Synthesis, Characterization and Gas Permeation study of CA/PEG/Zn-Co ZIF Mixed Matrix Membrane

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Certificate

This is to certify that work in this thesis has been carried out by **Mr. Nauman Hafeez** and completed under my supervision in MEMAR laboratory, School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

"We have enjoined on man kindness to parents."

(Quran 29:8 & 46:15)

-To my loving and beloved Parents-

Abstract

Exceptional permeabilities and perm-selectivities for CO_2, N_2, and CH_4 have been reported using Zeolitic Imidazole Framework in polymeric mixed matrix membranes. This research focuses on synthesis, characterization and permeation testing of mixed matrix membrane using Zn-Co ZIF and Cellulose Acetate. Gases used are N_2, CH_4 and CO_2. Zn-Co ZIF was synthesized using rapid room temperature method while mixed matrix membrane were synthesized using simple solution casting method. Excellent dispersion and morphology was obtained using Zn-Co ZIF and CA which was verified by various characterization techniques including SEM, X-ray Diffraction (XRD), FT-IR, Mechanical Testing using UTM and Thermo-gravimetric Analysis (TG). Characterization showed strong interaction between Zn-Co ZIF cages and cellulose acetate chains with excessive free volume elements for diffusion and excellent dispersion of Zn-Co ZIF on polymer surface. In permeability test system, pure CO_2, N_2, and CH_4 were used and perm-selectivities were calculated for CO_2/N_2 and CO_2/CH_4 gas pairs. For CO_2 maximum permeation of 160 barrer was obtained with 15wt% Zn-Co ZIF loading and 8 bar pressure. For N_2, and CH_4 maximum permeations of 6 and 5 barrer respectively were obtained. Perm-selectivity calculations showed very good results, for CO_2/CH_4 gas pair with 15wt% Zn-Co ZIF loading and 8 bar pressure was 26 which is very promising for industrial applications. For CO_2/N_2 gas pair, perm-selectivity was below industrially applicable value which might be enhanced by further modifications in composition. For this gas pair maximum perm-selectivity with 15wt% Zn-Co ZIF loading and 8 bar pressure was 32.

Acknowledgments

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Chapter – 1

Introduction

An Overview to Membrane Technology and its Applications.

1.1. Background

Membrane processes and their application constitutes a large part of industrialized and develop world. From health to industrial sector membrane process are found everywhere. Many research and developments sectors are working on betterment of existing membrane process and development of new ones. Due to their wide range of applications, usefulness, ease of operation and cost effectiveness these processes find home in almost all of the industrial processes.[1][2]

On industrial scale, membrane process are found in water purification and clarification, industrial waste separation, in food industry for purification of juices, in pharmaceutical industries, for separation of gasses. In health sector, membrane process for hemodialysis is extensively used. Each membrane process has its own merits and demerits and vary in operation conditions depending upon its use.[2]

Membrane Technology has taken great shift in terms of efficient performance and cost effectiveness. These process have grown simpler, have covered almost every field of operation, reduced its impact on environment to a great extent and stabilized the operating conditions. Not limited to this, membrane technology has emerged as a separate subject being taught at post graduate level due to its importance in industries and medicine.[3]

Amongst major industrial setups that employ membrane process for separation includes water treatment plants including Reverse Osmosis and Ultra Filtration, gas separation giants like Linde use gas separation membrane modules to separate and purify gases for industrial use. Such gas separation membrane operations are complex in their design and easy in operation. Development of these gas separation membranes have state of the art manufacturing units with nano scale engineering and design for efficient and commercial scale membrane development. In addition, membrane process are also finding their uses in refineries and fertilizer industries as post reactor treatment units and reactants and products treatment units.[4]

1.2. Science behind the membrane processes.

A membrane separation technique is a mass separation/transfer technique that uses membrane as a semi-permeable barrier which allows one of the component to pass through the membrane and disallow other components from separation thus dividing the feed into two separate components the retentate or the reject (R-R) and permeate or the product (P-P). But it does not necessarily means that permeate is always the product of the industry. Sometimes what is left on the feed side of the membrane is actually the required product of the industry.[4]

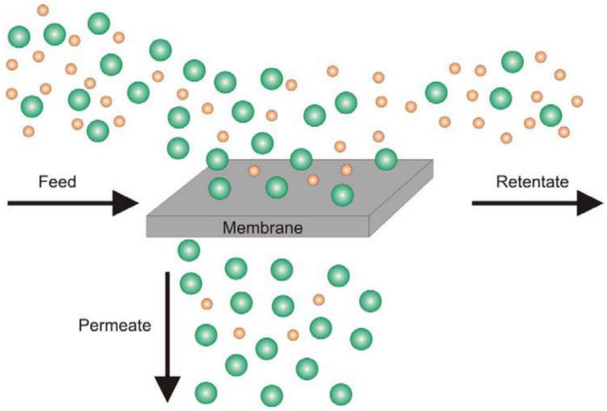

Figure 1: Schematic representation of Gas Separation Operation by Membrane

Mass transfer through the membrane is carried out by one or more of a driving forces acting on the membrane. These forces varies from process to process. For example in gas separation through membrane, pressure is the driving force acting on the membrane. Other forces that can act as driving force are electrical potential in process like electro-dialysis, thermal or concentration gradients can also act on the membrane resulting in separation. [5]

1.3. Types of filtration through membrane.

There are two types of filtration direction in which membrane process can be operated. These are Dead-end filtration and Cross-flow filtration.

1.3.1. Dead-end filtration

Dead-end filtration process in membrane separation techniques is rarely used mostly at small scale operations. This is due to its limitations caused by pileup of retentate or concentration polarization on the surface of the membrane reducing the overall surface area of the membrane. Such processes require frequent cleaning of the membrane module.[6]

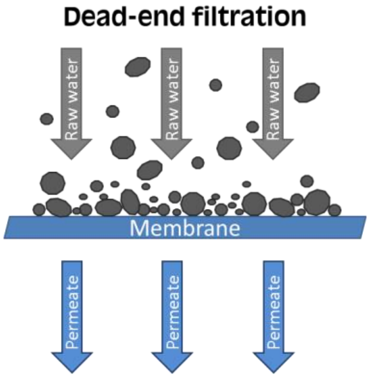

Figure 2: Schematic representation of Dead End Filtration

1.3.2. Cross-flow filtration

This type of filtration is frequently used in membrane separation process because it is less prone to concentration polarization. In this method, feed flows parallel to the membrane surface. Retentate does not pileup on the membrane surface and flows along the feed flow. This process is used in all major industrial membrane separation operations. More over these membranes require less cleaning and long membrane life. [6]

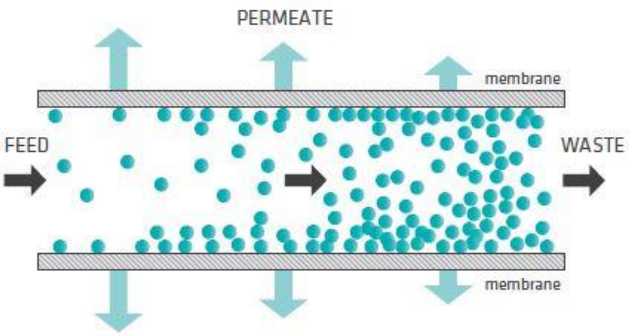

Figure 3: Schematic representation of Cross Flow Filtration

1.4. Classification of membrane.

Membrane are generally classified by:

- Naturally occurring membranes and artificially synthesized membranes.

  These includes:

  - Biological membranes that occur naturally in living beings.
  - Artificially synthesized membranes from organic and inorganic substances.
- Chemical and physical structure of the membranes.

1.4.1. Classification based on structure/morphology of the membrane.

Artificially synthesized membranes includes:

1.4.1.1. Symmetric Membranes.

Symmetric membranes are membranes having same symmetry in terms of morphology, structure and thickness across the membrane area. These membranes are mostly synthesized using single polymer layer. There is no visible division between the layers of the membrane. These are 10-200 micro meter thick and permeation decreases as the thickness increases.[7]

1.4.1.2. Asymmetric membrane

Such membranes are non-uniform across the membrane structure and consists of separately visible layers or chemical composition. Normally such membrane consist of two layers, one thin layer on top which plays central role in separation process and second the thick layer that acts as a supporting agent for the thin upper layer. Usually the thin layer is of the order of 0.1 to 0.5 micro meter and thick layer is 50-150 micro meter. Such membranes have good efficiencies both in term of permeability and perm-selectivity.[8]

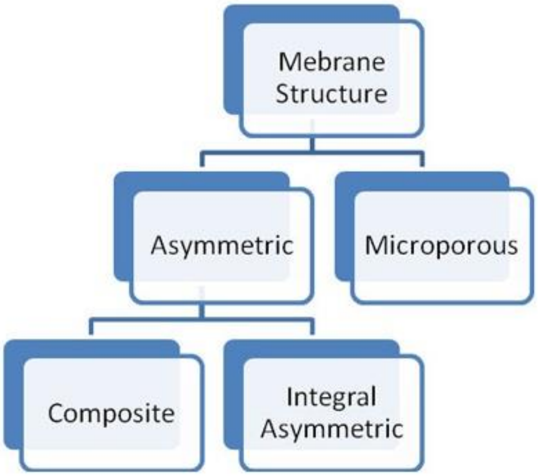

Figure 4: Classification of membranes

1.4.1.3. Composite Membranes

- Skinned Asymmetric Membranes

  Such membranes have two separate layers, the top layer originates from one polymer or element and the lower layer or the second layer originates from a different element and each layer is optimized separately according to separation requirement.

- Skinned symmetric membrane.

  In contrast to skinned asymmetric membrane, these membranes have skinned layer homogeneous to that of the bottom layer supporting it.[8]

1.4.1.4. Electrically Charged Membranes

These are less commonly used ion exchange membranes that are made from swollen gels carrying positive and negative charges.

1.4.1.5. Liquid Membranes

These membranes have high permeation rates and utilize metal ions to transport mass from one end to other.

1.4.1.6. Microporous membranes

For liquid and large particles separation in micro size, microporous membranes are used. These membranes works in the same fashion as that of a common filtration phenomena. Microporous membranes have pore size of the order of 0.01-10 micron. Like molecular sieving effect, these membranes allow particles smaller than its pore size to pass thorough the membranes and retaining the remaining particles from passing down the membrane.

For further understanding of microporous membranes, these membranes are classified into two types based on their physical structure.[9]

- ***Isotropic membranes:*** Such membranes have same isotropy i.e. the size of its pore throughout the membrane structure.
- ***Anisotropic membrane***: In these type of microporous membrane, the size of the pore varies from layer to layer randomly without any strict tend of pore sizes.

1.4.1.7. Thin-film composite membranes

These membranes are semipermeable membranes used in water filtration plants and chemical fuel cells. These membranes are composite membranes i.e. made from two different materials. One layer is top layer of the order of less than 200nm and the second layer i.e. the support layer is of the order of 50 microns. Top layer can be polycarbonate or cellulose acetate and the bottom layer can be polyether sulfone or simple polysulfide.[10]

1.5. Membrane separation processes:

1.5.1. Microfiltration (MF)

Microfiltration is the most widely used separation process in industries and commercial units. Separation range of microfiltration is 0.1 to 10 micron. It is used to separate suspended particles in liquid mixtures. Driving force in this process is pressure gradient that operates at 10-500KPa. This process is usually employed in initial stages of water purification before Reverse Osmosis to remove larger particles that would otherwise clog the RO membrane. These membranes can be synthesized from a number of different materials including CA, PC, PS etc. These membranes can operate in both cross flow and dead end flow filtration while cross flow is more preferred.[8]

Some common application of MF are given below:

- Sterile Filtration
- Clarification processes
- Industrial reject treatment
- Recovery of precious elements from industrial waste water.
- Separation of fruit juices, oils, effluents etc.

