



## ZIF-filler incorporated mixed matrix membranes (MMMs) for efficient gas separation: A review

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### ABSTRACT

Gas separation by employing polymeric membranes is one of the most developed branches of membrane based separation technology. But, polymeric materials are unable to meet the demands of present day membrane technology. Mixed matrix membranes (MMMs) which are combination of both polymeric and inorganic materials have appeared as an emerging membrane material as it combines the dimensional stability and efficient gas separation ability of inorganic material along with facile fabrication and low cost of polymeric material. In this review, main challenges that are encountered during fabrication of MMMs and the steps taken to overcome these challenges are reviewed in detail. Also, the basic criteria for the selection of suitable polymer and inorganic material for fabrication of MMMs is also discussed pertaining to chemical and physical compatibility between them. Zeolite imidazolate frameworks (ZIFs) because of their good compatibility with polymers along with their beneficial properties such as unsaturated sites, adjustable pore channels and simple functionalization are widely incorporated into polymer matrix for fabrication of MMMs. Influence of various types of ZIFs on MMMs fabrication along with their gas separation performances are also put together in this review article from different reports. Moreover, ZIF modification techniques in order to enhance the gas separation performance of MMMs are also discussed. This study reveals that modified filler's synergic effect can alter membrane's structure by improving interfacial voids and thus can overcome the trade-off effect. Besides this, the influence of ZIFs morphology on gas separation performance of MMMs is also analysed in this article.

### 1. Introduction

Membrane based gas separation technology is used to separate the gases from gaseous mixture by passing them through membrane which in most of the cases is made up of polymer. Ceramic membrane also has been used quite frequently for gas separation. The inlet feed stream that is usually at elevated pressure comes into contact with the surface of membrane. Because of the difference in rates of permeation, the components of gas that are more permeable pass through the membrane and

gather on the permeate side due to the existence of driving force, while on the contrary, the components of gas that transport a bit slower gather on retentate side. Driving force that is responsible for the separation of gaseous components is actually the partial pressure gradient between feed phase and permeate phase and can also be expressed as the product of total pressure and mole fraction.

Over the last few years, there has been an increase of usage of membranes in industries, especially in those industries that involve operations related to gas emissions and separations. Currently,

**Abbreviations:** MMMs, Mixed matrix membranes; ZIF, Zeolitic imidazolate framework; PSF, Polysulfone; PI, Polyimide; CA, Cellulose acetate; MOF, Metal organic frameworks; CNT, Carbon nanotubes; CMS, Carbon molecular sieves; VOC, Volatile organic compound; SAPO, Silicoaluminophosphate; ALPO, Aluminophosphate; PMO's, Periodic Mesoporous organic silicas; PBI, Polybenzimidazole; GO, Graphene oxide; EC, Ethyl Cellulose; PD, Poly dopamine; IL, Ionic liquid; CMC, Carboxyl methyl cellulose; PVAm, Polyvinyl amine; GCMC, Grand Canonical Monte Carlo.

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membrane based gas separation technology is being used in many gas separation applications such as separation of  $\text{CH}_4/\text{CO}_2$  for upgrading of biogas, for separation of  $\text{O}_2/\text{N}_2$  for enrichment of oxygen, in separation of  $\text{CO}_2/\text{N}_2$  to halt  $\text{CO}_2$  emission in atmosphere and etc. In order to purify gases that are industrially important, membrane technology is considered as an energy efficient option over other thermally driven conventional processes. Membranes when used for gas separations requires less investment cost and energy as compared to other competitive technologies such as adsorption, distillation, and absorption [1,2]. It was estimated by Sholl and Lively [3] that separations involving membranes utilize 90% less energy as compared to distillation process [3]. Other key advantages of membranes include less consumption of energy, flexibility in operations (which means that membranes can function as an independent unit or can also be retrofitted within existing processing unit), linear scale up (appropriate for medium and small scale operations) and, smaller carbon footprint [4–7]. It is believed that membrane based gas separation technology will help in reducing environmental burden by attaining high concentration of pure gases. Membrane based separation technology has predicted \$2.6 billion market value in 2022, that is approximately 86% greater than the market value that was in year 2018 [5,8]. Most of the membranes that are used commercially for gas separation applications are polymeric and 90 % of these membranes are used for separation of gases that are non-condensable, for example in treatment of natural gas, in production of  $\text{N}_2$  from air, and in purification of  $\text{H}_2$  [2,8,9].

Polymeric membranes have appeared as a superior and emerging separation process over other conventional gas separation techniques. Over past few decades, the research and study on polymeric membranes have acquired quite an attention because of its potential to differentiate gaseous species based on molecular size, moderate energy requirement, low capital cost and convenience of fabrication [10–13]. Polymeric membranes can be synthesized easily, they are extensively available and can be used commercially in gas separation applications. Even though quite a lot of polymers have been reported till date, but only some of them such as polysulfone (PSF), silicon rubber, polyimide (PI), cellulose acetate (CA) have been utilized to fabricate almost 90% of total deployed gas separation membranes [9]. Scalability and ease of fabrication are key advantages of polymeric membranes. In spite of advantages of polymeric membranes, Robeson upper bound between permeability and selectivity has restricted its applications as these membranes are bounded by permeability- selectivity trade off [14]. Plasticization as well as their sensitivity towards high temperatures and grim chemical environment also limits the use of polymeric membranes in realistic applications [15]. Higher concentration of gases at elevated pressure such as  $\text{CO}_2$  can cause swelling of polymer and can also increase polymer chain mobility which in turn results in decreasing membrane's selectivity [16]. These problems and challenges have led researchers to explore new categories of membrane materials.

Inorganic membranes for example zeolites, ceramics and carbon membranes provide many advantages over polymeric membranes because of their thermal and mechanical stability as well as resistance towards broad range of chemicals. For gaseous separations requiring strident chemical conditions and high temperatures, inorganic membranes could be the possible solution. Inorganic membranes, exceeding Robeson upper bound provide better selectivity and permeability than polymeric membranes. Despite of above mentioned advantages, fabricating defect free inorganic membranes is a challenging task because of their fragile structure, high temperature and long time required for synthesis. Also, they need extensive fabrication energy. In spite of the fact that inorganic membranes exhibited encouraging gas separation performance, quite a lot of challenges are faced in scaling up of inorganic membranes. Furthermore, inorganic membranes are much more expensive than polymeric membranes with an estimated module cost within range of \$1000 per  $\text{m}^2$  which is approximately 100 times greater than polymeric membranes [17]. Because, self-supported inorganic membranes are naturally brittle [18], and expensive inorganic porous

supports are needed which adds to the membrane system cost. Issues that are mentioned above together with other problems such as reproducibility restricts their widespread applications on industrial scale.

Hence, in order to overcome the limitations and flaws suffered by both inorganic and polymeric membranes new class of membranes, namely mixed matrix membranes (MMMs) was developed by researchers. MMMs are actually composite membranes and consist of inorganic particles dispersed homogeneously in continuous polymeric phase. In the field of gas separation membranes, MMMs, by combining the dimensional stability and excellent separation performance of inorganic membranes along with easy fabrication and low cost of polymeric materials have appeared as an alternative and appealing approach in membrane based separation technology [19]. MMMs are highly selective, require less energy and are easily and simply processable. Comparative to polymeric membranes, MMMs deliver enhancement in selectivity, permeability, mechanical strength and also in thermal and chemical stability. Previous studies related to MMMs have shown encouraging results by incorporating inorganic fillers such as metal organic frameworks (MOFs) [20], zeolites [21], carbon nanotubes (CNT) [22], carbon molecular sieves (CMS) [23] as a dispersed phase in MMMs as they aid in boosting membrane's performance.

Fabrication of MMMs that is defect free is a difficult task as the compatibility between filler and polymer is often inadequate to create homogeneous interfaces [15]. This incompatibility between polymer and filler would induce the filler to repel continuous phase and results in forming a sieve in cage morphology which in turn results in unselective interfacial voids. These voids are responsible for the penetrant to permeate across membranes as they offer negligible mass transport resistance without discriminating and differentiating the penetrants. So, adhesions between polymer and filler, disruption in polymer packing as well as the repulsive forces among two phases are some factors that result in formation of rigidified polymer layer and unselective voids [24]. Therefore, in order to fabricate a defect free MMMs, the selection of dispersed phase is a crucial part. MOFs through its organic ligands have exhibited better interaction and compatibility with polymer matrix as compared to other categories of fillers. They have gained quite an attention over the years because of their compelling properties. MOFs have small aperture size, higher  $\text{CO}_2$  affinity and adjustable chemical and physical properties through pre-post synthesis modification [25, 26]. MOFs are actually crystalline compounds and comprises of metal ions and organic ligands. They have high micropore volume, larger surface area, several pore sizes, moreover, its high metal content as well as crystallinity has allowed MOFs to emerge as remarkable porous materials meant for various applications [27].

Among various kinds of metal organic frameworks, zeolitic imidazolate frameworks (ZIFs) are caged compounds that are formed by self-assembling of molecules in which divalent cations i.e., Zn or Co are coordinated tetrahedrally and are connected with imidazolate linkers to form topologies that are similar to those of aluminosilicates zeolites [28]. ZIFs has several advantages over traditional porous materials such as they have diversified structure, adjustable and porous pore channels, high specific surface area, easy functionalization and unsaturated sites and are viewed as next generation membrane materials [29]. In order to fabricate MMMs, researchers have done huge progress in their efforts to blend ZIFs as inorganic filler with wide range of polymers [30]. ZIFs are flexible, porous and thermally stable crystals up till 400 °C and are considered as favorable material for gas separation and also for shape and size selective catalysis because of their pore size that is below 5 Å [29,31]. ZIFs also have the ability to enhance the restricted gas separation performance of polymeric membranes bounded by Robeson upper bound. Hence, ZIFs are considered as an attractive inorganic filler material in MMMs fabrication.

In the view of above mentioned literature, the aim of this novel review is to elaborate the principles of energy efficient membrane driven systems, especially, the MMMs followed by their classification and hindrances in their development. Many previous research studies have

highlighted the usefulness of ZIF membranes in gas purification and separation applications, and also have discussed their fabrication methods along with their performances in gas separation applications [32–35], but there are very few detailed research studies available on ZIF based mixed matrix membranes in which different types of ZIFs are used as an inorganic filler for MMMs fabrication. This review focuses on the selection criteria of polymers and fillers in fabrication of MMMs, especially, ZIF fillers based MMMs development and their performance. Finally, a critical review on experimental investigations on ZIF based MMMs for gas separation is discussed.

## 2. Basic principles and classification of membranes

In membrane systems, separation efficiency of membranes can be calculated by measuring permeability as well as selectivity of gases. Permeability of the membrane is defined as the membrane's ability to permit permeating gas to diffuse through membrane material as a result of pressure difference across the membrane and could be calculated in terms of thickness and area of membrane, permeate flow rate as well as difference of pressure across membrane. Whereas, membrane's selectivity is defined as the ratio of permeability of two gases permeating through membrane in case of binary separation [36]. In membranes, gas transport separations takes place via diffusion, adsorption and molecule desorption through membrane and is typically dependant on driving forces for example temperature ( $\Delta T$ ), pressure ( $\Delta P$ ), electric potential ( $\Delta V$ ) and concentration ( $\Delta C$ ). The basic principle of gas permeation and separation is depicted in Fig. 1.

The SI and non SI unit specified for permeability is GPU (Gas Permeability Unit) and Barrer. Permeance or pressure normalize flux will be calculated using Eq. 1.

$$\frac{P}{L} = \frac{Q_i}{(\Delta p)(A)} \quad (1)$$

$\frac{P}{L}$  = gas permeance of membrane in GPU, 1GPU = ( $10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ ).

$Q_i$  = Volumetric flow rate of permeated gas.

$(\Delta p)$  = pressure difference across membrane in (cm/Hg).

$(A)$  = effective membrane area in  $\text{cm}^2$ .

Selectivity will be calculated by Eq. 2 as pressure normalized flux ratio of gas component x over y.

$$\alpha_{x/y} = \frac{(P_x/L)}{(P_y/L)} \quad (2)$$

From the results of gas separation performance listed in many research papers, the increase in permeability and selectivity by addition

of fillers were measured by ratio between gas separation by mixed matrix membranes and sole polymer membranes, via equations listed below.

$$\text{Permeability factor} = \frac{P(\text{MMM})}{P(\text{POLYMER})} \quad (3)$$

$$\text{Selectivity Factor for } \alpha_{x/y} = \frac{\alpha_{x/y}(\text{MMM})}{\alpha_{x/y}(\text{POLYMER})} \quad (4)$$

The resulting increased gas transportation properties (selectivity and permeability) were then plotted for a comprehensive insight into filler impact.

Mostly, membranes can be classified based on their nature, structure, geometry and their separation mechanism. Membranes are extensively available in synthetic and natural material. Synthetic membrane material could possibly be organic for example polymers, or inorganic such as metals and ceramics, or combination of organic and inorganic [38]. Their morphology or structure could be asymmetric or symmetric and depending upon their structure, membranes can be thick or thin, heterogeneous or homogeneous. Depending upon the ability of membrane to change the chemical nature of species permeating across the membrane, transport across membrane could be active, passive or reactive [39]. Various means can direct passive transport such as electrical potential, pressure and concentration. Examples of membrane configuration or geometry include tubular or flat sheet membranes and their separation process is mainly based upon chemical and physical characteristics of components that are to be separated. The mechanism for separation could be charge interactions, sieve, solubility-diffusivity and so on. Fig. 2 below shows membrane classification based on their material, structure and configuration.

## 3. Energy efficiency and cost effectiveness of membrane systems

Every machine and factory along with all industrial operations and processes require energy to operate and is mostly supplied through oil reservoirs, fossil fuels and gas. Natural gas combustion, as well as of petroleum, coal and fossil fuels end up in higher emissions of  $\text{CO}_2$  which in turn causes global warming [40]. Hence, undesirable  $\text{CO}_2$  along with other hazardous gases should be removed and removal of  $\text{CO}_2$  is important because of its corrosive nature and its uncontrolled emission into the atmosphere has become a serious concern as it is hazardous for human health and also leads to climate change, flooding and acid rain. Conventional gas separation technologies such as adsorption, absorption and cryogenic separation consume high cost and energy and also exhibit operational complexity. To overcome these issues, membrane based gas

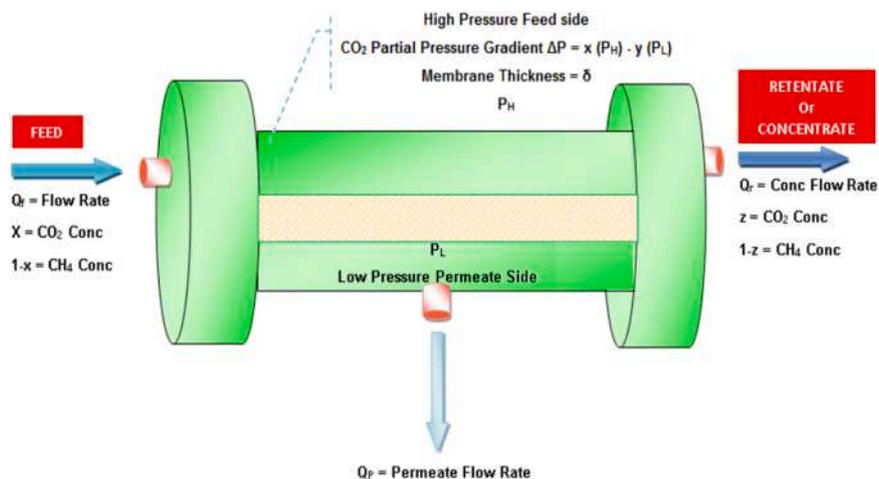


Fig. 1. Basic principle of permeation and separation of gas through membrane[37].

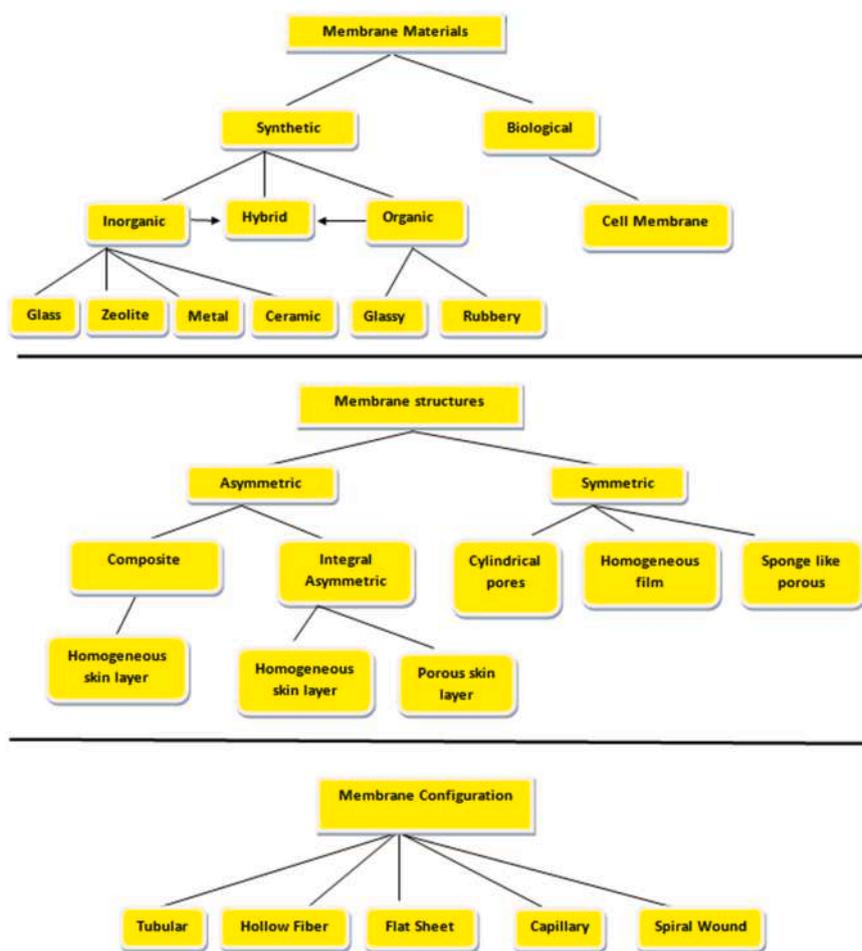


Fig. 2. Membrane classification based on material, structure and configuration.

separation technology has been employed as it offers convenient operational procedure and accessible scale up, and also it is cost effective and energy efficient [41,42]. Membrane based separation technology has played a vital part in several energy and environmental processes such as biogas upgrading [43], CO<sub>2</sub> capturing [44,45], natural gas sweetening [46,47], and also in volatile organic compound (VOC) recovery [48] and have the potential to compete with other traditional technologies in terms of economic cost and energy requirements.

It was announced by National Energy Technology that up till 2030, the electricity cost will surge for about 35% to eliminate over 90% of CO<sub>2</sub> arising out of power plants [49,50]. Though, the most commonly used and viewed technology in this area is amine absorption, but this technology suffered high CO<sub>2</sub> capture cost that is approximately \$40-\$100 per ton of CO<sub>2</sub> [49]. On contrary, membrane technology when used for gas separation can somehow decrease this cost if it is associated with adequate permselectivity by employing materials having high performance. For instance, in case of membrane systems having CO<sub>2</sub> permeance around 1000–2000 GPU and having CO<sub>2</sub>/N<sub>2</sub> selectivity that is around 25–50, the capture cost of CO<sub>2</sub> is reasonably reduced to \$20-\$23 per ton of CO<sub>2</sub> [50]. As discussed earlier, the most appealing benefit of using membranes for gas separation over other traditional techniques is high level of energy efficiency that is attained by employing membrane based gas separation technology [51]. Concentration of CO<sub>2</sub> in feed gas as well as pressure of feed stream, are major factors that will effect energy efficiency in gas separation process [52]. Input feed stream in membrane separation process have to be compressed frequently and this process requires energy. In processing of natural gas, the feed stream normally has enough pressure needed for membrane separation [42,53]. Furthermore, higher CO<sub>2</sub> concentration

in feed stream will increase diffusion rate of CO<sub>2</sub> and consequently increases membrane efficiency. Whereas in conventional processes employed for CO<sub>2</sub> separation such as amine absorption, higher CO<sub>2</sub> concentration in feed stream will usually increase energy requirements along with operational cost [54]. Since, in amine absorption system, high CO<sub>2</sub> concentration requires more amine circulation rate and in turn results in higher energy consumption [55].

