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Review Article

Selective Capture of CO_2 from Mixture of Different Gases using Cellulose Acetate, Polyimide, Polysulfone and some other Polymers based Mixed Matrix Membranes: A Review

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Abstract | Emission of Greenhouse gases is a major concern these days. A number of techniques are used for separation of CO_2, methane and other hydrocarbons but mixed matrix membrane based separation is gaining significant importance day by day. A number of different polymers have been employed for the fabrication of mixed matrix membranes for example cellulose acetate, polyimides, polysulfone, pebax, polybenzimidazole, polymer of intrinsic porosity, polyurethane, chitosan and many more. Likewise, along with other fillers, Metal organic frame works have also been tested as additive for the mixed matrix membranes as they offer several advantages over other fillers. This review majorly presents use of three polymers viz. cellulose acetate, polyimides and polysulfone, for fabrication of mixed matrix membranes. All of these polymers are of utmost industrial importance in the field of separation. Further use of different other polymers in this field is also discussed shortly.

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1. Introduction

Membrane based gas separation technology feature cost effectiveness, simplicity, no phase conversion, energy efficiency, small foot prints and high mechanical stability (Muhammad *et al.*, 2015; Marti *et al.*, 2018; Rezakazemi *et al.*, 2018) and hence gaining significant attention now a day (Hafeez *et al.*, 2015). A great attention is being paid on development of potential carbon capture technologies so that increasing emission of CO_2 can be controlled (Rehman *et al.*, 2020). The separation of methane and carbon dioxide is an important problem in different fields. Also the recovery of methane from biogas is used as potential alternative to energy sources such as electricity generation, automobile fuel, and grid injection (Baker, 2002; Marian *et al.*, 2007; Millar and Millar, 2003).

Inorganic membranes like Carbon Molecular Sieve Membranes (CMSMs) involve high cost due to their brittle nature so they are far more challenging (Caro *et al.*, 2000; He *et al.*, 2018). That is why polymeric materials are commonly used for CO_2/N_2 and CO_2/CH_4 separations (Adatoz *et al.*, 2015). Both glassy as well as rubbery polymers have been used for membrane preparation. The glassy polymers demonstrate higher perm-selectivity and higher chemical resistance as compared to rubbery polymers (Chen *et al.*, 2015). Furthermore, among the glassy polymers, polyimides demonstrate better performance in the CO_2/CH_4 separation.

The rapid growth in the field of polymer membranes has occurred after sighting the high flux asymmetric phase-inverted membranes in 1962. The successful trials of such membranes for gas separation encouraged for further testing and it was observed that these membranes appropriately separated helium gas from the natural gas (Gantzel and Merten, 1970). Later it was found that MMMs are associated with the superior separation performances as compared to that of the pure polymer membranes (Kulprathipanja *et al*., 1988).

The use of MMMs is promising alternative for extensive use of thermally rearranged polymers (Hu *et al*., 2020) and facilitated transport membranes (Wolińska *et al*., 2017), as well as blending of polymer membranes (Yong and Zhang, 2020) and cross-linking (Wang *et al*., 2020) etc. Despite all these advantages fabrication of a defect free MMM is still a hard challenge. However, such problems can be avoided by wise selection of polymer-filler pair and thus the performance of MMMs can be improved (Chung *et al*., 2007).

The use of filler particles of different shapes and sizes can help in this regard (Anjum *et al*., 2015a). Variation in the weight loadings of the filler particles as well as modification of filler particles surfaces (Venna *et al*., 2015) and use of different porous organic and inorganic fillers can improve the efficiency of MMMs modules towards gas separation (Goh *et al*., 2011; Song *et al*., 2012; Li *et al*., 2013).

The immensely explored materials for the fabrication of MMMs include porous and non-porous fillers for example activated carbons (He *et al*., 2018), carbon nano tubes (CNTs) (He *et al*., 2018), carbon molecular sieves (CMSs) (Ward and Koros, 2011), silica (Ariazadeh *et al*., 2020), Zeolites (Castruita-de León *et al*., 2020), TiO_2 nanoparticles and MOFs (Li *et al*., 2017; Tariq *et al*., 2020).

A large number of polymers have been used for fabrication of MMMs using the above fillers and a large number of other fillers while all of the polymers and fillers pairs cannot be summarized in a single review. Examples of polymers that have been used for fabrication of MMMs include Polymer of intrinsic microporosity (PIM), cellulose acetate (CA), polyimide (PI), polysulfone (PSf), Polydimethylsuloxane (PDMS), Polybenzimidazole (PBI), polyethersulfone (PES), poly (ether ether ketones) (PEEK), sulfonated poly (ether ether ketone) (SPEEK), polyurethane (PUR) etc.

A detailed description of Cellulose acetate (CA), Polyimide (PI), Polysulfone (PSf) and some other polymers based MMMs with regard to gas separation studies is presented below:

1.1 Cellulose acetate

Cellulose is a perfect natural, renewable, biodegradable and biocompatible polymer (Zhang *et al*., 2017) that has been exploited for preparation of self-standing and supported membranes that are cost effective and exhibit the characteristics of virtuous compatibility, good toughness, and good fouling resistance, ease of process-ability, stability and high CO_2 solubility (Moghadassi *et al*., 2014; Sanaeepur *et al*., 2014). It has been commercially used for gas separation specifically the separation of methane from CO_2 (Muhammad *et al*., 2015).

The first CA based membrane systems were introduced in the mid of 1980 by Cyanara which was meant for separation of carbon dioxide from the natural gas (Baker, 2002). The CA membranes usually exhibit relatively low permeability towards CO_2 and low CO_2/CH_4 and CO_2/N_2 gas pair selectivity (Mubashir *et al*., 2018a). The asymmetric hollow fiber membranes offer good permeability and selectivity and hence they have progressively gained importance in the gas separation processes (Tai-Shung *et al*., 1994).

1.1.1 Hollow fiber CA- MMMs

Among numerous configurations, hollow fiber membranes (HFMs) offer the benefits of high packing density, low pressure drops, high pressure stability, and easy scale up (Pang *et al*., 2018; Wahab *et al*., 2012). They show good industrial performances for gas separation but the limitations of instability at elevated temperatures and pressures are also associated with these membranes. Incorporation of filler such as CNTs (Widjojo *et al*., 2008), zeolites (Li *et al*., 2006a) Montmorrillonite (Zahri *et al*., 2016) and polysilsesquioxanes POSS (Zhang *et al*., 2016a) are known to improve the structural properties and thermal stability of resulting HFMMMs (Zhang *et al*., 2016a). But these fillers may suffer from the problem of incompatibility with polymer matrix as well as the defective membrane may be formed (Gao *et al.*, 2018). The defects can efficiently be avoided by using several suitable post-treatment methodologies such as polydimethylsiloxane (PDMS) coating, thermal treatment, and sometimes PDMS coating combined with thermal treatment (Zulhairun *et al.*, 2015). MOFs (Tsai *et al.*, 2018) have proven as prospective fillers which are inherently light weight. These replace the conventional fillers due to their unique properties. Therefore, extensive study on CO_2 adsorption has been carried out using several famous MOFs including the examples of UiOs, ZIFs and MILs (Kim *et al.*, 2016a).

The filler and the polymer chosen highly affect the permeation properties of HFMMMs (Cheng *et al.*, 2013). Commonly, HFMMMs are frequently fabricated using CA, cellulose triacetate, polysulfone (PSf) and polyimides. However, CA effectively removes CO_2 from mixture of CO_2 and CH_4 even when the humidity is present there (Saneepur *et al.*, 2014). Mubashir *et al.* (2019) published feasibility of application of combined use of thermal treatment and PDMS coating methodologies on NH_2-MIL-53(Al)/CA HFMMMs for significant improvement in their performance relating to the separation of CO_2 either from CH_4 (CO_2/CH_4 gas pairs) or from N_2 (CO_2/N_2 gas pairs). Thermal treatment of pristine CA-HFM and NH_2-MIL-53(Al)/CA HFMMM at 170°C resulted in improved selectivities of HFMMM for the CO_2/N_2 and CO_2/CH_4 gas pair from 7.7 to 8.4 and 9.1 to 9.9 respectively in comparison with untreated HFMMMs and neat CA membranes. Adhesion of the MOF with the CA polymer matrix reduced the CA chain mobility which resulted in an increased T_g value of 220 °C than the pristine CA-HFM (Mubashir *et al.*, 2018b).

The gas permeance exhibited a decreasing trend for $CO_2 > N_2 > CH_4$ as compared to that for CA-HFM that was accounted for the differences in the solubility of the two gases (Sanaeepur *et al.*, 2014). A decrease in permeability of CO_2 and separation factors for CO_2/N_2 and CO_2/CH_4 mixed gas pairs were attributed to the polarization effect and competition between the two gases which subsequently resulted in the reduced CO_2 adsorption-diffusion rates through this HFMMM. While CO_2 swelling effect trimmed down the CO_2 solubility coefficient and hence CO_2 permeance was observed to be decreased. An enhanced CO_2 pressure was also associated with its enhanced diffusion (Balçik and Ahunbay, 2018).

Asymmetric CA HFMs prepared by applying a dry/wet spinning procedure with non-solvent induced phase separation (NIPS) executed superior selectivity. In case of permeate; the CA HFM module exhibited a maximum of about 5% higher CO_2 concentration than the existing PSf membrane module at the same stage.

A smaller recyclable stage-cut condition was also observed for CA HFM module in contrast to the existing Polysulfone membrane module. Slightly increased recovery efficiencies were obtained for CH_4 in comparison with the existing Polysulfone membrane module at similar stage-cuts (Jeon and Shin, 2017).

1.1.2 Flat sheet CA-MMMs

The solvent system plays an important role in fabricating defect free membrane with non-selective voids (Mubashir *et al.*, 2018a). Mubashir *et al.* (2018a) used N-Methyl-2-pyrrolidone (NMP) as a solvent to fabricate CA membrane with improved fractional free volume and hence they executed improved gas permeance (Mubashir *et al.*, 2018a) as compared to those prepared in THF and acetone (Moghadassi *et al.*, 2014; Achoundong *et al.*, 2013). The membrane showed the ideal selectivity values of 10.71 and 8.80 respectively for CO_2/CH_4 and CO_2/N_2 gas pairs and the CO_2 permeability to be 15.56 Barrer. The solubility differences of gases in the CA matrix caused a decreasing gas permeability in the order $CO_2 > N_2 > CH_4$ (Moghadassi *et al.*, 2014). NMP enhanced the hydrogen bonding between OH- and C-OH of neighboring rings that increased the rigidity of the CA chain which rendered improved gas permeation efficiency. Thus, NMP was recommended as an effective solvent for fabrication of other types of membranes as well (Mubashir *et al.*, 2018a).

