Separation performance study of metal organic framework (MOF) based mixed matrix membrane for CO_2 and CH_4

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Dedication

Dedicated to my Family, beloved Teachers and Friends

Acknowledgments

All praises for Almighty Allah, the most Merciful and Beneficent, for providing me with the ability and strength to complete this study project. May Allah's peace and blessings be upon our Prophet Muhammad (PBUH), his Family, and all his Companions.

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Hassan Raza Khan

Abstract

The CO_2 capture is important not only in fuel upgrading but also for controlling global warming issues. The fossil fuels are major source of energy, which are the main contributors of greenhouse gas emission. So it is necessary to separate these gases. For controlling CO_2 emission, membrane technology has great potential because of its low energy consumption and maximum efficiency. Therefore, the work is designed to separate CO_2 from CH_4 with the help of membrane. In this study, a novel bimetallic NiO/CuO MOF based mixed matrix membranes (MMMs) were fabricated from polysulfone (PSf) and polyethylene glycol (PEG), and investigated for gas separation application. Polysulsone (PSf) was used as main polymer matrix, while polyethylene glycol (PEG) and NiO/CuO MOF were used as plasticizer and filler respectively. The four different composition of filler (NiO/CuO MOF) i.e. 0.05%, 0.1%, 0.15%, 0.2% and 2% of additive (PEG) was incorporated with polysulfone (PSf) to evaluate the results. All prepared membranes were characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) techniques. The obtained results revealed defects free membranes. The structure confirmed that MOF particles were uniformly embedded, which is the confirmation of good affinity of filler (NiO/CuO MOF) as well as additive/plasticizer (PEG) with polysulfone matrix. Furthermore, mechanical testing implied that by adding NiO/CuO MOF in Polysulfone, brittleness appeared and strength decreased from 2.84 MPa to 2.26 MPa. However, the strength increased to 4.11 MPa by adding PEG as plasticizer. The permeation was also performed to investigate the performance of pure PSf, PSf/MOF, PSf/PEG and PSf/PEG/MOF membranes. By adding 0.2% NiO/CuO Pyrazize and BDC MOF with 2% PEG, the CO_2 permeability increased from 6.82 Barrer (for pure PSf membrane) to 17.13 Barrer (for PSf/PEG with NiO/CuO MOF based membrane). Moreover, the best CO_2/CH_4 selectivity achieved was 20.70 for the same membrane at the pressure of 5 bar. The separation performance study was investigated in the pressure range of 2 to 5 bar, at room temperature. The study revealed a great potential of MMMs for CO_2 gas separation application.

Keywords

Mixed Matrix Membrane (MMM); Metal Organic Framework (MOF); Gas permeability; Gas separation; Membrane technology.

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Abbreviations

PSf	Polysulfone
PEG	Polyethylene Glycol
MOF	Metal Organic Framework
MMMs	Mixed Matrix Membranes
FT	Facilitated Transport
FTMs	Facilitated Transport Membranes
FSC	Fixed Site Carrer
CNTs	Carbon Nano Tubes
CMSs	Carbon Molecular Sieves
SBU	Secondary Building Unit
PI	Polyimide
PVAc	Polyvinyl Acetate
NiO	Nickel Oxide
CuO	Copper Oxide
FTIR	Fourier Transformed Infrared Spectroscopy
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
UTM	Universal Tensile Machine
BDC	Benzene Dicarboxylic Acid
CO_2	Carbon Dioxide
CH_4	Methane
CA	Cellulose Acetate
PU	Polyurethane
PPO	Polyphenylene Oxide
IUPAC	International Union of Pure and Applied Chemistry
γ-CD	Gamma-Cyclodextrin
ZIF-8	Zeolitic imidazole frame work
HKUST-1	Hong Kong university of science and technology-1

G-OH	Graphene Hydroxyl
TWh	Terawatt Hour
MIL-53	Material Institute Lavoisier
PES	Polyethersulfone

Chapter 1

Introduction

Background, Scope and Motivation

Global warming that results in the enormous emissions of greenhouse gases particularly CO_2, has become a social issue. It has been observed during last few decades the CO_2 concentration is keep on increasing in atmosphere and has reached up to its highest value of 413 ppm [1, 2]. This high value of CO_2 not only causes drastic climate changes but also critically affects the health of living beings. The energy demand is being fulfilled by burning of fossil fuels since the 18th century to run industry, power generation or for automobiles. British Petroleum published a report titled "Statistical Review of World Energy" in 2019 reporting the global production stats of oil, natural gas and coal for 2018. It shows the crude oil was highest consumed (4474.3 million tons) fossil fuel for energy generation followed by coal (3916.8 million tons oil equivalent) and then natural gas (3867.9 billion cubic meters) [3]. The excess use of fossil fuels not only depleting, but also the major source of CO_2 emission. Therefore, it is necessary that we must shift towards renewable, sustainable and green energy sources. One of the major sources of renewable energy is hydroelectricity, which was implemented on large scales since 1920s throughout the world [4]. However, alone hydroelectricity is not sufficient to replace fossil fuel consumption. The other sources of renewable energies are solar panels, geothermal energy, wind energy, wave and tidal energy and energy produced from biofuels. Biofuels are the most potential source of renewable energy and its contribution in renewable energy generation reached as high as 2480.8 TWh [3].

One of the most important renewable energy sources is biogas, which is produced by the anaerobic digestion of biofuel. Typically raw biogas consists of (30-45) % CO_2 and (50-65) % bio-methane CH_4 [4], where natural gas contains up to 9 percent of CO_2 and 80 percent of CH_4 [5]. The presence of high amount of CO_2 reduces its calorific value. Therefore, in order to use this raw gas as an efficient fuel it must be upgraded by removing CO_2. But this gas pair is difficult to separate due to identical size and physical properties (i.e. density, viscosity and solubility) of both gas molecules. Membrane technology has been widely used for CO2 separation in comparison to traditional chemical absorption, cryogenic separation, electrochemical separation, and pressure swing adsorption approaches. This is owing to its low energy usage, convenience of use, and minimal environmental impact. Membrane is a promising technology that can replace other conventional gas separation methods and it can easily be retrofitted in the existing gas plants [6-9]. Inorganic membranes, facilitated-transport membranes (FTMs), polymeric membranes, and mixed-matrix membranes (MMMs) are the four types of membranes used in gas separation applications [10].

Polymeric membranes are widely used for gas separation on a commercial scale due to their easy processing and low operating costs. However, there is a trade-off between these membranes' permeability and selectivity [11]. Therefore, rather than using pure polymeric membrane, Zimmerman introduced a new hybrid type membrane known as the mixed matrix membrane (MMM) [12], has gained large attention. In MMMs, additive has been incorporated in polymeric matrix that promotes the CO_2 transport through membranes. Therefore, CO_2 separation in MMMs also follows fixed site carrier (FSC) or facilitated transport (FT) mechanism. This helps to achieve optimized permeance and selectivity for gas separation applications [13, 14].

Number of organic and inorganic fillers has been reported in literature, such as carbon nano tubes (CNTs) [15], zeolites [16-18], carbon molecular sieves (CMSs) [19, 20], modified clays [21], graphene [22], fullerenes [23], inorganic oxides [24] and metal organic frameworks (MOF) [25, 26]. However, metal–organic frameworks (MOFs) are promising candidate to synthesize mixed matrix membranes (MMMs) for gas separation application. MOFs have high surface area, porosity, thermal stability, ordered, crystalline structure, controllable pore sizes and adjustable surface functionality. They are mainly composed of secondary building unit (SBU) with organic linkers, which work as a spacer and can be changed/ functionalized to control pore size, also enhances interaction with respective gases. According to the literature, MOF-based polymeric membranes increase gas permeability along with selectivity of gases [27-29]. The high surface area and porosity help to increase gas permeation by solution diffusion mechanism. However, the ability to functionalize the MOFs is beneficial towards increase in selectivity. The addition of MOFs to polymeric membranes can improve their mechanical and thermal stability. Therefore, it is highly required to synthesize specified MOFs for CO_2 capture application.

In addition, polymer selection for mixed matrix membrane (MMM) synthesis plays a significant role in the application of gas separation prior to filler dispersion. In literature, a wide range of polymer materials has been reported including polyimide (PI), cellulose acetate (CA), polysulfone (PSf), polycarbonates, phenolic resins, polyaramide, polyvinyl acetate (PVAc) [13], etc. Polysulfone (PSf), an amorphous glassy polymer, is one of the most extensively used polymers in gas separation application, having rigid, high strength structure and offers better gas transport when compared to rubbery polymers [30]. The incorporation of various fillers in PSf-based MMMs has been the subject of extensive investigation.

In early age of MMMs, different fillers, i.e. mesoporous molecular sieve (MCM 41) [31], $Cu_3(BTC)_2$ [32], zeolite (SAPO-44) [33], (MIL-101(Cr) and ZIF-8 [34], were used to evaluate their effects with PSf polumer matrix.. However, blends of PSf/PES (Polysulfone/Polyethersulfone) [35] and PSf/PEG (polysulfone/polyethylene-glycol) polymers with graphene hydroxyl nanoparticles (G-OH) [36], has also been studied to improve separation performance.

In this study a new type of MOF is being used, which was not been reported in gas separation application. However, it is bi-organic ligand (Pyrazine and BDC) incorporated with metal oxides (NiO and CuO) [37]. The Pyrazine and BDC (benzene dicarboxylic acid) behaved as strong organic linkers and they provided more adsorption surface area for the gases. The good thing about these organic linkers was that they had more affinity for CO_2 gas as compared to CH_4. As a result of the presence of these organic linkers, CO2 adsorption increased considerably in the polymer matrix. Moreover, the sorption coefficient was increased due to metal oxides (NiO and CuO). Hence, by applying more pressure on feed side, diffusion occurred due to the less pressure on exit side of membrane and CO_2 permeated through MMM. Therefore, significant increase in CO_2 permeability and selectivity was achieved by using NiO/CuO MOF as filler with polysulfone and polyethylene glycol. The key factors improving the MOF, polymer materials for the high CO_2 capture and selectivity uses for biogas upgrading to produce bio-methane. Also reduces the fossil-fuel CO_2 emission as well as the separation of CO_2 from natural gas will be addressed during this research work.

1.1. Membrane technology for gas separation

Membranes technology has been adopted of great importance for many applications, which include Water & Waste Water Treatment, Medical & Pharmaceutical, Food & Beverage, Industry Processing and Gas Separation applications [7, 38-41]. One of the fastest growing applications of membrane technology is gas separation [40, 42]. Membranes are barriers that selectively allow passage for one component to pass through from a gaseous mixture while retaining others. That is why these are called selective permeable membranes. While, the gas separation mechanism based on mainly two factors, pressure gradient and chemical potential, which act as driving force [43]. The general illustration of gas separation through membrane, showed in the following Figure 1.1.

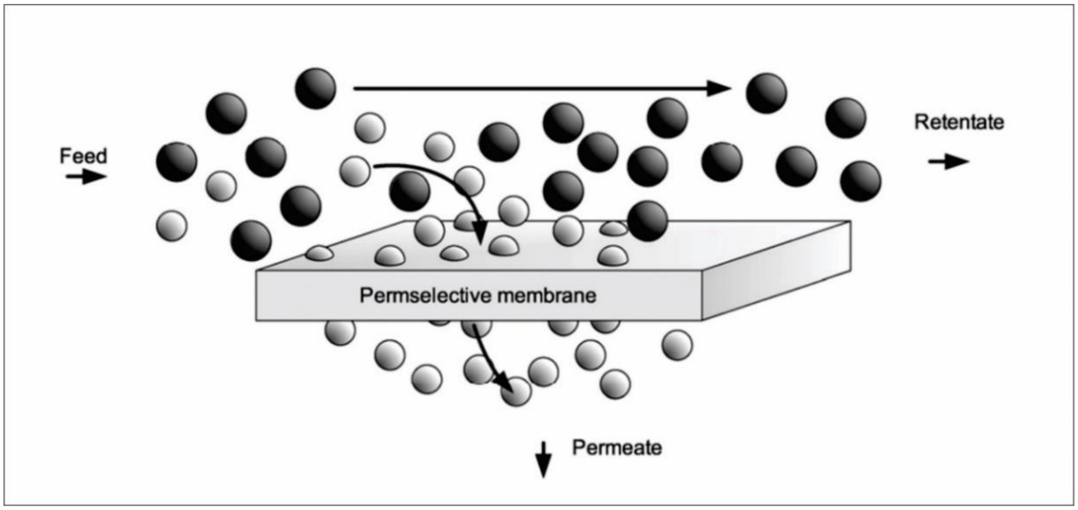

Figure 1.1. Schematic diagram of membrane separation [43]

In this research work, our focus is on the gas separation using membrane technology. This technique not only gained substantial consideration from the industries but also have a lot of potential in research point of view. The reason behind all this is its low cost and environment friendly nature. In Benny D. Freeman’s point of view, the membranes would contribute a lot towards environmental safety and low cost in purification of hydrogen and methane [44]. The major gas separation processes with the help of membrane technology are:

- H_2 removal from CH_4
- Air separation (separation of oxygen and nitrogen from air
- CO_2 Separation from flue gases
- CO_2 removal from natural and biogas sources for CH_4 upgrading

Separation performance of any membrane tells about the efficiency of that membrane to separate out gas mixture. Therefore, for the successful operation of gas separation, membranes must be more efficient in mechanical strength, thermally stable and chemically compatible. Furthermore, they must show better separation performance. The thermal and mechanical stability are important. They will directly affect performance of membrane. Similarly, chemical stability directly related to the nature of material that is being used during membrane synthesis. Therefore, it is good to use that material which will be able to cope up with hard industrial conditions [42]. The two most significant aspects of membrane performance are permeability and selectivity. These factors define membrane capability to separate out one gas from other. In other words, it tells that how much one component of gas mixture permeates preferentially as compared the other. Some other factors are the membrane morphology along with the design of system. These all factors in turn tell about the overall characteristic and performance of membrane.

However, membrane is a proven beneficial technology over other processes due to energy efficient, low cost and reliability. Since, no hazardous chemicals are required for the fabrication of membranes, therefore, membrane falls in the category of green technology. As reported in the literature, membrane technology has proven to be useful for low gas volumes and biogas with high CO_2 contents. In biogas, CO_2 composition may be 50% of total gas by volume depending upon the source of biogas generation. Membrane technology is therefore highly recommended in these contexts. Membrane is a promising candidate that can replace traditional chemical absorption, cryogenic separation, electrochemical separation and pressure swing adsorption techniques for gas separation and it can easily be retrofitted in the existing plants [7].

Polymer selection is one of the significant steps in membrane synthesis. Membrane performance highly depends on its material. The components of gas mixtures that are going to be separated along with process conditions are kept in mind during the selection of membrane material. This helps to get more separation efficiency, because these types of membranes permit one component of gas mixture as compared to other with better selectivity. Various materials are used for the fabrication of membranes e.g. polymers, ceramics, metals and glass [45-47]. Gas separation membranes are mainly classified as organic (polymeric) and inorganic membrane on the basis of material used [48].

1.1.1. Inorganic membranes

Inorganic membranes play a significant role in many applications, particularly in gas separation applications, due to their better stability in thermal, chemical and mechanical conditions. For a long period of time, inorganic carbon membranes have been center of attention for the researchers because of its outstanding permeability and selectivity. A lot of research has gone into improving membrane material along with membrane manufacturing process. The past work, successfully improved overall membrane performance, not only at normal but at elevated conditions as well [49]. As compared to organic or polymeric membranes which are applicable at low temperature application, the inorganic membranes are best candidate for elevated temperatures. These membranes are classified into three basic categories: Zeolites, palladium and sol-gel based micro porous membranes. These are synthesized from silica, zeolite and carbon based molecular sieve due to their substantial chemical and thermal resistivity. However, these membranes are facing challenges of high fabrication cost, difficulty in reproducibility, less membrane area to module volume ratio, high brittleness and reduced permeability values even after increased selectivity i.e. metal oxides at less than 400°C. Moreover, at high permeability, these membranes show very less selectivity. Due to these drawbacks, it is not convenient to use these membranes on commercial scale [50].

