Master Thesis

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# Manufacture and Characterization of Composite Membranes by Dip Coating for Gas Separation Applications

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Carried out for the purpose of obtaining the degree of Master of Science

Diplom-Ingenieur

By

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I confirm that going to press of this thesis needs the confirmation of the examination committee.

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In lieu of oath, I declare that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such.

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“Failure is an option here. If things are not failing, you are not innovating enough.”

– Elon Musk

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# Abstract

Separation processes got an important interest in chemical industries to isolate products and recover the reactants. A lot of separation techniques were built but one of the most famous and modern technique was membrane methods of separation, these methods help in reducing the capital investment, the cost of operating and increase the safety of process.

In these days a lot of membrane applications are used in gas separation process. Large scale gas filters have already been employed in industrial sectors in the US and some European countries.

Many of membrane types can be used in gas separation applications such as flat or hollow fibre membranes made of polymer composites. The gas separation performance of the membranes can be improved by coating the membrane with a suitable coating layer.

In this thesis different coating solutions with Pebax® copolymer have been prepared and tested to improve the selectivity in gas separation process.

The coating of polypropylene hollow fibres (PP) with different types of Pebax® copolymer was investigated at different concentration of each polymer and different speeds of coating. The trails were conducted in two modes, automatically (coating machine plant which is built by TU Wien university) and manually by normal dipping of the fibres in the coating solution. The automatically mode had been done only for the 1st type of Pebax® which is Pebax®-1657 and then all the work had been done in the manual mode under different concentrations of three types of Pebax® which are Pebax®-1657, Pebax®-5513, and Pebax®-1074. The coated fibres were analysed by SEM to determine the thickness and the uniformity of the coating layer. Besides, their performance in gas permeability and their selectivity was tested and determined by gas permeation (GP) unit which was constructed by Institute of Chemical, Environmental and Bioscience Engineering, TU Wien.

In machine coating the lower take up speed produce the lowest thickness of the coating layer, while the highest thickness had been obtained from the higher take up speed under the same conditions. On the other hand, selectivity of the higher take up-speed has higher values of selectivity than the other lower take up speeds. The results agrees with the trade-off relation between selectivity and permeability.

In manual coating the thickness of the coating layer increase with increasing the concentration of PEBAX®, regardless the specific type of that Pebax®. Pebax®-5513 had the lowest thickness under 3wt.% concentration, while Pebax®-1657 had the highest thickness at the same concentration.

The best result of selectivity has been obtained from PP fibres coated with 6wt.% Pebax®-1657, and the next best result of selectivity has been obtained from PP fibres coated with Pebax®-5513 under the same concentration.

As a future recommendation for this work, changing the PP fibres and deal with other less permeable fibres to be the support layer for the coating layer of Pebax® may lead to better results of selectivity under the same conditions of coating. Also, using PDMS polymer in coating as a gutter layer between the fibres support layer and the coating layer of Pebax® will prevent any penetration of the coating solution to the support layer and may lead to a better result. Finally, using the heat treatment for the fibres after coating would be possible to study the effect of oven-drying versus normal drying at room temperature.

# Zusammenfassung

Trennverfahren sind in der chemischen Industrie von großem Interesse, um Produkte zu isolieren und die Reaktanten zurückzugewinnen. Es wurden viele Trenntechniken entwickelt, aber eine der bekanntesten und modernsten Techniken war die Membran Trennung. Diese Methoden helfen bei der Reduzierung der Kapitalinvestitionen, der Betriebskosten und erhöhen die Sicherheit des Prozesses. Heutzutage werden viele Membrananwendungen in der Gastrennung eingesetzt. In den USA und einigen europäischen Ländern werden Gasfilter bereits in großem Maßstab in der Industrie eingesetzt.

Für die Gastrennung können viele verschiedene Membrantypen verwendet werden, wie z. B. Flach- oder Hohlfasermembranen aus Polymerverbundwerkstoffen. Die Gastrennleistung der Membranen kann durch Beschichtung der Membran mit einer geeigneten Beschichtung verbessert werden. In dieser Arbeit wurden verschiedene Beschichtungslösungen mit Pebax®-Copolymeren hergestellt und getestet, um die Selektivität im Gastrennverfahren zu verbessern.