Mubashir *et al.* (2018b) investigated the fabrication of new flat sheet MMMs by the incorporation of NH_2–MIL53–Al MOF as an additive into the CA polymer for getting better separation performances. The Brunauer Emmett and Teller (BET) surface area and micro pore volume of the prepared membranes were found to be 637 m^2/g and 0.28 cm^3/g, respectively (Kim *et al.*, 2012a). The agglomeration of MOF particles in CA based MMMs was observed upon increased filler loadings with an increase in glass transition temperature (*Tg*) of the obtained MMMs (Mubashir *et al*., 2018b).

The improved CO_2 permeability besides the CO_2/N_2 and CO_2/CH_4 ideal selectivities was observed upon incorporation of the aminated MOF into the CA matrix. A 200% increase (30 bar) in the CO_2 plasticization resistance was also observed as compared to the neat CA membrane. Thus, the fabricated MMMs were found to be the potential candidates for abstraction of CO_2 from the natural gas and flue gas at industrial scale (Mubashir *et al*., 2018b).

Two-dimensional MOF based nano-sheets possessing molecular sieving properties are exceedingly preferred as polymer additives for application in the separation of gases. But it is necessary to impose adhesion between the polymer matrix and that of the MOF module and to overcome the MOF particles agglomeration (Zhang *et al*., 2018).

The MOF membranes suffer from poor mechanical stability, defect formation during MOF membrane formation and a lack of interface interactions (Adatoz *et al*., 2015) that lead to compromised selectivity performance of the membranes due to the weaker interactions between the test polymer and the MOF particles (Zhang *et al*., 2016b). Furthermore, almost all MOFs cannot be dispersed well in aqueous system so organic solvents are usually used for synthesizing MOF/polymer composite membranes (Zhang *et al*., 2018).

Zhang *et al* successfully fabricated a carboxymethyl cellulose (CMC) cross-linked ZIF-L membrane by using an organic solvent free method. Here, CMC was used as the gas barrier and adhesive matrix through a facile, organic-solvent-free method. The dispersion stability of ZIF-L nanosheets was high in an aqueous system by successful combination of carboxymethyl cellulose and 2D zeolitic imidazolate framework ZIF-L nanosheets due to the interactions between CMC and ZIF-L nanosheets and the anion charge repulsion effect between the complex particles (Zhang *et al*., 2018).

These improved selectivities for mixed gas were achieved due to the gas barrier offered by the CMC matrix phase and sieving property of ZIF-L. The membranes loaded with 30-wt % ZIF-L nanosheets showed the highest separation ability. Moreover, CMC acted as a capping agent via simple synthesis technique and performed well as an adhesive matrix to fabricate a MOF-based membrane that could possibly be extended to various systems (Zhang *et al*., 2018).

Recently Kim *et al.* (2019) prepared the Zeolitic imidazolate framework-302 (ZIF-302) using 5(6)-methylbenzimidazole (mbImH) 2-methylimidazole (2-mImH) and embedded into the CA matrix using phase inversion technique. Similarly, Hou *et al.* (2017) fabricated HKUST-1 MOF based MMMs by selecting HKUST-1 MOF as additive and CA as the continuous matrix. The CA membrane was crack free while the fibers were twisted in the CA matrix. Further the particle size of HKUST-1 was in the range of 15-20 µm and 60 wt. % loading of HKUST-1 was used to fabricate the MMMs that yielded sufficiently high BET surface area of 459 $m^2\ g^{-1}$. However, both of these MMMs were not used for the gas separation tests (Hou *et al*., 2017).

A variety of layered nanoporous materials are in vogue, for instance layered silicates such as MCM-22, Nu-6 and UZAR-S1 (Roth *et al*., 2011; Gorgojo *et al*., 2012; Rubio *et al*., 2010), layered borogermanates (Xiong *et al*., 2007) and layered aluminophosphates (AlPOs) (Jeong *et al*., 2004) as well as 3D AMH-3 is another nano-porous layered silicate possessing pores without octa membered rings. Its crystallographic pore size is 3.4 Å that renders it potentially useful for significant separations of various gases for example CO_2/CH_4 and H_2/N_2 (Jeong *et al*., 2003).

Interest in nano-porous layered silicate/polymer composite or mixed matrix membranes is increasing day by day as the exfoliated selective layers or flakes present high aspect ratio (Kim *et al*., 2013). Thus the molecular sieving is enhanced which in turn creates an exceedingly high circuitous pathway for transportation of the slow moving molecules (Kim *et al*., 2013). Kim *et al.* (2013) performed membrane synthesis along with the detailed study of microstructural analysis, and evaluation of mixed gas permeation capacities and further established that the nanoporous flake/polymer based MMMs permit momentous improvement in the values of gas permeability while keeping the selectivity sustained.

So, the exfoliated flakes of SAMH-3 were used to fabricate CA membranes by using THF as solvent (Kim *et al.*, 2013). The layers of the used silicate possessed a high degree of exfoliation when present in the Cellulose Acetate module but merely 4–8 layers were found to compose the exfoliated flakes of thickness 15–30 nm. The resulting CA membrane module obtained after incorporation of SAMH-3 flakes in the range of 2–6 wt. % exhibited a significant increase in the CO_2 separation efficiency for the CO_2/CH_4 gas pair (Kim *et al.*, 2013). Moreover, the permeability values of CO_2 were observed to be significantly increased while the selectivity remained sustained. The transport phenomenon of such kind is governed by the competing effects of transport over the pores of layered SAMH-3 in addition to the interlayer spaces and is found potentially operative via the CA matrix of relatively lower-density. So the conventional models were unable to explain this transport (Kim *et al.*, 2013).

Figure 1 combines that the transport mechanism of CO_2 and CH_4 molecules, while the actual illustration describing the transport pathways of these gases can be found elsewhere (Kim *et al.*, 2013). Transportation of CO_2 is sieving through the layers of membranes. This also involves the CH_4 molecules exhibiting tortuous diffusion while Kundsen transport was observed for both the gases through inter layer species as illustrated in Figure 2.

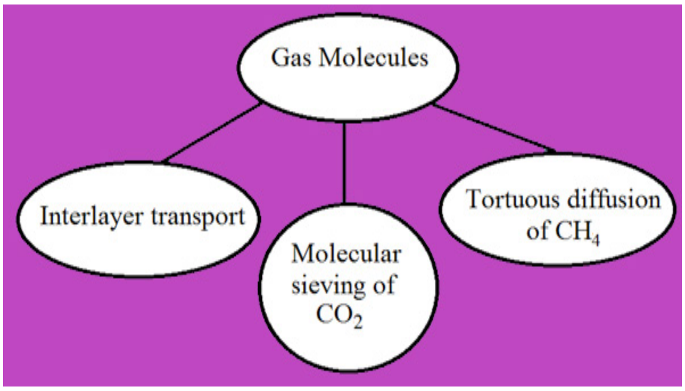

Figure 1: Schematic representation of transport mechanisms in composite membrane.

CAU-1-NH2 is well known for its microporosity, good stability and well established three-dimensional geometry. The octameric bricks consisting of Al in its constitution as $(Al_8(OH)_4(OCH_3)_8)^{12+}$ units are found to be arranged in the body-centered cubic as connected via twelve aminated terephthalate ligand connectors (Yin *et al.*, 2014; Si *et al.*, 2011). The resulting MOF possess highly rigid framework with exceptional thermal stability values up to 573 K (Yin *et al.*, 2014; Ahnfeldt *et al.*, 2009). It was in 2016 when Jian *et al.* (2017) reported the use of CAU-1-NH_2 MOF in its thin and tubular configuration to fabricate CA matrix. The obtained MMMs were tested against CO_2 and Nitrogen gas mixture constituting equal composition of both gases. A high separation factor of 14.8 was obtained for CO_2/N_2 gas pair for the resulting MMM in addition to the high permeance. Yeong and Khoo have demonstrated that the filler loadings greater than 5 wt. % lead to sedimentation as well as agglomeration that in turn increased the CO_2 permeability (149%) besides the increase in CO_2/N_2 selectivity (81%) in comparison to the pure cellulose acetate membrane module (Yeong and Khoo, 2019).

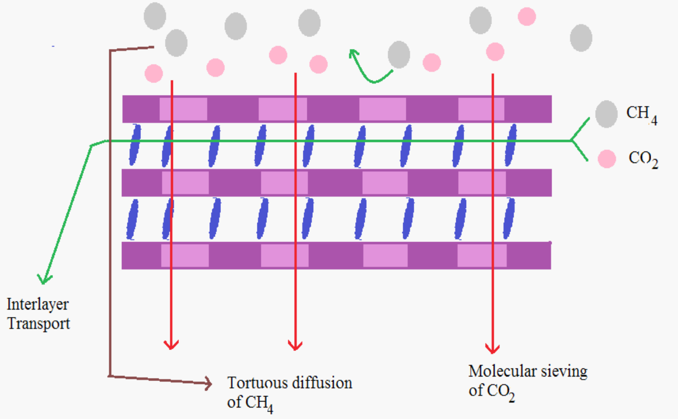

Figure 2: Transport mechanisms in composite membrane. (Redrawn form the reference; Kim *et al.*, 2013).

PDMS possess siloxane linkages which render it highly permeable for gas with a compromised selectivity (Pratibha and Chauhan, 2001). Although its mechanical strength is insufficient for industrial scale applications (Jeon and Shin, 2017) however the CA membranes coated with PDMS experience reduced defect flow to show appropriate permeability values in addition to the improved selectivity of gases (Jeon and Shin, 2017).

Zeolite-filled MMMs feature the potential to realize improved separation performances with nearly equal or comparatively greater fluxes in comparison with the prevailing polymer membranes sustaining their benefits (Li *et al.*, 2013b; Liu *et al.*, 2008). But non-selective "voids" created as a result of insufficient or weak interactions or prevalence of de-wetting phenomena in the polymer chains in addition to the impact of external zeolite surface can lead to a decrement in the performances of the obtained MMMs (Dong *et al*., 2013).

Different approaches may be followed to bring improvement in the polymer-zeolite adhesion in resulting zeolite-filled MMMs for improved gas separation. Such strategies include chemical treatment of the filler surface by introducing different organic functional groups; (Bae *et al*., 2009) creation of a roughened or nanoscopic non-organic whisker-like structure (Lydon *et al*., 2012; Shu *et al*., 2007; Kim *et al*., 2012b); surface initiated polymerization with preformed zeolites, (Shu *et al*., 2007); the in situ formation of zeolite particles inside the pre-fabricated polymer matrices; (Rezakazemi *et al*., 2014) annealing the membranes above the glass transition temperature of the polymer, (Rezakazemi *et al*., 2014) or addition of plasticizer and/or antiplasticizer additives into the membrane formulation (Şen *et al*., 2007).