Also, in order to control the energy consumption of membrane separation process, membrane's selectivity and permeability is considered as the most important element. Gas pressure drop will decrease by increasing membrane's permeability; therefore, the energy consumed for compression in each stage will in turn decrease. Conversely, if membrane's selectivity increases, membrane area and rate of circulation will decrease and consequently, the overall process cost will decrease [52]. Hence, it is inferred that overall energy efficiency as well as the process will improve on providing membranes with suitable performances for gas separation. Furthermore, factors that influence the design of membrane separation unit for example appropriate membrane modules as well as number of stages should be viewed as an effectual parameter for total energy consumption. Using multiple stage operation is considered as one of the techniques to increase efficiency of membrane as desirable separation ratio is not attained in single stage operation. In case of multiple stage units, on repeating operation in every stage to attain the desired concentration, the consumption of energy will increase yet it is much lower than the energy that is consumed to repeat entire process in single stage unit [56]. It was estimated by Yang et al. [57] on comparing single and multiple stage units during gas separation process that energy requirement amongst stages is approximately 107.5 KJ/m<sup>3</sup> in case of two stage membrane unit [57]. Results indicated

that higher energy is consumed in multiple stage units in order to generate suitable driving force after individual stage, yet it is not much when compared to consumption of energy in traditional amine absorption technique that is approximately  $600\text{--}900\text{ kJ/m}^3(\text{STP})$  [58].

Hence, it can be concluded that to carry out any desired gas separation process such as biogas upgrading,  $\text{CO}_2$  capturing, recovery of  $\text{H}_2$  or natural gas sweetening etc, high performance membrane material is needed, while considering some important factors such as permeability and selectivity, composition of feed gas, process conditions, mechanical and thermal stability as well as design of membrane module [59]. However, it is predicted that membrane based gas separation technique requires very little or no chemicals, have low energy consumption and can be scaled up quite easily as compared to conventional separation techniques, and in future it will be considered as an earth friendly technique for gas separation applications. Also, performances of membranes should be considered as a vital factor in membrane based gas separation units. Mixed matrix membranes as a new class of membranes having high permeability, selectivity along with higher energy efficiency could be an appropriate choice for this goal.

#### 4. Mixed matrix membranes

As reported earlier that the performance of polymeric membranes in gas separation applications is restricted by permeability/selectivity trade off. This issue led the researchers to develop new technology for membrane fabrication having the ability to fabricate high performance membrane material concerning the gas permeability and membrane selectivity in order to expand commercial applications of polymeric membranes. On contrary, in spite of encouraging performance of inorganic membranes in gas separation applications on laboratory scale, their scaling up encounters numerous challenges. Furthermore, inorganic membranes are likely to be excessively expensive having a module cost of  $\$1000/\text{m}^2$ , which is almost 100 times more than that of polymer membranes in flat sheet ( $\$10/\text{m}^2$ ) or hollow fiber ( $\$5/\text{m}^2$ ) geometry [17,60]. Hence, their high fabrication cost as well as their processability into modules for wide spread applications are important concerns related to their use in gas separation applications [61–63]. Polymeric membranes that are available commercially are comparatively cheap because of high processability but they provide relatively less separation capabilities in comparison to inorganic membranes. As mentioned earlier that inorganic membranes, in spite of their high selectivity and permeability, these chemically and thermally robust membranes demand higher capital cost because of its complicated fabrication process and highly priced precursors.

In order to address problems linked to inorganic and polymeric membranes, effort was done to combine the advantages of both inorganic and polymeric materials to fabricate advanced membranes namely mixed matrix membranes (MMMs). They have the ability to enhance permeability as well as selectivity at the same time, that is, without restraining any of it and by employing inorganic particles as dispersed phase and polymeric material as continuous phase. MMMs are fabricated by dispersing nano or micro sized inorganic particles (fillers) in continuous phase of polymeric matrix as shown in Fig. 3 below and resultant MMMs combines the benefits of both organic and inorganic phases.

The inorganic phase in MMMs generally enhances gas permeability and provides selectivity that is superior to polymeric phase, hence enhancing the performance and ability of polymeric membranes without disturbing the processing and economic conveniences of polymers. Table 1 below compares the characteristics of polymeric, inorganic and MMMs.

MMMs are actually polymer based composites involving phase separated membrane separation process. Within MMMs, inorganic fillers in order to enhance the separation performance of membranes, makes appropriate permeation pathways especially for selective permeability and at the same time creating a hurdle for unwanted permeation [65].

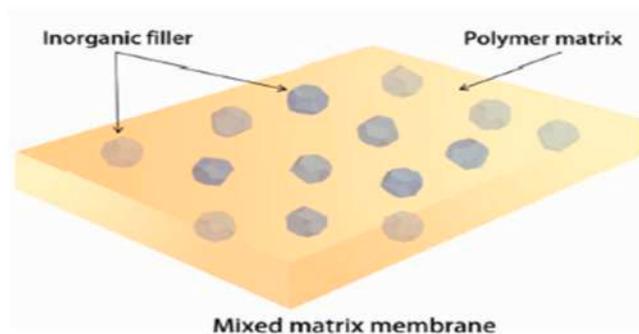


Fig. 3. Schematic illustration of mixed matrix membranes [64].

Table 1

Comparison between characteristics of polymeric, inorganic and mixed matrix membranes.

Characteristics	Polymeric membrane	Inorganic membrane	Mixed matrix membrane
Thermal and chemical stability	Moderate	Superior	Superior
Mechanical strength	Good	Low	Superb
Cost of fabrication	Low	High	Moderate
Processability and synthesis	Easy and simple	Tough	Easy and simple
Separation performance	Below Robeson upper bound	Above Robeson upper bound	Above Robeson upper bound
Resistant towards high pressure	Moderate	Higher	Higher
Plasticization	Susceptible	Unsusceptible	Unsusceptible

Inorganic membrane's exceptional permeability and selectivity along with polymeric membrane's processability are amalgamated to attain collaborative separation performance, during which inorganic phase delivers exceptional separation characteristics and continuous polymer phase allows perfection in membrane forming thereby resolving the problem related to inherit brittleness identified in inorganic membranes. It is expected that within polymer matrix, the addition of filler with molecular sieving characteristics would result in high permeability and selectivity in comparison to polymer membranes. The additions of inorganic fillers into polymeric matrix usually involve either fillers with spherical or low aspect ratio or, thin platelets of fillers with exceptionally higher ratios [66]. The last mentioned case is of great interest because it provides enhanced separation properties over traditional case [67]. Though inorganic fillers are employed in almost all preparation cases, the resultant separation performance of membrane as well as its morphology can be differed considerably, mainly arising from various capabilities of these molecular sieves (fillers), either on the basis of size or shape, in order to differentiate between distinctive molecules existing in feed mixture.

The benefits associated with employing MMMs encouraged further research to review gas separation capability of already existing polymer membranes. The exceptional performance of MMMs was first reported by Kulprathipanja et al. [68]. They perceived that by addition of silicate into cellulose acetate polymer resulted in increasing  $\text{O}_2/\text{N}_2$  selectivity in comparison to neat cellulose acetate polymeric membrane [68]. Although, MMMs must control and overcome some critical challenges associated with their fabrication for example, particle agglomeration and sedimentation as well as existence of interfacial voids at polymer-filler interface in order to achieve desired membrane morphology and gas separation characteristics. Within the polymer, too much filler loading results in agglomeration of filler particles which in turn reduces membrane performance [61,69]. Hence, in order to successfully fabricate MMMs, it is necessary to choose inorganic filler that is

compatible with polymer matrix meaning choosing a suitable pair of polymer/filler is challenging step in MMMs fabrication.

As discussed earlier that MMMs are fabricated by incorporation of inorganic particles within polymeric matrix. So, the method that is used to fabricate MMMs is somehow quite similar to the one that is used to fabricate regular polymer membrane. The initial step in fabrication of MMMs is to prepare a homogenous solution of particles and polymer. For the purpose of fabrication, different techniques can be employed. First technique involves dispersion of particles in the solvent and then mixture is stirred for predetermined amount of time and afterwards polymer is further added in it (Fig. 4a) [70–74]. In second technique, polymer is first dissolved into the solvent and it is then stirred and afterwards predetermined quantity of inorganic filler particles is then further added into the solution of polymer (Fig. 4b) [75–79]. In the third technique, inorganic filler particles are first dispersed in solvent and then continuously stirred for predetermined amount of time and similarly polymer is also dissolved into the solvent separately. In the end, filler particle suspension is finally added into polymer solution (Fig. 4c) [80,81]. Out of these three techniques, first and third technique is usually employed for better dispersal of filler particles as in dilute suspension, filler particles are normally restrained from agglomeration by higher shear rate while stirring. And, the second technique is normally

employed for the distribution of nanoparticles within the polymeric matrix. Fig. 4(a-c) below demonstrates different techniques for preparation of dope solution for MMMs fabrication.

#### 4.1. Challenges encountered in fabrication of MMM

In general, the dispersion of inorganic particles into continuous polymeric matrix is expected to enhance the properties of membrane because of the dispersed phase superiority. But, fabrication of MMMs in practical terms usually encounters the decline in membrane performance [19]. The interfacial morphology of polymer-filler is the most important factor that regulates general gas transportation properties. Weak interaction among filler and polymer often results in reduction in membrane's separation performance. Factors that normally lead towards poor interfacial morphology includes poor adhesion between filler and polymer, filler pore's partial blockage by polymeric chains and rigidification of polymer chains.

Incompatibility among filler and polymer is generally considered as the key factor that results in interfacial defects. This incompatibility also leads to non-selective interfacial voids. These voids could also occur because of forces of repulsion between filler and polymer, elongation stress during hollow fiber spinning and also interfacial cracking at very

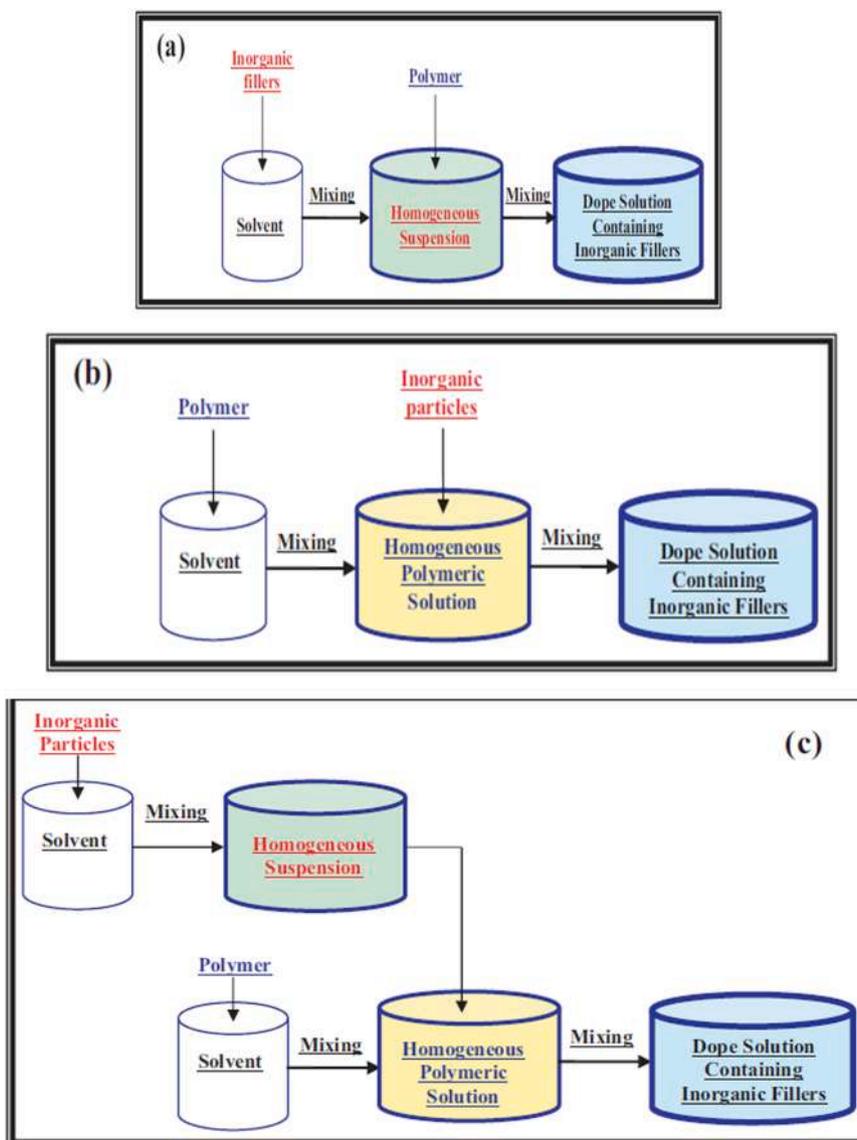


Fig. 4. Different techniques for preparation of dope solution for MMMs [15].

high loading [82]. Therefore, the existence of these interfacial voids would in turn leads towards low gas pair selectivity. The reduction in the formation of interfacial voids can be achieved by treating filler before dispersing it into polymer solution. In order to deal with this issue, filler particle treatment on mesoporous spheres of silica was suggested by Zornoza et al. by employing chemical extraction and calcinations [83]. Surface modification of filler is also considered useful in order to increase filler affinity towards polymeric matrix. This method helps in reducing the emergence of non-selective interfacial voids by acting as a cohesive agent at polymer-filler interface. The frequently used methods for surface modification include amine modification [84], silane coupling agent [85], octadecylamine [86] and also diethanolamine [87].

The fabrication of MMMs by employing polymer as a continuous phase is considered to be problematic because of agglomeration of filler particles during preparation of solution within which mixing techniques are essential in order to disintegrate agglomerated particles before the processing of membrane. Although, glassy polymers have quite appealing separation properties as compared to rubbery polymers because they possess high free volume but, poor mobility of polymer chain during membrane fabrication may leads to poor interaction between polymer matrix and inorganic filler particles. Interaction among inorganic filler particles and polymer matrix is of great concern because unacceptable channels might appear between two phases if polymeric chains do not interact completely with inorganic particles. Separating out of inorganic fillers from membrane matrix because of incompatibility and producing separate layers or phases of filler during MMMs fabrication is termed as classification and it can reduce membrane's gas separation performance [88]. Fig. 5 below demonstrates the formation of void at sieve-matrix interface. The emergence of these unselective interfacial voids permits escape of gases and thus results in reducing MMMs selectivity [89–92]. To resolve this issue, existence of bridging agent in order to provide ease in better interfacial interaction is of great significance as shown in Fig. 5c. Furthermore, techniques that involve creating of surface roughness and modifications of surface hydrophobicity along with varying pore architecture and composition of filler particle have too been explored [90].

Also other problem that is encountered during MMMs fabrication is partial filler pore blockage by polymeric chains rendering role of incorporated inorganic filler [93]. Partial pore blockage permits molecules that are smaller than blocked pores to go through whereas total pore blockage behaves as impenetrable filler and molecules of gas cannot pass through filler pores. Pores could get clogged with solvent or sorbent, or with some small component or contaminant in polymer chain or feed gas during, before or after membrane fabrication process. This phenomenon often results from too much filler loading that in turn results in creating impassable pores after occurrence of agglomeration.

Also, poor polymer-filler compatibility can lead towards blockage of pores. Through alteration or functionalization of filler or polymer via introduction of mutually interactive functional group will increase polymer filler compatibility and reduces pore blockage issue. At interface, rigidification of polymer induced by inhibition of polymer chain mobility within local region has the ability to change gaseous transport behavior around filler particles. The occurrences of this phenomenon could be reduced by plasticization of polymer matrix in order to enhance polymeric chain mobility [94]. Hence, to overcome aforementioned challenges and to reduce their negative effect, incorporation and effective dispersion of filler particles into polymeric matrix as individuals is one of the crucial tasks to be dealt with. In these conditions, several treatment approaches are employed to change inorganic filler's surface chemistry.

#### 4.2. Selection criteria for polymers

For fabrication of gas separation membranes, selection of polymeric materials has been studied extensively over last few decades and quite a lot of papers have been reviewed comprehensively on this topic [9, 95–97]. This topic in this review includes discussion about importance of selecting appropriate materials for preparing high performance MMMs. For fabrication of MMMs, selection of material for both polymer and inorganic filler is inherently important. Pair wise selection is of key importance for fabrication of MMMs as it is directly linked with separation performance as well as MMMs morphology. In MMMs that are defect free; the polymeric matrix generally determines minimum separation performance and inorganic filler regulates and determines enhancement of membrane's selectivity and permeability [98,99]. Commonly used polymeric materials for fabrication of MMMs usually includes polycarbonates, polyimides, polysulfone (PSF), poly(arylethers) and poly(arylketones) [100]. Several inorganic filler materials have been examined in order to fabricate MMMs including carbon molecular sieves [18], several zeolites [68,101], activated carbon [102], non-porous silica [103], carbon nanotubes [104], mesoporous materials [105–107], graphites [108] and lately metal organic frameworks [109, 110]. As discussed earlier, suitable combination of filler and polymer material plays a vital part in determining membrane's separation properties. For example, in case where diffusivity selectivity is a preferred choice within which fillers behave as molecular sieves to omit molecules of gas based on difference in their size, fillers having molecular sieving properties must be thought about. Under these circumstances, polymeric materials having the ability to separate gases based on difference in their diffusivity should be considered in order to match selected filler particles.

Generally, two types of polymers are often used for fabrication of gas separation membranes i.e., glassy and rubbery polymers. Most

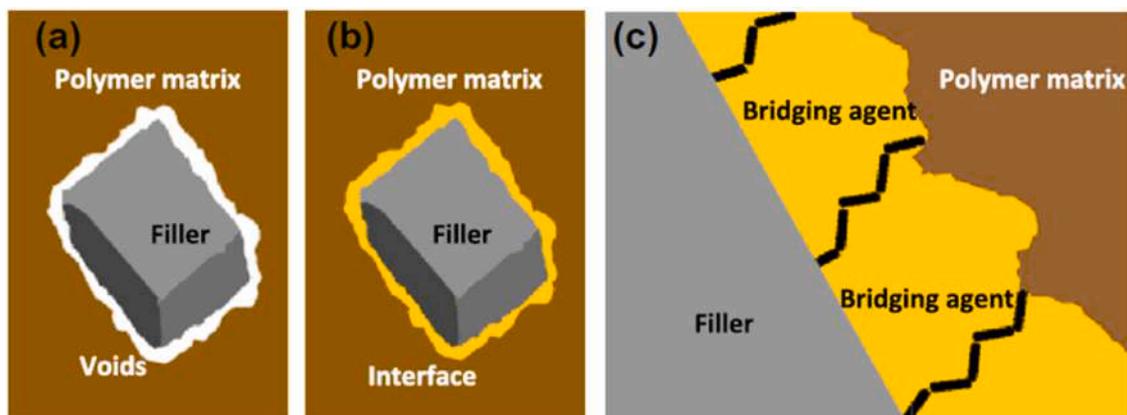


Fig. 5. MMMs interfacial properties (a) formation of void between two phases (b) Bridging of continuous polymer matrix and inorganic filler on surface modification [90].

important issue for polymeric material in MMM is ensuring appropriate adhesion between inorganic filler particles and polymer. In case of rubbery polymers, because of them having higher degree of mobility, stronger interaction with filler particles can be attained that in turn favors the development of zero-defect interface among two components. But, the disadvantage of rubbery polymer's higher mobility is that it makes up the membrane exceedingly permeable, hence the gaseous transport within membrane is mostly influenced by polymeric matrix and just a little portion of overall gaseous transport is accredited to filler particles. Whereas, glassy polymers in contrast, manifests higher separation performance because of them having rigid chain structure, which regrettably weakens and reduces interaction among filler and polymer. As a result, MMMs that are fabricated by employing glassy polymers generally have interfacial voids and these voids behave as an alternative path for molecules of gas and compromise membrane separation ability. Hence in this respect, a new category of polymeric material namely block copolymers having both soft and rigid polymeric segments was approved to fabricate MMMs by employing classic rigid-soft structure of block copolymer, hence possibly enhancing adhesion power. In recent past, many research studies have emerged narrating MMMs fabrication by employing block copolymers e.g., poly (imide siloxane) and filler particles (zeolite-Land carbon nanotubes). In those studies, good adhesion among inorganic filler particles and block copolymers was observed.