Die Beschichtung von Polypropylen-Hohlfasern (PP) mit verschiedenen Arten von Pebax® Copolymeren wurde bei unterschiedlichen Konzentrationen der einzelnen Polymere und unterschiedlichen Beschichtungsgeschwindigkeiten untersucht. Die Versuche wurden in zwei Modi durchgeführt, automatisch (Beschichtungsanlage, die von der TU Wien gebaut wurde) und manuell durch normales Eintauchen der Fasern in die Beschichtungslösung. Der automatische Modus wurde nur für den ersten Pebax®, Pebax®-1657, durchgeführt, während die gesamte Arbeit im manuellen Modus mit verschiedenen Konzentrationen von drei Pebax®, Pebax®-1657, Pebax®-5513 und Pebax®-1074, durchgeführt wurde. Die beschichteten Fasern wurden im REM untersucht, um die Dicke und die Gleichmäßigkeit der Beschichtung zu bestimmen. Außerdem wurde ihre Gasdurchlässigkeit und ihre Selektivität mit einer Gas Permeationsanlage (GP), die vom Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften der TU Wien gebaut wurde, getestet und bestimmt.

Bei der maschinellen Beschichtung führte die niedrigere Aufnahmegeschwindigkeit zu der geringsten Schichtdicke, während die höchste Schichtdicke unter den gleichen Bedingungen mit der höheren Aufnahmegeschwindigkeit erzielt wurde. Andererseits hat die höhere Aufwickelgeschwindigkeit höhere Selektivitätswerte als die niedrigeren Aufwickelgeschwindigkeiten. Die Ergebnisse stimmen mit der Trade-off-Beziehung zwischen Selektivität und Permeabilität überein. Bei der Handbeschichtung nimmt die Dicke der Beschichtungsschicht mit zunehmender Pebax®-Konzentration zu, unabhängig vom jeweiligen Pebax®. Pebax®-5513 wies bei einer Konzentration von 3m% die geringste Schichtdicke auf, während Pebax®-1657 bei der gleichen Konzentration die höchste Schichtdicke aufwies.

Das beste Selektivitätsergebnis wurde mit PP-Fasern erzielt, die mit 6m% Pebax®-1657 beschichtet waren, und das nächstbeste Selektivitätsergebnis wurde mit PP-Fasern erzielt, die mit Pebax®-5513 in derselben Konzentration beschichtet waren.

Als zukünftige Empfehlung für diese Arbeit könnte ein Wechsel der PP-Fasern und die Verwendung anderer, weniger durchlässiger Fasern als Trägerschicht für die Pebax®-Beschichtung zu besseren Selektivitätsergebnissen unter den gleichen Beschichtungsbedingungen führen. Auch die Verwendung von PDMS-Polymer bei der Beschichtung als Rinnenschicht zwischen der Faserstützschicht und der Beschichtungsschicht aus Pebax® verhindert das Eindringen der Beschichtungslösung in die Stützschicht und kann zu einem besseren Ergebnis führen. Schließlich könnte durch eine Wärmebehandlung der Fasern nach der Beschichtung die Wirkung der Ofentrocknung und der normalen Trocknung bei Raumtemperatur untersucht werden.

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# 1.Introduction

## 1.1 Overview of membrane science and technology

Membranes have a very important place in our daily life, as indicated by Richard Bowen, 'If you are tired of membranes, you are tired of life'. In the last 100 years, the membranes synthesis and their practical applications had been started.

Biological membranes in human body, plants and animals are doing a very complex processes especially in transportation like mass, energy, food, and water transport. They also can transport certain chemical components selectively with a specific concentration. As a comparison between biological membranes and synthetic membranes, biological membranes are very thin in range of several manometers, and they work under a special mechanism called active transport, which mean the transportation process happened without needing for any external force, while synthetic membranes are much thicker in range of several micrometres and the transport process need an external driving force to happen [1].

