Optimization of PVA Nano-composite Membranes in Membrane Contactor for CO2 Capture

Anne Marie Dominique

Yveline Maupilier

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Foreword and acknowledgements

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Finally I would like to thank my parents and my brother who supported me in my decision to come in Norway. This year has been an amazing experience for my studies and my personal life that I will always remember.

Contents

List of symbols

Symbol	Explaination	Unit/value
Latin letters		
a	Activity coefficient	
C	Concentration	$m^3(STP)/m^3$
D	Diffusion coefficient	m^2/s
g	Gravity	m/s^2
J	Flux	$m^3(STP)/(m^2s)$
l	Thickness	m
P	Permeability	Barrer
p	Pressure	Pa
S	Solubility coefficient	$m^3(STP)/(m^3.bar)$
T	Temperature	°C
v_f	Fractional free volume	(-)
W	weight	kg
w	Weight fraction	(-)
Greek letter		
α	Selectivity	
α	Coefficient of thermal expansion	K^{-1}
γ	Coefficient activity	
η	Viscosity	Pa.s
φ	Volume fraction	
μ	Chemical potential	
ρ	Density	Kg/m^3
Subscripts		
0	Feed side	
A	Component A	
B	Component B	
d	Dry	
l	Permeate side	
s	swollen	
Abbreviations		
CNTs	Carbon nanotubes	
IGCC	Integrated gasification combined cycle	
GA	Glutaraldehyde	
PSf	Polysulfone	
PVA	polyvinylalcohol	
SD	Swelling degree	
STP	Standard temperature and pressure	

Abstract

The aim of this report is to evaluate and optimize poly vinyl alcohol (PVA) composite membrane containing nanoparticles such as carbon nanotubes (CNTs), titanium dioxide or biofibers cross-linked with glutaraldehyde for application in membrane contactor to capture CO_2 at post combustion conditions.

Defect free PVA composite membranes were developed in lab by casting a 3 weight percent aqueous PVA solution and 1 weight percent or 2 weight percent nanoparticles on micro porous PSf support. These membranes were then subjected to chemical cross-linking by adding 3 weight percent or 5 weight percent glutaraldehyde and heat treatment for physical cross-linking at a temperature of 110°C and exposure time of 1, 5 hours.

Since PVA is a hydrophilic polymer and in a membrane contactor usually aqueous solutions are used to absorb CO_2, the developed membranes were tested twice for permeance and selectivity at 100% humid conditions. For experimentation pre mixed gas containing 10% CO_2 in nitrogen was feed to the membrane at three different pressures (1.2, 2 and 3bars). Helium was used as sweep gas. Swelling tests were performed to determine degree of swelling of each membrane, their theoretical equilibrium swelling degree and the swelling rate constant.

From the experimentation it was observed that a same operating pressure membranes containing 2 weight percent CNTs have higher permeance whereas the opposite phenomenon is observed with membranes containing TiO_2 and biofibers. However those results concerning TiO_2 membranes can be explained by probable presence of agglomerates which decrease the mean pore size and an increase of viscosity leading to suppression of macrovoids which hence decreases permeance (Yu L-Y et al., 2009). Furthermore an increase of glutaraldehyde leads to a reduction of free volume and consequently a decrease of permeance. It has been observed that membranes containing biofibers have the highest permeance values, and membranes with 1wt% of TiO_2 and 3% GA is then the best candidate. On the other hand membrane with 1wt% TiO_2 and 5wt% GA has similar results to membrane containing 2wt% CNTs and 5wt% GA.

Concerning swelling tests it was found that swelling degree increases rapidly before reaching a maximum and then remains stable which is similar to a typical swelling curve plot by Wu Q. and Feng Y. (2004) of a cross-linked polymer in solvent. Moreover it was observed that

membranes containing 1wt% TiO_2 have a higher swelling degree. Due to its hydrophilic nature TiO_2 nanoparticles enhance swelling capacity of PVA by absorbing more water which results in a high free volume. Furthermore TiO_2 membranes have also the smallest rate constant which means that they reach their maximum swelling degree faster than other membranes. Thus facilitate transport due to reaction between CO_2 and water enhances rapidly transport through the membrane. To conclude membranes containing 1wt% of TiO_2 particles seem to be the best option concerning swelling tests.

Thesis outline

The objective of this thesis is to present PVA membranes containing nanoparticles for application in membrane contactor based on lab experimentation.

The use of membranes is a novel technique in contacting technology. Membranes have to be highly permeable to transfer easily components from retentate side to permeate side. Moreover they have to be enhanced with nano-material to resist to all of the process constraints. PVA membranes with nanoparticles (carbon nanotubes, titanium dioxide or biofibers) were studied to remove CO_2 from a CO_2 / N_2 gas mixture. Permeation tests have been performed at three different pressures in order to determine permeance and selectivity of those membranes and compare their effectiveness. Moreover swelling tests have been performed to determine swelling degree, theoretical equilibrium swelling degree and rate the swelling rate constant of each membrane.

This report contains two sections. First part presents CO_2 separation techniques and focuses on membrane technology detailing membranes preparation, transport through membrane and enhancement of membrane properties with nanoparticles in hybrid membranes.

Second part described the experimental work and results obtained during this study. Explanations about solution preparation, membrane casting, permeation and swelling tests are detailed. Results and discussion from experiments and conclusions from this work are also given.

The title of this thesis is Optimization of PVA Nano-composite Membranes in Membrane Contactor for CO_2 Capture. The main objective is to synthetize and test membranes containing different loadings of different kind of nanoparticles such as carbon nanotubes, titanium dioxide and biofibers in order to compare their effect on permeance values and swelling degree of membranes. The experimentations for permeation tests were conducted at 1.2, 2 and 3 bar in a 100% humidified environment and swelling tests were performed in a sealed pot in a 100% humidified environment.

PART 1
Theoretical background

Introduction

The impact of CO_2 as a greenhouse gas on global warming has long been recognized. Primary source of CO_2 emissions are thermal power plants operating on fossil fuel. Almost 40% of CO_2 emissions from combustion are due to the use of coal as fuel for power generation (MIT interdisciplinary Study, 2007; Figueroa J.D et al., 2007). These emissions are expected to increase by 50% till 2030 in coal fired electricity generation (Energy Information Agency, 2007).

To reduce the CO_2 emissions, switching over to environment friendly and green fuels is necessary. Although much work has been done in this field but still in foreseeable future fossil fuels would be the primary source of energy. Until the development of some environmental friendly and cost effective fuel, CO_2 capture and storage is the only choice to control greenhouse gas emissions till date.

Several separation techniques have been investigated for CO2 capture; Adsorption, absorption, cryogenics and membranes are the most studied field in recent years. So far absorption has been recognized as the main capturing tool but appreciable amount of studies have been reported in the field of membrane technology; among the 1000 patents using those technologies, 60% have been published during the last decade and 25% the last three years around the world (figure 1.1):
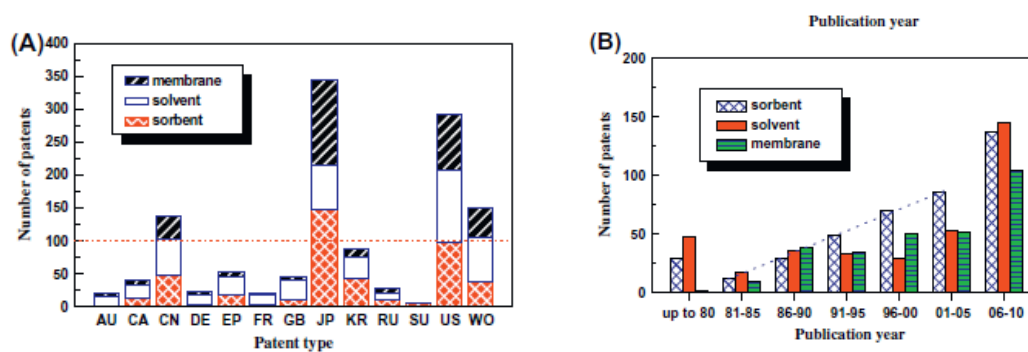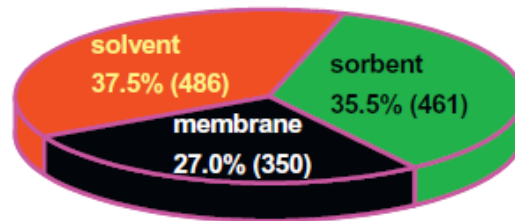

Figure 1.1: Overview of research activity (A), patents filled per year (B)

Distribution of patents among separation techniques:

Figure 1.2: Distribution of patents up to March 2012
(Li B., et al., 2013)

Up to now a large number of studies focus on CO_2 capture at post combustion conditions with membranes (Favre, 2007; Bounacoeur et al., 2006, Merckel T. C. et al., 2010). As a new generation of separation technique, membranes have a multidisciplinary character and can be used in a large range of processes such as gas separation, dialysis, reverse osmosis, microfiltration, ultrafiltration, pervaporation… Among many, some prominent advantages of membrane separation technology are continuous separation process, low energy consumption, easy up scaling, variable and adjustable membranes properties and can be easily couple with other separation processes.

A novel technique in the field of contacting equipment is the use of membrane as an interface to get non dispersive gas-liquid contact. A membrane contactor offers a specific surface area much higher than any other existing equipment. However some challenges remain unsolved. Such as the damage of the membrane after a long term contact with solvent and the right material allowing high permeability and high resistance to the process environment. So research has to be done on different materials to find the best balances between separation performance and resistivity.

Background and theory

2.1 CO$_2$ capture from power plant

Presently the use of fossil fuel for energy production contributes to three fourth of the global demand resulting in an increase in atmospheric CO$_2$ (IPCC. Climate change, 2001). Knowing that CO$_2$ contributes up to 60 per cent in global warming (Yamasaki A., 2003), its emission have to be reduced. According to Olajire (2010) there are only three options: reducing energy demand, carbon emissions or enhancing the sequestration of carbon. The most economical solution using the existing energy supply infrastructure seems to be the development of CO$_2$ capture and storage (CCS) technologies. Based on emission source CO$_2$ capture technologies can be classified into three main fields (A.Doukelis et al., 2009); post combustion, pre-combustion and oxyfuel combustion. The choice of the system has to be based on CO$_2$ concentration and operating.

Operating conditions of these three classes of CCS are schematically explained in figure 2.1.
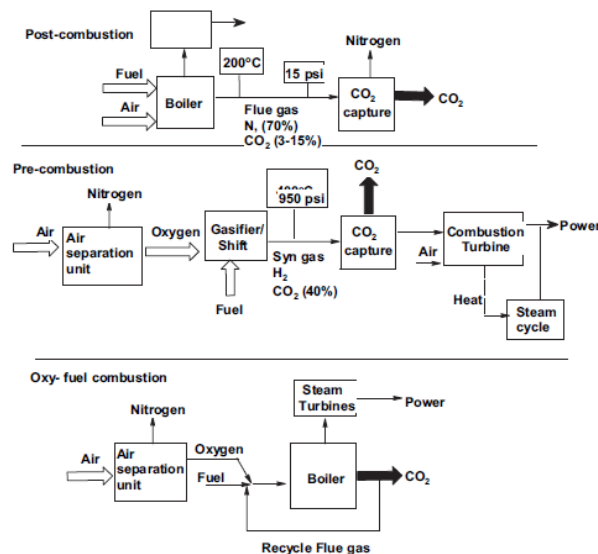

Figure 2.1: Block diagrams illustrating post-combustion, pre-combustion and oxyfuel combustion techniques. (Olajire.A, 2010)

- **Post combustion capture**: CO_2 is captured after complete combustion of fuel. Different technologies exist such as absorbers, membranes or low temperature distillation. Low CO_2 concentration in flow gas, high temperature, large volumes of gas to handle.

  So far absorption in liquid has been established as the most mature technology in this field but solvent regeneration and solvent losses are many challenges for which solution must be found (Olajire, 2010).

- **Oxy-fuel combustion**: In this post combustion process pure oxygen is used in combustion process which leads to a high concentration of CO_2 close to 80% and a small amount of NOx in flue gas. However a large quantity of oxygen is needed for this process which means high capital cost and energy consumption (Olajire, 2010).

- **Pre-combustion capture**: Carbon dioxide is removed before complete oxidation. This process is usually connected to integrated gas combined cycle (IGCC) power plant. Carbon dioxide is then removed from a mixture of H_2 and CO_2 resulting from water gas shift reaction (group, III and B. Metz, 2005). Pre-combustion capture is usually energy saving compared to post combustion capture. Moreover high pressures encouraged the use of physical absorption which also has a moderate energy penalty. However it requires high power generating costs (Olajir A.A., 2010).

2.2 CO_2 separation techniques

2.2.1 Overview of separation techniques

All CO_2 capture techniques involve a separation technique which has to be chosen based on the characteristics of the gas stream. There are many options for CO_2 separation such as chemical or physical absorption, adsorption or membranes Figure 2.2.
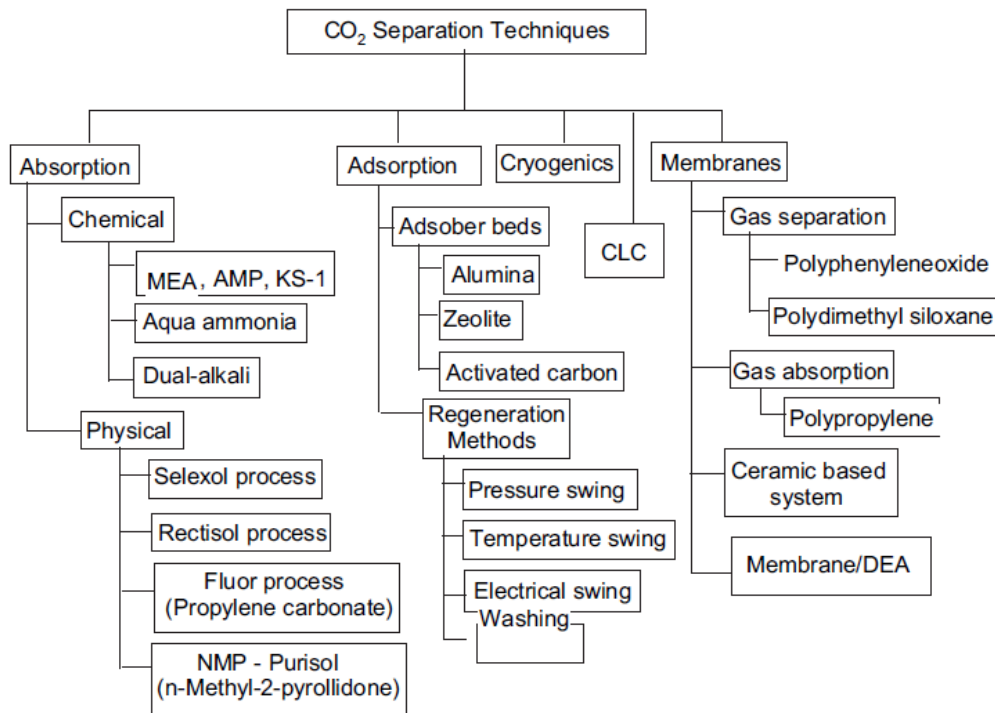
Figure 2.2: Technology options for CO$_2$ separation.

Solvent absorption process, which widely used in industry and membrane technology, an emerging technology, are discussed in this section.

2.2.2 Solvent absorption process

Absorption is the transfer of one component from a gas phase to a liquid phase (Khol and Nielsen, 1997). This process is the most commonly used process in gas purification. Absorption can be divided in three different classifications depending on nature of interaction between absorbent and absorbate: physical absorption, chemical absorption with reversible reaction and chemical reaction with irreversible reaction.

Physical absorption involves organic solvents (absorbant) which bind themselves with acid gas components (absorbate). No reaction takes place and no new components are formed. This absorption is mainly based on CO$_2$ partial pressure, absorbent's affinity and is usually governed by Henry's law. Hence absorption is favored by high pressure in feed stream

(Olajire, 2010) and desorption takes place by decreasing pressure down to atmospheric pressure or vacuum (Khol and Nielsen, 1997).

In chemical absorption a fast and reversible chemical reaction between CO_2 (acidic) and a basic absorbent through neutralization reaction takes place. Contrary to physical absorption it can operate at low partial pressures which make chemical absorption preferable for post combustion capture (Olajire, 2010). Solvents with alkalinoamine are acknowledged as chemical absorbents. In chemical absorption with irreversible reaction, component absorbed cannot be released by inverse reaction. This involves an absence of equilibrium vapor pressure of absorbate over the solution (Kohl and Nielsen, 1997).