Zeolite-filled porous MMMs harvest better permeation performance but couple with an unwanted reduction in selectivity in comparison with the dense MMMs (Funk and Lloyd, 2008; Chen *et al*., 2014). Sanaeepur *et al*. (2014) claimed the first time investigation of the proper modification of a homogeneous CA membrane using a micro-sized nanoporous zeolite employing the silylation reaction to attain good adhesion between the polymer and zeolite filler in the resulting MMMs. They used APDEMS to perform as the silane coupling agent and the precursor for zeolites synthesis was micro-sized nanoporous sodium zeolite-Y (Na-Y). The average diameter of the particles was increased as a consequence of Zeolite modification in addition to an increase in the overall volume and external surface area while the micropore surface areas concomitantly decreased. The modified zeolite particles exhibited improved crystallinity besides imparting improved morphological features to the obtained mixed matrix membranes in comparison with the CA/NaY MMMs. Additionally, the numbers and sizes of the unwanted agglomerates and cracks were considerably reduced. The MMMs fabricated with NaY-sm particles loading upto 20 wt. % exhibited the most favorable permselectivity behavior at pressure of 2 bar (Sanaeepur *et al*., 2014).

A schematic representation of membrane modification for enhanced CO_2/N_2 selectivity improvement via the facilitated CO_2 transport in the CA/NaY-sm membranes can be found in reference Sanaeepur *et al*., 2014. The most widely used kinetic diameter was chosen here for the effective molecular diameters of the penetrant gases which are respectively 3.3 and 3.64 A for CO_2 and N_2 molecules (Sanaeepur *et al*., 2014).

The CA/NaY-sm MMMs executed relatively reduced CO_2 permeability as compared to the CA/NaY MMMs. Moreover, the NaY-sm filled MMMs showed an average CO_2/N_2 selectivity of 6.34% in comparison to the MMMs filled with the unmodified NaY particles (≥ 4 bar). The characteristic crystalline peaks for both of the CA and zeolites were present in the membrane after incorporation of NaY or NaY-sm Zeolites but with a slight loss in number of crystallinity of CA after filler loading (Sanaeepur *et al*., 2014).

The particles were observed to be well distributed in unmodified NaY zeolite loaded membranes with a few agglomerates (Sanaeepur *et al*., 2014) at higher zeolite loadings (Sanaeepur *et al*., 2015; Amooghin *et al*., 2015). The gas molecules actually cannot access these points to move through and so these points are the dead zones in the membrane matrix. The surface modified zeolites appreciably improved the particle distribution. The modification of zeolite surface using APDEMS brings a high hydrophobicity in the resulting material as compared to the pristine zeolite. Further, the existence of some amount of moisture can be an additional factor for adsorption of CO_2 (Sanaeepur *et al*., 2014).

An increase in pressure was found associated with a decreased CO_2 permeability of all the membrane samples so the polymer chain densification reduces gas permeability.

Thermal annealing has proved to be an effective method for controlling the crack formation in CA based MMMs. Sanaeepur *et al*., 2014 fabricated dense CA based MMMs for separation of CO_2 from Nitrogen by using micro-sized nano-porous sodium zeolite-Y (NaY zeolite) particles up to 25 wt. %. They efficiently controlled some undesirable cracks in the selected cross sectional area of the well dried pristine CA membranes by annealing. However, further growth of cracks was possibly a result of enhanced NaY zeolites loading from 5 to 25 wt. %. The resulting membranes showed a two-fold permeability increase of CO_2 without compromising the CO_2/N_2 selectivity. Additionally, the CO_2-induced conditioning/plasticization of the glassy CA was reduced and the plasticization pressure was substantially increased (Sanaeepur *et al.*, 2015).

Bos *et al.* (1999) described that the intra-molecular hydrogen bonding present in the CA may be broken by providing sufficient thermal energy. Consequently, the polymer chains can achieve further mobility so as to establish inter-molecular hydrogen bonds between the polar (hydroxyl and acetyl) groups of different chains. These attractive interactions present within polymer chains cause efficient reduction in the free volume, which ultimately results in formation of more compact membranes. Thus, the membrane annealing reduces the permeability. The MMMs fabricated with different weight loadings of the filler ranging from 0 to 25 wt. % showed a small drop in the permeabilities of CO_2 with gradual increase in pressure at least up to plasticization pressure (Sanaeepur *et al.*, 2015). Beyond the plasticization pressure, the permeabilities of the same were observed to increase once again with the increase in pressure (Sanaeepur *et al.*, 2015).

Achoundong *et al.* (2013) used GCV-modification technique so as to modify the CA films by grafting vinyltrimethoxysilane (VTMS) to –OH functional groups. The hydrolyzed methoxy groups present on the silane subsequently underwent condensation to create a polymer network. The modified MMMs showed comparable CO_2/CH_4 and H_2S/CH_4 selectivities than that of the pristine CA membrane; nevertheless, the pure H_2S and CO_2 permeabilities were 165 and 139 barrers respectively which were far higher than the neat polymer. The GCV modified MMMs executed lower *Tg* and lower crystallinity in adition to increased flexibility in comparison to the neat CA. The vinyl substituents delivered by VTMS imparted improved flexibility in the resulting MMMs accompanied with reduced brittleness which could help with the structure of an asymmetric membrane (Achoundong *et al.*, 2013).

Najafi *et al.* (2018) used silica nanoparticles as fillers to study their effects on the permeance of pure gases such as N_2, O_2, and CO_2 while employing CA as polymer matrix. The thermal phase inversion method was used to fabricate CA and CA/silica nanocomposite membranes. SEM micrographs revealed the silica nanoparticles to be well dispersed into the polymer matrix with unavoidable agglomeration of the silica nanoparticles. These nanoparticles were quite compatible with the polymer.

Gas permeation experiments for the prepared composite membranes showed an increased permeability of condensed CO_2 gas with pressure increase. Nonetheless, increasing the silica loading up to 20 wt%. reduced the permeability of N_2 gas at pressure changes from 0.18 to 0.09 barrer. The addition of silica particles into the polymer matrix not only improves the total number of the $-OH^-$ groups but also induces the morphological changes at the polymer-silica interface. The solubility of the gas molecules increases in lieu of these changes, with a consequent reduction in diffusivity of the gas molecules. Consequently, improved CO_2/N2 selectivity was observed in the resulting nanocomposite membranes (Najafi *et al.*, 2018).

Lower mechanical stiffness and the consequent higher brittleness of MOFs in comparison to the zeolites is accompanied by undesirable effects of gate opening, breathing, and linker dynamics (Caro, 2011; Ferrey and Serre, 2009; Li *et al.*, 2009). Flexibility of the metal-organic backbone of MOFs makes their modulation as a self-assembled membrane to be easy; however, the flexible structure of MOFs prevents an appropriate separation based on the penetrant sizes (Caro, 2011) and leads to lower CO_2/CH_4 selectivity of MOF membranes as compared to the zeolites (Li *et al.*, 2006b).

The disadvantages of zeolites/MOFs which are the two best adsorbents in the case of MMMs could be overcome by tailoring the idea of "ship-in-a-bottle" (SIB). The SIB approach was first used to fabricate the zeolite catalysts (Sanaeepur *et al.*, 2019) by encapsulating the catalyst molecules in the zeolite (host) cavities. A guest molecule (like a ship) is formed by assembling its separate constituent species in the zeolite cavities and becomes larger than the pore aperture of the (bottle-like) zeolite. The guest nano-materials are confined and, can freely move around within nano-scale domains of the host cavities and, hence, prevent leaching (Kahlen *et al.*, 1998; Herron, 1986).

Thus gas separation properties of MMMs could be enhanced by interior modification of an inorganic nano-porous particle. Sanaepur *et al.* (2019) used

SIB, as a novel synthesis strategy to encapsulate a polyaza macrocyclic Ag-ligand complex into the zeolite Y, which resulted in a new host-guest nanocomposite. It was consequently incorporated into CA to fabricate a novel MMM for CO_2 separation. The results showed a promising increase in both the CO_2 permeability (45.71%) and CO_2/N_2 selectivity (40.28%) of the prepared MMMs over its pristine CA membrane (Sanaeepur *et al*., 2019).

The CO_2 separation using a membrane is not merely a procedure to physically sieve out CO_2 via a wise control over pore size of the selected membrane. The separation procedure specifically for composite dense membranes is primarily governed by diffusion and solubility phenomena of the gases. The blended constituents of composite membranes usually possess high CO_2 adsorption capability while, the adsorption kinetics of the gases directly influence their diffusion and the solubility. A complete understanding concerning the adsorption performance of CO_2 was explored in terms of its diffusion and solubility using pristine and composite CA. The CA-TiO_2 composite membranes were prepared using 20 wt. % of pure TiO_2 (Hafeez *et al*., 2015).

TiO_2 nanoparticles were homogenously dispersed in the blended membrane (Hafeez *et al*., 2015) but with appearance of some nanoscale granular morphology (Sijbesma *et al*., 2008). The hydrophilic TiO_2 nanoparticles impart increased thermodynamic instability towards the membranes, during solvent–water exchange. Accordingly, increasing the amount of TiO_2 nanoparticles within the polymer matrix could make the membrane porous. That is why optimized (20 wt. %) loading of TiO_2 nanoparticles in the CA matrix did not prompted the solvent–water exchange process. Also the porosity was not imparted in the blended membranes. The adsorption of CO_2 through both the pristine CA and blended membranes took place in a parallel fashion and this adsorption was increased with the pressure.

The blended CA membrane exhibited comparatively higher amount of CO_2 adsorption in comparison with the pure CA membrane because of inability of CO_2 gas to diffuse and its ease of solubilization in the dense pristine CA membranes. Furthermore, addition of TiO_2 nanoparticles caused an increase in the free volume between the polymeric chains that might enhance diffusion as well as adsorption of CO_2 in polymeric matrix. The –OH^- functionality on TiO_2 has its own role in increasing CO_2 adsorption (Hafeez *et al*., 2015).

Abedini *et al*. (2011) proposed that the temperature can easily affect the polymer chains in the absence of inorganic particles in the membrane. They also prepared CA/TiO_2 hybrid MMMs of different compositions by dispersing varying concentrations of inorganic filler in the casting solutions of CA. The addition of TiO_2 nanoparticles imparted porosity in the obtained hybrid membranes because of resultant increase in the mean pore size. The facilitated formation of macro voids occurred in the membrane sub-layer upon increasing the amount of TiO_2 nanoparticles in the cast module from 0 to maximum 25 wt. %. The addition of TiO_2 nanopaticles increased the thermal stability of hybrid membranes (Abedini *et al*., 2011).