Although the synthetic membranes are not efficient as biological membranes, but they are playing a very big role in our life due to the large number of their practical applications such like produce potable water from the sea, isolation of products and recovery of reactants, clean industrial effluents and recover valuable constituents, concentrate, fractionate macromolecular mixtures in food and drug industries, and to separate gases and vapors. Synthesis membranes also are very important components in systems work in energy conversion. Also, they are using in artificial organs and drug delivery systems.

Membranes used in different applications are vary in their shape, structure, their synthesis process, and their function. Therefore, it is not easy to get a complete overview of synthesis membranes and their applications. As Separation of binary gas mixtures are very important in companies, factories, and laboratories to reuse the good gases and control the pollution, now synthesis membranes are increasingly used in gas separation application, they have already used in industrial regions in the world.

Membrane technology in gas separation compete other techniques used in gas separation, and it becomes the most important technique because it could reduce the capital investment and the cost of operating. Also, membrane technology increase the process safety and have a multidimensional character, which give it many advantages over the others techniques. Advantages can summarised as the following: rapid mass transfer rate, high selectivity towards a specific gas, simplicity of operation and installation, feasibility under mild conditions, smaller footprint and flexibility of operation due to compactness of modules with huge reduction in consumption of electricity and fuel, no extra agents are required as compared to corrosive and polluting amine solvents in absorption process, continuous mode of operation with partial or complete recycle of retentate-permeate, membranes can be adjusted to adapt a specific separation target, possibility of integration with other separation units for achieving improved economy and desired purity levels [2].

In this thesis, the focus will be on $CO_2$ and $N_2$ gas separation application, manufacture, and characterization of composite membranes by dip coating of polypropylene hollow fibres with different types of a commercial polymer called Pebax for $CO_2$ and $N_2$ gas separation applications.

## *1.2 Milestones and previous studies in membrane gas separation technology*

Membrane technology in gas separation has been under growing interest in the last years. The first base for that technology was Graham's law of diffusion which had been proposed in 1850 [2]. The following figure illustrates the background and milestones in membrane gas Separation since 1850 – 2010.