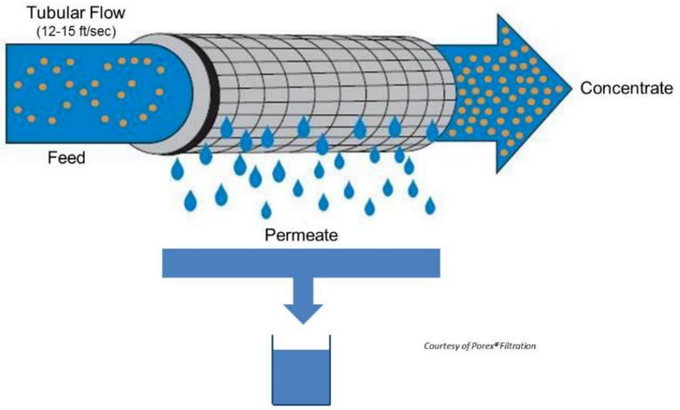

Figure 5: Schematic representation of Microfiltration

1.5.2. Ultrafiltration (UF)

Ultrafiltration is most commonly used where there is a need to separate undesirable impurities from a mixture. It is an intermediate process between NF and MF. Ultrafiltration operates due to difference in pressure gradients on both ends with pressure differentials of 0.1 to 1.0 MPa. The size of UF pores are 0.005 microns. This type of filtration to some extend depends on the charge of the particles but size of the particle is more important.[7] Common UF applications are jotted below:

- Recovery of oils.
- Feed clarifications
- Separation of colloidal materials
- Waste water treatment
- Removal of surfactants from industrial efflux
- In food industry for purification of fruit juices

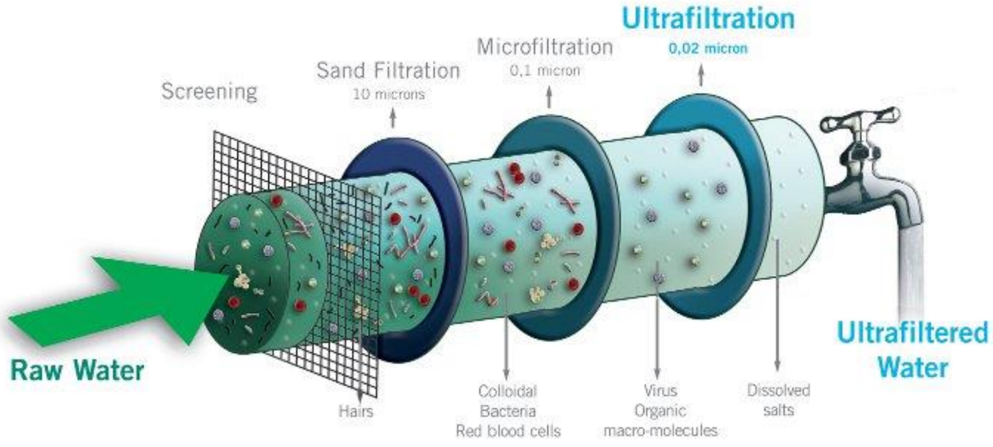

Figure 6: Schematic representation of Ultrafiltration process

1.5.3. Reverse Osmosis

Reverse Osmosis is most frequently used separation operation in water treatment plants and thermal power plants. This is a pressure driven separation process at operates at fairly high pressure 2 to 10 MPa. This process can also separate charged ions from water. Size of RO membrane pores are 0.5 to 1.5 nm.[11]

Common RO application are:

- Separation of ions, bacteria, viruses, salts, proteins and other unwanted nano size particles from the feed.
- For desalination of seawater
- Production of feed water for cooling towers to avoid rusting in towers.
- In metallurgical industry

1.5.4. Nano filtration

This process separates fluids and ions from a feed mixture. NF is nearly equal to RO process in terms of separation but RO separates more fine particles from the feed. Both NF and RO works on pressure difference but NF operates are lower pressure than RO. NF can operate at higher recoveries than RO. In separation of ions and salts, nano-filtration allows some of the salts to pass through the membranes thus not creating complete barrier for feed containing salt solutions. Size of NF pores are of the order of 1-10 nm. This process is much finer than UF and MF but less than RO.[12]

Common nano-filtration applications are:

- Softening of sea and feed water
- Purification of feed streams containing acids.
- In pre-treatment of feed for other separation processes like RO.
- In pharmaceuticals, pesticides and metallurgical industries.

1.5.5. Gas separation

Gas separation process uses membrane to efficiently separate gas mixtures. This technology has developed over time as one of the most significant membrane separation process. This in process dense membrane is used for separation of gases. These membranes do not have pores for separation but works on the basis of diffusion of gases through the membrane. This process works on pressure differential or concentration gradient basis.[13] Some of the common gas separation application are:

- Hydrogen separation and hydrogen recovery
- CH_4 separation and purification.
- Removal of undesired gases from gas mixture
- Air separation
- Helium recovery
- Separation of useful gases from landfill gas discharge.

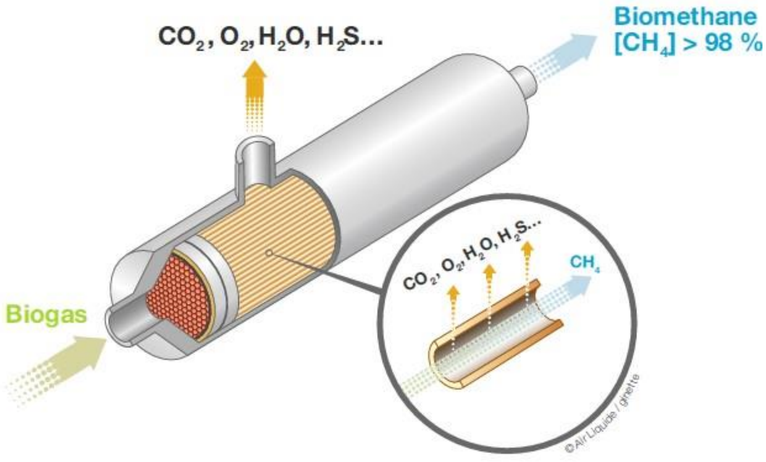

Figure 7: Schematic representation of a Gas Separation Membrane Module

1.6. Comparison between membrane processes vis-a-vis pore size and driving forces:

Sr. #	Membrane Process	Pore size of membrane	Driving force
1	Microfiltration	Symmetric microporous, 100-10000nm	Hydrostatic pressure difference (10-500 kPa)
2	Ultrafiltration	Asymmetric microporous, 1-10nm	Hydrostatic pressure difference (0.1-1 MPa)
3	Nano-filtration	Thin film membranes, order of nm	Hydrostatic pressure difference (9.3-15.9 bar)
4	Reverse Osmosis	Asymmetric skin-type, 0.5-1.5nm	Hydrostatic pressure difference (2-10MPa)
5	Gas separation	Non porous (or porous < 1nm)	Hydrostatic pressure and concentration gradient

Table 1: Comparison of pore size and driving force of different membrane separation operations.

Chapter – 2

Literature Review

This chapter concentrates on summary of research work reported for synthesis, characterization and gas permeation studies of mixed matrix membranes particularly using Zeolitic Imidazole in different polymers.

2.1. Gas Separation by Membrane

Gas separation by membrane technology has gained attraction of industrial processes from around the world in recent past years. Separation complexities and operational difficulties associated with conventional separation techniques like adsorption of solid surface, cryogenic distillation and absorption in liquids have turned researchers to concentrate on more easy, cost effective, environmental friendly and efficient process of gas separation by membranes. Membranes are making their place in most of the gas separation process and in almost all industries with great potential. Gas separation by membrane is already operational in gas processing units, gas separation units, gas purification units and part of other large industrial sectors like fertilizer industries and refineries. This process has not only proved very efficient and cost effective but it is helping developing countries to meet Clean Development Mechanism (CDM) of Kyoto Protocol to reduce carbon foot prints by minimizing energy consumption and reduction of CO_2 release in atmosphere.[14]

A lot of research has been done on membrane used for natural gas processing, nitrogen and air separation and separation of hydrogen from crude gas mixtures. Due to increased threats of global climate change, rise in greenhouse gasses and international conventions on reducing carbon contents from atmosphere, researchers have focused on producing more efficient membranes that can separate CO_2 from air and natural gas. This has created a lot of research space in this field.[15]

From industrial point of view, CO_2 separation by membrane processes has prime importance. Its major application includes separation of CO_2 from stack gases or industrial exhaust gases, from automobile exhausts, for air purification in polluted cities, CO_2

separation from natural gas extraction and pumping units. Successful attempts have been made in manufacturing polymeric gas separation membranes that are in operation. But the technology is still in maturity phase. Research is being carried out to develop more mature membranes that can give significant levels of permeability and perm-selectivity.[16]

Scientists are paving new ways to develop gas separation techniques. Introduction of new materials and methods, new innovations in nanotechnology, refining of existing membranes all has been extensively worked in this ongoing decade. In addition to different technologies, different scientific fields like materials science and technology, chemical and environmental engineering have joined hands in working together for developing new channels for efficient gas separation membrane processes. [17]

2.2. Choice of Material

Material selection is very important for membrane synthesis depending on requirement and separation condition. For example, operations carried out at high temperature and pressure requires materials with high thermal and physical stability. On the other hand some gas separation processes require materials that can withstand chemical reactions and acidic feeds, such processes require membranes materials that are inert and does not react chemically. Additionally, permeability and perm-selectivity greatly depends on choice of material.[18]

Choice of material can be made by keeping in consideration following parameters:

- Perm-selectivity and permeability requirements
- Membrane morphology
- Type of gas separation
- Physical and chemical parameters of feed gas.

Two important parameters that influence gas separation through nonporous membrane are permeability and perm-selectivity. A good tradeoff between permeability and perm-selectivity has to be adjusted as explained by Robeson. Permeability is the rate of diffusion of gases through the membrane while perm-selectivity is the ratio of permeation rates of two gases. Important task for scientists is to adjust a practical balance between permeability and perm-selectivity values.[19]

Among m any materials available for development of gas separation membranes including organic and inorganic, synthetic and natural, polymers have gained attention in recent years due to their flexibility in synthesis, good permeation rates and cost effectiveness.

Polymeric membranes have edge over other materials based on their good permeability vs perm-selectivity relationship. Moreover, polymers are flexible in changing their chemistry. Polymer chains can easily be changed and modified according to requirements by introducing other elements in polymer backbone. Polymeric materials are stable at good ranges of temperature are pressure and introduction of other materials in polymer chains make these materials more stable towards chemical and physical changes. State of polymer changes with change in temperature from glassy to rubbery state. These changes bring changes in permeability and perm-selectivity.[5]

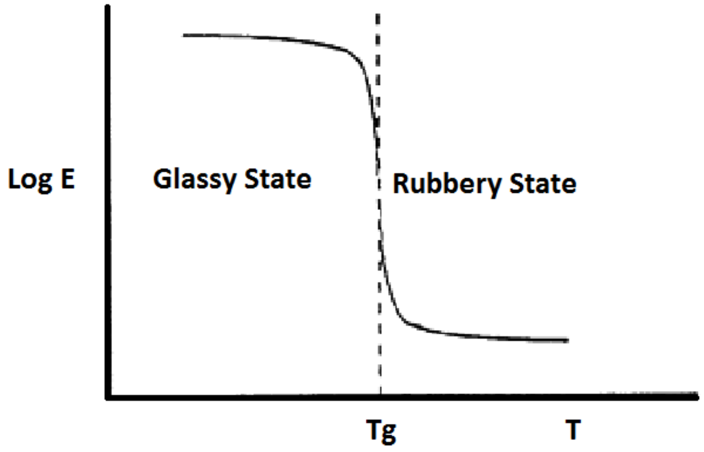

Figure 8: Graph between Log E (Modulus) and Tg (Glass Transition Temperature)

Fig. 8 shows graph of specific volume vs glass transition temperature. As the temperature rises, glassy state of polymer rapidly changes to rubbery state. Area on the left side is glassy while on the right side is rubbery. At line dividing the glassy and rubbery state is the glass transition temperature of the polymer. Both glassy and rubbery polymer shows different mechanical and thermal properties when synthesized into polymeric membranes.

There is a wide range of polymers being studied for gas separation membranes out of with a good number of polymers have made their ways to commercial applications. Polymers are being used both independently and in combinations in composite membranes. Some important polymers that are being researched are numbered below classified on the basis of their nature.[2]

Rubbery Polymers	Glassy Polymers
✓ Poly(dimethylsiloxane)	✓ Cellulose acetate
✓ Amide copolymers	✓ Polysulfone
	✓ Polyimides
	✓ Polycarbonates

Table 2: Important Glassy and Rubbery Polymers Used in Industrial Membrane Gas Separation[1]

Among disadvantages of polymeric membranes are its sensitive synthesis processes, difficult permeability-perm-selectivity tradeoff and difficult handling requirements. Polymeric membranes cannot be used as such and needs different kinds of modules based on application. Increasing permeability and perm-selectivity simultaneously is a difficult task as explained by modified 2008 Robeson upper bound tradeoff line.