The appropriate choice of polymeric material regulates MMMs interfacial morphology. To address the problem related to poor adhesion, the utilization of external linkers like silane coupling agents is considered as common approach. Though, the introduction of additional agent in system might leads towards undesirable pore blockage issue. To deal with it, selection of polymeric material having integral chemical linkages which are inherently part of chain backbone can enhance adhesion among filler and polymer and at the same time prevents pore blockage problem. Mahajan et al. examined the practicality of this approach by employing fluorinated polyimide created from 6FDA-6FpDA/4MPD/DABA having carboxylic groups on polymeric chain backbone in their research [92,111]. Presence of carboxylic group in this polymer possibly provides hydrogen bonding or rather covalently bondable sites to interact with filler surface as depicted in Fig. 6 below. Polymer will not be able to separate completely from filler surface because of these chemical ligands yet detachment may still occur at segmental level, hence administering good adhesion along with better interfacial morphology. By employing polymers having chemical linkers

that react with functional groups present on the surface of filler, the accomplishment of their research work specified a new direction towards improving adhesion related problem. This technique when combined with filler's surface functionalization has the potential to enhance interfacial morphology of MMMs.

#### 4.3. Selection criteria for fillers

As mentioned above, the continuous polymeric phase along with inorganic dispersed phase has influence on MMMs morphology as well as its separation properties. For fabrication of MMMs, porous and non-porous inorganic fillers are two main filler materials that are normally used. Carbon molecular sieves (CMS) and zeolites are examples of porous materials that are frequently used as inorganic filler particles in development of MMMs [18,70,71,81,112,113]. CMS are highly porous and have been explored widely as they have the ability to be used as membrane material for fabricating gas separation membranes [114, 115]. CMS assures higher gaseous permeability because of their high porosity as well as finer pore size distribution. Also, CMS pore opening size is almost of similar order as gas molecule size; hence it permits precise differentiation of particular gaseous species. Internal surfaces of CMS are hydrophobic and are employed in industries to separate CO<sub>2</sub> from landfill gases and also in air separation by adsorbing oxygen [116, 117]. CMS have ability to discriminate gases on basis of their kinetic diameters [118]. The potential of developing MMMs by employing CMS as filler was examined by many researchers. Gas separation performance of MMM incorporating CMS along with Matrimid 5218 was accessed by Vu et al. and 45 % enhancement in CH<sub>4</sub>/CO<sub>2</sub> selectivity was observed by them [18]. On the other hand, zeolites with their size selective nature as well as highly defined porous structure are also strong candidate for developing MMMs. Activated carbon, metal organic frameworks (MOF) and carbon nano tubes (CNT) are also different types of porous materials that have been incorporated as dispersed inorganic phase in development of MMMs.

When porous material is incorporated into polymeric matrix as inorganic filler, its surface chemistry, pore size distribution as well as functional groups should be compatible with molecules of gas pair. For instance, activated carbon is appropriate for CH<sub>4</sub>/CO<sub>2</sub> separation due of its high adsorption selectivity for CO<sub>2</sub> than for CH<sub>4</sub>, however this inorganic filler is not appropriate for O<sub>2</sub>/N<sub>2</sub> separation [102]. Zeolite 13x having aperture size of 10 Å is not likely to behave as molecular sieve for molecules of N<sub>2</sub> and O<sub>2</sub> having kinetic diameters of 3.64 Å and 3.46 Å

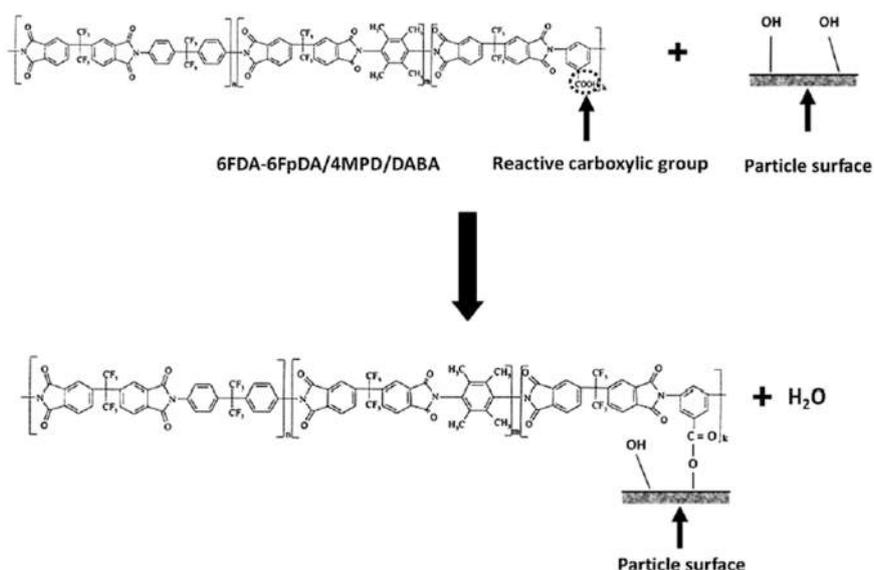


Fig. 6. Illustration of 6FDA-6FpDA/4MPD/DABA chemical attachment to surface of filler [61].

respectively. While on the contrary, zeolite 4A having aperture size of 3.8 Å have the ability to differentiate two molecules because of entropic factors [119]. Hence, it is important that molecular sieving phase should correspond exactly to shape and size difference of molecules of gas. On the other hand, as the influence of non-porous material on separation ability of mixed matrix membrane is quite different from porous materials with molecular sieving attribute, hence before adding these materials into polymeric matrix, interaction among nanofillers and polymeric chain fragments together with the functional groups on inorganic phase surface should be analysed and considered [75]. For example, the addition of silica into polyimide matrix could disrupt the packing of polymer chain which in turn increases the permeation rates of nitrogen and oxygen [120,121]. While on contrary, addition of TiO<sub>2</sub> into polyimide matrix could enhance the CH<sub>4</sub>/H<sub>2</sub> and CH<sub>4</sub>/CO<sub>2</sub> selectivities as the interactions of H<sub>2</sub> and CO<sub>2</sub> with TiO<sub>2</sub> are way stronger than interactions among TiO<sub>2</sub>-CH<sub>4</sub> [122]. Fullerenes (C60) [123], silica, TiO<sub>2</sub> [78,124] are most frequently used impermeable filler particles employed for fabricating nanocomposite MMMs.

Distinct properties of inorganic filler materials like morphology, dispersability, stability, size as well as hydrophobicity or hydrophilicity have the ability to affect MMMs overall performance. Hence, it is important to take account of these factors while fabricating MMMs [125]. Filler size greatly affects membrane's homogeneity. As an example, filler particles that are larger in size have tendency to agglomerate and this leads towards filler cluster formation within the membrane. These filler clusters are the reason behind membrane's non homogeneity as they dominate the polymeric phase within membrane and acts as a resistance. Therefore, a weak and poor interconnection is formed between inorganic filler and polymer which in turn decreases membrane's mechanical stability. Subsequently, membranes become sensitive towards high pressure and get damaged quite easily. Also, non-uniform filler dispersion within polymeric matrix results in formation of non-selective voids which consequently affects membrane's performance. Hence, in order to prevent the formation of voids and to attain stronger interaction between filler and polymer, good filler dispersion must also be taken into consideration [69].

#### 4.4. Mixed matrix membranes development

After the novel review on MMMs by Okumus et al, many reports on the likelihood of MMMs have been published [126]. In the fabrication of MMMs, solid polymer MMMs has received most attention. In this type of MMMs, both zeolitic and non-zeolitic inorganic fillers can be incorporated as fillers in polymer matrix. Silicoaluminophosphate (SAPO) and aluminophosphate (ALPO) molecular sieves are zeolitic inorganic particles and are considered as conventional zeolites. Because of their thermal stability and their permeation performances, these micro porous materials are used in the preparation of MMMs for the purpose of gas separation [87,127,128]. Zeolitic crystal properties such as specific adsorption and shape selectivity can enhance the selectivity and permeability of polymer films when combined with the process ability of polymeric matrix for the purpose of gas separation of various gas pairs. As a polymer matrix, both rubbery and glassy polymers were used in the fabrication of zeolitic mixed matrix membranes. The interaction between rubbery polymers and the zeolitic fillers is brilliant because of polymeric chains high mobility. In spite of the fact that they exhibit good permeation properties and high mechanical strength, MMMs that are fabricated using zeolites and glassy polymers end up having interfacial voids and defects. To eliminate the problem related to adhesion, various types of surface modifications are introduced that includes coating of a diluted solution of highly permeable silicone rubber to get rid of unselective voids mostly developing on polymers [129,130]. Plasticizer is added to decrease the intrinsic gas separation performance of polymers [101,131]. Amine coupling agents and silane is mostly used to enhance both gas selectivity and interfacial adhesion by modifying zeolites surface properties from hydrophilic to hydrophobic [71,80,132]. It was

seen that the selectivity of CO<sub>2</sub>/CH<sub>4</sub> decreased up to 80% by the embodiment of unmodified zeolites due to unselective void formation. Whereas by the incorporation of modified zeolites, CH<sub>4</sub>/CO<sub>2</sub> selectivity has boosted 50 % than neat membrane. By the absence of unselective voids after modification of surface, CH<sub>4</sub> followed a longer permeation path, whereas CO<sub>2</sub> can easily access through filler and hence selectivity of CH<sub>4</sub>/CO<sub>2</sub> improved. Till now many reports have been patented on zeolitic based MMMs as a better alternative to polymeric and inorganic membranes.

Non-zeolitic inorganic fillers have also received much attention in the development journey of MMMs. Metal oxide nanoparticles, carbon molecular sieves, porous and non-porous silica nanoparticles are some types of non-zeolitic fillers. CMS nanoparticles having micro pores are incorporated in the fabrication of MMMs as they exhibit remarkable permeation behavior and high productivity [133–135]. They also exhibit good affinity to glassy polymers ensuring good contact at interface [18]. However, in order to prevent the formation of interfacial voids and defects and to enhance selectivity as well as permeability many improvements are being done in CMS based MMMs [18,81]. Before undergoing pyrolysis at a temperature of 800 °C for 2 h in vacuum, CMS was made by using dense Matrimid5218 as a precursor. With the 200 selectivity of CO<sub>2</sub>/CH<sub>4</sub>, and 43.5 Barrer permeability of CO<sub>2</sub>, resulted MMM with CMS exhibited promising properties for separation. The increase in the properties of separation was due to incorporation of CMS into polymer matrix. During the process of gas separation, plasticization is another important phenomenon. At an elevated feed pressure, CO<sub>2</sub> plasticizes a broad range of glassy polymers [136]. Reduction in the interaction among filler and polymer can cause the plasticization of glassy polymers and declines the performance of membranes in gas separation applications. The CO<sub>2</sub> causes an increase in polymer chain mobility, thereby increases diffusion coefficients of all the penetrants within membrane. In order to improve plasticization resistance, modification and cross-linking methods were applied widely [137]. The process of cross-linking causes the reduction in polymeric chain mobility by enhancing the adhesion between inorganic filler and polymer. By overcoming the plasticization induced by CO<sub>2</sub>, long-term stability and gas separation performance can be achieved.

In order to fabricate heterogeneous mixed matrix membranes by sol-gel process, porous and non-porous nanoparticles of silica in forms such as ceramic, tetraethoxysilane, organosilicate, fumed or colloidal silica are usually dispersed in polymer matrix [78,138,139]. Because of weak permeability or intrinsic impermeability of silica particles, the addition of these particles in polymer matrix improves both selectivity and permeability by altering polymeric chains molecular packing [90,140]. MMMs which exhibits increase in polymer volume without the formation of non-selective voids have better permeation characteristics but decreased selectivity. Chemical modifications are expected to eliminate the formation of voids and are carried out with silane coupling agents containing hydroxyl or organo-functional groups [141,142]. Another form of silica particles i.e. mesoporous materials are used as filler to enhance the interaction between filler and polymer by penetration of mesopores through polymer chain. Because of their large surface area, the addition of mesoporous materials in polymer matrix can bridge polymeric chains through hydrogen bonding and no increase in selectivity was observed because diffusion of gas in mesopores is non selective [105,143,144]. Many approaches have been put forward to enhance the selectivity like creating mesopores in pure zeolites [145], incorporation of micropores in mesoporous materials [146] or modification of interface composition via functionalizing with organic groups i.e. PMO's (Periodic Mesoporous organic silicas) [147,148].

Rapid increase in publications has been observed directing towards the applications of above mentioned fillers used in fabrication of solid-polymer MMM. In spite of this, many alternative fillers such as layered silicates, graphene, carbon nanotubes (CNT), metal organic frameworks (MOFs) have been studied as a new material for filler having several attractive properties. MOFs as an emerging and new category of

crystalline porous materials have gained quite an attention recently as a promising candidate for fabrication of MMMs. Metal organic frameworks consists of secondary building units that are connected to organic ligands in order to create a repetitive cage like structure [149–152]. In them, the secondary building units are generally transition metal oxides and positive charged metal ions. MOFs can easily be synthesized in high purity as well as crystallinity via employing different techniques for example sonochemical, electrochemical, microwave and mechanochemical [149,153,154]. MOFs exhibit many distinctive structural properties as well as advantages such as high porosity and surface area [155], flexible and rigid framework [156], adjustable pore sizes [157], tunable porosity [158], low densities as well as chemical and thermal stability [159], and these advantages provides convenience to membrane researchers to utilize MOFs in several gas separation operations over other porous materials (activated carbons, silica, zeolites) [61,160,161]. During the last decade, many important structures of MOFs such as ZIF series,  $\text{Cu}_3(\text{BTC})_2$ , MIL-series, MOF-5, HKUST-1 etc have been utilized successfully in MMMs development.

Nik et al. employed five different types of MOFs that were  $\text{NH}_2\text{-UiO-66}$ ,  $\text{UiO-66}$ ,  $\text{MOF-199}$  ( $\text{Cu-BTC}$ ),  $\text{UiO-67}$ ,  $\text{NH}_2\text{-MOF-199}$  to fabricate Matrimid based MMMs [162]. Among all the fabricated membranes, the ones that were fabricated by employing  $\text{UiO-66}$  displayed high  $\text{CO}_2$  gas permeation, while on the contrary  $\text{NH}_2\text{-MOF-199}$  (amine functionalized MOF based MMM) enhanced both  $\text{CH}_4/\text{CO}_2$  selectivity as well as  $\text{CO}_2$  gas permeability. Reason behind enhancement in selectivity was due to hydrogen bonding existing between ( $-\text{NH}_2$ ) in filler and carboxylic group in polymeric chain that expedited polymeric chain rigidification at the interface. As a result, selectivity increased and permeability decreased [162].  $\text{ZIF-90}$  was impregnated successfully by Bae et al. in 6FDA-DAM polyimide to fabricate 6FDA-DAM/ $\text{ZIF-90}$  MMM by employing non solvent induced crystallization technique [163]. The addition of  $\text{ZIF-90}$  into 6FDA-DAM polyimide enhanced both gas permeability as well as selectivity of membrane.  $\text{CO}_2$  permeability adequately increased from 390 Barrer to 720 Barrer, while the selectivity of  $\text{CH}_4/\text{CO}_2$  improved from 27 to 37 [163].

As stated above, one of the advantages of MOFs is that they possess flexible structure. This permits the research workers to bring in desired functional groups linked to the main frameworks in order to provide extra affinity towards specific type of gases. For example, amine functional group possessing stronger  $\text{CO}_2$  affinity was employed to functionalize  $\text{Cu}_3(\text{BTC})_2$  in order to encourage  $\text{CO}_2$  solubility [85].  $\text{ZIF-7/polybenzimidazole(PBI)}$  MMM was fabricated by Yang et al. [164] via synthesizing  $\text{ZIF-7}$  with excess PBI and afterwards mixing it with Polybenzimidazole having reactive hydrogen atoms on polymeric chains without employing typical drying step, hence preventing aggregation of filler particles. The resultant MMM was packed with higher  $\text{ZIF-7}$  content (50 wt%) and exhibited ideal  $\text{H}_2/\text{CO}_2$  selectivity as well as enhanced  $\text{H}_2$  permeability [164]. Hence, MOFs are considered as favorable choice for fabrication of MMMs. The heart of development of MMMs is the selection of fillers that are compatible with the polymer matrix and boost the performance of membrane exceeding Robeson upper bound.

## 5. Various types of ZIF as a filler for MMM development

Zeolite imidazolate frameworks (ZIFs) belong to the family of MOFs and their structures resembles with that of zeolites. ZIFs exhibit higher chemical and thermal stabilities because of synergistic effect of metal and imidazole groups. They have been used extensively as filler in fabrication of MMMs as they can be prepared quite easily by energy efficient and uncomplicated method. Moreover, its size could also be adjusted and tuned via manipulating its synthesis procedure as well as formulation [165,166]. ZIF based materials were reviewed by Phan et al. for the purpose of  $\text{CO}_2$  capture and separation [167]. ZIFs are made up of transition metal nodes that are connected by imidazolate linkers which replaces the zeolite's bridging oxygen [168]. As mentioned

above, many structures of ZIFs having different organic linkers have been used as inorganic fillers for MMMs fabrication. Their narrower pore size and large cavities makes them appropriate fillers for gas selective MMMs, especially for separation of  $\text{CO}_2$  as the kinetic diameter of  $\text{CO}_2$  is 3.3 Å, which is very much comparable to pore openings in various ZIFs. ZIF also possess the flexibility to accommodate a second metal within its structure and this in turn provides a synergetic effect which results in higher and improved gas separation performance in MMMs [169].

MMM delivers separation properties that have the ability to overcome Robeson Upper Bound. Several different classes of fillers that are employed in fabricating MMMs have been discussed in different review papers [170–172]. This review focuses on the effects of incorporating different ZIF based fillers in fabrication and performance of MMMs. Many different ZIFs for example  $\text{ZIF-8}$ ,  $\text{ZIF-90}$ ,  $\text{ZIF-7}$ ,  $\text{ZIF-95}$ ,  $\text{ZIF-11}$ ,  $\text{ZIF-302}$ ,  $\text{ZIF-71}$  etc have been developed as sole-ZIF based MMMs [173–177] or modified ZIF based MMMs [174, 178–181] for several gas separation applications such as for separations of  $\text{CO}_2/\text{N}_2$ ,  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ ,  $\text{CO}_2/\text{CH}_4$ ,  $\text{H}_2/\text{CH}_4$  etc. The latest progress in research regarding ZIF based MMMs for separation of  $\text{CO}_2$  was highlighted by Guan et al. [182]. It was concluded that modified ZIF's synergetic effect can alter the membrane structure and enhances interfacial compatibility which in turn results in improving membrane's separation performance. Also, ZIFs characteristics such as its dispersibility, size as well as its hydrophobic or hydrophilic nature have influence on separation performance of membrane.

Pebax because of its admirable properties in terms of durability, flexibility as well as thermal and mechanical characteristics is considered as one of the most favorable polymeric matrices among other polymers. It also exhibits better selectivity towards polar and non-polar gases like  $\text{CO}_2/\text{N}_2$ . To fabricate MMMs, several ZIFs have been dispersed into Pebax polymeric matrix and other polymers [31,166,171,183].  $\text{ZIF-8}$  is one of the most explored Metal Organic Frameworks. It possesses a porous crystalline structure having M-Im-M angle that is near  $145^\circ$  and coincides with Si-O-Si angle present in many zeolites and having a large pore size of 11.6Å and 6-ring window aperture of 3.4Å as shown in Fig. 7 and it is studied frequently for separation performance of MMMs [174,184,185].