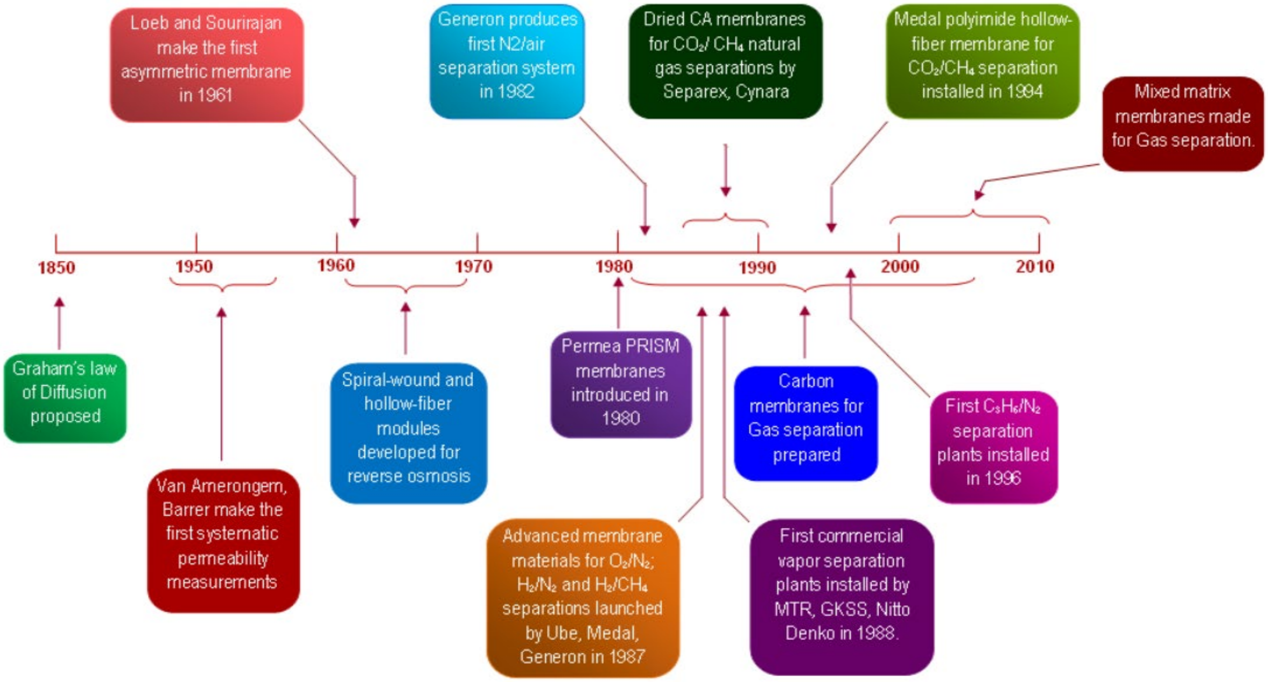


**Figure 1: Background and milestones in membrane gas Separation (1850 – 2010) [2].**

In 1979−1980, Monsanto was built the first successful industrial membrane gas separation, they were built to separate hydrogen gas from nitrogen, argon, and methane in ammonia. Then within a few years, Monsanto had installed many membrane separation systems around the world [3].

Since 1980s, membranes of gas separation have applied to many different processes, especially to separate nitrogen gas from air, and carbon dioxide gas from natural gas, and hydrogen from refinery and petrochemical process streams [3],[4].

Various studies have been conducted to deal about $CO_2$ separation using membranes made of polymers or coated with polymers. One of the most interesting polymers which used in $CO_2$ separation is Poly(ether-block-amide) copolymer known as "Pebax®" copolymers due to their rare chemical composition which contains glassy polyamide segment and rubbery PEO segment in different proportions depending on the commercial grade, more details about Pebax® copolymers will be discussed in the following sections of this thesis (section 2.6.3.1). Other researchers (Ahmadpour, Shamsabadi) investigated $CO_2$ separation with PVC/Pebax composite membrane in their study, poly (amide-6-b-ethylene oxide) (Pebax® MH 1657) copolymer was used as a selective layer to prepare PVC/Pebax® composite membrane for $CO_2$ capturing [4]. Also (Szwast, Makaruk, Harasek), investigated Pebax®-1074 copolymer on flat membranes and composite capillary membranes both made of copolymer Pebax®-1074 and their separation properties have been investigated [5].

## 1.3 Motivation and problem statement

Recently, Pebax® block copolymers have been the most interesting material for $CO_2$ separation membranes, because these polymers give a relatively high $CO_2$ permselectivity in $CO_2$/nonpolar gas separations such like $CO_2/N_2$ or $CO_2/CH_4$ separation. As mentioned before Pebax® copolymer had two segments soft and hard, the soft segment (polar polyether block) has a strong affinity to $CO_2$ due to dipole−quadrupole interaction, while the hard segment give a good mechanical strength to the material. Compared to $N_2$ Kinetic diameter (0.364 nm) and $CH_4$ kinetic diameter (0.38 nm), $CO_2$ has the smallest kinetic diameter (0.33 nm) [6]. Various parameters such as chemical structure, thickness, crystallinity, and thermal stability of Pebax® were investigated on the membrane performance [7]. In addition, many published studies have an aim to improve the properties of Pebax® copolymers for gas separation [7],[8], membranes based on chemically modified, cross-linked polymers, and composite membranes with organic or inorganic fillers are the outcomes of these studies [9].

The search for better membrane materials has got a big interest in many research groups. Currently all the used commercial membranes are polymeric membranes and separate gas mixtures by the solution diffusion mechanism.

## 1.4 Aim of work

As mentioned before, membranes made of Pebax® copolymer have very interesting separation properties for $CO_2$ and their applications will certainly increase due to its special chemical structure which contains soft and hard segments give the membrane high affinity to permeate $CO_2$ and a good mechanical strength.