Gas separation by polymeric membranes have fairly captured attention of R&D sector. This is because of its promising results and ease of modification. Recent research in polymeric membranes includes blending of polymers with organic and inorganic materials. These membranes are generally termed as mixed matrix membranes. In mixed matrix membranes, polymeric material is blended with a fixed amount of loading material. Recent studies shows single and multi-walled carbon nanotubes, graphene, metal organic framework, zeolitic imidazole framework and many other organic and inorganic loadings are being used to develop mixed matrix membrane giving good results of permeability and perm-selectivity. Moreover, MMMs can be enhanced by other physical and chemical methods such as modifying bond formation between organic and inorganic molecules, increasing or decreasing thickness of the membrane, changing casting temperature of the membrane, and application of a second more selective membrane layer on existing one. All these methods require extensive experimentations and changes in composition.[11]

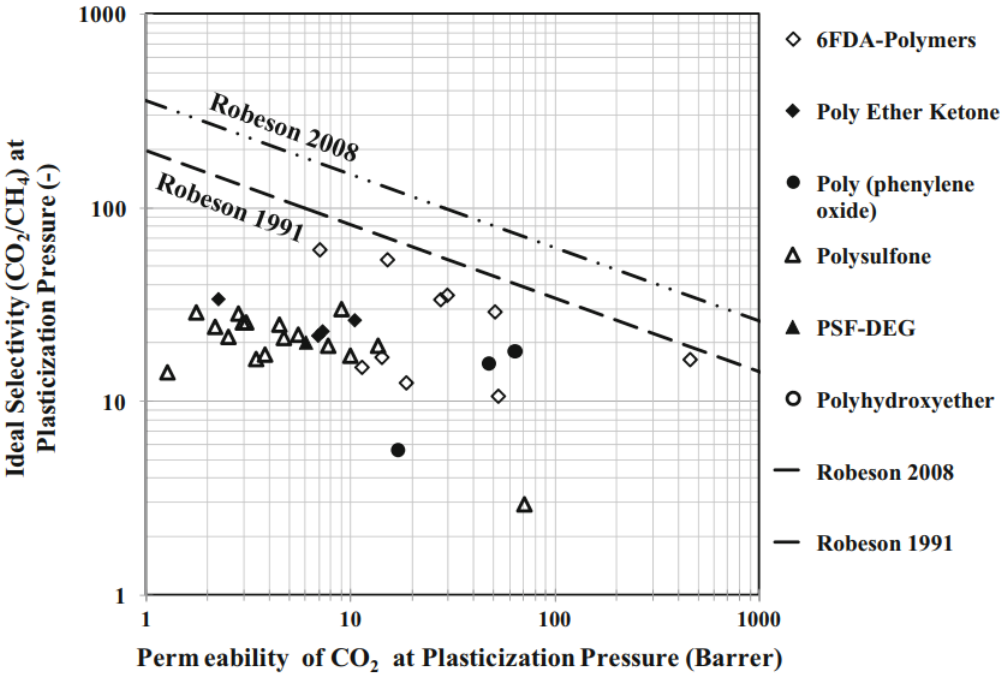

Figure 9: Ideal perm-selectivity (CO2/ CH4) and permeability of CO2 at plasticization pressure for polymeric membranes.

2.3. Membrane Development – Polymer Selection

First thing first – primary requirements of a good polymeric membranes are its good separation properties due to its good physical and chemical strength, ability to absorb gas molecules at high rate of absorption. Important parameters of a good polymer are:

- Resist swelling due to increase in pressure and temperature.
- Easy synthesis of polymer into thin film membranes.
- Good intermixing with loading component and solvent.
- Rubbery or glassy polymer choice is also very important while making decision in selection of polymer.[20]

2.4 Mixed Matrix Membranes

As simple polymeric membranes have limited permeation and perm-selectivity rates thereby cannot reach the Robeson Upper Bound Trade-off. On the other hand, inorganic membrane pose certain limitations in terms of economy, handling and industrial applications. MMMs are intermediate of polymeric and inorganic membranes. These membranes combine characteristics of both membranes into a hybrid approach. Many materials that have good attraction for specific gases depending on the kinetic diameter of the molecule. These materials when incorporated into polymers improve permeation rates and perm-selectivities. These materials include CNT's, MOF's ZIF's, different nanocomponents of carbon etc.[15]

Chung et al. first rolled out excellent properties of mixed matrix membranes for gas separation. They experimented with silicalite by blending it in polymer. As the loading of silicalite in polymer increased, perm-selectivity of the membrane increased. These membranes in comparison of simple polymeric membrane gives very encouraging results but their application on industrial scale still needs some refining. Even though, some MMM modules are already in use at natural gas extraction rigs for separation of sulphur from methane but these membrane have yet to be successfully implemented in every gas separation process. [21]

2.4.1. Adjustment of polymer-filler loading:

Adjustment of quantity of filler loading in polymer is very critical in getting good rates of permeability and perm-selectivity. Generally those polymers are used that give good perm-selectivities at cost of permeability. Such polymers when blended with a specific amount of filler can give considerably better results. Qilei Song et al. experimented Matrimid ® 5182 with loadings of ZIF-8 and Graphene Oxide. His experiments concluded that addition of ZIF-8 and GO markedly enhanced perm-selectivity of Matrimid ® 5182.[22]

2.4.2. Size of the filler

Particles in nano-range provides good dispersion in polymeric solution at casing stage. In membrane morphology, nano-size particles can have better polymer to loading surface structure. Moreover, smaller particles have large interfacial area giving more diffusion of molecules through the membrane. In addition, smaller particles do no agglomerate on the surface of the polymer hence less distraction is offered to gas molecules.[21]

2.4.3. Poor dispersion and agglomeration:

In most of the cases with MMMs, polymer is organic and fillers are inorganic and both have different phases. This causes agglomeration of nano-filler at dispersion and mixing stages. Agglomerated nanoparticles in membrane cause disrupted surface morphology and pores in the membrane surface which increases permeation of gases and decreases perm-selectivity. Such agglomerates can easily be detected by SEM.

2.5 Zeolitic Imidazole Framework (ZIF)

ZIF are new class of fillers that have attracted interest of membrane research scientists particularly in formation of mixed matrix membrane for gas separation. There is a wide range of ZIF's but frequently used ZIF's in polymeric membrane are ZIF-5, ZIF-8 and ZIF-67. Each ZIF has a single metal in its unit linked with imidazole framework. Each ZIF has a fixed size cavity that matches kinetic diameter of some gases including CO_2, CH_4, and N_2. That is why these fillers give good permeability and perm-selectivity values when added in polymers.[23]

2.5.1. Bi-Metallic ZIF

This research work is concentrated in using Bi-Metallic ZIF in polymeric MMM. These ZIF's are new in membrane synthesis and no such work has been done in finding permeation and perm-selectivities of membranes have Bi-Metallic ZIF's. Zn-Co based ZIF is shown in fig 9. [24]

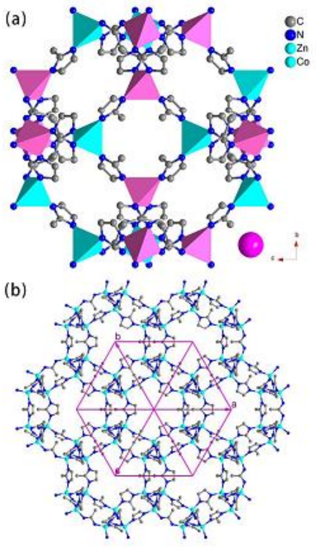

Figure 10: Structure of Zn-Co ZIF Cage

These ZIF's have two metals Zinc and Cobalt arranged in regular fashion repeated alternatively one after the other. The ZIF thus forms a cage like structure with fixed cage size. This size match the size of kinetic diameter of CO_2 molecule. That is why bi-metallic ZIF gives good permeation rates for CO_2.

2.6. Membrane Synthesis

Membrane synthesis process is very important in formation of good quality membranes. Membrane synthesis process varies depending upon type of membrane required and nature of separation needed. Porous and non-porous membranes have different methods of synthesis. Dense, nonporous polymeric mixed matrix membranes in turn have many available methods to synthesize. Some commonly employed methods are given as under:

- Solvent Evaporation Technique
- In-situ polymerization
- Solution-Gelation Method

2.6.1. Solvent Evaporation Technique

Solvent evaporation method is the most commonly used method for preparation of dense non-porous membranes at lab scale. In this method, polymer is dissolved in relevant solvent and stirred overnight for perfect mixing. In case, nano-particles are to be added in the membrane, nanoparticles are dispersed in the same solvent separately overnight and added in the polymeric solution and stirred again before casting. Other aiding instruments can also be used for better mixing like sonication etc.

Liangliang Dong et al. prepeared Pebax and ZIF-8/GO membrane by using solvent evaporation method by dispersing 6 wt% of ZIF-8/GO into polymeric solution and obtained optimum results. They reported that addition of ZIF-8/GO particles into polymer increased permeability of the Pebax. In comparison of standalone pebax, these membranes increased permeability to 191% and perm-selectivity to 174%.[25]

Qilei Song et al. reported ZIF-8 based polymeric nano-composite membrane in which he used Matrimid ® 5218 with ZIF-8 particles. Addition of ZIF-8 markedly increased permeation rates of Matrimid ® 5218 in comparison to simple Matrimid ® 5218 membrane. He reported that addition of ZIF-8 in Matrimid ® 5218 increased permeability of CO_2 from 8.07 to 28.28 (barrer) with 30 wt% loading. On the other hand perm-selectivity of CO_2/N_2 reduced from 22.4 to 17.1.[22]

Advantages and Disadvantages:

1. Advantages:
    - Easy process and practicable at lab scale.
    - Produces good quality membrane that can be tested easily.
    - Loading of nanoparticles can easily be changed and controlled.

2. Disadvantages
    - Less reliable scale for commercial use.
    - Need extensive experimentations.

2.6.2. In-Situ Polymerization

In this method, nanoparticles are incorporated within the polymer matrix by growing monomers into polymer in presence of nanoparticles. This results in intermixing of polymer and nanoparticles by chemical bonds. This method is difficult and relatively less commonly used on lab scale as growth of monomer into polymer does not guarantee successful results.

Junyong Zhu et al. fabricated MMM by in situ polymerization of quaternized polyethylenimine and soft nanoparticles that were then quaternized with bromoethane in polyethersulfone. It resulted in a novel method of developing MMMs that successfully grew monomers into polymers with covalent bonding between polymer and nanoparticles functional group.[18]

Rijia Lin et al. developed MMM by in situ polymerization of MOF with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride. They obtained excellent interaction of macro size MOF and polymer chains. They were also able to remove interfacial voids by control growth of polymer with MOF particles.[15]

Jiafeng Yu et al. prepared Pd-Zeolitic dense membrane for hydrogen separation by in-situ polymerization. Due to difficult trade of between permeation rates and thickness of membrane, they used in-site technique to repair defects in membrane. It resulted in thin membranes with high permeability rates of hydrogen. The growth of zeolites in membrane defects helped in maintaining the permeation-thickness tradeoff. They reported 91% hydrogen recovery from hydrogen-nitrogen gas mixture.[26]

Yue Zhang et al. prepared polyolefin membrane by in-situ chlorination graft polymerization. In-situ introduction of chlorine radicals in polymer layers helped in capturing hydrogen molecules. They reported a uniform and dense membrane with high permeation rates for hydrogen.[9]

Advantages and Disadvantages of In-situ polymerization.

1. Advantages
    - Thermodynamic reinforcement
    - Surface free of voids and contaminants
    - Provides good surface adhesion for any kind of loadings
2. Disadvantages
    - It causes difficulty in growth of polymer with inorganic particles.

2.7. Gas Separation Properties of Mixed Matrix Membranes

A number of parameters influence permeation of gas through polymeric mixed matrix membranes. In general terms, permeation of gas through MMM depends of Diffusivity (D) and Solubility (S) of the membrane. The relation is as under:

$$\text{Permeability} = D \times S$$

Generally permeability is taken in the units of barrer.