$\text{ZIF-8}$  possesses good chemical stability against non-polar and polar solvents [159], has high mechanical and thermal stability [187] and ability of reorientation of its structure at elevated pressure [188]. For instance, MMMs were developed by employing  $\text{ZIF-8}$  nano particles as filler into Pebax polymeric matrix. To prepare  $\text{ZIF-8}$  nanoparticles in different sizes of 40 nm, 60 nm, 90 nm, and 110 nm, micro emulsion technique was employed [166]. It was revealed from this study that smaller sizes of ZIF particles have a stronger affinity towards polymeric matrix hence, yielding a stronger interfacial interaction and zero-defect membrane. The outcome of  $\text{ZIF-8}$  particle size on gas selectivity as well as permeability of Pebax based MMM is shown in Fig. 8. Enhancement in  $\text{CO}_2$  permeability as well as  $\text{CO}_2/\text{N}_2$  selectivity was exhibited by MMM incorporating 5 wt% of  $\text{ZIF-8}$  having size of 90 nm in comparison to

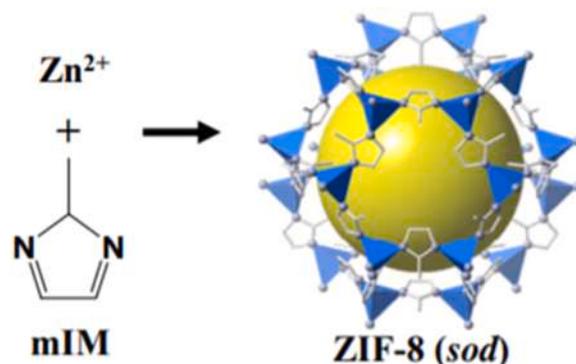


Fig. 7.  $\text{ZIF-8}$  crystal structure [186].

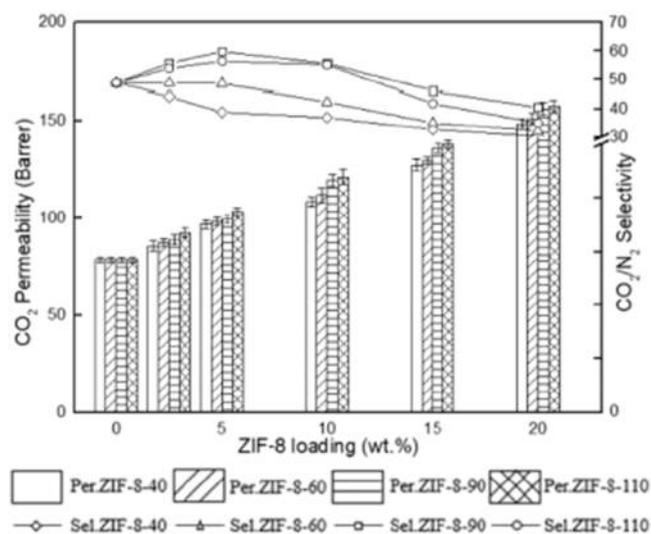


Fig. 8. Effect of ZIF-8 particle size and loading on  $\text{CO}_2/\text{N}_2$  selectivity as well as  $\text{CO}_2$  permeability of Pebax-ZIF-8 based MMM [193].

pristine Pebax membrane because of enhancement in free volume of polymer that is facilitated by ZIF-8 larger size particles. Though, in MMM, the selectivity of  $\text{CO}_2/\text{N}_2$  is reduced slightly because of micro-phase separation. Hence, it was concluded through this study that the separation efficiency of MMMs is strongly influenced by ZIF-8 particle size [166]. The utilization of ZIFs as a filler in development of MMMs was also reported by Ordonez et al. [189]. Matrimid/ZIF-8 based MMM having loading of ZIF-8 up to 80 wt% were fabricated. These filler loadings were quite higher than typical filler loadings that are attained through selected zeolite materials. This MMM displayed a reduction in mechanical strength only at highest loading which in turn lead towards reduction in flexibility. Permeability characteristics of fabricated MMMs were estimated for  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{C}_3\text{H}_8$ ,  $\text{H}_2$  and for gas mixtures  $\text{H}_2/\text{CO}_2$  as well as  $\text{CO}_2/\text{CH}_4$ . Increase in permeability of all gases was observed with loading of ZIF-8 upto 40 wt%. This enhancement in permeability is in opposition to the results narrated by Moore et al. where a decline in permeability was noticed with increase in filler loading in case of hybrid membrane material [190]. The decline in permeability was caused by rigidification of polymeric matrix. The enhancement in permeability up till 40 wt% of ZIF-8 loading in case of Ordonez et al. study could be because of the existence of polymeric free volume that is produced because of incorporation of nanoparticles of ZIF-8 into Matrimid that increased the distance among polymeric chains. It was noticed that nanoparticles disrupt the packing of polymeric chains in glassy polymers resulting in an increase in polymeric free volume as well as permeability [78,191,192]. No notable change in ideal selectivity was observed in most of the studied gaseous pairs including  $\text{H}_2/\text{N}_2$ ,  $\text{O}_2/\text{N}_2$ ,  $\text{H}_2/\text{CO}_2$ ,  $\text{CH}_4/\text{N}_2$ ,  $\text{H}_2/\text{O}_2$  up to ZIF-8 loading of 40 wt%. But, high ZIF-8 loading of 50 wt% and 60 wt% resulted in reducing the permeability of all the gases and enhanced the selectivities correspondent with ZIF-8 additive influence. 50 wt% loading of ZIF-8 enhanced the ideal selectivities in case of gaseous pairs involving small gases like  $\text{CO}_2/\text{CH}_4$ ,  $\text{H}_2/\text{O}_2$ ,  $\text{CO}_2/\text{C}_3\text{H}_8$ ,  $\text{H}_2/\text{CH}_4$ ,  $\text{H}_2/\text{C}_3\text{H}_8$ ,  $\text{H}_2/\text{CO}_2$ . This illustrated a conversion from polymer driven gas transport to ZIF-8 controlled gas transport because at higher loadings, the ZIF-8 nanocrystal's sieving effect is more dominant. ZIF-8 is considered as a favorable material for gas separation applications at high temperature and pressure conditions at which most of the industrial separation processes are carried out because ZIF-8 possesses the ability of selective transport of smaller molecules of gas such as  $\text{CO}_2$  and  $\text{H}_2$  and also because ZIF-8 exhibit stability at high temperature conditions. For Matrimid/ZIF-8 MMM, the separation performances were evaluated for gas mixtures of  $\text{CO}_2/\text{CH}_4$  (10/90 mol%) and of  $\text{H}_2/\text{CO}_2$  (50:50 mol%) at

50 wt% and 60 wt% of ZIF-8 loading. At both loadings of ZIF-8, both gas pairs exhibited selectivities identical to ideal selectivities keeping in view the experimental error [189].

MMMs were developed by Castro-Muñoz et al. [69] by employing Matrimid, ZIF-8 and PEG by using two different preparation methods, i. e., non-dried MOF method and traditional method. It was observed that addition of 30 wt% of ZIF-8 loading by employing traditional method enhanced the permeability of  $\text{CO}_2$  to 130 barrer. Whereas, MMM that was fabricated by adding 30 wt% of ZIF-8 loading by employing non dried MOF method lead towards increase in  $\text{CO}_2/\text{CH}_4$  selectivity of 15 in comparison to MMM that was fabricated by employing traditional method [194]. In another study by Zhang et al [195], ZIF-8 having a particle size of 200 nm was incorporated with 6FDA-DAM polyimide in order to fabricate MMMs dense films that were employed to investigate the sorption kinetics as well as equilibrium isotherms of propane ( $\text{C}_3\text{H}_8$ ) and propylene ( $\text{C}_3\text{H}_6$ ) at 35 °C. Good adhesion was exhibited by hybrid material between 6FDA-DAM and ZIF-8's effectively dispersed particles without the existence of sieve in cage morphology because of ZIF-8 hydrophobic nature. At high ZIF-8 loading (48 wt%), ZIF-8 filler clusters having sizes that are greater than single ZIF-8 crystal were created in 6FDA-DAM/ZIF-8 films. In spite the cluster formation, considerable increase in  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  selectivity as well as in  $\text{C}_3\text{H}_6$  permeability was observed in 6FDA-DAM/ZIF-8 MMM. The ideal selectivity  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  and permeability of  $\text{C}_3\text{H}_6$  in MMM having ZIF-8 loading of 48 wt% showed up to be 150 % and 258 % which was greater than pristine 6FDA-DAM membrane. Permeation characteristics of ZIF-8 were evaluated to an ideal selectivity ( $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ ) of 122 and permeability ( $\text{C}_3\text{H}_6$ ) of 277 Barrer by employing Maxwell model. It is proposed that amalgamation of ZIF material and polymer used possesses the ability for application in lowering  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  separation process's energy intensity [195].

Some of the materials of ZIFs including ZIF-11, ZIF-90, ZIF-8, ZIF-95, ZIF-301 and ZIF-67 possess larger cavities along with narrower pore apertures that are closer to  $\text{CO}_2$  kinetic diameter i.e. 0.33 nm, and this property allows the addition of suitable filler in sole ZIF based MMMs for separation of  $\text{CO}_2$ . Research studies that were done in previous 5 years on sole ZIF based MMMs are compiled in Table 2 below.

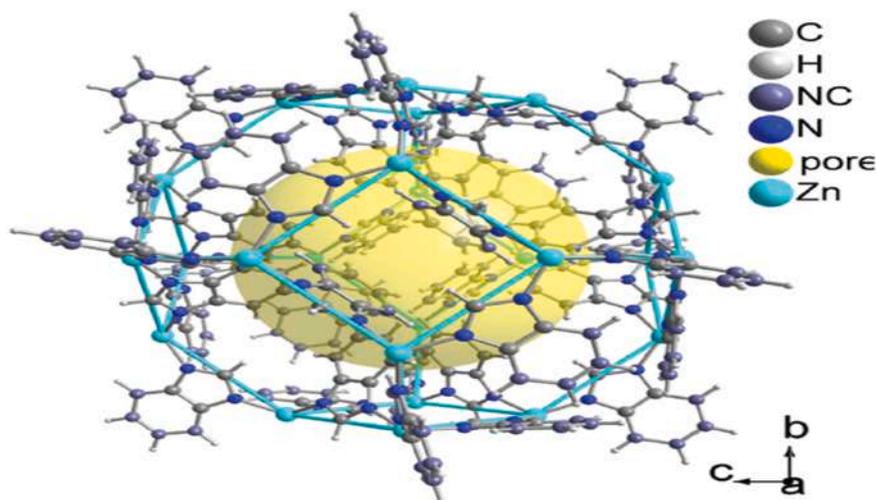
ZIF-67 has gained quite an attention because of its inherent family of metal organic frameworks (MOFs). ZIF67/6FDA-DAM mixed matrix membrane for the separation of  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  was first fabricated by An et al. [200], and ZIF-67 was incorporated successfully into Pebax 1657 rubbery membrane by Meshkat et al. (2020) in order to fabricate MMM [185]. This membrane not only enhanced gaseous permeability (130% enhancement in permeability of  $\text{CO}_2$ ) but it also improved the separation performance of membrane (58 % enhancement in  $\text{CH}_4/\text{CO}_2$  selectivity) in comparison with pristine Pebax membrane at 35 °C and feed pressure of 11 bar. ZIF-11 is considered as a favorable ZIF having structural features which makes it suitable for separation of  $\text{CO}_2$  or  $\text{H}_2$ . Ehsani et al. fabricated ZIF-11/Pebax 2533 MMM by incorporating ZIF-11 as a filler into Pebax 2533 membrane matrix [201]. The resultant membrane displayed higher  $\text{CO}_2$  permeability i.e. 402.9 barrer as well as selectivity  $\text{H}_2/\text{CH}_4$  (4.8),  $\text{H}_2/\text{N}_2$  (12.9) and  $\text{CO}_2/\text{CH}_4$  (12.5) at loading of 50–70 wt%.

In order to yield  $[\text{Zn}(\text{Purinate})_2]$ , ZIF-20, sodalite framework of ZIF-8 is converted into zeolite-A topology on replacing imidazole ligand with purinate as depicted in Fig. 9. Slightly agglomerated and small  $[\text{Zn}(\text{Purinate})_2]$ , ZIF-20 crystals with a loading of 8 wt% in ZIF-20/PSF MMM displayed improved performance than pure polymer in separation of equimolar mixture of  $\text{O}_2/\text{N}_2$ . Although the permeability of  $\text{O}_2$  displayed a minor decrease from 1.6 Barrer (for pristine polysulfone) to 1 Barrer for MMM while the selectivity of  $\text{O}_2/\text{N}_2$  enhanced from 4.7 to 6.7 [202]. The increase in sieving effect in mixed matrix membrane can be justified by fairly small difference in kinetic size among  $\text{N}_2$  (kinetic diameter=0.368) and  $\text{O}_2$  (kinetic diameter=0.343) [203]. High performance mixed matrix membrane was fabricated by Benavides et al. by incorporating ZIF-94 into 6FDA-DAM polymer, MMM having loading of

**Table 2**

Transport behavior of unmodified ZIF-based MMMs.

Polymers	ZIFs	ZIF Loading	Pressure/Temp	CH <sub>4</sub> (Barrer)	CO <sub>2</sub> (Barrer)	H <sub>2</sub> (Barrer)	N <sub>2</sub> (Barrer)	CO <sub>2</sub> /CH <sub>4</sub>	H <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>	Ref.
P84 polyimide	ZIF-8	17 wt%	3 bar/25 °C	0.068	6.33	–	–	93.6	–	–	[196]
PSF	ZIF-8	0.5 wt%	4 bar/30 °C	0.21	3.25	–	0.19	15.1	–	17.5	[174]
6FDA-DURENE	ZIF-8	10 wt%	3.5 bar/30 °C	49.71	1426	–	–	28.7	–	–	[177]
Pebax 1657	ZIF-8	2 wt%	11 bar/35 °C	5.5	118	–	2	21.4	–	59	[185]
Pebax 1657	ZIF-8	5 wt%	0.5 MPa°C	–	140	–	–	–	–	67	[184]
Pebax 1657	ZIF-67	4 wt%	11 bar/35 °C	5.8	16	–	2.2	27.6	–	72.7	[185]
6FDA-DAM	ZIF-11	20 wt%	4 bar/30 °C	8.3	257	272	–	31	32	–	[175]
6FDA-DURENE	ZIF-71	20 wt%	3.5 bar/35 °C	181	2560	–	186	14.2	–	13.8	[197]
Triptycene-PI	ZIF-90	10 wt%	9.8 atm/35 °C	0.6	26	61	1.1	42	99	24	[173]
6FDA-DAM	ZIF-301	20 wt%	4 bar/25 °C	–	891	–	–	29.3	–	–	[198]
Matrimid	ZIF-95	30 wt%	4 bar/35 °C	0.4	23.2	76.6	–	58	192	–	[199]

**Fig. 9.** Illustration of ZIF-20 crystal packing [16].

40 wt% ZIF-94 exhibited higher permeability of CO<sub>2</sub> (2310 Barrer) having CO<sub>2</sub>/N<sub>2</sub> selectivity of 22 at 1 bar [204]. ZIF-95 having larger voids (24.0 Å) is considered as a very essential material in gas purification as well as adsorption applications. Ilicak et al. [199] incorporated ZIF-95 as a filler in fabrication of polyimide based mixed matrix membrane [199]. ZIF-95/Matrimid5218 mixed matrix membrane attained adequate CO<sub>2</sub> separation performance having CO<sub>2</sub>/CH<sub>4</sub> selectivity of 58 and H<sub>2</sub>/CH<sub>4</sub> selectivity of 192. These results display compatibility among polymer and filler along with the likelihood of forming additional channels and increasing free Matrimid volume. MMM was fabricated by Li et al. [205] by utilizing porous PAN support and employing Pebax 1657 as polymer matrix, ZIF-7 in smaller size i.e. 30–35 nm as a filler and PTMSP as gutting layer in order to fabricate MMMs. At lower loading of filler both permeability of CO<sub>2</sub> and selectivity (CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>) of MMM was greater than pristine membrane. While, at higher ZIF-7 loading, CO<sub>2</sub>/CH<sub>4</sub> selectivity is increased to 44 but the permeability is reduced as compared to pristine Pebax 1657, as higher loading of ZIF-7 induced rigidification of polymer [205]. Hence, based on the studies it is depicted that the overall performance of MMM is influenced by size, loading as well as incorporation method of filler [206,207]. Also above studies shows that PSf, Pebax and 6FDA based polyimide are attractive options of polymer matrix to be used in ZIF based MMM. Also, ZIF-8 and ZIF-7 along with their functionalized counterparts attained quite an attention because of their superb separation performances.

## 6. Modification strategies to enhance performance of ZIF based MMMs

So as to enhance the interfacial compatibility among polymers and

ZIFs in MMMs and to improve the separation performance of membrane, many different techniques of functionalizing and modifying ZIFs in order to create covalent bonds between polymers and ZIFs within membrane matrix have been investigated. Defects are considered as one of the main concerns during the process of membrane fabrication, as they have a great influence on separation performance of membrane and are quite noticeable in ZIF based MMMs. This problem worsens when it comes right down to scale up fabrication which is necessary for membrane industrialization. Hence, ZIF modification provides a solution to reduce defects by plugging non selective gaseous transport paths and by enhancing interfacial interaction between filler and polymer. ZIF modification technique not only improves the separation ability of membrane by introducing extra functional groups in order to overcome the difficulty related to weak filler-polymer interfacial interaction [182] but; it also widens the scope of choice for fillers and polymer matrices. Researchers have incorporated a wide variety of inorganics and organics with ZIFs in order to develop modified fillers and modified ZIF based MMMs have been fabricated to enhance membrane's permeability as well as selectivity.

### 6.1. Amino functionalization

ZIFs can be functionalized quite easily and have many active sites, hence, the researchers had modified ZIF surface with amino group in order to form basic active sites that resulted in Lewis acid–base interaction with CO<sub>2</sub> which in turn increases selectivity of CO<sub>2</sub> [208]. ZIF-7-NH<sub>2</sub>/XLPEO mixed matrix membrane was fabricated by Xiang et al. [178] with high permeability and selectivity. On the surface of ZIF-7, efficient chelation of XLPEO with Zn ions improved the interfacial compatibility and, amino group introduction enhanced ZIF-7 pore size,

hence enhancing the diffusion selectivity as well as gas permeability. At 30 wt% loading of ZIF-7-NH<sub>2</sub>, permeability of CO<sub>2</sub> was 215 Barrer and CO<sub>2</sub>/CH<sub>4</sub> selectivity was 55 respectively, and that exceeded 2008 upper bound [178]. Micro emulsion based mixed linker approach was proposed by Ding et al. [180] in order to introduce amino groups during ZIF-8 growth [180]. At 6 wt% loading, great performance was achieved by MMM with CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 163.8 Barrer and 62 respectively that were 107.6% and 27% high in comparison to pure membrane [180]. Amino group's introduction improves the selective permeation of CO<sub>2</sub>. It is to be noted that different linkers have the ability to create different morphologies of ZIF particles, hence, influencing the specific surface area as well as polymer filler interface pattern.

