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REVIEW PAPER

Effect of nanofillers on selectivity of high performance mixed matrix membranes for separating gas mixtures

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Abstract−Techniques for separation of gas mixtures obtained from various sources, such as effluents from industries, and biogas, have always fascinated researchers. The advent of mixed matrix membranes (MMMs) has opened up a new window of opportunity for developing membranes coupled with flexibility, processability, and permeability of polymers and selectivity of inorganic nanomaterials. This review is a detailed overview of the effect of various nanofillers on the separation performance of MMMs including the major factors affecting the perm-selectivity and possible solutions for overcoming the emerging challenges. The paper also presents contemporary approaches for cost-effective implementation of MMMs. Methodologies for designing MMMs with improved interfacial morphology to exploit their full potential in tailoring the selectivity efficiency are also discussed in detail. This review can act be a guideline for the future development of high-performance MMMs for industrial applications without compromising long-term separation performance, durability, and stability to processing conditions.

Keywords: Gas Separation, Mixed Matrix Membranes, Nanomaterials, High Performance Polymers

INTRODUCTION

Emission of effluent gases from industries has been a major driving factor for changes in climatic conditions and increase of pollution in the environment. Separation and purification of these gas mixtures for isolation of products and recovery of reactants have always fascinated scientists and researchers, as a potential option towards environmental protection. For the last few years, membrane technology has been serving as a possible alternate choice in industries for separating and purifying these effluents. This technology offers relevance through reducing the environmental problems and costs by providing opportunities to conduct gas separation with minimal consumption of energy since no phase transition and regeneration of solvent is needed [1,2]. This separation process facilitates simple, inexpensive filtration through a clean process, feasibility under mild operation conditions, modular configuration, compact size, light weight, mechanical robustness. Moreover, this technology allows long-term stability of the membrane in the specified process environments with excellent separation performance. The configuration of the membrane for separation process depends mostly on the significant application areas where it will be implemented. A recent survey reveals a steady growth of ~30% of worldwide membrane market, and it is estimated that by 2025 the dependency on membrane-based gas separation would as high as five times the current status [3].

Transport of gases between the 'permeate' and 'retentate' phases can be modulated by the materials used for fabrication of membrane and the operating conditions such as pressure, temperature and concentration gradient apart from chemical potentials of components on feed and permeates side [1]. The targeted gas molecules are transported through transient free volume gaps in the membrane and these gaps mostly arise due to the thermal motion of polymeric chain segments [4,5]. The feed species penetrate through the membrane according to their size, solubility and diffusivity difference. Permeability portrays the potential of a particular feed component to drive through the membrane. Concurrently, selectivity is defined as the ratio of more permeable component to that of less permeable. The crucial physicochemical points influencing both these considerations are (i) flexibility of polymeric chains, (ii) intersegmental spacing stipulated by the free volume gaps within the polymeric chain segments, and (iii) the interactions between penettrant and polymer [3]. Two other important factors, including diffusivity and solubility, also play important roles in regulating the gas transport mechanism. The equilibrium between solubility selectivity and diffusivity selectivity determines the separation performance of feed components in gas mixtures [6]. Simultaneous improvement of both permeability rate and selectivity of a target gaseous species is the salient factor for the subsequent development of membranes and its successful utilization in large-scale industrial gas separation manipulations. Better permeability of the resulting membrane indicates better productivity and reduces the principal cost of the membrane units meantime; higher selectivity leads to more efficient separation of the target gas product. However, the chemical interaction between membrane materials and target gas penetrant to be separated determines the selectivity performance and its profitable implementation of large-scale industrial gas separation appli-

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Table 1. Kinetic Diameters and critical temperatures of various investigated gaseous species

Feed components	Kinetic diameter (A^o)	Critical temperature Tc (k)
Helium (He)	2.60	5.2
Water (H_2O)	2.65	647
Hydrogen (H_2)	2.89	33
Carbondioxide (CO_2)	3.30	304
Nitrogen (N_2)	3.65	126
Methane (CH_4)	3.80	191
Carbon monoxide (CO)	3.76	132
Oxygen (O_2)	3.46	118
Hydrogen sulphide (H_2S)	3.6	212
Argon (Ar)	3.40	175

cations.

Two important factors that predominantly affect the selectivity efficiency of the resulting membrane include critical temperature and kinetic diameter of the penetrant gases. The critical temperature correlates with condensability; the gases with higher critical temperature can able to permeate at a faster rate compared to lower one. This usually occurs with the utilization of rubbery polymers as continuous phase for fabrication of membrane. On the other hand, the diffusivity of the gas is dependent on the kinetic diameter of the gas molecules.

Table 1 depicts the kinetic diameter and critical temperatures of various feed components depending upon which only the targeted penetrants are transported throughout the membrane with acceptable separation efficiency.

Fig. 1 depicts the diagram of a membrane which separates various gas mixtures.

Dense polymeric membranes are the most potential candidates for industrial gas separation applications. Based on the applicability of polymeric membrane, it may be categorized as rubbery polymers, which separate gas mixtures based upon condensability, while glassy polymers segregate based on inequality of molecular size or kinetic diameter between the feed components [7]. Robeson explained the challenging reasons behind the performance trade-off in the case of polymeric membranes, i.e., selectivity is hampered with the increase rate of permeability and vice versa. Several other limitations, including high-temperature instability, swelling, poor chemical and thermal resistance and decomposition in most of the organic solvents [8] have substantially hindered their wide-ranging applications to separation processes.

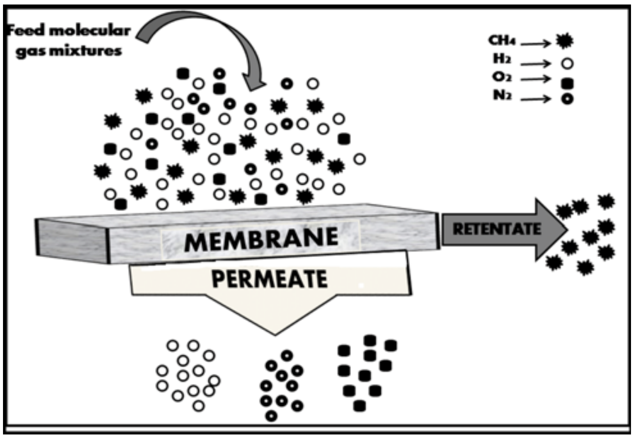


Fig. 1. Schematic diagram of a membrane for separating the different gas pair.

This has further motivated for the selection of inorganic membranes made of metals or pyrolyzed carbon, for overcoming most of the above drawbacks through the employment of polymeric membranes for gas separation applications. These inorganic membranes possess better molecular size discrimination, chemical selectivity, solvent-resistant properties, thermal stability, longer life span and resistance to swelling-induced plasticization [9]. However, the commercial scalability of these membranes is remarkably limited due to the high capital cost of the membrane fabrication, brittleness, low surface-to-volume ratio complexity in operation and deficiency of considerable technology for the development of continuous defect-free high performance membrane with acceptable separation characteristics [10,11].

Interest has thus been directed towards developing a new material, mixed matrix membrane (MMM), to overcome the complications arising from the utilization of trade-off limitation of polymeric and economical consideration of using inorganic membranes for gas separation applications. These MMMs are interpreted as organic-inorganic hybrids comprising both highly selective rigid filler phases dispersed in a continuous polymeric matrix phase. The incorporation of this filler phase with particle size close to the characteristic size of the macromolecules provides superior separation performance compared to the utilization of individual continuous or dispersed phase membrane. Carbon molecular sieves (CMS), zeolite, metal organic frameworks (MOFs), zeolite imadazole frameworks (ZIFs), carbon nanotubes (CNTs), silica, metal oxides are some of the high ranking filler, mostly used for fabrication of membrane for gas separation applications. The collaboration of both continuous and dispersed phases in the resulting membrane has evolved with synergistic effect: the rigid adsorptive filler phase contributing to high productivity and selectivity, while the polymeric phase provides desired mechanical strength, flexibility and hence processibility [12,13].

Separation of the various gas pair to acquire a certain level of purity of the target gas species occupies an essential position in the chemical feed stock industries. The primary membrane-based separation processes involve H_2/CO_2 separation of hydrogen production, CO_2/N_2 separation in flue gas or lime oven exhaust gases, CO_2/CH_4 separation for natural gas treatment or for biogas upgrading, removal of volatile components from effluent streams and O_2/N_2 separation for production of oxygen enriched air or pure nitrogen are the most currently used industrial gas separations through the membrane technology [14].

The present contribution reviews the potential of diverse inorganic fillers, especially prioritized for the prospective exploitation of CNTs as promising fillers which have the competency to achieve superior separation properties and frequently used polymers for fabrication of high performance mixed matrix membranes (MMMs) for a wide range of industrial gas separation applications. Moreover, the factors affecting the selectivity efficiency of MMMs and corresponding permeability have also been reviewed in detail. Various strategies for improving the membrane quality to achieve higher separation performance with desired interface morphology and concurrently overcoming the challenges arise in the way of successful industrial implementation of MMMs have been addressed in details.