This was one of the driving forces to investigate more about Pebax® copolymer and coating. This study aims to conduct an experimental investigation into the effect of coating the PP hollow fibre membrane with various types of Pebax® copolymer at different conditions (like changing the speed of coating, thickness of coating layer, and concentration of Pebax® in the coating solution) and then see the membrane performance in $CO_2/N_2$ separation.

To accomplish this, machine coating plant which had built in TU Wien was used to study the effect of different coating speeds with the same type of Pebax® and same concentration on the thickness of the obtained coating layer and the membrane performance in $CO_2/N_2$ separation. After finished with the machine coating the works of this thesis transferred to manual dip coating to study the effect of different types of Pebax® (Pebax®-1657, Pebax®-5513, Pebax®-1074) and different concentrations at a same coating speed on the thickness of the obtained coating layer and the membrane performance in $CO_2/N_2$ separation.

The thesis is divided into seven chapters, each covering a basic topic: Chapter 1 is an introduction to the field and gives some definitions and the historical development. Chapter 2 is a survey of Basics of membrane-based gas separation process. Chapter 3 gives an overview of experimental equipments and work procedure. Most of the coating process were done by dip coating and this technique will be described in detail. Chapter 4 is for results and discussion; it shows all kind of characterisation techniques. Chapter 5 summarise and conclude the whole work of the thesis and talks about the main final results. Chapter 6 illustrates the abbreviations and symbols had been mentioned in the thesis. Finally, in chapter 7 all references and citations had been used in this work are mentioned.

# 2.Basics of membrane-based gas separation process

## *2.1 Biological membranes*

Membranes can be made of many solid materials and also liquids. Membranes of living cells (biological membranes) are liquid in nature. They are composed of bilayers of phospholipids, which are amphiphilic with hydrophilic head group (conjugating group pointing towards inside and outside of the cell, while their lipophilic parts constitute the inner part of the double layer. Transport of molecules and ions occurs through specific proteins embedded in the bilayer [10]. Figure2 shows schematically a biological membrane, biological membranes are much more functional than any artificial membrane.

Biological membranes which separate the cell from its surrounding and controls the exchange of mass energy and electrical charges in a particular way are extremely. Also, biological membranes separate the cell from the surrounding. These membranes have very thin and small thickness, the thickness of the entire membrane is about relatively 10 nm thick, and they are permeable to relatively very small molecules, these molecules are soluble in a hydrophilic as well as and in a hydrophobic environment such parts like some certain gases. They are capable of so-transport via a mechanism called active transport, mechanism, it means that the transport usually occur without any external driving force. On the other hand the synthetic membranes are much thicker than the biological membranes, the thickness of the synthesis membranes is in the range of several micrometres, and the transport is the result always there is a need to an external driving force to make the transportation [11].

Although the simplicity of synthetic membranes in functions and structures comparing to biological membranes, they are main tools in a lot of technical and commercial process on industry. Many of uses of synthetic membranes on a large scale had been invited, like get a potable water from the ocean and sea, clean industrial pollution, concentrate macromolecules mixtures, and in the separation of gases and vapours.

