

**Permeation Behavior of Single and Mix Gases  
through Mixed Matrix Membranes**



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# **Permeation Behavior of Pure and Mixed Gases through Mixed Matrix Membranes**



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## **Certificate**

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## **Dedication**

To my Parents and Siblings

## Abstract

CO<sub>2</sub> presence in natural gas decreases the calorific value which makes its separation indispensable. Most of the polymers or their blends used for CO<sub>2</sub> separation are very expensive but cellulose acetate (CA) being cheap is a lucrative choice. Polyethylene glycol (PEG) has been utilized to enhance the chain flexibility of polymers which in turn modifies the permeability of different gases through these polymers while CNTs provides an extra free path for CO<sub>2</sub> molecules and augment its permeability. In this research, PEG and multi-wall carbon nanotubes (MWCNTs) were incorporated in CA using acetone as solvent via solution casting technique to study the permeation behavior of pure and mixed gases (CO<sub>2</sub> and CH<sub>4</sub>) through fabricated membranes. Membranes of pure CA, CA/PEG blend of different PEG concentrations (5%, 10%, 15%) and CA/PEG/MWCNTs blend of 10% PEG with different MWCNTs concentrations (5%, 10%, 15%) were prepared. Fabricated membranes were characterized using scanning electron microscopy (SEM), X-ray Diffraction (XRD), Thermo gravimetric analysis (TGA) and Tensile Testing. Permeation results demonstrate remarkable improvement in CO<sub>2</sub>/CH<sub>4</sub> selectivity. For pure gases CO<sub>2</sub>/CH<sub>4</sub> selectivity is enhanced from 5.74 to 39.47 in the case of 10%PEG/CA however maximum CO<sub>2</sub>/CH<sub>4</sub> selectivity of 48.92 is obtained for 10%MWCNTs/10%PEG/CA. In the case of mixed gas CO<sub>2</sub>/CH<sub>4</sub> selectivity augmented from 2.16 to 28.67 for 10%PEG/CA whereas maximum CO<sub>2</sub>/CH<sub>4</sub> selectivity of 38.5 is documented for 10%MWCNTs/10%PEG/CA.

**Keywords:** MMMs, natural gas, membrane separation, MWCNTs, mix gas, polymeric membrane

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## **ABBREVIATIONS**

Cellulose acetate	(CA)
Polyethylene glycol	(PEG)
Multi-wall carbon nanotubes	(MWCNTs)
Scanning electron microscopy	(SEM)
X-ray Diffraction	(XRD)
Thermo-gravimetric analysis	(TGA)
Facilitated transport membranes	(FTM)
Fixed site carrier	(FSC)
Mixed matrix membranes	(MMMs)
Metal organic frameworks	(MOFs)
Tetra-hydro-furan	(THF)
Carbon molecular sieve	(CMS)

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# Chapter -1

## Introduction

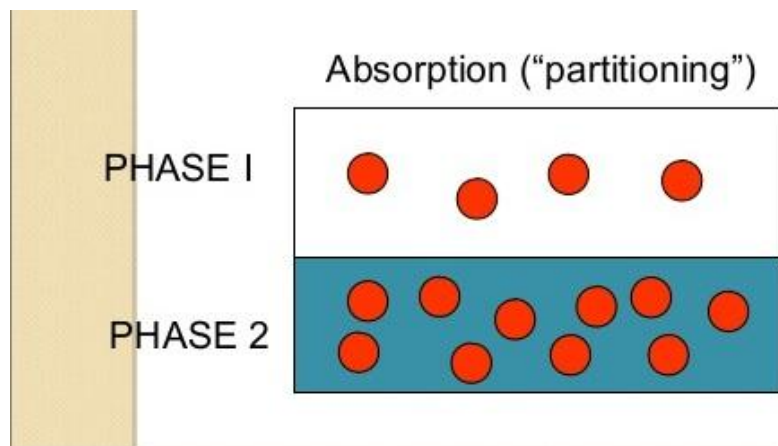
This chapter includes the common techniques used for CO<sub>2</sub> separation and the basics of membrane separation process including the preparation techniques and applications

CO<sub>2</sub> is present in natural gas, gasification products and flue gases[1]. 20% of natural Gas contains CO<sub>2</sub> which is above acceptable limits (2%) [2] and hence is responsible for lower calorific value. CO<sub>2</sub> is an acidic gas and corrosive in nature [3] and therefore damaging to both equipment and environment. So the removal of CO<sub>2</sub> from natural gas is indispensable. In order to remove CO<sub>2</sub> from natural gas and prevent its emission in atmosphere an efficient and cost effective separation technique is required [4] . Most common and conventional processes utilized for CO<sub>2</sub> capture are absorption and adsorption, whereas membrane separation is relatively new and is more efficient than the other processes.

### 1.1 Common Processes for CO<sub>2</sub> removal

#### 1.1.1 Absorption

Absorption is a process in which one or more components are transferred from gas phase to liquid phase (Figure 1) [5]. Absorption is normally utilized to remove impurities from gas mixtures. The component transferred is called solute and the absorption can be chemical or physical depending upon the kind of impurities needed to be removed. After absorption the impurities are removed by stripping. In absorption CO<sub>2</sub> can be removed either by chemical or physical absorption. Physical absorption follows Henry's Law in which CO<sub>2</sub> is absorbed under high pressure and low temperature. Processes like Selexol, Rectisol and Purisol are examples of physical absorption with dimethylether, Methanol and N-methylpyrrolidone as there solvents respectively. In chemical absorption solvents like Monoethanol Amine, Diethanol Amine, activated Methyl Diethanol Amine and Catacarb are used to capture CO<sub>2</sub>.



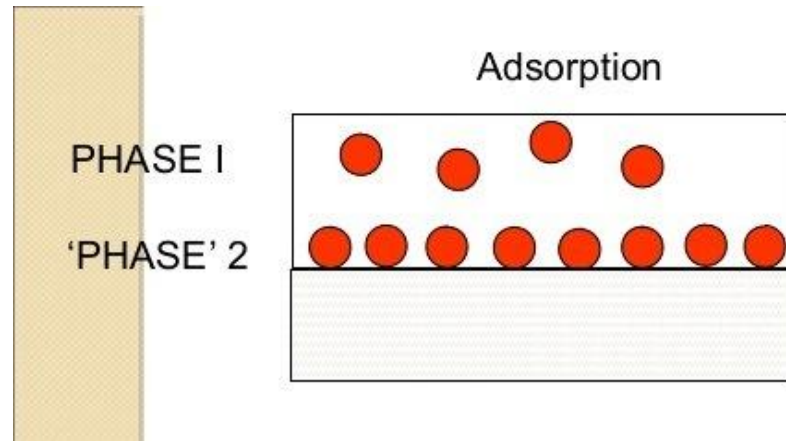
**Figure 1 Schematic of Absorption phenomena**

These are the most common solvents used for absorption processes. Absorption process consists of an absorber, stripper and flash drums. The process starts with the gases entering from bottom of absorber which is at low temperature and high pressure. The CO<sub>2</sub>-rich solution from the absorber is transferred to flash drums which are at lower pressure and high temperature to remove most of the CO<sub>2</sub> from solution while rest of the solution is sent to stripper for further removal of CO<sub>2</sub> and lean solution again enter the absorber. Ionic liquids also have good potential as CO<sub>2</sub> absorbing solvents.

They follow both chemical and physical absorption processes. In physical absorption species responsible for CO<sub>2</sub> capture are the anions as they have more influence on solubility of CO<sub>2</sub> while cations do not have any remarkable effect on solubility. In chemical absorption amino functional groups are used and there CO<sub>2</sub> absorption is found to be three times more, compared to physical absorption. During the process the viscosity of ionic liquid increases so in order to reduce the viscosity alkanolamine is added into the ionic liquid which keeps the viscosity under required limits. Activated Methyl Diethanol Amine is one of the best options compared to other solvents due to its high absorption capacity and least corrosive effects. A lot of industries are already using this process for CO<sub>2</sub> capture but there are problems associated with this process including foaming problem which causes level transducers to work inappropriately. To tackle foaming problems some fillers are added which reduces foaming but this process is still very expensive as we need heater, chillers and compressors.

### 1.1.2 Adsorption

Adsorption is a process in which a thin layer of molecules gets attached to a solid surface due to unbalanced forces (Figure 2) [5]. The specie getting adsorbed on the surface is called adsorbate while the surface is called adsorbent.

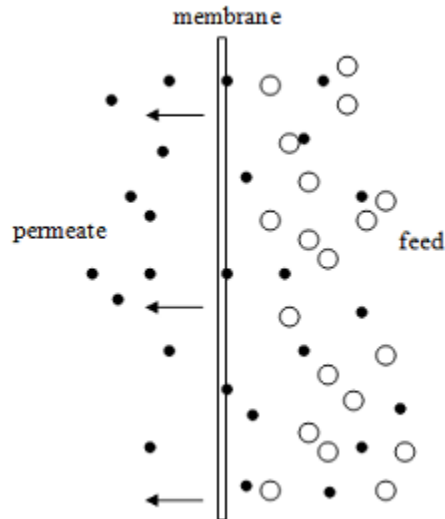


**Figure 2 Schematic of Adsorption phenomena**

In adsorption the removal of  $\text{CO}_2$  is obtained by solid materials which include carbonaceous adsorbents, zeolites, mesoporous silica and metal-organic frameworks (MOFs). Carbonaceous adsorbents have high activity and surface area for  $\text{CO}_2$  adsorption but have a limitation to be operated at high pressure. In order to improve  $\text{CO}_2$  adsorption single-wall carbon nanotubes and multi-wall carbon nanotubes are being modified. Zeolites being shape specific are very efficient in capturing  $\text{CO}_2$  but adsorption capacity is limited by cations presents in zeolites. By replacing cations  $\text{CO}_2$  adsorption can be increased but it has very little effect on selectivity of  $\text{CO}_2/\text{N}_2$ . Mesoporous silica although have high surface area but its  $\text{CO}_2$  adsorption capacity is not good enough to be utilized in industry. Metal-organic frameworks (MOFs) have attracted a lot of attention in last decade due to their high surface area, controlled pore diameter and tunable properties. MOFs have relatively higher  $\text{CO}_2$  adsorption capacity compared to other adsorbents but their adsorption capacities decrease sharply when mixtures of gases are used which put a limitation to their practical use. Chemically modified adsorbents are also used for  $\text{CO}_2$  capture including Amine-Impregnated Adsorbents and Amine-Grafted Adsorbents. At optimum amine loading on silica, enhanced  $\text{CO}_2$  adsorption is obtained but it lacks thermal stability so to overcome this problem Amine-Grafting is mostly used.

### 1.1.3 Membrane Separation

Membrane is a mechanical barrier which allows one component of the mixture to pass freely while hinders the movement of other components [6]. The component passing through the membrane is called permeate. Component retained on the surface is called retentate (Figure 3).



**Figure 3 Schematic of Membrane separation**

Absorption and Adsorption processes require regeneration of  $\text{CO}_2$  which needs energy and hence search for an alternative which require no regeneration is essential. In case of membranes  $\text{CO}_2$  separation is only single step in which a membrane selectively separates  $\text{CO}_2$  from other gases. Most of the polymeric membranes have  $\text{CO}_2/\text{CH}_4$  selectivity from 5-50. The separation is based on different permeation rates of the gases through membrane material. For  $\text{CO}_2$  capture mostly polymeric membranes are being utilized for their excellent  $\text{CO}_2$  selectivity. Membranes are far better alternatives and are industrially established processes due to compact size, ease of installation, no moving parts, no heating requirement, economical and being efficient. Membranes are being used at natural gas wells to purify natural gas to increase the calorific value and at the exit of coal fired power plants to reduce their environmental effects. Mixed matrix membranes (MMMs) include blending of metal-organic frameworks (MOFs) in different polymers and also have great potential for  $\text{CO}_2$  capture. Challenges associated with membranes are

thermal stability, mechanical strength, high permeation rates with high selectivity, plasticization resistance to cope swelling and manufacturing cost effective modules.

### **1.1.3.1 Types of membranes**

#### **1.1.3.1.1 Porous Membranes**

Porous membranes follow pore-flow model. Flow through these membranes is pressure based called convective flow. Pore-flow model is used to describe the flow through capillary medium. In porous membranes chemical and thermal stability are one of the important factors. Type of material does not affect the working of membranes whereas pore size and pore distribution are the only important factors in these kinds of membranes [7].

Mainly microfiltration and ultrafiltration are the examples of porous membranes. Adsorption affects the transport through these membranes.

The requirements of the polymers used are:

- Flux
- Selectivity
- Chemical and thermal stability

The techniques used to prepare microfiltration membranes are:

- Sintering
- Stretching
- Track-etching
- Phase Inversion

Since the pore size for ultrafiltration is much smaller the only technique used for this process is phase inversion.

#### **1.1.3.1.2 Nonporous Membranes**

Nonporous membranes follow solution diffusion model. Flow is dependent on the sorption and diffusion through the material. The driving force in dense membranes is



concentration gradient across the membrane [7]. Nonporous membranes are used for following processes

- Gas Separation
- Pervaporation

Following are the types of dense membranes based on morphology

- Asymmetric
- Composite

Asymmetric membranes are non-uniform over the cross section of the membrane it consists of different layers which differ in structure or type of material. Composite membranes contain a dense skin layer at the top of a porous substrate. The material of top skin layer is different from the substrate. Mass transfer of particular gas through these membranes is dependent on both the thickness and type of material whereas substrate is mostly to provide the mechanical support.

Since adsorption and absorption are very energy intensive processes membrane process suits the gas separation. Temperature and pressures manipulations are required for both adsorption and absorption while in case of membrane process only mechanical barrier in the form of membrane is needed. The pressure requirement is lower than the pressure at which the natural gas is obtained from wells.

In this study dense membranes are utilized for gas separation. Gas separation is mostly dependent on the solubility and diffusivity of a particular component in the polymeric material used.

### **1.1.3.2 Modes of Membrane Processes**

The modes of membrane processes are determined by the direction of flow. There are two major modes of membrane processes:

### 1.1.3.2.1 Dead-end membrane process

In dead-end membrane process the flow of feed is perpendicular to the membrane surface (Figure 4). This type of flow is not very common because of the limitations associated with this process. Its applications are limited because it blocks membrane pores due to cake build up on the surface of membrane and is not continuous [7].

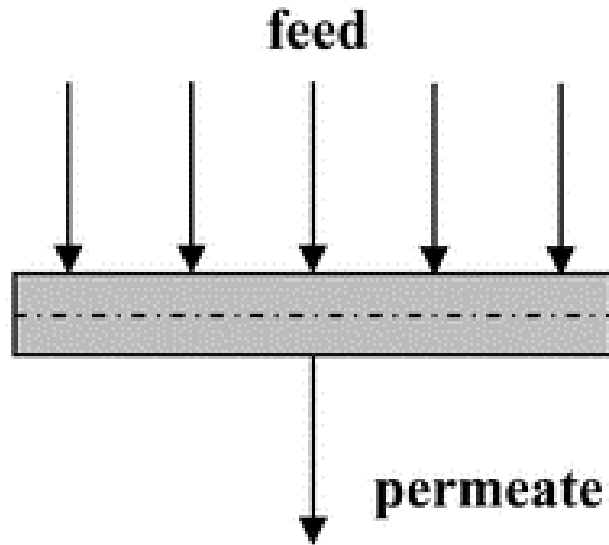


Figure 4 Dead-end Membrane process

### 1.1.3.2.1 Cross-flow membrane process

In cross flow membrane process the feed flows parallel to the surface of membrane. In this process the pores are not blocked because the flow of feed is parallel which does not allow the cake build up at the surface and this process is continuous as well (Figure 5). Hence cross-flow membrane process is the most common one [7] and is also utilized for this permeation study as well .