The MMMs offer the advantage to overcome the discrete deficiencies related to the inorganic particles as well as polymers in order to realize higher CO_2 separation performances (Scholes *et al*., 2008). Nevertheless, the membranes suffer from insufficient interfacial compatibility between the polymer and the inorganic phase which ends up in the creation of unselective voids within the membranes (Mahajan and Koros, 2000). Ahmed *et al* described synthesis of thin dense skin layer and defect free MMMs from cellulose acetate (CA) with homogeneous distribution of MWCNTs by using the wet phase inversion method. The separation efficiency of the obtained MMM for CO_2/N_2 gas pair was studied at 0.1 wt. % loading of MWCNTs functionalized with β-CD (MWCN-F). MWCNTs-F were also found to be less agglomerated in CA matrix (Ahmed *et al*., 2014).

Troota *et al*. (2011) described that β-CD can entrap CO_2 even at room temperature and atmospheric pressure. Neoh *et al*. (2006) made use of the β-CD cavity for encapsulation of CO_2. Considering the above work it can be deduced that embedding of β-CD into the CA polymer matrix could be beneficial for CO_2/N_2 separation.

The Nano channels were created as beneficiary of the smooth walls of MWCNTs so that gases can fastly be transported (Sanip *et al*., 2010, 2011) while the treatment using β-CD does not end up with the destruction of tubes with small diameter (Ahmed *et al.*, 2014). So the MMMs are expected to exhibit good separation efficiency.

There was a significant increase in the permeance of both the CO_2 and N_2 with the increase in loading of MWCNTs from 0.05 wt. % to 0.1 wt. % in the polymer matrix (Ahmed *et al.*, 2014). It was the result of presence of high diffusivity MWCNTs tunnels within the polymer matrix having good interaction between the MWCNTs and polymer phase (Kim *et al.*, 2006a). The selectivity was insignificantly changed with the increasing pressure (Ahmed *et al.*, 2014) which provided indication of the additional mechanical strength provided to the MMM by the presence of MWCNTs-F (Sanip *et al.*, 2011; Liu *et al.*, 2007).

Considering the importance for the design of membrane gas separation system, a number of models had been developed with the simultaneous growth of MMMs, so that CO_2 permeation performances could be estimated (Emovon *et al.*, 2017). Maxwell model (Mubashir *et al.*, 2016; Bouma *et al.*, 1997), Lewis-Nielsen model (Lewis and Nielsen, 1970), Bruggeman model (Goncharenko, 2003) and Pal model (Pal, 2007) are considered as basic models to predict permeability of CO_2 in the MMMs.

The estimation of CO_2 permeability of MMMs using models is important for the design of membrane separation system. The modified Maxwell model applied for NH_2-MIL-53(Al)/CA system, revealed the absolute average error (AARE %) of 1.66%, which was lower than the AARE% obtained from the other theoretical models (Mubashir *et al.*, 2018c).

Increase in filler loading simultaneously increased the viscosity of the NH_2-MIL-53(Al)/CA solution so as to create a stress between filler and polymer matrix (Ahmed *et al.*, 2014). This stress might have developed the pseudo dispersed phase in the CA polymer which could have increased the interfacial defects (θi) in MMMs (Abedini *et al.*, 2014; Emovon and Mgbemena, 2018; Adeeb *et al.*, 2018).

1.2 Polyimide

Polyimides (PI) are high performance glassy polymers with outstanding heat and chemical resistance (Mathew *et al.*, 2007) and high mechanical strength (Mathew *et al.*, 2007) and thus offers better selectivity in a number of major pairs of gases (for example O_2/N_2 and CO_2/CH_4). These exceptional properties render the PIs a striking candidate among a number of polymeric membranes for gas separation studies. Since the production of marketable PIs membranes, several of those have been commercialized for the purpose of gas separation. Their commercialized uses have been reported in the separation processes by the industries such as Ube (Japan) and the DuPont (USA) (Liaw *et al.*, 2012).

Imide functional group is the major unit constituting the PI backbone as can be seen in the Figure 3. Fully aromatic PIs possess linear structure and they are derivative of an aromatic dianhydride and a diamine. The semi aromatic PIs comprise any one of the aromatic monomer i.e. either of the constituting units that is dianhydride or a diamine are aromatic and the other monomeric unit may be the aliphatic one. Fully aliphatic PIs result from combination of aliphatic constituting monomers of diamine and dianhydride (Mathew *et al.*, 2007). PIs have broad applications in photoresists, dielectric films, passivation (Mathew *et al.*, 2007) and in synthesizing films and fibers, coatings molding powders and composites.

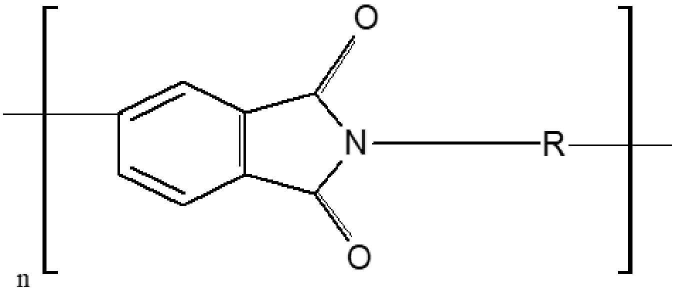

Figure 3: Chemical structure of Polyimide (Redrawn from referenec; Zhang *et al.*, 2019).

Raw multi wall carbon nanotubes (r-MWCNTs) with 0-6 wt. % were used to fabricate PI membranes which increased the separation factor for CO_2/CH_4 gas pair (from 19.05 to 45.75) and decreased the carbon dioxide (from 9.15 GPU to 5.49 GPU) and methane permeances. When the 2 wt. % r-MWCNTs were added into the spinning dope, the CO_2/CH_4 separation factor executed an increase from 46.61 to 72.20 that was comparable to the flat sheet MMMs. Sufficient segmental-level association existed between both of the phases comprising the MMMs which led to the formation of rigidification of polymer regions at the polymer/r–MWCNTs interfacial points and it was evident from increasing *Tg* values upon increased filler loadings (Aroon *et al.*, 2010).

In another work, Sanip and co-workers (Sanip *et al*., 2011) reported enhanced functionality of multi-walled CNTs (MWCNTs) by use of beta-CD (β-CD). The 0.7 wt. % loading of functionalized MWCNTs into polyimide membrane led to the formation of uniform finger-like structures in the resulting MMMs so as to facilitate the faster gas diffusion through the polymer matrix

MCM-41 functionalized with $-SO_3H$ was used to fabricate Matrimid® 9725 based MMMs. The functionalized fillers possessed a good contact with the polymer phase and were homogenously dispersed throughout the continuous phase. The activation energies of permeation in the resulting MMMs were higheras the introduction of massive $–SO_3H$ groups resulted in the creation of pores with reduced diameter. The highly porous filler along with functionalized polar groups led to a concurrent increase in the solubility co-efficients and diffusion of CO_2 as compared to the pristine membranes. Consequently, the functionalized MMMs showed upto 31% increase in CO_2 permeability and 14% increase in CO_2/CH_4 selectivity (Khan *et al*., 2013a).

Ordered mesoporous silica such as COK-12 particles featuring remarkably ordered 2D hexagonal structure possess short but straight pores that allowed a faster diffusion of penetrant gas when used as additives in MMMs based on Matrimid. The increased gas permeabilities of the test gases (N_2, CH_4 and CO_2) in comparison with pure Matrimid membrane resulted from the mesopores existing in the structure of additives. The addition of filler causes a decrease in activation energy of permeation. The mixed gas selectivity for both of the CO_2/CH_4 and CO_2/N_2 gas pairs was found to be lesser than the ideal gas selectivity for all of the tested MMMs; most probably the competitive sorption played its role (Khan *et al*., 2015).

Free volume causes a positive influence on gas permeability as well as selectivity. Increased sorption efficiency could be achieved for increased loading of carbon phase in the CSM@matrimid® 9725 MMMs. It was attributed to the increased affinity of the CO_2 gas molecules besides increasing free volume within the continuous phase and creation of extra porosity. The results showed a 2-fold increase in CO_2 mixed gas selectivity (up to 42.5) and a 6-fold increase in permeability for the CO_2/N_2 and CO_2/CH_4 gas mixtures which is a significant improvement (Anjum *et al*., 2015a).

Various factors influence the performance of polyimide membranes. Chaidou *et al*. (2012) prepared Matrimid® 5218 based MMMs by incorporating zeolite 13X, 4A and ZSM-5 by solution casting procedure. The results obtained after gas permeation trials indicated a significant rise in the permeability values of He, H_2, N_2 and CO_2 with increase in zeolite loadings (Chaidou *et al*., 2012). Slightly improved selectivity was obtained for H_2/N_2 gas pair for small addition of ZSM-5 and zeolite 13X however a decreasing trend in selectivity was observed for zeolite 4A and for high wt. % loadings of the other two zeolites. Moreover, an exceptionally improved selectivity was observed for the CO_2/N_2 gas pair with the addition of all of the three zeolites in the PI membrane in contrast to the selectivity of H_2/CO_2 gas pair which remained too low (1–3). The obtained permeabilities were quite higher than the predicted values of selectivity by employing the Maxwell model. However, the predicted permeabilities of H_2 and N_2 for the PI-4A system were an exception as they were in consistency with the observed permeabilities. The proposed modification in the Maxwell model helped in predicting the permeabilities of PI-zeolite 4A MMMs, but unfortunately they were incapable to simulate the increase in permeability induced by interfacial voids in the PI-zeolite 13X and PI-ZSM-5 MMMs systems (Chaidou *et al*., 2012).

Zeolite-T/6FDA-durene MMMs exhibited 172% rise in ideal selectivity (19.1) for the CO_2/CH_4 and 80% increase in CO_2 permeability (843.6 Barrer) with incorporation of only 1 wt. % zeolite-T loading in comparison with pure 6FDA-durene membrane. Furthermore, the MMMs showed a significant improvement in CO_2 plasticization resistance (up to 20 bar) in contrast to unfilled 6FDA-durene membrane which could show the CO_2 plasticiization resistance of only 5 bar (Jusoh *et al*., 2017a).

The MMMs comprising of 6FDA-based polyimide matrix fabricated with amine-functionalized T-type zeolite had enhanced polymer-zeolite adhesion in MMM compared with MMM loaded with unfunctionalized T-type zeolite which resulted in permeability value of 858 Barrer for CO_2 and selectivity of CO_2/CH_4 gas pair to be 22.5 on the other hand. While, MMM incorporated with unfunctionalized

T-type zeolite displayed permeability value of CO_2 to be 844 Barrer and selectivity of CO_2/CH_4 gas pair to be 19.1 (Jusoh *et al.*, 2018). Similarly, Nik *et al.* (2012) disclosed that the inclusion of amine-grafted MOF-199 in 6FDA-ODA matrix efficiently improved the dispersal of particle in the continuous phase and subsequently ended up with elevated values of permeability for CO_2 and selectivity of the CO_2/CH_4 gas pair (Nik *et al.*, 2012).