1.1.2. Polymeric membranes

Polymeric membranes have gained a lot of attention due to their low cost, ease of fabrication and optimum permeability and selectivity. Generally, polymers depicted increased selectivity and less through-put while relating to porous material because of less availability of free volume. Polymers can better transfer one chemical species over another in a mixture of gases. The penetration of gases through porous and dense gas separation membranes is governed by the Knudsen diffusion and solution diffusion models, respectively. In polymeric membranes increased permeability leads to decrease in selectivity and vice versa [51]. Robeson, also set an upper bound limits for permeability/selectivity in a graph by plotting values of permeability obtained of small gaseous molecule mainly CO_2, N_2, CH_4 and O_2 permeates through polymeric membranes fabricated by different polymers [52]. For gas separation, dense or non-porous polymeric membranes are commonly used. Gases are separated on the basis of their respective diffusion and solubility coefficient within polymer. Therefore, permeability is equal to the product of a gas's solubility "S" in a membrane multiplied by the gas's diffusivity "D" in a polymer. So permeation through non-porous polymeric membrane is through “solution-diffusion model” [53, 54]. Glassy polymers show more acceptability for fabrication of dense polymeric membranes to that of rubbery polymers, because former provide high selectivity and low permeability for gas mixtures such as CO_2/CH_4, O_2/N_2 and H_2/CH_4.

For the production of dense gas separation membranes, a wide range of polymers have been investigated, but only a few have gained acceptance on industrial scale. In rubbery polymers polydimethyl siloxane and in glassy polymers cellulose acetate (CA), polyurethane (PU), polyimides (PIs), polysulfone (PSf) and polyphenylene oxide (PPO) are most common. Selection of polymer for gas separation membrane should provide optimum selectivity and high permeability for particular component in a mixture of gases [55].

Initially, pristine polymers were used for the fabrication of membrane on lab scale and with successive triumphs on lab scale led to the fabrication of membrane modules of the same polymers on commercial scale. Cellulose acetate was the most common polymer employed for commercial purpose, in industrial plant in 1980 [56]. In addition hollow fiber module made from cellulose acetate were installed in Kelly-Snyder oil field for updating gas processing facility in 2006 [57]. These modules were made form pristine polymer and for further increase in permeability and selectivity some more modifications are necessary in gas separation membranes.

Later on, as research progressed, it was seen that polymeric materials are limited in their separation performance for gases, as far as current membrane technology is concerned. As a result, improved gas separation performance necessitated the use of novel materials. As a result, polymer blend membranes were proposed as a way to improve gas separation performance. The biggest advantage of blend membranes is that they combine the favorable properties of two different polymers into one membrane. For example, one tough polymer can be combined with a highly permeable one, to give the benefit of high permeability as well as mechanical toughness. A blend can also be the combination of highly porous polymer with a highly selective polymer. Polymers blend can be either miscible, if dissolve in common solvent and immiscible if solution system is required for their solubility. Miscible polymer blend have uniform composition, appear in single phase and shows single value of melting temperature and glass transition temperature [58, 59]. In immiscible polymer blend membrane polymers were dissolved in two different solvents and make solvent system for better performance. In immiscible polymeric blend the properties will depend on the phase distribution as well as the composition, and the different phases will act as separate pure polymers. Therefore, the polymer blends can be used when we need to combine the advantages of two different polymers. Of these two types of blends, immiscible polymer blends have the advantage of giving us better control of membrane morphology. This means that we can change the composition of the blend to see what effect it has on the morphology of the final membrane [59-61].

The current polymeric membrane materials are incapable of coping with the commercial scale requirement for separation of chemical species. If increase in permeability is achieved, then sudden decline in selectivity is observed and vice versa. An entirely new class of membrane materials were introduced by incorporating inorganic particle into polymers as filler particles, to make polymer/inorganic particle hybrid called mixed matrix membrane [50]. Inorganic particle has peculiar characteristics: specific pore size, pore size of precise shape and geometry, tunable pore diameter and very close distribution of pore size. These inorganic particles act as molecular sieve to enhance diffusivity and selectivity, therefore polymer/inorganic particle hybrid gives better separation performance surpassing pure polymer and polymer blend membranes. Most common inorganic particle used are carbon nano-tubes CNTs, Zeolites and metal organic frame work MOFs [19, 62]. Therefore, currently research has been shifted from zeolite to other inorganic or organic particle such as grapheme base material, carbon nano-tubes and metal organic frame work.

In one particular research work, mixed matrix membranes were fabricated by using zeolites 4A into polymeric matrix including Matrimid and polyvinyl acetate for O_2/N_2 separation. Pore size range of zeolite 4A (3.8-4.0A) and reported selectivity for O_2/N_2 separation of 37 was reported and permeability of O_2 just 0.8 Barrers. With this permeability and selectivity, zeolite/polymer hybrid membrane gained significant attention but not considered for commercial purpose. This is because of very low interfacial compatibility, which results in the development of non-selective interfacial defect and low mechanical strength. On contrary, if concentration of zeolite is increased, then dispersion in polymer is non-uniform [63-65].

Therefore, currently research has been shifted from zeolite to other inorganic or organic particle such as grapheme base material, carbon nano-tubes and metal organic frame work.

1.2. Metal organic frame works

Metal organic frame work, MOF, is two or three dimensional compounds having cavities in it. According to International Union of Pure and Applied Chemistry (IUPAC), a metal organic frame work, abbreviated to MOF is a coordination network with organic ligands that contain potential voids. Coordination networks refer to a coordination compound ranging through repeating coordination entities in two or three dimensions. Another name for MOF is porous coordination polymer, which is defined by IUPAC as, a coordination compound containing repeating coordination entities in one, two or three dimensions [66].

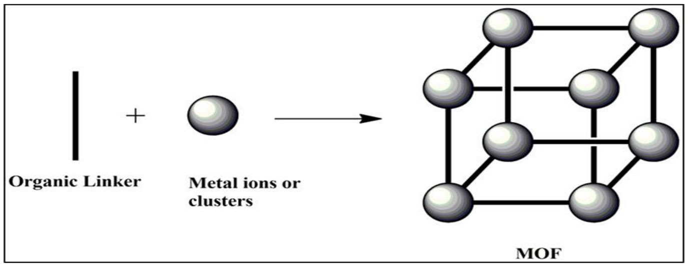

Figure 1.2. Structural representation of metallic organic frameworks [67]

1.2.1. History of MOF

The history of MOF traced back to 1700 when a pigment called Prussian blue was synthesized. Its XRD analysis represented the three-dimensional network of Fe (II) and Fe (III) ions connected to CN-1 forming a cubic network structure. This highly organized and symmetrical cubic topology encouraged chemists to synthesize more such compound with similar structure.

In 1990, a chemist named Robson anticipated the formation of a large compound composed of tetrahedral or octahedral metal nodes coordinated with linear shape organic ligand lead to the formation of material with the following characteristics:

- Compound having highly crystalline, potential cavities; possess chemical, thermal and mechanical stability with low mass to volume ratio.
- The presence of cavities within molecule capable of stores, permeate and separate guest molecules.
- These frameworks were capable of post-modification in its organic part i.e. chemical up gradation of ligand by replacing or incorporation by different nucleophile or electrophile.
- In heterogeneous catalytic application, these compounds possessed catalytically active sites for specific reaction to take place.
- Cooperative catalytic activity possesses between different catalytic sites.

In the field of metal organic frameworks, enough research has been done so far. The most of the assumptions that were in theory in the 1990s are now transformed into real time applications.

MOF is the term used as distinguished class of compound first introduced by Yaghi in 1995, but two compounds Cu2(4,4'-bipy)3(NO3)2 and Co(btc)(pyridine) synthesized at that time did not fit properly in the MOF category. The first coordination compound which gained the status of MOF was synthesized in 1999 by Yaghi and Williams were: MOF-5 and HKUST-1 [68-72].

1.2.2. Characteristics of MOF

MOFs can be synthesized with revolutionary high porosity and internal surface area equal to 10000 m^2/g, and capable of tunable pore structure. In addition, they are chemically and mechanically stable towards acidic gases. Comparing MOF with zeolites, organic ligands in MOF have tunable pore structure, permitting superior interaction with polymers, thus diminishing nonselective deficiencies in MOF-polymer interface. Hence, new methodologies being adopted to form MOF-polymer mixed matrix membrane that have better gas permeability and selectivity [73]. So far, a number of MOF have been developed and explored for their diverse applications for instance molecular recognition [74, 75], separation properties [76, 77], gas storage [78] and delivery of required component of drug in pharmaceuticals industry [79]. Following are the most commonly used MOF in different applications owing to their peculiar characteristics and also used as filler in fabrication of MOF-polymer membranes i.e. ZIF-8, HKUST-1, MIL-53, MOF-74 and Gamma-CD-MOF.

ZIF-8 acronym for Zeolitic imidazolate frame work. ZIFs are synthesized by linking zinc or cobalt tetrahedrally coordinated to imidazolate linker. Because of similarity in bond angle and topology with zeolites, they are called Zeolitic. ZIF-8 is most abundantly used among subclass of ZIFs in gas separation membranes, because of its crystallographic characteristics having pore aperture of 3.4A and cages of 11.6A. The pore aperture of 3.4A act as molecular sieve for separation of gas from a mixture and allow them to permit through it especially that have kinematic diameter greater than 3.4A i.e. C_3H_8, C_3H_6 to diffuse from ZIF-8 pore aperture. For the separation of C_3H_6/C_3H_8 ZIF-8 incorporated into 6FDA-DAM polyimide and fabricate mixed matrix membrane. The particle size of ZIF-8 is around 600 nm in diameter and it disperse homogenously in polymer matrix and being hydrophobic in nature it requires hydrophobic polymer for its dispersion and 6FDA-bases polyimide are of hydrophobic in nature and it resulted in permeability of 57 Barrer in case of C_3H_6 and selectivity of C_3H_6/C_3H_8 31. 260% improved in permeability and 150% improved in selectivity of ZIF-8/6FDA-DAM with respect to pure 6FDA-DAM [80-83].

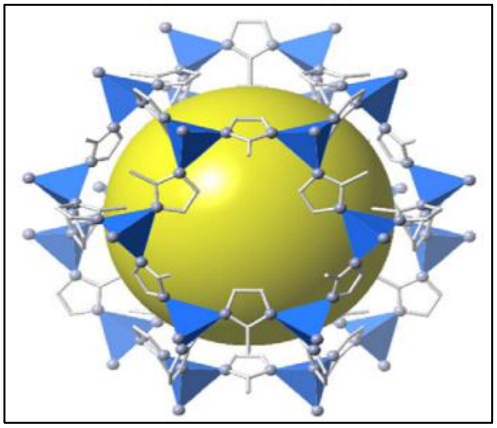

Figure 1.3. Structural representation of Zeolite imidazole framework-8 (ZIF-8) [84]

HKUST-1 stands for Hong Kong University of Science & Technology, HKUST-1, Chemically, this is synthesized by linking Cu2+ coordinated with benzene-1,3,5-tricarboxylate (btc) ligands. It is a cubic structure MOF with twisted boracite topology, with a 9A (Angstrom) main pore channel diameter and 5A diameter tetrahedral pockets, which enclose the main pore channel. It has significant thermal stability up to 300 ^oC in nitrogen environment. Moreover, its metal sites are open or coordinative unsaturated and rapidly exposed by temporary linked solvent or water molecule due to solvent exchange or some thermal procedure. Coincidently, these coordinatively unsaturated metal sites have an additional capability for gas sorption and act as Lewis acid in comparison to their coordinated saturated equivalent. HKUST-1 having particle size ~ 10μm was used as filler in Matrimid and Matrimid/polysulfone blend to make asymmetric mixed matrix membranes by Basu, for carbon dioxide separation. Because of large particle size of HKUST-1, it had been difficult to fabricate defect free membrane. Furthermore, the polymer and HKUST-1 defects resulted in insufficient gas separation. With another polymer, HKUST-1/6FDA-Durene MMMs and also the incorporation of ionic liquid result in considerably better permeation and perm selectivity values of CO_2/N_2 of 1100 Barrers and selectivity of 27, and in case of CO_2/CH_4 separation selectivity of 29, as compared to pristine 6FDA-Durene membrane [69, 85-89]. The schematic representation of this MOF is in following figure.

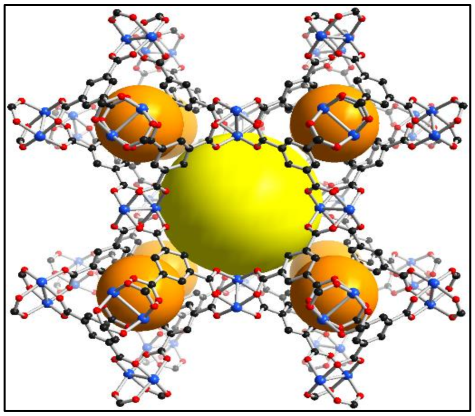

Figure 1.4. Structural representation of HKUST-1 MOF [90]

MOF-74 generally mentioned as M_2(dobdc), and it's comprises of magnesium Mg, iron Fe, nickel Ni, copper Cu and zinc Zn as metal cation coordinated with 2, 5-dioxide-1, 4-benzenedicarboxylate (dobdc) ligand having 12A wide hexagonal channels [91, 92]. Having maximum unsaturated coordinative active metal sites act as Lewis acid and dramatically intensified gas adsorption [93]. MOF-74 extensively used in fabrication of MMM for CO_2 removal by integrating in polyimide base polymers. Very distinct features observed of MOF-74 in MMM as it enhanced plasticization resistance and selectivity for mixed-gas separation. MOF-74 with nickel as metal cation Ni_2(dobdc) have large number of unsaturated active metal sites which help in increase in glass transition temperature in Ni_2(dobdc)/6FDA-DAM MMM for C_2H_4/C_2H_6 separation up to Tg = 397C while Tg = 393C in case of pure 6FDA-DAM [94].

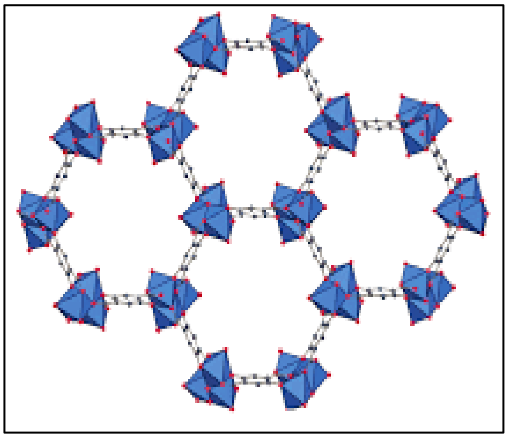

Figure 1.5. Structural representation of MOF-74 [91]

MIL-53 stands for Material Institute Lavoisier MOF fabricated by linking Aluminum, chromium, iron and scandium with terephthalic acid i.e. 1, 4-benzenedicarboxylate ligand [95-97]. It has three dimensional structure and pore size up to 8.5A. It has unique property of being elastic and have capability to contract or expand its pore size during the adsorption and desorption of certain gases i.e. CO_2. MIL-53 is fabricated by Cr3+

metal ion with terephthalic acid have pore aperture of 29 & 34A have chemical, thermal and humid environment stability. A CO_2 selective mixed matrix membrane (MMM) was developed by integrating ZIF-8 filler in 6FDA-DAM for CO_2/CH_4 separation. The membrane had a selectivity of 28 and a permeability of 660 Barrer [98-100].