The selection of a technology depends on process parameters such as: partial pressure of CO_2, absorption capacity of the solvent, cost of regeneration degree of capture, operating and capital costs.

2.2.3 Membrane technology

Membrane technology is an emerging candidate in gas separation. A membrane removes some components from gas stream by acting as a semi-permeable barrier. They can be defined in a structural way "A membrane is a region of discontinuity interposed between two phases" (Hwang and Kammermeyer, 1975) and in a functional way: "Any phase that acts as a barrier preventing mass movement but allowing restricted or regulated passage of one or several species through it may be defined as a membrane. This could be a solid or a liquid or even a gas. All membranes are active in an operational sense when used as a barrier to separate two solutions or phases unless they are too fragile or too porous" (Lakshminarayanaiah, 1979). Basis of membrane separation technique is illustrated in figure 2.3.
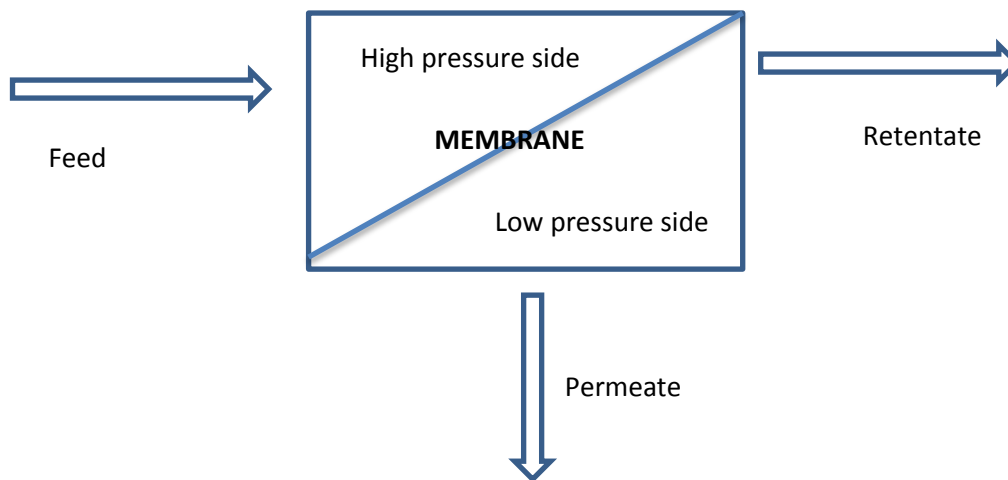
Figure 2.3: Schematic representation of membrane separation

As clear from figure 2.3, in a membrane based separation, the feed stream is divided in two streams: retentate and permeate. One component can be transported readily than the other through the membrane because of physical or /and chemical properties. Selectivity and flow through the membrane determine its efficiency. Flux is the volume flowing through the membrane per unit of area and time and selectivity is the ability of one component to go through the membrane relative to other (Mulder, 1996).

The driving force leading particles from one side to the other is defined as the gradient in potential across the membrane (ΔX) over the thickness of the membrane (l) (Mulder, 1996):

$$Driving\ force = \frac{\Delta X}{l} \qquad\qquad eq\ (2.1)$$

The gradient in potential can be the chemical potential, the electrical potential or the electrochemical potential. Particles are naturally transferred from the high potential to the low potential and equilibrium is reached when the potentials difference equals zero. The difference of potentials is the result of difference of pressure, concentration, electrical potential or temperature. Most of the time chemical potential ($\Delta\mu$) difference causes the

transfer of components. Chemical potential difference for a compound (i) is defined as following for isothermal conditions:

$$\Delta\mu_i = RT\Delta\ln(a_i) + V_i\,\Delta P \qquad eq\ (2.2)$$

Where V_i is the molar volume of the compound i, ΔP the pressure difference and a_i is the activity of i defined as following:

$$a_i = \gamma_i * x_i \qquad eq\ (2.3)$$

Where γ_i is the activity coefficient and x_i is the mole fraction of i.

Flux and driving force can be related by a proportionally equation such as Fick's law:

$$J = A * X \qquad eq\ (2.4)$$

Where J is the flux (N/mol), A a proportional factor and X the driving force.

This flux which is proportional to the driving force is illustrated in figure 2.4:
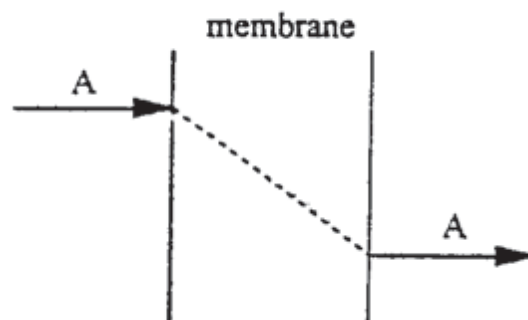

Figure 2.4: Diffusive transport through a membrane according to equation 2.4

However transport through the membrane can also be improved by facilitated transport mechanism. A mobile carrier enhances the component transport through the membrane. In this study H_2O acts as a carrier and facilitates CO_2 transport through the membrane by

dissolving carbon dioxide and forming bicarbonate ions on the retentate side which increases the amount of CO_2 absorbed, on the permeate side the reverse reaction occurs releasing CO_2.

$$CO_2 + H_2O \ = \ HCO_3^- \ + H_3O^+ \qquad\qquad eq \ (2.5)$$

2.2.4 CO2 capture by membrane technology

As mentioned earlier absorption is currently the separation process preferably chosen, but some authors argue that membrane could compete with absorption for a concentration of CO_2 over 10% (Hao et al., 2002). Indeed a lot of studies have been focused on membrane in order to improve membrane technology after a previous study of Hendricks et al in 1989 which considered membranes as non-competitive with absorption method. Recently Favre and co-workers studies emphasized that effectiveness of dense polymeric membrane to address the flue gas treatment problem may have been underestimated by comparing dense polymeric membranes to amine absorbing technology (Favre, 2007; Bounaceur et al., 2006). Both studies concluded that membranes for post combustion can easily reduce energetic consumption as feed mixture contents more than 20% of CO_2. This conclusion made membrane an interesting candidate for flue gas treatment processes.

2.3 Membranes for gas separation

A large range of material can be used to prepare synthetic membranes: organic (polymers) or inorganic (zeolite, ceramic, glass, metal, carbon). Hybrid membranes combine organic and inorganic material to enhance separation performance. Membrane composition is an important parameter which influences the transport mechanism through it; molecular size/shape selective mechanisms like Knudsen diffusion and molecular sieving dominate in porous membranes whereas, solution diffusion is responsible for transport through dense membranes.

Robust mechanical stability, good permeation properties, good processibility and flexibility are necessary for industrial membranes. Those conditions are most of the time satisfied by polymeric membranes which can be improved by adding nano material (Deng, 2009).

2.3.1 Characteristics of polymeric membranes

(1) Free volume

Free volume is volume unoccupied by the polymer between chains. It is highly dependent on polymer state. In glassy state, polymer is stiff and chains cannot have restricted movements thus free volume barely depends on temperature. On the other in rubbery state polymer is flexible which allows creation of free volume. The more the temperature increases, the more free volume there is (figure 2.5) according to equation 2.5:

$$v_f = v_{f,Tg} + \Delta\alpha(T - Tg) \qquad (eq\ 2.5)$$

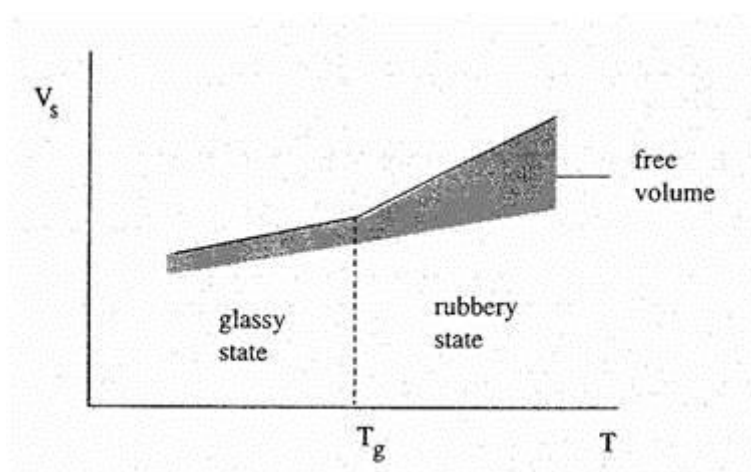Where $\Delta\alpha$ is difference between the value of thermal expansion coefficient above and below T_g.

Figure 2.5: Specific volume and free volume as a function of temperature (Mulder, 1996)

Generally the more free volume a membrane has, the easier the transportation through the membrane is.

(2) Solubility

Solubility quantifies the amount of compound sorbed through the membrane at thermodynamic equilibrium conditions (Mulder, 1996). Three different cases can be noticed:

-Solubility is independent of concentration which happens when the solubility is really low such as gas in elastomer polymers, it can be assumed then that gas diffusion coefficient is constant and Henry's law is followed, sorption isotherm is then linear (Figure 2.6 (a)). This can generally be observed with gases in elastomers

-Solubility is slightly dependent on concentration due to some weak interactions between molecules. In this model, named free volume model, two sorption mechanisms occur at the same time: Henry's law and Langmuir sorption (figure 2.6 & figure 2.7 (b)).

-Solubility is strongly dependent on concentration due to strong interactions according to Flory-Huggins thermodynamic (Figure 2.6 (c)).
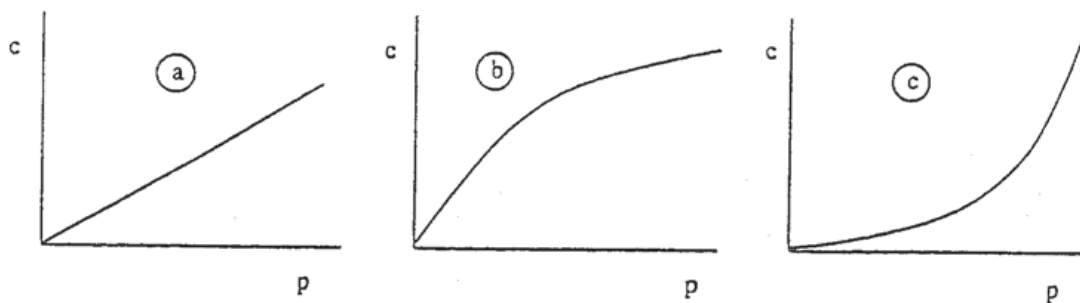
Figure 2.6: Schematic drawing of sorption isotherm for ideal sorption (a), dua sorption (b) and non-ideal sorption (c) (Mulder, 1996)
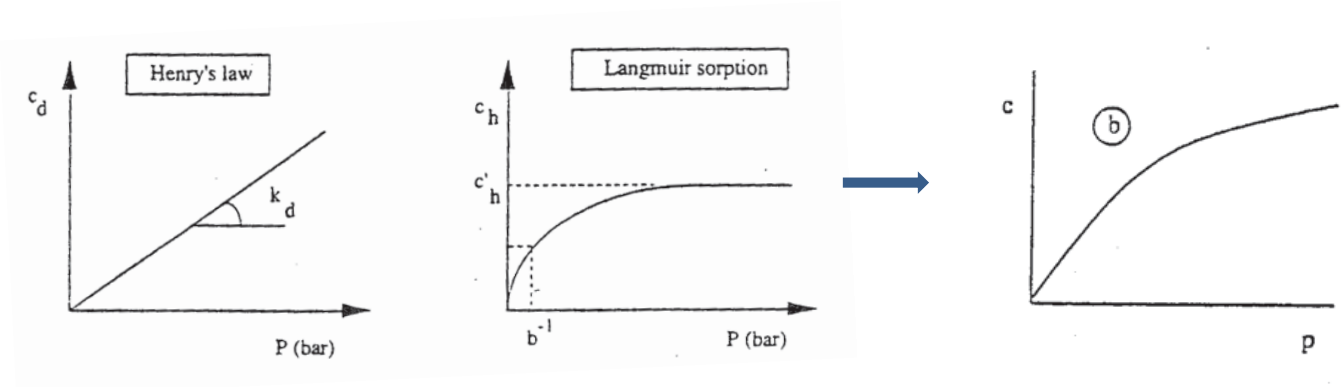
Figure 2.7 Dual sorption theory (Mulder, 1996)

(3) Diffusivity and swollen effect

Diffusivity is a kinetic parameter and is defined as the rate at which a penetrating molecule travels through the membrane. Moreover diffusion depends on component which diffuses, material through which diffusion occurs, state of the polymer, and its concentration dependent of the system (Mulder, 1996). Diffusion properties can strongly change in concentration dependent systems during swelling. Swollen effect causes strong interaction and an increase in polymer concentration and diffusion in the membrane (Figure 2.8).
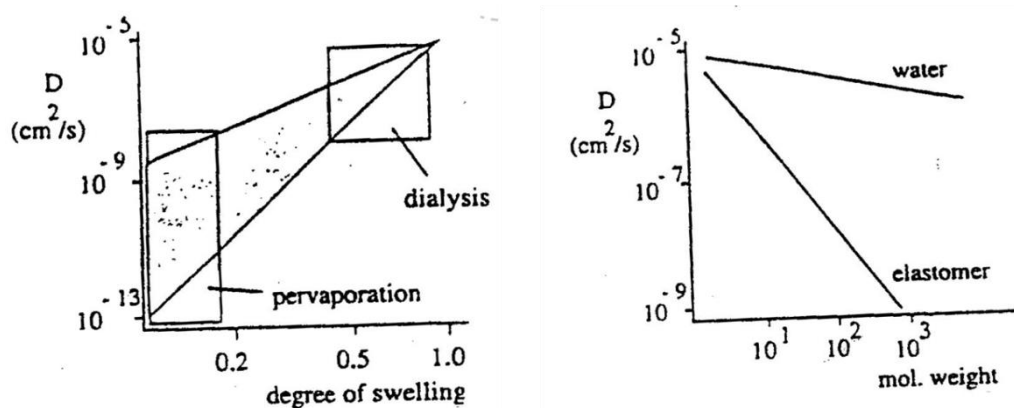

Figure 2.8: Diffusion coefficient of components in water and in a polymer as a function of the degree of swelling for a given low molecular weight penetrant (left figure) and in a elastomer membrane as a function of the molecular weight (right figure)(Muder, 1996)

2.3.2 Characteristics of hybrid membranes

Conventional organic and inorganic membranes have some limitations due to the trade off trend between gas selectivity and permeability according to Robeson (Robeson, 1991, Robeson, 2008). That is why hybrid membranes have been developed during the past 20 years to combine both advantages of polymeric and inorganic membranes which lead to enhanced properties (Guizard C. et al., 2001).

Hybrid membranes containing inorganic nanocomposite materials, which have mainly been explored for gas separation technology, are a promising solution to Robeson trade off of polymeric membranes (Peng F. et al., 2005; Pend F. et al., 2006). Thus, those membranes have high flux and selectivity, good mechanical properties, thermal and chemical resistance (Cong H. et al., 2007). However, previous studies show that gas permeability was particularly improved compared to selectivity which tends to remains similar to pure polymeric membranes (Merkel T.C et al. 2002; Moaddeb M., Koros W.J., 1997).

Network architecture

The membrane aptitude to reach some performances is determined by permeability, permeation rate and kinetic effects (Guizard C. et al., 2001) which highly depend on membrane structure. Degree of crosslinking and different type of connection between polymer and nano-composite material establish the membrane architecture (Cong H. et al., 2007). Different physicochemical effects influence permeation (Table 2.1).

Table 2.1: Physicochemical effects involved in component partioning and transport across polymer membranes (Guizard C. et al., 2001)

Debye forces	Dipole-induced dipole interaction (1–2 kcal/mole) in the case of polar molecules in presence of a polar matrix.
London – van der Waals dispersive forces	Attraction forces (0.1–2 kcal/mole) between permeant and membrane material or between polymer segments in the membrane.
Hydrogen bonding	Usually stronger than polar and dispersive forces (2–10 kcal/mole), important in the case of aqueous media with possibility of clustering effect.
Electrical charges:	
-ionic exchange	Ionic exchange between ions in the feed phase and the charged sites of the membrane. Charge
-charge interaction	interaction between charged sites and charged permeants
Selective complexation	Selective complexant sites in the membrane. Increase of partitioning for one specific component in the membrane.
Steric effects	Related to the effective size of the permeating components and the effective size of the permeation corridor in the membrane. Depend on polymer physical state (glassy, rubbery) and chain mobility.