Aminosilane grafted zeolite T/ 6FDA-durene MMMs also showed improved selectivity for CO_2/CH_4 gas pair (Jusoh *et al.*, 2017b) that was attributed to the capability of amino silane modified zeolite T to minimize the mobility of gases through the non-selective holes (Ismail *et al.*, 2008). Whereas the selectivity of MMMs embedded with the unmodified zeolite T for the same gas pair was found to be 19.1. The *Tg* values also supported the better performance of the MMMs embedded with grafted fillers used in this study. The success of this modification of the used zeolite as filler in the zeolite T/ 6FDA-durene MMMs is evident from the fact that these MMMs lie on the Robeson upper bound 2008 (Jusoh *et al.*, 2017b).

MMMs manufactured from continuous phase of cross-linkable co-polyimides *viz (*6FDA-Durene/ DABA (9/1) (MMM-1) and 6FDA Durene/DABA (7/3)) (MMM-2) were fabricated using ZIF-8 nanoparticles. The resulting MMMs were annealed at 400°C which facilitated the cross-linking reaction between the carboxyl groups present in the DABA moiety and thus caused characteristically high suppression in plasticization up to a CO_2 pressure of 30 atm. The MMM-1 fabricated with 40 wt. % of additives showed only a slight increase in ideal gas selectivity for CO_2/CH_4 gas pair in contrast to 134% increase in the same for C_3H_6/C_3H_8 gas pair. The loading of 20 wt. % of filler in MMM-1 exhibited CO_2/CH_4 selectivity to be 19.61 with a striking CO_2 permeability value of 728 Barrer in the binary mixture of gases (Askari and Chung, 2013). The experimental results argue upon the stronger dependency of gas pair selectivity and swelling resistance of the MMMs on the optimum annealing temperature and cross-linkable moiety (Askari and Chung, 2013).

The imidazolate likners constituting framework structure of ZIFs render them hydrophobic as a result ZIFs offer better interactions with the polymer matrix (Askari and Chung, 2013). 48 wt. % loading of ZIF-8 particles into ZIF-8/6FDA-DAM MMMs caused 250% increase in permeability and 150% increase in selectivity of propylene/propane (Zhang *et al.*, 2012). The studies have shown that the addition of breathing MOF *viz* MIL-53(Al), flexible ZIF-8 particles and rigid HKUST-1 MOFs dispersed in a Matrimid alleviated plasticization. Use of exceedingly higher pressures above the plasticization pressure of pristine Matrimid (recorded to be 10–12 bar) produced a slight elevation in the permeabilities of almost all MOF–MMMs in comparison with the neat polymer. Also, the increased MOF loading subsequently increases the plasticization pressure (Shahid and Nijmeijer, 2014).

Ploegmakers *et al.* (2013) indicated a constant permeability with increase in selectivity of the ethylene/ ethane gas pairs for the respective loading of HKUST-1. This was attributed to the higher diffusion coefficient of gases with sieve in cage morphology.

Increasing the loading of MOF-5 and Ni, Co and Cu doped MOF-5 into the PI as well as the increasing pressure was found to increase the permeability of CH_4, CO_2 and H_2 gases however, the selectivity for all of these three gas pairs *viz* CO_2/CH_4, H_2/CO_2 and H_2/CH_4 was observed to be reduced. Additionally, significant increase in the rates of permeation was observed for these gases with the use of obtained MMMs combined with a factor of gradual increment in the MOF loadings upto a maximum of 15 wt. % and at constant trans-membrane pressure (100-500 kPa) maintained at room temperature. Increasingly high feed pressures were found responsible for high gas transport via these MMMs (in the order; $CH_4>CO_2>H_2$) at the cost of reduction in selectivities of all of the above mentioned gas pairs. Here both MOFs had pore sizes in the range of 7-8 Å that were observed to be greater than the intersegmental spaces present within specific polymer chain comprising the MMMs. In fact, the application of trans-membrane pressure in turn increased the permeability of the bigger sized gas molecules specifically CH_4 and CO_2 that caused a reduction in the selectivities of H_2/CO_2 or H_2/CH_4 gas pairs (Ozen and Ozturk, 2019).

Adequate dispersion and good adhesion was observed between the continuous phase and additives in the Matrimid®5218/MIL-53 MMMs especially at lower MOF loadings. MMMs showed slightly increased permeability concerning CH4 as the increasing percentage of filler was embedded. For 20% loading of MIL-53, particles agglomeration and formation of voids was observed that finally led to 300% enhancement in permeability of CH_4 over pristine Matrimid membrane but a decrease in separation performance was observed. CO_2 permeability was observed to be increased up to 94% with a subsequent growth of 84% in CO_2/CH_4 selectivity for the MMMs loaded with 15wt. % of fillers in contrast to pure Matrimid membrane.

However, a complete destruction in membrane separation efficiency was observed for 20 wt. % loading of the filler in the MMMs (Dorosti *et al*., 2014).

Structural transformation of MIL-68(Al) upon water immersion under different sets of conditions followed a crackling core model to transform it to nanosheets of MIL-53(Al) of approximately 150 nm in size. The average thickness of nanosheets was 3.5 ± 0.9 nm. Also the nanosheets of the transformed MOF were disaggregated with an ease using PDMS solution. Both of the prepared fillers were deposited on the asymmetric P84® that was used as support to obtain the supported MMMs by applying vacuum filtration. The MMMs embedded with the filler in the nanosheets form brought improvements in the CO_2/CH_4 (28.4-28.7 *vs*. 22.4) and CO_2/N_2 (19.9-23.2 *vs*. 17.5) selectivities of the conventional MIL-53(Al)- MMMs with higher CO_2 permeance values (Perea-Cachero *et al*., 2019).

Coating is an efficient method to realize improvements in selectivity of gases. Coating of remarkably permeable silicone polymer layer performed on the surface of Matrimid® 9725 based MMMs embedded with 40 wt. % loading of HKUST-1, MIL-53(Al) and ZIF-8 were observed to overwhelm the likely existence of unselective voids. The CO_2/CH_4 and CO_2/N_2 selectivity as well as permeance for both dense and the asymmetric membranes fabricated with the above mentioned MOFs were improved as compared to the unfilled membranes taken as reference due to the breathing mechanism attributed to the MOFs and the interactions of CO_2 molecules with the hydroxyl groups present in the frame work (Basu *et al*., 2011).

The CO_2 molecules offer adsorptive interactions with the filler particles *Viz* NH_2-MIL-125 that accounted for the greater separation efficiency of this neat MOF membrane in addition to its role as an additive for the obtained MMMs comprising of Matrimid® 5218. Higher temperatures weakened the adsorptive interactions between the CO_2 molecules and amine groups so a decrease in the perm selectivity of CO_2 was observed in the thin supported MOF layer. The optimal loading of MOF was found to be 10 wt. % for casting efficient MMMs, capable of exhibiting a concomitant increase in both the selectivity as well as permeability relative to the neat polymer membrane. Whereas slightly increased loading (20 wt. %) of the respective MOF merely promotes permeability. Constant increase in the feed pressure caused no effect on the separation factor of both MMMs. While considering the performance of all of the membranes in relation to the Robeson upper bound and evaluating the performances of the MMMs with the Maxwell-model, it was revealed that all membranes inclusive of the supported thin membrane of MOF exceeded the Robeson upper bound (Friebe *et al*., 2016).

The combined use of modulation approach and amine-functionalized ligands, is recently being used for preparation of different MOF fillers (Anjum *et al*., 2015b). This approach is purposely employed so that the MOFs exhibit improved intrinsic separation efficiency and compatibility when present as fillers in MMMs *Viz* UiO-66@Matrimid ®9725. The amine groups present on the exterior surface of MOF either introduced via the ligand (2-aminoterephthalic acid) or by using suitable modulator (4-aminobenzoic acid) or by combined use of both resulted in formation of covalent linking between the Matrimid® 9724 and the fillers, which yielded precisely stable membranes (Anjum *et al*., 2015b). Additionally, the MOFs obtained through these approaches possess amine groups inside their pores and intimately offer linker vacancies so as to impart a positive influence on CO_2 transport. Here 30 wt. % loading of the MOF was proved to be appropriate towards the formation of MMMs so as to execute exceptional separation efficiency for CO_2/CH_4 gas mixtures. The resulting MMM exhibited substantially improved permeability of 19.4 Barrer (540%) and mixed gas selectivity of 47.7 (50%) when compared with the pristine Matrimid membrane (Anjum *et al*., 2015b). A careful and wise selection of the surface organic moiety for a MOF can harvest increased chances to obtain defect-free MMMs. Matrimid® 5218 based MMMs fabricated with surface optimized UiO-66-NH_2 particles exhibited improved thermal as well as mechanical properties. Functionalization of UiO-66 with –NH_2 and phenyl acetyl groups is known to offer favorable interactions with the imide groups present in the Matrimid® via π-π stacking and hydrogen bonding. On the other hand, robust interactions are expected to occur between the imide groups in the continuous phase and the –NH_2 groups. The amide linkages formed through hydrogen bonds are shown in Figure 4. So that truly defect free Polymer/ filler interface could be obtained.

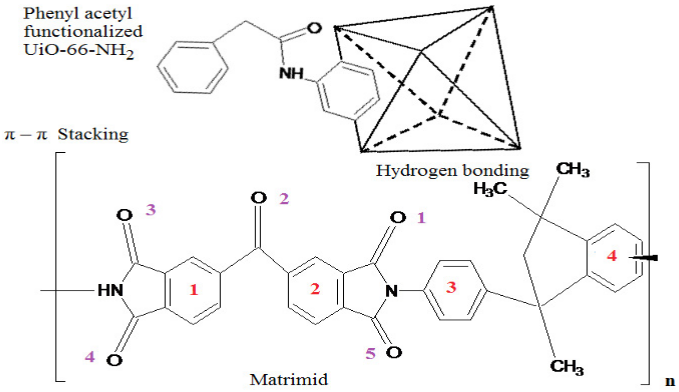

Figure 4: Schematic diagram depicting the promising interactions between the Matrimid® polymer and surface modified MOF (Redrawn from Reference; Venna *et al.*, 2015).

The obtained results indicated ~200% increase in CO_2 permeability and ~ 25% increase in ideal selectivity for CO_2/N_2 than the pure Matrimid®. These improvements were due to the molecular sieving offered by the MOF particles thus confirming the achievement of the anticipated technique so as to alleviate the defective MOF/Matrimid® interfaces (Venna *et al.*, 2015).

The fast solvent removal from NH_2-MIL-53(Al)@PI MMMs (25 wt. % of filler) of different thicknesses favorably contracted the MOF structure to a framework configuration possessing narrow pore size which then enhanced CO_2 permeability at trans-membrane pressure difference of 3 bar and 308 K and preserving the relatively high separation factor. Increased CO_2 permeability was also observed due to the same reason. These investigations revealed that even higher filler loadings (up to 25 wt%) did not affect the previously established exceptionally good filler polymer contact, while possessing void volume fraction to be almost 0.11% (Rodens *et al.*, 2014).