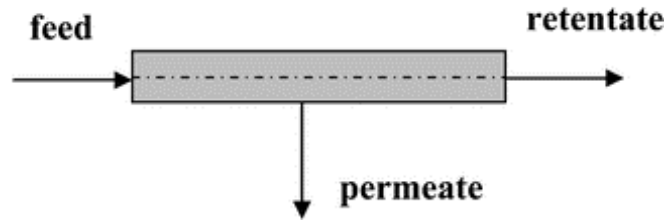


Figure 5 Cross-flow Membrane process

### 1.1.3.3 Common methods for Membrane Preparation

The method of membrane preparation determines the morphology and properties of these membranes. A lot of different methods are employed for membrane preparation but for MMMs solution blending, in-situ polymerization and sol gel methods are the most common.

#### 1.1.3.3.1 Solution blending

Solution blending is one of the simplest techniques utilized for membrane preparation. In this technique the first important factor to decide is the choice of solvent. The solvent should be able to dissolve the polymer at normal conditions and should not impart any chemical changes in the polymer. The second important factor is use of plasticizer. Plasticizer is very important to provide the flexibility and strength needed for the membrane to bear the constant pressure applied during separation process. Without plasticizer a lot of membranes tend to become brittle and gets damaged during the operation. Plasticizer is very important to keep the membranes intact for a longer period of time.

Choice of filler is a crucial part because unsuitable filler will lead to defective membrane. The filler should be compatible with the polymer and after membrane fabrication there should be a strong interaction between filler particles and polymer in order to ensure there are no gaps at the filler/polymer interface. Other important factors include drying time and rate of drying. Membranes should be allowed to dry at a lower rate so that the membranes should be homogeneous and defect free because higher drying rate lead to a

non-homogenous membrane. If possible use of vacuum drying oven would be best for membrane preparation.

In solution blending the polymer is dissolved in a particular solvent and then plasticizer is added. After addition of filler the solution is stirred and sonicated to ensure the homogeneity of solution. The solution is then allowed to settle in order to remove the bubbles and then poured into petri-dishes and placed in oven to remove the solvent. After the removal of solvent the membrane is obtained in the required form [8]

#### **1.1.3.3.2 Sol-gel method**

Sol-gel technique is also very attractive for researchers. A lot of work has been done in this field but is not very common at commercial level for gas separation. In this process a ceramic tube is coated with a dispersion of fine grains and then heating at a very high temperature. This process is mostly utilized to prepare ultra-filtration membranes which are normally in the form tubes.

#### **1.1.3.3.3 In-situ Polymerization**

In-situ polymerization is an interesting technique for researchers because in this process the polymerization and membrane preparation occur at the same time. Normally the inorganic particles are mixed with monomers of the polymer and then the monomers undergo polymerization. This process occurs at high temperature and functional groups get attached to the surface of inorganic material. The functional groups are attached at the surface covalent bonding between inorganic particles and polymer [9].

#### **1.1.3.4 Membrane process applications**

##### **1.1.3.4.1 Microfiltration**

Microfiltration is the most widely available membrane used to separate the suspended particles (greater than 0.1 micron). It requires the constant removal of particles which are removed from a feed stream [6]. The driving force in microfiltration is pressure difference around 10 to 500 kPa

Commonly utilized for following:

- Sterile Filtration
- Clarification
- Remove colloidal material

#### **1.1.3.4.2 Ultrafiltration**

Ultrafiltration is utilized to remove an undesired component from desirable ones normally used for biological and organic components [6]. The pore size for ultrafiltration is between 10 to 1000 Å. The driving force in this process is pressure difference higher than microfiltration around 0.1 to 1 MPa.

Commonly utilized for following:

- Recover oils
- Clarification of wines
- Produce ultra-pure water
- Remove Bacteria
- Remove Surfactants

#### **1.1.3.4.3 Reverse Osmosis**

Reverse osmosis is used to separate dissolved solids from water. It also removes bacteria, viruses, ions and salts. This process is utilized for desalination of water and produce drinkable water from seawater [6]. The driving force is pressure difference. The pressure requirement is very high in case of reverse osmosis because of the smaller pore size around 5 to 15 Å.

It can remove up to 99% of impurities from water including:

- Organic particles
- Inorganic particles
- Charged particles
- Biological impurities

#### **1.1.3.4.4 Nano-filtration**

Nano-filtration is utilized for the separation of fluids. It is also called loose RO because its separation is not as fine as RO and require less pressure difference as well [6]. Nano-filtration can have high recoveries than RO and have pore size in the order of nanometers.

Common applications include:

- Water Softening
- Removing contaminants from water
- High purity systems

#### **1.1.3.4.5 Gas Separation**

Gas separation is the type of separation process which mostly uses dense membranes which allow one component to pass through the membrane more readily. Components which passes through the membrane has more affinity for the polymeric material and diffuse through the polymeric material. The driving force in this process is concentration gradient and the pressure difference [6].

Common applications of gas separation include:

- Carbon capture
- H<sub>2</sub> separation
- Air separation
- He recovery
- N<sub>2</sub> production

### **1.2 Motivation**

Natural gas is one of the cleanest fuels because it produces less unwanted products compared to coal, diesel and other petroleum products. Natural gas after being recovered from underground reservoirs needs to be processed before it can be utilized. Main component in natural gas is methane while it also contains ethane, propane and butane. Along with the fuel components water, carbon dioxide and sulphur are also present in natural gas. CO<sub>2</sub> is a major greenhouse gas and primary contributor to global warming

and climate change. In order to make Natural gas available for industrial and domestic use a cost effective separation process is required. Since membrane separation process has fewer requirements in terms of energy, maintenance and cost, it gives us motivation to explore this area further and make it more feasible at industrial scale.

# Chapter - 2

## Literature Review

This chapter includes an overview of utilization of membrane technology for separation of different gases, selection of polymer material for certain applications, membrane preparation techniques and types of membranes available for gas separation

### 2.1 Membrane Technology for Gas Separation

Gas sweetening is done by membrane technology from many years because it is advantageous to other techniques and is environment friendly as well. It requires less energy, cost and space and also suitable for remote applications [10]. Fabrication of efficient membranes is the most important factor for this process to be more effective than other techniques. For membrane process permeability and selectivity are the most important parameters among all. Different kind of materials has been analyzed for CO<sub>2</sub> capture and ceramics have some applications in this regard but for larger applications polymers are found to be the more suitable.

Gas separation using polymeric membranes is considered as the most feasible technique due to easy scale up and least requirements in terms of energy, maintenance and cost [11]. Membrane separation process became economically competitive in 1970s [12] and since then it has always been more attractive than conventional processes like adsorption and absorption. CO<sub>2</sub>/CH<sub>4</sub> is at second place among the most investigated gas pairs [13]. Pure or modified polymeric membranes are utilized to separate CO<sub>2</sub> from natural gas, biogas and are being considered for flue gases as well [14][15].

In Europe coal and gas fired power plants emitting CO<sub>2</sub> are contributing to the increased concentration in the atmosphere. CO<sub>2</sub> concentration in the exhaust gases from these plants is around 13% [10]. Presence of other components (SO<sub>x</sub>, NO<sub>x</sub>) decreases the efficiency of membrane separation process by contaminating the surface and hence blocking the contact between membrane and gas mixture.



Plasticization due to CO<sub>2</sub> is a major challenge in membrane gas separation [16] a phenomenon associated with polymers which deteriorates their structure and increase the permeability of all the gases and hence decreases the selectivity [1].

## **2.2 Selection of Polymer and Membrane Preparation**

The selection of polymers or their blends used for membrane separation processes depends on the permeability, selectivity, cost, durability, ease of synthesis and fabrication. Wang et al. [10] obtained CO<sub>2</sub>/CH<sub>4</sub> selectivity of 49 however the CO<sub>2</sub> permeability was 22.6 barrer whereas Jose et al. [17] obtained permeability of 3800 barrer with CO<sub>2</sub>/CH<sub>4</sub> selectivity of 3.17. Usually a compromise between permeability and selectivity has to be made to set optimized values. Permeability and selectivity are recognized as trade-off parameters because an increment in one reduces the other.

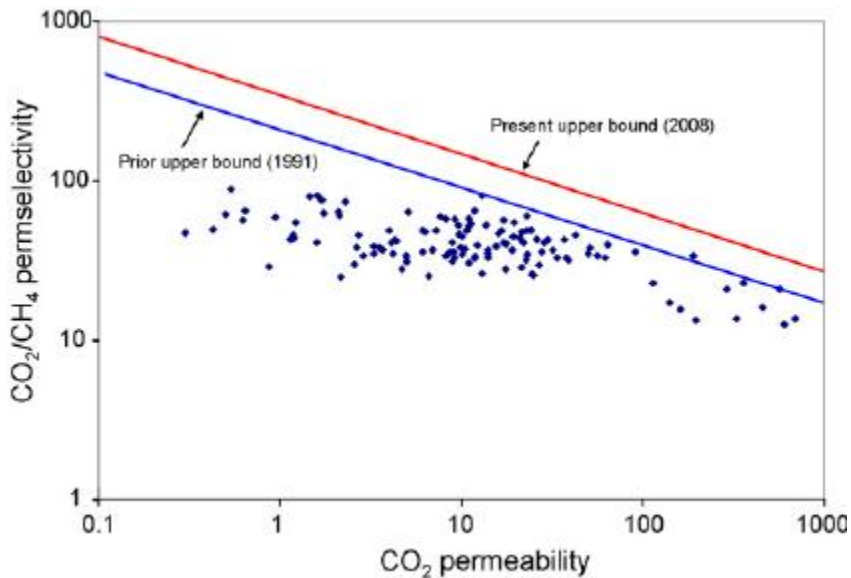
Poly(ethylene oxide) (PEO) are one of the polymers found very suitable for CO<sub>2</sub> capture. These polymers can capture CO<sub>2</sub> due to the presence of polar oxygen. Researchers have studied the removal of CO<sub>2</sub> using different blends of PEO which turned out to be very effective due to the presence of ethylene oxide linkage [10]. These membranes have problem of getting crystallize which in turn reduces the CO<sub>2</sub> permeability which can be overcome by using highly branched PEO or using lower MW PEO. Nijmeijer et al. found that use of PEBA<sub>X</sub> 1074 copolymer based on PEO have improved performance. Polaris<sup>®</sup> is also an important polymer which has been tested at pilot scale and it shows great potential for CO<sub>2</sub> removal and have acceptable selectivity [10].

Cellulose acetate (CA) is one of the economical polymers available which make it ideal for industrial use where large surface area is required to process gases. Research is still going on for membranes of pure CA and its blends however pure polymers are unable to provide required permeability and selectivity therefore blending of other polymers or their chemical modification is required.

A lot of different techniques have been employed for manufacturing the membranes. Glassy polymers are found to be the best in terms of mechanical strength and required permeability properties compared to rubbery polymers. In order to obtain both stability and permeability properties Loeb and Surirajan prepared asymmetric membranes. The

membranes obtained have a very thin skin layer consists of a dense material which is supported over a thicker bottom layer which provides the required mechanical strength. The thickness of skin layer is around 0.1 to 1 micron whereas of thick support is 100 to 200 micron [10].

The permeability and selectivity of the membrane is controlled by top skin layer. Membranes can differ in the thickness from 0.1-0.5 micron [18] prepared in laboratory to 50 nm prepared for commercial purpose. A lot of work has already been done in order to improve the performance of membranes which includes a major work by Robeson who investigated the properties of different polymers [13]. Robeson's upper bound curve elucidates the inverse relationship between permeability and selectivity for different polymers. The trade-off is related to upper bound in which the log of selectivity is plotted against the log of permeability for a certain membrane. Figure 6 shows Robeson's curve for different polymers which provide us the information about maximum selectivity obtained for a particular permeability. This plot determines the limit to achieve desired permeability with highest possible selectivity and vice versa. It can be seen that with improved methods and technology the Robeson's upper curve is moved upwards in 2008 from where it used to be in 1991.



**Figure 6 Robeson's upper bound Curve for CO<sub>2</sub>/CH<sub>4</sub>**

A defect free composite membrane prepared by Henis and Tripodi [19] consists of a thin silicon rubber on a asymmetric membrane. The top layer can have any required polymer for certain application including the inorganic filler as well and can be regarded as mixed matrix membrane. Researchers are attracted towards these kinds of membranes due to their improved performance [20].

Li et al [21] investigated the effect of polyethylene glycol (PEG) on the permeability and selectivity of CO<sub>2</sub> and CH<sub>4</sub> after addition of different molecular weights to CA. An increase in the permeability of membrane was observed when lower MW PEG200 was utilized but with a decreased CO<sub>2</sub>/CH<sub>4</sub> selectivity and best CO<sub>2</sub>/CH<sub>4</sub> selectivity was obtained by adding 10% of higher MW PEG-20000 which resulted in decreased permeability. An increase in transition temperature from 185.5 C for the pure CA to 197 C for membrane with 10% PEG20000 was also observed.

### **2.3 Facilitated Transport Membranes**

Facilitated transport membranes (FTM) gained popularity for their increased permeability behavior due to carbonate and bicarbonate formation in the presence of water. In most of the industrial processes the streams contains water vapors which compete with the CO<sub>2</sub> and reduces the permeability while in FTMs the presence of water facilitates the permeation and hence are more effective. Kim et. al. [22] reported increased CO<sub>2</sub> permeability in the presence of water using a PVAm membrane.

### **2.4 Fixed Site Carrier Membranes**

Recently fixed site carrier (FSC) membranes containing CO<sub>2</sub>-carriers have been found to increase CO<sub>2</sub> permeability due to its interaction with fixed sites. Deng et. al. [16] have worked on a crosslinked PVAm FSC membrane having amine group as CO<sub>2</sub>-carrier site. FSC membranes have limited application due to the loss of site carriers for long term operation by evaporation and degradation [23]. Polymer blends and facilitated transport membranes tackle the plasticization problem to some extent but fixed site carrier membranes are more effective due to presence of extra free volume for CO<sub>2</sub> created by site carriers [16][24].

## 2.5 Mixed Matrix Membranes

A major breakthrough is development of mixed matrix membranes (MMMs) in which different fillers are incorporated in polymers to modify their permeability properties. Particles like metal organic frameworks (MOFs), zeolites, TiO<sub>2</sub> nanoparticles, silica, CNTs [25][26][27] have been successfully incorporated.

S. Farrukh et. al. [11] studied the effect of TiO<sub>2</sub> nanoparticles on gas permeation and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 23.3 was reported. CO<sub>2</sub> permeability was enhanced due to the interaction between CO<sub>2</sub> and TiO<sub>2</sub> nanoparticles of size 5-10 nm. Cornelius et al. [28] studied effect of different alkoxy-silanes on permeability behavior of silica incorporated into polyimide. After thermal treatment permeability of CO<sub>2</sub> and CH<sub>4</sub> was enhanced up to 500% with little change in perm-selectivity.

A. L. Khan et al. [29] studied the effect of counter-ion on permeation behavior of mixed gases through sulfonated aromatic poly(ether ether ketone) (S-PEEK) at different pressures. CO<sub>2</sub>/CH<sub>4</sub> selectivity was slightly reduced justified by increased mobility of polymer chains allowing both CO<sub>2</sub> and CH<sub>4</sub> to pass and S-PEEK (Al) membranes exhibited the best CO<sub>2</sub>/CH<sub>4</sub> selectivity of 18.60.