There are mainly two different polymer-inorganic nanocomposite membranes in accordance with different bonds (Cong H. et al., 2007):

- Covalent bonds connect polymer material and inorganic material (Figure 2.9(a)).
- Van der Waals bonds or hydrogen bonds connect the two materials (Figure 2.9 (b)).
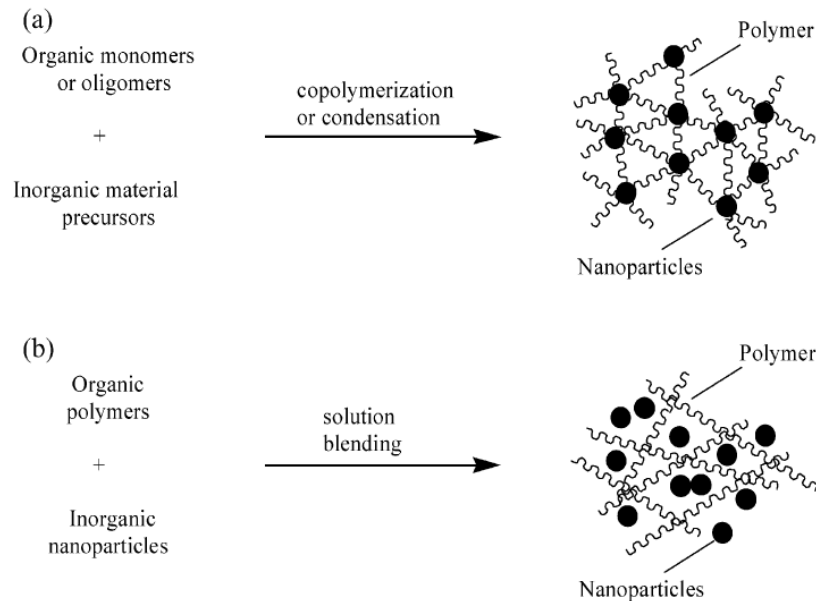
Figure 2.9: Illustration of different polymer-inorganic material structure. (a) Covalent bonds, (b) Van der Waals or hydrogen bonds (Cong H. et al., 2007)

Hybrid membranes preparation

Most commonly there are three different ways to prepare hybrid membranes (Li C. et al., 2003):

- Solution blending: polymer is dissolved in a solvent and particles are then dispersed in the solution by stirring. Hence membrane is cast by removing solvent. It is difficult to avoid aggregates of particles.
- In situ polymerization: Particles which often have some functional group and monomers are mixed together and then polymerization is initiated. Aggregates of particles are difficult to manage.

- <u>Sol-gel process</u>: In this method, which is the most popular, monomers or polymers and nanoparticles are mixed together, then inorganic precursors hydrolyze and condense in the polymer matrix (Li C. et al., 2003).

Presence of inorganic nanoparticles affects polymers interactions and thus changes permeation properties. Indeed nanoparticles can increase the void between polymer chains and so increase free volume which enhances gas permeation (Moaddeb M., Koros W.J., 1997; Shekhawat D. et al., 2003). In this work solution blending was used to prepare membrane solution.

2.3.3 Membrane contactor

Membrane contactor is a hybrid technique combining absorption and membrane technologies. "The term "membrane contactor" is used to identify membrane systems that are employed to "keep in contact" two phases." (Drioli E., Criscuoli A. & Curcio E., 2006). Membrane contactors avoid dispersion phenomena by acting as a barrier between two phases and ensure a definite and high interfacial area at all operating conditions (Roizard D. and Favre E., 2012). Species move from one phase to the other by diffusion. Membranes preferred for application in a contactor should have high permeability but should not necessarily be highly selective. Moreover membrane contactors appear to be more cost effective and perform better than other separation technologies such as membrane technology and absorption (Favre E. and Svendsen H.F.,2012; Feron, P.H.M. and A.E. Jansen, 2002).

Two different categories of membranes can be used in membrane contactors:

- Micro porous membrane contactors, in which the wetting and bubbling phenomena results in low separation efficiency.
- Dense skin membrane contactors, which can effectively prevent the wetting and bubbling problems.

One of the most important parameter is operating pressure. It has to be well controlled to avoid bubbling which causes dispersion of gas phase in liquid phase as well as wetting which causes penetration of liquid in membrane pores (figure 2.10).
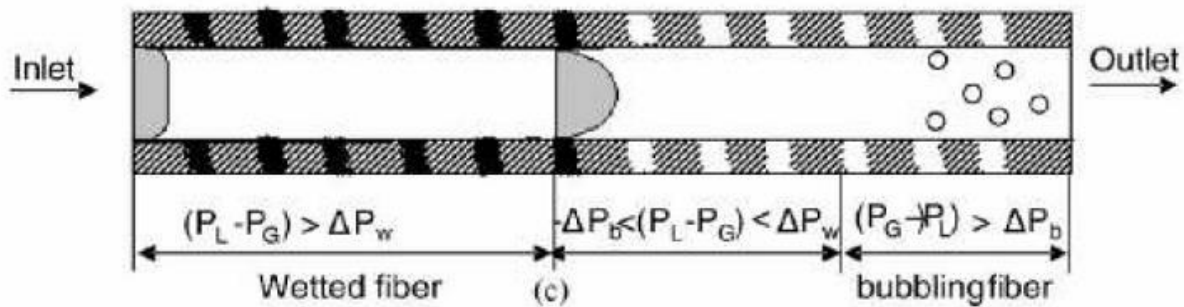

Figure 2.10: Wetting and bubbling phenomena (Wenten I.G, 2008)

These problems can be managed by using hydrophobic membranes, surface modification, and selection of dense composite membrane.

To overcome the challenge of pore wetting, use of dense composite membrane is a simple and convenient choice. Composite membranes have a non-porous thin layer coated which prevents wetting problems. This allows a wide range of operating pressure but since it adds a resistance to the mass transfer, this layer has to be highly permeable towards gases which have to be transported. A composite membrane is presented in figure 2.11. In a composite membrane the mass transfer resistance through dense layer is much higher than porous substrate or support layer. Therefore, characterization of dense layer is vital for evaluation of such membranes.
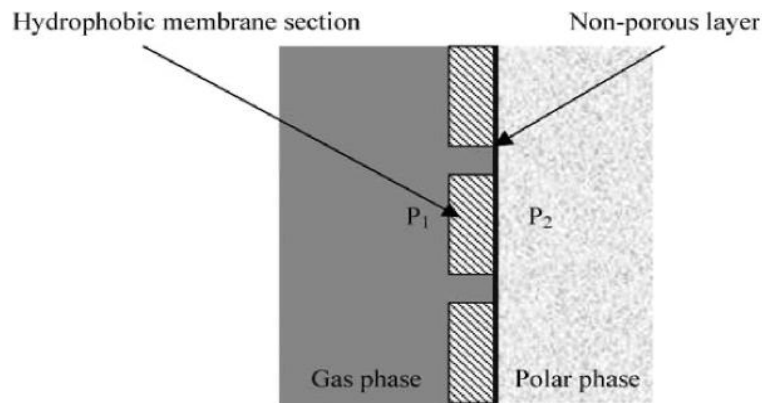
Figure 2.11: Composite membrane with dense thin layer coated on a microporous surface (Drioli et al., 2006)

Membrane contactors have several advantages compared to usual separation processes (Drioli et al., 2006):

- High interfacial area which results in smaller footprint.
- Low pressure drops
- Moduler design ensure easy and linear scale up

But membrane contactors have usually a short life time, a further resistance to transport and limited operating pressure allowed.

2.4 Preparation of membranes

2.4.1 Polymer material

Permeation rate is governed by the kinetic diameter of the molecule in glassy state polymers. Hence rate depends on molecules which are going through the membrane; Molecules can be classified as follows:

$$H_2O > H_2 > NH_3 > CO_2 > H_2S > O_2 > CO > N_2 > CH_4$$
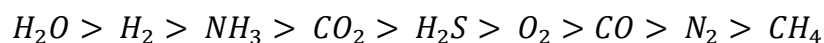
Glassy state polymers have a high selectivity which allows a good separation for molecules which have similar kinetic diameters. However this polymer state is not efficient for big

molecules and rubbery state polymers have to be used. Then solubility rate in polymer governs the permeation rate (Sun L-M., Thonnelier J-Y, 2004).

The polymer material has to be chosen according to several criteria which limit the choice of polymer for industrial applications:

- A good selectivity to obtain a gas as pure as possible.
- A good productivity to have reasonable membranes areas.
- A good chemical stability and mechanical resistance.

2.4.2 Inorganic material

Nano-particles are not only particles smaller than 20 nm, particles up to 1 μm can also be called nanoparticles depending on material and application involved (Ng L.Y, 2013).

Nanoparticles usually enhance permeability properties of polymeric membranes whereas selectivity properties remain the same. Especially for membrane contactor application optimization of permeability properties is one of the main objectives which make nanoparticles extremely attractive.

One of the most challenging problems is aggregation of particles in the membrane due to defective dispersion causes mainly by surface interactions; however other potential causes remain unclear (Ng L.Y, et al., 2013). Nonetheless a theory suggests that over a certain amount of particle, augmentation of concentration can lead to a decrease in dispersion of particle and thus promotes aggregates formation (Yu L-Y., et al. 2009).

A large range of nanoparticles can be added in polymeric membranes to enhance their properties such as CNTs (Peng F. et al., 2007), silica (Khayet M. et al., 2005), TiO_2 (Bae T.H., Tak T.M., 2005) , ZrO_2, polymeric nanoparticles (Xu Z.K et al., 2002)…

2.4.3 Preparation technique

Sintering, strenching, track-etching, template leaching, phase inversion are different techniques to prepare polymeric membrane, but the most used remains coating method.

Composite membranes

A thin polymeric selective layer is deposited on a porous support.

Top selective layer

Sub layer: Porous support
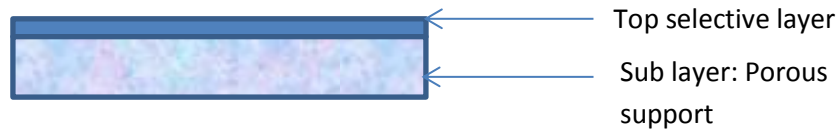
Figure 2.12: Schematic drawing of composite membrane

Dip-coating procedure

This technique provides a dense but very thin polymeric layer. The support is immersed in polymeric solution and a thin layer of solution adheres to it when membrane is removed from coating bath. Afterwards the membrane is heated in an oven to evaporate water and crosslink polymer (Mulder, 1996).

Thickness of the coating layer can be determined by using the Navier-Stockes equation:

$$h_\infty = \frac{2}{3}\sqrt{\frac{\eta v}{\rho g}} \qquad\qquad (eq\ 2.6)$$

Where: h_∞ is the equilibrium thickness, η the viscosity, ρ the density, g the gravity and v the coating velocity.

2.5 Transport through a membrane

Different transport mechanisms occur in membrane according to material used. Three different transport mechanisms can be considered (Mulder, 1996)(figure 2.13):

-Micro-porous membranes: the pore size and the mean free path of the gas have approximately the same size; Transport is then based on Knudsen diffusion. Such membranes are used in microfiltration and ultrafiltration.

-Dense polymeric membranes: based on solution-diffusion mechanism. Separation properties depend mainly on the material used for the dense layer. Such membranes are used in pervaporation, vapour permeation, gas separation and dialysis.

-Carrier membranes: The carrier can be either fixed to the membrane matrix or mobile into the membrane. The mechanism is based on reversible reaction; carrier reacts with the components which goes through the membrane, transports it and reverse reaction happens on the permeate side. This mechanism allows a higher flux through the membrane (Mulder, 1996).
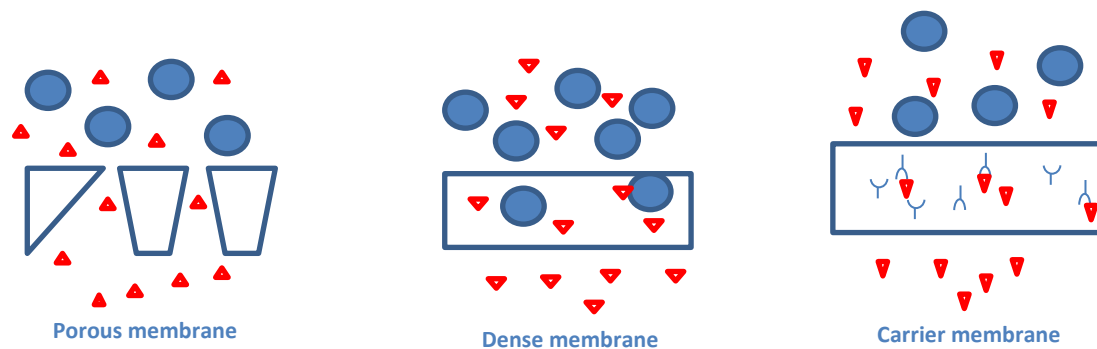

Porous membrane   Dense membrane   Carrier membrane

Figure 2.13: Transport through a membrane

The transport across membrane is due to a driving force which is mathematically represented by a gradient as previously mentioned. Moreover transport across a membrane is characterized by no equilibrium thermodynamics so only irreversible thermodynamic laws can be used.

The main mechanism which allows separation is the solution diffusion mechanism. Fick's first law describes this solution-diffusion mechanism as follows thanks to a chemical potential gradient:

$$J_A = D_A \frac{dC_A}{dx} \qquad (eq\ 2.7)$$

Where J_A (mol/(m^{2}s)) is the flux of gas component transported through the membrane, D_A (m^2/s) the diffusion coefficient indicating the movement's facility and $\frac{dC_A}{dx}$ (mol/m^4) which is the concentration gradient. This equation can be simplified as follows:

$$J_A = \frac{D_A}{l} \left(C_{A,0} - C_{A,l} \right)$$
(eq 2.8)

Where l (m) is the thickness of the membrane, $C_{A,0}$ and $C_{A,l}$ (mol/m^3)the concentrations of component A at the interfaces on the feed and the permeate sides of the membrane. The gas flux largely depends on the thickness of the membrane and the different concentrations of the component A. The separation factor is also a very important parameter for gas separation and it is defined as the ratio between the gas permeabilities:

$$\alpha = \frac{P_A}{P_B}$$
(eq 2.9)

Gas permeability for gas A is the product of diffusion coefficient D_A and its solubility S_A:

$$P_A = D_A * S_A$$
(eq 2.10)

Eventually the permeability factor can be written depending on diffusion coefficients and solubility values:

$$\alpha = \frac{P_A}{P_B} = \frac{D_A}{D_B} * \frac{S_A}{S_B}$$
(eq 2.11)

The diffusion coefficient is a kinetic property and describes the molecules mobility into the polymer when the molecular size increases the diffusion coefficient decreases. On the other hand the solubility is a thermodynamic property describing the dissolved molecules concentration in balance with the gaseous phase.

Moreover in ideal systems it can be supposed that the Henry's law which describes a linear relationship between concentration inside the membrane C and pressure outside the membrane p can be applied:

$$C = S * p$$
(eq 2.12)

Then equation (2.8) becomes:

$$J_A = \frac{S_A D_A}{l} \left(p_{A,0} - p_{A,l} \right) \qquad (eq\ 2.13)$$

With: $p_{A,0}$ the pressure on the feed side and p_{Al} the concentration on the permeate side.

And using equations (eq 2.10) and (eq 2.13):

$$J_A = \frac{P_A}{l} \left(p_{A,0} - p_{A,l} \right) \qquad (eq\ 2.14)$$

Addition of inorganic nanoparticles in polymeric membranes can increase free volume by disrupting polymer chains due to interactions between polymer and nanoparticles which then enhances permeability properties.

2.6 Crosslinked PVA membrane

2.6.1 PVA membrane

Poly(vinylalcohol) is a polymer formed from repetition of ethanol monomer (figure 2.14).
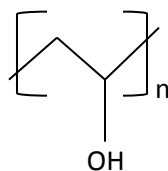
Figure 2.14: Poly(vynil alcohol)

Alcohol group makes it hydrophilic and linear structure gives it high crystallinity, tensile strength and high flexibility which allow easy film forming for membrane casting on support. This polymer is largely used in industry due to its resistance to organic solvent and oil and impermeability for most of the natural gases. Moreover its good thermal and chemical stability are crucial for CO_2 capture in post combustion to handle process parameters and resist to the solvent without chemical reactions. Furthermore transport through the membrane is facilitates by PVA high capacity to swell.

PVA glass transition temperature is Tg= 85°C.

2.6.2 Catalytic reaction with Glutaraldehyde

Due to its poor stability in aqueous solution PVA must be cross-linked to resist to process stresses. This chemical reaction reinforces mechanical properties and thus creates a stable membrane (Yeom C-K, Lee K-H., 1996).