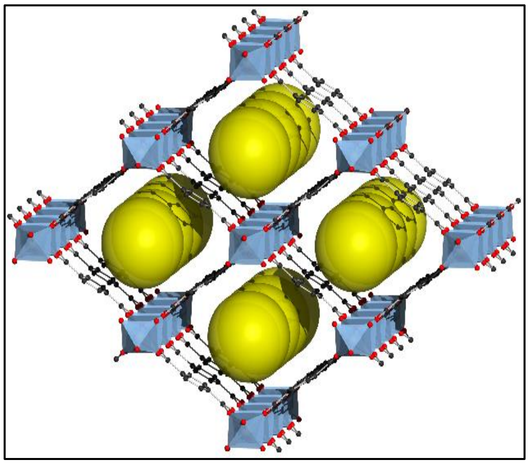

Figure 1.6. Structural representation of MIL-53 [99]

In recent times, an environment friendly and renewable MOF has been reported, this MOF also called green MOF as it is prepared from natural raw material, i.e. starch. Basic raw materials for this MOF are γ-cyclodextrin (γ-CD) and alkali metals salts mainly potassium hydroxide (KOH) and this MOF is called "Gamma-CD-MOF". The method involved for the preparation of this MOF is "vapor diffusion method" [101, 102]. This gamma-CD-MOF has a porous framework having body-centered cubic structure, with an aperture of 7.8 A and cavity size of 17 A. In this MOF, potassium cation coordinatively bonded with –OCCO- unit present in D-glucopyranosyl ligand of gamma-cyclodextrin unit [103]. Gamma-CD-MOF has the ability to use for particular gas storage and adsorption from mixture of gases.

This can be attributed to the s ideal cavity size of 1.7nm and presence of three hydroxyl groups on each glycosidic ring and total of 24 hydroxyl group in single crystal of gamma-CD-MOF. Major application of gamma-CD-MOF are separation of halo aromatic compound, separation of saturated, unsaturated and chiral aromatic as well as alicyclic compounds, separation of benzene and toluene and also removal of CO_2 from natural gas also subject of extensive research on lab scale and efforts are being made to implement at industrial level [104].

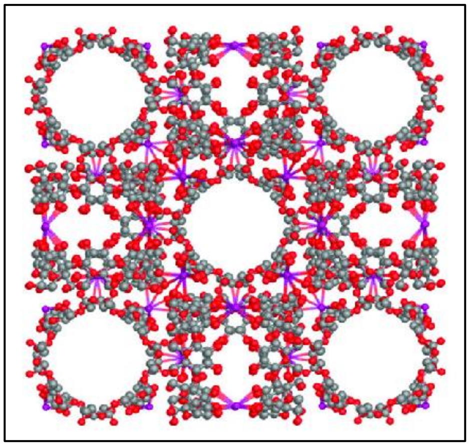

Figure 1.7. Structural representation of Gamma Cyclodextrin (γ-CD) MOF [105]

1.3. Selection of polymer

Membrane efficiency is affected by the material used in its fabrication. The combination of these material helps in gas separation application. Therefore, the better affinity of membrane materials with each other as well as with specific gas from mixture will result in better separation. MOF loses its crystallinity and flexibility, if employed in powder form for gas adsorption. So its efficacy can be retained by integrating into polymeric matrix and fabricating MOF-polymer MMM.

For fabrication of polymer/MOF MMM, two polymers were selected in this work, i.e. polysulfone and polyethylene glycol. The selected polymers were incorporated by NiO/CuO pyrazine and BDC MOF. After fabrication, synthesized membranes undergo permeation testing for single gas and mix gas of CO_2 and CH_4.

1.3.1. Polysulfone

Polysulfone is one of the best polymer for the gas separation application because MOF shows good adhesion with this polymer by synthesizing more defects free MMMs [106]. In this work, PSf is selected as the basic polymer in mixed matrix membrane. PSf is a thermoplastic with high performance. The high performance is depicted in form of toughness, chemical and thermal stability over wide pressure range [107]. The repeating unit of PSf is shown in Figure 1.8.

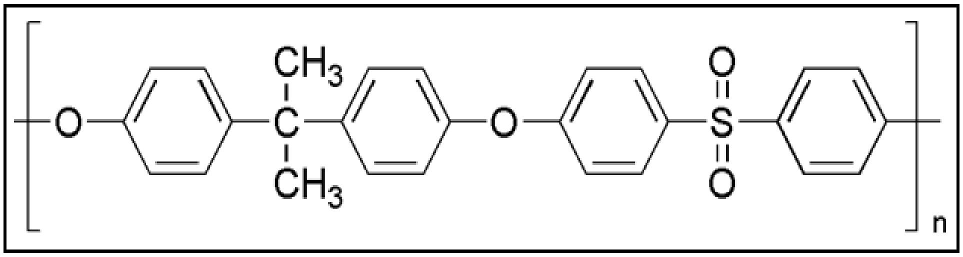

Figure 1.8. Polysulfone repeating unit [107]

PSf can perform over a temperature range of -100 – 200 °C. PSf is an amorphous polymer with excellent mechanical and thermal properties. The added advantages of PSf are as follows:

1. Presence of aromatic rings render PSf resistant to gamma radiations.
2. PSF is transparent and has high thermal, hydrolytic and oxidative stability.
3. It has the ability to be extruded, molded and thermoformed into different desired shapes based on requirements.

4. PSf have high flame retardancy properties [108]

PSf can be easily molded into membranes with pore size of at least 40ηm. Gas separation, hemodialysis, and water purification are some of the applications for these membranes.

1.3.2. Polyethylene glycol

Polyethylene glycol has numerous advantage based on its structure and properties. It is one of the best plasticizer in membranes, which increases flexibility of polymeric membrane. The added advantage of PEG is its contribution in enhancement of permeability in gas separation application. The repeating unit of PEG is shown in Figure 1.9.

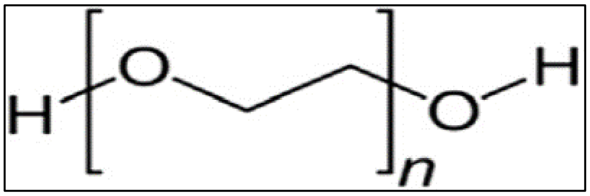

Figure 1.9. Polyethylene glycol repeating unit [109]

PEG is available in a variety of molecular weights for diverse uses that can have minor influence on its features, most notably its form and physical appearance. PEG is defined by a number of qualities, including non-toxicity, inertness, odorlessness, colorlessness, and non-volatility.

Polyethylene glycol is extremely soluble in water as well as organic solvents like chloroform, carbon tetrachloride and benzene for the application of gas separation [109].

1.3.3. NiO/CuO BDC and Pyrazine MOF

In this study, bimetallic Ni/Cu oxides based metal organic framework was used as filler. Although, this has not been used in gas separation application but it proposed morphology encourages to use it in the gas separation application. It was developed by incorporating NiO/CuO with two organic ligands: Benzene dicarboxylic acid (BDC) and Pyrazine with the help of hydrothermal process.

The proposed amount of pyrazine and terephthalic acid was dissolved in DMF. After that equal amount of $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ was added in solution and stirred until the solution became homogeneous. The solution was gradually heated up to 200 ^oC in Teflon-lined autoclave and bluish green product was produced after the process. The product was washed with ethanol and used as filler in our mixed matrix membrane after drying [37]. The organic linkers and metal oxides provided more permeation for CO_2 by providing more surface area for adsorption.

The interaction of MOF with polymers is explained in following Figure 1.10. The Polyethylene glycol (PEG) molecules (used as plasticizers) linked the Polysulfone (PSf) with Pyrazine-MOF that is used as filler. During the cross linking the C=O double bonds of the pyrazine- MOF are opened up and link with one of the hydroxyl group of Polyethylene glycol (PEG) molecule via hydrogen bonding and alternatively, the S=O double bonds of the Polysulfone (PSf), are also opened up and link to the other hydroxyl group of Polyethylene glycol (PEG) via dipole-dipole interactions.[110, 111] Therefore strong interactions are established between Polysulfone and the metal organic framework filler material due to their compatibility with each other in terms of functionalities.

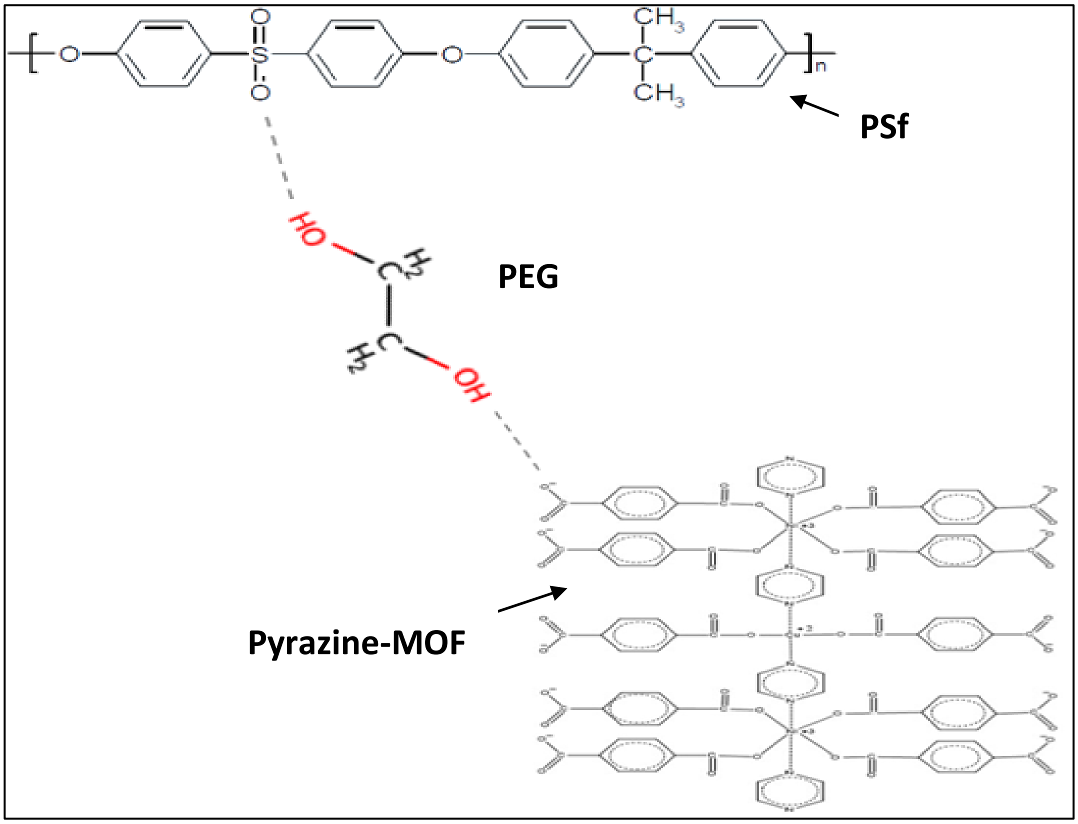

Figure 1.10. Schematic Interaction of MOF with PSf and PEG

1.4. Motivation

Metal organic frame work has been used extensively for carbon dioxide adsorption in different conditions. Their results showed that these membranes have much potential for both the above mentioned applications. Although the selected MOF (i.e. NiO/CuO BDC and Pyrazine MOF) was not used in gas separation application. However, on the basis of reported structure and morphology of this MOF, it is bi-organic ligand (Pyrazine and BDC) incorporated with metal oxides (NiO and CuO) [37]. The Pyrazine and BDC (benzene dicarboxylic acid) behaved as strong organic linkers and they provided more adsorption surface area for the gases. Therefore, it is been advised to use NiO/CuO MOF as filler and incorporated in polymeric matrix and fabricate polymer/MOF mixed matrix membrane. Furthermore, this mixed matrix membrane undergo permeation study for single gas testing of CO_2 and CH_4 along with some supporting characterization techniques. The aim of this work is to incorporate NiO/CuO MOF into polymeric matrix, fabricate mixed matrix membrane and enhanced the permeation as well as selectivity of CO_2 and CH_4. This will make it easier to separate CO_2 from the mixture of CO_2/CH_4 gases.

Keeping in view the above facts, the objectives of this work are summarized as under:

1. Optimize the weight percentage of filler concentration in pure polymeric and blend matrix.
2. Fabricate pure polysulfone, PSf/MOF, PSf/PEG and PSf/PEG/MOF mixed matrix membranes.
3. Characterization of the resulting membrane by using the following techniques;
    - ➢ Scanning electron microscopy analysis (SEM)
    - ➢ Fourier transform infrared microscopy (FTIR)
    - ➢ X-ray diffraction (XRD)
    - ➢ Mechanical testing (i.e. Strength and Strain)
4. Permeability and selectivity measure of prepared membranes for pure CO_2 and CH_4 gas.

Finally, after getting results from both polymeric mixed matrix membrane, comparison was performed with already published literature and also predict future recommendation for optimizing permeation and perm selectivity of CO_2 and CH_4.

1.5. Outline of thesis

1st Chapter details the introduction of metal organic frame works, their properties and their use in the adsorption of different gas. The integration of metal-organic frameworks

(MOFs) into various polymeric matrixes and their potential use for gas separation along with brief introduction of gas separation membranes are also covered in this chapter. Finally, NiO/CuO MOF also studied, to see their use in mixed matrix membranes and polysulfone and polyethylene glycol also studied in detail.

2nd Chapter includes examples of the research work carried out in the use of different MOFs in mixed matrix membranes for gas separation application at different pressures (i.e. very high and low pressure applications).

3rd Chapter summarizes the materials and experimental technique employed in fabrication of mixed matrix membranes. The characterization techniques used to study their various physical and chemical properties are discussed here in detail, along with permeation testing technique.

4th Chapter studies the results obtained from different characterization techniques for all the synthesized membranes, and these results are then discussed in detail to explain their significance in my work.

5th Chapter gives a concise summary of the entire work along with future recommendations.

Chapter 2

Literature Review

The increase in concentration of carbon dioxide in atmosphere will enhance the greenhouse gases that become the cause of global warming. Globally, scientists and researchers are working on other fuel resources (i.e. biogas) to fulfill energy demand. Efforts are being made all over the world to reduce CO_2 concentration in atmosphere by different procedures i.e. by carbon dioxide sequestration, carbon dioxide separation from natural gas using membrane system etc. most efficient process is through membrane separation. And membrane is being employed for its separation, among membrane system mixed matrix membrane gain significant appreciation and most widespread topics among researcher.

2.1. Metal organic frame work

Metal organic frame work has achieved tremendous acceptability in the last 15-20 years. Basic components of MOF are: metal ions and organic ligands or linker. These metal ions and organic linkers have too much diversity and that results in assembling into different morphologies and crystalline structure [112]. In addition, MOF have remarkably high porosities, tunable but uniform pore size and high absorption capacity. That’s why MOF is under extensive research in chemistry, chemical and material engineering fields [113-115]. Major areas where there is potential to use MOFs are: gas storage, separation of mixture of gases, as catalyst, sensing and proton conduction and others.

2.1.1. Recent development in membrane technology using MOF

One of the most common applications of MOF is to use for the separation of mixture of gases. The separation of mixtures requires energy intensive process for its accomplishment, which is the most vital unit process or unit operation in the chemical industry. This separation process for gas mixtures has more significance in chemical industries. The most common gas separations include: CO_2 capture (CO_2/air, CO_2/H_2), acidic gases removal from natural gas (CO_2/CH_4, N_2/CH_4, and CO_2/H_2S), O_2/N_2 separation, noble gas separation, separation of light hydrocarbons (olefin/paraffin) and so on so forth.