The molecular sieving ability, adsorption at the surface, enhanced tensile strength and availability of extra path through the inorganic filler makes MMMs far more superior [30]. CNTs are one of the attractive organic fillers with CO<sub>2</sub> adsorption capacity of 22.7 mg/g [25].

M. M. Khan et al. [27] investigated the effect of CNTs on gas permeation. Chemical modification of CNTs with PEG in a polymer blend enhanced the CO<sub>2</sub> permeability due to better interaction and hence CO<sub>2</sub>/CH<sub>4</sub> selectivity of 16.3 was attained. Liyuan et al. [16] studied separation of CO<sub>2</sub>/CH<sub>4</sub> using PVAm/PVA blend membranes with CNTs as fillers at elevated pressure. An increase in CO<sub>2</sub> permeance up to 0.35 m<sup>3</sup>(STP)/m<sup>2</sup>.h was observed while CO<sub>2</sub>/CH<sub>4</sub> selectivity of 45 was documented.

A. R. Moghadassi et al [30] fabricated cellulose acetate based MMMs using MWCNTs as fillers which enhanced the mechanical strength and CO<sub>2</sub>/CH<sub>4</sub> selectivity from 13.41 to 21.81. Highest CO<sub>2</sub>/CH<sub>4</sub> selectivity obtained at 2 bar pressure was 53.98.

## **2.6 Objective**

It is observed from above discussion that CNTs are good choice as filler for MMMs but have only been tested for pure gases with tetra-hydro-furan (THF) as a solvent [31] . Effect of MWCNTs weight percentages with a different solvent and mixed gas experiments need to be analyzed in order to make these membranes industrially viable.

In this study cellulose acetate is blended with PEG and MWCNTs using acetone as a solvent. PEG enhances the chain mobility and MWCNTs provides the thermal stability, tensile strength [31] and an extra path for transport of CO<sub>2</sub> molecules. Resulted membrane can be more CO<sub>2</sub> permeable and CO<sub>2</sub>/CH<sub>4</sub> selective. Fabricated membranes were tested for CO<sub>2</sub> and CH<sub>4</sub> permeation and effect of different weight percentages of PEG and MWCNTs on permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity is observed at different pressure for both single and mixed gases.

# Chapter - 3

## Experimental Methods

In this chapter membrane materials, membrane preparation and casting technique, gas permeability test system and its working are discussed in detail

### 3.1 Materials:

- Cellulose acetate (MW-50000) from Sigma-Aldrich
- Acetone and PEG (MW-1000) from Sigma-Aldrich.
- 95% pure MWCNTs with 8-15nm outer diameter (OD) and 3-5nm inner diameter (ID) from Yurui Shanghai Chemicals.
- 99.5% CO<sub>2</sub> and CH<sub>4</sub> from Linde, Pakistan.

### 3.2 Solution Preparation:

Solution casting method was adopted to fabricate Pure CA, CA/PEG and CA/PEG/MWCNTs membranes. Casting solution was prepared by adding CA in 15 ml acetone in 7 different bottles while 5, 10 and 15 weight percentage of MWCNTs were added in 10 ml acetone in 3 separate bottles and were stirred overnight. 10%PEG and prepared MWCNTs solutions were added into 3 of the bottles containing CA/acetone solution whereas 5, 10 and 15 weight percentages of PEG were added to other 3 bottles containing CA/acetone solution and stirred for 24hrs. After stirring, solutions were sonicated for 6hrs to obtain homogeneity. Bottles were placed at room temperature for half hour to remove any bubbles.

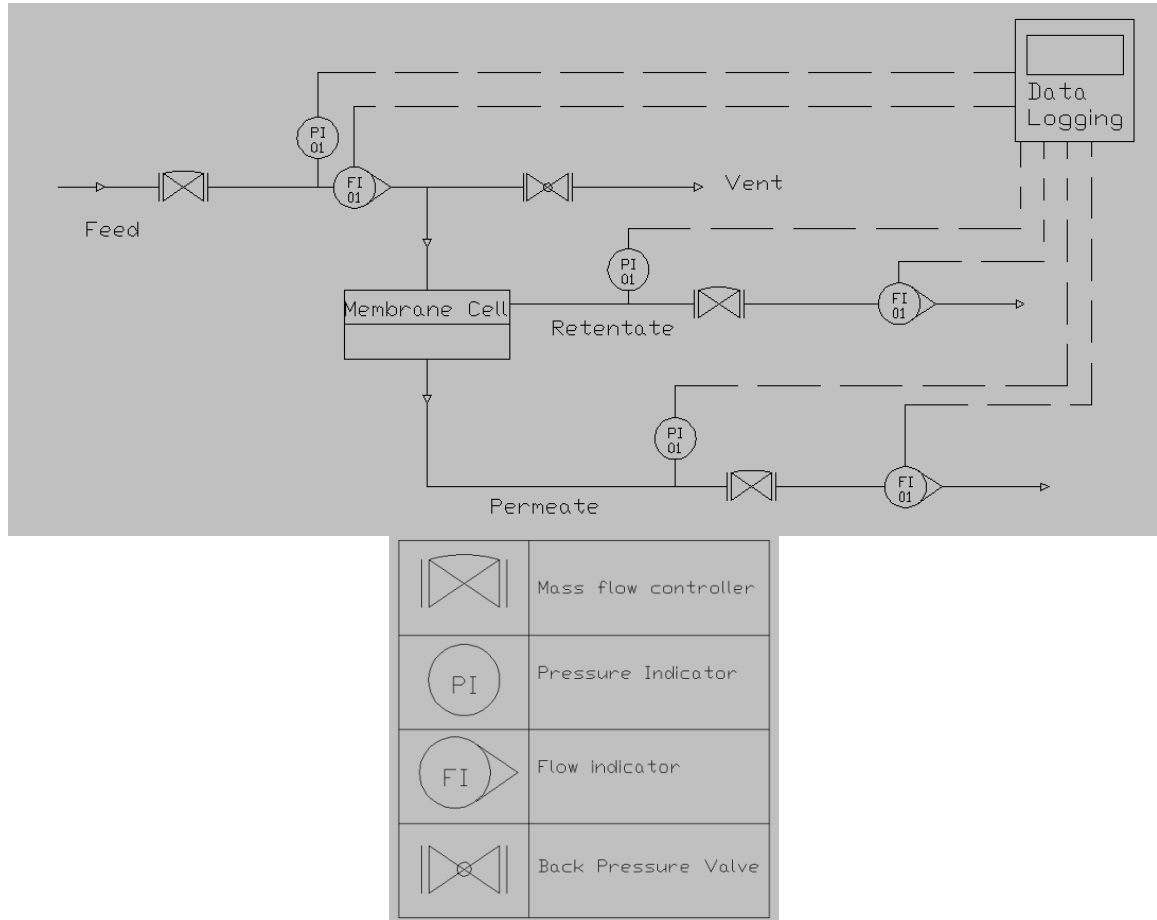
### 3.3 Membrane Casting:

The prepared solutions were then poured into petri dishes very slowly in order to avoid any bubble formation and retained at a horizontal surface for 10 min at room temperature and then placed in the oven at 40 °C for 2 days. The thickness of membranes was 35 to 50 um.

### 3.4 Permeation Setup:

#### 3.4.1 Equipment Description:

Permeability of CO<sub>2</sub> and CH<sub>4</sub> is measured both as single and mixed gas using Gas Permeability Test System (PHILOS, Korea). The layout of system is shown in Figure 7.



**Figure 7 Layout of Gas Permeability Test System**

This system contains porous ceramic support with effective area of 8.5cm<sup>2</sup>. A bubble flow meter is also utilized to determine the flow rates below 10 ml/s. The permeability test system provides us with very accurate values for pressure and flow rate which are used to determine the permeability.

#### 3.4.2 Instrumentation:

Gas permeability test system contains following instrumentation

- Mass flow controllers
- Back pressure valve
- Flow indicators
- Pressure indicators
- Stainless steel membrane cell
- Bubble flow meter

### 3.4.3 Working of Gas Permeability Test System:

Single and mix gases are provided from cylinders to feed side and membranes are tested at constant volume and variable pressures from 2 to 4 bar. A certain pressure difference is maintained across the membrane to determine the flux through membranes. The pressure difference is calculated by subtracting the pressure at feed side from the permeate side pressure. The pressure difference is increased gradually to determine the effect of increasing pressure difference.

Mass flow controllers control and detect the feed and permeate flow rates in order to keep the flow rate and pressure within allowable limits while back pressure valve is used to maintain a given differential pressure across the membrane. Flow and pressure indicators display gas flow and pressure on feed, concentrate and permeate side.

Permeability of the gases is determined by solution diffusion model [6] represented by Eq. (3.1).

$$P = \frac{Q.L}{\Delta P.A} \quad (3.1)$$

Where Q is volumetric flow rate (ml/min), L is membrane thickness (cm), P is Pressure difference between feed and permeate side (bar) and A is the effective area of membrane (cm<sup>2</sup>). Ratio of CO<sub>2</sub> and CH<sub>4</sub> permeability is the permselectivity [6] represented by Eq. (3.2).

$$\alpha_{A/B} = P_A/P_B \quad (3.2)$$

Where P<sub>A</sub> is permeability of CO<sub>2</sub> and P<sub>B</sub> is permeability of CH<sub>4</sub>

For mixed gas, permeability is determined by Eq. (3.1) while the selectivity depends on the molar fractions of the components both in feed and permeate. Hence the selectivity of mixed gas is measured by following equation.



$$\alpha_{i/j} = (y_i/y_j) / (x_i/x_j) \quad (3.3)$$

Where y and x are the molar fractions of gases in permeate and feed respectively. i and j are used for CO<sub>2</sub> and CH<sub>4</sub> respectively.

# Chapter - 4

## Resources and Approaches

In this chapter the characterization techniques used for fabricated membranes are discussed also includes some of their application and working as well.

### Characterization Techniques

#### 4.1 Scanning Electron Microscopy (SEM):

Scanning electron microscope (SEM) is used to analyze the structure and morphology of membranes. High energy electrons are focused on the surface of the material. The analysis is performed to determine the surface and cross sectional morphology. Membranes were prepared by sputter coating of gold and analyzed at 10mm distance and 90mA current in SEM.

##### 4.1.2 Components of SEM:

SEM consists of following components (Figure 8):

- Electron column
- Scanning system
- Detector
- Display
- Vacuum system
- Electronic control

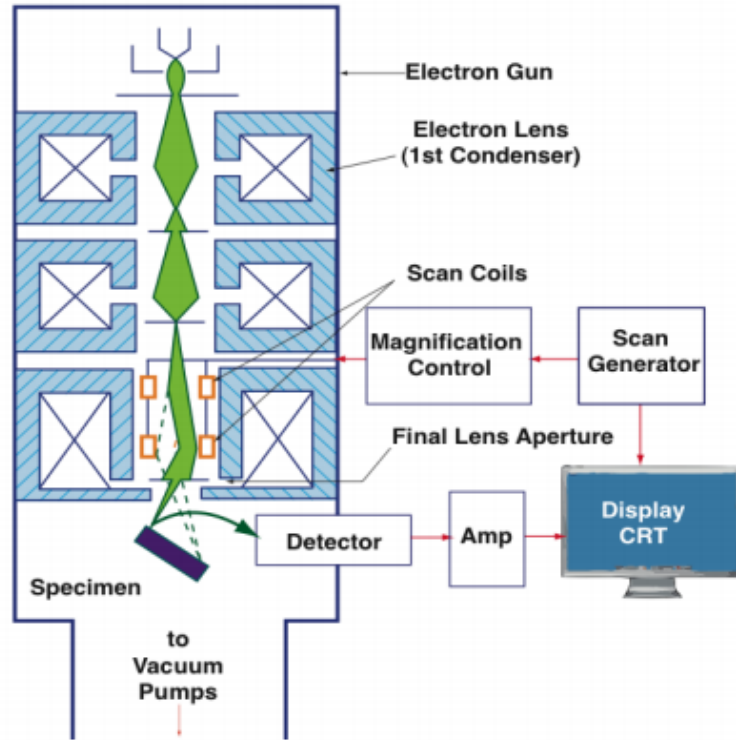


Figure 8 Schematic of Scanning Electron Microscope (SEM)

#### 4.1.1 Working Principle:

Electron of high energy are decelerated which dissipated in different kind of signals are focused on the surface of material. Secondary electrons form the image of material while the backscattered electrons are important for phase determination. The secondary electrons elucidate the morphology and topography of the sample. SEM is a non-destructive technique because the sample because the interaction of electrons does not damage the sample.

#### 4.1.3 Magnification in SEM:

There is no optical transformation in SEM. The magnification in SEM is obtained by increasing or decreasing the length of scan ( $L_{spec}$ ) on the material under observation. Before magnification the calibration of microscope is very important. With a constant length of scan of monitor ( $L_{mon}$ ) the linear magnification ( $M$ ) can be determined by following formula.

$$M = L_{mon} / L_{spec} \quad (4.1)$$

#### 4.1.4 Quality of the Image:

SEM image formation is dependent on determining the events collected at detector. Signal (S) is measured by counting the number of electrons (n) at the detector. The Noise (N) presence abates the signals and the quality of the signals is decreased.

Increased number of counts increases the quality as it is the ratio of signal to noise (S/N).

The Contrast (C) is defined as:

$$C = (S_2 - S_1) / S_2 \quad (4.2)$$

#### 4.1.5 Image Formation:

SEM forms a two dimensional intensity map and each pixel on the map is representative of a point of the sample which is directly related to the intensity of the signal (Figure 9). It is not possible for SEM to generate a true image rather the image is displayed electronically.

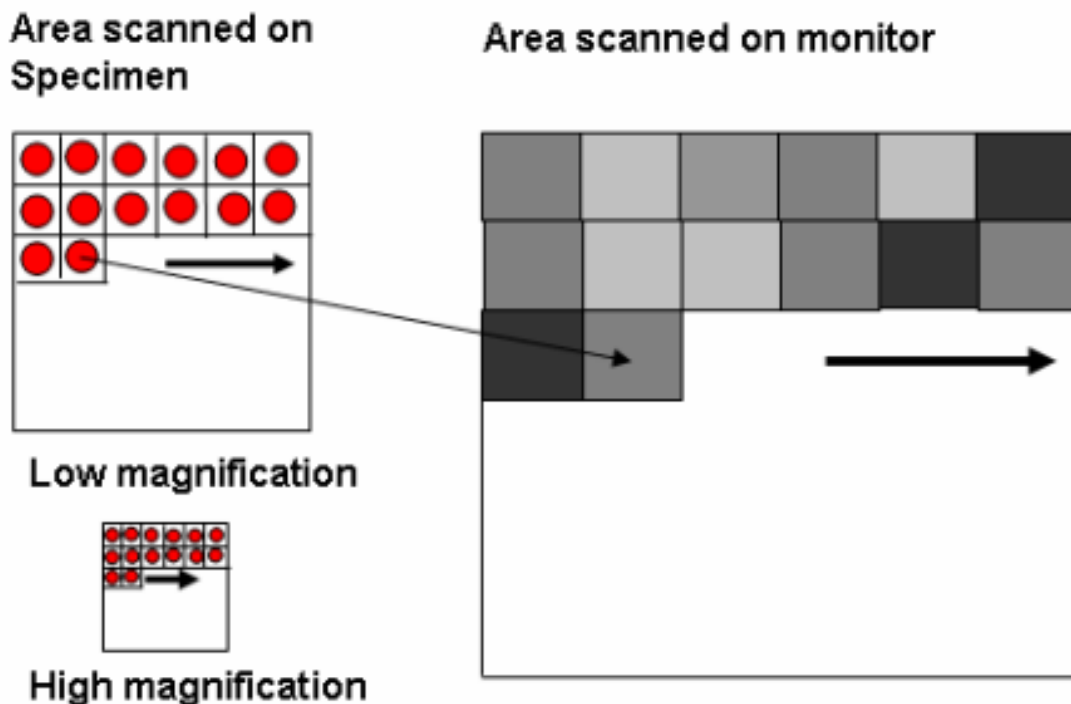


Figure 9 Image formations in Scanning Electron Microscope (SEM)

The information obtained from the image formed by SEM is:

- Morphology of the material
- Topography of the material

## 4.2 Thermal Gravimetric Analysis (TGA):

Weight changes and thermal stability of fabricated membranes were investigated by TGA. The weight change can be determined as a function of temperature or time at constant temperature. The atmosphere contains either N<sub>2</sub> or He. TGA can analyze polymers, composites or metals. Analysis was performed under nitrogen flow from 30 to 500 °C at a rate of 10 °C/min and 80ml/min of gas flow [32].