MIXED MATRIX MEMBRANES (MMMs): CONCEPT AND BENEFITS

Hybridizing both polymeric and inorganic membranes would result in synergistic improvement of separation efficiency and thus, the new class of MMMs has attained great demand as a next generation membrane for various industrial gas separation applications. MMMs have potential to enhance both permeability and selectivity while improving permeability or elevating selectivity at constant permeability. The utilization of two different materials for fabrication of membrane with divergent properties such as density, flux, and different permeation characteristics leads to feasibility for enhancing gas separation performance of MMMs [15]. Incorporating suitable inorganic fillers in polymeric matrices can provide a significantly improved performance of the membrane with better stability to the processing environments, but a minimal compromise can be attained in processability and cost. The rigid adsorptive-type dispersed phase contributes towards achieving better separation properties which can overcome the upper bound trade-off line, while the continuous phase has the perfect membrane-forming ability [16]. The behavior of filler phase, including a large surface-to-volume ratio of these inorganic fillers, facilitates chain packing, enhanced free volume and maximum gas/filler interaction, thus exhibiting the perspective capability to tailor the gas separation performance. MMMs are generally characterized by higher flexibility, durability, and stability while maintaining other advantages like targeted functionalities, enhanced physical, mechanical, thermal properties and adaptability to harsh processing environments [17]. In the case of MMMs, the selected inorganic fillers upgrade the gas selectivity efficiency depending on homogeneity and uniformity of their dispersion throughout the matrix phase; even at a very low concentration, they are able to alter the entire performance of the polymeric membranes. Currently, the exploitation of MMMs propounds the rapid, minimal energy consumption and lower cost effective route to be utilized as next generation commercial membranes for separation of various gas pairs of huge industrial gas separation application processes. Numerous reports previously demonstrated that MMMs have shown tremendous improvement in separation performance with superior desired characteristics in comparison to their membrane counterparts both polymeric and inorganic membrane [18]. The various aspects that can influence the interface morphology and consequently affect the separation properties are: (i) intrinsic properties of both phases, (ii) morphology and polarity of MMMs, (iii) uniform dispersion and proper alignment of fillers throughout the matrix phase, (iv) interfacial defects such as void formation and matrix chain rigidification around the filler particles (if any), and (v) fabrication methods of MMMs (Ahn Chung et al., 2008) [19].

Polymer nanocomposite membranes manifest apparently different permeability and selectivity performance in contrast to their isolated complementary polymeric and inorganic membranes. The distinguishable changes in behavior have been recognized because of the incorporation of these specific inorganic fillers and its beneficial effects on the membrane performance, which are summarized as follows:

- The specific interaction between nanofillers and polymer matrix may disrupt the polymer-chain packing, thereby leading to more “relaxed” structure. Furthermore, the increased tortuosity pattern and rigidification of the polymeric chain because of the intimate contact between both polymer and filler phase conduct for the decrement in gas diffusivity characteristics and consequently result in an enhancement in membrane separation performance [12].
- The nature of the interaction between nanofillers and feed components can possibly change the solubility of penetrant gases in the membranes. For example, functional moieties on a filler surface like OH- that tends to interact more strongly with polar molecules like carbon dioxide (CO_2), sulfur dioxide (SO_2). This confirms that the presence of functional groups on the surface of fillers has an influential role on the separation performance of the resulting membrane [13].
- The non-selective voids at the polymer-filler interface are formulated primarily due to the difference in physical properties between both the continuous and dispersed phases deteriorate the separation performance of the membrane. Moreover, strong bonds providing extra links and contacts between fillers and polymeric chains can eventually hinder the permeation of gas molecules [15,16].

Nevertheless, the decisive consideration for large scale fruitful implementation of the membrane includes (i) inherent permeability of membrane, (ii) resistance to swelling induced plasticization, (iii) better interaction with one of the components of gas mixtures, and (iv) ability to obtain defect-free interfacial morphology with superior separation performance. MMMs’ structure can be controlled by either the cross-linking degree of the polymer matrix or the types of connection bonds between polymer and inorganic phases in the composite material. Suitable selection of membrane forming materials, additionally good interaction between two phases, control of filler concentration, surface functional groups, the affinity of fillers towards the gases to be separated and their dimensions are essential factors to be considered to achieve a synergistic defect-free MMMs performance [3].

Consequently, the performance of MMMs in the gas separation field of large-scale industrial application is still needs to be figured out with the development and interpretation of new techniques and methods for the formation of defect-free, longer life span membrane along with the aim to attain high separation efficiency with better purity of the target gas product. This complication is predominantly attributed to the obstructions to develop membrane materials with the desired characteristics, difficulties appear during the preparation of defect-free membrane with acceptable enhancement simultaneously in permeability, selectivity properties, and long-term separation performance. However, the most significant challenges persist in preparing industrially efficient MMMs,

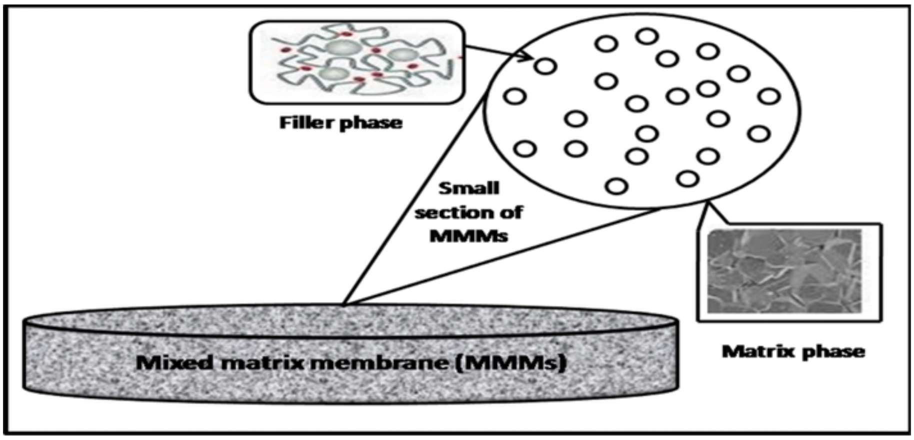


Fig. 2. Diagram for a Mixed Matrix Membrane for gas separation.

including better separation performance for target gas species, greater chemical and physical resistance to higher operating conditions, even at excessive filler loadings as well as with improved thermal stability and durability. The interface morphology in MMMs is one of the predominant factors which have the ability to regulate the permselectivity performance of the as-synthesized membranes. The development of better polymer-filler interfacial compatibility with defect-free morphology and homogeneous dispersion and proper distribution of filler within a matrix phase are the most complicated challenges that are limiting the successful implementation of hybrid membranes of large-scale industrial gas separation applications. Fig. 2 displays MMM comprising the desired matrix and dispersed filler phase for separation of target gas with remarkable selective performance compared to both polymeric and inorganic membrane.

1. Applicability of Different High Performance Polymers for MMMs

The endeavor to coordinate the basic structure of composite membrane materials with superior permeability and selectivity has promoted the utilization of different polymeric phase to attain significant improvement in gas separation performance of the membrane. It is effectively demonstrated that chemical structures coupled with subtle physical properties of the polymeric material have a direct impact on permeability and selectivity performance of the membrane. Even through the selection of appropriate inorganic fillers, it has been established that special attention should be given to the choice of the suitable polymer as the hosting matrix for the fabrication of MMMs [8]. Basically, the predominant benchmarking properties for choosing specific polymeric materials for preparation of MMMs include chemical resistance, processing flexibility, better sorption capacity, price, ability to resist swelling induced plasticization stability at moderate temperatures and good mechanical strength. However, the selected polymer should have good interaction with the dispersed filler phase, and also with one of the feed component of the gaseous mixture for inducing effective separation performance. Several other properties of polymeric phase that affect the separation characteristics of the resulting membrane include free volume content, molecular structure, inter-segmental chain spacing (d-spacing), crystallinity, cross-linking, polarity, average molecular weight, the degree of crystallization, and glass transition temperature. Nevertheless, the transport properties of the gaseous species are actively dependent on the adhesion and better affinity between the filler and bulk phases and appropriate interfacial contact between them [9].