The literature describes, the physical and chemical aspects along with adsorption capacities of some common MOFs i.e. MOF-5 ($Zn_4O(bdc)_3$, bdc= 1,4-benzenedicarboxylate) [112, 116], (UiO-66) ($Zr_6O_4(OH)_4(bdc)_6$, bdc= 1,4-benzodicarboxylate) [117, 118], MIL-53 (Al(OH)(bdc), bdc= 1,4-benzodicarboxylate) [98], NOTT-100 (Cu_2(bptc), bptc= biphenyl tetra-carboxylate) [119], HKUST-1 ($Cu_3(btc)_2$, btc= **1**,3,5-benzene tricarboxylate), Chromium terephthalate metal–organic framework [MIL-101(Cr)] etc.

For adsorption of particular component in MOF, it should have adsorption capacity. It's divided into two basic categories i.e. gravimetric uptake and volumetric uptake. The gravimetric uptake is defined as the amount of gas adsorbed inside a unit mass of material, whereas volumetric uptake is the volume of gas adsorbed under standard conditions divided by volume of adsorbent. Mass of particular MOF required for gravimetric uptake and volume of adsorbent required comes under volumetric uptake. For the separation of one component from a mixture over the other component the MOF should be highly selective for one component than other [120].

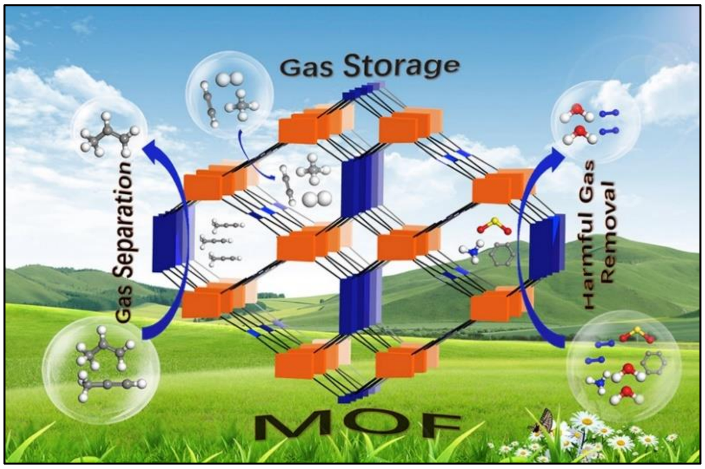

Figure 2.1. Gas separation mechanism with MOF [120]

Due to the depletion of fossil fuels, world is shifting towards green sources of energy. Metal organic frameworks (MOF) are the best candidate for application of green energy and environment by gas upgrading and removing harmful toxic gases [120]. They adsorbed these gases and separate out from the mixture. With the separation characteristics of MOFs as well as the mechanism explained above, the different MOFs with their selectivity and adsorption capacity are summarized in the table below:

Table 2.1. Adsorption capacity and selectivity of CO_2/CH_4 using MOFs

Sr. No	MOF	Surface area (m^2g^{-1})	CO_2 uptake (mmol g^{-1}) at 1.0 bar	Selectivity CO_2/CH_4	Temperature (K)	Reference
1	PEI-MIL-101-125	183	4.35	230	298	[121]
2	NENU-520	386	2.71	12.8	298	[122]
3	UTSA-16	627	2.36	29.7	298	[123]
4	MgMOF-74	1494	6.1	104	298	[123]

5	UPC-12	270	1.5	691	298	[124]
6	PEI-MIL-101-125	183	4.35	230	298	[121]

The adsorption capacities of different MOFs in high and low pressure gas separation applications are listed in following table 2.2 and Table 2.3, respectively.

Table 2.2. High pressure CO_2 adsorption capacity in MOFs

Sr. No	MOF	Surface area BET m2/g	Capacity (wt %)	Pressure (bar)	Temperature (K)	Reference
1	HKUST-1	1268	43	30	313	[125]
2	MOF-177	4490	61	48-50	297	[126]
3	MOF-200	4528	74	48-50	300	[126]
4	NU-100	6142	70	38-40	297	[127]

Table 2.3. Low pressure CO_2 adsorption capacity in MOFs

Sr. No	MOF	Surface area BET m2/g	Capacity (wt %)	Pressure (bar)	Temperature (K)	Reference
1	Co-MOF-74	956	25	1	298	[128]
2	MIL-101(Cr)	2673	4.1	1	318	[129]
3	MOF-177	-	6.7	1	299	[130]
4	Zn-MOF-74	-	20	1	295	[128]

Chapter 3

Materials and Method

3.1. Materials

Polysulfone (PSf) (Mw~35000) was purchased from Sigma-Aldrich, which was used as main polymer in membrane synthesis. Polyethylene glycol (PEG) (Mw~1000) and Chloroform (analytical reagent grade) were also purchased from Sigma-Aldrich. Pyrazine based metal organic framework (NiO/CuO MOF) was kindly supplied by catalysis research group of SCME, NUST and used as filler [37]. Pure CO_2 and CH_4 (99.99% purity) gases were purchased from Paradise Gases.

3.2. Method

The MMMs were synthesized using the solution casting process. The membrane procedure along with their compositions is discussed below.

3.2.1. Pretreatment of polysulfone

The pretreatment of polysulfone polymer was required to remove entrapped moisture as polysulfone immediately catches moisture present in air [131]. Therefore, before making solution, the required amount of polysulfone was preheated at 65 ^{0}C to remove moisture content present in it.

3.2.2. Solution preparation

Polysulfone based polymeric membrane was synthesized by the method of solution casting. Polysulfone (PSf) 6 Wt % was precisely assed in the required amount of chloroform [132]. To make solution complete homogeneous, polysulfone was well mixed in chloroform at room temperature, with the help of magnetic plate. This required one complete day to be homogeneous through stirring. The clear solution was obtained after mixing. This solution was used for the casting of pure PSf membranes. Similarly, PSf/PEG blended membrane solution (6 wt% of total polymer in solvent) was prepared using similar method, keeping composition of PEG at 2 wt.% in PSf.

For the solution preparation of MMMs with MOF loadings, different concentrations of MOF (preheated at 40 ^{o}C) were added to the solution with respect to weight percent of the polymer. MMMs with 0.05 wt%, 0.1 wt%, 0.15 wt% and 0.2 wt% loading of NiO/CuO MOF into the 6% pure PSf and 0.2 wt% loading of NiO/CuO MOF into the blend of 6% polymers were prepared. Firstly, to get uniform dispersion of NiO/CuO MOF, required amount of MOF was dispersed in half amount of chloroform and stirred at room temperature. The polymer in required amount (i.e. 6 wt% of total polymer) was introduced in remaining solvent and stirred continuously to get homogeneous solution. After this, the polymers solution was introduced to the filler suspension using a priming method to reduce particle polymer interface tension [133]. A small amount of polymers solution was added with filler solution before adding whole solution of polymers. The solution was stirred for 2 h before being sonicated for 15 min. Before adding further little quantity of total polymer solution, sonicated NiO/CuO MOF solution was again stirred for 15 min. The steps were repeated until the filler solution had received all of the polymer solution. After all of the polymer solution had been added, the final solution was stirred for another 24hrs. Following that, the MMMs were prepared in the same way as the pure polymeric membrane described before. After this all membranes are characterized before permeation testing. The membranes with their respective PSf, PEG and NiO/CuO MOF concentration along with the concentration of chloroform (solvent) are provided in Table 3.1.

Table 3.1. Membranes with their composition

Sr. No.	Membrane Type	Composition (%)			
		Polymer (6%)			*Solvent (94%)*
		PSf	PEG	MOF	Chloroform
1	PSf	100	0	0	94
2	PSf0.05MOF	99.95	0	0.05	94
3	PSf0.1MOF	99.9	0	0.1	94
4	PSf0.15MOF	99.85	0	0.15	94
5	PSf0.2MOF	99.8	0	0.2	94
6	PSf2PEG	98	2	0	94
7	PSf2PEG0.2MOF	97.8	2	0.2	94

3.2.3. Membrane casting

The resultant solution was poured into a flat-bottomed 10 cm glass petri dish. For 24 hours, the petri dish was covered with a glass lid to allow the solvent to slowly evaporate at ambient temperature (i.e. 25 ^{o}C). A thin film started appearing with evaporation of chloroform. After 24 h, remaining solvent was removed by annealing. To acquire same thickness of membranes, equal amount of solution was added to all petri dishes and conditions were kept constant for all samples. Solution preparation and membrane casting methodology is shown in Figure 3.1.

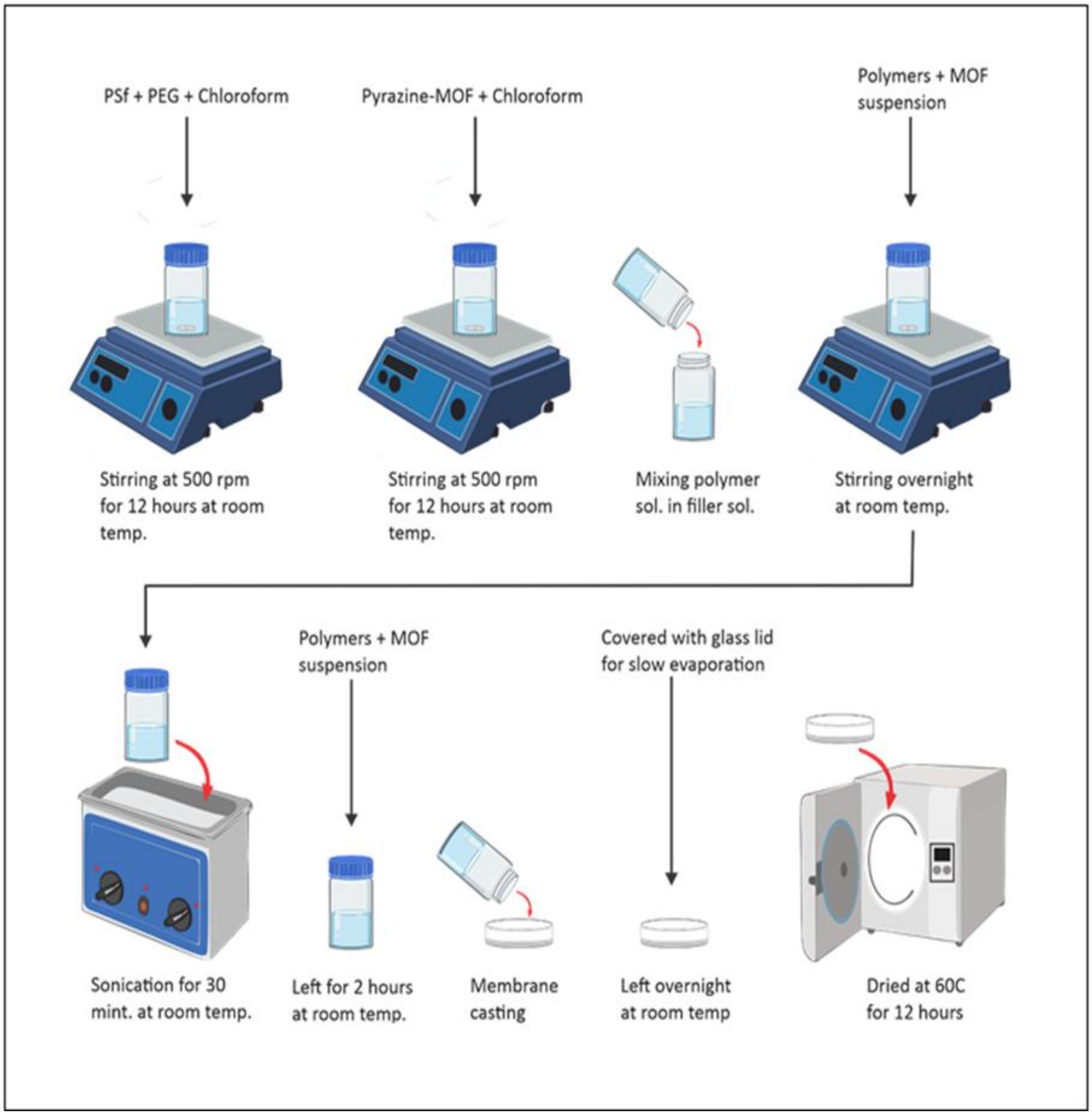

Figure 3.1. Solution preparation and membrane casting process

3.3. Testing and Characterization

3.3.1. Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared is an analytical method for identifying the presence of functional groups in organic molecules, both qualitatively and quantitatively. This technique is used for detecting the type of chemical bond in molecule and explaining precise information about molecular structure. FTIR helps in the recognition and determination of functional group present in required sample [134].

In FTIR when infrared beam incident on sample, it is absorbed by the sample. A sample contains numerous energy states level. When molecule absorbed infrared radiation from the energy source, these molecules jump to higher energy states level from ground state. And wavelength it absorbed proportional to transfer the molecule from ground state to respective energy state level. Different functional groups present in a sample and absorb infra-red of different specific wavelength. This is called fingerprint of that functional group. All the characteristic absorption peak of different functional group combine to complete the spectrum of sample and hence detail study can be done using FTIR spectrometer [135].

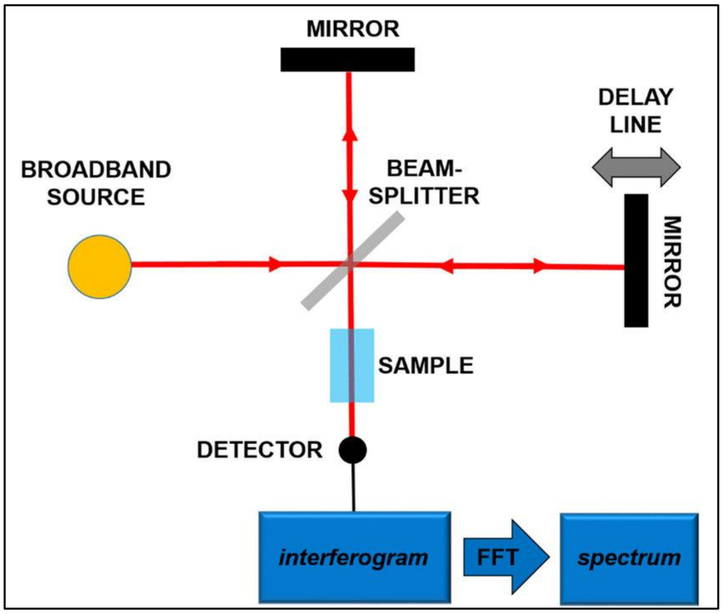

Figure 3.2. Schematic diagram of FTIR Spectroscopy [136]

The Perkin-Elmer Spectrum 100 FT-IR Spectrometer was used to perform FTIR spectroscopy with a wave number range of 4000-400 cm^{-1} and a resolution of 4 cm^{-1}. Membrane samples for FTIR spectrometry were prepared by using potassium bromide KBr to make appropriate pallets and then exposed to FTIR spectroscopy. Membrane samples were examined by simply fitting the membrane into a sample cell and exposing it to infrared radiation. The spectrum was utilized to study different functional groups in membranes. [137].

3.3.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is an analytical technique used to study the membrane surface topography and morphology. Furthermore, it is employed to study the cross-sectional structure of membrane, pores geometry and crystalline structure of membranes and other samples (i.e. MOFs etc.).

Components of SEM:

- Electron generating source
- Column where electron moves along with electromagnetic lenses
- Electron detector
- Sample chamber
- Display screen or computer

The detailed schematic diagram of SEM is shown in following figure along with incident beam.