### 4.2.1 Instrumentation:

A schematic of TGA is shown in Figure 10 which contains following components.

- IR Detector
- Sample changer
- Furnace
- Optical filter
- Electronic microbalance

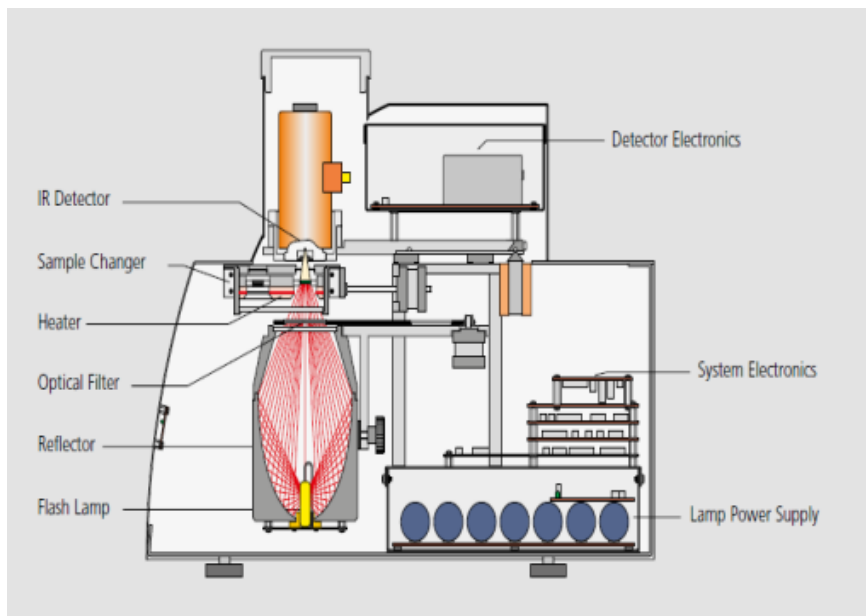


Figure 10 Schematic of Thermal Gravimetric Analysis (TGA)

#### 4.2.2 Working Principle:

TGA contains a sample holder in the form of a pan where sample is analyzed. The sample pan is heated through a furnace throughout the experiment. The weight change of the sample is recorded as the furnace provides constant heating. The sample atmosphere is controlled using the inert gas which usually is  $N_2$ , He or Ar. Through this procedure the thermal stability of membranes is determined. Figure 11 shows the components of furnace used in TGA.

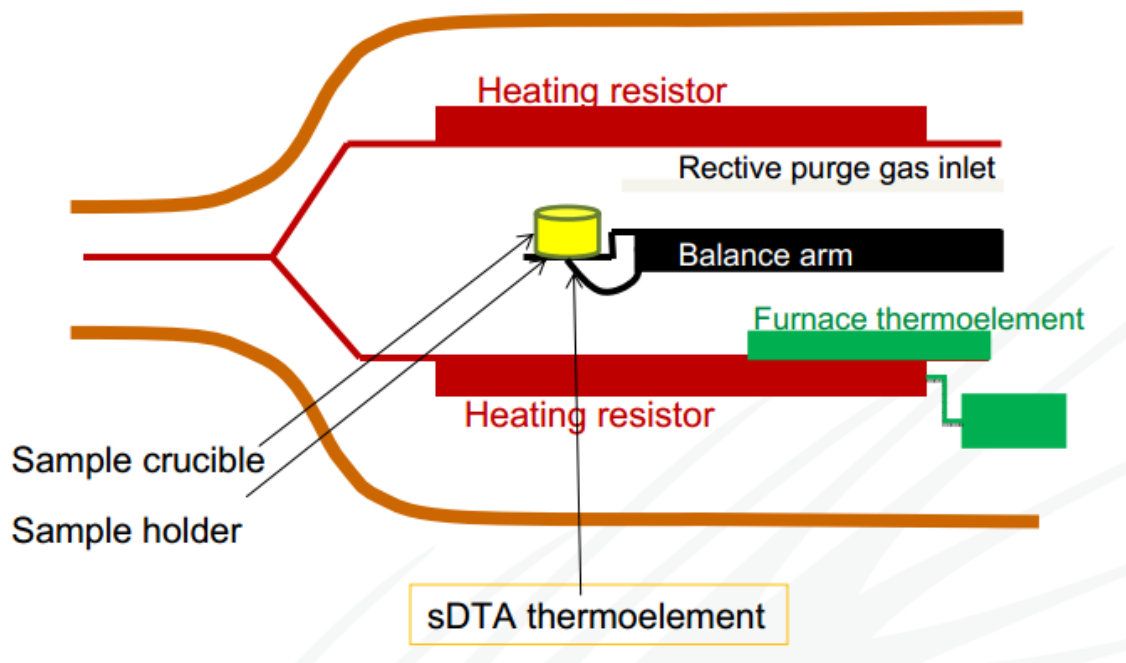


Figure 11 Furnace of TGA

#### 4.2.3 Types of Thermogravimetry:

##### Isothermal TGA:

A constant temperature is used for a fixed time period and the change in the weight of sample is determined.

##### Dynamic TGA:

A constant heating rate is employed and the change in the weight of the sample is determined.

### Quasistatic TGA:

Sample is heated to a constant rate at series of increasing temperature.

#### 4.2.4 Performance of TGA:

Performance of TGA is determined by decomposition of oxalate monohydrate (Figure 12). It exhibits three weight losses with increasing temperature in inert ( $N_2$ ) atmosphere. The decomposition process of oxalate monohydrate occurs when the gaseous products ( $H_2O$ ,  $CO$ ,  $CO_2$ ) are identified as they evolve.

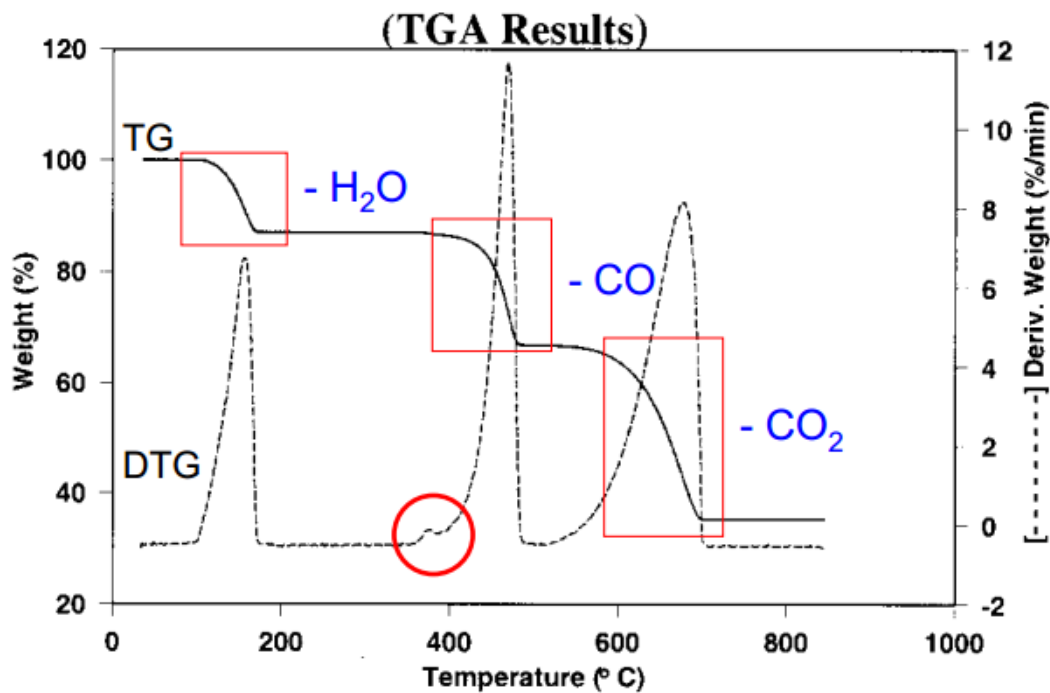


Figure 12 TGA Results for standard oxalate monohydrate

#### 4.2.5 Factors affecting the TGA curve:

Increasing the heating rate and sample size increases the temperature at which decomposition occurs whereas the progress of the reaction is affected by packing, crucible shape and gas flow of the system.

#### 4.2.6 Information obtained from TGA:

The measured weight loss curve obtained from TGA gives us information about following:

- Changes in the sample composition
- Thermal stability
- Kinetic parameters for chemical reactions in the sample

### **4.3 Mechanical Testing:**

Tensile testing is utilized to determine the mechanical stability of the material. In this test the material is subjected to controlled stress and the deformation produced is measured. It is used to determine the strain produced in the material under certain stress. The primary use of tensile testing is to determine the stress-strain curve. The strength of material is determined by simply stretching operation. Normally the material is taken in a standard shape and stretched at a constant rate to determine the strain produced by a specific stress. Stress and strain are defined as:

$$\text{Stress} = \text{Force/Area} = F/A \quad (4.3)$$

$$\text{Strain} = \text{Change in length/Original length} = \Delta L/L \quad (4.4)$$

#### **4.3.1 Purpose of Mechanical Testing:**

Purpose of mechanical testing is normally to determine its elasticity, ductility, resilience and toughness.

#### **4.3.2 Universal Testing Machine (UTM):**

UTM is used to test tension, compression, bending or hardness of the materials. The components of UTM include (Figure 13):

- Frame
- Engine
- Gear
- Screws
- Crosshead
- Gripping Jaws
- Extensometer
- Specimen



- Hardware and Software Control

### 4.3.3 Working Principle:

The material to be tested is placed in between the jaws of testing machine and an axial force is applied while the strain produced is recorded. The strain is determined until the material fracture. The change in the length is determined to measure the relationship between stress and strain.



Figure 13 Universal Testing Machine (UTM)

### 4.4 X-ray Diffraction (XRD):

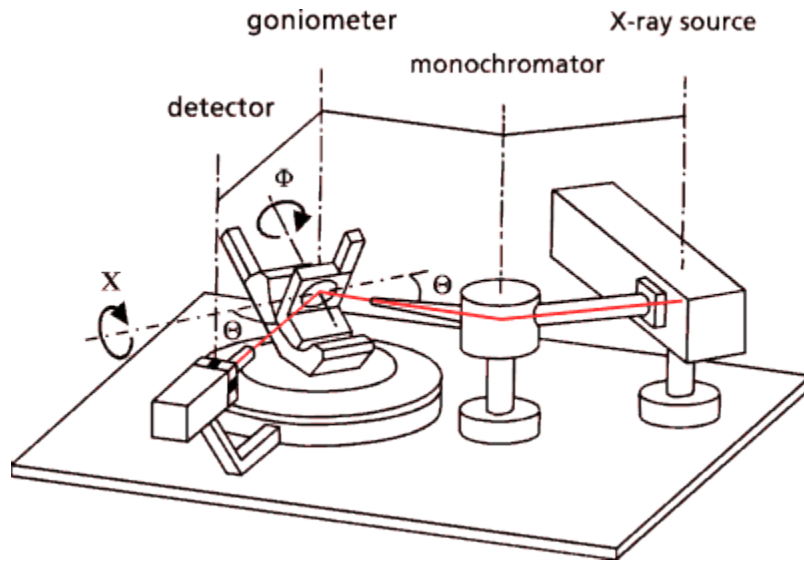
XRD analysis was performed to determine the phase purity or crystallinity of material. X-rays have provided the researchers means to determine the properties of material at atomic level. It can determine how the atoms are packed, the bond lengths and angles.

#### 4.4.1 Instrumentation:

Figure 14 shows a schematic of X-ray Diffractometer (XRD) which have four main components.

- X-ray Source
- Monochromator

- Goniometer
- Detector



**Figure 14 Schematic of x-ray Diffractometer (XRD)**

#### **4.4.2 Working Principle:**

The working principle of XRD is dependent on the interference of monochromatic ray. Generated X-rays are directed on to the sample under observation. Each material have their atoms arranges in regular planes in a crystal lattice. The X-rays after striking the material are both refracted and transmitted while some of it is diffracted and absorbed in the sample material as well. The diffraction of light is different for different material and phases depending upon the atoms arrangement in crystal lattice. The distance between the atoms is measured by Bragg's Law which is defined as:

$$n\lambda = 2d \sin\theta \quad (4.5)$$

$n$  = order of diffracted beam

$\lambda$  = wavelength of incident x-ray beam

$d$  = distance between adjacent planes of atoms

Distance between the adjacent planes of atoms generated in the x-ray scan gives the 'fingerprint' of the sample. Material can be easily identified by comparing this scan with the reference pattern.