Other parameters that can influence diffusivity and solubility of polymeric membrane are addition of another polymeric material or addition of organic/inorganic particles/filler of nanosize such as ZIF, MOF, CNT's or other nanoparticles. These particles can contribute in polymeric membranes by:

- Incorporation of filler in polymer changes the polymeric chemistry by attaching itself to chains of the polymer thereby altering the structure of the polymer. This introduce free volume elements in the polymer that acts as a channel to diffuse gas molecules gown the membrane thickness.
- In case of inorganic fillers, functional groups can chemically interact with polymer to create covalent bonds with polymer chain. This attract gas molecules due to bond interaction. This readily increases permeability of polymeric mixed matrix membranes.[27]

Addition of Zeolitic Imidazole Framework (ZIF's) or Metal Organic Framework (MOF's) has introduced new grounds of preparation of polymeric mixed matrix membranes. Many such studies have been carried out by using different kind of ZIF's and MOF's. Such nanoparticles have significantly enhanced permeabilities and perm-selectivities of mixed matrix membranes.[28]

Several success cases have been reported for good permeability and perm-selectivity rates using polymeric mixed matrix membranes by addition of ZIF's which is related to the work presented in this thesis. Some of them are summarized below:

Yohannan Subin Sabilon et al. prepared Polyamideimide (PAI) MMM by adding ZIF-8 and carbon molecular sieves as fillers. He reported preparation of ZIF-8 and CMS in laboratory. Membrane was prepared by phase inversion method and presence of nanoparticles was tested by characterization using SEM, TEM and XRD. Filler loading of 1%, 2% and 3% by weight was added in PAI. Mechanical testing showed increase in strength of mixed matrix membrane. FTIR and other characterization studies represented good morphology and even distribution of particles in the membrane structure.[29]

Hamid Reza Amedi et al. reported synthesis of Aminosilane-functionalized ZIF-8/PEBA mixed matrix for gas separation. In this study carbon dioxide was separated from methane by using organic nano-fillers of ZIF-8. He prepared a 40 micron thick membrane by addition of 40 wt% loading of ZIF-8 in polymer. It resulted in membrane with uniform morphology and surface structure which was characterized by various techniques including XRT, FTIR, DLS and BET. He reported increased permeability by addition of ZIF-8 as compared to pure polymer membrane. Permeability testing gave 250 barrer permeability for carbon dioxide and perm-selectivity of 16.[30]

Shuwen Yu et al. reported carbon dioxide separation from nitrogen by using polyamide/ZIF-8 mixed matrix membrane. By in-site monomer growth to polymer in presence of hybrid ZIF-8 nanoparticles resulted in less defect free thin film nanocomposite membrane as characterized by FTIR, SEM and XPS. TFN membrane exhibited both high perm-selectivities and permeabilities by achieving Robeson upper bound curve.[31]

Mehtap Safak Boroglu et al. reported preparation of Matrimid/ZIF-12 mixed matrix membranes by solvent evaporation or solution casting method. He used commercially available Matrimid and added (0, 10, 20, 30 and 40) wt% of ZIF-12. Resulted membrane was characterized by XRD, SEM, FT-IR, BET and TGA. In continuous phase, excellent dispersion of ZIF-8 particles was obtained. Gas permeation experiments were obtained using hydrogen, carbon dioxide and methane. Up to 20 wt% loading of ZIF-8, the permeability of gases showed increasing trend and decreased till 40 wt%. However at higher loadings greater than 20 wt%, perm-selectivity of both gas pairs increased. The separation factor for carbon dioxide-methane gas pair was 66.70 and 212.00 for hydrogen-methane gas pair. All gas permeation experiments were conducted at 4 bar pressure and 25^{o} C temperature.[32]

Shoichi Hasebe et al. prepared polymeric membranes containing silica nanoparticles for gas separation. For carbon dioxide separation from nitrogen, nano-spaces created by silica in polymer aided in high permeation rates with compromise on perm-selectivity of gas pair. He added 25 wt% silica particles in polymer to produce mixed matrix membrane. Permeability achieved was 1920 barrer while perm-selectivity was 23. They used Maxwell model for permeability calculation before experimental testing. Surface morphology, functional group analysis and other parameters were verified by SEM, XRD and FTIR.[16]

Ali Ehsani et al. reported gas permeability through ZIF-11/Pebax® 2533 mixed matrix membranes. They synthesized ZIF-11 nanocrystals and incorporated them in Pebax with loading ranging from 10-70 wt%. For permeation testing, H_2, N_2, CH_4 and CO_2 were used. At filler loading of 10 wt%, the membrane became rigid and permeability reduced. At higher loading values greater than 40 wt%, rigidity reduced and permeability increased. Highest perm-selectivities were obtained at 50 and 70 wt%. Permeability obtained was around 400 barrer and perm-selectivity was at an average of 12. TGA and SEM showed excellent interfacial adhesion and surface morphology.[20]

Susilo Japip et al. reported synthesis of Polyimide-ZIF-71 based MMMs for gas separation. Gases used were H_2, O_2, N_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. ZIF-71 particles were synthesized at lab scale and were incorporated with loading percentage of 20 wt% in 6FDA-Durene polyimide polymer. Final membrane resulted in uniform and agglomeration free membrane. Addition of ZIF-71 in polymer helping in reducing plasticization of membrane and increased overall perm-selectivity of the membrane. For CO_2/CH_4 perm-selectivity was reduced from 16 to 12 while permeability increased. Membrane was able to bear operation pressure of 30 atm. With increase in pressure, permeability rose from 56 barrer to 371 barrer. For characterization and verification, PLAS and sorption studies were carried out. PLAS showed that increase in permeation was due to increase in diffusion of gas molecules aided by ZIF-71 nanoparticles.[28]

2.8. Conclusion from literature review

Although a lot of research has been reported for synthesis of Cellulose Acetate based mixed matrix membranes for gas separation using ZIFs and MOF, following gaps have been identified on with research needs to be performed

- Use of Bi-Metallic ZIFs in glassy polymers.
- Enhancement of Permeability values
- Enhancement of perm-selectivity values
- Improvement in mechanical properties of membranes i.e. strength

Chapter - 3

Experimental Methods

This chapter focuses on synthesis of mixed matrix membrane using carefully selected materials and methodologies.

3.1 Selection of Materials

Careful selection of material is very important step towards successful synthesis of membrane. In this research, materials were selected based on thorough literature review and requirements for gas separation.

Sr. No.	Materials	Source	Primary Information
1.	Cellulose Acetate	Sigma Aldrich	MW = 50000
2.	Acetone	Sigma Aldrich	Purity = 99.9 %
3.	PolyEthylene Glycol	Sigma Aldrich	
4.	Zn-Co based Bi-Metallic ZIF	Borrowed from peer	Freshly synthesized
5.	Carbon Dioxide	Rehmat Gas (Pvt.) Ltd.	Food Grade, 99.9% pure
6.	Nitrogen	Rehmat Gas (Pvt.) Ltd.	Purity = 99.5 %
7.	Methane	Rehmat Gas (Pvt.) Ltd.	Purity = 99.5 %

Table 3: Material list, source and primary information.

3.2 Membrane Synthesis

Membrane synthesis is the most difficult yet most important stage in membrane technology. In this research, synthesis of Cellulose Acetate, Zn-Co Based mixed matrix membrane consisted of following stages:

3.2.1. CA/ZIF/PEG solution preparation

We employed solution casting by solvent evaporation method to synthesis membranes. For a single membrane preparation, a fixed amount of acetone, depending on size of the petri dish and thickness of the membrane required, was taken in media bottle. Part of this acetone, let say 1/4th was taken in another media bottle for suspension of ZIF particles. 15 wt% (of acetone) cellulose acetate was added in acetone. Then 10 wt% (of cellulose acetate) PEG was added. Addition of PEG is necessary because it helps in reducing the brittleness of membrane. Solution obtained was stirred overnight at 650 rpm on hot plate magnetic stirrer. On the other hand, freshly prepared Zn-Co ZIF as synthesized was taken 20 wt% of cellulose acetate and dispersed in 1/4th of the acetone reserved from polymeric solution acetone. The suspension was stirred overnight to complete suspend the ZIF particles in acetone.

After 24 hours, ZIF suspension in acetone was added into polymeric solution in stages and at each stage, the polymeric solution was stirred for 1 hour. Whole process was complete in 4 stages. To conform complete suspension of ZIF particles in polymeric solution, sonication was performed on final solution for 1-2 hours. The whole process was carried out at room temperature and normal atmosphere.

3.2.2 Membrane Casting and Drying

After complete stirring and sonication, solution was left idle for 10-15 min to let any possible bubbles set that might have otherwise created holes in the membrane. Petri dishes with six inch diameter were taken for casting membrane. Solution was poured carefully in the petri dish without splashing. Minor splashes in petri dish can introduce bubbles due to high viscosity of the solution. Casted film in petri dish was kept in room temperate in a room free of air currents for initial evaporation of acetone. Acetone evaporated in about 60 min to 90 min and thin film of membrane was obtained. To completely remove any residual solvent in membrane, it was placed in vacuum oven at 40^{o}C for 2-4 hours. High temperature in vacuum oven introduced brittleness in the membrane and difficulty in handling and testing stages.

3.3. Gas permeation and test system

For gas permeation experimentation, PHILOS Permeation Test System was used. It consist of a central membrane module, whose one end is attached to feed gas inlet and other end takes two outlets, one to permeate and other to retentate. Pressures of inlet and outlet streams, flow rates and change in pressure all can be monitored on screen.

Membrane module consisted of a ceramic disc on which membrane was placed. The disc was mounted on module casing which was sealed with gaskets. Membrane was trimmed to the size of disc and placed on it carefully to avoid any possible cracks or rupturing of the membrane film.

To study gas permeation, PHILOS Test system was operated without aid of Gas Chromatogram when single gas was tested. For mixed gas permeation, Test System was attached with GC to study permeation of gases with 10/90 ratio, where 10% being CO_2 and 90% either CH_4 or N_2. During experimental stages, volume was constant and pressure was from 1 bar to 8 bar. Each reading was taken after an increase of 0.5 bar pressure. Each gas was passed separately at one time from the module and changing trends in permeation was measured at each increasing interval of pressure. Change in pressure (ΔP) was taken as standard for pressure readings. Enough time was allowed before reading to let the membrane attain equilibrium in terms of diffusion through the membrane.

When feed was shifted from one gas to the other, ventilation valve was released to let the residual gases purge from the pipelines. Alternative gas testing also helped in avoiding plasticization of the membrane. All experimentation was performed with commercially available pure gases with purity greater than 99%.

Principle law that explains diffusion of gas molecules through mixed matrix membrane is Fick's Law of Diffusion. It was derived by Adolf Fick in 1855[33]. Under condition of steady state, Fick's law relates diffusive flux with concentration gradient. In actual, flux travels from high concentration regions to low concentration region. In case of diffusion of gases, gas transfer from high pressure region to low pressure region.

Mathematically, Fick's law is represented as;

$$\mathrm{J} = -\mathrm{D}\,\frac{\mathrm{d}\varphi}{dx}$$

For permeability calculation in barrer, following relation was used derived from solution diffusion model[6]:

$$P = \frac{Q * L}{\Delta P * A}$$

Here;

Q is the volumetric flow rate measured in ml/min, A is membrane area i.e. area of the ceramic disc measured in m^2, L is the thickness of the membrane measured in meter and ΔP is the change in pressure measured in bar.

The perm-selectivity of membrane is defined as ratio of permeability of one gas to other. For two gasses A and B, perm-selectivity can be mathematically represented as:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

Here;

P_A is the permeability of gas A and P_B is the permeability of gas B. Both are measured in Barrer. In this research, P_A was CO_2 and P_B was N_2 and CH_4 in both gas pair cases.

3.4. Gas Permeation Rig Equipment Setup and Instrumentation

Philos Gas Permeation Rig used for permeation testing works both on single gas permeation testing and dual gas permeation testing when attached to Gas Chromatogram. Gas permeation rig setup and instrumentation is shown below.