High performance MMMs doped with ZIF-94 as filler into the 6FDA-DAM polymer matrix are known to selectively separate the CO_2 from a mixture of gases testing ($15CO_2$:$85N_2$) at room temperature with a trans-membrane pressure difference ranging between 1-4 bar. The addition of ZIF-94 particles caused an increase in CO_2 permeability through the membrane system while sustaining a constant selectivity (~22) for CO_2/N_2 gas mixture. The biggest increase of~ 200% was observed in CO_2 permeability for 40 wt. % loading of ZIF-94 into the continuous phase thus paving its way towards the highest ever reported permeability of 2310 Barrer while sustaining quite similar selectivity among the 6FDA-DAM MMMs. The ZIF-94 MOF crystals used in this work were prepared for the first time possessing smaller particle size (< 500 nm) by using methanol and THF that are termed as nonhazardous solvents instead of using DMF in a scalable process. These results demonstrated a very good dispersal and sufficient interaction of the filler particles even at their high loadings in the layer of continuous phase (Etxeberria-Benavides *et al.*, 2018).

High-performance ZIF-8/MMM were produced using in-situ controlled thermal treatment that was performed in air at a temperature 350°C in the presence of air to remarkably boost the gas separation performance up to the highest ever reported selectivity for CO_2/CH_4 to date for the MMMs loaded with MOFs (Kertik *et al.*, 2017). The amorphisation of the MOF occurred due to the protection of the surrounding continuous phase that in-situ created a porous molecular sieve network. Role of the thermal treatment unveiled when it improved the adhesion between filler and continuous phase and together induced oxidative cross-linking of the continuous phase. Thus increasingly stable MMMs were formed that offered plasticization resistance at considerably higher pressure of 40 bar (Kertik *et al.*, 2017). Hence, the Matrimid® membranes displayed a substantial increase in selectivity of CO_2/CH_4 from a range of 22 to 40 at 250°C. While annealing at 350°C increased the selectivity nearly 4 times than the reference pristine Matrimid® films (selectivity of CO_2/CH_4 = 20) (Kertik *et al.*, 2017). However, annealing at shorter applied treatment times at 350°C yielded lower selectivities (Kertik *et al.*, 2017) and MMMs treated at low temperatures range of 100-160°C did not exhibit well enhanced selectivity (Kertik *et al.*, 2017).

The thermally treated MMMs embedded with 20 wt. % loading of ZIF-8 at temperature range of 100-160°C exhibited permeabilities of 20 Barrer that were more than twice the permeability (8 Barrer) of reference Matrimid® film. The higher ZIF-8 loading in the range of 30 to 40 wt. % ended up with achievement of permeability up to 57 Barrer. An increase in CO_2 permeabilities was attributed to the defects created at the interface of continuous phase and ZIF-8 nanoparticles in addition to the residual DMF entrapped within ZIF-8. The continuous phase in this study underwent densification after cross-linking which subsequently decreased the permeability of CH_4 while the CO_2 permeability was affected to a much lesser extent and thus resulted in general improvement in CO_2/CH_4 selectivity (Kertik *et al*., 2017). The building blocks of non-crystalline ZIF-8 filler acted as virtual source for rich abundance of imidazolate linkers and unsaturated Zn^{2+} ions which could further promote the robust quadrupolar interactions with CO_2 (Hu *et al*., 2013).

Another report describes (Castro-Muñoz *et al*., 2019) use of 30 wt. % ZIF-8 particles as fillers for fabrication of Matrimid MMM which exhibited improved CO_2 permeability (33.3 Barrer) and selectivity (15.4). Similarly, the molecular sieving characteristic of MOF-76(Y) also improved the CO_2/CH_4 and CO_2/N_2 selectivity of the Matrimid ®5218 MMMs (Bano *et al*., 2019). LaBTB/6FDA-DAM based MMMs are also reported to be potential candidate for selective CO_2 capture even under water/moisture and these have surpassed the 2008 Robeson's upper bound (Hua *et al*., 2018).

1.3 Polysulfone (PSf)

Polysulfone (PSf) is a characteristically high-strength, transparent tough and rigid thermoplastic polymer with good thermal and chemical stability over temperatures ranging broadly from -100°C to above 160°C. The exceptionally high mechanical strength and superb oxidative resistance render it a favored material to be used as a membrane substrate. It is extensively used in fabricating membranes for applications in ultra-filtration systems for water (Kaeselev *et al*., 2001; Kilduff *et al*., 2000) and the gas separations Liu *et al*. (2004) such as heterogeneous MMMs based on PSf which were prepared with copper terephthalate (CuTPA) particles.

PSf embedded with amine-impregnated zeolite particles were observed to be more selective towards CO_2 over methane as compared with pristine PSf module (Castruita-de León *et al*., 2020). Similarly, three different kinds of CuTPA particles each with varying pore size distribution, pore volume and surface areas were used as inorganic dispersed phase. CuTPA particles having high porosity increased the permeability values of the heterogeneous membranes to He, N_2, O_2 and CO_2. Comparatively, a decrease in permeability was recorded for the two other variants of CuTPA particles possessing characteristically lower porosity. The annealing of the resulting MMMs embedded with greatly porous CuTPA particlesat a temperature of 200°C resulted in CO_2 permeability that was 3.3-times greater than the reference PSF film. The MMMs annealed at 150°C also exhibited 1.65-times higher permeability for CO_2 than reference PSF film. The substantial improvement in membrane permeability was related to the removal of residual solvent from pores of CuTPA particles after annealing (Kubica *et al*., 2016).

Ordered mesoporous silica (OMSs) particularly MCM-41 (Kim and Marand, 2008) and the other commercially employed MCM-48 (Kim *et al*., 2006b) are known to effect positively towards the permeability of unfilled PSF membranes while sustaining the selectivity at the same time. This suggests enhanced interactions with the continuous polymer phase which positively affects the sieving effect derived from the mesoporosity (2-3 nm) present in them. The small quantities of such ordered mesoporous silica spheres (MSS) or exfoliated layered microporous titanosilicate such as UZAR-S1 (produced from JDF-L1, a layered material) are reported to be used as inorganic fillers into PSf Udel® P-3500 matrix (Zornoza *et al*., 2011). The embedding of MSS in quantities as low as 8 wt. % to fabricate the MSS–PSf MMMs resulted in specifically pronounced increase in selectivities of H_2/CH_2 (79.2) and CO_2/N_2 (36.0) gas mixtures and permeability values as well for H_2 (26.5 Barrer) and CO_2 (12.6 Barrer). UZAR-S1-PSf membrane loaded with 4 wt. % of filler executed H_2 permeability of 11.5 Barrer and H_2/CH_2 gas pair selectivity value to be 69.2. The mesoporous phase favored H_2 diffusivity instead of CH_2, while the increased permeability was credited to the disruption of polymer chain packing which led to an increment in polymer-free volume (Zornoza *et al*., 2011).

Reid *et al*. (2001) recorded positive impact of large pore sized MCM-41 when used as an additive for PSf

(Reid *et al.*, 2001) on the permeability value of CO_2 while selectivity stayed unchanged. Kim and Marand (2008) described that 40 wt. % nanosized (80 nm) MCM-41 loading into the PSf caused 300% increase in permeability of CO_2 Kim and Marand (2008). However, the functionalized silica particles slightly improved the CO_2/CH_4 selectivity (Sakamoto *et al.*, 2007). Also, the increased void formation upon 8 wt. % loading of mesoporous silica resulted in a decreased selectivity of the PSf based MMMs (Zornoza *et al.*, 2009).

The silanol groups on the exterior surface of 3D MCM-48 offer good interactions with PSf matrix which in turn increased the permeability without compromising the selectivity (Kim *et al.*, 2006b).

Mesoporous silica particles extracted from rice husk ash were functionalized with 4-aminophenazone (4-AMP) so as to improve the CO_2-philic characteristics of the resulting PSf based MMMs. The filler particles were well adhered and nicely dispersed into the continuous phase. The presence of large mesopores in the filler caused relatively quicker diffusion of the penetrant gas that was accountable for the high gas permeabilities of all MMMs compared to pristine PSf membrane. The presence of functionalized silica at a highest 40% loading in the MMMs caused them to exhibit considerably higher ideal selectivities for CO_2/CH_4 (32.79) and CO_2/N_2 (33.31) pairs than the un-functionalized silica based MMMs and pristine PSF membranes.

Change in temperature caused a direct effect on the free volume which in turn affected the flexibility of the polymer chains and that caused faster diffusion of molecules and so higher chain mobility of the polymer matrix and hence permeability of CO_2 was pronouncedly increased. The same factors were responsible for the decreased selectivity of the CO_2 through the MMM of the same composition. The use of such extremely ordered structures possessing small but straight pore channels provide improvement in gas permeation properties thus warranting the silica extracted from the rice husk to be a promising additive for commercial gas separation processes under variable temperature conditions (Waheed *et al.*, 2016).

The performance of acrylate derivatization on PSf (PSfAc) to obtain a series of MMMs fabricated by using amine functionalized mesoporous MCM-41(NH_2-MCM-41) resulted in a good contact between the aminated silica and PSfAc matrix (Khan *et al.*, 2013b). The covalent linkages were formed between functionalized silica and PSf, that enhanced the permeability of PSfAc-NH_2-MCM-41 series of MMMs slightly due to three factors i.e., rigidification of polymer chains at the interface, (Zhang *et al.*, 2008), reduced pore size offered by surface functionalized fillers and elimination of the immensely permeable unselective voids. So the improved gas performance for the (selectivity of CO_2/N_2 (32.97) and CO_2/CH_4 (31.48) gas, and CO_2 permeability (9.13) Barrer) was observed (Khan *et al.*, 2013b).

ZIFs possess tunable pore structure with well famed thermal and chemical stabilities (Phan *et al.*, 2010). The 0.5 wt. % loading of ZIF-8 in PSf matrix caused 1.37 fold increase in CO_2 permeation and 1.19 fold increase in selectivity due to creation of increase free volume within polymer chains. However, a dramatice decrease in selectivity was observed upon increasing the filler loading upto 10 wt. % due to non-selective channeles formed within PSf layers (Nordin *et al.*, 2015)

The presence of a number of active sites in ZIF-108 makes it able to accommodate substitutions offered from other metals. The doping of ZIF-108/PSF MMMs using Cobalt as secondary metal executed almost a 7-fold enhancement in CO_2 permeability over ZIF-108/PSf and a 17-fold higher permeability of the same than the pure PSf membrane. The doped metal in fact enlarged the pore size in ZIF-108 framework which in turn increased the filler compatibility with the continuous phase so as to achieve superior separation factors and improved permeability of CO_2 (Ban *et al.*, 2014).