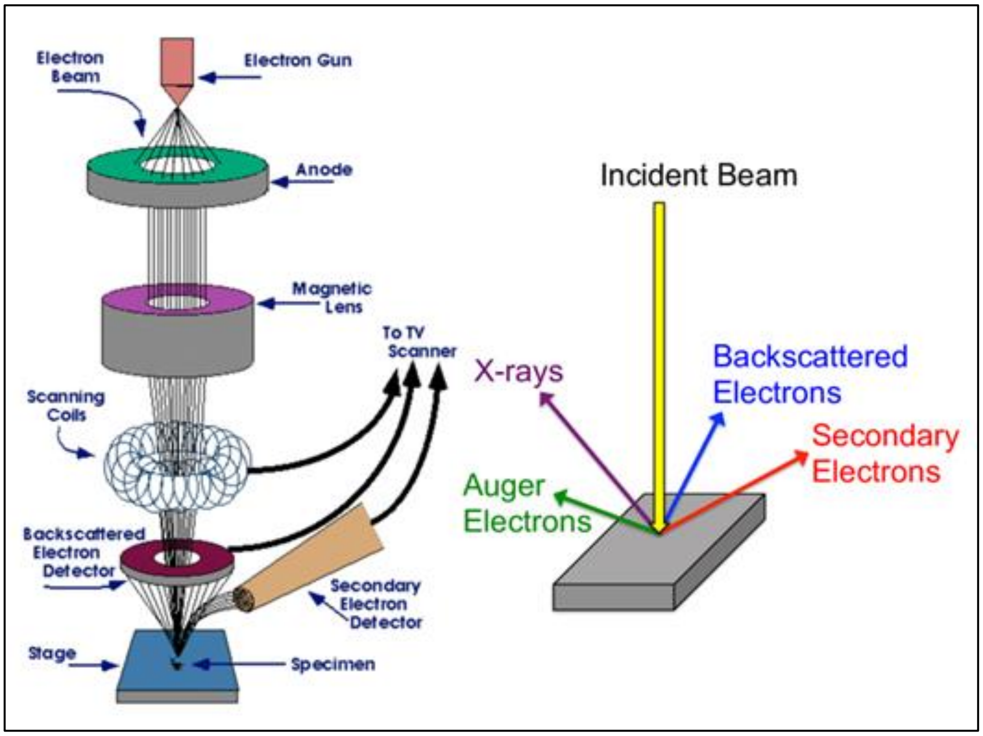

Figure 3.3. Schematic diagram of SEM along with Incident Beam [138]

When electron beam is incident on sample, it aids in studying and examining the characteristics of specific area of sample with greater accuracy and precision. Signals generated between the interaction of electron beam and sample were received by the detectors and analyzed accordingly.

SEM analysis was performed using a Hitachi S-4700 SEM, and gold sputtering was performed on the membrane with a JEOL Ltd. JFC-1500 ion sputtering machine. All membrane sample including pure polysulfone and PSf/MOF MMMs, blend of PSf/PEG and PSf/PEG/MOF MMM samples of 0.2, 0.4, 0.6, 0.8 and 1 wt. % were undergo SEM analysis with magnification of 2000x and voltage of 5Kv. Their best images of surface and cross- section were presented and studied in detail [139].

3.3.3. X-ray diffraction analysis

X-ray diffraction is an analytical technique for studying the crystallinity structure of a material that uses a dual wave/particle of x-ray. X-ray diffraction helps in find out size and shape of crystallites, phase purity, lattice parameters and crystallinity [140].

X-ray diffraction of pure polysulfone and PSf/MOF mixed matrix membrane sample and blend of PSf/PEG and PSf/PEG/MOF MMM at different compositions were done by equipment "STOE Germany". Scan angle was kept 50-600 with a step size of 0.4 degree and step time of 1 sec, respectively. Radiation adopted for performing characterization was Cu K α-1. According to Bragg's law, XRD was used to determine the d-spacing between structural layers at a certain angle, such as:

$$\mathrm{N}\lambda = 2\mathrm{d}\,\sin\theta \tag{3.1}$$

Bragg's law is used to understand the diffraction process and is generally used in crystal diffraction. The crystallite size of the crystals can be find using the Debye-Scherrer equation. Every crystalline material has a distinct X-ray pattern that serves as a fingerprint for its identification. [141].

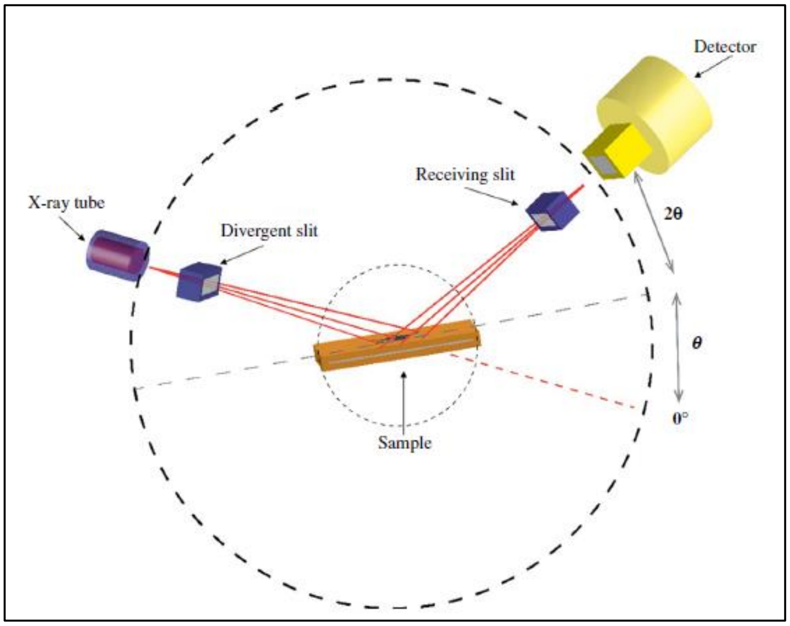

Figure 3.4. Schematic diagram of XRD [142]

3.3.4. Ultimate tensile machine

Tensile strength of a material can be defined as the maximum stress that a material can stand before its structure permanently deforms. Material are either glassy or rubbery on the basis of their mechanical strength [143]. Ultimate tensile machine is used to calculate the stress bearing strength of pure and hybrid polymeric membranes.

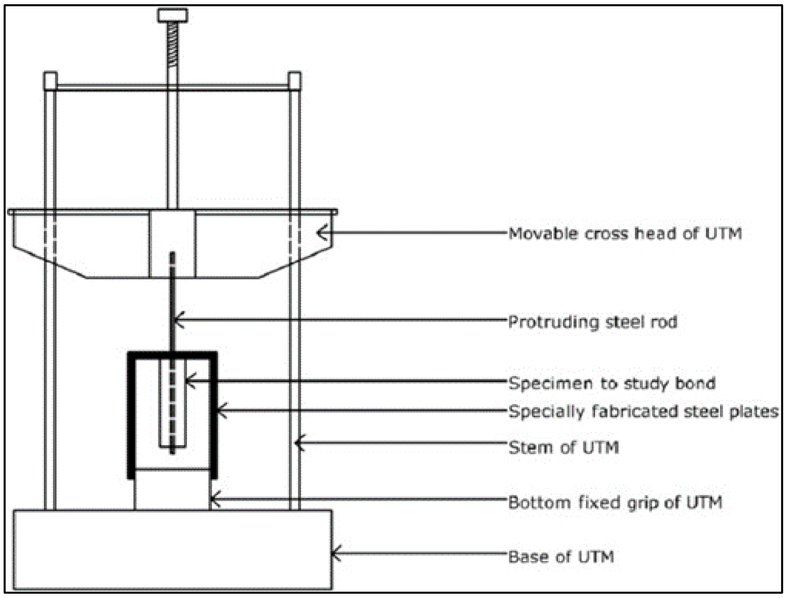

Figure 3.5. Schematic diagram of ultimate tensile machine [144]

Tensile strength of pure polysulfone and PSf/MOF based mixed matrix membrane as well as PSf/PEG blended membrane and PSf/PEG/MOF mixed matrix membrane samples were tested using “SHIMADZU ADS-X” series precision ultimate tensile tester with a full load of 20KN. Samples were tested adopting ASTM standard D882-02 and strips were made according to the dimension mention in standard (i.e. 5.0-25.4 mm wide, and at least 50 mm longer than the grip separation used during testing). Lastly detail study of sample were made after the results drawn from testing [144].

3.3.5. Permeation testing

The membrane separation performance was investigated using a permeation equipment, shown in Figure 3.6. For single gas permeation testing, a stainless steel gas permeation rig is used. The membrane is fitted into the membrane cell. Feed gas is introduced at the top of the cell while permeate is exited from the bottom of the cell. A portion of permeate gas is passed through a bubble flow meter to determine the flow rate, and the time it takes for the bubble to flow a fixed volume tells us the gas flow rate.

Pure CO_2 and CH_4 gases were fed through membranes in the pressure range of 2-5 bar to perform the test at room temperature. For each run, the pressure was maintained at the same level. While the permeate side was kept at a constant pressure of 1 atm during each run, by varying feed pressure. These gases were passed through all formulated membranes and each membrane tested repeatedly for the validation of results. The permeability was then calculated by following equation [145]:

$$P = \frac{Q \times L}{\Delta P \times A} \tag{3.2}$$

Where Q represents volumetric flowrate of permeate gas passing through effective area of membrane (cm^3/s), L refers to membrane thickness (cm), ΔP is the pressure difference between feed and permeate side (cm Hg) and A represents membrane effective area (cm^2).

While for CO_2/CH_4 selectivity (α) was calculated by the equation [145]:

$$\alpha = \frac{P_{CO_2}}{P_{CH_4}} = \frac{D_{CO_2}}{D_{CH_4}} \times \frac{S_{CO_2}}{S_{CH_4}} \tag{3.3}$$

Where P_{CO2}/P_{CH4} is the ratio of pure CO_2 & CH_4 gas permeability. The product of diffusivity selectivity and solubility selectivity is the overall permeation selectivity.

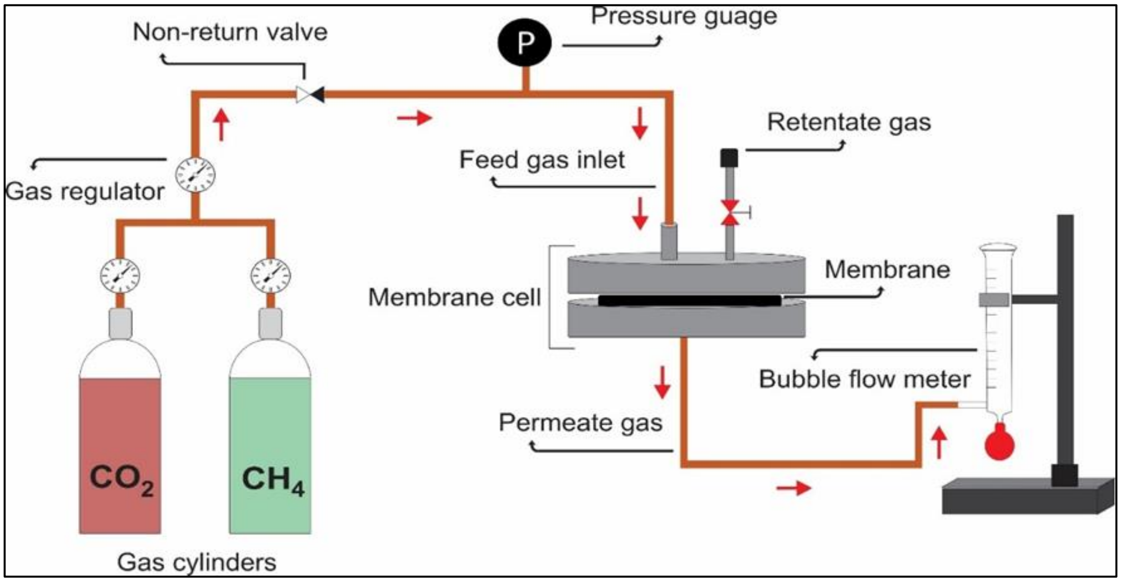

Figure 3.6. Schematic diagram of permeation rig

Chapter 4

Results and Discussion

All characterization techniques along with permeation testing are discussed here for the prepared membranes. Their results are also shown in graphical formats.

4.1. FTIR analysis:

The structural interaction of pure PSf, PSf/MOF, PSf/PEG blend and PSf/PEG/MOF based MMMs with the help of FTIR analysis is illustrated in Figure 4.1. The FTIR analysis of pure PSf membrane showed -CH_3 stretching vibration at 2955 cm^{-1} and 1388 cm^{-1}. A sharp peak at 1167 cm^{-1} assigned to Ar-SO_2-Ar (Ar for aromatic) symmetric stretching, which ascribed stretching of C-C. Moreover, spectra at 1230 cm^{-1} exhibiting Ar-O-Ar stretching, while spectra at 1289 cm^{-1} representing to symmetric stretching in the spectral vibration of S=O [146, 147]. After incorporation of NiO/CuO MOF in polysulfone matrix, a visible and strong spectral appeared in the band range at 1625-1725 cm^{-1} appeared. This was ascribed to the presence of benzene ring in Pyrazine [37]. The shifting of spectral bands from 1578 and 1501 cm^{-1} for pure PSf to 1582 and 1510 for blend of PSf/PEG matrix appeared by adding 2 wt% of PEG in PSf matrix. This slightly shift in position of band to some degree, indicating about an interaction of polysulfone and polyethylene glycol. Also the shifting of band spectra for both sulfones of symmetric and asymmetric confirmed interaction between PSf and PEG, which changed from 1148,1321 and 1289 cm^{-1} to 1153, 1326 and 1298 cm^{-1} , respectively [148, 149]. The same shift in FTIR spectra occurred, when PSf/PEG/MOF MMM was analyzed, although the bands absorption intensity was slightly higher as compared PSf/PEG membrane.

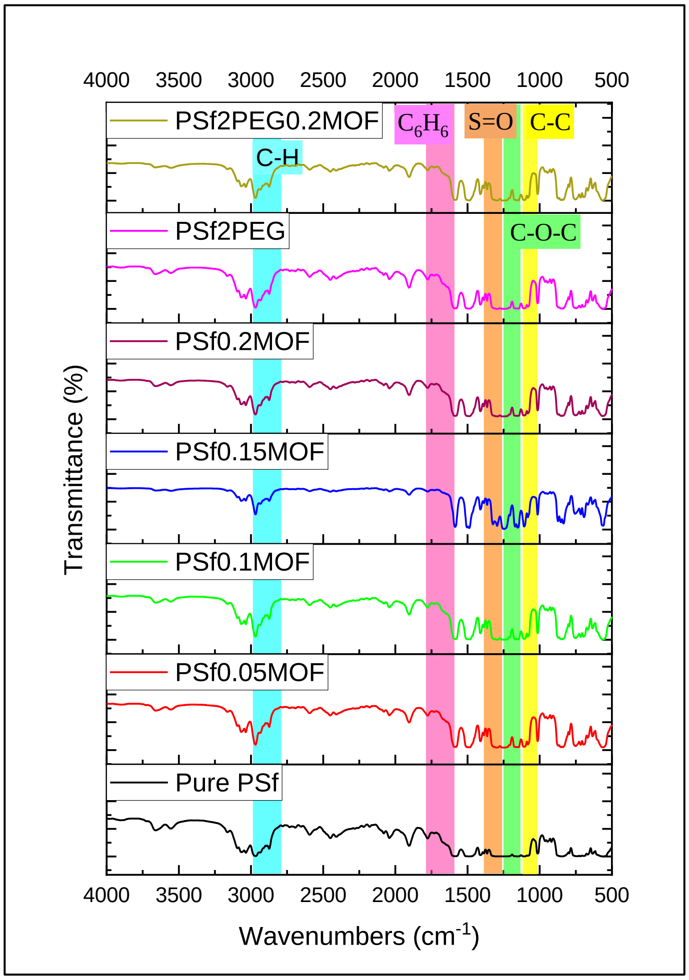

Figure 4.1. FTIR of pure PSf, PSf0.05MOF, PSF0.1MOF, PSf0.15MOF, PSf0.2MOF, PSf2PEG and PSf2PEG0.2MOF

4.2. SEM analysis

SEM morphology was studied for all formulated membranes and the results are presented in Figure 4.2. The structural morphology of pure PSf membrane showed a homogenous flat structure. However, the structure was changed after the addition of filler and additive i.e. PEG and NiO/CuO MOF respectively. The SEM images showed that polymer layer wrapped NiO/CuO MOF and was embedded into polymer matrix without any defects, which confirmed its good compatibility with polymer matrix and showed uniformity in structure. The good compatibility of organic linkers (i.e. Pyrazine and BDC) present in MOF can be due to this. Furthermore, the porous structure of nanoparticles allows polymer chains in the vicinity of NiO/CuO MOF, which helped in good adhesion [150]. Similarly, cross section of PSf/PEG blended membrane showed more roughly as compared to pure membrane, which implies good adhesion between the two polymers.