## 6.2. Carbon nano tube (CNT) –ZIF based MMM

Small diameter, smooth surface, larger surface area as well as high mechanical strength of CNT make them suitable filler for fabrication of MMMs. The incorporation of CNT has the ability to enhance the mechanical strength of polymeric membrane. Also, CNT's nanostructures and their larger interfacial area enhances interaction among polymeric matrix and CNTs, that in turn enhances organic-inorganic interfacial compatibility [209]. CNTs possess low resistance transport channels and several adsorption sites, such as pore sites and gap channel sites having large surface energy that are useful in order to enhance membrane's gas permeability [210]. CNT-ZIF based mixed matrix membrane amalgamates advantages of both ZIF and CNTs that in turn results in high permeability and selectivity. ZIF-302@CNT/PSF mixed matrix membrane was fabricated by Sarfraz et al. [211] and the results depicted that membrane with 12 wt% loading of ZIF-302 and 8 wt% loading of CNT showed remarkable performance with CO<sub>2</sub> permeability of 18 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 35. Under wetting conditions, permeability was improved slightly [211]. The comprehensive details of ZIF@CNT MMM are shown in Fig. 10 below. Series of ZIF-301 @CNT/PSF mixed matrix membrane was also synthesized by Sarfraz et al. [212]. It was revealed by gas permeation test that membrane having 6 wt% loading of CNT and 18 wt% loading of ZIF-301 showed remarkable separation performance with CO<sub>2</sub>/N<sub>2</sub> selectivity and CO<sub>2</sub> permeability of 48 and 19 Barrer respectively [212].

Because of the inner Van der Waals forces, CNT aggregates quite easily

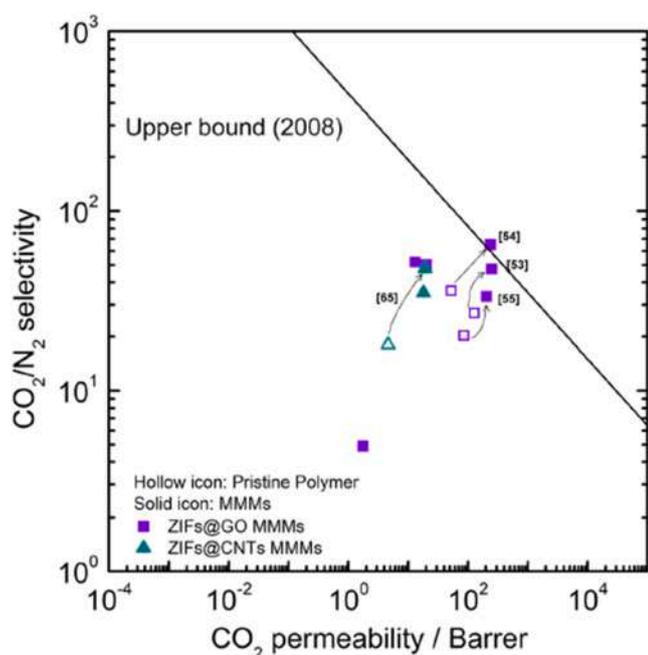


Fig. 10. Separation properties of CO<sub>2</sub>/N<sub>2</sub> of inorganic ZIF based MMM [182].

within polymeric matrix [213]. It is believed by authors that in order to solve the problem related to aggregation researchers should use two methods in future. One of the methods includes the addition of surfactant in casting solution. The other method involves the introduction of functional groups within tail or defects in CNTs [213] or non covalently functionalizing them with functional polymeric materials and organic macromolecules. Membrane's separation performance when combined with inherent properties of ZIFs can be enhanced further. Actually the structure of nanotube with hollow channels is a beneficial incorporation into MMMs. And also, ZIF@CNT approach provides a favorable structure with great possibilities.

## 6.3. Incorporation of PEG

PEG possesses exceptional lubricity as well as it has great compatibility with many different polymers. Ethylene oxide unit, which is PEG's polar ether segment, has the ability to interact with CO<sub>2</sub>'s electric quadrupole moment. Some of the previous studies have suggested that smaller amount of PEG possessing low molecular weight has the ability to improve the structure of membrane greatly by enhancing compatibility among polymers and nanoparticles as well as by encouraging uniform dispersion of particles. Because of these advantages, PEG is frequently used to fabricate CO<sub>2</sub> separation membranes. PEG-200@ZIF-8/Matrimid5218 mixed matrix membrane was fabricated by Castro-Munoz et al. having (10–40) wt% loading of ZIF-8. In case of CO<sub>2</sub>/CH<sub>4</sub> system, mixed matrix membrane that is fabricated by 30 wt% loading of ZIF-8 showed remarkable separation performance having CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 33.12 Barrer and 15.4 respectively [214]. Such type of MMMs have the potential to be used in separation applications involving CO<sub>2</sub> separations because of PEG's universality and also PEG being remarkable CO<sub>2</sub>-phillic additive along with its interface modification effect. As PEG is considered just an additive to the membrane separation system, hence fundamental characteristics are mainly determined via choice of ZIF and polymer.

## 6.4. GO@ZIF based MMM

Graphene oxide possesses one atom thick layered unique structure having superior mechanical strength along with larger aspect ratio. Because of abundance of oxy-groups present on its surface, it possesses advanced dispersal properties as well as modification capacity [215]. GO possesses excellent thermal stability along with high specific surface area. Because of it having higher aspect ratio and 2D structure, GO incorporation into polymeric matrix has the ability to make gaseous transfer channel tortuous and longer, supporting the diffusion of smaller gas molecules and by decreasing the diffusion of large gas molecules and enhancing selectivity diffusivity of gases [216]. Also, GO incorporation enhances the material's mechanical properties, hence can be incorporated as an inorganic filler in order to fabricate MMMs. To sum up, amalgamation of GO layers with ZIF has the ability to enhance the gas separation performance.

Polyimide (PI)/ZIF-8 @GO mixed matrix membrane was fabricated by Huang et al. and tested for gas permeation [217]. Membrane having 20 wt% of ZIF-8 @GO loading exhibited outstanding performance having CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 238 Barrer and 65 respectively and it was a remarkable improvement when compared with intrinsic characteristics of PI membranes [217]. Also, CO<sub>2</sub>/N<sub>2</sub> separation property surpassed 2008 upper bound. Series of Pebax/ZIF-8 @GO mixed matrix membranes were fabricated by Dong et al. [218]. Membrane having 6 wt% loading of ZIF-8@GO showed remarkable performance having CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 249 Barrer and 47.6 respectively and it is an escalation of 91 % and 74 % as compared to pristine Pebax membrane [218]. ZIF-8@GO nanosheets were prepared by Yang et al. by employing two step ultrasonic synthesis technique in order to fabricate EC(Ethyl Cellulose)/ZIF-8@GO mixed matrix membrane [219]. MMM having 20 wt% filler loading displayed

CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 203.3 Barrer and 34.4 respectively, which is, an improvement of 139 % and 65 % as compared to pure EC membrane [219]. This performance of EC/ZIF-8@GO membrane was also much superior than MMM having independent ZIF-8 or GO. Result of above study depicted that modification technique that involves amalgamating 2D nanosheets and ZIFs has significant capability to fabricate CO<sub>2</sub> separation membranes having high performance. Ultrason/ZIF-300@GO mixed matrix membrane was fabricated by Sarfraz et al. and gas separation performance was examined [220]. Results depicted that at 1 wt% loading of GO and 30 wt% loading of ZIF-300, the CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity were 3.4 and 2.3 times greater than that of pure Ultrason membrane [220]. Sarfraz et al also fabricated PSF/ZIF-302 @GO mixed matrix membrane [221]. At 30 wt% loading of ZIF-302 and 1 wt% loading of GO, the CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity was 13 Barrer and 52 respectively and that surpassed 1991 upper bound [221]. Hence, from above studies it was inferred that ZIF@GO modification technique enhanced membrane separation performance.

### 6.5. PD (poly dopamine) coating

ZIF-8/PD-PI mixed matrix membrane was fabricated by Wang et al. [222] via simplistic technique by producing polymer/ZIF interface through PD coating [222]. By employing self polymerization method of dopamine, a uniform and thin layer of PD having controllable thickness was applied onto the ZIF-8 nano crystal surface. At 30 wt% loading, CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity was 1056 Barrer and 14 respectively [222]. The gas separation performance showed substantial improvement as compared to pristine membrane. PD coating helps by preventing direct contact among polymeric matrix and ZIF-8 crystal and reduces interface structural differences. Also, within the PD coating the presence of amine groups (primary or secondary) have H-bonding interaction with Polyimide (PI) segments, hence improving interfacial compatibility. Hence, PD coating technique can be considered as a promising technique in order to improve gas separation performance of MMMs. The comprehensive details of modified ZIF based mixed matrix membranes are listed in Table 3.

### 6.6. Ionic liquid (IL)@ZIF based MMMs

In order to analyse and utilize the advantages of ionic liquids, researchers have proposed a new technique of enclosing ionic liquids to ZIF cages. In recent years, many research studies revealed that ionic liquids were encapsulated into ZIF nanocages in order to carefully control the pore size of ZIF for separation of gas pair possessing comparable kinetic diameter. The outcome displayed that IL@ZIF based MMMs exhibited remarkable gas separation performance for CO<sub>2</sub>/N<sub>2</sub> by surpassing Robeson upper bound [223–225]. Therefore, ionic liquids can potentially be used in order to modify the microenvironment of ZIF cavities within MMMs to further enhance the membrane's molecular discrimination ability and gas separation performance.

ZIF-8 effective cage size was fine tuned by Ban et al. [224] to stand between N<sub>2</sub> and CO<sub>2</sub> kinetic diameters by enclosing [Bmim][Tf<sub>2</sub>N] to SOD cages of ZIF-8 via in situ ionothermal synthesis. [Bmim][Tf<sub>2</sub>N]@ZIF-8/PSF MMM's gas permeation test revealed that modification technique brought about outstanding improvements in both CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> separation. In case of CO<sub>2</sub>/CH<sub>4</sub> system, the permeability of CO<sub>2</sub> was 253 Barrer while selectivity was 45.7 and, in case of CO<sub>2</sub>/N<sub>2</sub> system, the CO<sub>2</sub> permeability and selectivity was 279 Barrer and 130 respectively, and all of them exceeded Robeson upper bound 2008 [224].

The data reported in Table 3 shows the most common modification strategies employed to enhance the performance of ZIF based MMMs. Other modification techniques such as multiple metal ion ZIFs [226] are also employed in some uncommon cases. Table 3 shows that even though the separation characteristics of modified ZIF based MMMs does

**Table 3**  
Comprehensive details of modified ZIF based MMMs.

Modification method	Polymer	ZIFs	wt% of ZIF	Testing condition	Characteristics of pristine polymeric membranes					Characteristics of modified ZIF based MMMs				
					Permeability in Barrer	Ideal selectivities	Permeability in Barrer	Ideal selectivities	Permeability in Barrer	Ideal selectivities				
Amine functionalization Carbon nanotubes (CNTs)	XLPEO	ZIF-7	30%	35 °C/5 bar	CO <sub>2</sub>	H <sub>2</sub> /CO <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> /CO <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>	References	
	PSF	ZIF-301/ZIF-302	18%/12%	25 °C/2bar/25°C/2 bar	110	-	21	-	215	-	55	-	[178]	
	Matrimid 5218	ZIF-8	30%	25 °C/8 bar	6.756.75	-	-	2727	1918	-	-	4835	[212]	
Graphene Oxide (GO)	PI	ZIF-8	20%/6%	30 °C/1bar/25°C/6 bar	7.16	-	17.4	-	33.12	-	15.4	-	[221]	
	PSF	ZIF-8	6%	30 °C/6 bar	6.62165	-	-	33.121	238249	-	-	6547.6	[214]	
PD coating	US	ZIF-300	30%	25 °C/2 bar	6.2	-	-	27	19.90	-	-	50.08	[217]	
	PI	ZIF-8	30%	35 °C/1 bar	285	1.4	35	24	1056	1.8	20	1.4	[218]	
ILs	PSF	ZIF-8	6%	30 °C/6 bar	208	1.26	24.76	26.33	307	1.38	26	53	[220]	
	PSF	ZIF-8	6%	30 °C/6 bar	208	1.26	24.76	26.33	307	1.38	26	53	[222]	

not normally exceed the Robeson upper bound, but the permeability as well as selectivity is enhanced simultaneously as the organic-inorganic interfacial defects are somehow reduced to a certain degree, which result in exceptional improvements as compared to pristine polymeric membranes.

## 7. Effect of ZIF morphology on MMMs separation performance

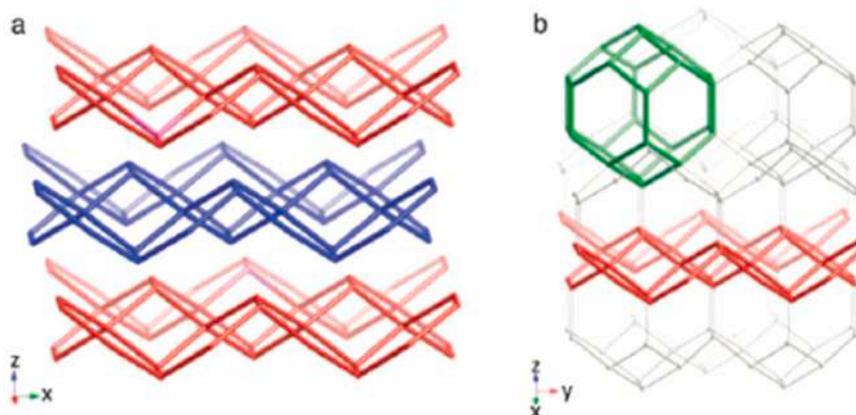
Most of the ZIFs possess a 3D framework and are particle like [227]. Lately, different new types of ZIFs having other shapes have been fabricated and incorporated as a filler for preparation of MMMs. MMM was prepared by Wang et al. by dispersion of ZIF-8 hollow nanotubes as a filler into Pebax 1657 polymeric matrix [184]. MMM having 5 wt% loading of H-ZIF-8 exhibited remarkable separation performance having CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 147 Barrer and 68 respectively, nearing 2008 Robeson upper bound and surpassing most of the previously reported CNT/Pebax MMM. Also, nanoporous 2D nanosheets have gained quite an attention because of their advantageous characteristics related to low diffusion resistance as well as larger external surface area that permits the exposure to more active sites. 2D ZIFs that possess a cushion shape cavity among layers, are new type of ZIFs having a leaf like structure and having dimensions of 0.94 nm × 0.7 nm × 0.53 nm is commonly termed as ZIF-L as depicted in Fig. 11 [228]. 2D ZIF derived and 2D ZIF nanoporous nanosheets were employed by Feng et al. in many different applications because of their pore features as well as their special morphology [229] such as in gas separation [230–232], metal removal [233], solvent separation [234] as well as in water purification [235] etc. Deng et al. studied and investigated the effect of ZIF morphology on separation capability of CO<sub>2</sub> in case of ZIFs/Pebax2533 mixed matrix membrane [232]. So, three different shapes of ZIFs i.e particle (0D), microneedles (1D) and leaves (2D) were investigated. The results depicted that increase in permeability of CO<sub>2</sub> was linked to the morphology of ZIF and it followed 0D < 1D < 2D order. Whereas, selectivity followed the opposite order with ZIF (0D) exhibiting the greatest selectivity. 2D ZIF-L nanosheets were synthesized by Zhang et al. by employing 2- methylimidazole aqueous solution and zinc salt, and then incorporating them into CMC (carboxyl methyl cellulose) solution in order to make uniformly mixed aqueous suspension via employing one step solution blending technique [236]. Resultant MMM having loading of 30 wt% of ZIF-L displayed greatest separation capability with selectivities of H<sub>2</sub>/N<sub>2</sub>, N<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/CO<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> to be 21.54, 8.93, 10.62 and 17.87 respectively [236].

## 8. Research progress on ZIF based MMMs for gas separation

As explained earlier that ZIFs belong to the category of MOFs and are created by amalgamation of metal clusters like Zn or Co with

imidazolate linkers. ZIFs, as compared to MOFs have better characteristics including high chemical, thermal as well as moisture stability. Among different varieties of ZIFs, ZIF-8 is considered as the most preferred ZIF for fabrication of MMMs. It is made up of metal cation of (Zn<sup>2+</sup>) that is linked with 2-methylimidazole ligands and provides SOD zeolitic network topology that comprises of large cavities. Hence, it can be used and considered appropriate for applications related to gas storage and separation processes [26,237]. ZIF-8 possesses high chemical and thermal stability and is considered as an appropriate filler to be used in MMMs [238,239]. Amine modifications have been used in an attempt to enhance the CO<sub>2</sub>-philicity of ZIF-8. It is considered as challenging effort as modification can lead towards pore blockage that may deteriorate the performance of MMMs. Hence, there is still a need of extensive research in order to analyse the performance and outcome of modified ZIF particles when they are incorporated as filler in MMMs [240]. ZIF-8 was synthesized by Nordin et al. under amine modification via several ammonia solutions [240]. The incorporation of unmodified and modified ZIF-8 into polysulfone (PSF) matrix exhibited that this ZIF-8 modification caused a decline in permeance of CO<sub>2</sub> but at the same time the selectivity of CO<sub>2</sub>/CH<sub>4</sub> was increased, this was because of the reduction in mesopore contribution and enhancement in micropore contribution to gas permeation pathway [240]. The N-H group affinity in modified ZIF-8 towards CO<sub>2</sub> contributed in increasing the permeance of CO<sub>2</sub> e.g., on dispersing ZIF-8 that was modified in 25 ml of ammonia solution at a temperature of 60 °C within PSF matrix, the selectivity of CO<sub>2</sub>/CH<sub>4</sub> was increased to 72 % and the permeability of CO<sub>2</sub> was increased to 43 % when compared with pristine PSF membrane [240].

Li et al. applied a chelation assisted interfacial reaction approach in order to assimilate vertically oriented ZIF within the polyvinyl amine (PVAm) polymeric matrix [241]. PVAm/PVA-ZIF-L vertically aligned continuous mixed matrix membrane was fabricated on functionalized polysulfone membrane. Good polymer filler interfacial adhesion with the absence of non selective interfacial voids was observed in the fabricated membrane because of the good capability of polyvinyl amine to complex with Zn<sup>2+</sup>. Consequently, the fabricated composite membrane exhibited high tensile strength as well as higher flexibility. The pure polysulfone (PS) membrane displayed tensile strength of 13.20 MPa, elongation at break of 10.96 % and young's modulus of 120.36 MPa while on the contrary, PVA/PVAm membrane exhibited tensile strength, elongation at break, and young's modulus of 40.01 MPa, 22.52 % and 177.69 MPa respectively. Also, PVA/PVAm-ZIF-L composite membrane displayed tensile strength, elongation at break and young's modulus of 44.70 MPa, 22.98 % and 194.50 MPa respectively. These results indicated that PVA/PVAm-ZIF-L membrane possesses excellent mechanical and structural stability and it also displayed reversed selectivity of N<sub>2</sub>/CO<sub>2</sub> gas pair having N<sub>2</sub> permeance and N<sub>2</sub>/CO<sub>2</sub> selectivity of 174.9 GPU and 51.9 respectively.



**Fig. 11.** (a) ZIF-L (2D) along z(b)ZIF-8 sod topology Correlation between ZIF-L and ZIF-8. Framework of ZIF-8 in gray color along with a sodalite cage featured in green and layer analogous to ZIF-L in red.[228].

Hwang et al. applied the microimaging by IR microscopy to track record the progression of CO<sub>2</sub> concentration in case of ZIF-8@6FDA-DAM MMMs [242]. Time resolved images displayed that molecules of CO<sub>2</sub> propagated from filler (ZIF-8) to surrounding polymer, where filler behaves as a highway for mass transport of CO<sub>2</sub>. Increase in the concentration of CO<sub>2</sub> at polymer filler interface was also noticed at equilibrium. At elevated gas pressures, this occurrence was even more prominent. The existence of microvoids at polymer filler interface was revealed by atomic simulations. GCMC (Grand Canonical Monte Carlo) simulations displayed that accumulation of molecules of CO<sub>2</sub> is supported within the microvoids that in turn initiate the first move towards forming higher concentration layer of CO<sub>2</sub> at interface with MOF and also advocates the significance of polymer filler compatibility in mixed matrix membrane separation performance (refer Fig. 12) [242]. Also, Table 5 below summarizes the performance of various ZIF based MMMs for CO<sub>2</sub> separation.