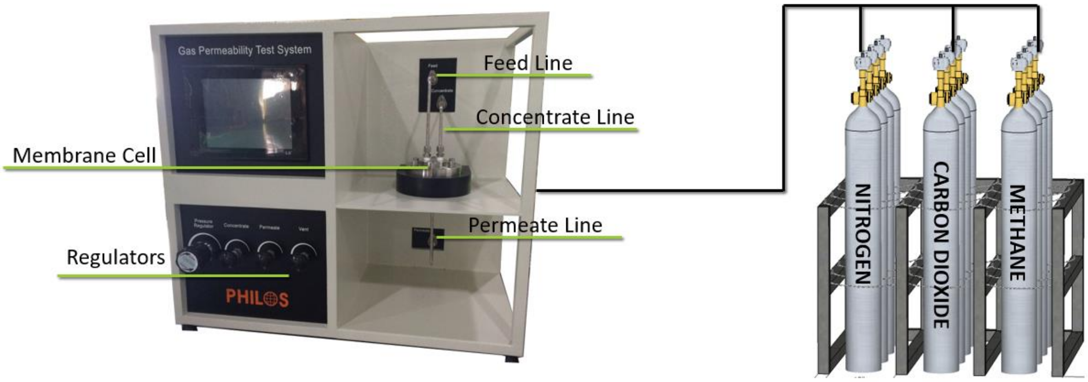

Figure 11: Gas Permeation Rig Setup

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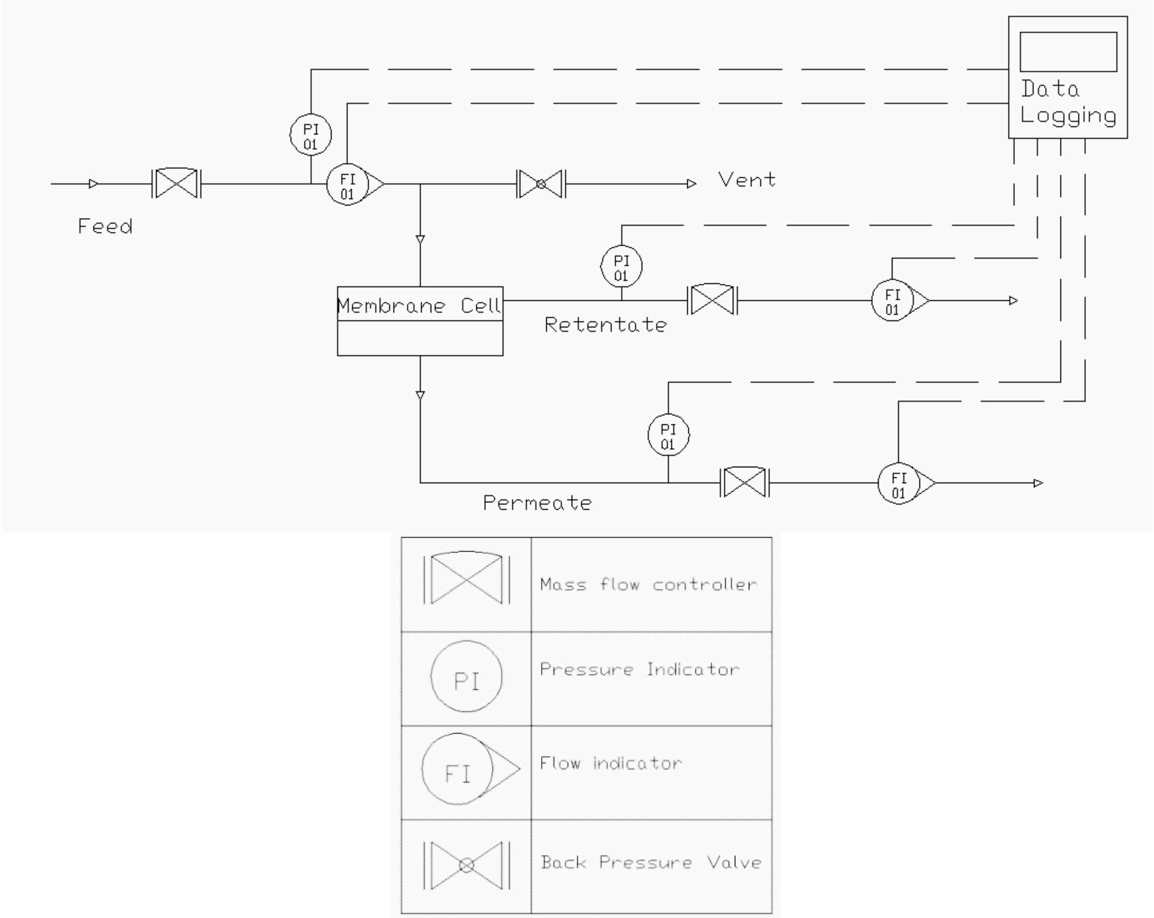

Figure 12: Gas Permeation Rig Instrumentation

Chapter - 4

Experimental Methods

This chapter includes characterization performed to study the synthesized membranes.

4.0. Characterization techniques

4.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is one of the most reliable characterization technique to study morphology, topography and crystallography. Nano-sized magnification helps in attaining insights of the membrane structure and interaction of polymer with filler. Both surface and cross section of the membrane can be analyzed. Possible pore in dense membrane, agglomeration of filler particles, irregularities in morphology and layering of polymer all can be identified by different levels of magnification. SEM as a standard characterization technique was used in this research to conform non-porosity of membrane and any possible existence of agglomerates of filler in membrane. [34]

4.1.1. Mechanism of SEM

In scanning electron microscopy, membrane is first made brittle and easy to crack by using liquid nitrogen. Membrane piece is placed in magnification compartment. A high energy electron beam is focused on the membrane depending on the heat bearing properties of polymer. Some polymers degrade upon dissipating electron beam and burn away making higher magnification impossible. Electron scattered and bouncing back from the membrane surface retunes to the signal collector where signals are turned into image. This image is created by backscattered electrons. They mostly divide the phase of the membrane while SE are more helpful in giving topography and morphology. Falling electrons on the surface of the polymer creates X-Rays that are result of the electron interaction with the electrons of the membrane sample.[35]

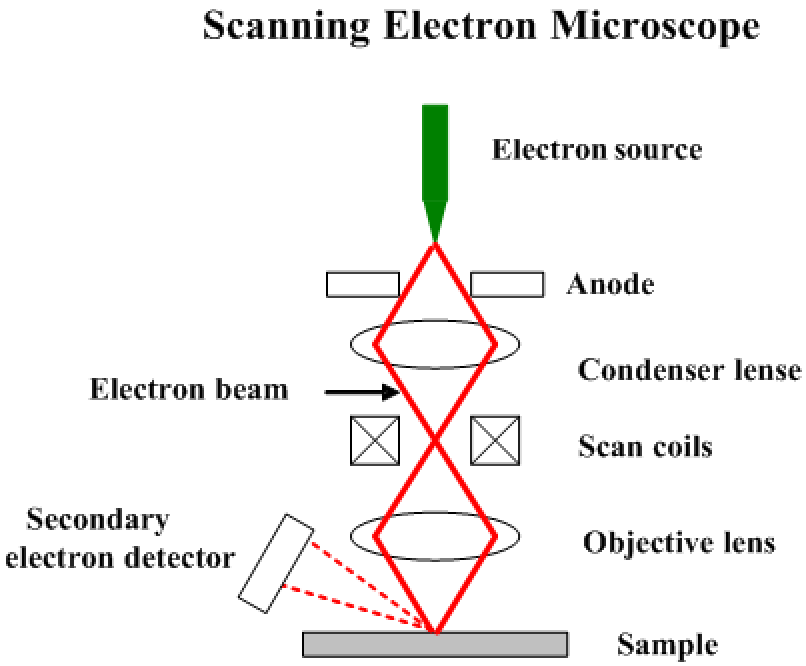

Figure 13: Working principle of Secondary Electron Microscopy

4.1.2. SEM outputs:

SEM is useful in finding morphology of the membrane, presence of crystal structure of the membrane and fillers, and topography of the membrane. SEM is equally useful and capable of studying surface and cross section of the membrane. SEM can give information about the size of fillers, thickness of layers, arrangement of atoms and size of pores if present. Usually SEM can focus up to 20000 times.

4.1.3. Parts of SEM

SEM consists of an electron gun from where electrons are bombarded on membrane sample. Second, electron lenses give direction to the electrons. Sample stage is where sample is placed in SEM. Detector is part of SEM which collects X-Rays or reflected electrons from the membrane. Data output devices give results of the SEM on display screen.

4.2. X-ray diffraction (XRD)

X-Ray Diffraction of commonly known as XRD is a standard characterization technique to find out crystalline nature of the sample. XRD uses X-rays to study crystalline nature of the sample at atomic level. This method is equally good in explaining atomic packing of the sample. This works on the same principal as retina detector works. Like every individual has one's own kind of retina, each crystal sample is unique and separate from other. XRD targets the sample and give peaks that can be identified by matching with the standard peaks of the materials already available.

4.2.1. Working Principle

This technique uses X-rays monochromatic constructive interference to generate monochromatic radiation. At cathode rays tube, rays are developed. These rays by using focusing lens focus on the material to be tested. As the arrangement of crystals is specific for specific crystal with plane angles geometry, the rays are refracted back from the planes to detector while the other rays are transmitted as such. The difference between the bombarded rays and the rays refracting back helps in detecting the crystalline nature of the material.

The working principle of XRD is Bragg's Law, by which the rays are focused on the sample and the identification of crystalline structure is possible as [36]

Bragg's Law[37]; basis of XRD working principle:

Mathematical Formula: $n\lambda = 2d \sin\theta$

Here;

n = order of diffracted beam

λ = wavelength of rays

d = distance b/w atoms, it is used to identify type of crystalline material present in the sample as distance varies from material to material

4.2.3. Instrument parts

XRD instrument has following major parts:

- X-ray bombarding tube
- Sample holding part
- X-ray detection unit

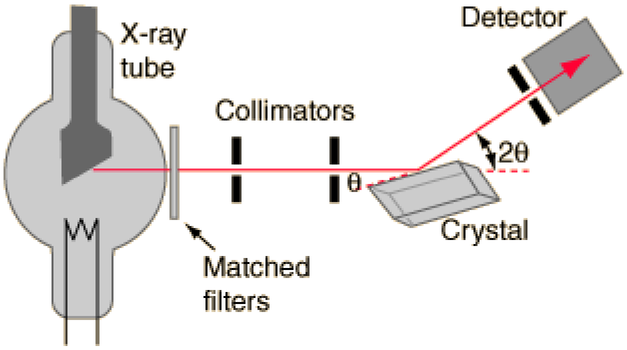

Figure 14: X-ray Diffraction Principle Diagram.

4.2.4. Applications

XRD is useful in:

- Finding impurities in the sample
- Measuring size of the material at unit level
- Finding nature of the crystalline material

4.3. Thermo-gravimetric Analysis (TG)

Thermo-gravimetric analysis or TGA helps in determining change in weight of the material with gradual increase in temperature over time. This technique can also study material isothermally over time change in weight of the material. TGA can work both in inert atmosphere and in presence of gases was required. Mostly inert atmosphere is used while studying this method. In case, oxidation is required to slow down, oxygen can be used to create atmosphere. [38]

4.3.1 Working Principle

TGA working principle is very simple. A pan containing sample under observation is placed in a furnace vacuumed by an external pump. If environment is required, air, He, Ar or N_2 can be used. The furnace temperature is monitored and heated at constant rate.

Material sample under test passes through many physical changes including absorption, desorption, oxidation, evaporation, decomposition, and sublimation. These processes introduces rapid and visible changes in the sample. Hence thermal stability of material and kinetics related with it are easily studied.

4.3.2. Instrumentation of TGA

TGA is a simple analytical technique and consists of a;

- Well calibrated and sensitive microbalance that can easily detect minute changes in weight.
- A furnace, well insulated to avoid thermal leakages and attached to a vacuum.
- Temperature monitor and recorder to plot graph isothermally and temperature change vs weight loss.
-

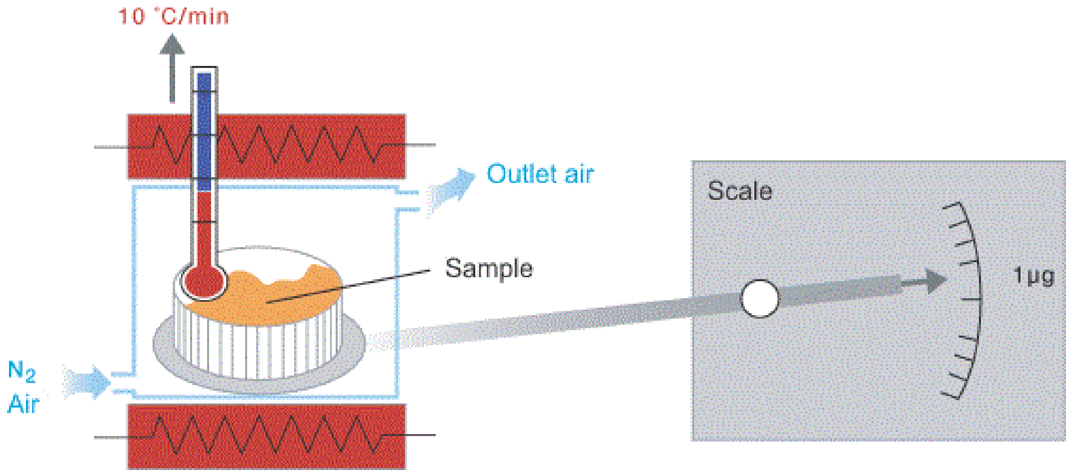

Figure 15: Thermogravimetric Analysis Working Principle.

4.3.3. Uses of TGA

TGA can be used to study:

- Thermal stability of the material
- In studying kinematics of the material
- The composition of the material under test

4.4. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy or FT-IR is a standard analytical technique. It is called Fourier Transform because it uses Fourier transform mathematical model to study the spectrum of light. It helps in studying type of chemical bonding in the material and functional groups of different elements in compound. It uses infrared band gap of emission/absorption of all kinds of sample. This technique is flexible for both qualitative/quantitative and organic/inorganic sample. That is why it is a popular technique in characterization studies.[39]

4.4.1. Mechanism of FT-IR

In FTIR technology, infrared radiations are used to study the sample. Radiations emitted from the source are partially absorbed into the sample and partially transmitted through the sample. The spectrum thus absorbed and transmitted gives FTIR spectrum in range of 4000 to 400 cm^{-1}. Spectrum obtained in this range gives indication of type of sample according to standard values of each type available in the literature.