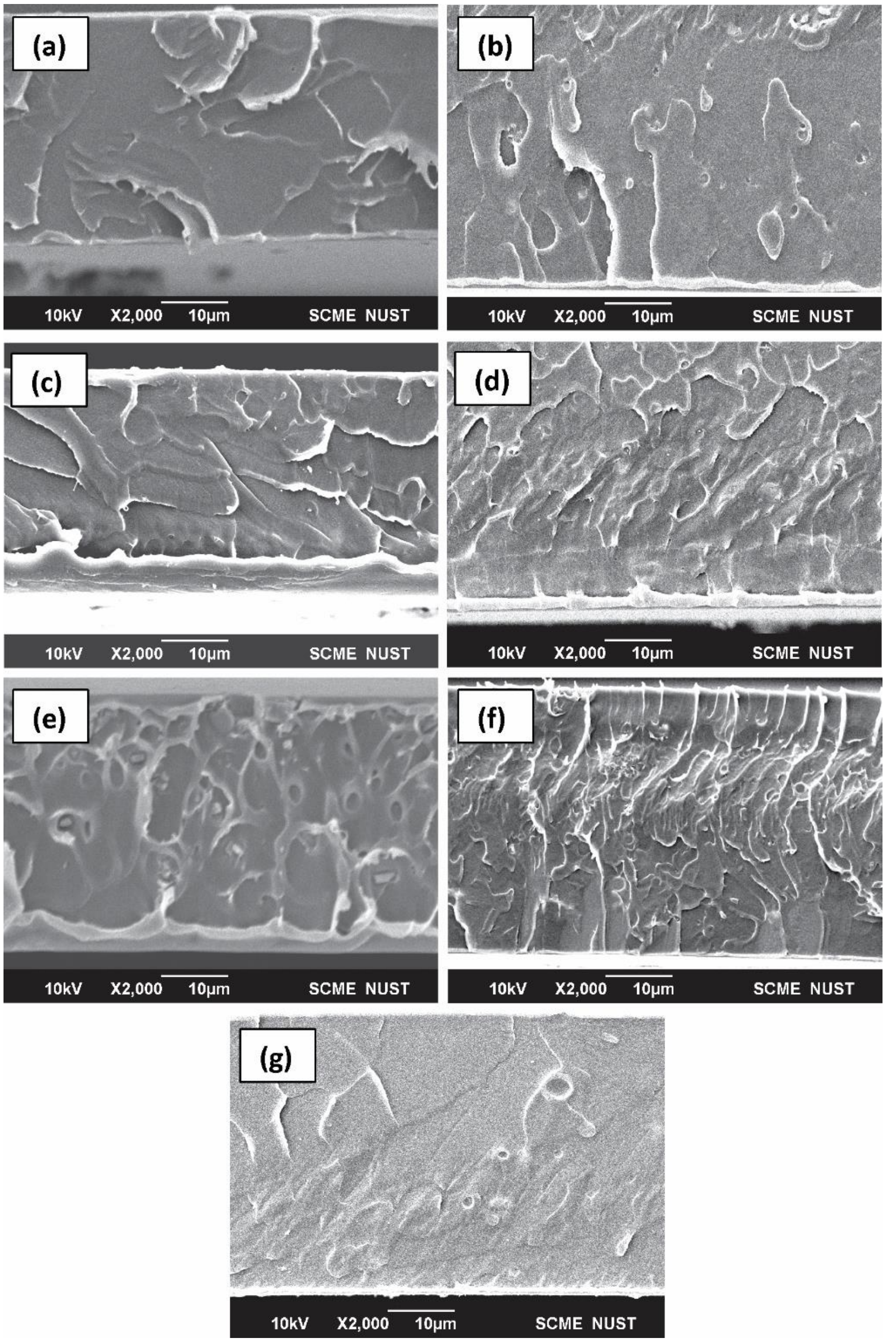

Figure 4.2. SEM cross sectional images of (a) Pure PSf, (b) PSf0.05MOF, (c) PSf0.1MOF, (d) PSf0.15MOF, (e) PSf0.2MOF, (f) PSf2PEG, (g) PSf2PEG0.2MOF

4.3. XRD analysis

XRD was used to characterize the change in crystallography of pure PSf and manufactured membranes caused by the addition of NiO/CuO MOF and PEG. As shown in Figure 4.3, the X-ray diffraction patterns of PSf/MOF, PSf/PEG, and PSf/PEG/MOF membranes of various compositions were compared to those of pure PSf membrane. In general, the sharp peak is observed in XRD patterns, when a polymeric material contains more crystalline region, and the intensity is high, whereas the amorphous polymeric material shows rather a broad peak [151]. Fig. 4.3 illustrates that pure PSf membrane showed peak in the region from 17 to 22 degree. This broad peak demonstrates the rigid and amorphous polymer structure of PSf [152]. Furthermore, there was a small but no significant shift in this peak observed after addition of MOF. The small decrease in peak broading indicated its crystallinity of NiO/CuO MOF. However, this crystallinity reduced when PEG was used as plasticizer in pure PSf as well as with NiO/CuO MOF. Hence, the resultant membranes were amorphous. Moreover, these broad peaks confirmed compatibility and homogeneity of incorporation of filler as well as additive. Moreover, these broad peaks confirmed compatibility and homogeneity of incorporation of filler as well as additive. Based on these results of structural characterization combing by FTIR, SEM and XRD techniques revealed that through the present methodology with the assistance of additive/plasticizer, the MOF particles can be uniformly embedded into PSf matrix which not only can guarantee good and homogeneous affinity for CO_2 of MMMs, but also would offer a fine interfacial-tuning to enable defect-free membrane which is promising for efficient separation performance of CO_2 from CH_4.

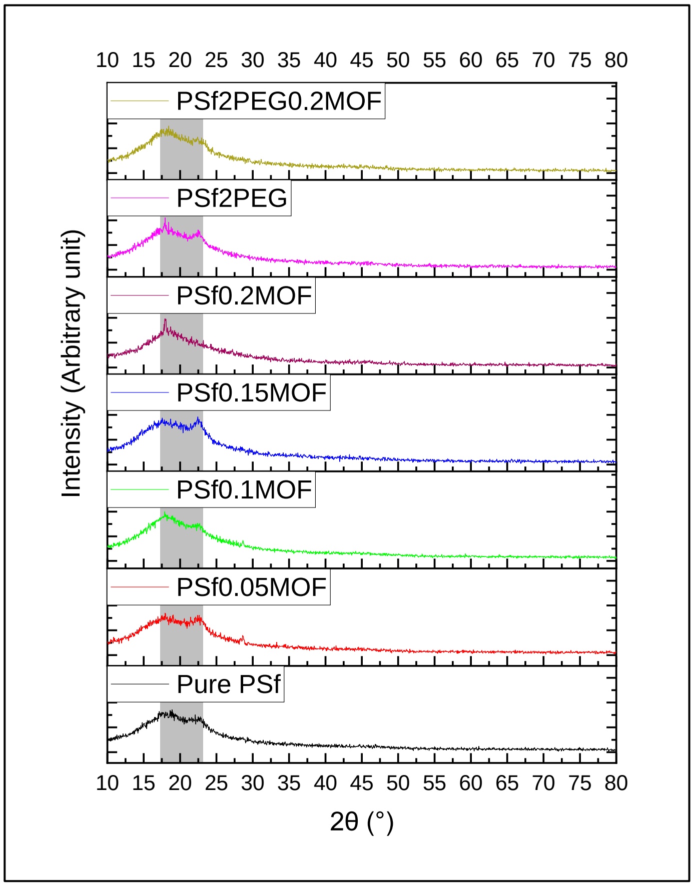

Figure 4.3. XRD analysis of pure PSf, PSf/MOF, PSf/PEG and PSf/PEG/MOF based MMMs at different composition

4.4. Mechanical Testing

The mechanical properties of all prepared membranes are showed in figure 4.4. Initially, there is a small gradual decrease in tensile strength of MMMs by adding filler in polymer matrix, which indicates a little crystalline nature of prepared membrane. Therefore, membranes showed small but not significant brittleness after addition of MOF as discussed previously. By adding PEG as plasticizer, the increase in mechanical strength occurred. Based on these results combing by XRD and FTIR, pure polymeric membrane was truly amorphous but addition of MOF made it crystalline. The maximum mechanical strength was observed in MOF based PSf/PEG blend membrane, indicating amorphous nature of MMMs as compared to pure PSf synthesized membrane. On the other hand, the percentage strain showed random trend for membranes at different composition as can be seen in the following Figure 4.4.

The results of mechanical testing implied that by adding MOF in PSf, brittleness appeared and strength decreased from 2.84 MPa to 2.26 MPa, but this go increased to 4.11 MPa by adding PEG as plasticizer. With the help of PEG additive, the interfaces of PSf/PEG/Pyrazine-MOF membranes were self-adaptively controlled, which not only assured the robust mechanical properties of the resulted MMMs, but also may enable a self-adaptive interface for promoting the permeability and suppressing the possible loss of selectivity for CO_2.

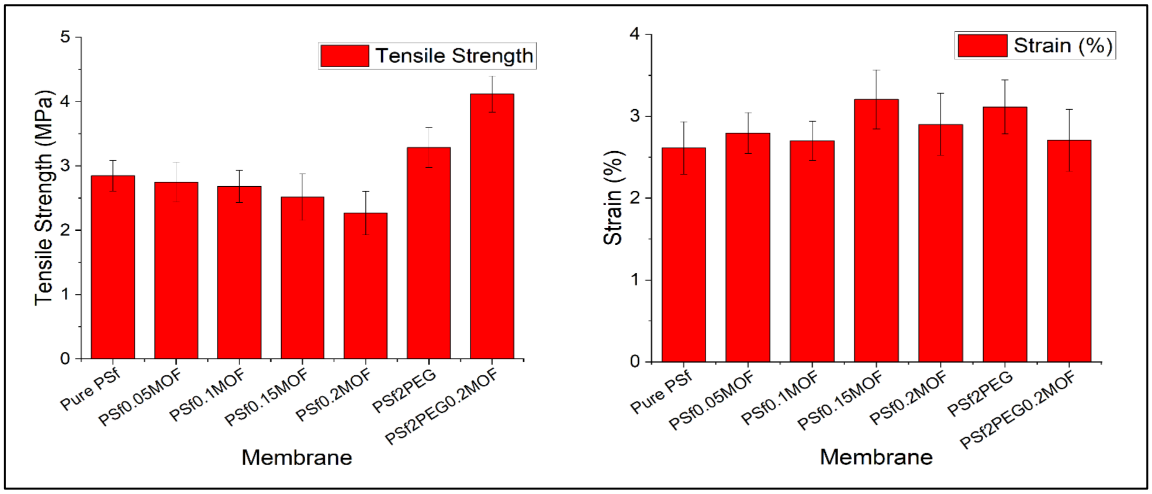

Figure 4.4. Tensile Strength (MPa) and Strain (%) of Pure PSf and all prepared MMMs

4.5. Membrane performance

The permeability of CO_2 and CH_4 gases through pure PSf, PSf/MOF, PSf/PEG and PSf/PEG/MOF based mixed matrix membranes have been tested in the pressure range of 2-5 bar, at room temperature. The permeation performance and ideal gas selectivity are presented in Figure 4.5. It can be seen that there is a progressive increase in permeation of pure gas with increasing filler loading. Similarly, for blended membranes, improved results were achieved. This increase in permeation rate is due to the formation of additional pores or which allowed more gas to pass through these channels. Also this increased the free volume for diffusion of gas molecules to pass through mixed matrix membranes [153]. Furthermore, the addition of the plasticizer PEG changed intermolecular interaction with other molecules matrix. This increased not only PSf chain flexibility but also gas molecule transport through the polymer matrix. [154]. This enhancement of free volume was achieved by the successful incorporation of filler as well as additive in pure PSf matrix. Hence, addition of the filler and the plasticizer has increased permeability of pure gases. At 0.2 wt % of filler loading with PSf/PEG blend, highest CO_2 permeability of 17.13 Barrer was achieved. The considerable increase in gas permeability can be attributed to the adsorption-controlled gas permeation process of CO2 through the pores. The results were also consistent with Henry's law, which stipulates that the solubility of any gas moving through a membrane is proportional to the feed pressure applied to the membrane [155]. It should be clear that permeability values of different gases through polymeric membrane can vary from the literature [33, 156]. This change in permeation values can due to the different properties of polymer, mainly molecular weights along with variation in operating conditions, casting gap, synthetic methods, membrane uniformity, variation in the solvent evaporation (slow or fast), and thickness of membrane [157].

The calculated values of ideal selectivity of MMMs for CO_2 and CH_4 demonstrate defect free membranes. The values were well above the pure PSf membrane, which also confirmed about uniform distribution of our selected MOF as well as PEG plasticizer in the matrix of PSf polymer. The observed ideal selectivity increased from 9.8 to 20.2 at 2 bar feed pressure. It was raised even further by progressively raising feed pressure from 2 to 5 bar at room temperature (Figure 4.5). This can be explained by the strong affinity of CO_2 gas with filler pores. The presence of basic sites like as pyrazine and BDC decorated the pores and due to comparatively small pore dimensions in MOF greatly enhanced adsorption of CO_2 gas molecules.