## 9. Conclusions and future direction

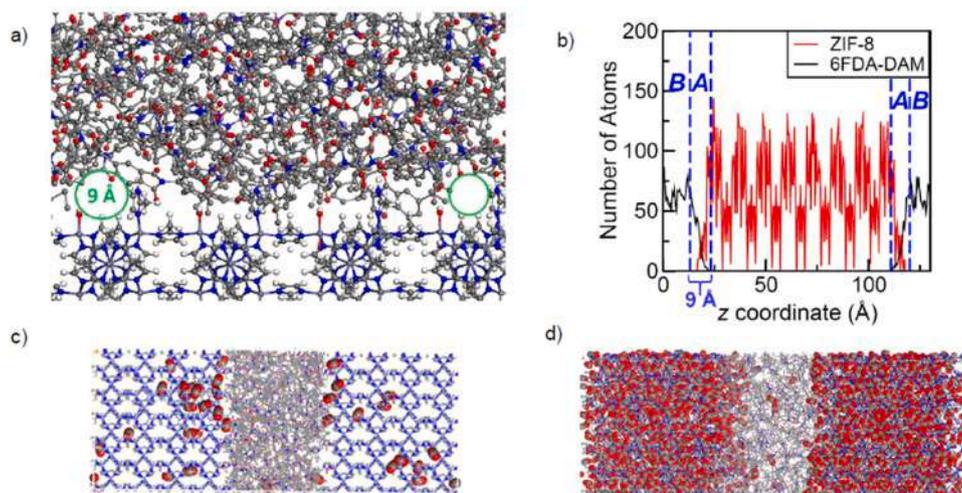
In recent years, the use of mixed matrix membranes in gas separation applications has gained quite an attention. MMMs normally comprises of different inorganic fillers that are incorporated into polymeric matrix having ultimate goal of surpassing Robeson upper bound. Various researches have already been done for choosing a suitable polymer filler pair for fabrication of MMMs as material selection is considered as one of the major aspect in fabrication of high performance MMMs. In this review, by using different examples we have investigated the advances made in (ZIF)-based MMMs for gas separation. This review discusses the worthiness of (ZIF)-based mixed matrix membrane over inorganic and polymeric membranes, and also that ZIF based MMMs have the ability to overcome permeability/selectivity trade off limit. This review highlights that ZIFs are an attractive filler option in fabrication of MMMs and offers exceptional performance attributes to MMMs in terms of higher selectivity and permeability considering that interaction between polymeric phase and filler (inorganic phase) is appropriately configured. ZIF's organic part provides the opportunity to increase the compatibility among polymeric chains and ZIFs, and hence regulates and controls ZIF-polymer interfacial structure. Pure (ZIF)-based MMMs possess better and enhanced separation characteristics as compared to pure polymeric membranes. In order to further enhance the separation properties of (ZIF) - based MMMs, researchers have prepared modified filler that amalgamates the benefits of several materials and hence can further improve the performance of ZIF based MMMs. Filler (ZIF) modifications possess the ability to alter the structure of membrane and can also

**Table 4**

Mechanical strength characteristics of PVA/PVAm-ZIF-L membrane, PVA/PVAm membrane and pristine membrane[241].

Samples of membrane	Tensile strength	Elongation at break	Young's modulus
PVA/PVAm-ZIF-L	44.70 MPa	22.98%	194.50 MPa
PVA/PVAm	40.01 MPa	22.52%	177.69 MPa
Pure PSF	13.20 MPa	10.96%	120.36 MPa

improve interfacial voids and refines the structure of ZIF. Many different types of ZIFs, especially ZIF-8 have been used widely for MMMs fabrication and promising results were achieved by its incorporation into polymeric matrix. Previous researches have revealed that ZIF based MMMs are promisingly next generation membranes for gas separation applications. Efficient performance is also linked with hybrid fillers that offer diversity by serving more than one targets and requirements as compared to mono fillers. For instance, CNT and GO are combined with ZIFs in order to tune selectivity, permeability, dispersion of filler as well as interfacial properties in resultant MMMs. Comprehensively, ZIFs are an appropriate fillers in MMMs fabrications but there is still a need of further research especially on hybridization and functionalization of ZIFs in order to achieve the goal of high permeability, selectivity, better thermal, chemical and mechanical stability and scalability, hence facilitating the path for ZIF based MMM to comply with the requirements in today's challenging gas separation needs. Presently, research related to (ZIF)-based MMMs is merely at material analysis stage. But, actual requirement is the production of thin MMMs i.e. MMMs having thinner selective layer instead of thicker membranes. On comparison with thicker membranes, the fabrication of thinner membranes involves membrane materials possessing remarkable properties along with maturity and process viability. So, materials that are proposed recently and have exhibited remarkable performance at laboratory scale could not be thinned due to their brittle structure. Also, the separation ability of thicker membranes is not even a precise reflection in comparison to thinner membranes. For instance, the interfacial defects existing in thicker membranes might bring about an increase in permeability of gases at steady tendency and also, in thicker membranes the free volume fraction of polymer is not as considerable as in thinner membranes. It is therefore difficult for conventional fabrication techniques of MMMs to minimize the selective layer thickness. Hence, the development of new fabrication technique for MMMs is urgently required.



**Fig. 12.** (a) illustration of microvoids at polymer-filler interface (b) atomic density of polymer (6FDA-DAM) and filler (ZIF-8) as function of coordinate perpendicular to surface of ZIF-8. (c,d) configuration of MMMs model at lower and elevated pressure[242].

**Table 5**  
Performance of various ZIF based MMMs for CO<sub>2</sub> separation.

Polymer	ZIF	Filler loading (wt%)	Testing conditions	Permeability of CO <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub> selectivity	CO <sub>2</sub> /CH <sub>4</sub> Selectivity	CO <sub>2</sub> /H <sub>2</sub> Selectivity	References
PVAm	ZIF-8	9(13)23	22 °C	297GPU	83	–	–	[237]
PSF	Amine modified ZIF-8	0.5	27 °C and 4 bar	7.26 Barrer	–	34.09	–	[240]
Ultem	ZIF-8	030	35 °C	1.535 Barrer11.1 Barrer	26.5231.11	37.940.4	–	[243]
Pebax	ZIF-8 @GO	(6)	25 °C and 1 bar	249Barrer	47.6	–	–	[218]
P84	ZIF-8	27	25 °C and 3 bar	10.92Barrer	92.6	–	–	[196]
PEGMEA	ZIF-8	1.5	35 °C and 2 bar	730.8 Barrer	–	13.3	–	[244]
Pebax	PDA@ZIF-8	051015051015	25 °C and 1 barDry stateHumid state	94.56Barrer158.16Barrer187.08Barrer220.06Barrer113.96Barrer196.69Barrer233.13Barrer267.74Barrer	29.3646.1150.6856.1430.1249.0256.6562.65	–	–	[245]
XLPEGDA	ZIF-8	20	35 °C and 2 bar	840Barrer	48.0	16.0	9.2	[246]
Pebax –2533	ZIF-8	05101520253035	room Temp and 2 bar	351Barrer365Barrer427Barrer574Barrer854Barrer1082Barrer1176Barrer1287Barrer	33.829.631.430.328.931.331.632.3	8.38.18.510.49.28.58.79.0	–	[247]
Matrimid	ZIF-8	10203040	35 °C and 5 bar	13Barrer18Barrer25Barrer45Barrer	–	43485242	–	[26]
PVC-g-POEM	ZIF-8	010203040	35 °C	70.2Barrer197.6Barrer446.3Barrer687.7Barrer1195.4Barrer	30.531.432.134.926.1	14.014.414.212.410.9	–	[248]
Pebax-2533	ZIF-11	70	20 °C and 2 bar	402.89Barrer	–	12.49	–	[201]
Matrimid	ZIF-11	30	35 °C and 4 bar	31.36Barrer	–	42.95	–	[249]
PBI	ZIF-7/8 core-shell	32	250 °C and 3 bar	141.2Barrer	–	–	0.018	[250]
6FDA-DAM	ZIF-11	0102030	30 °C and 4 bar	20.60Barrer109.70Barrer257.50Barrer73.05Barrer	–	32.6931.3431.0230.44	–	[175]
Ultrason® S 6010	ZIF-302	40	25 °C and 2 bar	13Barrer	33	–	–	[251]
PSF	ZIF-301	010203040	298 K and 2 bar	6.32Barrer10.17Barrer13.75Barrer17.12Barrer21.36Barrer	26.3329.0630.5628.0722.72	–	–	[252]

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## References

- [1] J. Caro, Are MOF membranes better in gas separation than those made of zeolites? *Curr. Opin. Chem. Eng.* 1 (1) (2011) 77–83.
- [2] E. Adatoz, A.K. Avci, S. Keskin, Opportunities and challenges of MOF-based membranes in gas separations, *Sep. Purif. Technol.* 152 (2015) 207–237.
- [3] D.S. Sholl, R.P. Lively, Seven chemical separations to change the world, *Nature* 532 (7600) (2016) 435–437.
- [4] M.R.A. Hamid, H.-K. Jeong, Recent advances on mixed-matrix membranes for gas separation: opportunities and engineering challenges, *Korean J. Chem. Eng.* 35 (8) (2018) 1577–1600.
- [5] Q. Qian, et al., MOF-based membranes for gas separations, *Chem. Rev.* 120 (16) (2020) 8161–8266.
- [6] C. Zhang, et al., Ultrathin metal/covalent-organic framework membranes towards ultimate separation, *Chem. Soc. Rev.* 48 (14) (2019) 3811–3841.
- [7] S. Qiu, M. Xue, G. Zhu, Metal-organic framework membranes: from synthesis to separation application, *Chem. Soc. Rev.* 43 (16) (2014) 6116–6140.
- [8] M. Galizia, et al., 50th anniversary perspective: polymers and mixed matrix membranes for gas and vapor separation: a review and prospective opportunities, *Macromolecules* 50 (20) (2017) 7809–7843.
- [9] R.W. Baker, Future directions of membrane gas separation technology, *Ind. Eng. Chem. Res.* 41 (6) (2002) 1393–1411.
- [10] A. Wonders, D. Paul, Effect of CO<sub>2</sub> exposure history on sorption and transport in polycarbonate, *J. Membr. Sci.* 5 (1979) 63–75.
- [11] A. Houde, S. Stern, Permeability of ethyl cellulose to light gases. Effect of ethoxy content, *J. Membr. Sci.* 92 (1) (1994) 95–101.
- [12] C. Cao, et al., Chemical cross-linking modification of 6FDA-2, 6-DAT hollow fiber membranes for natural gas separation, *J. Membr. Sci.* 216 (1–2) (2003) 257–268.
- [13] A.A. Shamsabadi, et al., Separation of hydrogen from methane by asymmetric PEI membranes, *J. Ind. Eng. Chem.* 19 (5) (2013) 1680–1688.
- [14] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.* 320 (1–2) (2008) 390–400.
- [15] M. Aroon, et al., Performance studies of mixed matrix membranes for gas separation: a review, *Sep. Purif. Technol.* 75 (3) (2010) 229–242.
- [16] H.B.T. Jeazet, C. Staudt, C. Janiak, Metal-organic frameworks in mixed-matrix membranes for gas separation, *Dalton Trans.* 41 (46) (2012) 14003–14027.
- [17] J. Caro, Hierarchy in inorganic membranes, *Chem. Soc. Rev.* 45 (12) (2016) 3468–3478.
- [18] D.Q. Vu, W.J. Koros, S.J. Miller, Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results, *J. Membr. Sci.* 211 (2) (2003) 311–334.
- [19] T.-S. Chung, et al., Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, *Prog. Polym. Sci.* 32 (4) (2007) 483–507.
- [20] S. Basu, A. Cano-Odena, I.F. Vankelecom, MOF-containing mixed-matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> binary gas mixture separations, *Sep. Purif. Technol.* 81 (1) (2011) 31–40.
- [21] R.T. Adams, et al., CO<sub>2</sub>-CH<sub>4</sub> permeation in high zeolite 4A loading mixed matrix membranes, *J. Membr. Sci.* 367 (1–2) (2011) 197–203.
- [22] A. Ismail, et al., Gas separation performance of polyethersulfone/multi-walled carbon nanotubes mixed matrix membranes, *Sep. Purif. Technol.* 80 (1) (2011) 20–31.
- [23] D.Q. Vu, W.J. Koros, S.J. Miller, Effect of condensable impurity in CO<sub>2</sub>/CH<sub>4</sub> gas feeds on performance of mixed matrix membranes using carbon molecular sieves, *J. Membr. Sci.* 221 (1–2) (2003) 233–239.
- [24] H. Vinh-Thang, S. Kaliaguine, Predictive models for mixed-matrix membrane performance: a review, *Chem. Rev.* 113 (7) (2013) 4980–5028.
- [25] B. Ge, et al., High performance gas separation mixed matrix membrane fabricated by incorporation of functionalized submicrometer-sized metal-organic framework, *Materials* 11 (8) (2018) 1421.
- [26] S. Shahid, et al., MOF-mixed matrix membranes: precise dispersion of MOF particles with better compatibility via a particle fusion approach for enhanced gas separation properties, *J. Membr. Sci.* 492 (2015) 21–31.
- [27] J. Yao, H. Wang, Zeolitic imidazolate framework composite membranes and thin films: synthesis and applications, *Chem. Soc. Rev.* 43 (13) (2014) 4470–4493.
- [28] O.M. Yaghi, Metal-Organic and Zeolite Imidazolate Frameworks (MOFs and ZIFs) for Highly Selective Separations, University of California-Los Angeles, 2012.
- [29] M. Shah, et al., Current status of metal-organic framework membranes for gas separations: promises and challenges, *Ind. Eng. Chem. Res.* 51 (5) (2012) 2179–2199.
- [30] S. Mashhadikhan, et al., Interlocking a synthesized polymer and bifunctional filler containing the same polymer's monomer for conformable hybrid membrane systems, *J. Mater. Chem. A* 8 (7) (2020) 3942–3955.
- [31] A. Phan, O. Keeffe, O.M. Yaghi, et al., *Acc. Chem. Res.* 43 (1) (2010) 58–67.
- [32] V.M.A. Melgar, J. Kim, M.R. Othman, Zeolitic imidazolate framework membranes for gas separation: a review of synthesis methods and gas separation performance, *J. Ind. Eng. Chem.* 28 (2015) 1–15.
- [33] Y. Li, et al., Zeolitic imidazolate framework ZIF-7 based molecular sieve membrane for hydrogen separation, *J. Membr. Sci.* 354 (1–2) (2010) 48–54.
- [34] L. Dumée, et al., Seeded growth of ZIF-8 on the surface of carbon nanotubes towards self-supporting gas separation membranes, *J. Mater. Chem. A* 1 (32) (2013) 9208–9214.
- [35] J.-W. Wang, et al., Preparation and gas separation properties of Zeolitic imidazolate frameworks-8 (ZIF-8) membranes supported on silicon nitride ceramic hollow fibers, *Ceram. Int.* 42 (7) (2016) 8949–8954.
- [36] K. Chong, et al., Recent progress of oxygen/nitrogen separation using membrane technology, *J. Eng. Sci. Technol.* 11 (2016) 1016–1030.
- [37] S. Sridhar, S. Bee, S. Bhargava, Membrane-based gas separation: Principle, applications and future potential, *Chem. Eng. Dig.* 1 (1) (2014) 1–25.
- [38] K. Nath, Membrane Separation Processes, PHI Learning Pvt. Ltd., 2017.
- [39] Lloyd, D.R., Membrane materials science: an overview, 1985.
- [40] D.F. Sanders, et al., Energy-efficient polymeric gas separation membranes for a sustainable future: a review, *Polymer* 54 (18) (2013) 4729–4761.
- [41] A. Otani, et al., Molecular design of high CO<sub>2</sub> reactivity and low viscosity ionic liquids for CO<sub>2</sub> separative facilitated transport membranes, *Ind. Eng. Chem. Res.* 55 (10) (2016) 2821–2830.
- [42] T.E. Rufford, et al., The removal of CO<sub>2</sub> and N<sub>2</sub> from natural gas: a review of conventional and emerging process technologies, *J. Pet. Sci. Eng.* 94 (2012) 123–154.
- [43] A. Makaruk, M. Miltner, M. Harasek, Membrane biogas upgrading processes for the production of natural gas substitute, *Sep. Purif. Technol.* 74 (1) (2010) 83–92.
- [44] A. Brunetti, et al., Membrane technologies for CO<sub>2</sub> separation, *J. Membr. Sci.* 359 (1–2) (2010) 115–125.
- [45] J. Huang, J. Zou, W.W. Ho, Carbon dioxide capture using a CO<sub>2</sub>-selective facilitated transport membrane, *Ind. Eng. Chem. Res.* 47 (4) (2008) 1261–1267.
- [46] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: an overview, *Ind. Eng. Chem. Res.* 47 (7) (2008) 2109–2121.
- [47] L. Peters, et al., CO<sub>2</sub> removal from natural gas by employing amine absorption and membrane technology – a technical and economical analysis, *Chem. Eng. J.* 172 (2–3) (2011) 952–960.
- [48] R.W. Baker, Membranes for vapor/gas separation, *Membr. Technol. Res.* 25 (2006).
- [49] J.D. Figueroa, et al., Advances in CO<sub>2</sub> capture technology – the US Department of energy's carbon sequestration program, *Int. J. Greenh. Gas. Control* 2 (1) (2008) 9–20.
- [50] T.C. Merkel, et al., Power plant post-combustion carbon dioxide capture: an opportunity for membranes, *J. Membr. Sci.* 359 (1–2) (2010) 126–139.
- [51] J. Fu, et al., Fabrication of COF-MOF composite membranes and their highly selective separation of H<sub>2</sub>/CO<sub>2</sub>, *J. Am. Chem. Soc.* 138 (24) (2016) 7673–7680.
- [52] P. Luis, T. Van Gerven, B. Van der Bruggen, Recent developments in membrane-based technologies for CO<sub>2</sub> capture, *Prog. Energy Combust. Sci.* 38 (3) (2012) 419–448.
- [53] I.U. Khan, M.H.D. Othman, A. Jilani, High performance membrane for natural gas sweetening plants, in: Z. Zhang, W. Zhang, M.M. Chehimi (Eds.), Membrane Technology Enhancement for Environmental Protection and Sustainable Industrial Growth, Springer International Publishing, Cham, 2021, pp. 59–72.
- [54] S. Budhathoki, et al., High-throughput computational prediction of the cost of carbon capture using mixed matrix membranes, *Energy Environ. Sci.* 12 (4) (2019) 1255–1264.
- [55] G. George, et al., Polymer membranes for acid gas removal from natural gas, *Sep. Purif. Technol.* 158 (2016) 333–356.
- [56] X. He, et al., Membrane system design for CO<sub>2</sub> capture: from molecular modeling to process simulation, in: Athanasios I. Papadopoulos, Panos Seferlis (Eds.), Membrane Technology Enhancement for Environmental Protection and Sustainable Industrial Growth, Wiley, 2017.
- [57] D. Yang, et al., Parametric study of the membrane process for carbon dioxide removal from natural gas, *Ind. Eng. Chem. Res.* 48 (19) (2009) 9013–9022.
- [58] A.E. Amoghini, et al., Substantial breakthroughs on function-led design of advanced materials used in mixed matrix membranes (MMMs): a new horizon for efficient CO<sub>2</sub> separation, *Prog. Mater. Sci.* 102 (2019) 222–295.
- [59] I.U. Khan, et al., ZIF-8 based polysulfone hollow fiber membranes for natural gas purification, *Polym. Test.* 84 (2020), 106415.
- [60] Gemmer, R., Membrane technology workshop summary report. Washington, DC, 2012.
- [61] G. Dong, H. Li, V. Chen, Challenges and opportunities for mixed-matrix membranes for gas separation, *J. Mater. Chem. A* 1 (15) (2013) 4610–4630.