### **4.4.3 Applications:**

X-ray diffraction analysis is widely used for following applications

- To identify unknown crystalline material
- To Determine unit cell dimensions
- To check the purity of sample

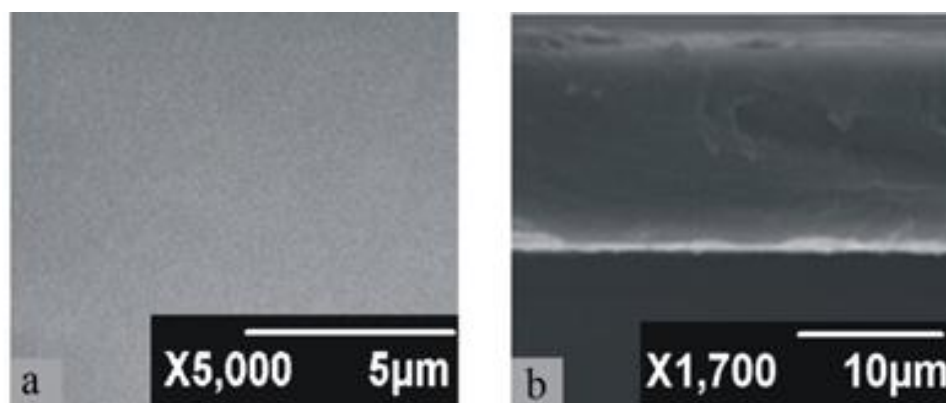
# Chapter - 5

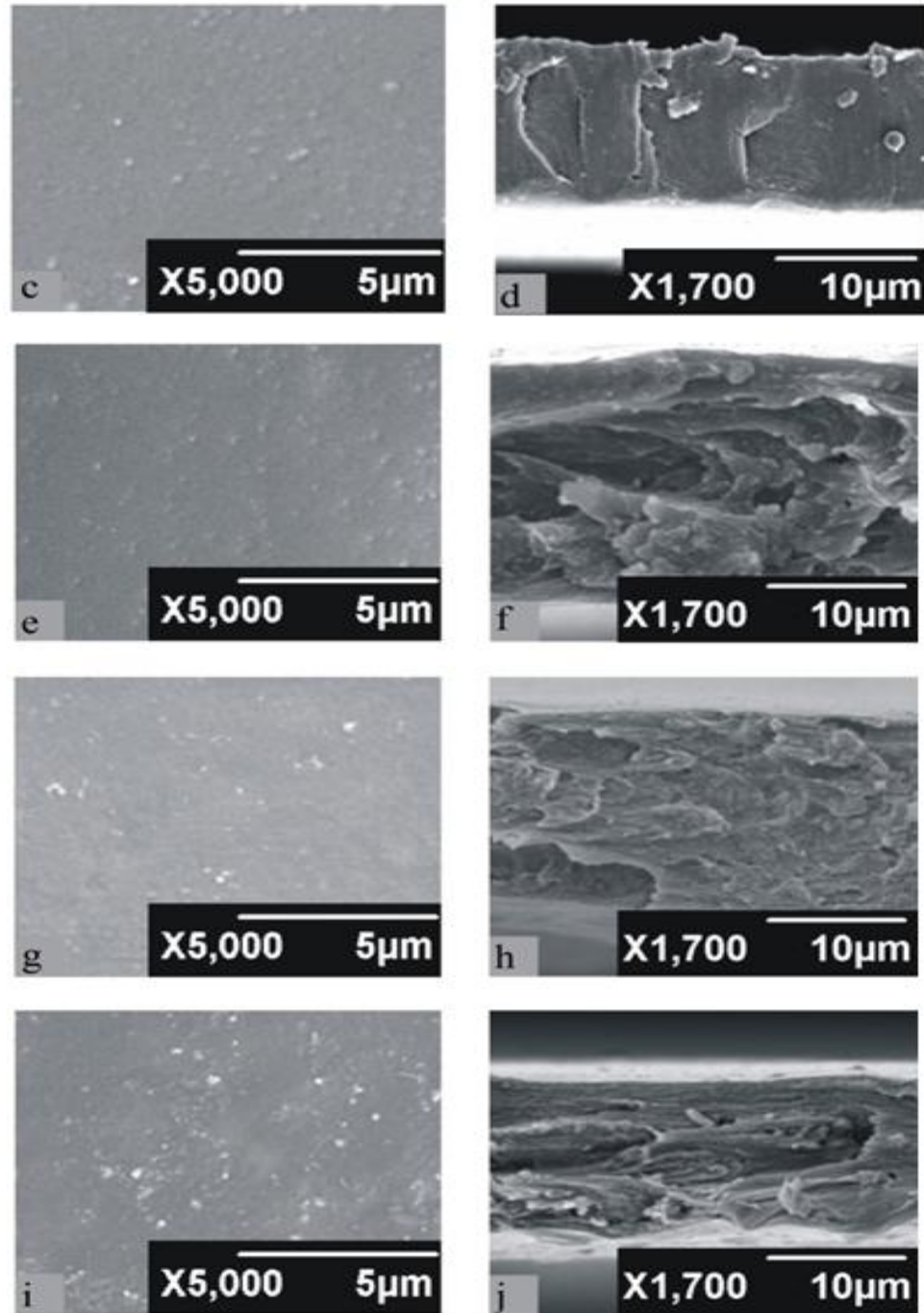
## Results and Discussions

In the first part of this chapter results obtained from characterization are discussed in detail. This chapter also includes the permeation study and effect of pressure and weight fraction of filler on permeability and selectivity of the fabricated membranes

### 5.1 Scanning electron microscope (SEM):

Morphology of the membranes is compared using SEM micrographs of Pure CA, 10%PEG/CA and MMMs at a resolution of x5000 for surface and x1700 for cross section. The SEM analysis revealed that fabricated membranes have dense structure (Figure 15). Pure CA has smooth surface (Figure 15a) but 10%PEG/CA has slightly rough surface (Figure 15c). SEM micrograph (Figure 15(e,g,i)) depicts the presence of MWCNTs at the surface of MMMs. The cross sectional micrographs (Figure 15(b,d,f,h,j)) demonstrates that in case of pure CA and 10%PEG/CA the cross sections are smooth and dense however in case of MMMs according to Figure 15(f,h,j) there is sub-layer void formation which increment in case of filler incorporation because it disturb the proper packing of the chains [31]. In case of pure CA which is a glassy polymer the chains are rigid and there are free spaces in the forms of voids between the chains. These voids are non-selective passages which are not being able to separate the gases. Addition of PEG increases the density of polymer thereby decreasing the voids between the chains but since the flexibility of the chains increase, the diffusion of CO<sub>2</sub> also increases and hence the permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity as well.





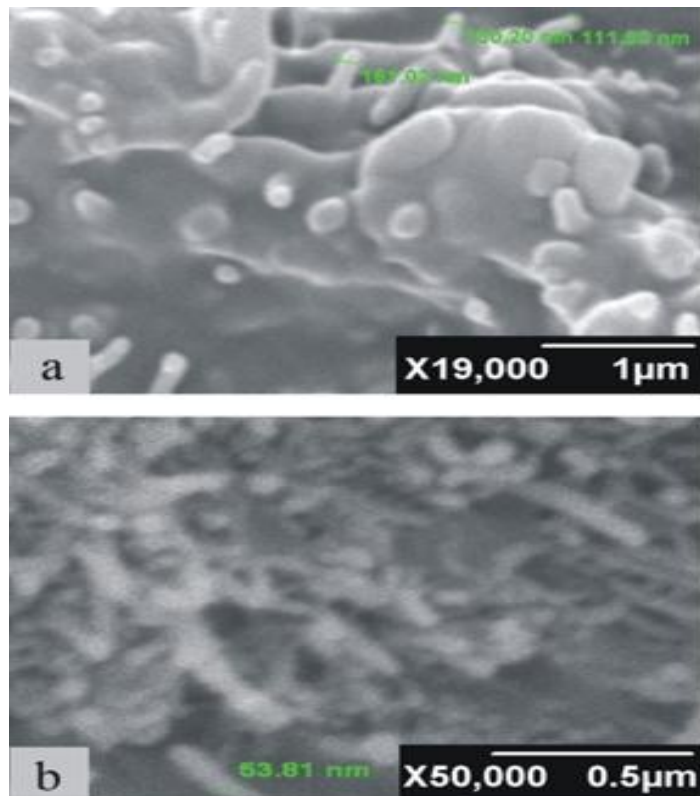
**Figure 15** Surface and Cross sectional SEM images (a) Pure CA (b) Pure CA cross section (c) 10%PEG/CA d) 10%PEG/CA cross section (e) 5%MWCNTs/10%PEG/CA (f) 5%MWCNTs/10%PEG/CA cross section (g) 10%MWCNTs/10%PEG/CA (h) 10%MWCNTs/10%PEG/CA cross section (i) 15%MWCNTs

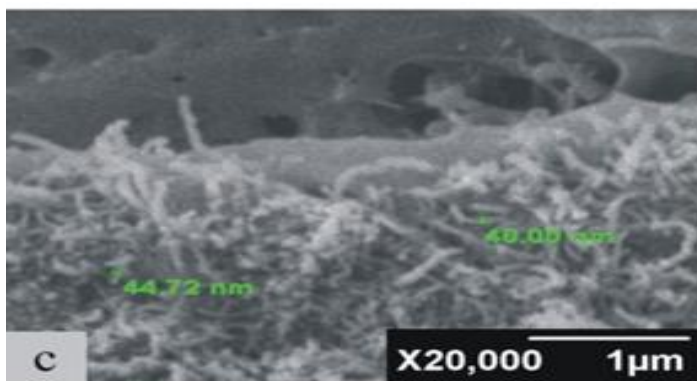
The cross sectional micrographs are taken at different resolutions due to different sizes of MWCNTs. In the cross sectional micrographs (Figure 16(a,b)) the homogeneity of MWCNTs in 5 and 10% MWCNTs was observed however micrograph (Figure 16c)

confirms agglomeration in case of 15% MWCNTs. The augmented size of MWCNTs in case of 5% MWCNTs compared to 10 and 15% MWCNTs is depicted in Figure 5.2. The OD in case of 5% MWCNTs is enlarged from 15 nm to 134.37 nm on average which shows strong interaction between MWCNTs and polymeric chains.

In case of 10% MWCNTs OD improved from 15 to 53.81 nm (Figure 16b) whereas for 15% MWCNTs the OD is enhanced from 15 to 42.36 nm (Figure 16c). Although the interaction in 5% MWCNTs is stronger but the amount of MWCNTs are not enough to give required permeability. In case of 10% MWCNTs the homogeneity, optimum amount of MWCNTs and slightly better interaction between MWCNTs and polymer chains results in less void formation at the edges of MWCNTs.

In case of 15% MWCNTs agglomeration enhances in such a way that voids are generated at the interface of MWCNTs which are non-selective allowing both the gases to pass through consequently increasing the permeability and decreasing the selectivity. In order for the gases to be separated they have to go through the process of diffusion. Since CO<sub>2</sub> can diffuse readily through the polymer because of OH groups attached to the polymer chains the permeability of CO<sub>2</sub> is more compared to CH<sub>4</sub> and ultimately more CO<sub>2</sub>/CH<sub>4</sub> selectivity.





**Figure 16 SEM images for increased size of MWCNTs (a) 5%MWCNTs/10%PEG/CA (b) 10%MWCNTs/10%PEG/CA (c) 15%MWCNTs/10%PEG/CA**

## 5.2 Permeation study:

The permeation setup was evacuated for 5hrs before membrane testing. Membranes were cut into a circular shape of 5 cm diameter and were placed on porous support in a way that the edges extend pass the polymeric seals in order to ensure the proper sealing. The experiments were performed to determine the permeate flow rate at different pressures. Using constant area and thickness permeability is determined by inserting the values obtained for flow rate and pressure difference. Table 5.1 to 5.7 shows the permeability and selectivity obtained at different pressures for fabricated membranes.

**Table 1 Change in Permeability and Selectivity with increasing Pressure of CA membranes**

$\Delta P$ (bar)	Permeability	(Barrer)	Selectivity
	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
2.00	38.32	6.67	5.74
2.50	38.94	6.40	6.09
3.00	35.23	7.10	4.96
3.50	32.58	8.55	3.81
4.00	29.90	9.98	3.00

**Table 2 Change in Permeability and Selectivity with increasing Pressure of 5%PEG/CA membranes**

$\Delta P$ (bar)	Permeability	(Barrer)	Selectivity
	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
2.00	16.90	0.47	35.80
2.50	14.58	0.63	23.03
3.00	13.28	0.65	20.33
3.50	12.52	0.65	19.38
4.00	12.84	0.75	17.04

**Table 3 Change in Permeability and Selectivity with increasing Pressure of 10%PEG/CA membranes**

$\Delta P$ (bar)	Permeability	(Barrer)	Selectivity
	CO2	CH4	CO2/CH4
2.00	19.32	0.49	39.47
2.50	19.70	0.59	33.53
3.00	19.15	0.65	29.35
3.50	17.34	0.70	24.80
4.00	16.23	0.73	22.10

**Table 4 Change in Permeability and Selectivity with increasing Pressure of 15%PEG/CA membranes**

$\Delta P$ (bar)	Permeability	(Barrer)	Selectivity
	CO2	CH4	CO2/CH4
2.00	16.68	0.57	29.50
2.50	15.69	0.68	23.13
3.00	15.68	0.75	20.80
3.50	16.19	0.81	20.04
4.00	15.66	0.85	18.47

**Table 5 Change in Permeability and Selectivity with increasing Pressure of 5%MWCNTs/10%PEG/CA membranes**

$\Delta P$ (bar)	Permeability	(Barrer)	Selectivity
	CO2	CH4	CO2/CH4
2.00	22.23	0.54	41.47
2.50	19.10	0.51	37.11
3.00	17.63	0.48	37.00
3.50	18.38	0.51	36.00
4.00	18.94	0.50	37.86

**Table 6 Change in Permeability and Selectivity with increasing Pressure of 10%MWCNTs/10%PEG/CA membranes**

$\Delta P$ (bar)	Permeability	(Barrer)	Selectivity
	CO2	CH4	CO2/CH4
2.00	26.95	0.65	41.64
2.50	28.14	0.58	48.92
3.00	25.88	0.72	35.99
3.50	24.17	0.78	30.96
4.00	24.13	0.72	33.55



**Table 7 Change in Permeability and Selectivity with increasing Pressure of 15%MWCNTs/10%PEG/CA membranes**

$\Delta P$ (bar)	Permeability	(Barrer)	Selectivity
	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
2.00	64.82	39.96	1.62
2.50	67.45	44.45	1.52
3.00	68.88	45.16	1.53
3.50	74.92	46.79	1.60
4.00	73.59	46.54	1.58

The permeation behavior of gases can be divided into two parts:

- (i): Effect of PEG and PEG/MWCNTs weight percentages on single and mixed gas permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity of membranes
- (ii): Effect of pressure on permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity of membranes

### **5.2.1 Effect of PEG and PEG/MWCNTs on single and mix gas permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity in pure and modified membranes.**

Permeability of CO<sub>2</sub> and CH<sub>4</sub> is less in CA/PEG blend compared to pure CA membrane but CO<sub>2</sub>/CH<sub>4</sub> selectivity is higher. Table 8 depicts the effect of PEG weight percentage on the permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. Pure CA has more CO<sub>2</sub> permeability followed by 10% PEG while 5 and 15% PEG have least permeability values. Higher permeability of pure CA is due the presence of non-selective voids between the polymer chains attributed by improper fixing of chains and hence free path for both CO<sub>2</sub> and CH<sub>4</sub> is available resulted in reduced CO<sub>2</sub>/CH<sub>4</sub> selectivity. In case of 5%PEG/CA the chains are compact and hence CO<sub>2</sub> permeability is reduced, moreover enhanced CO<sub>2</sub>/CH<sub>4</sub> selectivity is attributed by presence of OH functional group responsible for CO<sub>2</sub> transport through the membrane but the movements of chains are not as free as they are in 10%PEG/CA which have slightly better CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. Further increment in weight percentage to 15%PEG increases the density consequently reducing the CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity also reported by Li et al [21].

**Table 8 Permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity of Pure, 5%, 10% and 15% PEG/CA membranes at 2.5 bar**

Membranes	Permeability (Barrer)		Selectivity
	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
Pure CA	38.31	6.67	5.74
5%PEG/CA	16.90	0.47	35.8
10%PEG/CA	19.31	0.48	39.47
15%PEG/CA	16.67	0.56	29.5

Presence of MWCNTs decreases the permeability compared to pure CA membrane which is in accordance with Maxwell model. According to this model diffusion of a gas through membrane decreases with the addition of a filler [26]. Effect of filler weight percentage on permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity is shown in Table 9. The permeability was reduced by increasing the weight percentage from 5 to 10% and augmented for 15%. Increasing the percentage of filler from 5 to 10% decreased the permeability due to its inverse relation with filler weight percentage while improved CO<sub>2</sub>/CH<sub>4</sub> selectivity is acquired.