Both rubbery and glassy polymers can be accepted as continuous phase for the preparation of MMMs. Rubbery polymers are soft and elastic due to the flexibility of polymer backbone segments and depicted to perform above the glass transition temperature; whereas glassy polymer is rigid and tough with low intersegmental mobility, emerging from steric hindrance along the polymer backbone and operating below the glass transition temperature. Glassy polymers are mostly used as polymeric matrices for fabrication of MMMs, as they provide a rigid and high-strength structure, with better thermal stability, resistance to many solvents, more free volume gaps and better separation performance compared to that of rubbery materials [11]. Therefore, some researchers adopted glassy polymers as the continuous matrix phase instead of rubbery polymer for the preparation of MMMs because the separation competence of the former is below the upper bound limit. The MMMs obtained from glassy polymers evolve increased selectivity with lower permeability, whereas with the utilization of rubbery polymers, high permeability can be obtained with the cost of low selectivity due to the paucity of polar groups, the absence of crystallinity and low degree of cross-linking [8]. Hence, high permselectivity can only be obtained with polymers having rigid backbone structures and inter-segmental gaps, i.e., high T_g and resistance to plasticization. Generally, rubbery polymers show low selectivity for common gas pairs such as O_2/N_2, H_2/CH_4, and CO_2/CH_4, whereas glassy polymers display higher selectivity performance with lower permeability for different gas pairs. The current research focuses on the utilization of various glassy polymers such as polysulfone (PSf), polyethersulfone (PES), polyetherimide (PEI), polyimide (PI), cellulose acetate (CA), poly (phenylene oxide) (PPO), polycarbonate (PC), polyarylates with higher intrinsic perm-selectivity [8], as the bulk phase with acceptable membrane forming qualities with the aim of achieving superior performance in terms of both higher permeability and selectivity [7]. Currently, the new class of promising polymeric materials that are mostly used for

Table 2. Transport properties of some commercially used polymers for fabrication of MMMs [7-11]

Commercial polymers	Permeability				
	H_2	N_2	O_2	CH_4	CO_2
Cellulose acetate (CA)	2.63	0.21	0.59	0.21	6.3
Ethyl cellulose	87	3.2	11	19	26.5
Polycarbonate (PC)	--	0.18	1.36	0.13	4.23
Polydimethylsiloxane (PDMS)	550	250	500	800	2700
Polyimide (PI)	28.1	0.32	2.13	0.25	10.7
Polymethylpentene	125	6.7	27	14.9	84.6
Polyphenyleneoxide (PPO)	113	3.81	16.8	11	75.8
Polysulfone (PSf)	14	0.25	1.4	0.25	5.6
Polyetherimide (PEI)	7.8	0.047	0.4	0.035	1.32

fabrication of high-performance MMMs with better separation efficiency and other esteemed properties include thermally rearranged (TR) polymers, polymers of intrinsic microporosity (PIMs) and perfluoropolymers.

Table 1 displays the transport properties of different gases by some commercially used polymers.

Fig. 3 depicts a systematic comparison between favorable utilization of glassy and rubbery polymers for gas separation application to achieve superior separation performance.

2. Effects of Different Nanofillers in MMMs

Inorganic fillers possess unique structural and transportation properties for separation of various gas pairs; they offer high temperature resistance, mechanical and chemical stability when dispersed within the continuous matrix phase and provide better performance in terms of higher selectivity efficiency than conventionally prepared membranes. The specific characteristics of these fillers that are responsible for modulating gas separation performance include nanofiller material type, dimension, density, morphology, pore size, dispersion and distribution of filler throughout the polymeric matrix phase [13]. The dominant variables that customarily influence the suitable selection of filler phase mainly are the chemical structure of filler particles, its surface chemistry, particle size distribution, textural properties and aspect ratio. However, dispersion and distribution of fillers within the matrix phase, compatibility and interaction between both the phases, the presence of different functional groups on the filler surface are the key points for successful industrial implementation of MMMs for divergent gas separation applications [18].

Basically, two types of inorganic fillers are used in MMMs: porous and non-porous. The transport of gas molecules through non-porous fillers (such as nanoclay, silica and metal oxide) depends upon solubility selectivity. They disturb the packing of polymeric chains and enhance the free volume gaps within the chain segments, which facilitates the transport of gases. But substantial matrix tortuous pattern established through the use of this kind of filler particles leads to the decrement of diffusion of gas molecules and hence diminishes the performance. On the contrary, porous type fillers have a concise aperture, discriminate the gas molecules according to their size and shape differentiation; thereby, the transport takes place through the diffusion process [20]. Porous fillers are mostly encouraged as their distribution is more uniform and homogeneous in the matrix phase as compared to the micro-sized particles, since smaller particles yield more polymer/particle contact area and also support for enhancing the interfacial compatibility between both the continuous and dispersed phases. Hence, the adaptation of porous type fillers as dispersed phase to fabricate of MMMs for gas separation application is considered to be a more effective and coherent option to accomplish exceptional separation performance of the membrane. Carbon molecular sieve (CMS), carbon nanotube (CNT), metal organic framework and zeolite are some common examples of porous type fillers frequently used for fabrication of MMMs for various gas separation applications [16].

2-1. Metal Oxide Nanoparticles

Metal oxide nanoparticles such as magnesium oxide (MgO), zinc oxide (ZnO) and titanium dioxide (TiO_2) are prominent materials for the membrane-based gas separation process. These particles are combined with attractive properties, including high specific area, higher stability, and a better potentiality to be dispersed indi-

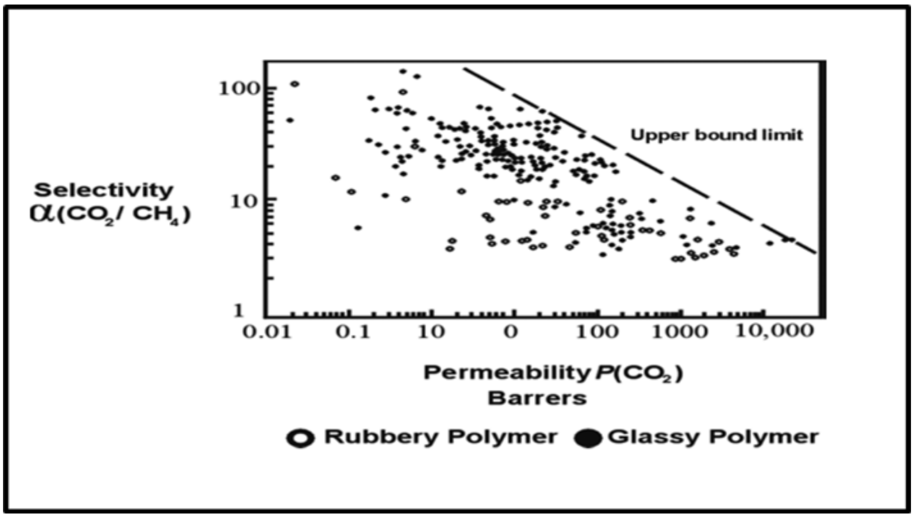
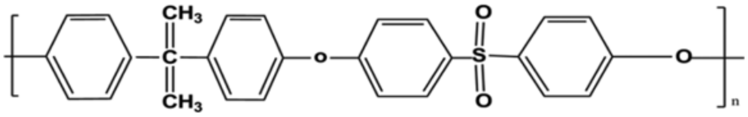
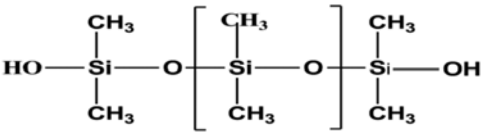
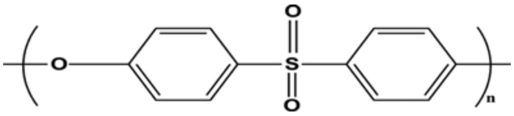
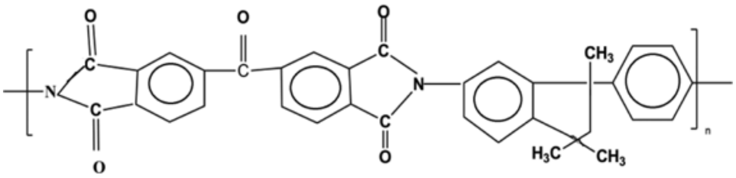
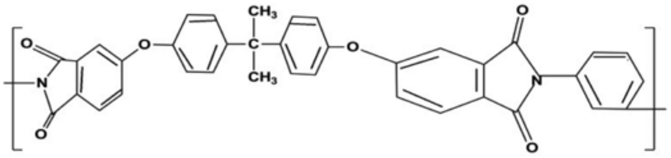
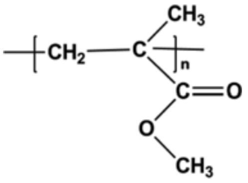
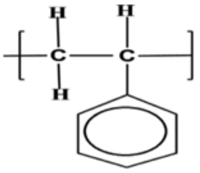
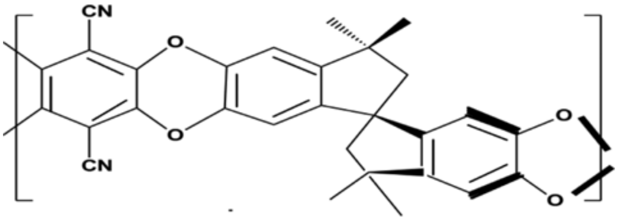
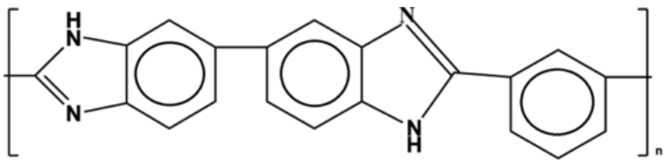
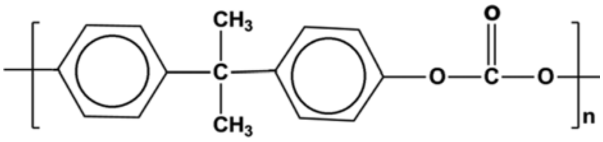


Fig. 3. Comparison between performances of rubbery and glassy polymers for separation of a CO_2/CH_4 gas pair.