- [62] M.N. Nejad, M. Asghari, M. Afshari, Investigation of carbon nanotubes in mixed matrix membranes for gas separation: a review, *ChemBioEng Rev.* 3 (6) (2016) 276–298.
- [63] I. Sreedhar, et al., Process and engineering trends in membrane based carbon capture, *Renew. Sustain. Energy Rev.* 68 (2017) 659–684.
- [64] R. Lin, et al., Metal organic framework based mixed matrix membranes: an overview on filler/polymer interfaces, *J. Mater. Chem. A* 6 (2) (2018) 293–312.
- [65] G.L. Jadao, P.S. Singh, Synthesis of novel silica-polyamide nanocomposite membrane with enhanced properties, *J. Membr. Sci.* 328 (1–2) (2009) 257–267.
- [66] J. Johnson, W.J. Koros, Utilization of nanoplatelets in organic–inorganic hybrid separation materials: separation advantages and formation challenges, *J. Taiwan Inst. Chem. Eng.* 40 (3) (2009) 268–275.
- [67] S. Clémenson, et al., Nanocomposite membranes of polyetherimide nanostructured with palladium particles: processing route, morphology and functional properties, *J. Membr. Sci.* 361 (1–2) (2010) 167–175.
- [68] Kulprathipanja, S., R.W. Neuzil, and N.N. Li, Separation of gases by means of mixed matrix membranes. 1992, Google Patents.
- [69] R. Castro-Muñoz, V. Ffla, Effect of the ZIF-8 distribution in mixed-matrix membranes based on Matrimid® 5218-PEG on CO<sub>2</sub> separation, *Chem. Eng. Technol.* 42 (4) (2019) 744–752.
- [70] L.Y. Jiang, et al., Fundamental understanding of nano-sized zeolite distribution in the formation of the mixed matrix single-and dual-layer asymmetric hollow fiber membranes, *J. Membr. Sci.* 252 (1–2) (2005) 89–100.
- [71] T.W. Pechar, et al., Fabrication and characterization of polyimide–zeolite L mixed matrix membranes for gas separations, *J. Membr. Sci.* 277 (1–2) (2006) 195–202.
- [72] P. Gorgojo, et al., Development of mixed matrix membranes based on zeolite Nu-6 (2) for gas separation, *Microporous Mesoporous Mater.* 115 (1–2) (2008) 85–92.
- [73] Y. Zhang, et al., Gas permeability properties of Matrimid® membranes containing the metal-organic framework Cu–BPY–HFS, *J. Membr. Sci.* 313 (1–2) (2008) 170–181.
- [74] A. Ismail, T. Kusworo, A. Mustafa, Enhanced gas permeation performance of polyethersulfone mixed matrix hollow fiber membranes using novel Dynasylan Amino silane agent, *J. Membr. Sci.* 319 (1–2) (2008) 306–312.
- [75] H. Cong, et al., Polymer–inorganic nanocomposite membranes for gas separation, *Sep. Purif. Technol.* 55 (3) (2007) 281–291.
- [76] Y. Zhang, et al., Preparation and characterization of zirconium oxide particles filled acrylonitrile-methyl acrylate-sodium sulfonate acrylate copolymer hybrid membranes, *Desalination* 192 (1–3) (2006) 198–206.
- [77] N.M. Wara, L.F. Francis, B.V. Velamakanni, Addition of alumina to cellulose acetate membranes, *J. Membr. Sci.* 104 (1–2) (1995) 43–49.
- [78] J. Ahn, et al., Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation, *J. Membr. Sci.* 314 (1–2) (2008) 123–133.
- [79] G. Ciobanu, G. Carja, O. Ciobanu, Structure of mixed matrix membranes made with SAPO-5 zeolite in polyurethane matrix, *Microporous Mesoporous Mater.* 115 (1–2) (2008) 61–66.
- [80] S. Husain, W.J. Koros, Mixed matrix hollow fiber membranes made with modified HSSZ-13 zeolite in polyetherimide polymer matrix for gas separation, *J. Membr. Sci.* 288 (1–2) (2007) 195–207.
- [81] W. Rafizah, A. Ismail, Effect of carbon molecular sieve sizing with poly (vinyl pyrrolidone) K-15 on carbon molecular sieve–polysulfone mixed matrix membrane, *J. Membr. Sci.* 307 (1) (2008) 53–61.
- [82] R. Xing, W.W. Ho, Synthesis and characterization of crosslinked polyvinylalcohol/polyethyleneglycol blend membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *J. Taiwan Inst. Chem. Eng.* 40 (6) (2009) 654–662.
- [83] B. Zornoza, et al., Combination of MOFs and zeolites for mixed-matrix membranes, *ChemPhysChem* 12 (15) (2011) 2781–2785.
- [84] N. Nordin, et al., Aqueous room temperature synthesis of zeolitic imidazole framework 8 (ZIF-8) with various concentrations of triethylamine, *RSC Adv.* 4 (63) (2014) 33292–33300.
- [85] O.G. Nik, X.Y. Chen, S. Kaliaguine, Amine-functionalized zeolite FAU/EMT-polyimide mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *J. Membr. Sci.* 379 (1–2) (2011) 468–478.
- [86] S. Hashemifard, A.F. Ismail, T. Matsuura, Effects of montmorillonite nano-clay fillers on PEI mixed matrix membrane for CO<sub>2</sub> removal, *Chem. Eng. J.* 170 (1) (2011) 316–325.
- [87] G. Clarizia, et al., Zeolite-based composite PEEK-WC membranes: gas transport and surface properties, *Microporous Mesoporous Mater.* 115 (1–2) (2008) 67–74.
- [88] H. Cong, et al., Carbon nanotube composite membranes of brominated poly (2, 6-diphenyl-1, 4-phenylene oxide) for gas separation, *J. Membr. Sci.* 294 (1–2) (2007) 178–185.
- [89] R. Mahajan, W.J. Koros, Factors controlling successful formation of mixed-matrix gas separation materials, *Ind. Eng. Chem. Res.* 39 (8) (2000) 2692–2696.
- [90] P. Goh, et al., Recent advances of inorganic fillers in mixed matrix membrane for gas separation, *Sep. Purif. Technol.* 81 (3) (2011) 243–264.
- [91] S. Shu, S. Husain, W.J. Koros, A general strategy for adhesion enhancement in polymeric composites by formation of nanostructured particle surfaces, *J. Phys. Chem. C* 111 (2) (2007) 652–657.
- [92] R. Mahajan, W.J. Koros, Mixed matrix membrane materials with glassy polymers. Part 1, *Polym. Eng. Sci.* 42 (7) (2002) 1420–1431.
- [93] E.V. Perez, et al., Mixed-matrix membranes containing MOF-5 for gas separations, *J. Membr. Sci.* 328 (1–2) (2009) 165–173.
- [94] Y. Li, et al., The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite A mixed matrix membranes, *J. Membr. Sci.* 260 (1–2) (2005) 45–55.
- [95] H. Lin, B.D. Freeman, Materials selection guidelines for membranes that remove CO<sub>2</sub> from gas mixtures, *J. Mol. Struct.* 739 (1–3) (2005) 57–74.
- [96] M. Ulbricht, Advanced functional polymer membranes, *Polymer* 47 (7) (2006) 2217–2262.
- [97] W.J. Koros, R. Mahajan, Pushing the limits on possibilities for large scale gas separation: which strategies? *J. Membr. Sci.* 175 (2) (2000) 181–196.
- [98] M. Rezakazemi, et al., State-of-the-art membrane based CO<sub>2</sub> separation using mixed matrix membranes (MMMs): an overview on current status and future directions, *Prog. Polym. Sci.* 39 (5) (2014) 817–861.
- [99] S. Kim, Y.M. Lee, Rigid and microporous polymers for gas separation membranes, *Prog. Polym. Sci.* 43 (2015) 1–32.
- [100] L.M. Robeson, Polymer membranes for gas separation, *Curr. Opin. Solid State Mater. Sci.* 4 (6) (1999) 549–552.
- [101] R. Mahajan, et al., Challenges in forming successful mixed matrix membranes with rigid polymeric materials, *J. Appl. Polym. Sci.* 86 (4) (2002) 881–890.
- [102] M. Anson, et al., ABS copolymer-activated carbon mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *J. Membr. Sci.* 243 (1–2) (2004) 19–28.
- [103] T. Merkel, et al., Ultrapermeable, reverse-selective nanocomposite membranes, *Science* 296 (5567) (2002) 519–522.
- [104] S. Kim, T.W. Pechar, E. Marand, Poly (imide siloxane) and carbon nanotube mixed matrix membranes for gas separation, *Desalination* 192 (1–3) (2006) 330–339.
- [105] B. Zornoza, C. Téllez, J. Coronas, Mixed matrix membranes comprising glassy polymers and dispersed mesoporous silica spheres for gas separation, *J. Membr. Sci.* 368 (1–2) (2011) 100–109.
- [106] J. Kim, J.W. Grate, P. Wang, Nanobiocatalysis and its potential applications, *Trends Biotechnol.* 26 (11) (2008) 639–646.
- [107] D. Zhao, et al., Triblock copolymer synthesis of mesoporous silica with periodic 50 to 300 angstrom pores, *Science* 279 (5350) (1998) 548–552.
- [108] G. Clarizia, C. Algieri, E. Drioli, Filler-polymer combination: a route to modify gas transport properties of a polymeric membrane, *Polymer* 45 (16) (2004) 5671–5681.
- [109] S. Basu, A. Cano-Odena, I.F. Vankelecom, Asymmetric Matrimid®/[Cu3 (BTC) 2] mixed-matrix membranes for gas separations, *J. Membr. Sci.* 362 (1–2) (2010) 478–487.
- [110] A. Car, C. Stropnik, K.-V. Peinemann, Hybrid membrane materials with different metal–organic frameworks (MOFs) for gas separation, *Desalination* 200 (1–3) (2006) 424–426.
- [111] W. Koros, R. Mahajan, Mixed matrix membrane materials with glassy polymers. Part 2, *Polym. Eng. Sci.* 42 (7) (2002) 1432–1441.
- [112] L.Y. Jiang, T.S. Chung, S. Kulprathipanja, Fabrication of mixed matrix hollow fibers with intimate polymer–zeolite interface for gas separation, *AIChE J.* 52 (8) (2006) 2898–2908.
- [113] Y. Li, et al., Dual-layer polyethersulfone (PES)/BTDA-TDI/MDI co-polyimide (P84) hollow fiber membranes with a submicron PES–zeolite beta mixed matrix dense-selective layer for gas separation, *J. Membr. Sci.* 277 (1–2) (2006) 28–37.
- [114] A. Singh, W. Koros, Significance of entropic selectivity for advanced gas separation membranes, *Ind. Eng. Chem. Res.* 35 (4) (1996) 1231–1234.
- [115] D.Q. Vu, W.J. Koros, S.J. Miller, High pressure CO<sub>2</sub>/CH<sub>4</sub> separation using carbon molecular sieve hollow fiber membranes, *Ind. Eng. Chem. Res.* 41 (3) (2002) 367–380.
- [116] J.-M. Duval, et al., Adsorbent filled membranes for gas separation. Part 1. Improvement of the gas separation properties of polymeric membranes by incorporation of microporous adsorbents, *J. Membr. Sci.* 80 (1) (1993) 189–198.
- [117] H.S. Zakria, et al., Fabrication of high performance PVDF hollow fiber membrane using less toxic solvent at different additive loading and air gap, *Membranes* 11 (11) (2021) 843.
- [118] R.T. Yang, *Gas Separation by Adsorption Processes*, World Scientific, 1997.
- [119] R. Mahajan, *Formation, Characterization and Modeling of Mixed Matrix Membrane Materials*, The University of Texas at Austin, 2000.
- [120] M. Moaddeb, W.J. Koros, Gas transport properties of thin polymeric membranes in the presence of silicon dioxide particles, *J. Membr. Sci.* 125 (1) (1997) 143–163.
- [121] H.S. Zakria, et al., Immobilization techniques of a photocatalyst into and onto a polymer membrane for photocatalytic activity, *RSC Adv.* 11 (12) (2021) 6985–7014.
- [122] Q. Hu, et al., Poly (amide-imide)/TiO<sub>2</sub> nano-composite gas separation membranes: fabrication and characterization, *J. Membr. Sci.* 135 (1) (1997) 65–79.
- [123] A. Higuchi, et al., Preparation and gas permeation of immobilized fullerene membranes, *J. Appl. Polym. Sci.* 77 (3) (2000) 529–537.
- [124] Y. Kong, et al., Study on polyimide/TiO<sub>2</sub> nanocomposite membranes for gas separation, *Desalination* 146 (1–3) (2002) 49–55.
- [125] R. Castro-Muñoz, et al., Pervaporation-assisted esterification reactions by means of mixed matrix membranes, *Ind. Eng. Chem. Res.* 57 (47) (2018) 15998–16011.
- [126] E. Okumus, T. Gurkan, L. Yilmaz, Development of a mixed-matrix membrane for pervaporation, *Sep. Sci. Technol.* 29 (18) (1994) 2451–2473.
- [127] L.Y. Jiang, T.S. Chung, S. Kulprathipanja, An investigation to revitalize the separation performance of hollow fibers with a thin mixed matrix composite skin for gas separation, *J. Membr. Sci.* 276 (1–2) (2006) 113–125.
- [128] S. Khoonsap, S. Amnuaypanich, Mixed matrix membranes prepared from poly (vinyl alcohol)(PVA) incorporated with zeolite 4A-graft-poly (2-hydroxyethyl methacrylate)(zeolite-g-PHEMA) for the pervaporation dehydration of water–acetone mixtures, *J. Membr. Sci.* 367 (1–2) (2011) 182–189.
- [129] D. Şen, H. Kalıpcılar, L. Yilmaz, Development of polycarbonate based zeolite 4A filled mixed matrix gas separation membranes, *J. Membr. Sci.* 303 (1–2) (2007) 194–203.

