgium) for grants as doctoral research fellow. A.C.O. acknowledges the *Departament d'Universitats, Recerca i Societat de la Informació* (DURSI) from the *Generalitat de Catalunya* for the postdoctoral scholarship awarded. We thank K. U. Leuven for support in the frame of the CECAT excellence and the Flemish Government for the Methusalem funding and the Federal government for an IAP-grant.

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