Dialdehydes such as glutaraldehyde have been well investigated to cross-link PVA membranes (Hirai T et al., 1992 (a) & (b)). Aldehyde groups react with hydroxyl groups of PVA to crosslink the structure. Three different structures can be obtained:
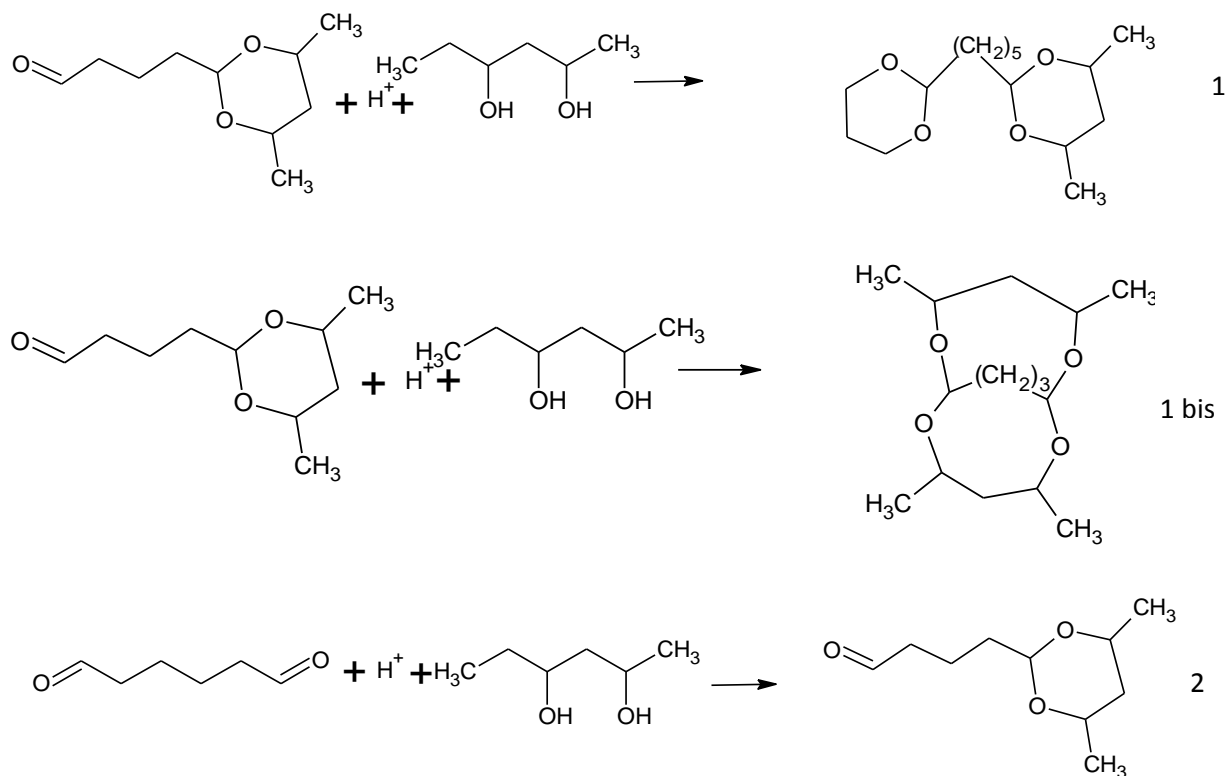
Figure 2.15: Crosslinking products of reaction between PVA and Glutaraldehyde (Yeom C-K, Lee K-H., 1996)

2.7 Nano-composites: CNTs, TiO$_2$ and biofiers

According to Maxwell model (Maxwell C., 1873), based on the analysis of dielectric properties of diluted suspension of spheres under steady state, adding of nanoparticles is expected to reduce permeability properties of polymeric membranes:

$$P_c = P_p \left(\frac{1 - \varphi_f}{1 + 0.5\varphi_f} \right) \qquad\qquad eq(2.15)$$

With P_c and P_p permeabilities of membrane with and without nanocomposites and φ_f the volume fraction of the nanofiller.

The loss of polymer volume caused by presence of nanocomposite decreases the sorption capacity and an increasing pathway length decreases diffusivity (Merkel T.C., et al., 2003). As a consequence, permeability is decreasing with increasing particle volume. However a lot of studies showed an increasing permeability when nanoparticles were added (Merkel T.C., et al., 2002; Moaddeb M. and Koros W.J., 1997; He Z., et al., 2002). Cong H. et al., 2007, explain that difference by strong interactions between polymer and nanoparticles which change solubility and diffusivity of penetrants in membranes.

2.7.1 CNTs

Since carbon nanotubes have been discovered in 1991 (Iijima S, 1991) a lot of studies on their extraordinary mechanical, electrical and thermal properties have been made and addition to different polymeric material have been tested (Andrews R. and Weisenberger M.C., 2004; Ounaies Z. et al., 2003). It has been proved that CNTs considerably enhance the mechanical strength of polymer material (Zeng J. et al., 2004). Consequently carbon nanotubes magnify polymeric membrane properties which can then be able to transcend Robeson upper bond (Robeson L.M , 1991) which is one of the main problems in membrane technology research. Considering that, inside of carbon nanotubes is atomically smooth (Skoulidas A.I. et al., 2002) which creates reflections of gas molecules on nanotube walls, membranes with CNTs can exceed Robeson upper bonds. Hence gas transport through membrane is very rapid (Majumder, M.et al., 2005).
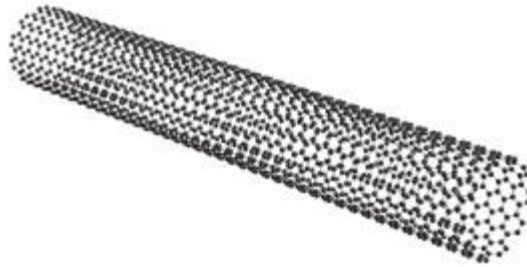
Figure 2.16: Multiwall carbon nanotub (Mgrdichian L., 2006)

2.7.2 TiO_2

Previous investigations on effect of TiO_2 nanoparticles show that voids formation and chain packing disruption due to TiO_2 particles increase the gas permeability of polymeric membranes (Madaeni S.S. etal., 2012). This nanomaterial has several advantages for membrane applications such as great hydrophilicity, innocuity, UV resistance and it can decompose bacteria. Moreover a homogenous dispersion and a minimum of aggregate phenomenon can be obtained thanks to good affinity of TiO_2 with organic solvents (Yang Y. et al., 2005).

It has been noticed in several studies (Yang Y. et al., 2005; Yu L-Y et al., 2009) that an increasing of nanoparticle amount in membranes leads to an increasing viscosity and a slowdown of solvent/non-solvent rate exchange. As a consequence thickness of the skin layer increases which leads to a decrease or a suppression of macro voids in the membrane. Hence the proper amount of TiO_2 can enhance significantly membrane properties but too much TiO_2 can also decrease those properties.

2.7.3 Biofibers

Last few years number of studies investigated natural fibers properties as new ecological, cheap and having renewable sources composite material (Jiang, L. & Hinrichsen, G., 1999; Takagi, H. & Asano, A.,2008). Biofibers which are sustainable, biodegrable, eco-efficient are

often refer today to be "green" composites. Cellulose is one of the most famous bio-composite which is used. This is a macromolecule of 1–4-linked-d-anhydroglucopyranose units.
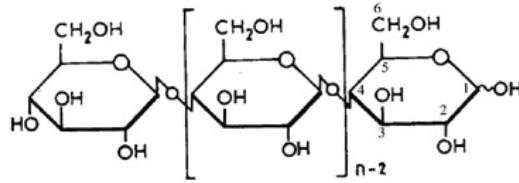

Figure 2.17: Cellulose (Fiber Source)

Moreover cellulose fibers have a high specific strength and stiffness, are nonabrasive and their production requires low energy; many advantages which promote membrane reinforcement and low cost production.

PART 2
Experimental results and discussion

Material and experimental study

3.1 Material

3.1.1 Polymer

PVA powder was supplied by Aldrich chemistry. (PVA lot# MKBH1410V MW=89,000 - 98,000,99+%hydrolyser).

3.1.2 Nanocomposites

CNT nanoparticles were supplied by Showa Denko K. K. (VGCF® (Vapor-grown carbon fiber) VGCF®-H (Vapor-grown carbon fiber))

TiO_2 nanoparticles were supplied by Evonik Industry (TiO_2 P25 Aeroxide, hydrophilic fumed metal oxide, CAS No 13463-67-7).

Biofibers were supplied by Sygma-Aldrich (Microcrystalline cellulose (water content above saturated solutions) CAS No 9004-34-6).

3.1.3 Support

Polysulfone (PSf) ultrafiltration flat sheet membranes (from Alfa Lava, MWCO 20,000-100,000) have been used as a microporous support to make flat sheet membranes.
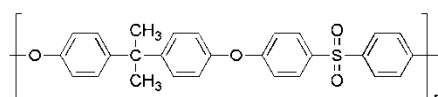
Figure 3.1: Polysulfone

3.1.4 Gases

All gases Helium 4.6 and gas mixture of N_2 (90%) and CO_2 (10%) were supplied in 50L cylinders by Yara Praxair AS, Norway.

3.2 Membrane preparation

3.2.1 Solution preparation

A calculated amount of PVA powder has been mixed in determined amount of distilled water to make a 3 wt% PVA solution. Since PVA is not dissolvable at room temperature, the solution has been heated at 90°C for 2 hours and then polymer was dispersed overnight in water with a rotating machine.

A calculated amount of particles (CNT, TiO_2 or biofibers) has been added to PVA solution to make either a 1wt% or 2wt% solutions. Afterwards solution has been sonicated 10 minutes amplitude 40 and 1 hr amplitude 20 to disperse well all particles in the solution. Then glutaraldehyde has been mixed at 60°C overnight in order to obtain either a 3 wt% or 5 wt% solutions.

3.2.2 Membrane coating

The dip coating procedure has been used to coat membranes. The PVA was casted on a PSf supports which have been fixed to a glass plate. Afterwards PSf supports have been put under water during few minutes to prevent PVA from going into PSf pores. Those supports were then immersed in PVA solution during 5 seconds before being fixed from upside 2 hours. To obtain an even continuous and defect free solution layer supports have been coated a second time and fixed from down side. Before coating solutions were sonicated 10 minutes amplitude 40 to disperse correctly all particles. Thereafter membranes were heated at 110°C during 1.5 hours.

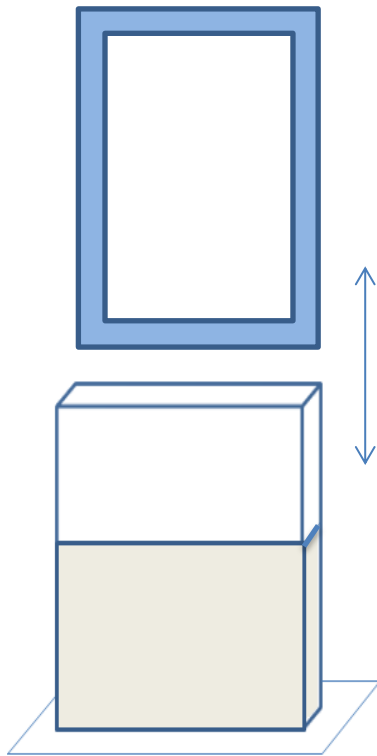Schematic draws of dip coating procedure are presented in figures 3.2 and 3.3.
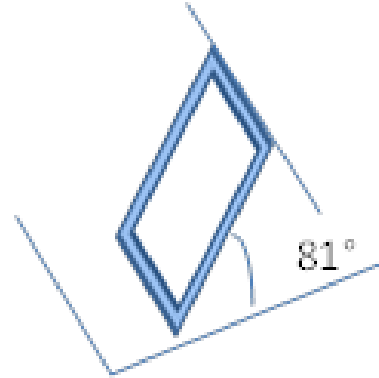
Figure 3.3: Illustration of the drying procedure

Figure 3.2: Dip coating procedure

3.3 Permeation measurement

Permeability and selectivity are two important parameters to determine effectiveness of membrane and to compare it with Robeson upper bound. "Permeation is the diffusion, through a barrier, of a substance in solution" (Encyclopedia britannica).

$$P_i = \frac{J_i}{\Delta P_i} = \frac{q_{p,i}}{A * \Delta P_i} \qquad (eq\ 3.1)$$

Where permeance of gas i Pi (m^3 (STP)/(m^2 h bar)), is defined as ratio of gas i flux J_i over partial pressure difference between upstream and downstream of component i. A (m^2) is the effective membrane area and $q_{p,i}$ (m^3/h) is the permeation flow rate (Deng L., 2009).

Selctivity α was calculated in this study as the ratio of permeablities of CO_2 over N_2.

$$\alpha = \frac{P_{CO_2}}{P_{N_2}} \qquad (Eq\ 3.2)$$

3.3.1 Permeation set up

Permeance and selectivity are tested in a gas permeation rig designed within Memfo Group and processed at the department of chemical engineering (IKP) at NTNU (Figure 3.4 and appendix A.1).

Feed gas was a pre-mixed gas (CO_2/N_2) and sweep gas was Helium supplied from cylinders. Both of those gases were saturated in water by humidifiers (2). CO_2 was separated from N_2 by a flat sheet membrane (3) in which feed flow and sweep flow were in counter current.

A flow controller (FC) and a flow indicator (FI) and pressure transmitters (PI-1 and PI-2) recorded flow rate and pressure. Those data were recorded on a computer with Labview program (National Instruments).

The relative humidity of feed gas was adjusted by the bypass line with the V4 valve, and relative humidity of feed gas was measured by humidity analyzers (HI-1 and HI-2). Humidity's data were recorded on a computer with Rotronic HygroData HTS HW3 program.

An auto-sampling gas chromatograph analyzed the composition of the permeate gas.

Helium was used as sweep gas to reduce the partial pressure of CO_2 in permeate side which was maintained at atmospheric pressure (Sun L-M., Thonnelier J-Y., 2004).

Pressure, humidity and temperature were varied and controlled to study different influences on membrane performances. The gas composition was analyzed using a micro GC (G2801A).
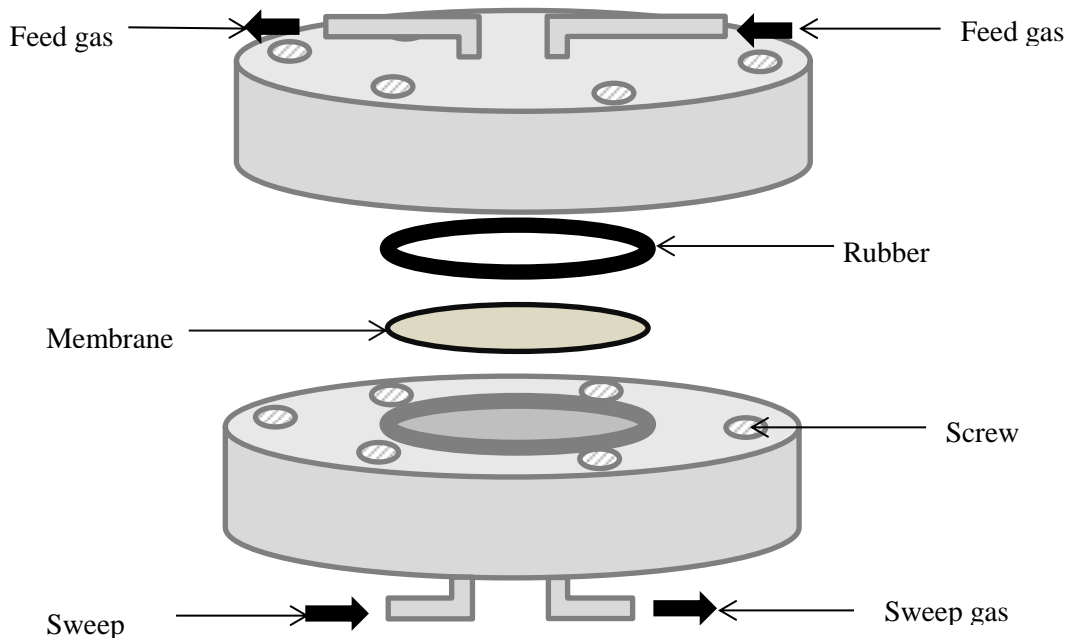
Figure 3.4: Set up for gas permeation test

3.3.2 Membrane cell preparation

Membrane is placed into a cell before being set in the permeation rig (figure 3.5). The membrane has to be cut in order to be placed in the cell. The area of the membrane is thus 3.74 cm². This membrane was sandwiched between two parts of the cell and a rubber ring was placed in order to get a sealed system. Moreover the cell was closed with 6 well tightened screws. Feed flow and sweep flow were in counter flow. Then membrane was placed into the set up one night before tests to get it well humidified.