The combined use of ZIF-8 and MIL-101(Cr) in 1:1 ratio for fabrication of MMMs consisting of Polysulfone harvested 500% increase in CO_2 permeability in the resulting MIL-101(Cr)/ZIF-8@ PSF MMMs over the pure PSf due to the synergistic effects of membrane with combined fillers with the same CO_2/CH_2 selectivity. The ZIF-8/PSf executed about 300% increase and the MIL-101(Cr)/PSf based MMMs exhibited 260% increment in CO_2 permeability than that of the control (Jeazet *et al.*, 2016).

Similarly, dispersion of hybrid GO/ZIF-302 into the PSf matrix caused improved CO2 permeability and a 2-fold increase in CO2/N2 selectivity as a result of better interaction of the hybrid filler with the polymer matrix (Sarfraz and Ba-Shammakh, 2016a, b).

Similarly, incorporation of MIL-101 (Al) caused 60% increase in gas permeability in the PSf based MMMs with selectivity remained unchanged (Rodens *et al.*, 2014).

Ishaq *et al* developed high performance MMMs comprising of nano bars of Bio-MOF-1 and PSf matrix. The resulting MMMs obtained after 30 wt. % loading with Bio-MOF-1 showed 168% increase in CO_2 permeability (16.57 Barrer) and 58% increase in ideal selectivity of (42.6 and 45.6 for CO_2/CH_4 and CO_2/N_2) as compared to the unfilled reference membranes. The Bio-MOF-1 created additional channels upon loading into the PSf matrix thus the concomitant increase in free volume of membrane facilitated the diffusion of gas molecules via the MMMs which in turn positively influenced the permeability.

The existence of pyrimidine and adeninate amino Lewis basic sites decorate the pores and thus offer reasonably contracted pore dimensions in the Bio-MOF-1 so as to greatly increase the adsorption of the CO_2 gas molecules with increased selectivity (Ishaq *et al.*, 2019)

Similarly, NH_2-MIL-125 (Ti)/ PSf MMMs also show better gas permeability and selectivity as compared to pristine membranes (Anjum *et al.*, 2016).

The appropriately textured nanosized UiO-66-GO hybrids in size range 30– 100 nm were embedded into the PSF to obtain MMMs with varying quantities of 0 and 32 wt. %. A good hybrid filler-polymer interaction, the barrier effect offered from the GO and the micro porous nature of the MOF were found responsible to affect the separation phenomena in different MMMs. An increase in temperature from 30 to 90°C positively influenced the permeability of all test gases with a simultaneous decline in the corresponding selectivity of H_2/CH_4 and CO_2/CH_4 mixtures (Castarlenas *et al.*, 2017).

The highly stable sulfonated UiO-66 MOFs employing the zirconium metal were grafted by using silane coupling agent namely mercaptopropyl trimethoxysilane. They were then used to fabricate the PSf based MMMs along with the non functionalized UiO-66. The modified sulfonated UiO-66 functionalized with silane, adhered properly with the continuous phase. Thus there was a higher affinity of the same filler towards the CO_2 gas molecules upon increasing concentration of the sulfonic group which in turn improved the selectivity and CO_2 permeability for pure and mixed gases. The resulting PSf based MMMs employing functionalized sulfonated UiO-66 exhibited high separation performance that were very close to the Robeson upper bound when compared with several other MMMs of such kind. Thus the functionalized MOFs are assumed as efficient materials for gas separation purposes (Tahir *et al.*, 2019).

1.4 Miscellaneous polymer based MMMs

A number of other polymers are also tested for fabrication of MMMs by embedding of various kinds of fillers into them. The examples include Sulfonated poly (etheretherketone) (SPEEK) which is a polyelectrolyte and is considered to be a potential candidate for gas separation applications (Khan *et al.*, 2011). Figure 5 illustrates structure of SPEEK. The glassy SPEEK membranes involved facilitated transport as an efficient method to influence positively their CO_2 separation efficiency by reversible reaction between CO_2 molecules and facilitated transport carriers (Shen *et al.*, 2013; Zhang *et al.*, 2013).

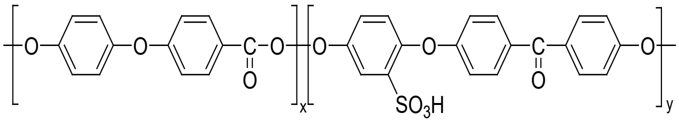

Figure 5: Chemical structure of SPEEK (Redrawn from reference; Xin *et al.*, 2014).

MIL-101 (Cr) exhibits high CO_2 adsorption capacity and stability in water and it is found to retain its morphology upon sulfonation (S-MIL-101(Cr)) or embedding within the SPEEK matrix to form MMMs. The gas performance measurements indicated that the addition of SPEEK/S-MIL-101 and SPEEK/MIL-101caused an increase in the selectivity of the resulting MMMs for CO_2/CH_4 and CO_2/N_2 systems by positively affecting the CO_2 solubility. The maximum value of ideal selectivity obtained for CO_2/CH_4 was 50 and for CO_2/N_2 system was 53, CO_2 permeability was 2064 Barrer in humidified state. The water molecules present in bound state facilitate the hydration of CO_2 resulting in its easy permeation through the membrane module with a sufficiently lower energy barrier. As a result, in humidified state, comparatively low transport resistance offered towards CO_2 as compared with N_2 and CH_4 and hence high CO_2/gas selectivity is obtained (Xin *et al.*, 2015).

Compared with the unfilled SPEEK membrane, the MMMs embedded with 40 wt. % MIL-101(Cr) and S-MIL-101 (Cr) exhibited an increase in CO_2 solubility coefficient by 39% and 61%, correspondingly. Moreover, the quadrupole moment of CO_2 and availability of extra polar interaction sites of $-SO_3H$ were found responsible for higher values of solubility selectivity of SPEEK/S-MIL-101 MMMs as compared with SPEEK/MIL-101 MMMs. Furthermore, the MMMs embedded with 40 wt. % sulfonated MIL-101 showed a corresponding increase of 74% and 38% in the CO_2/CH_4 and CO_2/N_2 selectivities in contrast with the MMMs embedded with same loading of unmodified MIL-101 (Xin *et al.*, 2015).

The MMMs of SPEEK/S-MIL-101 series executed increased CO_2 permeability in comparison with the MMMs doped with the non-sulfonated MOFs as a result of reduced chain rigidification and increased size of ionic nano-channel of the SPEEK/S-MIL-101 MMMs, the increased total water and the higher solubility of CO_2 (Xin *et al.*, 2015).The mixed gas CO_2 permeability and CO_2/CH_4 as well as CO_2/N_2 system's selectivity were observed to be slightly lower as compared with the results of pure gas tests for both dry and humidified membranes. The primary reason for improved results in case of mixed gas systems may be the competitive sorption effect (Raymond *et al.*, 1993) as the CO_2 pressure did not reached up to the plasticization pressure (Xin *et al.*, 2015) during gas separation experiments.

The CO_2 permeability was observed to be increased with the temperature while the opposite was found true for the selectivities of CO_2/CH_4 and CO_2/N_2 systems. MMMs embedded with sulfonated MOFs exhibited fairly good gas separation efficiency surpassing the Robeson's upper bound reported in 2008 in their humidified state. Conclusively, the use of exceedingly permeable MOFs and tuning their functional groups effectively improved their contact and affinity with the continuous phase thereby making it possible to execute improved gas separation performance of the pristine polymer (Xin *et al.*, 2015).

Fluorinated and sulfonated Polyether ether ketones are prospective candidates for membrane based separation of CO_2. This property is the result of their effective chain packing and reduced formation of charge transfer complexes that renders an increased free volume and permeability (Calle *et al.*, 2010; Ayala *et al.*, 2003). Incorporation of zeolite 4A into fluorinated sulfonated poly (ether ether ketone) polymer (F-SPEEK) having fixed degree of sulfonation yielded perm-selectivities closer to the Robeson's upper bound along with the execution of superior anti-plasticization properties (Tahir *et al.*, 2018).

Tahir *et al* fabricated MMMs containing F-SPEEK (prepared through 4, 4-difluorobenzophenone (m), sodium 5, 5′-carbonylbis (2-fluorobenzene-sulfonate) (n), and 4, 4¢-difluorobenzophenone (DFBP)) using zeolite 4A filler. Zeolite 4A with a distinctive pore size ca. 3.8Å that possesses a potential to perform as a molecular sieve with high mechanical, and thermal stability. The cubic-structured alumino silicates are also present here with ordered cavities and channels for the penetration of ions and molecules. The zeolite 4 A possess unit cell with high negative charge due to presence of AIO_4^{5-} and SiO_4^{4-} which is guilty of cationic propagation and thus eventually causes a better adsorption. The higher selectivity was obtained for CO_2/CH_4 and CO_2/N_2 systems, as a result of synergistic behavior of F-SPEEK/zeolite 4A. The facilitation ratio of all of the three gases increased with the filler loading. Consequently, each gas experienced an increase in permeability through the membrane. The separation performance results of these membranes were found closer to the Robeson upper bound in contrast with other such MMMs (Tahir *et al.*, 2018).

Another example of polymer used for formation of MMMs is Chitosan (CS), poly (β (1→4) 2 amino 2 deoxy D glucopyranose). is an abundantly available, cheaper in cost and linear polysaccharide that is obtained by deacetylation of chitin. It is usually acquired from certain renewable natural sources, *i.e.* the shell of crustaceans so it is biodegradable, biocompatible and non-toxic as well as hydrophilic in nature. Casado-Coterillo *et al.* (2015) combined a small quantity of non-toxic and highly absorbing ionic liquid *viz* (emim)(Ac) (IL) with the CS and embedded them with HKUST-1 and ZIF-8 particles of nanometer size so as to prepare MMMs. The molecular sieving ability of ZIF-8 particles was found to be due to the presence of cavities that were11.6 Å in diameter and were connected through small apertures of 3.4 Å. Presence of IL and ZIF-8 improved the thermal stability in addition to the ability of retaining a water content of about 20 wt. %, featuring the successful development of high temperature water resistant membranes for CO_2 separation. The MMMs with 10 wt. % ZIF-8 and 5 wt. % HKUST-1/IL-CS membranes were observed to show correspondingly best CO_2 permeability and CO_2/N_2 selectivity performance recorded as high as 5413 ± 191 and 11.5, and 4754 ± 1388 Barrer and 19.3, respectively. This was attributed to a better adhesion and smaller particle size of ZIF-8 than HKUST-1 nanoparticles with respect to the IL-CS continuous phase, as inferred by Hansen solubility parameters and Maxwell-based models that were modified to account for pore blockage, rigidification, and crystallinity of the CS matrix, with exactly precise predictions (Casado-Coterillo *et al*., 2015).