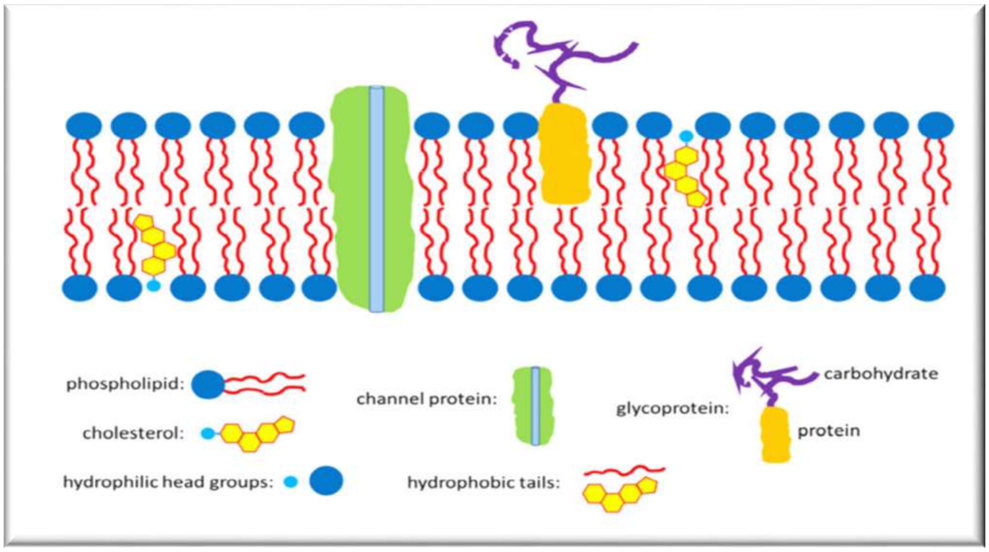


**Figure 2: Cell membrane composed of phospholipid bilayer, cholesterol, , glycolipids, and glycoproteins [10].**

## *2.2 Types of membranes*

Many factors can separate membranes into categories such like the membrane nature, geometry, structure, or transport process through the membrane.

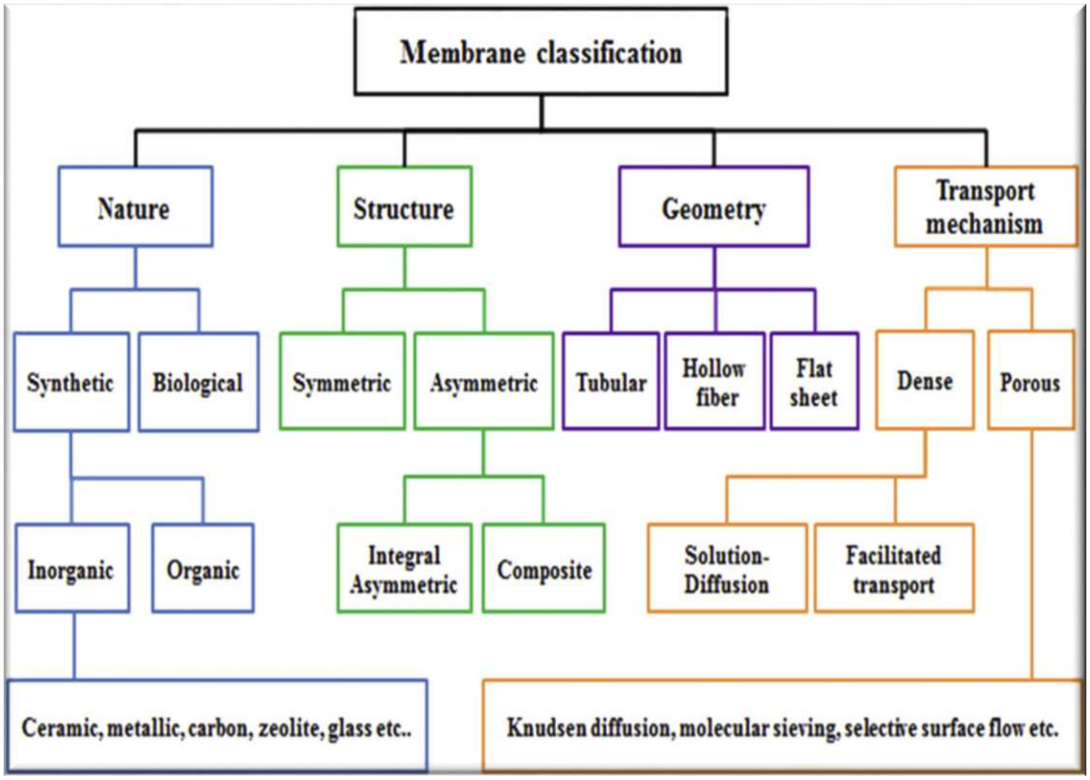


**Figure 3: Membranes Classification based on their nature, internal structure, geometry, and transport mechanism [12].**

As clarified in figure 3, membranes can be classified into biological membranes, (mentioned at the beginning of this thesis in detail) And synthetic membranes. Two types of synthetic membranes are existed, solid and liquid membranes. For synthetic solid membranes, organic or inorganic materials can be used to build them [12].