Table 3. List of different polymers with structures used for MMMs

Polymer	Structure
Polysulfone (PSf)	
Poly(DimethylSiloxane) PDMS	
Polyethersulfone (PES)	
Polyimide (MATRIMID)	
Poly etherimide (PEI)	
Polymethylmethacrylate (PMMA)	
Polystyrene (PS)	
Polymer intrinsic microporosity (PIM)	
Polybenzimidazole (PBI)	
Polycarbonate (PC)	

vidually and uniformly throughout the bulk phase, thus inhibiting the chances for agglomeration and aggregation of filler particles. Proper dispersion of filler particles within matrix phase prevents the generation of non-selective voids at nanoparticles/polymer matrix interface, thus improving the performance of membrane by significantly enhancing permeability while maintaining selectivity efficiency at a constant or favorable rate [21,22]. The average pore size of this filler is much larger than the kinetic diameters of different gas species, particularly for CO_2; thus the permeability increases as a function of particle content and significantly the selectivity drops. Research works associated to MgO, ZnO and TiO_2 inserted into MMMs have been described previously by many authors [23-26].

2-2. Layered Silicates

Incorporation of layered silicates into the matrix phase can enhance mechanical, dimensional, thermal, and barrier performance of the resulting membrane, even at very lower percentages of filler loading. The filler particles are able to disperse as individual layers with an aspect ratio of 1000 (for fully dispersed individual layers) throughout the matrix phase during the fabrication of membrane [1]. The uniform, homogeneous dispersion of filler phase improves the separation performance of MMMs with a better or constant level of permeability. The existence of this filler phase in polymeric matrix diminishes the free volume, thus influencing sorption process, which can be particularly suitable for separation of more condensable gases. This clay is considerably accepted for MMMs, since it possesses reasonable characteristics such as easy availability, compositional variability, acceptable pore size, suitably costwise and the most essential factor is environmental friendliness. Different studies [27-29] conducted on such clay minerals as promising inorganic fillers for transportation of gas molecules showed sufficient improvement in separation performance.

2-3. Graphene Oxide (GO)

Graphene is a crystalline allotrope of carbon with SP^2 bonded atoms having molecular bond length 0.142 nanometers. It is a impermeable filler with high aspect ratio. It has a high electronic density for the carbon rings, so can repel atoms and gas molecules and offers very low solubility to maximum penetrant gases. It is inert and has poor dispersion in many solvents as well as imperfect interfacial interaction with the continuous polymeric matrix. Therefore, the prepared membrane will be not that much efficient and effective for gas separation purpose. So it is inevitable to introduce active functional groups on its planar sheet in order to formulate its adeptness as reasonable filler for fabrication of membrane, which can be profitably proposed for gas separation applications. The attachment of these functional groups such as epoxy, hydroxyl and carboxyl groups on the filler surface can alleviate the chances for agglomeration and aggregation tendency and improve its dispersion in polymeric phase; thus, the homogeneous and uniform dispersion of filler throughout the matrix can directly influence membrane gas separation performance [31]. After incorporating functionalized graphene into the polymeric matrix, it creates a tortuous path in the composite membrane to allow the gas with the smaller size to effortlessly pass through; meanwhile, the gas molecules with larger size are hindered from passing. The resulting membrane separates the penetrant gases according to their size selective nature with acceptable membrane performance. Currently, many studies have been conducted on using oxidized graphene GO (the oxygen-containing groups contributing to the formation of interacting sites with the polymeric chains) as filler for fabrication of MMMs for separation of various gas pairs [32,33].

2-4. Zeolites

Zeolites are silicalite or aluminosilicate microporous crystalline materials with tetrahedral structure, consisting of elements of Si and Al with cations such as Na, K, Ca and Mg. It can be demonstrated by empirical formula of $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ where M is the alkali or alkaline earth atom, n is the cation valence, x is a number from 2 to 10, and y is a number from 2 to 7 which represents the Si/Al ratio, porosity of the framework and the existence of cations, respectively [16]. This inorganic filler exhibits fascinating sorption and diffusion characteristics because of its accurate size and shape discrimination nature, resulting from the narrow pore distribution. CO_2 adsorbs stronger on zeolites than other light gases such as H_2, CH_4, and N_2 because CO_2 has a higher molecular weight and electrostatic quadrupole moment. Although there are more than 190 zeolite structures investigated, only 20 have been shown to give authentic separation. Several reports [35-37] have suggested a favorable outcome by incorporating zeolite in the matrix phase for a variety of gas pairs. Most of the research indicated that the type of zeolite with pore sizes ranging from 4 to 10 Å incorporated within the matrix phase has greater impact on the gas separation properties. Zeolite-4A and Zeolite-L have emerged as the potential fillers for ensuring superior selectivity and improving the long-term performance of the resulting membrane in contrast to the utilization of other type of zeolites for fabrication of MMMs [35].

2-5. Silica Nanoparticles (SiO_2)

Silica nanoparticles are among the most widely used inorganic fillers for fabrication of organic-inorganic composite membranes for gas separation applications due to advantageous characteristics, including their high specific surface area, mechanical, thermal and chemical stability, owing to reactive silanol groups, well-defined mesoporous array, and improved porosity. The pore size of this filler is sufficiently porous, leading to unusually intimate interactions between polymer and inorganic phase. The cross-sectional areas per chain of mostly selective synthetic polymers are around 1 nm^2 or less. Polymer chains penetrate into the pores of silica nanoparticles and improve the interfacial interaction between both the phases [38]. With the incorporation of this filler, the static free volume gap increases by disrupting the polymer chain packing and improving the membrane interfacial morphology. The better interfacial morphology between both the phases contributes to higher gas separation performance with acceptable permeability rate. Recently, many studies have been based upon using this inorganic filler as the dispersed phase in the polymeric matrix for preparation of high performance of MMMs [38-41].

2-6. Carbon Molecular Sieves (CMS)

CMS is basically carbonaceous materials originating from pyrolysis of thermosetting polymer. CMS have been manifestly described to be very capable for gas separation applications owing to their better adsorptivity for specific gas pairs. They have some advantageous characteristics such as high surface area, void volume with better porosity and uniform pore size distribution. The molecular sieving discrimination due to their size and shape selective nature of CMS permits smaller-sized gas penetrants to diffuse at higher rates compared to larger-sized penetrants across the membrane

[38]. Several studies report the selectivity and permeability performance improvement of CMS based MMMs for separation of smaller gas pairs such as CO_2/N_2, the O_2/N_2 and C_2 and C_3 alkene/alkane [42]. The CMS displays the appropriate affinity to glassy polymers than rubbery polymers for fabrication of membranes with superior adhesion at the interface and less processing complexities. These materials have hydrophobic internal surfaces and are mostly used for separation of air by adsorption of O_2 and removal of CO_2 from landfill gases [7].

2-7. Metal Organic Frameworks (MOFs)

Metal organic framework (MOF) (a hybrid of organic and inorganic microporous material) is typically a coordination polymer that consists of transition metals and metal oxides connected by the organic linkers. MOF enables tuning of pore geometries, which creates an interesting avenue to be utilized as effective filler for fabrication of MMMs for various gas separation applications. This filler is mainly categorized as rigid and dynamic: rigid structure displays inflexibility and variable pore size with small change in volume; whereas the latter exhibits significant rate of flexibility. However, their implementation of the separation process is not only based on size and aperture of the gas species, but also on the adsorption conditions. Two principal mechanisms responsible for selective gas adsorption in MOF are adsorbed-adsorbent surface interactions and size exclusion [43]. High surface area, which contributes to better sorption capacity, controlled porosity, greater thermal stability, low density, better affinity for particular gases and good interfacial contact with the matrix phase (due to existence of the organic linkers) are the major positive attributes of MOFs to be utilized as promising filler for diverse gas separation applications. These dominant properties of the filler have the competency to intensify the resulting membrane performance, even with the incorporation of small concentrations of particles. Numerous experimental and computational reports of gas sorption capacity in MOFs have been published with impressive performance enhancements for some gas pairs [44-46].

2-8. Zeolitic Imidazolate Frameworks (ZIFs)

ZIF, a subset of metal-organic frameworks MOF, is a promising crystalline porous material with exceptional thermal and mechanical strength, chemical stability against polar and nonpolar solvents and with the ability to reorient the structure at high pressure. It has a tetrahedral network exhibiting zeolite-like structures with ultra high level porosity. Generally, divalent metal cations such as Zn, Co and N atoms of bridging imidazolate anions are bonded for ZIF production, which contributes to the formation of solids with exceptionally small pores, reveals zeotype architectures such as SOD, RHO or LTA. It exhibits thermal and mechanical stability up to 400 °C and has Brunauer-Emmett-Teller (BET) surface area around 1,300 to 1,600 m^2/g or even more, which can explain its suitability as promising filler for membrane based gas separation application [43]. ZIF has a narrower pore size of about 3 Å, which is between the kinetic diameter of H_2 (2.9 Å) and CO_2 (3.3 Å). Thus, this filler acquires specific attention for separation of these two gas pair as it is supposed to exhibit a clear cutoff with higher separation efficiency. It was found that this filler has high adsorption ability to CO_2 and H_2, which is an attractive property for development of selective membrane materials [44]. The pore size as well as adsorption properties of ZIF can be customized by altering or chemically modifying the anionic imidazolate linker. Numerous interests have been reported by using this promising filler as dispersed phase for fabrication of MMMs as given in the reference list [47].