Figure 3.5: Mounting the membrane

3.4 Swelling tests

Swelling tests were performed to determine the swollen degree of each membrane and their swelling rate constants. For this test membranes have been cast without support and dried over night at 50°C. Afterwards they were crosslinked at 110°C during 1.5 hour.

Dry membranes were weighted before testing; they were then placed into a hermetic sealed pot containing water in the bottom which by evaporation of water creates an environment with 100% humidity. Membranes were regularly weighted during 288 hours (Figure 3.6).

Swelling degree which characterizes the mass of water absorbed by the membrane is calculated as following:

$$SD = \frac{W_s - W_d}{W_d} * 100 \qquad\qquad eq \ (3.3)$$

Where Ws is the weight of swollen membrane and Wd the weight of dry membrane.
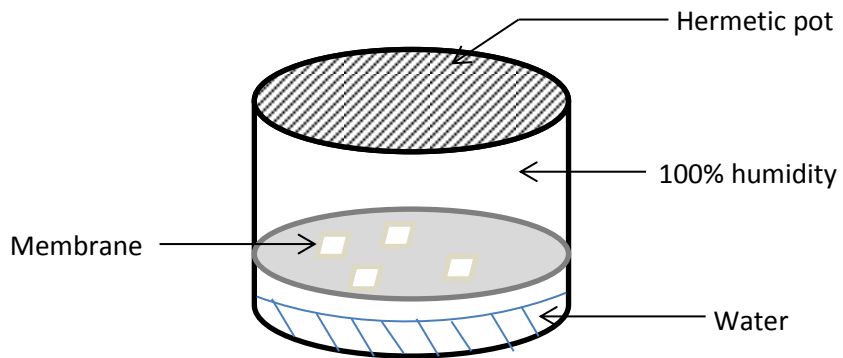
Figure 3.6: Swelling test set up

Results and discussion

This report is a summary of experimental evaluation of PVA membranes developed and optimized for application in a membrane contactor. As mentioned earlier, chemically cross-linked thin film PVA membranes were developed over PSf support with two different concentrations (1wt% and 2 wt %) of 3 types of nano practical (CNTs, TiO_2 and bio fibrils). The membranes were chemically cross linked using two concentrations of glutaraldehyde (3 wt% and 5 wt %).

To evaluate the developed each membrane, following tests were conducted.

- Permeation test with mixed gas in humid conditions
- Swell test

4.1 Permeation tests

Mixed gas containing 10% CO_2 in N_2 was used to test presence and selectivity of CO_2 for each membrane at $25^{o}C$ and 100% humidity. PVA is a hydrophilic material with excellent film forming ability. A dense membrane of PVA with a thickness in nano meters was casted over PSf support to produce a composite membrane. The only mode of transport for CO_2 through PVA layer is solution diffusion. Permeance of CO_2 is highly depended on swelling of membrane. To ensure a stable degree of swelling with water, all membrane samples were subjected to testing conditions for a time period of 12 hours approximately prior to experimentation. Based on findings from previous work, all permeation tests were conducted with Helium as sweep gas with a flowrate of 4 ml/min.

Since PVA is an inert material towards both CO_2 and N_2 and facilitated transport is not expected so, experiments were conducted at three different pressures (1.2, 2 and 3 bar(a)) to study the influence of driving force on CO_2 flux and membrane selectivity. Gas chromatography has been used to analyze permeate sample. After observing a stable operation

for one hour, permeate samples were taken at an interval of 20 minutes each. Each experiment consisted of 5 to 8 stable readings (as presented in figure 4.1).

Experiments were also repeated to verify the reproducibility of results. From these experiments the influence of degree of crosslinking and particle loading were studied and optimum configuration was suggested based on high permeance and selectivity towards CO_2.
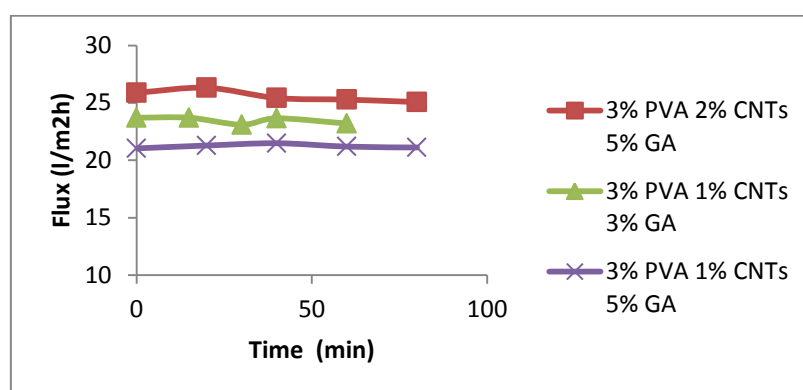

Figure 4.1 Flux of CNTs membrane with time

4.1.1 Permeation experiments with CNTs

Carbon nano tubes were investigated by Deng L. (2009) and an optimal loading of 1 wt% was suggested for physically cross-linked PVA/PVAm membrane. Since the membrane developed in this work is intended for application in a gas-liquid membrane contactor, it is necessary to chemically crosslink the PVA film. Besides ensuring the integrity of membrane, chemical crosslinking also reduces the chain flexibility and permeance. To ensure high permeance CNTs were added to the membrane. Two concentrations of GA (3 and 5 wt %) were used in this work to cross-link PVA so, two different loadings of CNTs (1 and 2 wt %) were considered to experimentation. CNTs are hydrophilic nano particles which help to maintain high degree of swelling even in chemically cross-linked dense membrane.

(a)   (b)
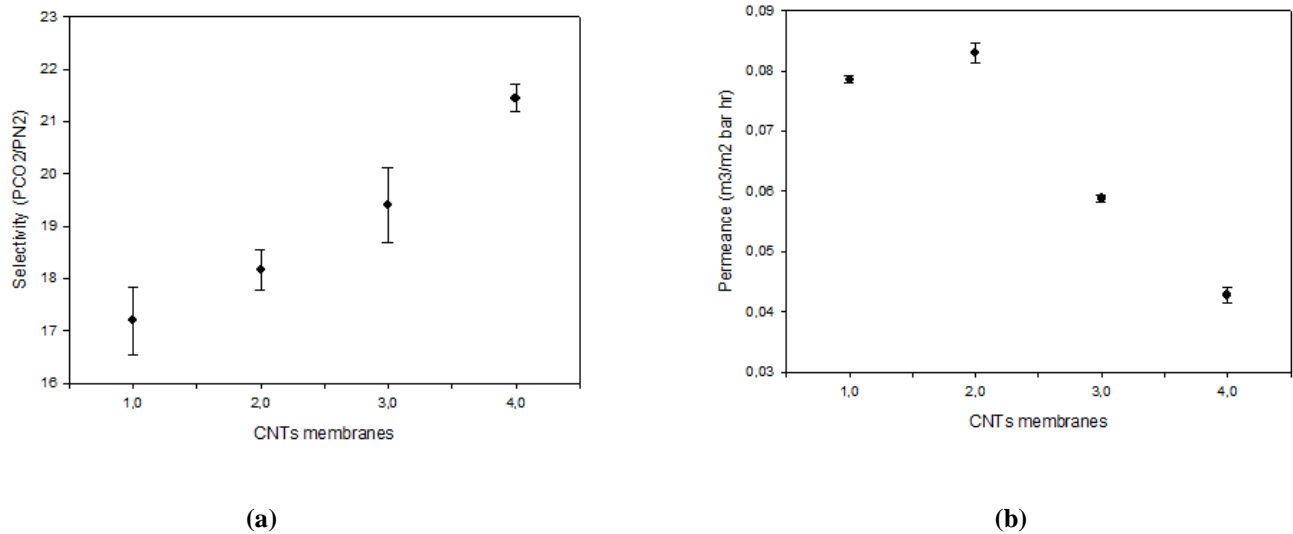
Figure 4.2: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on CNTs loading and glutaraldehyde concentration under P= 2 bars. (1) 3% PVA 2% CNTs 5% GA, (2) 3% PVA 2% CNTs 3% GA, (3) 3% PVA 1% CNTs 5% GA, (4) 3% PVA 1% CNTs 3% GA.

Under humid conditions PVA membrane loaded with CNTs absorbs water and increases chain mobility. This results in higher diffusion coefficient for any gas passing through the membrane. Theoretically an increase in CNTs should not only increase the diffusivity of CO_2 but it also should increase the permeance of N_2 through the membrane. Since the solubility of CO_2 in water is much higher than that of N_2, PVA membrane acts as facilitated membrane under humid conditions and presence of nano particles like CNTs increases the swelling capacity of PVA film hence resulting in a facilitated transport of CO_2. Selectivity and permeance of CNT membranes operating at 2 bars pressure are presented in figure 4.2 and all experimental results for these membranes are given in table 4.1. All the selectivity and permeance values are graphically compared in appendix A.2 & A.3

Table 4.1: Flux and permeance values of CNTs membranes

Membrane	Flux (l/(m2h))	Permeance (m^3/ m^2 bar hr)
1.2 bar		
3% PVA 2% CNTs 3% GA	26.21	7.90E-02
3% PVA 2% CNTs 5% GA	25.59	7.29E-02
3% PVA 1% CNTs 3% GA	23.46	5.20E-02
3% PVA 1% CNTs 5% GA	21.22	6.13E-02
2 bars		
3% PVA 2% CNTs 3% GA	47.09	8.30E-02
3% PVA 2% CNTs 5% GA	44.39	7.86E-02
3% PVA 1% CNTs 3% GA	39.04	4.28E-02
3% PVA 1% CNTs 5% GA	32.73	5.88E-02
3 bars		
3% PVA 2% CNTs 3% GA	68.56	7.94E-02
3% PVA 2% CNTs 5% GA	64.61	7.48E-02
3% PVA 1% CNTs 3% GA	49.87	3.92E-02
3% PVA 1% CNTs 5% GA	45.71	5.73E-02

It can be noticed that membranes containing 2% of CNTs have higher CO_2 permeance and flux values than membranes containing only 1% of CNTs. At same degree of crosslinking permeance of CO_2 is increased by 25 $\pm$ 4% by doubling the CNT loading. This means that by increasing the CNT loading performance of membrane can be improved. However, it is fairly difficult to maintain a homogeneous suspension of casting solution with high concentration of nano particles. Deng L. (2009) also faced difficulties in keeping a homogeneous suspension of CNT particles in polymer solution at high concentrations. Keeping this challenge in mind and a short time frame for this project, 3, 4 wt% and higher loadings were not tested.

In figure 4.2, besides the influence of CNT loading, a clear influence of crosslinking on permeance can also be seen. As the degree of crosslinking is increased from 3 to 5 wt% of GA solution, the permeance has decreased by 7 $\pm$ 3% for same CNT loading. Degree of crosslinking is a function of GA concentration, temperature and time for reaction. In this work all membranes were cross-linked at 60°C for 24hrs at two concentrations of GA only. Influences of time and temperature have not been studied in this work due to a fixed timeframe for master thesis.

It can be notice that selectivity is increasing with decreasing permeance. Membranes containing 1% of CNTs have higher selectivity values than membranes containing 2% of CNTs. It means that decreasing the CNTs loading increases selectivity of membranes. Moreover selectivity increases with increasing glutaraldehyde concentration. As mention earlier an increase of CNTs also increases the permeance of N_2 which decreases selectivity.

Results obtained during experimentations deviate of 0.60% to 4.60%. It can be concluded that those results are stable. Moreover membranes have been tested a second time and small deviations between 3% and 8.5% have been recorded. It can be concluded that those results are reliable. The biggest instabilities have been noted during tests under 1.2 bar. Sweep pressure was approximately 1.152 bars and flow pressure was oscillating between 1.108 bar and 1.380 bar. Sweep pressure was then sometimes higher than flow pressure which can make results unstable.

4.1.2 Experimentation with TiO_2

Experiments were conducted with PVA containing TiO_2 membranes at same conditions as for CNT membranes. Somewhat similar effect of degree in crosslinking was observed for these membranes but a completely different trend appeared for nano particle loading. Unlike CNT membranes TiO_2 membranes show a reverse effect of particle loading on permeance. Selectivity and permeance of TiO_2 membranes at 2 bars are presented in figure 4.3 and flux and permeance data are presented in table 4.2. All results are graphically compared in appendix A.4 & A.5.

(a)　　　　　　　　　　　　　　　　　　　**(b)**
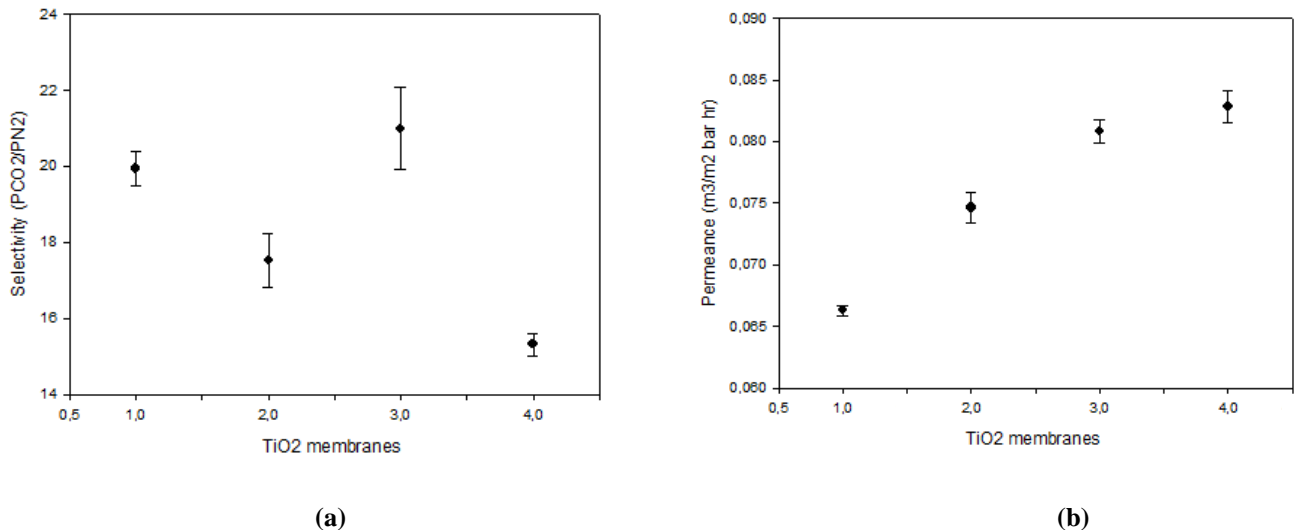
Figure 4.3: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on TiO$_2$ loading and glutaraldehyde concentration under P= 2 bars. (1) 3% PVA 2% TiO$_2$ 5% GA, (2) 3% PVA 2% TiO$_2$ 3% GA, (3) 3% PVA 1% TiO$_2$ 5% GA, (4) 3% PVA 1% CNTs 3% GA.

Experiments were repeated to verify these observations. Repeated experiments showed same results with 5 to 17% difference for respective pressures. Same problems concerning tests under 1.2 bar than the ones for membranes containing CNTs nano-particles were noticed during those tests.

In a mixed matrix membrane, nano particles produce an inconsistency. There are then two phases within a membrane i.e. continuous polymer phase and dispersed particles. Maxwell theory has been used to understand the influence of particles on transportation of gas. The higher permeance of CO$_2$ for 1% loading compared to that of 2% TiO$_2$ can be justified on the basis of aggregate forming ability of TiO$_2$. Yu Li-Yun et al.(2002) studied the influence of TiO$_2$ loading (0.5 to 5 wt%) on the performance of PVDF membrane and observed a similar behavior. They studied the contact angle of prepared membranes to see the influence of particle concentration on hydrophylicity of membrane and concluded that at concentration higher than 1 wt%, TiO$_2$ starts agglomerating and results in big lumps of particles which decreases the mean pore size. Hence the assumption of homogeneous dispersion of particles becomes questionable and a decline in flux is observed. Moreover addition of TiO$_2$ increases viscosity which slows down the exchange rate between solvent and non-solvent and decreases hydrophilicity of the membrane whereas low concentration of TiO$_2$ increases hydrophilicity which can capture more molecules of water and then facilitate permeance. It can be noticed that membranes containing 5% glutaraldehyde have higher selectivity.