- [130] A.M. Hillock, S.J. Miller, W.J. Koros, Crosslinked mixed matrix membranes for the purification of natural gas: effects of sieve surface modification, *J. Membr. Sci.* 314 (1–2) (2008) 193–199.
- [131] T.T. Moore, W.J. Koros, Non-ideal effects in organic–inorganic materials for gas separation membranes, *J. Mol. Struct.* 739 (1–3) (2005) 87–98.
- [132] A.L. Khan, et al., Hydrogen separation and purification using polysulfone acrylate–zeolite mixed matrix membranes, *J. Membr. Sci.* 350 (1–2) (2010) 340–346.
- [133] Tin, P.S., et al., Carbon-zeolite composite membranes for gas separation. 2005.
- [134] S. Bertelle, et al., Study of polymer-carbon mixed matrix membranes for CO<sub>2</sub> separation from flue gas, *Desalination* 199 (2006) 401–402.
- [135] M. Das, J.D. Perry, W.J. Koros, Gas-transport-property performance of hybrid carbon molecular sieve– polymer materials, *Ind. Eng. Chem. Res.* 49 (19) (2010) 9310–9321.
- [136] C.A. Scholes, et al., Plasticization of ultra-thin polysulfone membranes by carbon dioxide, *J. Membr. Sci.* 346 (1) (2010) 208–214.
- [137] J. Adewole, et al., Current challenges in membrane separation of CO<sub>2</sub> from natural gas: a review, *Int. J. Greenh. Gas. Control* 17 (2013) 46–65.
- [138] C. Hibshman, C. Cornelius, E. Marand, The gas separation effects of annealing polyimide–organosilicate hybrid membranes, *J. Membr. Sci.* 211 (1) (2003) 25–40.
- [139] M. Linlin, et al., Poly (2, 5-benzimidazole)–silica nanocomposite membranes for high temperature proton exchange membrane fuel cell, *J. Membr. Sci.* 411 (2012) 91–98.
- [140] M.-C. Ferrari, et al., Gas and vapor transport in mixed matrix membranes based on amorphous Teflon AF1600 and AF2400 and fumed silica, *Ind. Eng. Chem. Res.* 49 (23) (2010) 11920–11935.
- [141] A. Ladhe, et al., Thiol-functionalized silica–mixed matrix membranes for silver capture from aqueous solutions: experimental results and modeling, *J. Membr. Sci.* 326 (2) (2009) 460–471.
- [142] H.B. Park, et al., Imide-siloxane block copolymer/silica hybrid membranes: preparation, characterization and gas separation properties, *J. Membr. Sci.* 220 (1–2) (2003) 59–73.
- [143] S. Kim, E. Marand, High permeability nano-composite membranes based on mesoporous MCM-41 nanoparticles in a polysulfone matrix, *Microporous Mesoporous Mater.* 114 (1–3) (2008) 129–136.
- [144] A. Jomekian, et al., Fabrication or preparation and characterization of new modified MCM-41/PSf nanocomposite membrane coated by PDMS, *Sep. Purif. Technol.* 80 (3) (2011) 556–565.
- [145] H. Vinh-Thang, et al., Effect of the acid properties on the diffusion of C7 hydrocarbons in UL-ZSM-5 materials, *Microporous Mesoporous Mater.* 92 (1–3) (2006) 117–128.
- [146] V.-T. Hoang, et al., Structure and diffusion characterization of SBA-15 materials, *Langmuir* 21 (5) (2005) 2051–2057.
- [147] B. Nohair, et al., Functionalized mesostructured silicates as supports for palladium complexes: synthesis and catalytic activity for the suzuki– miyaura coupling reaction, *J. Phys. Chem. C* 112 (15) (2008) 6065–6072.
- [148] N. Mizoshita, T. Tani, S. Inagaki, Syntheses, properties and applications of periodic mesoporous organosilicas prepared from bridged organosilane precursors, *Chem. Soc. Rev.* 40 (2) (2011) 789–800.
- [149] V. Ve Butova, et al., Metal-organic frameworks: structure, properties, methods of synthesis and characterization, *Russ. Chem. Rev.* 85 (3) (2016) 280.
- [150] R. Adams, et al., Metal organic framework mixed matrix membranes for gas separations, *Microporous Mesoporous Mater.* 131 (1–3) (2010) 13–20.
- [151] L. Ma, et al., Engineering of the filler/polymer interface in metal–organic framework-based mixed–matrix membranes to enhance gas separation, *Chemistry– Asian J.* 14 (20) (2019) 3502–3514.
- [152] K. Sumida, et al., Carbon dioxide capture in metal–organic frameworks, *Chem. Rev.* 112 (2) (2012) 724–781.
- [153] V. Remya, M. Kurian, Synthesis and catalytic applications of metal–organic frameworks: a review on recent literature, *Int. Nano Lett.* 9 (1) (2019) 17–29.
- [154] Y.-R. Lee, J. Kim, W.-S. Ahn, Synthesis of metal-organic frameworks: a mini review, *Korean J. Chem. Eng.* 30 (9) (2013) 1667–1680.
- [155] H. Furukawa, O. Snurr, R.Q. O’Keefe, M. Kim, J. Yaghi, et al., *Science* 329 (5990) (2010) 424–428.
- [156] S. Kitagawa, R. Kitaura, Si Noro, Functional porous coordination polymers, *Angew. Chem. Int. Ed.* 43 (18) (2004) 2334–2375.
- [157] H. Furukawa, et al., The chemistry and applications of metal-organic frameworks, *Science* 341 (2013) 6149.
- [158] N. Rangnekar, et al., Zeolite membranes—a review and comparison with MOFs, *Chem. Soc. Rev.* 44 (20) (2015) 7128–7154.
- [159] K.S. Park, et al., Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, *Proc. Natl. Acad. Sci. USA* 103 (27) (2006) 10186–10191.
- [160] Z. Zhao, et al., Gas separation properties of metal organic framework (MOF-5) membranes, *Ind. Eng. Chem. Res.* 52 (3) (2013) 1102–1108.
- [161] H. Li, et al., Recent advances in gas storage and separation using metal–organic frameworks, *Mater. Today* 21 (2) (2018) 108–121.
- [162] O.G. Nik, X.Y. Chen, S. Kaliaguine, Functionalized metal organic framework–polyimide mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *J. Membr. Sci.* 413 (2012) 48–61.
- [163] T.H. Bae, et al., A high-performance gas-separation membrane containing submicrometer-sized metal–organic framework crystals, *Angew. Chem.* 122 (51) (2010) 10059–10062.
- [164] T. Yang, Y. Xiao, T.-S. Chung, Poly-/metal-benzimidazole nano-composite membranes for hydrogen purification, *Energy Environ. Sci.* 4 (10) (2011) 4171–4180.
- [165] G. Zhong, D. Liu, J. Zhang, The application of ZIF-67 and its derivatives: adsorption, separation, electrochemistry and catalysts, *J. Mater. Chem. A* 6 (5) (2018) 1887–1899.
- [166] W. Zheng, et al., ZIF-8 nanoparticles with tunable size for enhanced CO<sub>2</sub> capture of Pebax based MMMs, *Sep. Purif. Technol.* 214 (2019) 111–119.
- [167] A. Phan, et al., Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks, *Acc. Chem. Res.* 43 (1) (2010) 58–67.
- [168] A.G. Kontos, et al., CO<sub>2</sub> captured in zeolitic imidazolate frameworks: Raman spectroscopic analysis of uptake and host-guest interactions, *ChemSusChem* 7 (6) (2014) 1696–1702.
- [169] M. Mirqasemi, M. Homayoonfal, M. Rezakazemi, Zeolitic imidazolate framework membranes for gas and water purification, *Environ. Chem. Lett.* 18 (2019).
- [170] M. Wang, et al., Recent advances on mixed matrix membranes for CO<sub>2</sub> separation, *Chin. J. Chem. Eng.* 25 (11) (2017) 1581–1597.
- [171] M. Vinoba, et al., Recent progress of fillers in mixed matrix membranes for CO<sub>2</sub> separation: a review, *Sep. Purif. Technol.* 188 (2017) 431–450.
- [172] A.R. Kamble, C.M. Patel, Z. Murthy, A review on the recent advances in mixed matrix membranes for gas separation processes, *Renew. Sustain. Energy Rev.* 145 (2012), 111062.
- [173] Y. Liu, et al., Transforming from planar to three-dimensional lithium with flowable interphase for solid lithium metal batteries, *Sci. Adv.* 3 (10) (2017), eaao0713.
- [174] B. Sasi Kumar, et al., Performance of polysulfone hollow fiber membranes encompassing ZIF-8, SiO<sub>2</sub>/ZIF-8, and amine-modified SiO<sub>2</sub>/ZIF-8 nanofillers for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> gas separation, *Sep. Purif. Technol.* 264 (2021), 118471.
- [175] M.S. Boroglu, A.B. Yumru, Gas separation performance of 6FDA-DAM-ZIF-11 mixed-matrix membranes for H<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation, *Sep. Purif. Technol.* 173 (2017) 269–279.
- [176] S. Park, H.-K. Jeong, In-situ linker doping as an effective means to tune zeolitic-imidazolate framework-8 (ZIF-8) fillers in mixed-matrix membranes for propylene/propane separation, *J. Membr. Sci.* 596 (2020), 117689.
- [177] N. Jusoh, et al., Transport properties of mixed matrix membranes encompassing zeolitic imidazolate framework 8 (ZIF-8) nanofiller and 6FDA-durene polymer: Optimization of process variables for the separation of CO<sub>2</sub> from CH<sub>4</sub>, *J. Clean. Prod.* 149 (2017) 80–95.
- [178] L. Xiang, et al., Amino-functionalized ZIF-7 nanocrystals: improved intrinsic separation ability and interfacial compatibility in mixed-matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *Adv. Mater.* 29 (32) (2017), 1606999.
- [179] N.H. Suhaimi, et al., Amine-functionalized metal organic framework (MOF)/6FDA-durene composite membranes for CO<sub>2</sub> removal from CH<sub>4</sub>, *Mater. Today: Proc.* 19 (2019) 1730–1737.
- [180] R. Ding, et al., Amino-functional ZIF-8 nanocrystals by microemulsion based mixed linker strategy and the enhanced CO<sub>2</sub>/N<sub>2</sub> separation, *Sep. Purif. Technol.* 236 (2020), 116209.
- [181] J. Gao, et al., Functionalized ZIF-7/Pebax® 2533 mixed matrix membranes for CO<sub>2</sub>/N<sub>2</sub> separation, *Microporous Mesoporous Mater.* 297 (2020), 110030.
- [182] W. Guan, et al., Zeolite imidazolate framework (ZIF)-based mixed matrix membranes for CO<sub>2</sub> separation: a review, *J. Appl. Polym. Sci.* 137 (33) (2020), 48968.
- [183] A.G. Kontos, et al., CO<sub>2</sub> captured in zeolitic imidazolate frameworks: raman spectroscopic analysis of uptake and host-guest interactions, *ChemSusChem* 7 (6) (2014) 1696–1702.
- [184] Q. Wang, et al., ZIF-8 hollow nanotubes based mixed matrix membranes with high-speed gas transmission channel to promote CO<sub>2</sub>/N<sub>2</sub> separation, *J. Membr. Sci.* 630 (2021), 119323.
- [185] S. Meshkat, S. Kaliaguine, D. Rodrigue, Comparison between ZIF-67 and ZIF-8 in Pebax® MH-1657 mixed matrix membranes for CO<sub>2</sub> separation, *Sep. Purif. Technol.* 235 (2020), 116150.
- [186] S.U. Azam, et al., Enhancement in the selectivity of O<sub>2</sub>/N<sub>2</sub> via ZIF-8/CA mixed-matrix membranes and the development of a thermodynamic model to predict the permeability of gases, *Environ. Sci. Pollut. Res.* 27 (19) (2020) 24413–24429.
- [187] Tan, J.C., T.D. Bennett, and A.K. Cheetham, Chemical structure, network topology, and porosity effects on the mechanical properties of Zeolitic Imidazolate Frameworks. *Proceedings of the National Academy of Sciences*, 2010. 107(22): p. 9938–9943.
- [188] S.A. Moggach, T.D. Bennett, A.K. Cheetham, The effect of pressure on ZIF-8: increasing pore size with pressure and the formation of a high-pressure phase at 1.47 GPa, *Angew. Chem. Int. Ed.* 48 (38) (2009) 7087–7089.
- [189] M.J.C. Ordenez, et al., Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes, *J. Membr. Sci.* 361 (1–2) (2010) 28–37.
- [190] T.T. Moore, et al., Hybrid membrane materials comprising organic polymers with rigid dispersed phases, *AIChE J.* 50 (2) (2004) 311–321.
- [191] T. Merkel, et al., Sorption, transport, and structural evidence for enhanced free volume in poly (4-methyl-2-pentyne)/fumed silica nanocomposite membranes, *Chem. Mater.* 15 (1) (2003) 109–123.
- [192] S. Matteucci, et al., Gas transport properties of MgO filled poly (1-trimethylsilyl-1-propyne) nanocomposites, *Polymer* 49 (6) (2008) 1659–1675.
- [193] X. Zhang, H. Lin, B. Hu, The effects of electrocoagulation on phosphorus removal and particle settling capability in swine manure, *Sep. Purif. Technol.* 200 (2018) 112–119.
- [194] R. Castro-Muñoz, V. Fíla, Effect of the ZIF-8 distribution in mixed-matrix membranes based on matrimid® 5218-PEG on CO<sub>2</sub> Separation, *Chem. Eng. Technol.* 42 (4) (2019) 744–752.
- [195] C. Zhang, et al., High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations, *J. Membr. Sci.* 389 (2012) 34–42.

- [196] A. Guo, et al., Metal-organic framework-based mixed matrix membranes: synergetic effect of adsorption and diffusion for CO<sub>2</sub>/CH<sub>4</sub> separation, *J. Membr. Sci.* 562 (2018) 76–84.
- [197] S. Japip, Y. Xiao, T.-S. Chung, Particle-size effects on gas transport properties of 6FDA-Durene/ZIF-71 mixed matrix membranes, *Ind. Eng. Chem. Res.* 55 (35) (2016) 9507–9517.
- [198] Z. Wang, et al., ZIF-301 MOF/6FDA-DAM polyimide mixed-matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *Sep. Purif. Technol.* 264 (2021), 118431.
- [199] I. Ilicak, et al., Influence of ZIF-95 on structure and gas separation properties of polyimide-based mixed matrix membranes, *J. Nat. Gas. Sci. Eng.* 91 (2021), 103941.
- [200] H. An, et al., A new superior competitor for exceptional propylene/propane separations: ZIF-67 containing mixed matrix membranes, *J. Membr. Sci.* 526 (2017) 367–376.
- [201] A. Ehsani, M. Pakizeh, Synthesis, characterization and gas permeation study of ZIF-11/Pebax® 2533 mixed matrix membranes, *J. Taiwan Inst. Chem. Eng.* 66 (2016) 414–423.
- [202] H. Hayashi, et al., Zeolite A imidazolate frameworks, *Nat. Mater.* 6 (7) (2007) 501–506.
- [203] B. Seoane, et al., Insight into the crystal synthesis, activation and application of ZIF-20, *RSC Adv.* 1 (5) (2011) 917–922.
- [204] M. Etxeberria-Benavides, et al., High performance mixed matrix membranes (MMMs) composed of ZIF-94 filler and 6FDA-DAM polymer, *J. Membr. Sci.* 550 (2018) 198–207.
- [205] T. Li, et al., Carbon dioxide selective mixed matrix composite membrane containing ZIF-7 nano-fillers, *J. Membr. Sci.* 425 (2013) 235–242.
- [206] F. Uribe-Romo, et al., Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks, *Acc. Chem. Res.* 43 (2010) 58–67.
- [207] N.A.H.M. Nordin, et al., Utilizing low ZIF-8 loading for an asymmetric PSf/ZIF-8 mixed matrix membrane for CO<sub>2</sub>/CH<sub>4</sub> separation, *RSC Adv.* 5 (38) (2015) 30206–30215.
- [208] K.Y. Cho, et al., Synthesis of amine-functionalized ZIF-8 with 3-amino-1, 2, 4-triazole by postsynthetic modification for efficient CO<sub>2</sub>-selective adsorbents and beyond, *J. Mater. Chem. A* 6 (39) (2018) 18912–18919.
- [209] M. Majumder, et al., Enhanced flow in carbon nanotubes, *Nature* 438 (7064) (2005) 44–44.
- [210] D.S. Sholl, J.K. Johnson, Making high-flux membranes with carbon nanotubes, *Science* 312 (5776) (2006) 1003–1004.
- [211] M. Sarfraz, M. Ba-Shammakh, Combined effect of CNTs with ZIF-302 into polysulfone to fabricate MMMs for enhanced CO<sub>2</sub> separation from flue gases, *Arab. J. Sci. Eng.* 41 (7) (2016) 2573–2582.
- [212] M. Sarfraz, M. Ba-Shammakh, Harmonious interaction of incorporating CNTs and zeolitic imidazole frameworks into polysulfone to prepare high performance MMMs for CO<sub>2</sub> separation from humidified post combustion gases, *Braz. J. Chem. Eng.* 35 (2018) 217–228.
- [213] A. Ismail, et al., Transport and separation properties of carbon nanotube-mixed matrix membrane, *Sep. Purif. Technol.* 70 (1) (2009) 12–26.
- [214] R. Castro-Muñoz, et al., Enhanced CO<sub>2</sub> permeability in Matrimid® 5218 mixed matrix membranes for separating binary CO<sub>2</sub>/CH<sub>4</sub> mixtures, *Sep. Purif. Technol.* 210 (2019) 553–562.
- [215] D. Zhao, et al., Effect of graphene oxide on the behavior of poly (amide-6-b-ethylene oxide)/graphene oxide mixed-matrix membranes in the permeation process, *J. Appl. Polym. Sci.* 132 (2015) 41.
- [216] H.W. Kim, et al., Selective gas transport through few-layered graphene and graphene oxide membranes, *Science* 342 (6154) (2013) 91–95.
- [217] D. Huang, et al., Synergistic effects of zeolite imidazole framework@ graphene oxide composites in humidified mixed matrix membranes on CO<sub>2</sub> separation, *RSC Adv.* 8 (11) (2018) 6099–6109.
- [218] L. Dong, et al., Metal-organic framework-graphene oxide composites: a facile method to highly improve the CO<sub>2</sub> separation performance of mixed matrix membranes, *J. Membr. Sci.* 520 (2016) 801–811.
- [219] K. Yang, et al., ZIFs-modified GO plates for enhanced CO<sub>2</sub> separation performance of ethyl cellulose based mixed matrix membranes, *Sep. Purif. Technol.* 214 (2019) 87–94.
- [220] M. Sarfraz, M. Ba-Shammakh, Pursuit of efficient CO<sub>2</sub>-capture membranes: graphene oxide-and MOF-integrated Ultrason® membranes, *Polym. Bull.* 75 (11) (2018) 5039–5059.
- [221] M. Sarfraz, M. Ba-Shammakh, Synergistic effect of incorporating ZIF-302 and graphene oxide to polysulfone to develop highly selective mixed-matrix membranes for carbon dioxide separation from wet post-combustion flue gases, *J. Ind. Eng. Chem.* 36 (2016) 154–162.
- [222] Z. Wang, et al., Interfacial design of mixed matrix membranes for improved gas separation performance, *Adv. Mater.* 28 (17) (2016) 3399–3405.
- [223] Z. Guo, et al., Ionic liquid tuning nanocage size of MOFs through a two-step adsorption/infiltration strategy for enhanced gas screening of mixed-matrix membranes, *J. Membr. Sci.* 605 (2020), 118101.
- [224] Y. Ban, et al., Confinement of ionic liquids in nanocages: tailoring the molecular sieving properties of ZIF-8 for membrane-based CO<sub>2</sub> capture, *Angew. Chem. Int. Ed.* 54 (51) (2015) 15483–15487.
- [225] J. Ma, et al., Fabrication of mixed-matrix membrane containing metal-organic framework composite with task-specific ionic liquid for efficient CO<sub>2</sub> separation, *J. Mater. Chem. A* 4 (19) (2016) 7281–7288.
- [226] X. Zhang, et al., Mixed-matrix membranes based on Zn/Ni-ZIF-8-PEBA for high performance CO<sub>2</sub> separation, *J. Membr. Sci.* 560 (2018) 38–46.
- [227] K. Noh, J. Lee, J. Kim, Compositions and structures of zeolitic imidazolate frameworks, *Isr. J. Chem.* 58 (9–10) (2018) 1075–1088.
- [228] R. Chen, et al., A two-dimensional zeolitic imidazolate framework with a cushion-shaped cavity for CO<sub>2</sub> adsorption, *Chem. Commun.* 49 (82) (2013) 9500–9502.
- [229] Y. Feng, H. Wang, J. Yao, Synthesis of 2D nanoporous zeolitic imidazolate framework nanosheets for diverse applications, *Coord. Chem. Rev.* 431 (2021), 213677.
- [230] W. Zhu, et al., Introducing hydrophilic ultra-thin ZIF-L into mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *RSC Adv.* 9 (40) (2019) 23390–23399.
- [231] S. Kim, et al., The enhanced hydrogen separation performance of mixed matrix membranes by incorporation of two-dimensional ZIF-L into polyimide containing hydroxyl group, *J. Membr. Sci.* 549 (2018) 260–266.
- [232] J. Deng, Z. Dai, L. Deng, Effects of the morphology of the ZIF on the CO<sub>2</sub> separation performance of MMMs, *Ind. Eng. Chem. Res.* 59 (32) (2020) 14458–14466.
- [233] P. Zhao, et al., Removal of arsenic (III) from water by 2D zeolitic imidazolate framework-67 nanosheets, *Environ. Sci.: Nano* 7 (11) (2020) 3616–3626.
- [234] F. Şahin, B. Topuz, H. Kalıpçılar, ZIF filled PDMS mixed matrix membranes for separation of solvent vapors from nitrogen, *J. Membr. Sci.* 598 (2020), 117792.
- [235] T. Li, et al., A novel water-stable two-dimensional zeolitic imidazolate frameworks thin-film composite membrane for enhancements in water permeability and nanofiltration performance, *Chemosphere* 261 (2020), 127717.
- [236] F. Dou, H. Zhang, Mixed membranes comprising carboxymethyl cellulose (as capping agent and gas barrier matrix) and nanoporous ZIF-L nanosheets for gas separation applications, *Polymers* 10 (12) (2018) 1340.
- [237] S. Zhao, et al., Mixed-matrix membranes for CO<sub>2</sub>/N<sub>2</sub> separation comprising a poly (vinylamine) matrix and metal-organic frameworks, *Ind. Eng. Chem. Res.* 54 (18) (2015) 5139–5148.
- [238] E. Mahdi, J.-C. Tan, Mixed-matrix membranes of zeolitic imidazolate framework (ZIF-8)/Matrimid nanocomposite: Thermo-mechanical stability and viscoelasticity underpinning membrane separation performance, *J. Membr. Sci.* 498 (2016) 276–290.
- [239] A. Kertik, A.L. Khan, I.F. Vankelecom, Mixed matrix membranes prepared from non-dried MOFs for CO<sub>2</sub>/CH<sub>4</sub> separations, *RSC Adv.* 6 (115) (2016) 114505–114512.
- [240] N.A.H.M. Nordin, et al., Facile modification of ZIF-8 mixed matrix membrane for CO<sub>2</sub>/CH<sub>4</sub> separation: synthesis and preparation, *RSC Adv.* 5 (54) (2015) 43110–43120.
- [241] H. Li, et al., Oriented Zeolitic imidazolate framework membranes within polymeric matrices for effective N<sub>2</sub>/CO<sub>2</sub> separation, *J. Membr. Sci.* 572 (2019) 82–91.
- [242] S. Hwang, et al., Revealing the transient concentration of CO<sub>2</sub> in a mixed-matrix membrane by IR microimaging and molecular modeling, *Angew. Chem. Int. Ed.* 57 (18) (2018) 5156–5160.
- [243] D. Eiras, Y. Labreche, L.A. Pessan, Ultem®/ZIF-8 mixed matrix membranes for gas separation: transport and physical properties, *Mater. Res.* 19 (2016) 220–228.
- [244] X. Ding, et al., Partial pore blockage and polymer chain rigidification phenomena in PEO/ZIF-8 mixed matrix membranes synthesized by in situ polymerization, *Chin. J. Chem. Eng.* 26 (3) (2018) 501–508.
- [245] L. Dong, et al., Multi-functional polydopamine coating: simultaneous enhancement of interfacial adhesion and CO<sub>2</sub> separation performance of mixed matrix membranes, *N. J. Chem.* 40 (11) (2016) 9148–9159.
- [246] L. Hu, et al., Highly permeable mixed matrix materials comprising ZIF-8 nanoparticles in rubbery amorphous poly (ethylene oxide) for CO<sub>2</sub> capture, *Sep. Purif. Technol.* 205 (2018) 58–65.
- [247] V. Nafisi, M.-B. Hägg, Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO<sub>2</sub> capture, *J. Membr. Sci.* 459 (2014) 244–255.
- [248] W.S. Chi, et al., Enhanced performance of mixed-matrix membranes through a graft copolymer-directed interface and interaction tuning approach, *ChemSusChem* 8 (4) (2015) 650–658.
- [249] A.B. Yumru, M. Safak Boroglu, I. Boz, ZIF-11/Matrimid® mixed matrix membranes for efficient CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> separations, *Greenh. Gases: Sci. Technol.* 8 (3) (2018) 529–541.
- [250] J. Sánchez-Lafnez, et al., Tuning the separation properties of zeolitic imidazolate framework core-shell structures via post-synthetic modification, *J. Mater. Chem. A* 5 (48) (2017) 25601–25608.
- [251] M. Sarfraz, M. Ba-Shammakh, ZIF-based water-stable mixed-matrix membranes for effective CO<sub>2</sub> separation from humid flue gas, *Can. J. Chem. Eng.* 96 (11) (2018) 2475–2483.
- [252] M. Sarfraz, M. Ba-Shammakh, A novel zeolitic imidazolate framework based mixed-matrix membrane for efficient CO<sub>2</sub> separation under wet conditions, *J. Taiwan Inst. Chem. Eng.* 65 (2016) 427–436.