2-9. Covalent Metal Organic Frameworks (COFs)

Covalent organic frameworks are porous, crystalline, based on fully organic materials, and made entirely of light elements (such as H, B, C, N, and O). The crystallinity of COFs is derived from the reversible covalent bond formation reactions. The building

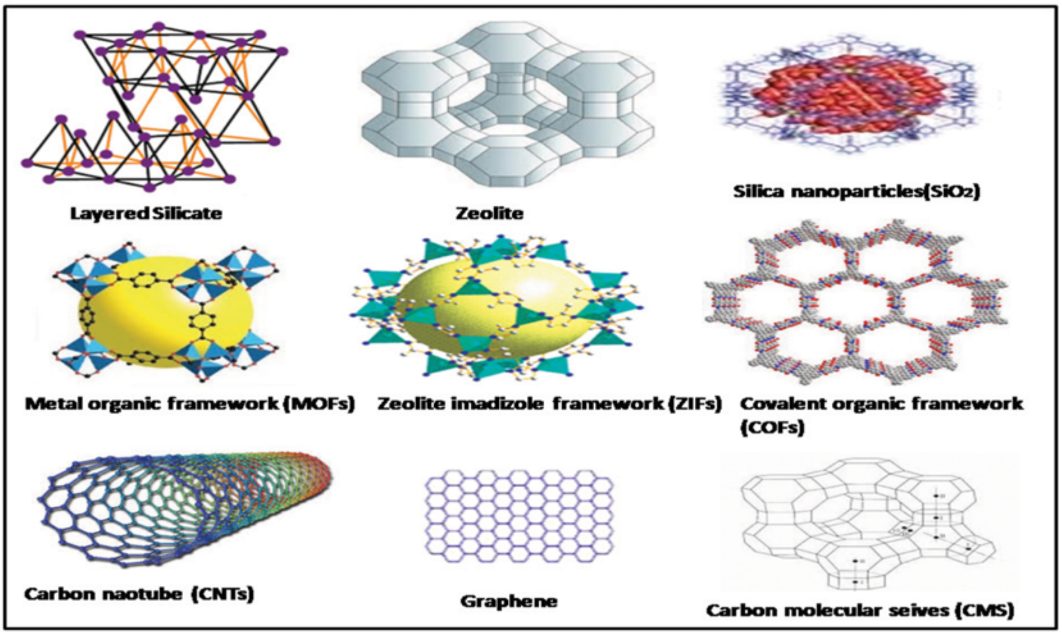


Fig. 4. Structure of different inorganic fillers for fabrication of MMMs.

blocks (generally the rigid monomers) are linked to each other by strong covalent bonds which provide permanent porosities for this filler. The utilization of filler in the polymeric matrix for fabrication of MMMs can provide excellent compatibility between both the phases based on the theory of similarity and inter-miscibility. It possesses exceptional stability, well-defined tunable porous nanochannels with higher chemical stability (long lifetimes) as an efficient filler for gas separation application. In comparison to MOFs, COF-based MMMs have superior separation performance for various gas pairs under high pressure process by virtue of their uniform organic composition. The incorporation of this potential filler as the dispersed phase for the fabrication of gas separation

Table 4. Summarizes the different kind of literature with the advantages and limitation of their works

Author	Membrane forming materials	Techniques adopted to improve the performance of membrane	Advantages	Drawbacks	Reference
P. Safaei et al.	Polystyrene (PS) and Titanium nanoparticles (TiO_2)	Selection of suitable membrane fabrication method	Selective separation of CO_2/N_2	Higher permeability rate at higher processing parameters	[26]
S. A. Hashemifard et al.	Polyetherimide (PEI) and nanoclay	Perfect interfacial adhesion even at higher particle loading	Selective removal of CO_2 from CO_2/CH_4 gas mixture	Formation of non-selective interfacial defects	[27]
Qingping Xin et al.	Sulfonated poly(ether ether ketone) (SPEEK) and Graphene oxide (GO	Amino acid-functionalized filler phase can able to improve the solubility rate and hence better separation performance	Long-term separation performance for CO_2/CH_4 and CO_2/N_2 gas pairs	At higher water content the performance of the membrane can be decreased	[33]
Muhammad Hussain et al.	Polydimethylsiloxane (PDMS) and Zeolite (ZSM-5)	Incorporation of suitable filler particles	Permeability of CO_2/N_2 increased three times compared to that of pure polymeric membrane	Permeability rate is higher compared to selectivity efficiency of the membrane	[37]
M. Pakizeh et al.	Polysulfone (PSf) and Silica nano particles (SiO_2)	Effect of both optimized loading of polymer and modified filler particles	The permeabilities for H_2/CH_4, H_2/CO_2 was improved with the incorporation of modified filler	The selectivities performance for H_2/CO_2 gas pair was poor	[41]
A. F. Isimil et al.	Polysulfone (PSf) and Carbon molecular sieves (CMS)	Better polymer-seive adhesion was achieved at higher loading and by maintaining casting temperature close to T_g of polymer, interfacial voids can be avoided	At 20 wt% CMS loading the O_2/N_2 selectivity was 5.97 with the O_2 permeability 7.9617 barriers	The chosen filler is a conventional one but the selection of other advanced filler may show higher separation performance	[42]
X. Chen et al.	Polyimide (PI) and Metal organic frameworks (MOFs)	Amino functionalized fillers and copolyimide matrix phase	Selective separation of CO_2/CH_4 even without addition of any compatibilizing agent	Higher matrix rigidification may decrease the permeation rate of the gaseous species	[46]
Abolfazl Jomekian et al.	Pebax 1657 and Zeolite imidazole Framework (ZIF-8)	Selection of appropriate polymeric and filler phase for fabrication of membrane	Higher separation performance for CO_2/CH_4 gas pairs	Plasticization effect is more at higher processing parameters	[47]
Xiaochang Cao et al.	Poly(vinylamine) (PVAm) and Covalent organic framework (COF)	Formation of appropriate size of pore for selective separation of gas	CO_2/H_2 selectivity is 15 and CO_2 permeance is 396 GPU at 0.15 MPa was achieved	The separation performance was decreased at higher processing parameters	[49]
A. Mustafa et al.	Polyethersulfone (PES) and Carbon nanotubes (CNTs)	Surface functionalization of fillers	Selectivity of CO_2/CH_4 gas was enhanced	Poor dispersion of filler particles	[50]

MMMs has been reported by many authors [48,49].

2-10. Carbon Nanotubes (CNTs)

Contemporary research based on CNTs as potential inorganic filler in various gas separation applications have encouraged their utilization as they possess unprecedented physical and chemical properties for fabrication of MMMs. CNT is allotrope of carbon with graphitic hollow cylindrical nanostructure sheets rolled at specific and discrete ("chiral") angles and the combination of rolling angles and radius. It can be categorized as single-walled carbon nanotubes (SWCNT) or multiwalled carbon nanotubes (MWCNT). Yang and Xie (2011) reported that CNT is an excellent candidate for substituting or complementing conventional fillers for the synthesis of multifunctional polymer nanocomposites membrane owing to their unique advantageous properties [50]. It has been demonstrated that utilizing composite membranes composed of nanotubes may result in an appealing route for the fabrication of fast MMMs with high separation efficiency. Gas permeation rates through CNTs are several orders of magnitude higher than any other inorganic filler such as zeolites and CMS, due to their distinctive extraordinarily smooth walls and large diameter pores. Gas transport through CNTs is dramatically accelerated due to their smooth and structurally stable internal walls with uniform channels which also can be formed in various sizes. Among all choices, most of the researchers have suggested CNTs to be promising and suitable filler for membrane based gas separation application with spectacularly high fluxes and high selectivity for a wide range of gas mixtures [51].

The following figure displays the structure of different promising inorganic fillers which are frequently used to prepare of mixed matrix membrane for gas separation applications.

MMMs BASED ON CARBON NANOTUBES

Theoretically, it is proved that CNTs have ideal superlative characteristics as potential inorganic fillers for the fabrication of composite membrane, according to their relative size difference between its smooth inner diameter and the permeating molecules. Therefore, many researchers have focused their attention towards utilization of CNTs as an important component for various separation technologies such as water purification, desalination, solvent filtration, and gas separation [51]. In the past few decades, considerable research has been put forth through the incorporation of CNTs within polymeric matrix to prepare MMMs for application in gas separation. The separation performance of CNTs based systems explores the possibilities of overcoming the trade-off between selectivity and permeability as found in conventional counterparts [52].