4.4.2. Parts of FT-IR spectrometer

It consist of following major components:

- Point source from which radiations emits.
- Sample point where sample is hold in chamber.
- Radiation detection meter and display unit

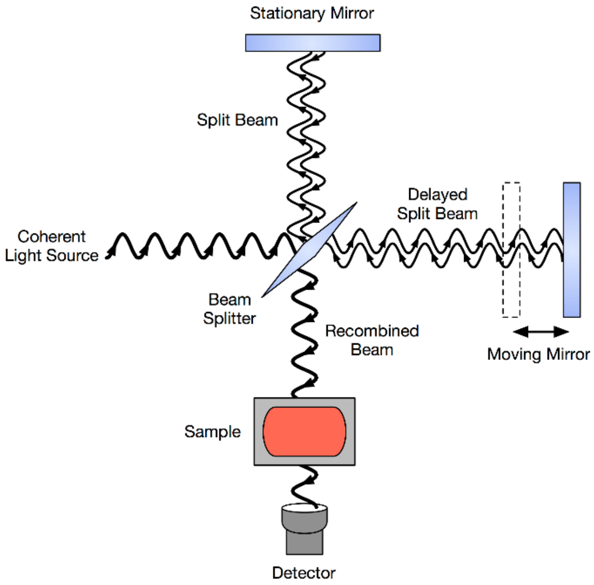

Figure 16: FT-IR Spectrometer Schematic Diagram.

4.4.3. Uses of FT-IR

It is used for following purposes

- Functional group identification
- Study of bonding and functional groups
- Identification of anonymous materials
- Qualitative and Quantitative analysis

4.5. Mechanical Testing

For materials that need to work or operate under high pressures and stresses, mechanical testing is used to conform their physical stress bearing properties. In this method, sample is tested under gradually increasing stress unless it reaches its rupture/break point. This determines its pressure/load/stress bearing capacity. It gives stress strain curve, tensile stress over strain curve and determines young's modulus. Ultimate Tensile Strength (UTS) is the basic test conducted in this method.[40]

4.5.1. Operation

Original length of the material is known. The sample is subjected to stress and change in length is measured due to elongation in the sample. Due to elongation, the sample shrinks in cross section thus reducing its strength. The sample is stretched till the fracture point. At this point final length is measure and change in length is noted. Graph is plotted accordingly.

4.5.2. Instrumentation

Apparatus consists of a load cell in which sample is kept. Moving cross head applies stress on the sample. Other head is fixed to a point. Base and actuator is at the bottom.

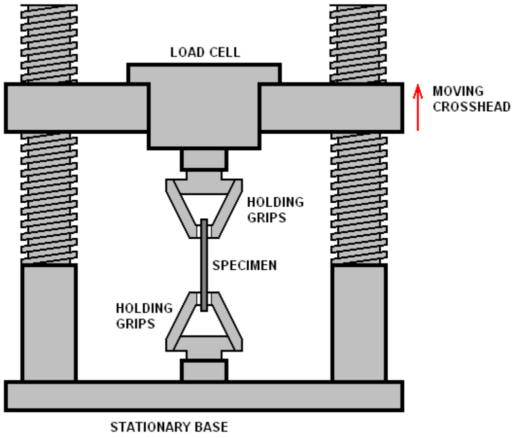

Figure 17: Tensile Testing Apparatus Diagram.

Chapter - 5

Results and Discussion

This chapter includes results of all characterization techniques and gas permeation experiments performed on membrane.

5.1. Thermal Gravimetric Analysis:

5.1.1. Experimentation:

Weighted samples (Approx. 3mg) of membrane and ZIF particle sample were taken in aluminum pans in presence of nitrogen atmosphere. Temperate was increased from 10°C to 500°C. Values were noted after every minute with an increase of 10 °C per minute. Flow of gas in the chamber was kept constant at 80-100 ml/min. Same experiment was obtained for all three samples of Cellulose Acetate / PEG membrane, Cellulose Acetate / PEG / Zn-Co ZIF membrane and Zn-Co ZIF particles.

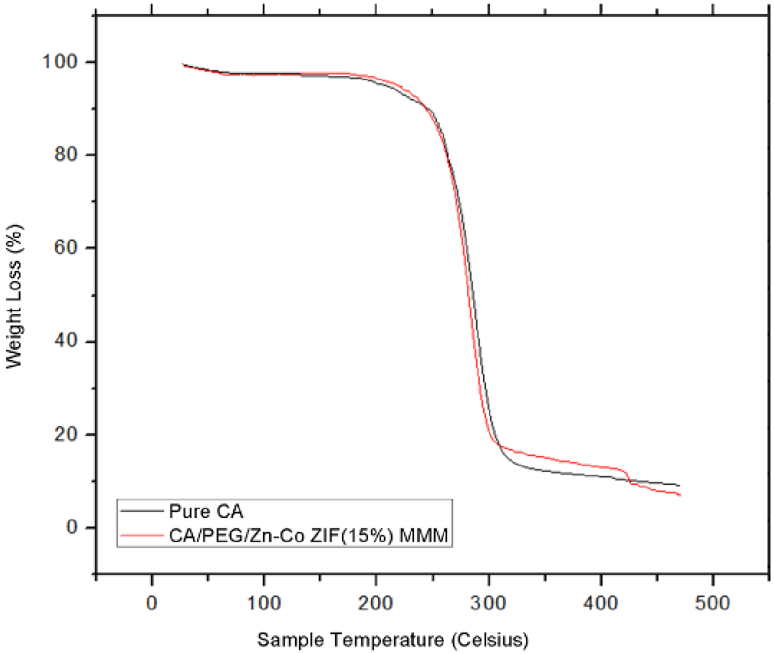

Figure 18: Plot of TGA showing curves of Weight Loss (%) vs Temperature for CA/PEG and CA/PEG/Zn-Co ZIF MMM.

Figure 18 illustrates TGA weight loss % versus temperature curves. Two curves are obtained one for CA/PEG sample and other for CA/PEG/ZIF membrane. For CA/PEG curve, sample starts to lose weight at around 250^{o}C. At roughly 340^{o}C process of final decomposition starts. Most of the weight is lost between temperatures of 230^{o}C to 310^{o}C. On the other hand, CA/PEG/ZIF membrane is more stable towards change in temperature. Visible weight loss initiates from 260^{o}C which is greater than CA/PEG membrane and final decomposition initiates from 360^{o}C which is much greater than CA/PEG membrane. Greater stability of CA/PEG/ZIF membrane is due to better interaction of polymer and ZIF particles. This provides stabilization to the polymer matrix thus making polymer backbone more rigid and resistive to temperature changes.

In case when different loadings of ZIF are added in membrane. With increase in ZIF loading, decomposition temperature of polymer remained same while increased amount of ZIF resulted in increased final weight % left as residue. Decomposition of Cellulose Acetate completed at 390^{o}C. This implies that CA/PEG/ZIF mixed matrix membranes are operable at temperature ranges within 300^{o}C. After this temperature decomposition begins resulting in bigger voids causing increase in permeability and rapid decrease in perm-selectivity of membrane.

5.2. Scanning Electron Microscopy Results Analysis

To study surface and cross section morphology, structure and incorporation of filler in membrane, SEM analysis was carried out using JEOL JSM-64900 electron microscope was used. Two different samples, one with CA/PEG membrane and other CA/PEG/ZIF mixed matrix membrane was carried under test. Images obtained at varies magnifications showed that in both cases membrane was complete dense and no pores were observed at magnification up to x20000. In case of CA/PEG/ZIF membrane, surface analysis showed smooth morphology with good interaction of CA and ZIF particles. No agglomeration of ZIF was observed on the surface. In cross section analysis, ZIF particles are evenly distributed throughout the cross section with no voids or channels. In addition no pores were observed in the membrane.

CA/PEG/ZIF membrane showed uniform and excellent blended morphology both on surface and in cross section till 20 wt% loading of ZIF particles. Further increase in ZIF particles resulted in agglomeration of particles are various places on membrane surface. These agglomerated nono-cakes of ZIF offer hindrance to transport of gases through membrane thereby decreasing permeation rates of gases.[41] Well below 20 wt% membrane was homogeneously blended and uniform in morphology conforming controlled high permeation rates through membrane.

Figure 19a and 19c illustrates cross sectional and surface images of CA/PEG and CA/PEG/ZIF mixed matrix membranes taken by SEM. In both the cases membrane were completely dense and no indication of pores were observed. In MMM imaging, pore free surface and cross section were observed. Cross section of CA/PEG/ZIF showed through intermixing of CA and ZIF particles throughout the cross section. This resulted in creation of free volume elements that aid in diffusion of gas molecules down the membrane thickness. Cage like structure of ZIF particles present in polymer layers across the membrane also acts like free volume elements fixed to their points that attracts gas molecules with kinetic diameter equal to the size of their cages. This greatly enhanced the permeability of gas molecules as compared to simple CA/PEG membrane.

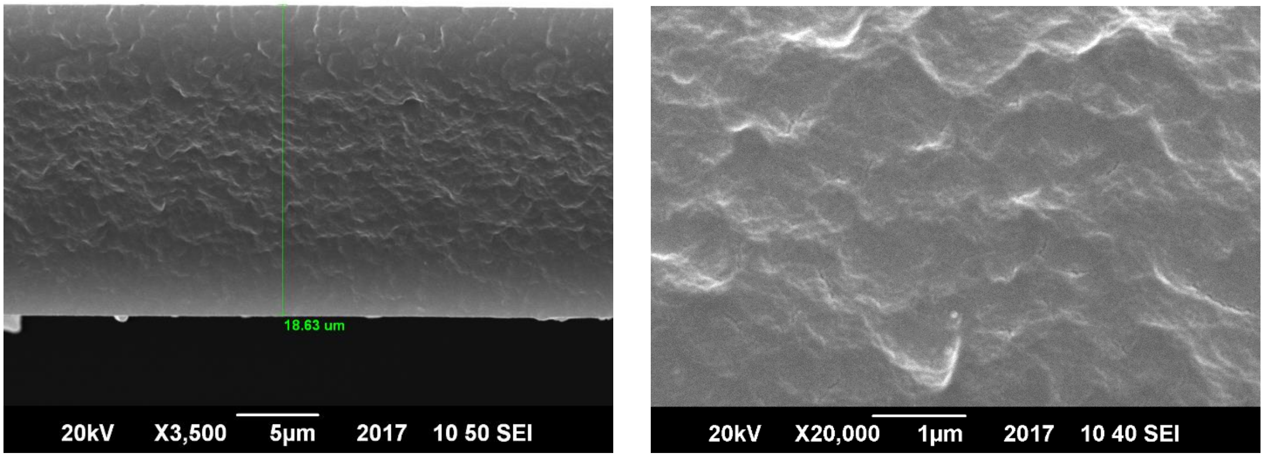

Figure 19a: Zn-Co ZIF/CA/PEG Cross Section view at different magnifications

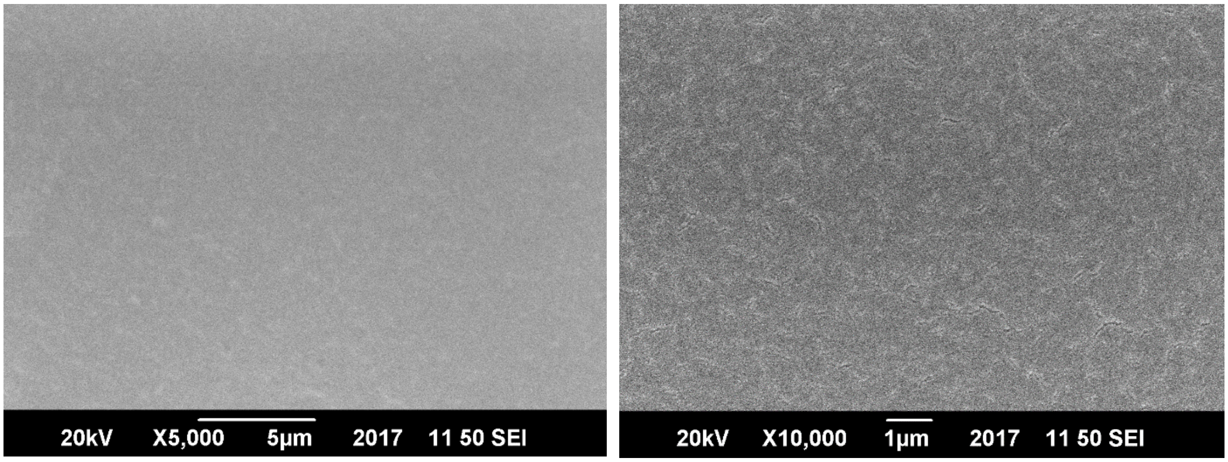

Figure 19b: Zn-Co ZIF/CA/PEG surface view at different magnifications.