Contrary to CNTs membrane particle loading doesn't seems to be the main parameter for selectivity. It can be assume that the more the membrane crosslinked is the more selective it is. Furthermore the membrane containing 1wt% of TiO_2 and 5wt% of glutaraldehyde shows the best parameters with the highest selectivity and almost the highest permeance.

In this project only two concentrations of TiO_2 have been tested. 1wt% TiO_2 was selected for this study because of the observation published by Yu Li-Yun et al.(2002). 2wt% TiO_2 was selected to compare the results with CNT membranes. Keeping the short time scale for this thesis lower loadings of TiO_2 were not tested.

Table 4.2: Flux and permeance values of TiO_2 membranes

Membrane	Flux (l/m2h)	Permeance (m^3/m² bar hr)
Pressure = 1.2 bar		
3% PVA 2% TiO$_2$ 3% GA	30.01	9.10E-02
3% PVA 2% TiO$_2$ 5% GA	23.94	7.18E-02
3% PVA 1% TiO$_2$ 3% GA	25.94	7.79E-02
3% PVA 1% TiO$_2$ 5% GA	24.12	7.24E-02
Pressure = 2 bars		
3% PVA 2% TiO$_2$ 3% GA	42.31	7.46E-02
3% PVA 2% TiO$_2$ 5% GA	37.79	6.63E-02
3% PVA 1% TiO$_2$ 3% GA	46.89	8.29E-02
3% PVA 1% TiO$_2$ 5% GA	45.63	8.08E-02
Pressure = 3 bars		
3% PVA 2% TiO$_2$ 3% GA	61.61	7.14E-02
3% PVA 2% TiO$_2$ 5% GA	54.72	6.31E-02
3% PVA 1% TiO$_2$ 3% GA	71.18	8.27E-02
3% PVA 1% TiO$_2$ 5% GA	67.74	7.52E-02

4.1.3 Experiments with Bio micro fibrils

Membranes containing 1 and 2 wt% bio fibrils were subjected to study at same operating conditions as CNTs and TiO_2 membranes. Results similar to TiO_2 were observed in this case as well. The flux and permeance of CO_2 decreased with increasing particle concentration. Experiments were repeated to verify the results. Permeance and flux were calculated with less than 10% difference for each pressure. Experimental results for selectivity and permeance are presented in figure 4.4. All the results concerning flux and permeance data are given in table 4.3.

(a)

(b)
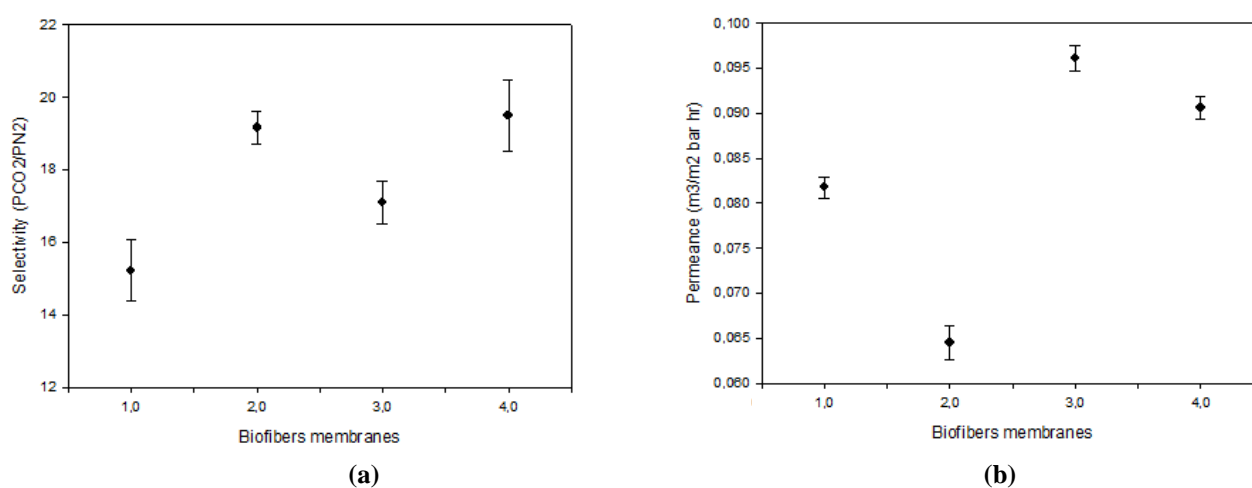
Figure 4.4: Selectivity evolution with deviation (a) and permeance evolution with deviation depending on biofibers loading and glutaraldehyde concentration under P= 2bars. (1) 3% PVA 2% Biofibers 5% GA, (2) 3% PVA 2% Biofibers 3% GA, (3) 3% PVA 1% Biofibers 5% GA, (4) 3% PVA 1% Biofibers 3% GA.

The decline in flux with increase in loading may be caused by aggregation of fibers but increase in permeance with increase in GA concentration cannot be explained theoretically. Repeated experiments showed less than 10% deviation in permeance. Unfortunately no literature is available on bio fibrils used for such application to verify this strange behavior. This strange behavior of bio fibers shows interesting results in permeance experiments. Swell and durability test of bio fibers shall be conducted to see if there was any defect in membrane otherwise bio fibers have highest permeance even at higher degree of crosslinking. Further investigation shall be conducted to understand the transport mechanism in these membranes. All results are also graphically compared in appendix A.6 & A.7.

Concerning selectivity values, the opposite behavior to membranes containing TiO_2 particle is observed. Membranes with 3wt% concentration of glutaraldehyde have highest selsctivity values. High crosslinked membranes have the best selectivity properties. Moreover membrane containing 1wt% of Biofibers and 3wt% of glutaradehyde seems to be the most beneficial membrane.

Table 4.3: Flux and permeance values of Biofibers membranes

Membrane	Flux (l/m2h)	Permeance (m3/m² bar hr)
Pressure = 1.2 bar		
3% PVA 2% Biofibers 3% GA	23.58	6.37E-02
3% PVA 2% Biofibers 5% GA	23.61	7.07E-02
3% PVA 1% Biofibers 3% GA	32.28	8.85E-02
3% PVA 1% Biofibers 5% GA	30.69	8.41E-02
Pressure = 2 bars		
3% PVA 2% Biofibers 3% GA	42.31	6.45E-02
3% PVA 2% Biofibers 5% GA	37.79	8.17E-02
3% PVA 1% Biofibers 3% GA	46.89	9.06E-02
3% PVA 1% Biofibers 5% GA	45.63	9.61E-02
Pressure = 3 bars		
3% PVA 2% Biofibers 3% GA	52.14	6.01E-02
3% PVA 2% Biofibers 5% GA	67.57	7.87E-02
3% PVA 1% Biofibers 3% GA	72.13	8.43E-02
3% PVA 1% Biofibers 5% GA	75.24	8.82E-02

4.1.2 Comparison of membranes and optimal configuration

Permeance of CO_2 as a function of pressure for each membrane is plotted to understand and compare the performance of developed membranes. Figure 4.5 illustrates the trend of permeance as a function of pressure for membranes containing 1% nano particles at different degree of crosslinking.

(a)

(b)
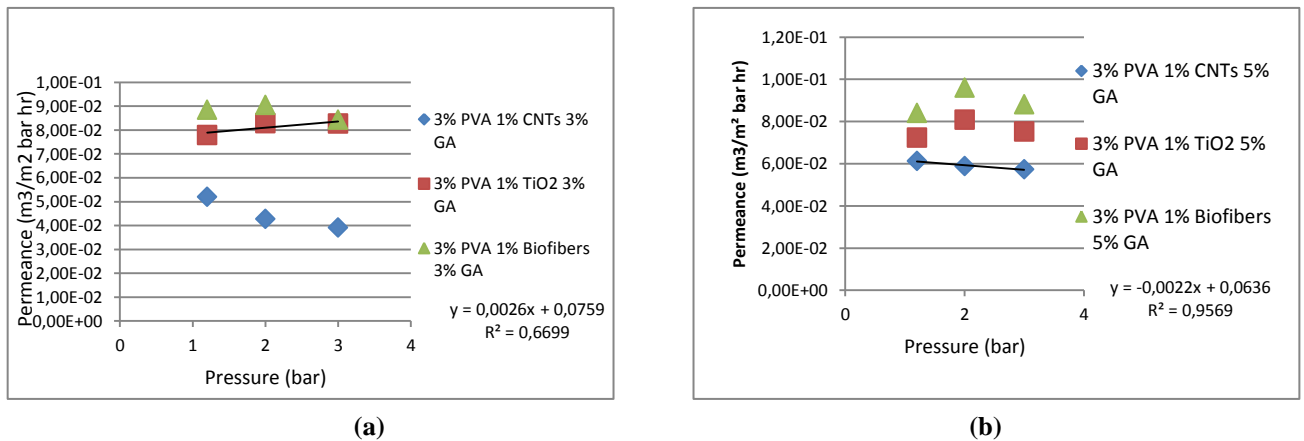
Figure 4.5: Evolution of permeance with pressure; (a) 1 wt% particles in 3% GA (b) 1% particles in 5% GA.

It can be seen that at both levels of crosslinking membranes with bio fibers are the most permeable towards CO_2. Degree of crosslinking has a pronounced effect of permeance of CNT membranes but it has a much elusive effect on membranes with TiO_2. However, degree of crosslinking has an opposite effect on permeance of bio fiber membranes as compared to CNT and TiO_2 membranes.

(a)

(b)
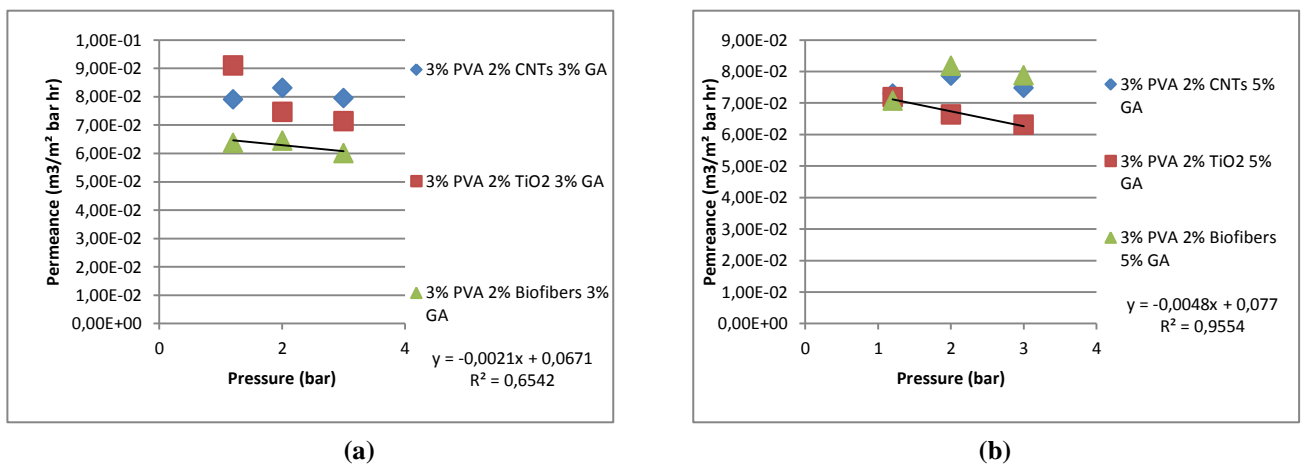
Figure 4.6: Evolution of permeance with pressure; (a) 2wt% particles in 3% GA, (b) 2wt% particles in 5% GA

Contrary to above discussion, the permeance of CO_2 is lowest for membrane containing 2 wt% biofibers at lower degree of crosslinking. However, permeance increases with increase in crosslinking. Considering our results to be authentic for bio fibers, it is then recommended to

use a highly cross-linked membrane with high concentration of biofibers. This configuration not only guarantees a stable membrane in water rich environment but also ensures high permeance.

1 wt% TiO_2 is then the second best candidate which shows higher permeance than CNTs. 1wt% TiO_2 and 5 wt% GA membrane is comparable with 2 wt% CNT and 5 wt% GA membrane. However, 2wt% TiO_2 is the worst possible configuration. As at 3wt% GA its permeance is less than CNTs and even lesser than 1wt% TiO_2 at same level of crosslinking.

CNT based membrane is much simpler and easier to explain. Its performance increases with increase in particle loading and decreases with crosslinking. At 2wt% CNT loading and low levels of crosslinking its performance is better than other two membranes and at higher degree of crosslinking its performance is comparable with bio fiber membrane. In short it can be said that CNT based membrane is the most reliable as the results shows a consistent trend and unlike TiO_2 it shows a homogenous dispersion of particles at the two studied concentrations.

Permeance of all membranes along with its standard deviation is presented in table 4.4.

Table 4.4: Permeance of membranes depending on pressure and standard deviation

Pressure (bar)	1.2	2	3	Standard deviation	Average	Relative standard deviation
2% CNTs 3% GA	7.90E-02	8.30E-02	7.94E-02	1.71E-03	8.05E-02	2.12%
2% TiO₂ 3% GA	9.10E-02	7.46E-02	7.14E-02	7.99E-03	7.90E-02	10.11%
2% Biofibers 3% GA	6.37E-02	6.45E-02	6.01E-02	1.78E-03	6.28E-02	2.84%
2% CNTs 5% GA	7.29E-02	7.86E-02	7.48E-02	2.10E-03	7.54E-02	2.79%
2% TiO₂ 5% GA	7.18E-02	6.63E-02	6.31E-02	3.17E-03	6.71E-02	4.73%
2% Biofibers 5% GA	7.07E-02	8.17E-02	7.87E-02	4.22E-03	7.71E-02	5.48%
1% CNTs 3% GA	5.20E-02	4.28E-02	3.92E-02	4.88E-03	4.46E-02	10.93%
1% TiO₂ 3% GA	7.79E-02	8.29E-02	8.27E-02	2.18E-03	8.12E-02	2.68%
1% Biofibers 3% GA	8.85E-02	9.06E-02	8.43E-02	2.31E-03	8.78E-02	2.64%
1% CNTs 5% GA	6.13E-02	5.88E-02	5.73E-02	1.43E-03	5.91E-02	2.42%
1% TiO₂ 5% GA	7.24E-02	8.08E-02	7.52E-02	3.12E-03	7.61E-02	4.10%
1% Biofibers 5% GA	8.41E-02	9.61E-02	8.82E-02	4.44E-03	8.94E-02	4.10%

4.2 Swelling tests

Previous studies show that there is a strong dependence between permeability and selectivity of a membrane and its swelling degree (Deng L., Hägg M.-B., 2010). Furthermore it has been proven that water-swollen membranes enhance CO_2 transport by forming HCO_3^- (Kim T.J., Li B.A. and Hagg M.B.,2004). Hence swelling capacity is a crucial parameter in this study. Swelling tests have been performed 3 times and graphs have been plotted taking into account the average of each series and deviation. Graphs of each category of particles have been plotted to determine which membrane is the best in each category. The best membranes have then been compared in figure 4.7.All the results can be found in appendix A.9.
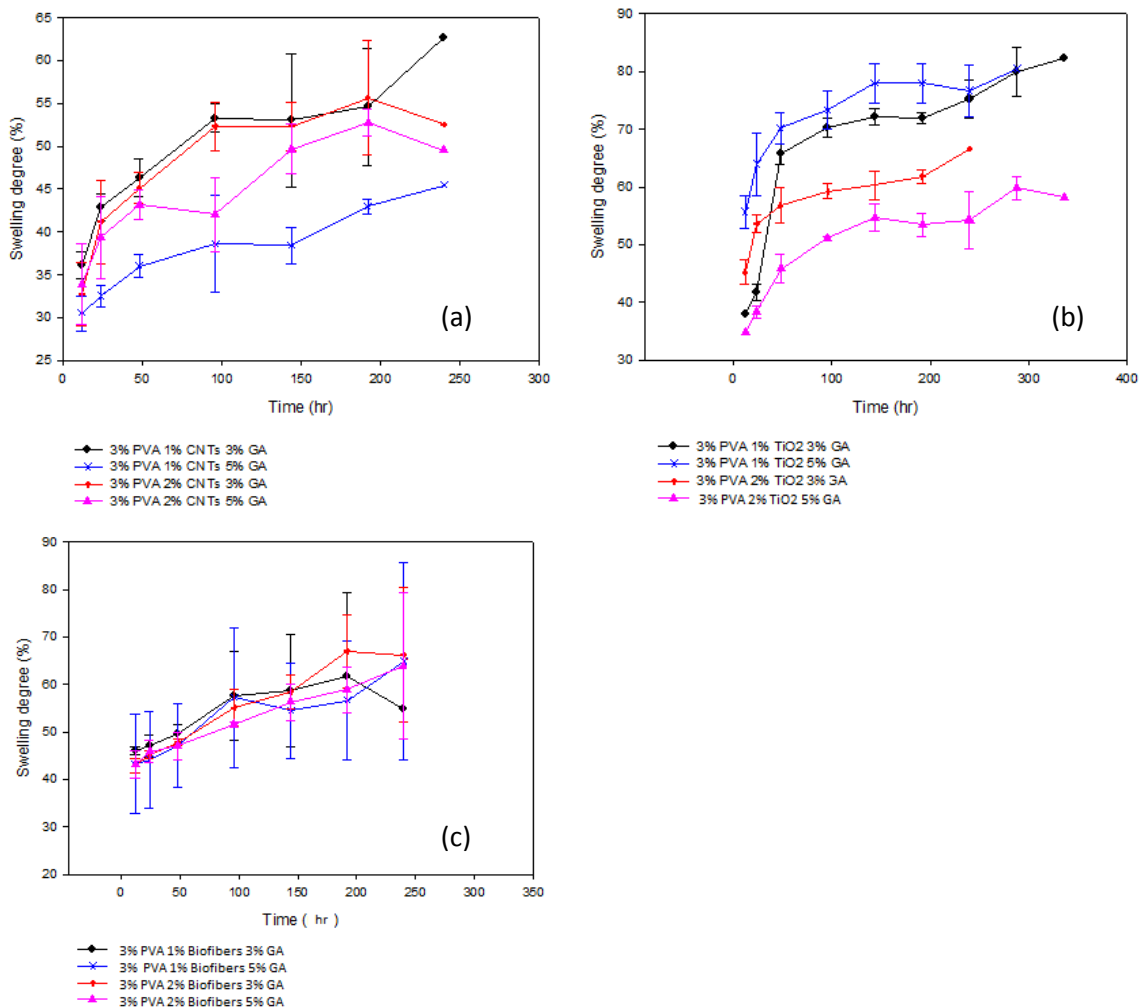
Figure 4.7: Evolution of swelling degrees and their deviations with time; (a) Membranes with CNTs, (b) Membranes with TiO$_2$; (c) Membranes with Biofibers.