Critically, the permeability of all gas species was shown to be strongly correlated with the free volume the membrane, the particle size and hydrophobicity. Matching the pore size of filler to that of target penetrant gas molecules is a crucial factor in the case of membrane based gas separation process [53]. Moreover, it would be favorable to fabricate ideal membrane structures having an initial pore diameter of the filler close to that of the target penetrant molecule. The nanotube size can be controlled during the growth of CNTs through the utilization of various catalyst particles with the different diameter. By manipulating the growth time and catalyst, the dimension (length and diameter) of CNT can be customized to achieve precise size exclusion capability and to suit a wide range of gas separation applications. Hence, it is recommended that a feasible avenue for regulating filler pore diameter along with porosity tuning can be achieved in the resulting membrane and thereby the performance can be modulated to a certain degree. The prospective interaction between target gas molecules and CNTs is more intense when the diameter of CNTs dropss. Moreover, the dynamic flow of gas molecules is further rapid in the case of smaller CNTs compare to larger ones [54].

CNT have several possible structurally perfect and stable interstitial adsorption sites with high binding energy, which in turn helps to exhibit extremely high separation performance. The expanding exploration of CNTs for membrane gas separation application can also be ascribed to their distinctive advantageous properties, such as high aspect ratio (>1,000) in combination with low blending amount, surface area, frictionless surfaces, strong chemical property, potential to elevate mechanical strength with small filler content chemical inertness and also competency for better control of pore dimension at the nanometer scale, which amplifies the chances of the permeate gas molecules to interact more strongly with their surfaces [55]. Moreover, CNTs are found to carry more strain in compression side through the polymer composites membrane due to their better load transfer behaviour, thereby providing supplementary strength for the resulting membrane. Therefore, when CNT based MMMs are exposed to high pressures, the large load pressed on the polymer matrix was efficiently transferred to the rigid nanotube lattice via polymer-nanotube interfacial bonding, rendering the whole membrane structure tougher and more stable under a high-pressure feed gas stream. The significantly improved membrane stability is mainly attributed to the enhancement of polymer mechanical strength and anti-compaction property due to the incorporation of CNTs. On the other hand, the presence of extremely inherent smoothness of hydrophobic graphite wall forming confined nano-channels with one-dimensional structure is ascribed to distinctive circumstance for ultra-efficient transport of various gases [56,57].

In fact, molecular dynamic simulation and detailed predictions demonstrated that the unique combination of properties and rapid mass transport behavior of CNTs gives the ability to exceed the selectivity to several orders of magnitude higher than compared any other porous filler. Therefore, currently, researchers are stimulating an appreciable attempt to employ CNT filled polymeric matrix membranes in order to engineer advanced molecular separation systems in the field of industrial gas separation applications.

Sholl and co-workers [56] were first to estimate that transport diffusivities and fluxes of gases in single walled carbon nanotubes (SWNTs) are orders of magnitude faster than in zeolites having comparable pore sizes. The high selectivities of the resultant membrane are theoretically possible due to the precise diameters of nanotubes. SWNT-based membranes are basically new nanoporous materials having the potential for transcending Robeson's upper bound limit. Based on most of the exploratory investigations, the selectivity performance for CNT-MMMs was enhanced because the strong interaction between matrix phase and nanotubes can disturb the chain packing, thus intensifying the gas diffusion (by introducing more free volume voids between polymeric chains and defects at the polymer/nanofiller interface). The experimental appraisal concluded that the decrease in gas permeability can be attributed to the impermeable behavior of raw CNTs (closed-ended), but the increase of permeability with an enhancement in selectivity can be obtained by using open-ended nanotubes with better adhesion between nanotubes and polymeric matrix phase at the interface. An ideal defect-free CNT membrane structure can be achieved if the space gap between individual CNTs is only occupied by matrix phase with polymers having high wettability with nanotubes to enable better interaction between both the phases [58].

The properties of CNT-based composite membrane structures depend upon several factors, such as properties of synthetic polymer, the process used to produce nanotubes, its purification and modification process (if any), amount and type of impurities, diameter, length and aspect ratio apart from the most important factor, which is the direction of nanotube orientation in the host polymeric matrix. Moreover, the discontinuity between both the phases would lead to loss of mechanical properties, especially at high filler loadings, which reduces the processibility and hence reduce its utility for large-scale industrial applications. However, two critical issues challenging the successful implementation of CNT/polymeric membrane are interphase chemistry and better alignment of the nanotube in the chosen matrix phase [59].

CRITICAL FACTORS AFFECTING THE PERFORMANCE OF MMMs

Many experimental investigations have revealed that regardless of the presence of conceptually promising, highly selective inorganic fillers in MMMs, the performance is found to be unsatisfactory for specific gas pairs. The efficiency of MMMs not only depends on the elementary attachment of intrinsic properties of both the individual phases, but also on the durability, stability and mechanical integrity at higher operating conditions, productivity and separation efficiency of the membrane forming materials [4]. Due to the huge physical property difference between filler and bulk polymeric phases, it is quite challenging to fabricate defect-free MMMs with higher separation performance. The lack of selectivity performance is attributed by virtue of the drawbacks such as weak contact between two phases, non-uniform dispersion, and distribution of filler particles throughout the continuous polymeric matrix phase and poor stability of the prepared membrane for higher operating conditions. Nanoparticle aggregation, agglomeration and interfacial defects are some prime factors responsible for generating large free volume gaps between both the phases, and often the gaps are much bigger than the size of a chosen gas molecule to be transported. Therefore, the generation of these gaps destroys the separating efficiency of the membrane and finally, the utilization of filler particles for fabrication of MMMs becomes worthless. The above-elucidated issues describe the circumstances that are predominantly responsible for deterioration regarding the expected performance of MMMs.

The factors that exemplify the performance and efficiency of MMMs for outstanding large-scale industrial implementation are highlighted below,

- **Selection of appropriate membrane forming materials for MMMs**

An appropriate combination of both continuous and dispersed phases is considered as most promising and technologically challenging aspect to develop successful MMMs with excellent separation efficiency. The option for choosing membrane materials for a particular gas separation application to attain superior performance depends upon the preferred affinity between both the phases. Furthermore, compatibility and adhesion between two phases at the polymer-filler interface are needed to be focused on fabricating defect-free MMMs. Thus, special attention must be put forth for the selection of suitable membrane materials for preparing high performance MMMs with the aim to achieve exceptional separation efficiency and long-term stability [60].

- **Fillers loading within the matrix phase**

Optimized loading of filler particles in continuous polymeric phase is an essential factor for fabricating ideal defect-free MMMs with impressive separation efficiency. If the loading of filler is insufficient, then it results in heterogeneous filler distribution throughout the matrix phase and contributes to the inferior membrane separation performance. Unfortunately, with increasing loadings of fillers, it compelled for the formation of aggregation and agglomeration of filler particles across the matrix phase. This can produce non-selective voids and pinholes, over the membrane, thus increasing the diffusion distance and generating more free volume gaps between individual particles and the polymeric matrix. These gaps create extra channels to permit the feed gas molecules to drive across the membrane without any size selective nature and eventually destroy the utilization of inorganic filler for fabrication of MMMs by disintegrating membrane separation performance [13].

- **Agglomeration and sedimentation of fillers in matrix phase**

Throughout the fabrication of MMMs, precipitation may occur (due to the differences in physico-chemical properties between both the phases), resulting in the configuration of separate inhomogeneous layers of filler and polymeric phases in MMMs. It also emerges for the generation of agglomeration and aggregation of fillers and improper adhesion between both the phases. It results in the generation of pinholes that are lean in bulk phase, forming non-selective interfacial defects through MMMs, and thus reducing membrane gas separation performance [61].

- **Incompatibility between inorganic and continuous phase**

The defect-free polymer/filler interface especially assures better membrane integrity as well as providing superior separation performance with greater stability to processing conditions. The usage of glassy polymers has predominantly spread in most gas separation industries for fabrication of MMMs; however, their rigid structure gives poor contact with the chosen particle surface, resulting in the formation of non-selective voids (Aroon et al., 2010). The presence of these voids is undesirable for a membrane because feed gases will flow through it, thus eliminating the fillers' function with lowering the separation performance. Thus, the performance of the membrane is degenerated by contributing higher permeability at the cost of decreased selectivity rate, and therefore the potentiality of existing MMMs becomes ineffective for various gas separation applications [62,63].

- **Poor distribution of dispersed phase**

Non-uniform, heterogeneous distribution of fillers in polymeric matrix contributes to agglomeration, aggregation, and sedimentation throughout the prepared membrane surface. Especially when dealing with excessive filler loading at higher operating conditions for industrial scale applications, this factor might be the main cause for deteriorating the properties of the membrane to attain better separation performance. Thus, the membrane obtained has less selectivity for the diffusion of target gas molecules, while the permeability rate increases enormously, affecting the separation efficiency and stability, and hence the overall performance of the membrane is reduced [60,63].

- **Interfacial defects**

The polymer-filler interfacial morphology is the most crucial aspect that can alter the whole gas separation performance of the resulting MMMs. Polymer-inorganic filler incompatibility, disruption in packing of polymeric chain in the vicinity of fillers, improper adhesion between both the phases, repulsive force among them and difference in thermal expansion coefficients between them are the prime causes for defective interfacial morphology, which can promote the formation of non-identical interfacial defects across the surface of the resulting membrane. The presence of these interfacial non-selective voids is supposed to be the major reason for the deterioration in membrane performance as the feed gas molecules pass through these non-selective and less resistant by-pass voids instead of transporting through the pores of fillers and ultimately degrade the separation efficiency of membranes [63,64].