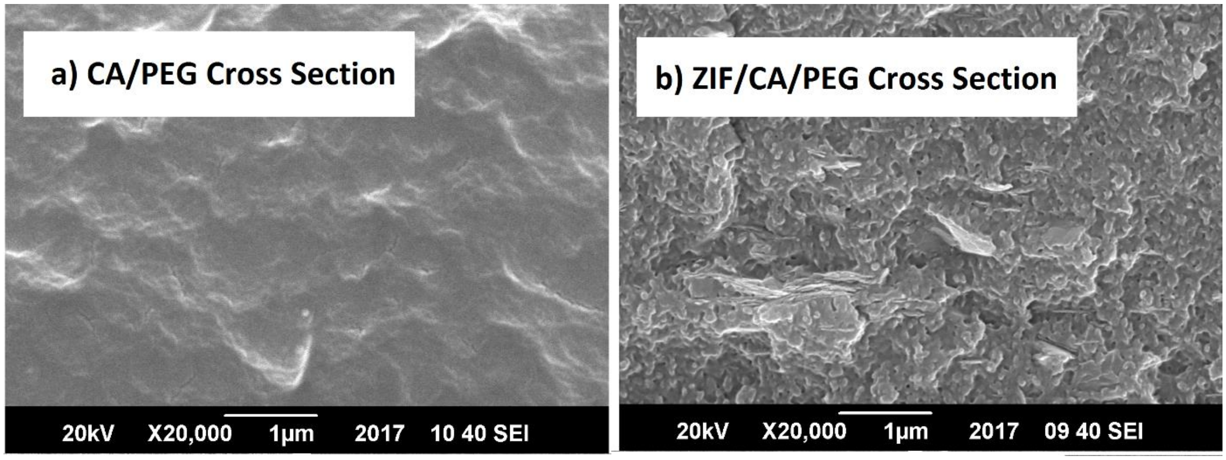

Figure 19c: Comparison of pure CA/PEG (a) and Zn-Co ZIF/CA/PEG MMM (b) with 15% Zn-Co ZIF loading cross section view at same magnifications.

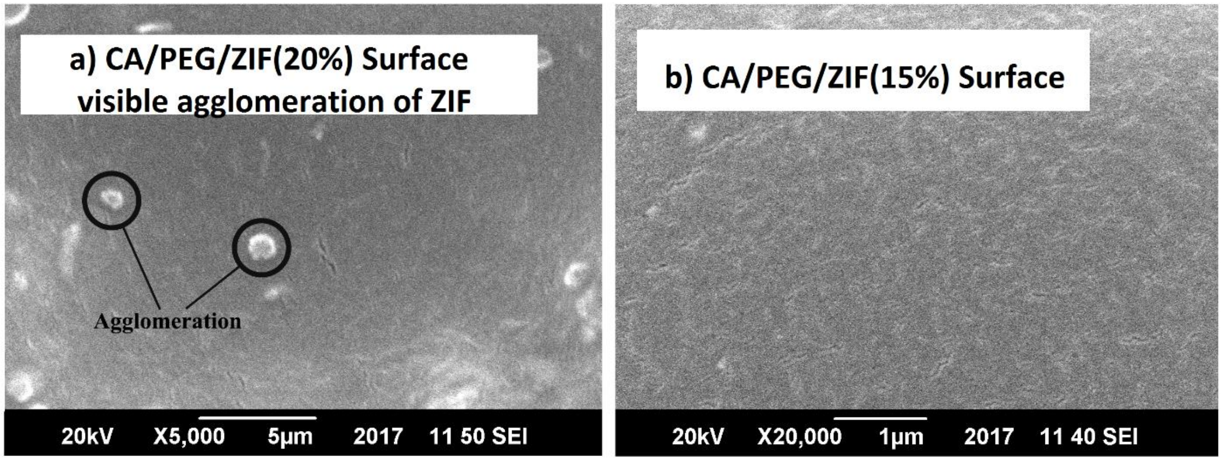

Figure 19d: a) CA/PEG/ZIF(20%) surface with visible agglomeration of ZIF. b) CA/PEG/ZIF(15%) with even distribution of ZIF across the surface and no visible agglomeration.

5.3. Mechanical Testing Results

Mechanical Testing of CA/PEG and CA/PEG/ZIF mixed matrix membranes were carried out to study tensile strength of the membrane. Mixed matrix membrane was also tested with changing weight percentage of ZIF in polymer. Following are some details of the experiments carried out:

- Apparatus: Universal Testing Machine (AG-XPlus Shimadzu)
- Temperature: Average room temperature
- Membrane cross sectional area: 8.5mm
- Gauge length: 10 ± 0.5 mm

Figure 20 illustrates graph between stress and strain for CA/PEG membrane. It was observed that membrane had a tensile strength of 60 MPa with 28% strain. Membrane showed good flexibility and stress bearing properties. This is due to addition of PEG in membrane that reduces the rigidity of membrane imparting flexibility which in turn enhances its stress bearing property.

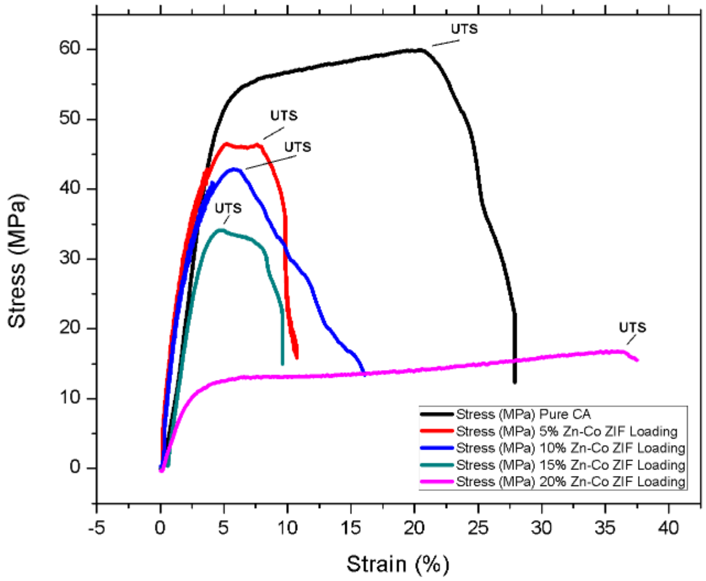

Figure 20: Comparison of Stress-Strain curves at different Zn-Co ZIF Loadings.

In case of mixed matrix membrane containing Zn-Co ZIF as filler, stress showed different results than simple CA/ZIF membrane. Membranes with ZIF loading of 5, 10, 15 and 20 wt. % were studied. It was observed that addition of ZIF made membrane brittle and hard. As the amount of ZIF increased brittleness also increased till 20 wt. %. This was due to presence of ZIF particles in the polymer structure. The free rotation of polymer backbone in case of pure polymer membrane was retarded by presence of less flexible and more crystalline ZIF particles. This made membrane to show less resistance to stress thus reducing its tensile stress and strain properties.

Results of above plotted graphs showed interesting trends. At loading of 5 wt. % rise in tensile strength and elongation was observed. This was particularly due to strong bonding between ZIF particles and polymer chains. At loadings higher than 5 wt. %, tensile strength and % elongation both started to decrease. This can be attributed to rigidity introduced in the polymeric structure by ZIF particles making it more brittle. This fashion kept on increasing with increase in ZIF loading. The presence of large agglomerates of ZIF particles on the surface of membrane above 20 wt. % as observed by SEM can also be attributed to this observation. From 0 to 5 wt. % tensile strength reached 45MPa, while from 5 to 20 wt. % tensile strength reduced from 45MPa to 14MPa. Also percentage elongation decreased from 26% to 11% from 0-5 wt. %.

From 5 to 20 wt. % of ZIF loading, percentage elongation decreased from 30% to 6.5% thereby decreasing its stress bearing properties and making it more rigid and brittle. Though loading higher than 20 wt. % offer higher permeability rates but such membrane cannot work at high pressure operation such as industrial gas separation operations.

This shift in tensile strength and percentage elongation can be explained by molecular studies. Increasing weight ratios of ZIF in polymer matrix undergoes bonding with polymer chains. This bonding change the flexible nature of polymer into rigid crystalline nature of ZIF particles. On the other hand, ZIF particle acts as free volume element due to empty cages at their center, also ZIF particles due to their metal-organic framework and cubic structure offer less resistance to stress, making membrane structure weaker.

Another reason that can lead in reduction of tensile strength is agglomeration. As explained above, at 20 wt. % loading of ZIF in polymer, they start to agglomerate in polymer layers. This agglomerates also creates voids in the membrane decreasing its tensile strength and percentage elongation.

Membrane	Tensile Strength (MPa)	Elongation (%)
CA/PEG/Zn-Co ZIF (0 wt. %)	58.55	26.65
CA/PEG/ Zn-Co ZIF (5 wt. %)	46.00	11.22
CA/PEG/ Zn-Co ZIF (10 wt. %)	43.54	16.16
CA/PEG/ Zn-Co ZIF (15 wt. %)	34.65	9.05
CA/PEG/ Zn-Co ZIF (20 wt. %)	28.88	36.66

Table 4: Mechanical Properties of CA/PEG/Zn-Co ZIF Mixed Matrix Membranes with Increasing Concentration of ZIFs

5.4 X-Ray Diffraction (XRD) Analysis

X-ray Diffraction Analysis was conducted to study nature of polymer and ZIF in mixed matrix membrane. XRD helped in carrying out analysis of structure of mixed matrix membrane. XRD results were plotted in form of graphs with peaks representing each compound added in membrane. Peaks for both Cellulose Acetate and ZIF were obtained at different points.

Due to rather semi-crystalline nature of cellulose acetate, its peak was obtained roughly at 2θ of 23[42]. This position on XRD graph when analyzed with available literature on cellulose acetate XRD patterns conforms its semi-crystalline nature and its presence in mixed matrix membrane without degradation of its polymeric semi-crystalline structure due to excessive heating.

On the other hand, Zn-Co ZIF has crystalline nature and its peak falls much before cellulose acetate peak. For Zn-Co ZIF, peak was observed at 2θ of 5. This verifies its crystalline nature which was also attested with available literature on similar finding on nature of Zn and Co ZIF. This peak also verifies the presence of ZIF particles in mixed matrix membrane without any structural changes and changes in crystallinity during synthesis stages.

Low crystallinity of cellulose acetate is subjected to interaction of hydroxyl and acetyl groups while crystalline nature of ZIF is due to the presence of linker and Zn-Co framework.

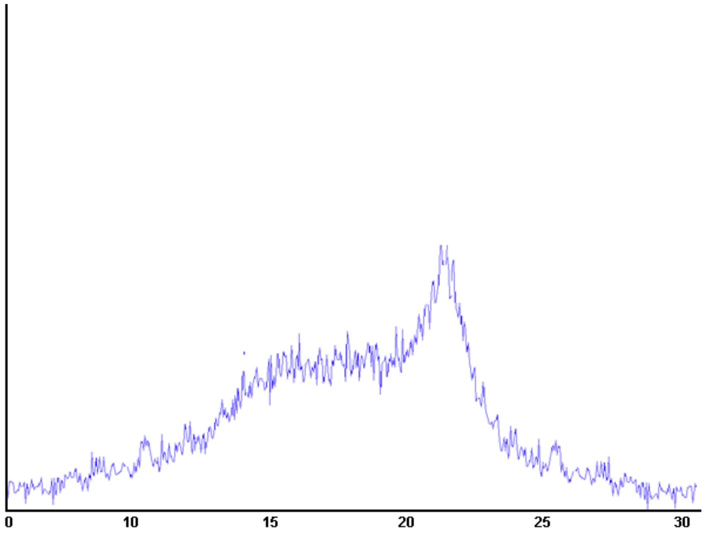

Figure 21: XRD Patterns of Pure CA/PEG.

Figure 21 illustrates X-ray Diffraction peaks for CA/PEG. For CA, peak can be observed at roughly 2θ of 23. While for Zn-Co ZIF peak is observed at 2θ of 5 and 13. All these peaks are confirmed by Expert high score ICCT1 database. This result of XRD analysis verifies intermixing of Zn-Co ZIF and CA particles homogeneously and presence of each compound with its standard properties without any degradation in structure and nature.

5.5. Gas Permeation Test System Results

Gas permeation test system was used to study permeation of gases through mixed matrix membrane formulated with different loadings of Zn-Co ZIF. In gas permeation testing, membranes were placed in membrane cell by trimming membranes into circular shape each with size of 2 inches dia to match the size of the ceramic disc placed in the membrane cell. To initiate the procedure, gas permeation rig was purged with gas under test by opening completely the vent valve to allow residual gases present in the system to evacuate them. Each gas was passed separately when test system was operated alone. When test system was used in combination with gas chromatography, mixed gases were used.