Secondly, the orientation of MWCNTs in the membranes and kinetic diameters (Table 10 [33]) play an important role because some of MWCNTs with ID up to 3.7 nm are vertical and allow a straight path only for CO<sub>2</sub> thereby increasing its permeability and decreasing the permeability of CH<sub>4</sub> however MWCNTs with ID more than 3.8 nm behave just like sub layer voids allowing passage for both molecules but at the exit mostly CO<sub>2</sub> molecules gets adsorbed on the polymer chains due to their affinity for OH group and diffuse through the membrane.

Further addition of 15%MWCNTs enhanced the permeability which is not consistent with Maxwell model justified by the agglomeration of MWCNTs. Moreover the presence of excessive MWCNTs disturbs the proper packing of molecular chains and voids are produced allowing both gases a non-selective path and decreasing the CO<sub>2</sub>/CH<sub>4</sub> selectivity. Hence increasing weight percentage of MWCNTs beyond 10% causes inhomogeneity due to agglomeration which is also reported by A. Raza et al [31]

**Table 9 Permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity of Pure, 5%, 10% and 15% MWCNTs/PEG/CA membranes at 2.5 bar**

Membranes	Permeability (Barrer)		Selectivity
	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
Pure CA	38.31	6.67	5.74
5%MWCNTs/10%PEG/CA	36.84	2.86	12.86
10%MWCNTs/10%PEG/CA	26.95	0.64	48.92
15%MWCNTs/10%PEG/CA	64.81	39.96	1.62

**Table 10 Kinetic Diameter of CO<sub>2</sub> and CH<sub>4</sub>**

Gas	Kinetic Diameter (nm)	Ref.
CO <sub>2</sub>	3.3	[27]
CH <sub>4</sub>	3.8	[27]

For mixed gas permeation study of fabricated membranes, a binary mixture of CH<sub>4</sub> and CO<sub>2</sub> (60:40) was utilized. Composition and CO<sub>2</sub>/CH<sub>4</sub> selectivity of permeate is determined by mole fraction using areas under the curves obtained from Gas Chromatograph (GC). Compositions and CO<sub>2</sub>/CH<sub>4</sub> selectivity of pure and modified membranes are given in Table 11.

**Table 11 Mix gas composition of feed and permeate and CO<sub>2</sub>/CH<sub>4</sub> selectivity of pure and modified membranes at 2.5 bar**

Membranes	Composition		Selectivity (CO <sub>2</sub> /CH <sub>4</sub> )
	(CH <sub>4</sub> :CO <sub>2</sub> )		
	Feed	Permeate	
Pure CA	60:40	68:32	2.16
10%PEG	60:40	5:95	28.67
10%MWCNTs/10%PEG/CA	60:40	4:96	38.5

The CO<sub>2</sub>/CH<sub>4</sub> selectivity rises from 2.16 to 28.67 for 10%PEG/CA while further incorporation of 10% MWCNTs increases the CO<sub>2</sub>/CH<sub>4</sub> selectivity from 28.67 to 38.5 for 10%MWCNTs/10%PEG/CA. The purity of CO<sub>2</sub> gas in the permeate increases from 32 to 95% for 10%PEG/CA while it becomes 96% for 10%MWCNTs/10%PEG/CA. In mixed gas separation the sorption and diffusion of gases becomes competitive and

consequently the permeability and selectivity in case of mixed gas is different from pure gas [34].

### 5.2.2 Effect of pressure on permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity of pure and modified membranes

Figure 17 demonstrates a slight decrease in permeability in most cases except 15% MWCNTs/10% PEG/CA which depicts that flow of gases through dense membranes is not too much dependent on pressure and there is a very slight increase in the flowrate with pressure and hence permeability decreases as we increase the pressure while 15% MWCNTs/10% PEG/CA does not behave like other membranes due to poor interaction of MWCNTs with the polymer caused by agglomeration.

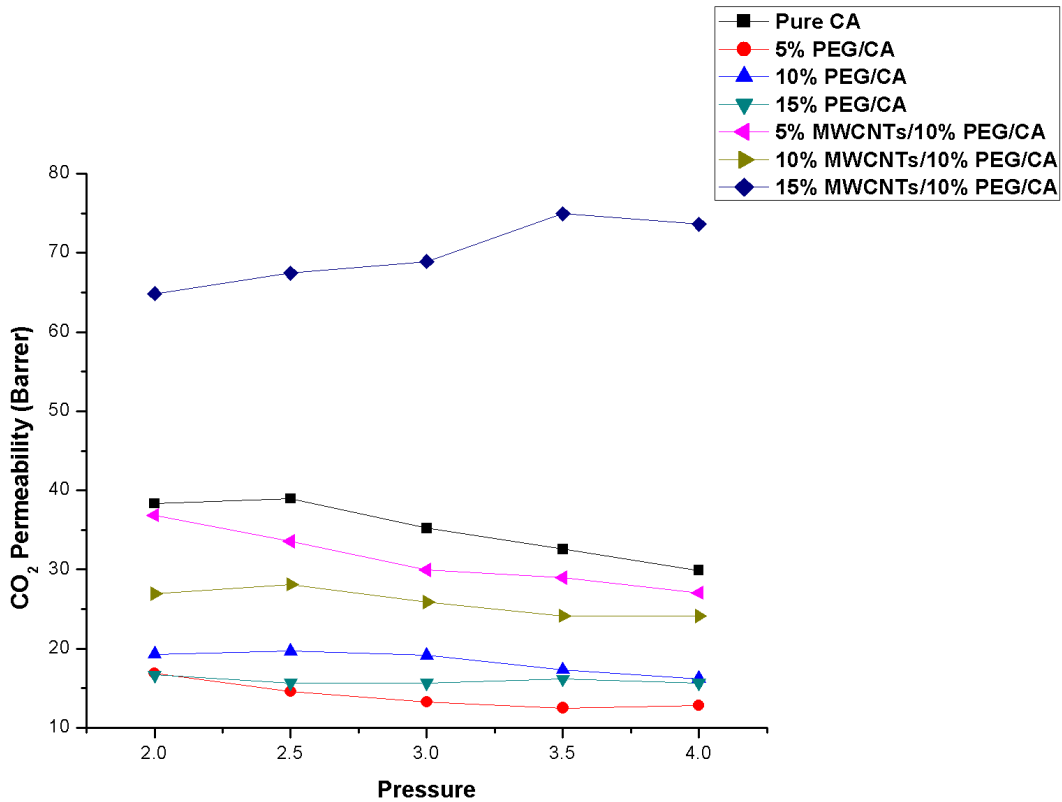


Figure 17 Pressure vs CO<sub>2</sub> Permeability graph for pure and modified membranes

According to Figure 18 the change in permeability of CH<sub>4</sub> with pressure for pure and modified membranes can be observed. There is a very slight change in permeability of

CH<sub>4</sub> for 5, 10 and 15% PEG/CA. According to solution diffusion model permeability is inversely related to differential pressure. The decrease in permeability is due to the fact that the flow rate of gas is not increasing as much at higher pressure as it was on the lower pressure.

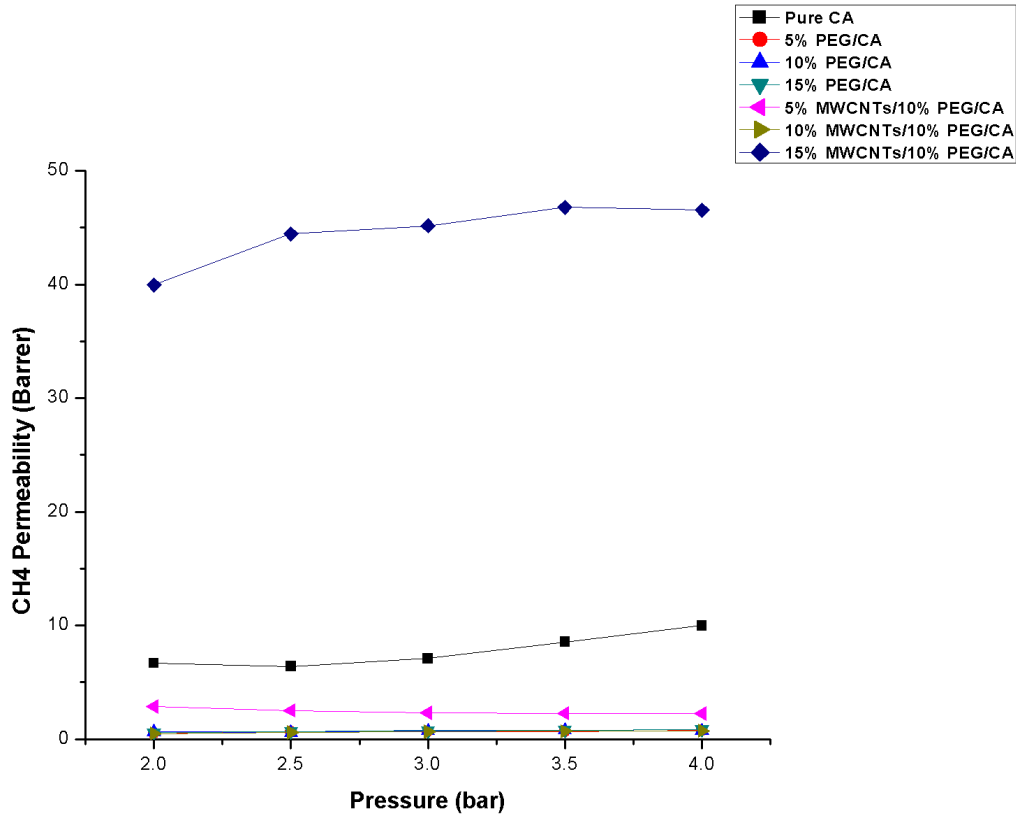


Figure 18 Pressure vs CH<sub>4</sub> Permeability graph for pure and modified membranes

Also the chains are packed and permeability mainly depends upon the interaction of gas molecule with the OH functional group attached to the chains, which in case of CO<sub>2</sub> facilitate its diffusion due to quadrupole moment associated with CO<sub>2</sub>. In case of MWCNTs the interaction between MWCNTs and CA determines the permeability of CH<sub>4</sub>. In case of 15% MWCNTs the interaction between MWCNTs and CA is weak (Figure 16) producing small spaces between MWCNTs and CA matrix allowing the gas a non-selective path while in case of 5 and 10% MWCNTs the interaction is strong and the permeability is either through the MWCNTs or due to movement of chains which hinders the movement of CH<sub>4</sub> molecules and allow CO<sub>2</sub> to pass preferably.

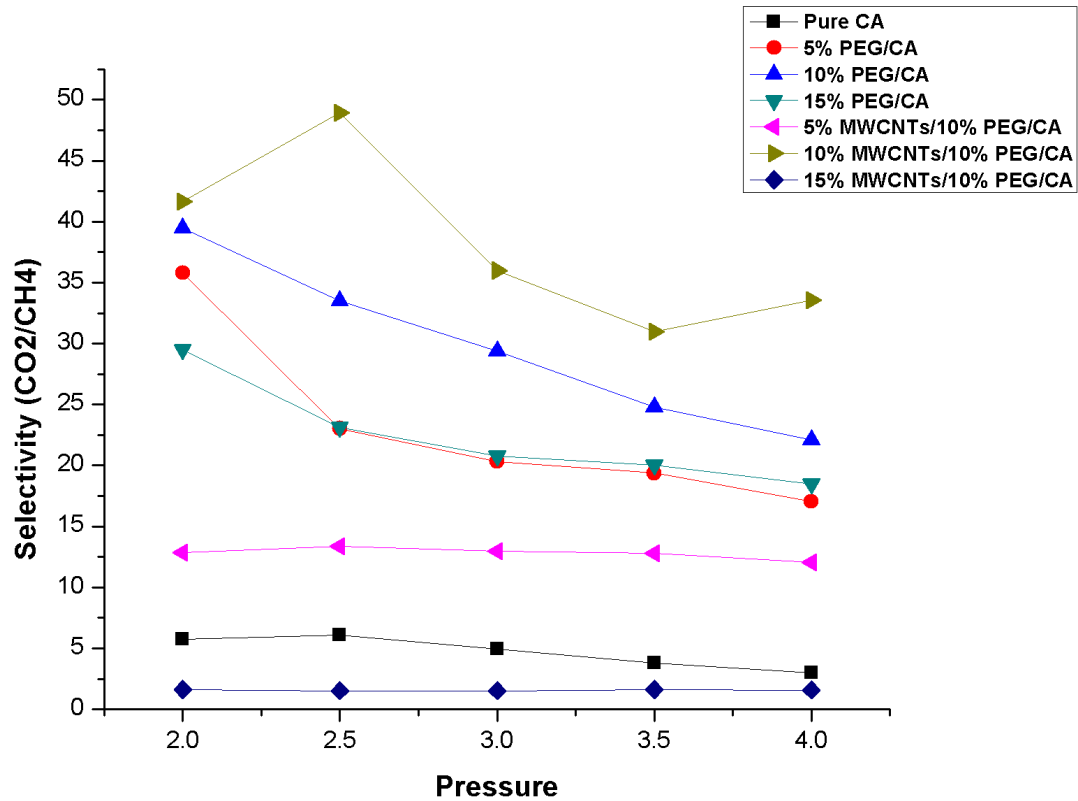
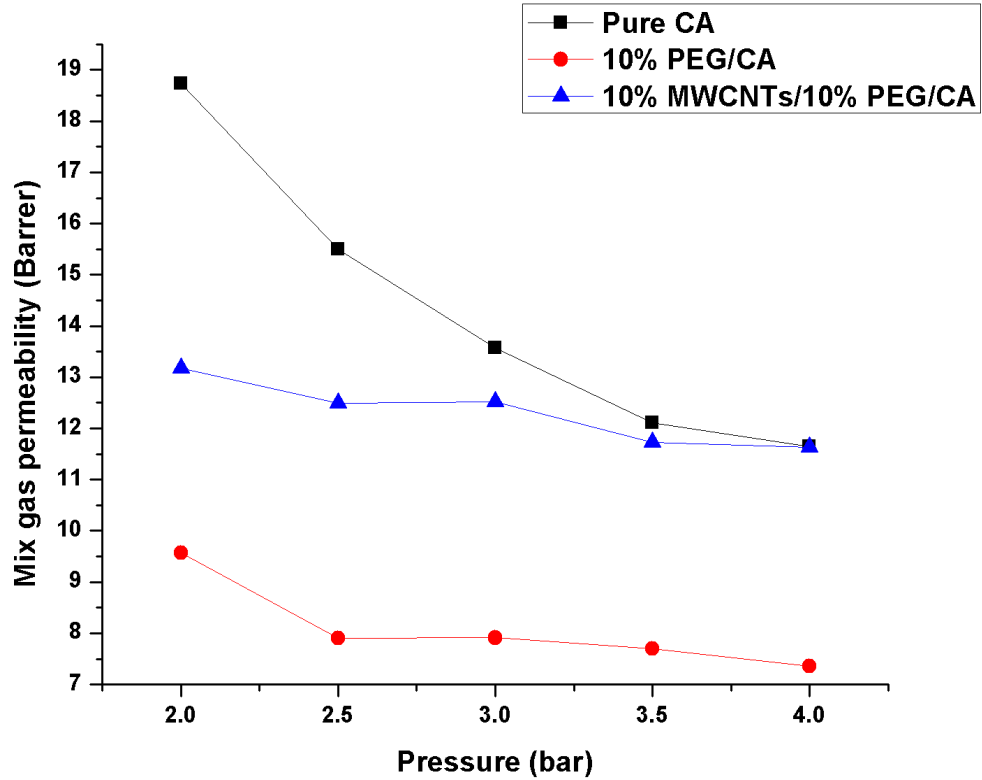