1. Impact of Interfacial Morphology on MMMs Performance

The possible reasons for the formation of non-selective interfacial defects are due to the imperfect contact and poor interaction between dispersed and continuous phases (mainly due to the strong aggregation tendency of filler) at the organic-inorganic interface, different values of shrinkage and high stress generated during the solvent removal and poor relaxation of rigid polymeric matrix material. These voids at sieve-matrix interphase act like fast transport channels for the feed gas mixtures to get separated, thus rendering the membrane with high permeation rate and hence drastically hampering the overall membrane separation performance. Different composition of polymers and fillers can ensure the formation of varying percentage of interface morphologies, which can bring on divergent influences on gas transport properties [61,62].

The most common types of interface morphologies found in MMMs are (i) sieve-in-a-cage, (ii) leaky interface, (iii) matrix rigidification, and iv) plugged sieves. Fig. 3 displays a schematic diagram for various nanoscale interface morphologies of MMMs. Case (i) depicts an ideal morphology, which has no defects. Case (ii) shows the detachment of bulk phase from filler surface; Case (iii) indicates rigidification of polymeric chain segments in the vicinity of inorganic filler, and in Case (iv) the pore has been slightly plugged within the surface section of fillers [65].

'Sieve-in-a-cage' is produced when the filler is located freely in a cage formed by the polymeric matrix. The interfacial voids thus formed comprise the pore size of the filler particles since the void size is larger than that of the size of penetrating gas molecules. These non-selective-voids provide the path of least resistance, so penetrating gas molecules can easily pass through them instead of the pore of dispersed phase. It causes much higher permeability rate at the cost of selectivity performance. The second case, leaky interface, is obtained when the formed voids have sizes much larger than the permanent gas molecule; thus, the flux escalates notably while the selectivity drops drastically. It can generate non-selective resistance path, thereby elevating the enhancement in permeability and depletion in selectivity as a contrast to that in the case of sieve-in-a-cage [60,66].

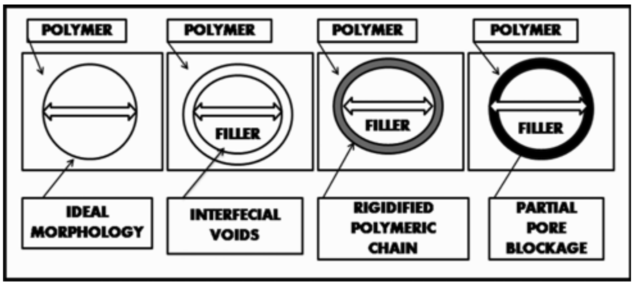


Fig. 5. Schematic of various interface structures of MMMs.

The reduction of free volume in polymeric chains in the vicinity of fillers results in a significant difference in mobility between the dispersed and continuous phases causing localized stresses. If the applied stress directions are not uniform around the inorganic particles, interfacial voids will be formed at the polymer-particle interface. This stress is the main cause for the formation of rigidified polymer layers around the filler and is called matrix rigidification. This interfacial rigidified layer diminishes the permeation of penetrant gases, while synchronously increasing the diffusive selectivity than intrinsic bulk polymer because of the reduction in free mobility of polymeric chain [63]. Rigidified polymer lowers the gas sorption as well as permeation in the semi-crystalline structure. Furthermore, the increase in glass transition temperature (T_g) of MMMs is exhibited as a significant confirmation for the existence of rigidification effect in MMMs. MMMs with polymer chain rigidification have a higher T_g than the original polymeric membranes. Most researchers described that the depletion of permeability in polymer rigidified chain layer ranges from one-fourth to one-third of the permeability of the intrinsic polymer [65,67].

Another type of interfacial morphology is pore blockage. It is a unique type of defect found in the case of porous fillers embedded MMMs. These inorganic particle pores may get blocked with sorbent, solvent, contaminant or minor components from feed gases or even by rigidified polymeric chain segments. This pore blockage can be categorized as total and partial based on the difference in pore size of inorganic fillers. Total pore blockage will not allow the feed gas molecules to pass through the particle pores as filler pores are plugged completely, and hence porous inorganic particles in MMMs behave as impermeable filler for transport of gases. But in the case of partial pore blockage, penetrants of interest enter or pass through the pores more deliberately, depending upon the intensity of blockage, the dimension of the target gas molecule and blockage degree. Although this defect hampers the permeability of the membrane, selectivity increases as a result of reduced pore size

[63,65]. Before blockage, if the size of the porous filler is in the range of the molecular diameter of gases, (such as 4A zeolite filler for separation of O_2/N_2 and CO_2/CH_4), after blockage it will not allow the gases to permeate and hence pore blockage is considerably responsible for the reduction of membrane performance in terms of selectivity. When the actual size of the porous filler is larger than the molecular diameter of targeted gases (e.g., 5A and beta zeolites for O_2/N_2 and CO_2/CH_4 separation), pore blockage can improve the selectivity performance of the resulting membrane [7].

2. Suitable Techniques to Diminish the Defects

For the resulting MMMs to accomplish adequate separation performance with exceptional long-term stability to processing conditions, the presence of these dispensable non-selective interfacial defects must be regulated. Researchers mostly investigated the following methods to eliminate interfacial voids and to fabricate defect-free MMMs possessing superior separation performance along with the advantageous properties,

- When glassy polymers are utilized for fabrication of MMMs, casting must occur at a temperature above the glass transition temperature of the polymer used. By means of this, the flexibility of the matrix can be maintained to maximize stress relaxation with the gain of higher free volume gaps. This activity facilitates realizing the superior performance of the resulting membrane. Predominantly, a low volatile solvent is more favorable for the casting of a membrane [68].

- Uniform and homogeneous dispersion of inorganic particles in bulk matrix phase can be achieved through the insertion of fillers in a suitable solvent prior to mixing (rather than directly used in polymeric solution). By vigorous stirring, the obtained dilute suspension reduces agglomeration and aggregation of filler particles when incorporated within the matrix phase. Another significant aspect that contributes for poor dispersion of filler particles throughout the polymeric phase is the sedimentation of particles [12]. This complication can be diverted by selecting ultra-fine crystalline particles. Through the utilization of these particles, the sedimentation rate can be decreased and dope viscosity of the suspension may be upgraded. Also, matching the polarity of polymer medium to that of filler particle surface may minimize sedimentation problems. The concentration of casting solution should be high enough to enhance the viscosity and thereby retard the sedimentation rate of inorganic filler particles across the polymeric phase [69]. By these above-explained methodologies, one can achieve improved dispersion of the dispersed filler phase and have a direct link on the separation performance of the prepared membrane.

- Incorporation of low molecular weight plasticizers into the polymeric solution such as RDP Fyroflex, di-butyl phthalate and 4-hydroxy benzophenone, decreases the polymer glass transition temperature. Thus, polymer chain mobility and flexibility can be maintained during fabrication of membrane. It enhances the performance of the membrane in terms of selectivity by reducing the free volume gaps between the chain segments [68].

- Surface modification of inorganic particles by hydroxyl, carboxyl or any other functional groups can reduce the possibility of agglomeration and the sedimentation tendency of fillers. The modified filler can interact more strongly with polar gases (CO_2 and SO_2) to improve the penetrant solubility of prepared membranes. Moreover, the functionalization of filler particles helps to attain improved dispersion of dispersed phase throughout the matrix. This method has been demonstrated as a suitable choice to accomplish defect free MMMs with the high gas separation ability [70].

- The addition of copolymers such as polyimide siloxane with rubbery segments during the preparation of MMMs enhances flexibility and interfacial contacts between the continuous and dispersed phases. Thus, the improved polymer-filler interface can fabricate defect-free high performance MMMs. However, it is very difficult to find an industrially favorable copolymer, and also the synthesis of desired copolymers enhances additional membrane fabrication steps [71,72].

- Priming is a method that involves coating of filler surface with the suitable dilute polymer dope prior to dispersing in the bulk polymeric phase, which reduces the stresses at the polymer-filler interface. It eliminates the chances for the formation of agglomeration and the aggregation tendency of filler particles and encourages better interaction between bulk polymeric phase and the polymer primed filler particles, according to Aroon et al. (2010). Through the usage of priming technique, compatibility between both the phases may be enhanced, and thus better dispersion of filler particles is attained which directly influences membrane separation performance. However, priming method requires that the filler particles should be evenly dispersed in the desired solvent before the inclusion of polymer dope solution to prevent priming of filler agglomerates and aggregates [73].

- The introduction of low-molecular-weight additive (LMWA) for membrane formulation as a third component is yet another promising solution to diminishing these non-selective interfacial defects. The chosen additive must be soluble in the solvent used for preparing the polymeric dope solution. The selection of LMWA is based upon the consideration of multiple functional groups on its surface such as amine, nitro, and hydroxyl (Karatay et al., 2010). The presence of these functional groups within LMWA causes the formation of hydrogen bonds with other existing functional groups on the polymeric chain and the inorganic filler surface. Long aliphatic and polyaromatic based compounds containing polar atoms, rigid and planar structure such as 2, 4, 6-triaminopyrimidine (TAP) and pnitroaniline (pNA), 4-amino 3-nitro phenol (ANP), 2-Hydroxy 5-Methyl Aniline (HMA) are customarily used as additives for fabrication of high performance MMMs [74]. The simultaneous interaction of the LMWA with the polymer/inorganic interface can produce void-free inorganic-glassy polymer based MMMs with superior gas separation performance (Yong et al., 2001).