Following gases were used in gas permeation testing:

- Carbon Dioxide (99.9 % Pure)
- Nitrogen (99.5 % Pure)
- Methane (99.5 % Pure)

Pressure:

Feed pressure was varied from 1 bar to 8 bar. Reading were obtained after every 0.5 bar change in pressure.

Zn-Co ZIF Loadings

Membranes were tested with different loadings of Zn-Co ZIF. Loadings were varied from 5, 10, 15 and 20 (wt. %).

5.5.1. Effect of Zn-Co ZIF loading on gas permeability of CA/PEG/Zn-Co ZIF based mixed matrix membrane

Figure 22 illustrates graph drawn between permeability and loading of Zn-Co ZIF in membrane. Graphs are drawn for CO2, CH4 and N2. It was observed that permeability of CO2 markedly increased with increase in loading of Zn-Co ZIF from 5 wt. % to 20 wt. %. While for CH4 and N2 change in permeability was low as compared to CO2. This can be attributed to attraction of CO2 in cages of Zn-Co ZIF molecules. The cage size of Zn-Co ZIF matches that of carbon dioxide kinetic diameter that allows gas molecules to rapidly pass through cages that acts as free volume elements in the polymer chains. While on the other hand, kinetic diameter of methane and nitrogen is bigger as compared to Zn-Co ZIF cage size thus increase in its loading does not impart prominent increase in permeabilities. Figure 23 illustrates a comparative analysis of CO_2 and N_2 permeabilities. As the concentration of Zn-Co ZIF in polymer increased the permeability of both gases increased. But in comparison, carbon dioxide showed much higher increase in permeabilities as compared to nitrogen. The kinetic diameter of carbon dioxide is 3.6 Å which is roughly equivalent to the size of the Zn-Co ZIF cage. While the kinetic diameter of nitrogen molecule is 3.64 Å which is much larger than the size of the cages thus cages provide practically no diffusion path to nitrogen molecules and they only uses free volume elements of polymeric membrane to diffuse thought the membrane.

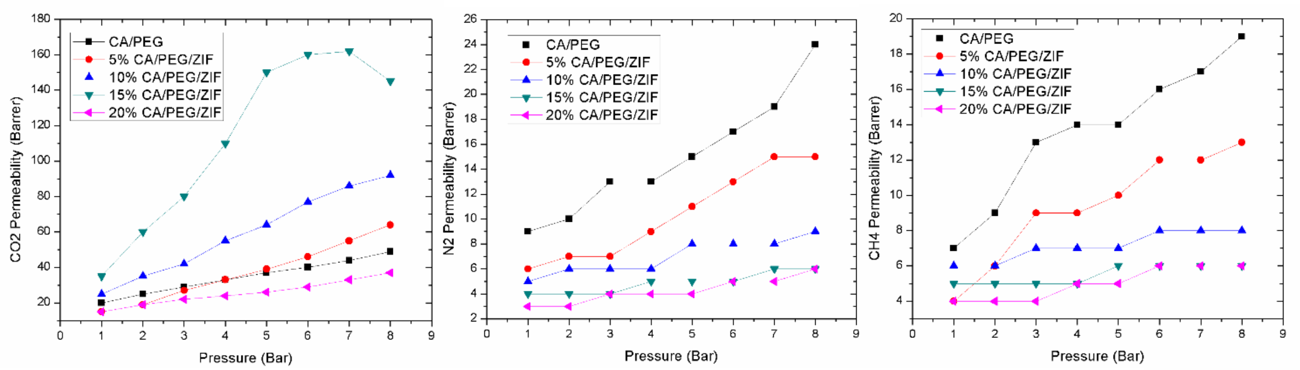

Figure 22: Effect of Zn-Co ZIF on permeability of CO_2, N_2 and CH_4

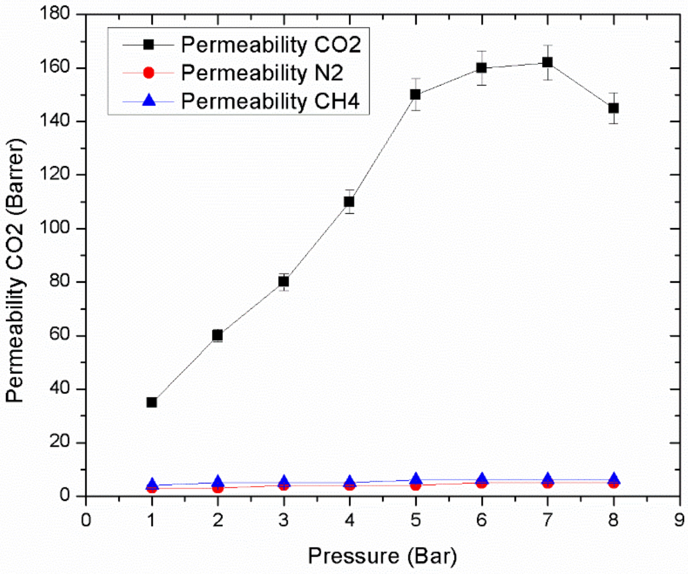

Figure 23: Permeability vs Pressure Comparison of CO_2, N_2 and CH_4 with 15% Zn-Co ZIF Loading.

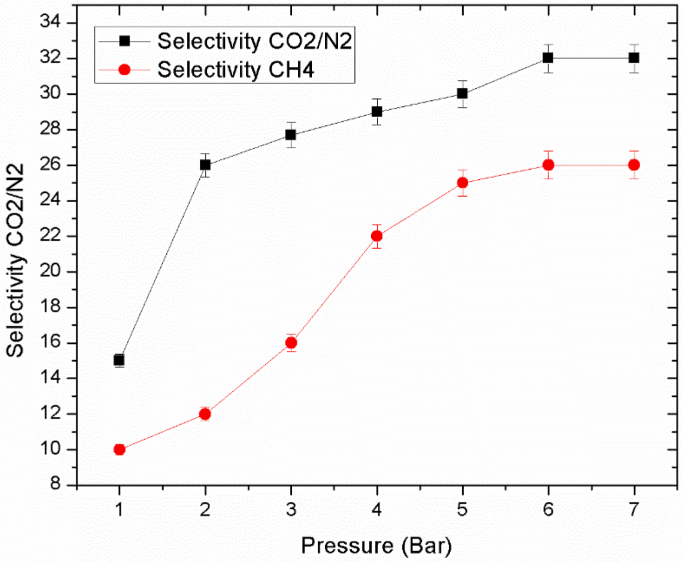

Figure 24: Pressure vs Perm-selectivity Comparison of CO_2/N_2 and CO_2/CH_4 with 15% Zn-Co ZIF Loading.

Similar trends were observed in case of comparison between permeabilities of carbon dioxide and methane. Figure 24 illustrates graph between permeabilities of both gases. Here too, the size of methane kinetic diameter is much bigger than the size of Zn-Co ZIF cage thereby disallowing it to penetrate thought the voids created by Zn-Co ZIF. Methane molecules only used free volume elements of the polymer matrix.

Specimen	Diameter (Å)
Zn-Co ZIF	3.30
Nitrogen	3.64
Carbon Dioxide	3.30
Methane	3.80

Table 5: Comparison of gases kinetic diameter and Zn-Co ZIF cage

5.5.2. Effect of Zn-Co ZIF loading on perm-perm-selectivity of CA/PEG/Zn-Co MMMs.

In perm-selectivity studies of CA/PEG/Zn-Co MMMs, two gas pairs were studied i.e. CO_2/N_2 and CO_2/CH_4. Membranes with different Zn-Co ZIF loadings were studied. Optimum results were obtained at 6 bar pressure (Delta).

For CO_2/N_2 gas pair at 6 bar pressure and 15wt% loading of Zn-Co ZIF, maximum perm-selectivity was recorded. At higher loadings, permeability of N_2 markedly increased. This anomaly can be attribute to abundance of Zn-Co ZIF particles in polymer matrix that caused agglomeration on surface of membrane. Also increase in loading resulted in weakening of strength that caused plasticization of membrane. Increase in voids and creation of pin holes increased permeability of both gases thereby reducing the perm-selectivity of membrane. Results of perm-selectivity for CO_2/N_2 gas pair is shown is figure 24.

Similar results were witnessed in case of CO_2/CH_4 gas pair. At loading of 15 wt. % and pressure of 7 bar, optimum results for perm-selectivity were obtained. At higher loadings, permeability increased for both gases and perm-selectivity was reduced. It was also observed that increase in Zn-Co ZIF loading introduced brittleness in the membrane that resulted in cracks at nano-level that act as voids in the membrane. These voids offer free passage for gases to permeate through the membrane without perm-selection. Perm-selectivity of CO_2/CH_4 gas pair is illustrated in figure 23.

5.5.3 Changing permeation rates with change in pressure for CA/PEG/Zn-Co ZIF MMM.

To study effect of pressure on permeation of gases through CA/PEG/Zn-Co ZIF mixed matrix membrane different loadings of Zn-Co ZIF were used to create MMM. These membranes were tested at pressures from 1 bar to 8 bar with intervals of .05 bar each. Gas permeation for carbon dioxide, nitrogen and methane increased from 1 to 6 bar while at higher pressures increased in permeation rate slowed down. Perm-selectivity also increased with increase in pressure till 7 bar. At higher pressures, perm-selectivity decreased. This phenomena own its roots to dual sorption model that describes effect of pressure on permeation of gases through glassy polymers. Permeation is directly proportional to pressure.

5.5.4. Pressure vs Perm-selectivity of CA/PEG/Zn-Co ZIF MMMs

Perm-selectivity studies were carried out at various pressure ranges. Both gas pairs, CO_2/N_2 can CO_2/CH_4 were studied at pressures ranging from 1 bar to 8 bar. Readings were noted after every 0.5 bar rise in pressure. During all these observation, temperature was kept constant at room temperature.

It was observed that perm-selectivity increased with increase in pressure till 6 bar. While with ZIF loading of 15 wt. % perm-selectivity increase rated slowed down. Best perm-perm-selectivities were obtained with 15 wt. % ZIF loading. The membrane was flexible, less brittle, and easy to handle during test phase.

Conclusions and Recommendations.

5.6 Conclusions

Vast and extensive studies on polymers for synthesis of gas separation membranes have been carried out keeping in view their successful results at laboratory scale and some of its commercial applications particularly in natural gas purification. One of the major studied portion in polymeric gas separation membrane is the incorporation of additives and fillers that helps in achieving the permeability and perm selectivity tradeoff. In case of pure polymeric membrane obtaining good values for both permeability and perm selectivity is very difficult.[4, 17]

This study reports effect of Zn-Co ZIF filler on permeation and perm selectivity of Cellulose Acetate polymeric membrane. The CA/PEG/Zn-Co ZIF membrane were synthesized with different loading of filler from 5% to 20%. Cellulose acetate as a base polymer has been tested and verified as high strength, easy to synthesis and cost effective polymer for membrane synthesis. Addition of PEG further enhances its strength by increasing its flexibility and inducing rubbery characteristics in CA.[43]

Although, perm-selectivity of CO_2/N_2 and CO_2/CH_4 obtained in this research is not mature enough to be used in industrial application, a good permeability and perm selectivity tradeoff was calculated with CA/PEG/Zn-Co ZIF membranes at 15% loading of Zn-Co ZIF. Permeation of carbon dioxide was 160 barrer at 8 bar pressure as compared to nitrogen and methane i.e. 6 barrer and 5 barrer. For CO_2/N_2 gas pair, perm-selectivity was 32 and for CO_2/CH_4 perm-selectivity was 26. It was also revealed that at higher loading of ZIF in membrane, membrane morphology and mechanical properties sharply changes due to change in polymer structure. Membranes with better morphology and permeability were obtained between 10%-15% ZIF loadings.

It has been concluded that addition of Zn-Co ZIF in polymer can be a potential candidate commercial gas separation membrane applications. A lot of space has been left in this study to further enhance the permeation and perm selectivity by introducing variations in amount of Zn-Co ZIF loadings and amount of Cellulose Acetate used.

5.7. Future Recommendation

Study of effects of Zeolitic Imidazole Frameworks on permeation rates of polymeric mixed matrix membrane has a vast area of research. In continuation of this research work, several other ZIF’s can be added in combination of Zn-Co ZIF to study changing permeabilities and perm-selectivities of polymeric membrane. Also varying amount of ZIF loadings in polymer can also be studied to observe change in membrane morphology and strength.[44]

A very important recommendation that requires extensive research is to scale up this membrane model successfully to industrial application. For industrial applications, pressure and temperature requirements have to be met in order successfully execute this research. In addition, this combination of CA/PEG/Zn-Co ZIF might also work for other gas combinations that have remained untouched in this research work due to time and resources limitation and due to extension of this research work from the scope.

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