Figure 19 Effect of pressure on selectivity (CO<sub>2</sub>/CH<sub>4</sub>) at 25oC

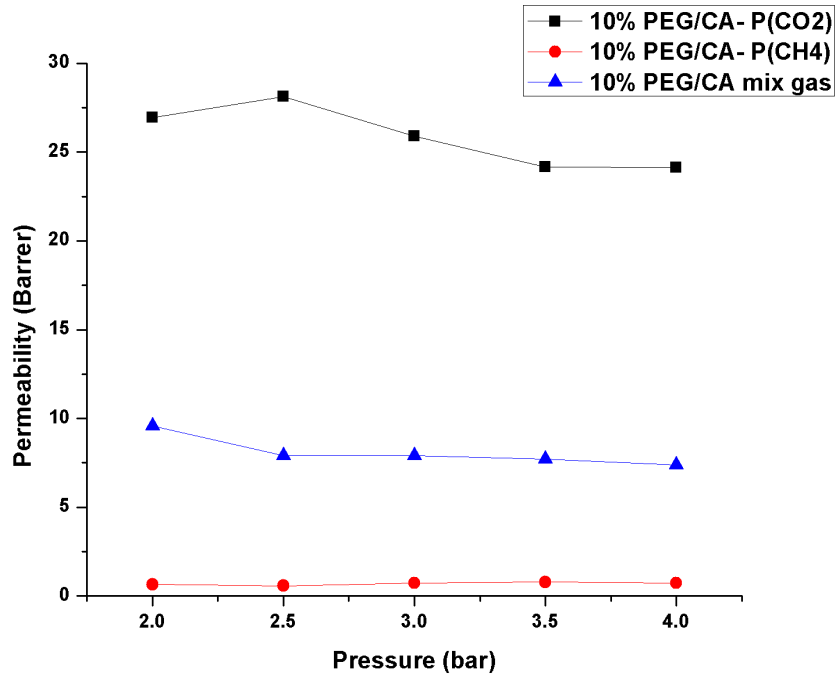
The effect of pressure on CO<sub>2</sub>/CH<sub>4</sub> selectivity with the addition of PEG and MWCNTs can be observed in Figure 19. Maximum CO<sub>2</sub>/CH<sub>4</sub> selectivity obtained is for 10%MWCNTs/10%PEG/CA because the gap between the surface of MWCNTs and polymer matrix disappear due to good interaction which is also confirmed by SEM whereas 15%MWCNTs/10%PEG/CA is the least selective due to poor interaction between MWCNTs and CA (Figure 15,16).

Permeability of mixed gas for pure and modified membranes at different pressures is depicted in Figure 20. It can be seen that the trend of permeability for mixed gas is almost the same as it is for single gases. The permeability increases a little at 2.5 bar while it decreases for the increasing pressure because the effect of pressure on flow rate at high pressure difference is not same as it is at lower pressure difference.

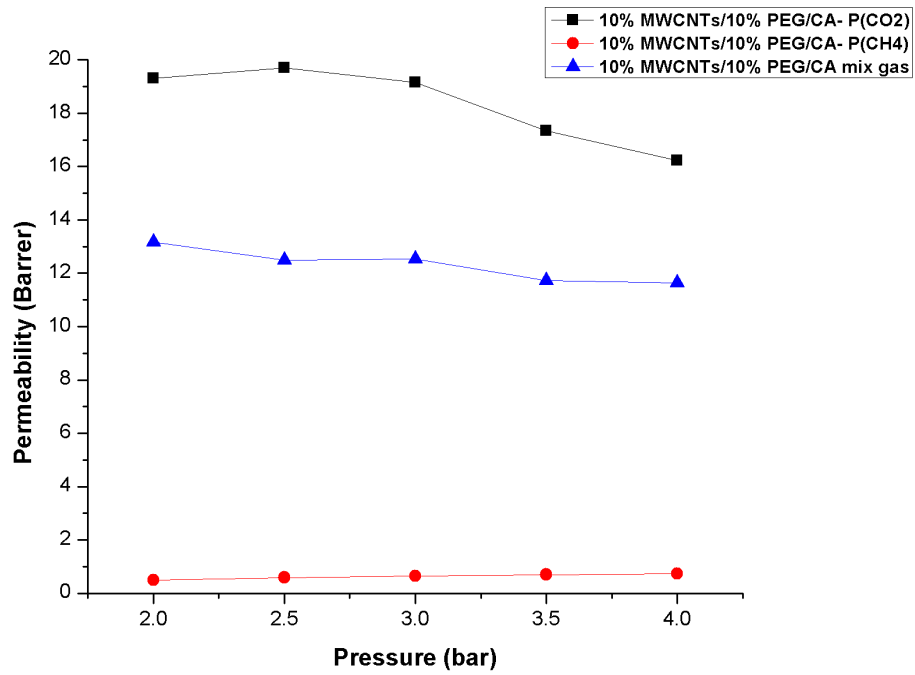


**Figure 20** Mix gas Permeability of Pure CA, 10%PEG/CA and 10%MWCNTs/10%PEG/CA at different pressures.

The comparison of pure CA, CA/PEG and CA/PEG/MWCNTs membranes for CO<sub>2</sub>, CH<sub>4</sub> and mixed gas is depicted in Figure 21(a, b, c). In all the cases the permeability of CO<sub>2</sub> is more compared to CH<sub>4</sub> and the permeability of mix gas is different from the situation when single gases are used it is somewhere in between the permeability of single gases which is due to the fact that when mixed, the area of membrane available to the gases is same but the type of molecules are different and both the gas molecules compete and hinder the movement of other molecule through membrane. Hence the presence of another gas reduces the permeability [34][35].

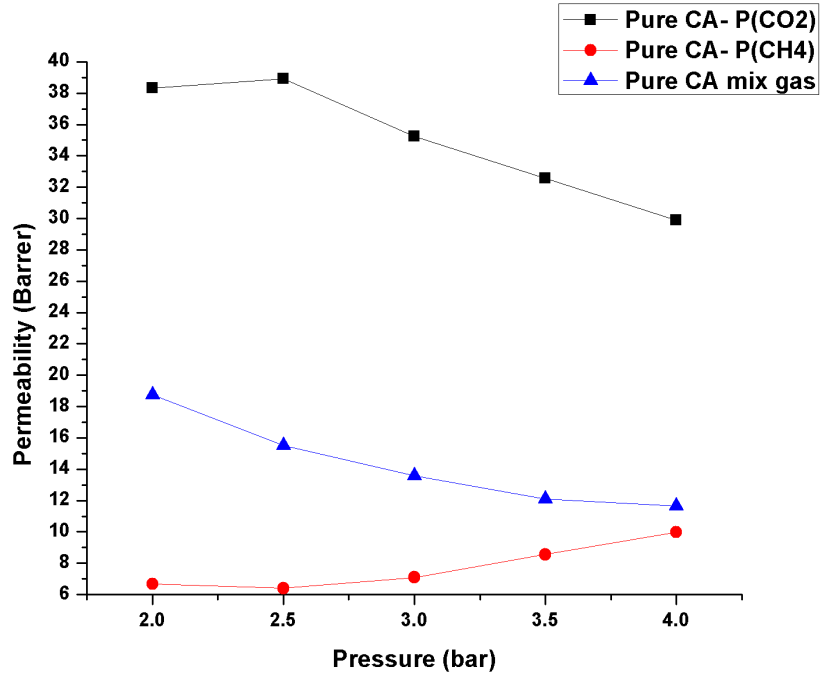


(a)



(b)





(c)

Figure 21 Mix gas Permeability of Pure CA, 10%PEG/CA and 10%MWCNTs/10%PEG/CA at different pressures.

### 5.3 XRD:

XRD patterns of Pure CA, 10%PEG/CA and 10%MWCNTs/10%PEG/CA are shown in Figure 22.

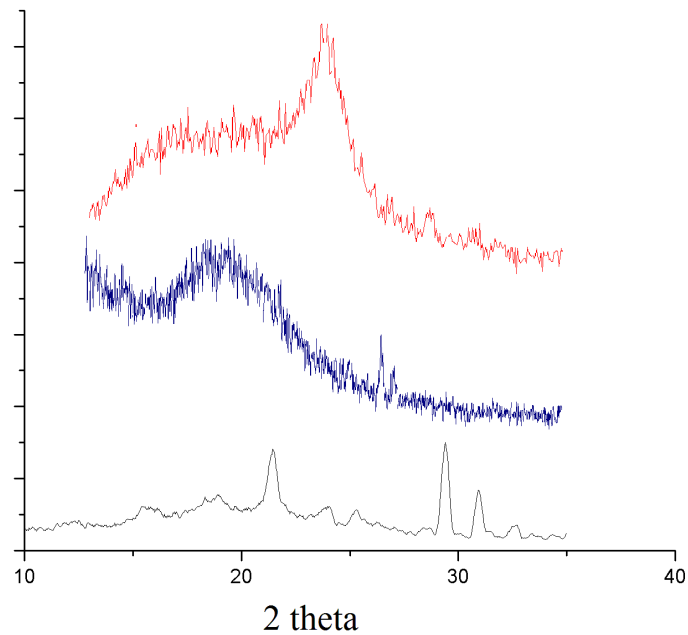


Figure 22 XRD images of Pure CA (Red), 10%PEG/CA (Blue) and 10%MWCNTs/10%PEG/CA (Black)

For pure CA a sharp peak at 23° is obtained and addition of 10% PEG causes a shift towards left generating a broader peak at 18° while in case of 10% MWCNTs three peaks at 23°, 29° and 32° are observed. Peak at 29° and 32° are due to the presence MWCNTs containing carboxylic groups while peak at 23° is slightly shifted towards left confirming good interaction between CA and MWCNTs.

#### 5.4 TG/DTA:

The weight loss for 10%MWCNTs/10%PEG/CA membrane starts at 290 °C and decomposition occurs at 350 °C (Figure 23). For pure CA weight loss starts at 180 °C and decomposition occurs at 330 °C. In case of 10%PEG/CA weight loss starts at 160 °C and it is decomposed at 320 °C. Presence of PEG increase the chain mobility causing an early weight loss in case of 10%PEG/CA but presence of MWCNTs in case of 10%MWCNTs/10%PEG/CA improves the thermal stability and hence weight loss occurs at 290°C which makes this membrane industrially very useful where separation occurs at higher temperatures.

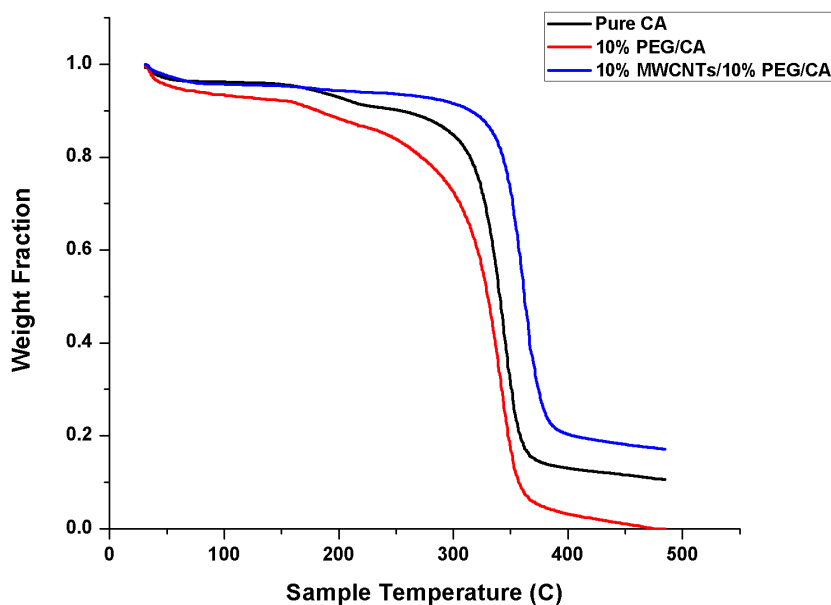


Figure 23 TGA curves of Pure CA, 10%PEG/CA, 10%MWCNTs/10%PEG/CA

## 5.5 Tensile Testing:

The results of tensile strength and % elongation of pure CA, 10%PEG/CA and 10%MWCNTs/10%PEG/CA (Figure 24) depicts that 10%PEG/CA has better tensile strength than pure CA due to reduced free volume between the chains whereas both pure CA and 10%PEG/CA have less tensile strength compared to 10%MWCNTs/10%PEG/CA which is due to the strong interaction between MWCNTs and polymer chains.

The % elongation for both pure CA and 10%PEG/CA is greater than 10%MWCNTs/10%PEG/CA because it can be seen in Figure 15(f,h,j) that there is sub layer void formation in case when filler is incorporated but no sub layer void formation occur in case of pure CA and 10%PEG/CA s Figure 15(b,d). Moreover, the augmented size of MWCNTs proves that the sudden breakage of MWCNTs membrane is due to cohesive fracture in which the polymer between outer surfaces of MWCNTs suddenly breaks preventing it from interfacial breakage.

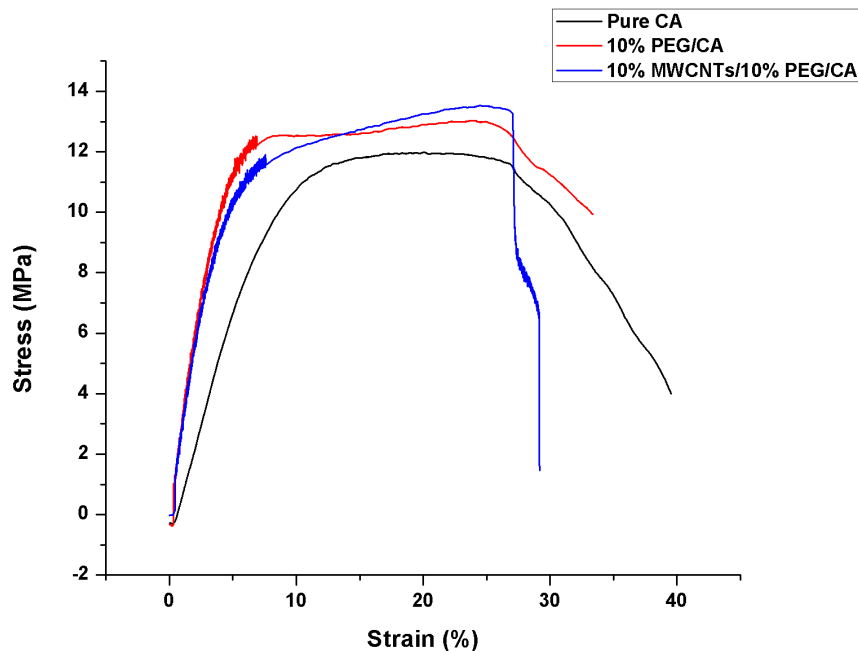


Figure 24 Stress Strain curves of Pure CA, 10%PEG/CA and 10%MWCNTs/10%PEG/CA

## 5.6 Comparison with other work:

Table 12 shows the CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity from different study in which different fillers are used for single and mixed gas separation. Increasing silica weight fraction from 10 to 40% increases the permeability from 6.6 to 14.8 but decreases the CO<sub>2</sub>/CH<sub>4</sub> selectivity from 23 to 15 [29]. Addition of 17% carbon molecular sieve (CMS) has a slight effect on permeability and increases the CO<sub>2</sub>/CH<sub>4</sub> selectivity from 35.71 to 44.78 [30]. However, in this study CO<sub>2</sub> permeability decreases from 38.31 to 19.31 for 10%PEG/CA and CO<sub>2</sub>/CH<sub>4</sub> selectivity increases from 5.74 to 39.47. There is further increment in permeability from 19.31 to 26.95 for 10%MWCNTs/10%PEG/CA and CO<sub>2</sub>/CH<sub>4</sub> selectivity is improved from 39.47 to 48.92.