- Initial attempts to refine the interfacial contact between continuous bulk and dispersed phases have been based on thermal annealing above the glass transition temperature (T_g) of membrane materials under vacuum condition. It enlarges the flexibility and mobility of polymeric chain segments, elevates the free volume gaps, leading to better attachment of polymer chains to the filler surface. By adopting the annealing technique the compatibility between both the phases can be enhanced and thereby improve the gas separation performance of the prepared membrane. This process is the most effortless and reasonable post-treatment technique to minimize stress and remove traces of solvent from the resulting membrane, and therefore has the potentiality to achieve superior purity of the target gas product [64].

After the annealing method, the cooling protocol is indispensable to inhibit the emergence of non-selective voids at the polymer-filler interface. Two cooling protocols are confirmed: immediate quenching, and natural cooling. After annealing, immediate quenching may be the reason for detachment of polymeric chains from the inorganic filler surface (as the chains are still in a random state) because of the rapid freezing. This process can result in the formation of non-selective voids between polymer and filler interfaces because of the difference in properties between both the phases, i.e., thermal coefficients of expansion, density, and thermal stability. However, the natural quenching method has been widely employed in the membrane fabrication process to decrease the formation of voids and for improving the membrane separation performance. The strong motivation for assigning natural cooling after annealing is to formulate the polymeric chains as harder and shrink much more slowly and gradually. This method facilitates the formation of a desirable polymer-filler interface through an effective contact between both the phases [75].

Out of all above-mentioned methods for promoting better polymer-filler interface through the minimization of the presence of these non-selective interfacial defects is by surface modification of inorganic filler. This modification method is the most customarily used technique for the fabrication of high performance MMMs with superior separation efficiency.

INDUSTRIAL VIABILITY ANALYSIS OF MMMs

The implementation of MMMs for industrial gas separation applications has greatly expanded during this last 25 years because of its multidisciplinary features over other conventional separation processes: (i) potential for saving energy and costs, (ii) light weight and modular designs, (iii) compactness, (iv) easy expansion or operation at partial capacity and requirement of no phase change, (v) high demand, and (vi) reduced environmental pollution. The membrane industry itself has a profound perspective as illustrated by the higher implemented growth rates, the steadily increasing diversity of gas separation applications and the increasing number of technically feasible membrane processes for separating various gaseous mixtures in order to control the environmental pollution [5]. As a result, this membrane-based separation process has acquired a remarkable aspect in the industrial scenario in terms of economical consideration and superior gas separation performance with the higher purity of the target gas product.

The fruitful prediction of membranes for gas separation processes in both lab and industrial scale is mostly based on the preference of membrane materials with acceptable chemical, thermal mechanical and permeation properties. Nowadays, the critical challenge in extensive utilization of MMMs for practical industrial gas separation application is to attain higher selectivity and greater purity of the target product, with adequate productivity and long-term membrane stability. Moreover, the membrane must have the ability to sustain in realistic, complex, and aggressive feeds at higher temperature and pressure. Furthermore, properties of the membrane-forming materials, sustainable performance and competence of the resulting membranes to actual operating conditions at higher loading of filler particles are the extreme consequences. Most of the prepared membranes are tested on bench scale with relative absolute conditions; however, when the membranes are employed in real industrial gas stream operating conditions, their performance remains uncertain. Therefore, the performance of the membrane should be estimated under realistic industrial feed conditions, as the actual conditions fluctuate over time with different operating conditions. Hence, long-term performance and stability for successful fulfillment of MMMs demand its estimation under realistic conditions to evaluate the actual viability of the membrane for diverse gas separation applications. An industrially qualified MMM for particular separation application demands in-depth realization of factors affecting membrane performance and generalized methodology for mitigating the difficulties arising during the fabrication of membranes for attaining greater separation efficiency.

Table 5. Major applications of gas separation in industries

Gas mixtures	Applications
H_2/CO_2	Fuel cells
O_2/N_2	Oxygen enrichment, inert gas generation
H_2/hydrocarbon	Refinery hydrogen recovery
H_2/N_2	Hydrogen recovery from Ammonia pure gas
H_2/CO	Synthesis gas ratio adjustment
CO_2/N_2	Digester gas treatment
CO_2/hydrocarbon	Acid gas treatment, greenhouse gas capture
H_2O/hydrocarbon	Natural gas dehydration
H_2S/hydrocarbon	Sour gas treating
He/hydrocarbon	Helium separation
He/N_2	Helium recovery
Hydrocarbon/air	Hydrocarbon recovery
H_2O/air	Air dehumidification
Hydrocarbon/air	Pollution control
	Stack gas or solvent recovery

Primarily, the fabrication of ideal defect-free MMMs for industrial scale application is absolutely challenging because the actual compatibility difference between continuous and dispersed phases, greater tendency of fillers for the formation of agglomerates and aggregates at higher loading results in non-uniform dispersion of fillers within the polymeric phase promoting weak polymer-particle adhesion. Consequently, a systematic investigation is required for proper dispersion of nanofillers in the continuous phase to fully realize its potential under real-life conditions and to provide acceptable separation performance. Although MMMs have the potential to overcome the Robeson trade-off curve for achieving high separation efficiency, there is a long way to go for commercializing the membranes for large-scale industrial gas separation applications.

CONCLUSION

Among the miscellaneous initiative movements, to effectively utilize the developing opportunities of MMMs in the field of gas separation application, intense fascination prevails in recognition of new appropriate membrane forming materials with desired characteristics and which have the potential to adhere to the current requirements to achieve favorable separation performance. Nevertheless, the extensive implementation of these MMMs for various applications is mostly incidental to the employment of new classes of inorganic ingredients with the combination of high performance polymers to achieve defect-free separation performance. However, the development of MMMs comprising CNTs as inorganic filler is currently dominating the research interest as the gas permeation rates in CNTs are several orders of magnitude higher than any other inorganic fillers such as zeolites, carbon molecular sieves because of their extraordinarily smooth walls, large diameter pores, high aspect ratio, excellent mechanical and thermal properties. Hence, the incorporation of CNTs as the dispersed phase in the polymeric matrix is appreciative to achieve the long-term high performance of the as-synthesized MMMs in terms of better separation efficiency of the target gas products. Despite the significant achievements of CNT-MMMs in gas separation applications; the difficulties in addressing uniform dispersion and distribution of fillers as individuals within the matrix phase and poor compatibility between both the phases must be resolved properly, as these features have the direct link on separation performance of the membrane unit. The intrinsic properties of CNTs, including hydrophobic nature, lack of interfacial interaction, tendency to form aggregates are some of the most essential factors, which interrupt the well uniform dispersion throughout the continuous polymeric matrix during the fabrication of composite membrane. Improper dispersion is the consequence towards the formation of agglomeration and aggregation of fillers in the fabricated MMMs and leads to non-selective interfacial voids at the polymer-filler interface, which provides discontinuous and tortuous paths for gas transport and thereby intensely mitigates the effectiveness of CNTs as filler to fabricate MMMs. Therefore, it is desirable to disperse filler particles homogeneously and uniformly in the matrix phase to take the full advantage of the characteristics of fillers and maximize the membrane permselectivity. Different appropriate techniques are needed in order to disperse and distribute the filler particles uniformly throughout the matrix phase to intensify the performance of MMMs.

Moreover, the modification of fillers and matrices has displayed as an expanding field of research as with the insertion of these functional groups on the surface of membrane materials; it can able to improve the dispersion of fillers, enhance the interfacial contact between the phases and with the higher potentiality to alter the chemical affinities of penetrants in nanocomposite membrane, and thereby promote the superior outcome on both permeation rate and selectivity performance. The development of high performance polymer matrices for the fabrication of MMMs via copolymerization, blending, grafting, crosslinking, etc., to overcome the different shortcomings generally appears during the utilization of single polymeric phase such as swelling, weak resistance to realistic conditions and plasticization. Recent molecular dynamic simulations of MMMs have demonstrated that the complicated situation which deviates the results from presumed performance is attributed to the lessened polymer chain mobility and higher permeability at the polymer-filler interface, and which principally occurs because of the weak compatibility between both the phases. Thus, the gas transport properties of the membrane system largely depend upon the characteristics of defect-free interfacial morphology. The mechanisms behind these phenomena demand extensive investigations and development of suitable techniques to improve the interfacial morphology and thereby assist in order to intensify the upper bound trade-off curve in terms of higher separation performance in combination with better permeation properties.

Much effort is dedicated towards the formation of MMMs for gas separation, but additional research and development approaches are still required to exploit the prospective of this technology for large industrial-scale gas separation applications with the aim to achieve better stability, longer life span and outstanding separation performance to obtain better purity of the target gas product. Currently, research emphasis is on overcoming the present challenges and developing new membrane materials having better qualities and characteristics to eliminate the arising drawbacks for large-scale industrial gas separation applications.

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