It can be noticed that results match with a typical graph showing evolution of swelling degree of a cross linked polymer in a solvent as a function of time illustrated in figure 4.8. The swelling degree increases first rapidly and then slows progressively down trying to reach an equilibrium.
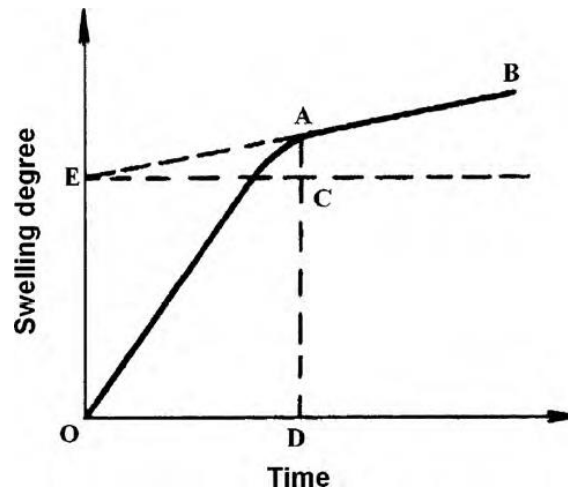
Figure 4.8: Evolution of swelling degree as function of time of a cross linked polymer in a solvent (Wu Q., Feng Y., 2004)

From those graphs it can be concluded that membranes with 1% of TiO_2 and 5% of GA, 1% of CNTs and 2% of Biofibers and 3% of GA have the best capacity to swell. Figure 4.9 compare those three membranes.
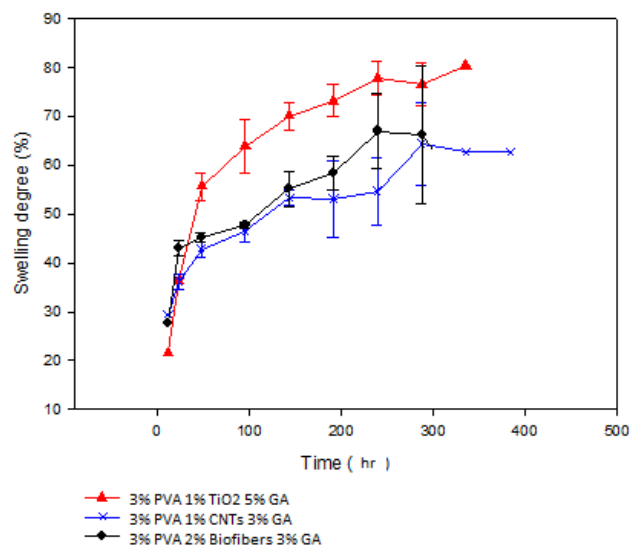
Figure 4.9: Comparison of swelling capacity of synthetized membranes

Membrane containing TiO_2 particles have higher swelling degree than other membranes. TiO_2 is highly hydrophilic which can enhance membrane capacity to swell. Moreover it can be assumed that membranes containing cellulose have higher swelling degree because of presence of hydroxyl groups which enhance membrane capacity to swell.

Furthermore a simple second order equation (equation 4.1) can, once integrated (equation (4.2)), evaluate the theoretical equilibrium swelling degree of membranes (Wu Q., Feng Y., 2004).

$$\frac{dS}{dt} = k_s \left(S_{eq} - S\right)^2 \qquad\qquad eq\ (4.1)$$

$$\frac{t}{S} = \frac{1}{k_s S_{eq}^2} + \left(\frac{1}{Seq}\right) t \qquad\qquad eq\ (4.2)$$

Where S is the swelling degree, S_{eq} the theoretical equilibrium swelling degree, t the time, and k_s the swelling rate constant. To find the theoretical equilibrium swelling degree and the kinetic constant t/S versus t graphs have been plotted in figure 4.10 and appendix A.8.
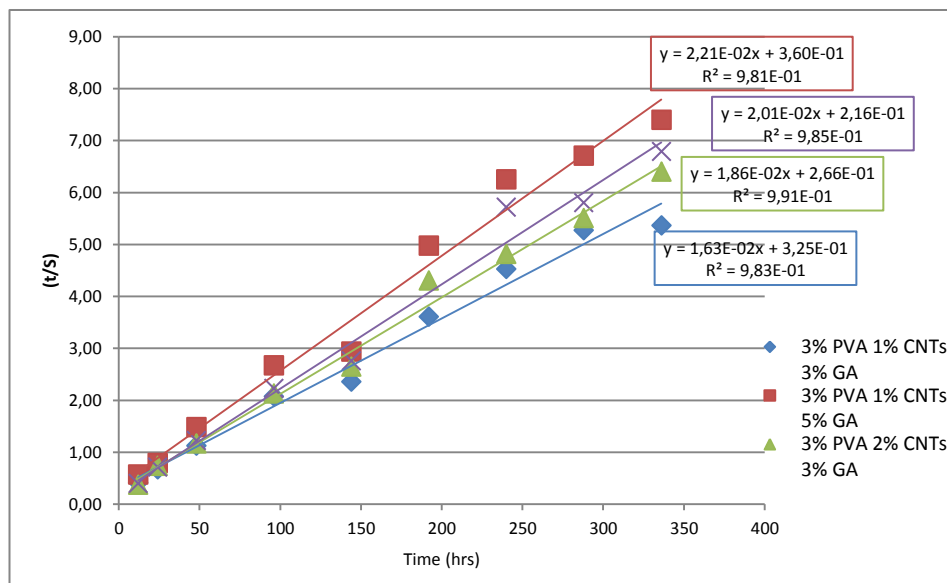
Figure 4.10: Time/ swelling degree as function of time for data concerning membranes with CNTs

All the results are reported in table 4.5:

Table 4.5: Swelling degree equilibrium (S_{eq}) and kinetic constant (k) values

Membranes	1/Seq	Seq	1/kSeq	K ((g gel/ g water)/hrs
1% TiO2,3% GA	1.18E-02	8.47E+01	2.50E-01	5.58E-04
1%TiO2,5% GA	1.15E-02	8.70E+01	3.97E-01	3.33E-04
2%TiO2,3% GA	1.46E-02	6.85E+01	2.41E-01	8.84E-04
2%TiO2,5% GA	1.66E-02	6.02E+01	2.48E-01	1.11E-03
1CNT%,3% GA	1.63E-02	6.13E+01	3.25E-01	8.19E-04
1%CNT,5% GA	2.21E-02	4.52E+01	3.60E-01	1.36E-03
2%CNT,3% GA	1.86E-02	5.38E+01	2.66E-01	1.30E-03
2%CNT,5% GA	2.01E-02	4.98E+01	2.16E-01	1.87E-03
1%Biofibers,3% GA	1.77E-02	5.65E+01	1.60E-01	1.96E-03
1%Biofibers,5% GA	1.72E-02	5.81E+01	1.82E-01	1.62E-03
2%Biofibers,3% GA	1.68E-02	5.95E+01	2.39E-01	6.33E-04
2%Biofibers,5% GA	1.49E-02	6.71E+01	3.51E-01	1.18E-03

Theoretical swelling degree gives information for the long term use of the membrane. Indeed beyond this limit membrane can be damage and start to dissolve, thus equilibrium must not be exceed. Theoretical equilibrium swelling degree is between 49.8% and 87% depending on membranes. Moreover swelling rate constants are between 3.33E-04 (g gel/g water)/hrs and 1.96E-3 (g gel/g water)/hrs. Membranes with high swelling degree reach faster their equilibrium. It can be conclude that membranes containing 1% TiO_2 are the best to handle swelling since they have the highest theoretical equilibrium swelling degree with the fastest reaction which allow rapidly and good transfer. TiO_2 membranes are also membranes which presented the best stability during swelling test (figure 4.7).

Membranes containing biofibrils show high rate of swelling in the beginning. During permeance tests membranes were left for 12 hours to get humidified. Due to higher swelling cellulose membranes with higher crosslinking degree show a better permeance.

4.3 Safety measures during this study

All the lab work required the wearing of a lab coat, protection glasses and gloves. Moreover special safety measures had to be followed during manipulations of nanocomposites. Since they are highly toxic a mask had to be wear to prevent any particle breathing. As CNTs particles are less toxic after being humidified a wet environment created by placing wet paper on the work bench and special gloves avoiding all electrostatic interactions were worn. Furthermore headphones were worn during sonication of solutions. The use of permeation set up which needs gases under pressure required surveillance during working time and low pressure and sweep flow were set during the night. Risk assessment tables have been filed in (table 4.6) following the risk assessment matrix code (appendix A.10) before starting to be fully aware of all the risks and act in consequences.

Table 4.6: Risk assessment

ID no.	Activity from the identification process form	Potential undesirable incident/strain	Likelihood: Likelihood (1-5)	Consequence: Human (A-E)	Environment (A-E)	Economy/ material (A-E)	Reputation (A-E)	Risk value Human	Comments/status Suggested measures
1	Solution preparation	Spill of solution to the floor/bench	4	A	A	A		A4	The bench/floor will be washed with water after every preparation of solution
2		Spill of solution on humans	4	A	A	A		A4	Safety equipment must be used!
3		Spill of solution into the eyes	2	C	A	A		C2	Safety glasses must be used!
4		Breathing of nano particles	1	E	A	C		E1	Safety mask must be worn
5		Burns due to the use of oven at high temperatures	2	A	A	A		A2	Safety gloves must be worn
6	Membrane casting	Spill of solution on the floor/bench	4	A	A	A		A4	The bench/floor will be washed with water after every
7		Spill of solution on humans	4	A	A	A		A4	Safety equipment must be used!
8		Spill of solution in the eyes	2	C	A	A		A4	Safety equipment must be used!
		Possible hearing damages	2	B	A	A		B2	Headphones must be worn
9	Membrane testing	leakage of gas	1	E	A	C		E1	Use of gas detector
10		Too much pressure in the gas going to the apparatus	1	E	A	C		E1	Check the regulator regularly

Conclusion

From experimentations it can be conclude that:

- Permeance is higher in membranes containing 2 weight percent CNTs than in membranes containing 1 weight per cent.

- Due to its hydrophilic nature, PVA swells by absorbing water from gas stream which results in a high free volume. The water absorbed not only increases the permeability of membrane by swelling it but also helps in selective transport of CO_2 from a mixed gas feed based on its higher affinity to absorb CO_2 than N_2. Hence the dense PVA layer acts as a facilitated membrane in presence of moisture.

- Membranes containing 1wt% TiO_2 have higher permeance values than membrane with 2wt% TiO_2. High percentage of TiO_2 nanoparticle can clog the pores and thus reduces mean pore size which decreases permeance. Moreover it increases viscosity which slows down solvent/nonsolvent exchange rate which decreases hydrophilicity and consequently decreases swelling capacity of the membrane and permeance.

- Crosslinking reduces free volume which decreases permeance. This has been corroborated by results for membranes with CNTs and those with TiO_2.

- An opposite behavior concerning crosslinking has been observed for membranes with biofibers. Permeance values are higher for membranes with 5wt% concentration of glutaraldehyde than membranes with 3wt%. Nonetheless results have been confirmed after second tests. Swelling tests showed high swelling rate in the beginning of experiment. During permeation test membranes were left 12 hours to get humidified in the set up. Biofibers membranes with 5wt% GA swelled rapidly which explains better performance compared to membranes containing 3wt% GA.

- Swelling degree increases rapidly and then tends to reach slowly equilibrium. Results obtained match with typical swelling/time curve of cross-linked polymer in solvent observed in previous study (Wu Q., Feng Y., 2004).

- TiO_2 due to its hydrophilic character allocates a higher swelling degree to membranes. Membranes with 1wt% TiO_2 nano particle also have the highest theoretical equilibrium swelling degree and a smallest swelling rate constant which means that those membranes have ability to swell rapidly and thus enhance the facilitate transport which increases permeance.

- Membranes with CNTs have the lowest swelling degree; however their results appear to be more stable than those for Biofibers membranes.

- After this study it can be noticed that membrane with 1wt% TiO_2 have permeance values amongst the best and the best results for swelling test.

Recommendation for further work

Due to the short time scale for this thesis lot of tests had not been performed. However experimentations could help for a better understanding of phenomena which have been observed. Difficulties have been faced to keep a homogeneous suspension of CNTs particles in polymer solution at high concentration. 3wt% and 4wt% loading of CNTs should be tested to corroborate previous results and verify if permeance values still increase with an increasing particle loading. Moreover tests should be performed with lower loading of TiO_2 to compare results with the work of Yu Li-Yun et al.(2002). Results concerning membranes with biofibers should be verified due to the unexpected behavior of membranes with degree of cross-liking. Studies leading to a better understanding of transport mechanism through membranes with biofibers should be conducted. Influence of time and temperature on membranes has not been tested. However they are two key parameters in membrane contactor processes. Permeation test should be performed over on longer time scale to confirm that better permeance results of biofibers membranes with 5wt% are due to high rate of swelling in the beginning. Membrane should also be able to resist a long time to process conditions. Moreover SEM analysis should be performed to measure the thickness of the membrane and then calculate permeability values of membranes. Dispersion of particles in membranes could be also be evaluated.

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Appendix A.4: Selectivity evolution (a) and permeance evolution (b) depending on TiO_2 loading and glutaraldehyde concentration under P= 1.2 bar. (1) 3% PVA 2% TiO_2 5% GA, (2) 3% PVA 2% TiO_2 3% GA, (3) 3% PVA 1% TiO_2 5% GA, (4) 3% PVA 1% CNTs 3% GA.

Appendix A.5: Selectivity evolution (a) and permeance evolution (b) depending on TiO_2 loading and glutaraldehyde concentration under P= 3 bars. P= 1.2 bar. (1) 3% PVA 2% TiO_2 5% GA, (2) 3% PVA 2% TiO_2 3% GA, (3) 3% PVA 1% TiO_2 5% GA, (4) 3% PVA 1% CNTs 3% GA.

Appendix A.6: Selectivity evolution (a) and permeance evolution (b) depending on Biofibers loading and glutaraldehyde concentration under P= 1.2 bar. (1) 3% PVA 2% Biofibers 5% GA, (2) 3% PVA 2% Biofibers 3% GA, (3) 3% PVA 1% Biofibers 5% GA, (4) 3% PVA 1% Biofibers 3% GA.

Appendix A.7: Selectivity evolution (a) and permeance evolution (b) depending on Biofibers loading and glutaraldehyde concentration under P= 3 bars. (1) 3% PVA 2% Biofibers 5% GA, (2) 3% PVA 2% Biofibers 3% GA, (3) 3% PVA 1% Biofibers 5% GA, (4) 3% PVA 1% Biofibers 3% GA.