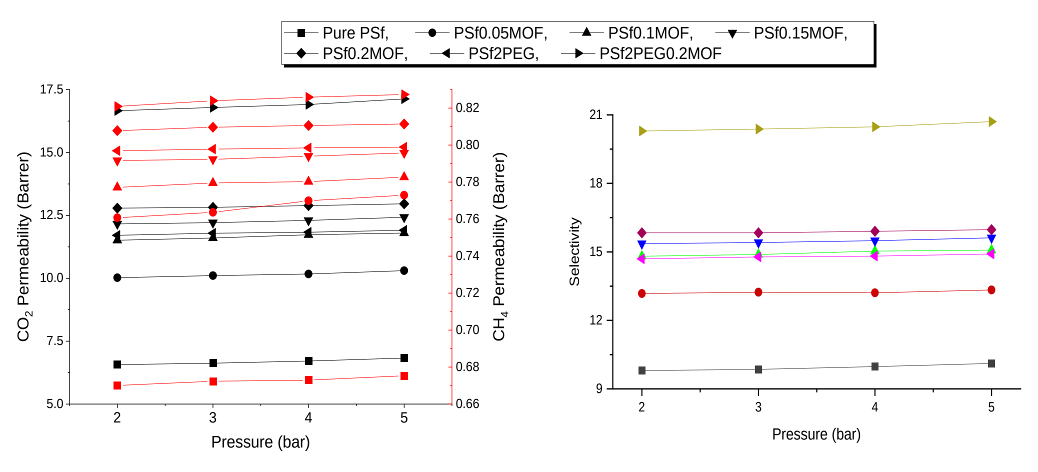

Figure 4.5. Pure CO_2 and CH_4 permeability and ideal selectivity for all prepared membranes

Conclusion and Recommendations

Conclusion

The study reports the synthesis of PSf based MMMs for gas separation application. In which, NiO/CuO MOF was used as filler and PEG as plasticizer, to make ternary MMMs for CO_2 and CH_4 gas separation. When a filler and a plasticizer were added to the synthesized MMM, the CO2 permeability and selectivity increased by up to 2-3 times when compared to a pure polymeric membrane. FTIR results showed shifting in adsorption band which indicates the interaction of MOF and PEG as compared to pure PSf membrane. Moreover, the SEM images confirmed that PSf/PEG and ternary MMMs were defect free which implies that PEG and NiO/CuO MOF was successfully distributed in the polymer matrix. The X-ray diffraction band pattern of all MMMs and PSf/PEG blend membrane did not show significant shift of peaks and mainly was broader peaks, indicating the amorphous nature with little crystallinity of membranes. The mechanical properties of membrane decreased by adding filler but increased by adding PEG. Moreover, permeation testing for CO_2 separation showed increased permeability as well as selectivity for CO_2. The synthesized MMM performed best at 5 bar, with CO_2 permeability and selectivity of 17.13 Barrer and 20.70, respectively. The synthesized membranes result showed that theses membranes have much potential in the separation of CO_2. The comparison study of PSf based mixed matrix membranes with our work is listed below.

Table 5.1. A performance comparison of different PSf based dense membranes for CO_2 separation

Polymer	Filler loading	T (ºC)	P (bar)	CO_2 Permeability (Barrer)	CO_2/CH_4 Selectivity	Reference
PSf	CNF (1%)	RT	4	4.87	12.7	[158]
PSf	f-SWNT (10%)	35	4	5.19	18.53	[158]
PSF	ZSM5 (10%)	35	5	2.00	4.13	[159]
PSf	DMS (10%)	n.g	n.g	12.81	23.7	[160]
PSf/PEG	GO (5%)	35	8	23.14	15.21	[149]
PSf/PES	GO (10%)	35	5	17.54	14.31	[35]
PSf	ZIF (5%)	35	8	17.31	17.11	[34]
PSf	NiO/CuO MOF (0.2%)	RT	5	12.96	15.97	This work
PSf/PEG	NiO/CuO MOF (0.2%)	RT	5	17.13	20.7	This work

Recommendations

On the basis of results obtained from this study, following recommendations are to be kept in mind.

- Since selected MOF was used for the first time in gas separation application but it showed good potential in CO_2 separation. Hence, it should be tested with different polymers as well as for other gas separation applications.

- Durability of membranes should be tested for longer period of time against pressure, plasticizing and swelling resistance.
- Simultaneously focus should be given on the utilization of new polymers i.e. polymeric intrinsic microporosty PIM, 6FDA-DABA, PDMS etc. because literature narrates the significant rise in permeability and selectivity in CO_2, CH_4, N_2 and O_2 from membrane fabricated from these polymers.

References

[1] Nocito, F., A.J.C.O.i.G. Dibenedetto, and S. Chemistry, *Atmospheric CO2 mitigation technologies: carbon capture utilization and storage.* **2020**. 21: p. 34-43.

[2] IEA, *World Energy Outlook*. **2019**.

[3] *BP Statistical Review of World Energy*. **2019**: p. 1633-1648.

[4] Selvaraj, R., et al., *Monitoring of CO2 and CH4 composition in a biogas matrix from different biomass structures.* **2017**. 249: p. 378-385.

[5] Al-Megren, H., *Advances in Natural Gas Technology*. **2012**: BoD–Books on Demand.

[6] Basu, S., et al., *MOF-containing mixed-matrix membranes for CO2/CH4 and CO2/N2 binary gas mixture separations.* **2011**. 81(1): p. 31-40.

[7] Baker, R.W.J.I. and e.c. research, *Future directions of membrane gas separation technology*. **2002**. 41(6): p. 1393-1411.

[8] Peer, M., et al., *Separation of hydrogen from carbon monoxide using a hollow fiber polyimide membrane: experimental and simulation.* **2007**. 30(10): p. 1418-1425.

[9] Lin, D., et al., *Gas permeation through polydimethylsiloxane membranes: comparison of three model combinations.* **2012**. 35(10): p. 1833-1841.

[10] Nasir, R., et al., *Material advancements in fabrication of mixed-matrix membranes.* **2013**. 36(5): p. 717-727.

[11] Shen, J., et al., *UiO-66-polyether block amide mixed matrix membranes for CO2 separation.* **2016**. 513: p. 155-165.

[12] Zimmerman, C.M., *Advanced gas separation membrane materials: Hyper rigid polymers and molecular sieve-polymer mixed matrices*. **1998**, University of Texas at Austin.

[13] Saqib, S., et al., *Perylene based novel mixed matrix membranes with enhanced selective pure and mixed gases (CO2, CH4, and N2) separation.* **2020**. 73: p. 103072.

[14] Kardani, R., et al., *Mesoporous copper zinc bimetallic imidazolate MOF as nanofiller to improve gas separation performance of PEBA-based membranes.* **2020**. 83: p. 100-110.

[15] Sanip, S., et al., *Gas separation properties of functionalized carbon nanotubes mixed matrix membranes.* **2011**. 78(2): p. 208-213.

[16] Huang, Z., et al., *Enhanced gas separation properties by using nanostructured PES-Zeolite 4A mixed matrix membranes.* **2006**. 101(6): p. 3800-3805.

[17] Ozturk, B. and F.J.C.e.j. Demirciyeva, *Comparison of biogas upgrading performances of different mixed matrix membranes.* **2013**. 222: p. 209-217.

[18] Li, Y., 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.* **2006**. 277(1-2): p. 28-37.

[19] Vu, D.Q., W.J. Koros, and S.J.J.J.o.m.s. Miller, *Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results.* **2003**. 211(2): p. 311-334.

[20] Anson, M., et al., *ABS copolymer-activated carbon mixed matrix membranes for CO2/CH4 separation.* **2004**. 243(1-2): p. 19-28.

[21] Zulhairun, A., et al., *Asymmetric mixed matrix membrane incorporating organically modified clay particle for gas separation.* **2014**. 241: p. 495-503.

[22] Van Rooyen, L., et al., *Gas barrier properties of oxyfluorinated graphene filled polytetrafluoroethylene nanocomposites.* **2016**. 109: p. 30-39.

[23] Chung, T.-S., et al., *Characterization of permeability and sorption in Matrimid/C60 mixed matrix membranes.* **2003**. 211(1): p. 91-99.

[24] Ahmad, J. and M.B.J.J.o.m.s. Hågg, *Polyvinyl acetate/titanium dioxide nanocomposite membranes for gas separation.* **2013**. 445: p. 200-210.

[25] Perea-Cachero, A., et al., *A new zeolitic hydroxymethylimidazolate material and its use in mixed matrix membranes based on 6FDA-DAM for gas separation.* **2017**. 544: p. 88-97.

[26] Sutrisna, P.D., et al., *Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fibre membranes.* **2017**. 524: p. 266-279.

[27] Zhang, J., et al., *Mixed matrix membranes comprising aminosilane-functionalized graphene oxide for enhanced CO2 separation.* **2019**. 570: p. 343-354.

[28] Ahmad, M.Z., et al., *Enhanced gas separation performance of 6FDA-DAM based mixed matrix membranes by incorporating MOF UiO-66 and its derivatives.* **2018**. 558: p. 64-77.

[29] Jamil, A., et al., *Polyetherimide-montmorillonite mixed matrix hollow fibre membranes: Effect of inorganic/organic montmorillonite on CO2/CH4 separation.* **2018**. 206: p. 256-267.

[30] Zornoza, B., et al., *Mesoporous silica sphere− polysulfone mixed matrix membranes for gas separation.* **2009**. 25(10): p. 5903-5909.

[31] Reid, B.D., et al., *Gas permeability properties of polysulfone membranes containing the mesoporous molecular sieve MCM-41.* **2001**. 13(7): p. 2366-2373.

[32] Car, A., C. Stropnik, and K.-V.J.D. Peinemann, *Hybrid membrane materials with different metal–organic frameworks (MOFs) for gas separation.* **2006**. 200(1-3): p. 424-426.

[33] Junaidi, M., et al., *Carbon dioxide removal from methane by using polysulfone/SAPO-44 mixed matrix membranes.* **2013**. 112: p. 1-6.

[34] Tanh Jeazet, H.B., et al., *Increased selectivity in CO2/CH4 Separation with mixed-matrix membranes of polysulfone and mixed-MOFs MIL-101 (Cr) and ZIF-8.* **2016** (27): p. 4363-4367.

[35] Abdul Mannan, H., et al., *Polysulfone/poly (ether sulfone) blended membranes for CO2 separation.* **2016**. 133(5).

[36] Raouf, M., et al., *A favored CO2 separation over light gases using mixed matrix membrane comprising polysulfone/polyethylene glycol and graphene hydroxyl nanoparticles.* **2020**. 133: p. 394-407.

[37] Noor, T., et al., *Nanocomposites of NiO/CuO Based MOF with rGO: An Efficient and Robust Electrocatalyst for Methanol Oxidation Reaction in DMFC.* **2020**. 10(8): p. 1601.

[38] Scott, K., *Handbook of industrial membranes*. **1995**: Elsevier.

[39] Nunes, S.P. and K.-V. Peinemann, *Membrane technology*. **2001**: Wiley Online Library.

[40] Baker, R.W., *Membrane technology and applications*. **2012**: John Wiley & Sons.

[41] Lin, Y., et al., *Microporous inorganic membranes.* **2002**. 31(2): p. 229-379.

[42] Bernardo, P., et al., *Membrane gas separation: a review/state of the art.* **2009**. 48(10): p. 4638-4663.

[43] De Meis, D., *Overview on porous inorganic membranes for gas separation.* **2017**.

[44] Ismail, A.F., K.C. Khulbe, and T.J.S.S. Matsuura, *Gas separation membranes.* **2015**. 10: p. 978-3.

[45] Saufi, S. and A.J.C. Ismail, *Fabrication of carbon membranes for gas separation—a review.* **2004**. 42(2): p. 241-259.

[46] Zhang, Y., et al., *Current status and development of membranes for CO2/CH4 separation: A review.* **2013**. 12: p. 84-107.

[47] Pandey, P. and R.S. Chauhan, *Membranes for gas separation.* Progress in Polymer Science, **2001**. 26(6): p. 853-893.

[48] Mohshim, D.F., et al., *Latest development on membrane fabrication for natural gas purification: a review.* **2013**.

[49] Wu, Z., *Inorganic Membranes for Gas Separations*, in *Membrane Separation Principles and Applications*. **2019**, Elsevier. p. 147-179.

[50] Galizia, M., et al., *50th anniversary perspective: polymers and mixed matrix membranes for gas and vapor separation: a review and prospective opportunities.* **2017**. 50(20): p. 7809-7843.

[51] Gao, C., et al., *The effect of nanoparticles on gas permeability with polyimide membranes and network hybrid membranes: a review.* Reviews in Inorganic Chemistry, **2020**. 1(ahead-of-print).

[52] Comesaña-Gándara, B., et al., *Redefining the Robeson upper bounds for CO 2/CH 4 and CO 2/N 2 separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity.* Energy & Environmental Science, **2019**. 12(9): p. 2733-2740.

[53] Javaid, A.J.C.E.J., *Membranes for solubility-based gas separation applications.* **2005**. 112(1-3): p. 219-226.

[54] Budd, P.M. and N.B.J.P.C. McKeown, *Highly permeable polymers for gas separation membranes.* **2010**. 1(1): p. 63-68.

[55] Hofmann, D. and E. Tocci, *Molecular modeling, A tool for the knowledge-based design of polymer-based membrane materials*, in *Membrane Operations*. **2009**, Wiley Online Library. p. 3-18.

[56] Park, H.B., et al., *Thermally rearranged (TR) polymer membranes for CO2 separation.* **2010**. 359(1-2): p. 11-24.

[57] Wind, J.D., D.R. Paul, and W.J.J.J.o.M.S. Koros, *Natural gas permeation in polyimide membranes.* **2004**. 228(2): p. 227-236.

[58] Deng, L., T.-J. Kim, and M.-B.J.J.o.M.S. Hägg, *Facilitated transport of CO2 in novel PVAm/PVA blend membrane.* **2009**. 340(1-2): p. 154-163.

[59] Barlow, J., D.J.P.E. Paul, and Science, *Polymer blends and alloys—a review of selected considerations.* **1981**. 21(15): p. 985-996.

[60] Wang, D., K. Li, and W.J.J.o.M.S. Teo, *Polyethersulfone hollow fiber gas separation membranes prepared from NMP/alcohol solvent systems.* **1996**. 115(1): p. 85-108.

[61] Panapitiya, N., et al., *Compatibilized immiscible polymer blends for gas separations.* **2016**. 9(8): p. 643.

[62] Zornoza, B., et al., *Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential.* **2013**. 166: p. 67-78.

[63] Barrer, R.M.J.Z., *Zeolites and their synthesis.* **1981**. 1(3): p. 130-140.

[64] Mahajan, R., W.J.J.P.E. Koros, and Science, *Mixed matrix membrane materials with glassy polymers. Part 1.* **2002**. 42(7): p. 1420-1431.

[65] Dahe, G.J., R.S. Teotia, and J.R.J.C.E.J. Bellare, *The role of zeolite nanoparticles additive on morphology, mechanical properties and performance of polysulfone hollow fiber membranes.* **2012**. 197: p. 398-406.

[66] Batten, S.R., et al., *Terminology of metal–organic frameworks and coordination polymers (IUPAC Recommendations 2013).* **2013**. 85(8): p. 1715-1724.

[67] Férey, G., et al., *Hydrogen adsorption in the nanoporous metal-benzenedicarboxylate M (OH)(O 2 C–C 6 H 4–CO 2)(M= Al 3+, Cr 3+), MIL-53.* Chemical communications, **2003**(24): p. 2976-2977.

[68] Li, H., et al., *Design and synthesis of an exceptionally stable and highly porous metal-organic framework.* **1999**. 402(6759): p. 276-279.

[69] Chui, S.S.-Y., et al., *A chemically functionalizable nanoporous material [Cu3 (TMA) 2 (H2O) 3] n.* **1999**. 283(5405): p. 1148-1150.

[70] Hoskins, B.F. and R.J.J.o.t.A.C.S. Robson, *Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related frameworks [N (CH3) 4][CuIZnII (CN) 4] and CuI [4, 4', 4'', 4'''-tetracyanotetraphenylmethane] BF4. xC6H5NO2.* **1990**. 112(4): p. 1546-1554.

[71] Yaghi, O.M. and H. Li, *Hydrothermal Synthesis of a Metal-Organic Framework Containing Large Rectangular Channels.* Journal of the American Chemical Society, **2002**. 117(41): p. 10401-10402.

[72] Yaghi, O.M., G. Li, and H.J.N. Li, *Selective binding and removal of guests in a microporous metal–organic framework.* **1995**. 378(6558): p. 703-706.

[73] Furukawa, H., et al., *The chemistry and applications of metal-organic frameworks.* **2013**. 341(6149).

[74] Cui, J., et al., *Photonic metal–organic framework composite spheres: A new kind of optical material with self-reporting molecular recognition.* **2014**. 6(20): p. 11995-12001.