PBI is another polymer that is extensively used for formation of MMMs. Hafnium based UiO- 66-type MOF formulated as UiO-66(Hf)-$(OH)_2$ possess distinct nanoparticle size and exhibited good compatibility with (PBI) in the resulting MMMs (Hu *et al*., 2016a). When compared with UiO-66(Zr), the UiO- 66(Hf)-$(OH)_2$ showed a smaller BET surface (922 m^2 g^{-1}) area and reduced pore sizes at 4 Å, most probably due to the introduction of heavier Hf cations and relatively bulkier linkers (Hu *et al*., 2016b). But the unexpected, high gravimetric uptake of CO_2 (4.06 mmol g^{-1}) and volumetric uptake of CO_2 (167 v/v at 1 bar and 298 K) exhibited by this MOF was among the highest of all the water-stable pristine MOFs, without chemical decorations (e.g., amine grafting). The embedding of 10 wt. % of these MOF particles into the PBI matrix has resulted into the outstanding gas permeability and selectivity values which has put this membrane above the 2008 Robeson upper bound (Hu *et al*., 2016b).

It was found that elevated pressure and reduced temperature promoted the gas separation efficiency of the PDMS MMMs embedded with microporous adsorptive carbon nanoparticles as the penetrant gas molecules can follow the capillary condensation through the micropores within the filler particles that were embedded in these MMMs (Heidari *et al*., 2019). Similarly, HKUST-1@PDMs (Zulhairun, *et al*., 2015) and ZIF-8@PDMS (Fang *et al*., 2015) acted as increasingly good adsorptive filler into the PDMS matrix for improved CO_2 and higher hydrocarbons respectively.

Similarly, PIM fabricated with unfunctionalized and nano MIL-101 (ca. 50 nm) strongly shifted the permeability towards higher values for all gas pairs, specifically for CO_2 i.e. up to 35,600 Barrer, highest among the PIM-1 based MMMs while selectivity remained almost same (Khdhayyer *et al*., 2019).

Similarly, nanosized ZIF-8 crystals with varying particle sizes exhibit different capacities of gas permeability and selectivity upon embedding into the PES matrix. A ternary component of ZIF-8/PES/pNA which consisted of 10 wt. % of ZIF-8 particles exhibited CO_2/CH_4 selectivity 52.6 at 35°C (Ayas *et al*., 2018).

Embedding of different MOFs into the poly (vinylidene fluoride) (PVDF) phase such as CuBTC @ PVDF, CuBDC @ PVDF, MIL-53 (Al) @ PVDF and NH_2-MIL-53(Al) @ PVDF MMMs has witnessed improvement in the gas separation performance. This improvement is explained to the chain rigidification induced due to the Cu BDC (Feijani *et al*., 2015). Further, more than 100% increase in gas selectivity for the He/CH_4, He/N_2 and CO_2/CH_4 systems was observed for the PVDF MMMs that were fabricated with CuBDC in along with GO nanosheets. These MMMs exhibited homogeneous dispersal of fillers, nice polymer/filler interactions and filler morphologies (Feijani *et al*., 2018).

Poly (ether block amide) commercially available with the brand name of PEBAX is one of the outstanding polymers employed for separation of gases particularly CO_2. Its structure constitutes polyamide (PA) part possessing extraordinarily increased hardness and exceptional mechanical resistance as shown in Figure 6. On the other hand, the flexible PE segment contributes towards permeability (Tocci *et al*., 2008; Reijerkerk *et al*., 2010) particularly for the polar gas species like CO_2 due to the interactions of ether group of the flexible segment with the CO_2 molecules (Lin and Freeman, 2005). So, relatively improved diffusion and adsorption is obtained for this molecule in comparison with the non-polar gases. Many different

MOFs e.g. ZIF-7 (Sutrisna *et al.*, 2018), Cu-MOF (Kim *et al.*, 2016b), MIL-53 (Meshkat *et al.*, 2018), UiO-66 (Sutrisna *et al.*, 2018), 7.5wt. % MOF- 801@ PEBA (Sun *et al.*, 2019) as well as FeBTC/PEBAX (Dorosti and Alizadehdakhel, 2018) and many other inorganic fillers such as Attapulgite (Xiang *et al.*, 2016), Carbon nanotubes (Zhao *et al.*, 2017), Graphene oxide (Zhao *et al.*, 2015), silica (Ariazadeh *et al.*, 2020) and Zeolite 4A (Murali *et al.*, 2014) were previously reported to fabricate MMMs using PEBA.

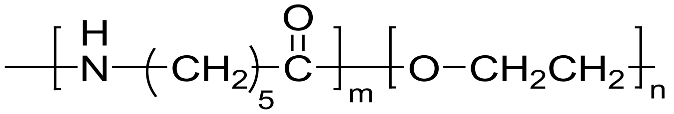

Figure 6: Chemical structure of (a) Pebaxs MH 1657 (Redrawn from reference; Wu *et al.*, 2014).

Polyurethane (PUR) is a block copolymer including a soft but rubbery segment (SS) which is able to impart increasingly good permeability properties along with a hard but glassy part (HS) (Figure 7) meant to introduce suitable mechanical properties. A decent combination of both these segments results in robust mechanical structure that may seldom compromise over the amount of permeability concerning the resulting PUR membranes (Hepburn, 2012; Isfahani *et al.*, 2016a).

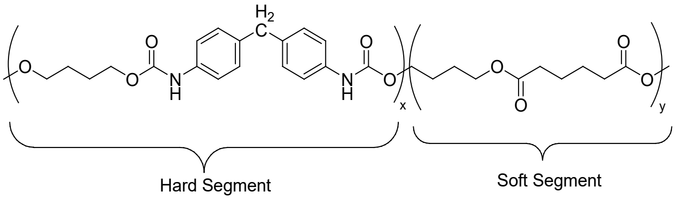

Figure 7: Chemical structure of polyurethane (Redrawn from reference; Isfahani *et al.*, 2016b).

ZSM-5, silica nanoparticle, and ZIF-8 sufficiently interact with these segments to bring a change in the balance of hydrogen bonding between the both segments (Amedi *et al.*, 2016). The cross-linking property of Silica particles resulted in decreased free space within polymer. Consequently, increased selectivity of carbon dioxide to methane was observed from 15.9 to 23.4 (Amedi *et al.*, 2016).

The low cost PU/ZIF-8 MMMs exhibited a proper permeability of 74.6 barrer. The increasing amount of zeolite particles inside the PUR membrane could lead to compliance of two different behaviors. Firstly, the 5% improvement in performance of MMM was observed by addition of ZSM-5 particles so as to cause some void space around the particle that increased the sorption selectivity. But the mobility selectivity remained constant as the pore size of these particle was (5 Å) but larger than the kinetic diameter of the both gases. But on overall selectivity was increased.

The second behavior was related to the increase in amount of particles from 5% to 20% with a consequence of increase in permeability of carbon dioxide at its compromised selectivity due to CO_2 plasticity which brought an ease in the mobility of continuous phase of PUR that increased empty spaces between the PU chains. Thus creation of voids pores and the particle aggregation positively affected permeability of the large CH_4 molecules. The permeability of CO_2 molecules on the other hand was decreased as a result of decreasing molar fraction of CO_2, existence of methane in the pure feed and the course of permeation and dissolution phenomena are followed by existence of competition between the species (Amedi *et al.*, 2016).

Similarly, Gholami *et al.* (2017) reported that ZIF-8/PU MMMs showed increased thermal stability, improved tensile strength and strain at break (Gholami *et al.*, 2017). CO_2 and CH_4 transport was positively affected upon incorporation of ZIF-8 as additive into the PU matrix which resulted in significant improvement in separation performances of all of the tested membranes in their work. (Gholami *et al.*, 2017).

Likewise, Ismail *et al.* (2011) also incorporated 0.5-3 wt. % loadings of the un-functionalized MWCNTs into the polyethersulfone matrix. Their results revealed that attainment of highest gas selectivity (α) ($\alpha_{CO2=CH4}$ = 250:13; $\alpha_{O2=N2}$ = 10:65) was possible with the use of 0.5 wt. % loading of MWCNTs. The gas selectivity showed a decline upon addition of 3 wt. % of the MWCNTs as a result of formation of interfacial voids and the higher loading of MWCNTs content made them more prominent.

In view of considerations laid in the literature review section, the present study was formulated to prepare the MOF based MMMs as the polymer and explore their CO_2 separation potential for CO_2/CH_4 pair.

Conclusions and Recommendations

Cellulose acetate, polyimide and polysulfone were discussed here as chief polymer matrices for the MMMs with a brief discussion on some other polymer matrices. A number of different fillers have been used in order to improve the separation properties of the resulting MMMs, and to find one that could surpass the Robeson's upper bound and to remove or decrease the shortcomings of the pure polymers or inorganic membranes, cost effectiveness and to make the resulting MMMs as viable commercial candidate in the field of MMMs based separation. After going through the practical applicability of various fillers, it was found that although other fillers like silica or titania nanoparticles, activated charcoal, silane based modified fillers, and amino functionalization of various fillers result in the improvement in the efficiency of resulting MMMs after their embedding in different polymer matrices, the MOFs have their own chemistry with the different polymer matrices. They are also proved to be affective filler towards various polymer matrices due to their porosity, sieving effect and thereby offering the facilitated transport through the MMMs. The brittleness, cracks and voids in the resulting MMMs were found to be compromised and so, improved permeability and selectivity could be obtained by careful selection of MOF-polymer pair. Nicer distribution and compatibility with the polymer and plasticization resistance shown by different resulting MMMs tested argue upon their usefulness in the field of separation. Surface functionalization and use of some other filler as co-filler can further improve the separation efficiency. In view of considerations laid in the literature review section, a study can be formulated including preparation of the MOF based MMMs as the polymer and their CO_2 separation potential for CO_2/CH_4 pair can be explored. There are ample possible polymer-MOF pairs available in the literature which can be tested experimentally to fully explore their potential in this field. In this context our research group has studied MMMs comprising of Matrimid® 5218 incorporating $Tb(BTC)(H_2O).(DMF)_{1.1}$ MOF with three different percentages for selective separation of CO_2/CH_4 (Tariq *et al*., 2020). Such studies can lead to the selection of most suitable MOF for the commercial applicability of the selected MMMs embedded with optimum loadings of the most appropriate MOF.

Novelty Statement

This review article highlights the gas separation performance applications of mixed matrix membrane technology and their industrial applicability.

Author's Contribution

Misbah Sultan and Tariq Mahmud presented the idea regarding content of the article, Asma R. Tariq collected data and wrote the article and Saadia R. Tariq performed proof reading and language correction of the article.

Conflict of Interest

The authors have declared no conflict of interest.

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