Appendix A.8: Time/ swelling degree as a function of time for TiO2 membranes (a) and Biofibers membranes (b)

Appendix A.10: Risk assessment matrix

List of tables
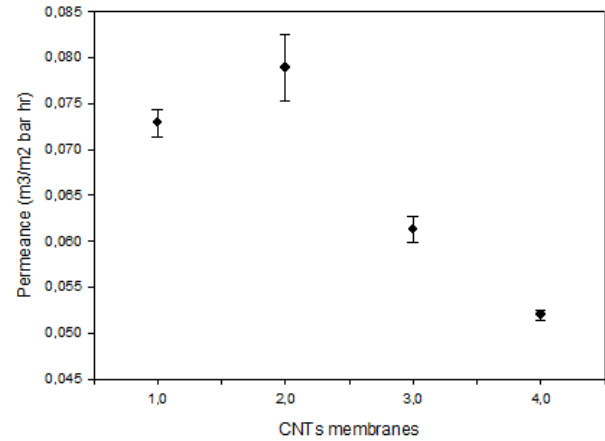
Appendix

Permeation test set up

Appendix A.1: Permeation set up (a & b) and permeation rig (c)

Effect of particle loading and glutaraldehyde concentration

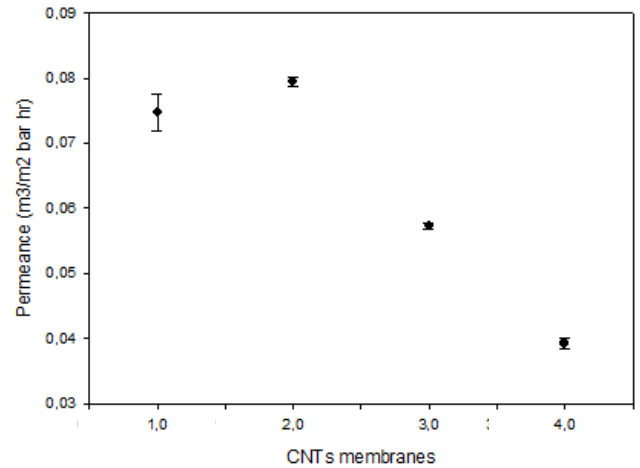**CNTs**
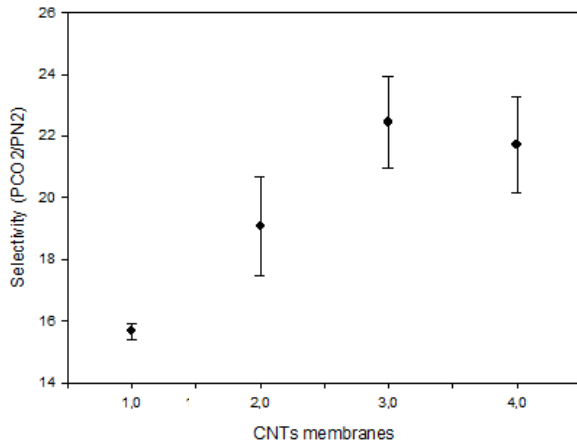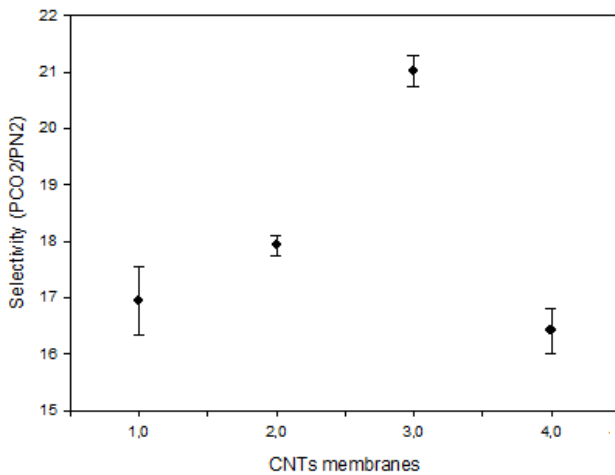

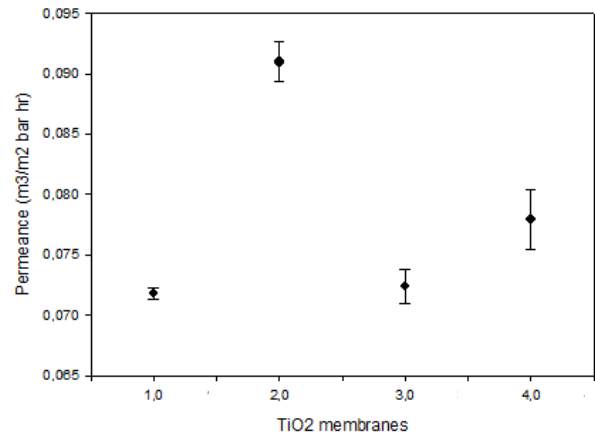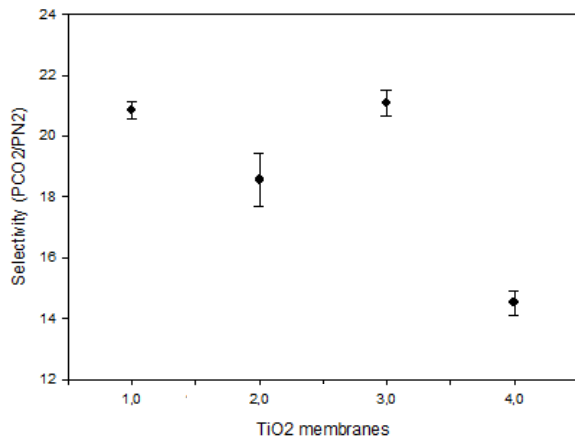(a)   (b)

Appendix A.2: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on CNTs loading and glutaraldehyde concentration under P= 1.2 bar. (1) 3% PVA 2% CNTs 5% GA, (2) 3% PVA 2% CNTs 3% GA, (3) 3% PVA 1% CNTs 5% GA, (4) 3% PVA 1% CNTs 3% GA.
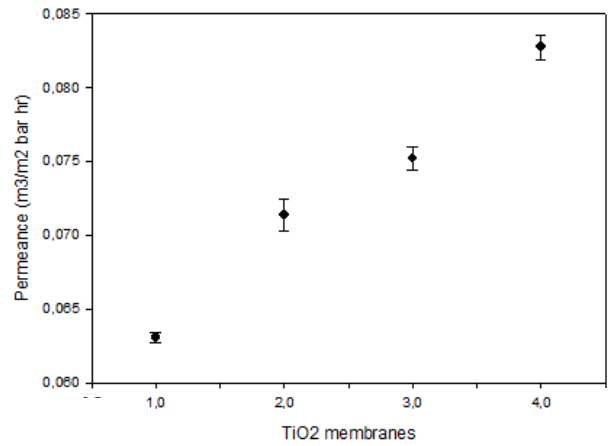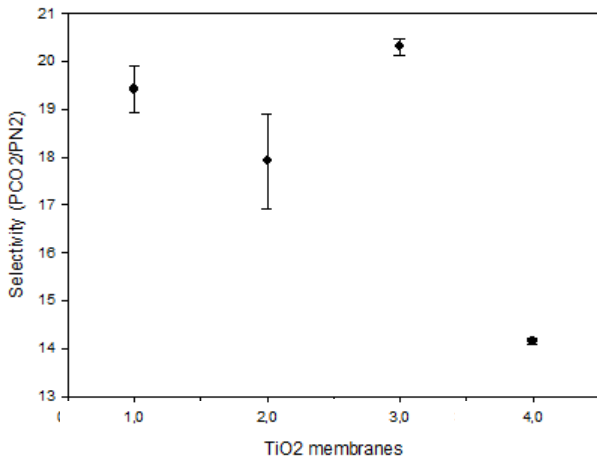

Appendix A.3: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on CNTs loading and glutaraldehyde concentration under P= 3 bars. (1) 3% PVA 2% CNTs 5% GA, (2) 3% PVA 2% CNTs 3% GA, (3) 3% PVA 1% CNTs 5% GA, (4) 3% PVA 1% CNTs 3% GA.
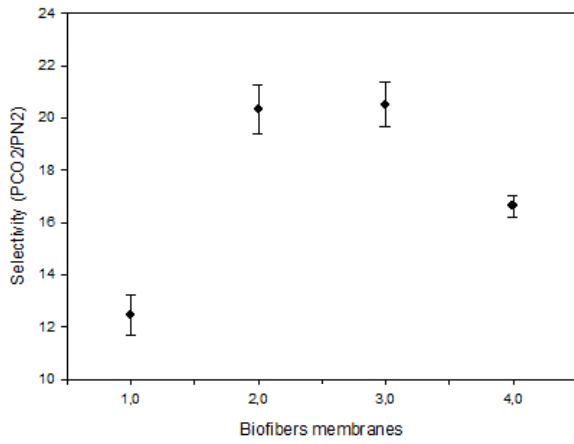
TiO$_2$

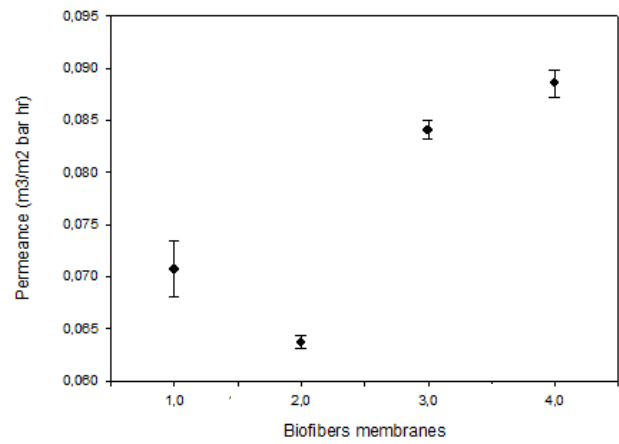(a)   (b)

Appendix A.4: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on TiO$_2$ loading and glutaraldehyde concentration under P= 1.2 bar. (1) 3% PVA 2% TiO$_2$ 5% GA, (2) 3% PVA 2% TiO$_2$ 3% GA, (3) 3% PVA 1% TiO$_2$ 5% GA, (4) 3% PVA 1% CNTs 3% GA.

(a)   (b)

Appendix A.5: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on TiO$_2$ loading and glutaraldehyde concentration under P= 3 bars. P= 1.2 bar. (1) 3% PVA 2% TiO$_2$ 5% GA, (2) 3% PVA 2% TiO$_2$ 3% GA, (3) 3% PVA 1% TiO$_2$ 5% GA, (4) 3% PVA 1% CNTs 3% GA.

Biofibers

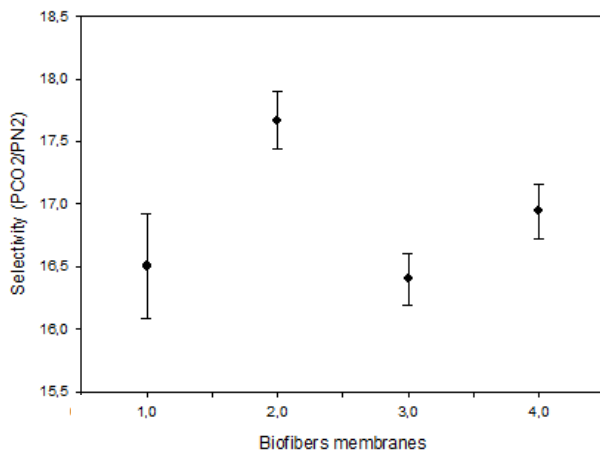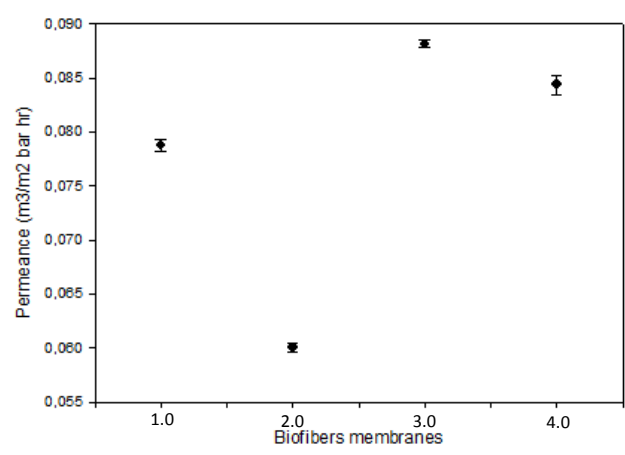|	
(a)	(b)

Appendix A.6: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on Biofibers loading and glutaraldehyde concentration under P= 1.2 bar. (1) 3% PVA 2% Biofibers 5% GA, (2) 3% PVA 2% Biofibers 3% GA, (3) 3% PVA 1% Biofibers 5% GA, (4) 3% PVA 1% Biofibers 3% GA.

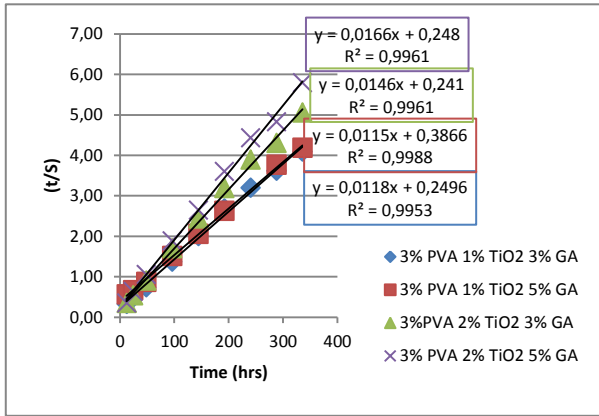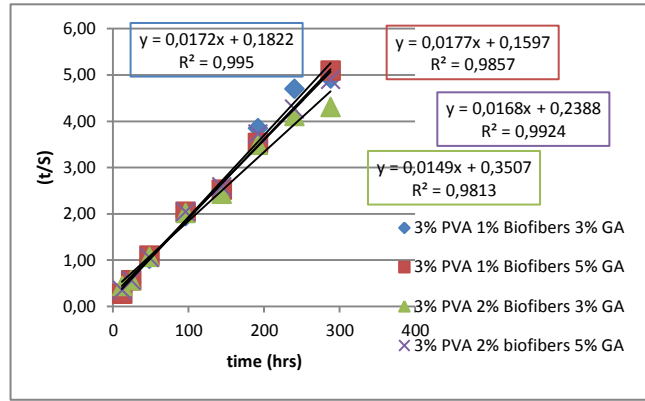|	
(a)	(b)

Appendix A.7: Selectivity evolution with deviation (a) and permeance evolution with deviation (b) depending on Biofibers loading and glutaraldehyde concentration under P= 3 bars. (1) 3% PVA 2% Biofibers 5% GA, (2) 3% PVA 2% Biofibers 3% GA, (3) 3% PVA 1% Biofibers 5% GA, (4) 3% PVA 1% Biofibers 3% GA.

Swelling tests results

(a)   (b)

Appendix A.8: Time/ swelling degree as a function of time for TiO2 membranes (a) and Biofibers membranes (b)

Appendix A.9: Swelling tests results

Time (hrs.)	12	24	48	96	144	192	240	288
1% TiO₂ 3% GA	38.03	41.73	65.76	70.28	72.13	71.83	75.21	79.89
1%TiO₂ 5% GA	21.60	36.32	55.68	63.89	70.14	73.23	77.93	76.64
2%TiO₂ 3% GA	35.16	45.22	53.64	56.77	59.20	60.36	61.82	67.07
2%TiO₂ 5% GA	34.74	38.37	45.84	51.07	54.64	53.44	54.23	59.78
1CNT5% 3% GA	29.31	36.14	42.81	46.34	61.22	53.31	53.05	54.66
1%CNT5,5% GA	21.11	30.50	32.50	36.04	49.07	38.60	38.44	42.96
2%CNT5,3% GA	32.38	32.76	41.21	45.14	54.45	44.67	49.89	52.35
2%CNT5,5% GA	30.53	33.88	39.39	43.13	52.29	447.05	42.03	49.67
1%Biofibers,3% GA	36.53	46.09	47.09	49.54	57.59	49.96	51.16	58.63
1%Biofibers,5% GA	45.16	43.27	44.11	47.11	57.24	54.50	147.92	56.59
2%Biofibers,5% GA	35.25	43.19	45.87	47.05	55.89	51.60	56.34	58.87
2%Biofibers,3% GA	27.66	43.00	45.20	47.77	59.38	55.13	58.42	67.02

Appendix A.10: Risk assessment matrix