[75] Kumar, P., et al., *Luminescent nanocrystal metal organic framework based biosensor for molecular recognition.* **2014**. 43: p. 114-117.

[76] Kılıç, A., et al., *Sod-ZMOF/Matrimid® mixed matrix membranes for CO2 separation.* **2015**. 489: p. 81-89.

[77] Li, R.-J., et al., *ROD-8, a rod MOF with a pyrene-cored tetracarboxylate linker: framework disorder, derived nets and selective gas adsorption.* **2014**. 16(28): p. 6291-6295.

[78] Kumar, A. and S.J.J.o.D.R. Maskara, *Revealing clinicians' experiences towards healthcare software usability using human–centred design approach.* **2015**. 13(1): p. 36-54.

[79] Miller, S.R., et al., *Biodegradable therapeutic MOFs for the delivery of bioactive molecules.* **2010**. 46(25): p. 4526-4528.

[80] Park, K.S., et al., *Exceptional chemical and thermal stability of zeolitic imidazolate frameworks.* **2006**. 103(27): p. 10186-10191.

[81] Casco, M.E., et al., *Gate-opening effect in ZIF-8: the first experimental proof using inelastic neutron scattering.* **2016**. 52(18): p. 3639-3642.

[82] Zhang, K., et al., *Exploring the framework hydrophobicity and flexibility of ZIF-8: from biofuel recovery to hydrocarbon separations.* **2013**. 4(21): p. 3618-3622.

[83] Zhang, C., et al., *High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations.* **2012**. 389: p. 34-42.

[84] Yaghi, O.M.J.R., *High-throughput synthesis of zeolitic.* **2008**: p. 939-943.

[85] Al-Janabi, N., et al., *Mapping the Cu-BTC metal–organic framework (HKUST-1) stability envelope in the presence of water vapour for CO2 adsorption from flue gases.* **2015**. 281: p. 669-677.

[86] Sorribas, S., et al., *Pervaporation and membrane reactor performance of polyimide based mixed matrix membranes containing MOF HKUST-1.* **2015**. 124: p. 37-44.

[87] Kim, H.K., et al., *A Chemical route to activation of open metal sites in the copper-based metal–organic framework materials HKUST-1 and Cu-MOF-2.* **2015**. 137(31): p. 10009-10015.

[88] Basu, S., A. Cano-Odena, and I.F.J.J.o.m.s. Vankelecom, *Asymmetric Matrimid®/[Cu3 (BTC) 2] mixed-matrix membranes for gas separations.* **2010**. 362(1-2): p. 478-487.

[89] Lin, R., et al., *Ionic liquids as the MOFs/polymer interfacial binder for efficient membrane separation.* **2016**. 8(46): p. 32041-32049.

[90] Nakagaki, S., et al., *Chemical reactions catalyzed by metalloporphyrin-based metal-organic frameworks.* **2013**. 18(6): p. 7279-7308.

[91] Rosi, N.L., et al., *Rod packings and metal− organic frameworks constructed from rod-shaped secondary building units.* **2005**. 127(5): p. 1504-1518.

[92] Millward, A.R. and O.M.J.J.o.t.A.C.S. Yaghi, *Metal− organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature.* **2005**. 127(51): p. 17998-17999.

[93] Britt, D., et al., *Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites.* **2009**. 106(49): p. 20637-20640.

[94] Bachman, J.E., et al., *Enhanced ethylene separation and plasticization resistance in polymer membranes incorporating metal–organic framework nanocrystals.* **2016**. 15(8): p. 845-849.

[95] Boutin, A., et al., *The behavior of flexible MIL-53 (Al) upon CH4 and CO2 adsorption.* **2010**. 114(50): p. 22237-22244.

[96] Bourrelly, S., et al., *Explanation of the adsorption of polar vapors in the highly flexible metal organic framework MIL-53 (Cr).* **2010**. 132(27): p. 9488-9498.

[97] Llewellyn, P., et al., *Complex adsorption of short linear alkanes in the flexible metal-organic-framework MIL-53 (Fe).* **2009**. 131(36): p. 13002-13008.

[98] Serre, C., et al., *Very Large Breathing Effect in the First Nanoporous Chromium (III)-Based Solids: MIL-53 or CrIII (OH)⨀{O2C− C6H4− CO2}⨀{HO2C− C6H4− CO2H} x⨀ H2O y.* **2002**. 124(45): p. 13519-13526.

[99] Loiseau, T., et al., *A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration.* **2004**. 10(6): p. 1373-1382.

[100] Sabetghadam, A., et al., *Metal organic framework crystals in mixed-matrix membranes: impact of the filler morphology on the gas separation performance.* **2016**. 26(18): p. 3154-3163.

[101] Forgan, R.S., et al., *Nanoporous carbohydrate metal–organic frameworks.* **2012**. 134(1): p. 406-417.

[102] Furukawa, Y., et al., *Nano-and Microsized Cubic Gel Particles from Cyclodextrin Metal–Organic Frameworks.* **2012**. 124(42): p. 10718-10721.

[103] Smaldone, R.A., et al., *Metal–organic frameworks from edible natural products.* **2010**. 49(46): p. 8630-8634.

[104] Gassensmith, J.J., et al., *Strong and reversible binding of carbon dioxide in a green metal–organic framework.* **2011**. 133(39): p. 15312-15315.

[105] Smith, M.K., S.R. Angle, and B.H. Northrop, *Preparation and analysis of cyclodextrin-based metal–organic frameworks: laboratory experiments adaptable for high school through advanced undergraduate students.* Journal of Chemical Education, **2015**. 92(2): p. 368-372.

[106] Jeazet, H.B.T., C. Staudt, and C.J.D.T. Janiak, *Metal–organic frameworks in mixed-matrix membranes for gas separation.* **2012**. 41(46): p. 14003-14027.

[107] Fink, J.K., *High performance polymers*. **2014**: William Andrew.

[108] Kyriacos, D., *High-temperature engineering thermoplastics*, in *Brydson's Plastics Materials*. **2017**, Elsevier. p. 545-615.

[109] Zarrintaj, P., et al., *Application of compatibilized polymer blends in biomedical fields*, in *Compatibilization of Polymer Blends*. **2020**, Elsevier. p. 511-537.

[110] Liang, H.-q., et al., *Polysulfone membranes via thermally induced phase separation.* Chinese Journal of Polymer Science, **2017**. 35(7): p. 846-856.

[111] Ding, Z., et al., *Enhancing the compatibility, hydrophilicity and mechanical properties of polysulfone ultrafiltration membranes with lignocellulose nanofibrils.* Polymers, **2016**. 8(10): p. 349.

[112] Eddaoudi, M., et al., *Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage.* **2002**. 295(5554): p. 469-472.

[113] Li, J.-R., R.J. Kuppler, and H.-C.J.C.S.R. Zhou, *Selective gas adsorption and separation in metal–organic frameworks.* **2009**. 38(5): p. 1477-1504.

[114] Li, J.-R., J. Sculley, and H.-C.J.C.r. Zhou, *Metal–organic frameworks for separations.* **2012**. 112(2): p. 869-932.

[115] Nugent, P., et al., *Porous materials with optimal adsorption thermodynamics and kinetics for CO 2 separation.* **2013**. 495(7439): p. 80-84.

[116] Eddaoudi, M., H. Li, and O.J.J.o.t.A.C.S. Yaghi, *Highly porous and stable metal− organic frameworks: structure design and sorption properties.* **2000**. 122(7): p. 1391-1397.

[117] Cavka, J.H., et al., *A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability.* **2008**. 130(42): p. 13850-13851.

[118] Garibay, S.J. and S.M.J.C.C. Cohen, *Isoreticular synthesis and modification of frameworks with the UiO-66 topology.* **2010**. 46(41): p. 7700-7702.

[119] Lin, X., et al., *High capacity hydrogen adsorption in Cu (II) tetracarboxylate framework materials: the role of pore size, ligand functionalization, and exposed metal sites.* **2009**. 131(6): p. 2159-2171.

[120] Wang, B., et al., *Applications of metal–organic frameworks for green energy and environment: New advances in adsorptive gas separation, storage and removal.* Green Energy & Environment, **2018**. 3(3): p. 191-228.

[121] Lin, Y., et al., *Polyethyleneimine incorporated metal-organic frameworks adsorbent for highly selective CO 2 capture.* **2013**. 3(1): p. 1-7.

[122] Bao, S.-J., et al., *A stable metal–organic framework with suitable pore sizes and rich uncoordinated nitrogen atoms on the internal surface of micropores for highly efficient CO 2 capture.* **2015**. 3(14): p. 7361-7367.

[123] Xiang, S., et al., *Microporous metal-organic framework with potential for carbon dioxide capture at ambient conditions.* **2012**. 3(1): p. 1-9.

[124] Wang, R., et al., *A Zn metal–organic framework with high stability and sorption selectivity for CO2.* **2015**. 54(22): p. 10587-10592.

[125] Möllmer, J., et al., *High pressure adsorption of hydrogen, nitrogen, carbon dioxide and methane on the metal–organic framework HKUST-1.* 2011. 138(1-3): p. 140-148.

[126] Furukawa, H., et al., *Ultrahigh porosity in metal-organic frameworks.* **2010**. 329(5990): p. 424-428.

[127] Farha, O.K., et al., *De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities.* **2010**. 2(11): p. 944-948.

[128] Yazaydın, A.O.z.r., et al., *Screening of metal− organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modeling approach.* **2009**. 131(51): p. 18198-18199.

[129] Chowdhury, P., C. Bikkina, and S.J.T.J.o.P.C.C. Gumma, *Gas adsorption properties of the chromium-based metal organic framework MIL-101.* **2009**. 113(16): p. 6616-6621.

[130] Saha, D., et al., *Adsorption of CO2, CH4, N2O, and N2 on MOF-5, MOF-177, and zeolite 5A.* **2010**. 44(5): p. 1820-1826.

[131] Ida, S., *PES (Poly(ether sulfone)), Polysulfone,* in *Encyclopedia of Polymeric Nanomaterials,* S. Kobayashi and K. Müllen, Editors. **2021**, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1-8.

[132] Waheed, N., et al., *Mixed matrix membranes based on polysulfone and rice husk extracted silica for CO2 separation.* Separation and Purification Technology, **2016**. 170: p. 122-129.

[133] Mahajan, R., W.J.J.I. Koros, and E.C. Research, *Factors controlling successful formation of mixed-matrix gas separation materials.* **2000**. 39(8): p. 2692-2696.

[134] Shabanian, M., M. Hajibeygi, and A. Raeisi, *FTIR characterization of layered double hydroxides and modified layered double hydroxides,* in *Layered Double Hydroxide Polymer Nanocomposites*. **2020**, Elsevier. p. 77-101.

[135] Wongthong, S., et al., *Attenuated total reflection: Fourier transform infrared spectroscopy for detection of heterogeneous vancomycin—intermediate Staphylococcus aureus.* **2020**. 36(2): p. 1-12.

[136] Faghihzadeh, F., et al., *Fourier transform infrared spectroscopy to assess molecular-level changes in microorganisms exposed to nanoparticles.* **2016**. 1(1): p. 1.

[137] McCluskey, M.J.J.o.A.P., *Local vibrational modes of impurities in semiconductors.* **2000**. 87(8): p. 3593-3617.

[138] Walock, M.J., *Nanocomposite coatings based on quaternary metal-nitrogen and nanocarbon systems*. **2012**: The University of Alabama at Birmingham.

[139] Goldstein, J.I., et al., *Scanning electron microscopy and X-ray microanalysis*. **2017**: Springer.

[140] Rajeswari, A., et al., *Characterization studies of polymer-based composites related to functionalized filler-matrix interface.* Interfaces in Particle and Fibre Reinforced Composites, **2020**: p. 219-250.

[141] Inaba, K., et al., *High resolution X-ray diffraction analyses of (La, Sr) MnO 3/ZnO/Sapphire (0001) double heteroepitaxial films.* **2013**.

[142] Falsafi, S.R., H. Rostamabadi, and S.M. Jafari, *X-ray diffraction (XRD) of nanoencapsulated food ingredients*, in *Characterization of nanoencapsulated food ingredients*. **2020**, Elsevier. p. 271-293.

[143] Fontananova, E., *Tensile Strength*, in *Encyclopedia of Membranes*, E. Drioli and L. Giorno, Editors. **2015**, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1-3.

[144] Gunasekaran, K., et al., *Mechanical and bond properties of coconut shell concrete.* **2011**. 25(1): p. 92-98.

[145] Mozafari, M., R. Abedini, and A.J.J.o.M.C.A. Rahimpour, *Zr-MOFs-incorporated thin film nanocomposite Pebax 1657 membranes dip-coated on polymethylpentyne layer for efficient separation of CO 2/CH 4.* **2018**. 6(26): p. 12380-12392.

[146] Pihlajamäki, A., et al., *Characterization of clean and fouled polymeric ultrafiltration membranes by Fourier transform IR spectroscopy–attenuated total reflection.* **1998**. 138(2-3): p. 323-333.

[147] Junaidi, M., et al., *Fouling mitigation in humic acid ultrafiltration using polysulfone/SAPO-34 mixed matrix membrane.* **2013**. 67(9): p. 2102-2109.

[148] Karimi, S., et al., *Assessment of gas separation properties and CO2 plasticization of polysulfone/polyethylene glycol membranes.* **2019**. 173: p. 13-19.

[149] Zahri, K., P. Goh, and A. Ismail. *The incorporation of graphene oxide into polysulfone mixed matrix membrane for CO2/CH4 separation*. in *IOP Conference Series: Earth and Environmental Science*. **2016**. IOP Publishing.

[150] Shahid, S., K.J.S. Nijmeijer, and P. Technology, *Matrimid®/polysulfone blend mixed matrix membranes containing ZIF-8 nanoparticles for high pressure stability in natural gas separation.* **2017**. 189: p. 90-100.

[151] Sadeghi, M., et al., *Gas permeation properties of ethylene vinyl acetate–silica nanocomposite membranes.* **2008**. 322(2): p. 423-428.

[152] Muntha, S.T., et al., *Mixed matrix membranes of polysulfone/polyimide reinforced with modified zeolite based filler: Preparation, properties and application.* Chinese Journal of Polymer Science, **2018**. 36(1): p. 65-77.

[153] Swapna, V.P., V.S. Abhisha, and R. Stephen, *Polymer/polyhedral oligomeric silsesquioxane nanocomposite membranes for pervaporation*, in *Polymer Nanocomposite Membranes for Pervaporation*. **2020**, Elsevier. p. 201-229.

[154] Yampolskii, Y., *1.3 Basic Aspects of Gas Transport in Membranes*, in *Comprehensive Membrane Science and Engineering*. **2017**, Elsevier Oxford. p. 57-64.

[155] Kanehashi, S. and K.J.J.o.M.S. Nagai, *Analysis of dual-mode model parameters for gas sorption in glassy polymers.* **2005**. 253(1-2): p. 117-138.

[156] Aroon, M., et al., *Morphology and permeation properties of polysulfone membranes for gas separation: Effects of non-solvent additives and co-solvent.* **2010**. 72(2): p. 194-202.

[157] Anastasiou, S., et al., *Metal-organic framework/graphene oxide composite fillers in mixed-matrix membranes for CO2 separation.* **2018**. 212: p. 513-522.

[158] Kim, S., et al., *Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: theory and experiment.* **2007**. 294(1-2): p. 147-158.

[159] Dorosti, F., et al., *Fabrication and characterization of polysulfone/polyimide–zeolite mixed matrix membrane for gas separation.* **2011**. 171(3): p. 1469-1476.

[160] Park, S., et al., *3-Dimensionally disordered mesoporous silica (DMS)-containing mixed matrix membranes for CO2 and non-CO2 greenhouse gas separations.* **2014**. 136: p. 286-295.