For mixed gas, addition of Grignard treated zeolites reduces the permeability from 13.8 to 6.8 GPU while augment the selectivity from 39.6 to 46.9 [31]. Here, in this study the permeability of mixed gas reduces from 18.74 to 9.57 barrer for 10%PEG/CA whereas CO<sub>2</sub>/CH<sub>4</sub> selectivity improve from 2.16 to 28.67 and a rise in permeability is obtained from 9.57 to 13.17 barrer and an augment in CO<sub>2</sub>/CH<sub>4</sub> selectivity from 28.67 to 38.5 is observed for 10%MWCNTs/10%PEG/CA.

Table 12 Comparison with other work

Membrane	Pressure (bar)	CO <sub>2</sub> Permeability/Permeance	Selectivity (CO <sub>2</sub> /CH <sub>4</sub> )	Single (S)/Mixed (M)	Ref.
				(CO <sub>2</sub> :CH <sub>4</sub> )	
Barrer <sup>a</sup> /GPU <sup>b</sup>					
PSf+MCM-41 silica (10%)	4	6.6	Barrer	23	S [34]
PSf+MCM-41 silica (40%)	4	14.8	Barrer	15	S [34]
Matrimid® 52 18	3.4	10	Barrer	35.71	S [35]
Matrimid® 52 18 + CMS (17%)	3.4	10.3	Barrer	44.78	S [35]
Cellulose acetate + PEG (10%)	2	19.31	Barrer	39.47	S This study
Cellulose acetate + PEG (10%)+ MWCNTs (10%)	2	26.95	Barrer	48.92	S This study
Ultem® 1000	7.8	13.8	GPU	39.6	M (20:80) [36]
Ultem® 1000 + Grignard treated zeolites	7.8	6.8	GPU	46.9	M (20:80) [36]
Cellulose acetate + PEG (10%)	2	9.57	Barrer	28.67	M (40:60) This study
Cellulose acetate + PEG (10%)+ MWCNTs (10%)	2.5	13.17	Barrer	38.5	M (40:60) This study

<sup>a</sup>1Barrer= 10<sup>-10</sup>cc(STP)cm.cm<sup>-2</sup>s<sup>-1</sup>cmHg<sup>-1</sup>

<sup>b</sup>1GPU= 10<sup>-6</sup>cc(STP)cm<sup>-2</sup>s<sup>-1</sup>cmHg<sup>-1</sup>

# Chapter - 6

## Conclusion

This chapter contains an overview of the entire research work with future recommendations

### 6.1 Conclusion:

Membranes with 5, 10 and 15% PEG in CA and 5, 10 and 15% MWCNTs with 10% PEG in CA with acetone as a solvent were fabricated. Solution casting method was adopted to fabricate the membranes. Incorporation of PEG and MWCNTs provide a more selective passage to gases because incorporation of PEG decreases the voids present between the chains of polymers and make it denser but increases the flexibility of the chains thereby increasing the possibility of CO<sub>2</sub> diffusion through the polymer.

Experiments are run for both single and mix gases. The permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity for mix gas is found to be less because due to the presence of other gas both the gases compete and hinders the flow through membranes. 10%PEG/CA and 10%MWCNTs/10%PEG/CA produced the best results. PEG enhances the permeability of CO<sub>2</sub> compared to CH<sub>4</sub> due to free movement of chains and attached OH functional group consequently CO<sub>2</sub> permeability of 19.31 barrer and CO<sub>2</sub>/CH<sub>4</sub> selectivity up to 39.47 for single and mix gas permeability of 9.57 barrer with CO<sub>2</sub>/CH<sub>4</sub> selectivity up to 28.67 for 10% PEG/CA is obtained.

In case of MWCNTs the interaction of polymer and MWCNTs at the interface is very important. The voids between the surface of MWCNTs and CA polymeric chains are minimized due to good interaction between MWCNTs and polymer matrix in 10%MWCNTs/10%PEG/CA and MWCNTs preferably provide an extra selective path for CO<sub>2</sub> molecules which further enhances both the permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. CO<sub>2</sub> permeability of 26.95 barrer with CO<sub>2</sub>/CH<sub>4</sub> selectivity of 48.92 for single

and mix gas permeability of 13.57 with CO<sub>2</sub>/CH<sub>4</sub> selectivity of 38.5 for mixed gas is obtained for 10%MWCNTs/10%PEG/CA.

Experiments were performed from 2 to 4 bar and it is observed that pressure has a very slight inverse effect on both permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. TGA results show that weight loss for 10%MWCNTs/10%PEG/CA starts at 290 °C and decomposition occurs at 390 °C while weight loss for pure CA and 10%PEG/CA membranes starts at 180 °C and 160 °C and decomposition occurs at 370 °C and 360 °C respectively which indicates that 10%MWCNTs/10%PEG/CA membranes are more stable and suitable for industrial applications.

## **6.2 Future Recommendations:**

Permeability of the membranes should be enhanced. Different polymers or their blends can be utilized and can be further incorporated with the MWCNTs. Different fillers can be added in cellulose acetate to enhance the permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. Thickness of the membranes is one of the most important parameters. Membranes with reduced thickness and reasonable thermal and mechanical stability can have remarkable effect on the permeability.

## Appendix-A

### **Basic Definitions:**

**Membrane:** A physical barrier which have the ability to separate the components on the basis of their affinity for the membrane material.

**Permeate:** Components which pass through the membrane material are called permeate

**Retentate:** Components which are not being able to pass are retained on the feed side and are called retentate

**Mixed Matrix Membrane (MMM):** Membranes containing filler particles in polymer blend are called mixed matrix membranes

**Facilitated Transport Membranes (FTM):** Membranes in which diffusion of components is facilitated by presence of water are called facilitated transport membranes.

**Fixed Site Carrier Membranes (FSC):** Membranes which contain functional groups ( $\text{NH}_2$  or  $\text{OH}$ ) helps the diffusion of components through the membrane and hence these membranes are called fixed site carrier membranes

**Permeability Test System:** Permeability test system is a semi-automated system which have the ability to determine the pressure difference across the membrane and the flow rate of feed, permeate and retentate which can be utilized to determine the permeability of the system

**Solution Blending:** Solution blending is a process in which different polymer is dissolved into a solvent and after addition of further chemical species the solution.

**Membrane Casting:** Process of spreading the prepared solution in the forms of sheets and evaporation of solvent to obtain a solvent free polymeric sheet is called membrane casting

## References:

- [1] Y. Zhang, J. Sunarso, S. Liu, and R. Wang, “Current status and development of membranes for CO<sub>2</sub>/CH<sub>4</sub> separation: a review,” *Int. J. Greenh. Gas Control*, vol. 12, pp. 84–107, 2013.
- [2] A. L. Kohl and R. Nielsen, *Gas purification*. Gulf Professional Publishing, 1997.
- [3] D. Y. C. Leung, G. Caramanna, and M. M. Maroto-Valer, “An overview of current status of carbon dioxide capture and storage technologies,” *Renew. Sustain. Energy Rev.*, vol. 39, pp. 426–443, 2014.
- [4] L. Yang, F. Lu, X. Zhou, X. Wang, X. Duan, and B. Sun, “Progress in the studies on the greenhouse gas emissions from reservoirs,” *Acta Ecol. Sin.*, vol. 34, no. 4, pp. 204–212, 2014.
- [5] J. D. Seader and E. J. Henley, “Separation process principles,” 2011.
- [6] R. W. Baker, *Membrane technology*. Wiley Online Library, 2000.
- [7] J. Mulder, *Basic principles of membrane technology*. Springer Science & Business Media, 2012.
- [8] I. Genne, S. Kuypers, and R. Leysen, “Effect of the addition of ZrO<sub>2</sub> to polysulfone based UF membranes,” *J. Memb. Sci.*, vol. 113, no. 2, pp. 343–350, 1996.
- [9] S. P. Nunes, K. V. Peinemann, K. Ohlrogge, A. Alpers, M. Keller, and A. T. N. Pires, “Membranes of poly (ether imide) and nanodispersed silica,” *J. Memb. Sci.*, vol. 157, no. 2, pp. 219–226, 1999.
- [10] S. Rafiq, L. Deng, and M. Hägg, “Role of Facilitated Transport Membranes and Composite Membranes for Efficient CO<sub>2</sub> Capture—A Review,” *ChemBioEng Rev.*, vol. 3, no. 2, pp. 68–85, 2016.
- [11] S. Farrukh, S. Javed, A. Hussain, and M. Mujahid, “Blending of TiO<sub>2</sub> nanoparticles with cellulose acetate polymer: to study the effect on morphology



- and gas permeation of blended membranes,” *Asia-Pacific J. Chem. Eng.*, vol. 9, no. 4, pp. 543–551, 2014.
- [12] T. Matsuura, *Synthetic membranes and membrane separation processes*. CRC press, 1993.
- [13] L. M. Robeson, “The upper bound revisited,” *J. Memb. Sci.*, vol. 320, no. 1, pp. 390–400, 2008.
- [14] A. Brunetti, F. Scura, G. Barbieri, and E. Drioli, “Membrane technologies for CO<sub>2</sub> separation,” *J. Memb. Sci.*, vol. 359, no. 1, pp. 115–125, 2010.
- [15] G. George, N. Bhorla, S. AlHallaq, A. Abdala, and V. Mittal, “Polymer membranes for acid gas removal from natural gas,” *Sep. Purif. Technol.*, vol. 158, pp. 333–356, 2016.
- [16] L. Deng and M.-B. Hägg, “Carbon nanotube reinforced PVAm/PVA blend FSC nanocomposite membrane for CO<sub>2</sub>/CH<sub>4</sub> separation,” *Int. J. Greenh. Gas Control*, vol. 26, pp. 127–134, 2014.
- [17] N. M. José, L. A. S. de A. Prado, and I. V. P. Yoshida, “Synthesis, characterization, and permeability evaluation of hybrid organic–inorganic films,” *J. Polym. Sci. Part B Polym. Phys.*, vol. 42, no. 23, pp. 4281–4292, 2004.
- [18] M. Wang, X. Zhu, and L. Zhang, “Hole structure and its formation in thin films of hydrolyzed poly (styrene maleic anhydride) alternating copolymers,” *J. Appl. Polym. Sci.*, vol. 75, no. 2, pp. 267–274, 2000.
- [19] J. M. S. Henis and M. K. Tripodi, “Composite hollow fiber membranes for gas separation: the resistance model approach,” *J. Memb. Sci.*, vol. 8, no. 3, pp. 233–246, 1981.
- [20] P. Bernardo, E. Drioli, and G. Golemme, “Membrane gas separation: a review/state of the art,” *Ind. Eng. Chem. Res.*, vol. 48, no. 10, pp. 4638–4663, 2009.

- [21] J. Li, S. Wang, K. Nagai, T. Nakagawa, and A. W. H. Mau, "Effect of polyethyleneglycol (PEG) on gas permeabilities and permselectivities in its cellulose acetate (CA) blend membranes," *J. Memb. Sci.*, vol. 138, no. 2, pp. 143–152, 1998.
- [22] T. Kim, B. Li, and M. Hägg, "Novel fixed-site-carrier polyvinylamine membrane for carbon dioxide capture," *J. Polym. Sci. Part B Polym. Phys.*, vol. 42, no. 23, pp. 4326–4336, 2004.
- [23] A. S. Kovvali and K. K. Sirkar, "Carbon dioxide separation with novel solvents as liquid membranes," *Ind. Eng. Chem. Res.*, vol. 41, no. 9, pp. 2287–2295, 2002.
- [24] E. L. Cussler, R. Aris, and A. Bhowan, "On the limits of facilitated diffusion," *J. Memb. Sci.*, vol. 43, no. 2–3, pp. 149–164, 1989.
- [25] C. Lu, H. Bai, B. Wu, F. Su, and J. F. Hwang, "Comparative study of CO<sub>2</sub> capture by carbon nanotubes, activated carbons, and zeolites," *Energy & Fuels*, vol. 22, no. 5, pp. 3050–3056, 2008.
- [26] L. Ge *et al.*, "Investigation of Gas Permeability in Carbon Nanotube (CNT)–Polymer Matrix Membranes via Modifying CNTs with Functional Groups/Metals and Controlling Modification Location," *J. Phys. Chem. C*, vol. 115, no. 14, pp. 6661–6670, 2011.
- [27] M. M. Khan *et al.*, "Enhanced gas permeability by fabricating mixed matrix membranes of functionalized multiwalled carbon nanotubes and polymers of intrinsic microporosity (PIM)," *J. Memb. Sci.*, vol. 436, pp. 109–120, 2013.
- [28] C. Cornelius, C. Hibshman, and E. Marand, "Hybrid organic-inorganic membranes," *Sep. Purif. Technol.*, vol. 25, no. 1, pp. 181–193, 2001.
- [29] A. L. Khan, X. Li, and I. F. J. Vankelecom, "Mixed-gas CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> separation with sulfonated PEEK membranes," *J. Memb. Sci.*, vol. 372, no. 1, pp. 87–96, 2011.
- [30] A. R. Moghadassi, Z. Rajabi, S. M. Hosseini, and M. Mohammadi, "Fabrication

and modification of cellulose acetate based mixed matrix membrane: Gas separation and physical properties,” *J. Ind. Eng. Chem.*, vol. 20, no. 3, pp. 1050–1060, 2014.

- [31] A. Raza, S. Farrukh, and A. Hussain, “Synthesis, Characterization and NH<sub>3</sub>/N<sub>2</sub> Gas Permeation Study of Nanocomposite Membranes,” *J. Polym. Environ.*, pp. 1–10.
- [32] R. Gurdeep Chatwal and S. K. Anand, “Instrumental method of chemical analysis.” Himalaya publishing House, 2002.
- [33] N. Mehio, S. Dai, and D. Jiang, “Quantum mechanical basis for kinetic diameters of small gaseous molecules,” *J. Phys. Chem. A*, vol. 118, no. 6, pp. 1150–1154, 2014.
- [34] C. P. Ribeiro, B. D. Freeman, and D. R. Paul, “Pure-and mixed-gas carbon dioxide/ethane permeability and diffusivity in a cross-linked poly (ethylene oxide) copolymer,” *J. Memb. Sci.*, vol. 377, no. 1, pp. 110–123, 2011.
- [35] S. Kim and E. Marand, “High permeability nano-composite membranes based on mesoporous MCM-41 nanoparticles in a polysulfone matrix,” *Microporous Mesoporous Mater.*, vol. 114, no. 1, pp. 129–136, 2008.
- [36] S. Husain and W. J. Koros, “Mixed matrix hollow fiber membranes made with modified HSSZ-13 zeolite in polyetherimide polymer matrix for gas separation,” *J. Memb. Sci.*, vol. 288, no. 1, pp. 195–207, 2007.