Most number of synthetic membranes are solid membranes and can be built of many materials like polymers, metals, ceramics, or mix of them. Polymer membranes got huge interest in this time as there are a lot of different types of polymers one can choose from, they are not expensive to produce, and they are easy to treat mechanically [13]. However, for membrane-based separation techniques under harsh conditions, the only suitable membranes will be the inorganic membranes. Also, sometimes there is a need for an absolute selective transportation in the membrane layer which is not happen in polymer membranes.

There are dense or porous membranes formed  symmetrically, they have all over the cross section the same structure, and there is asymmetric dense or porous membranes, they have a thin selective layer which is strengthened by a porous substructure as shown in Figure 4. The asymmetric membranes can have a thin selective layer help in lowering the resistance for the molecules can enter the membrane.

Hence, these molecules can enter the membrane layer at a higher flow rate. The large porous substructures give the mechanical strength to the membrane. Different way can be used to build asymmetric forms of membranes, it also referred to the type of the used material and in this work we focus on polymers. In thin film composite membranes, one can coat the top of the support layer by a certain polymer and get a thin effective selective layer [10].

Many ways of coating can be done, such like casting a polymer solution on the top of the support layer and then evaporate the solvent. Also, it is possible to add some additives and some fillers particles in the solution, these additives can improve specific properties of the membrane like the stability and electric conductivity. On the other hand, these additives may also affect the permeability and selectivity properties of the membrane [14].

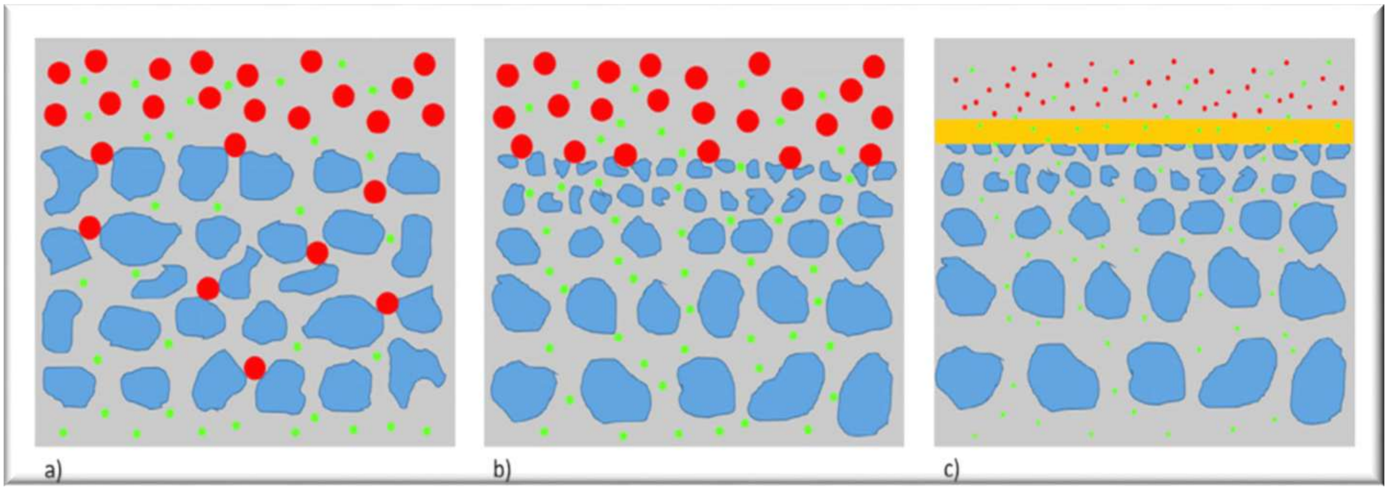


**Figure 4: Cross sections of different membranes. (a) Symmetric porous, (b) Asymmetric porous, and (c) Thin film composite membrane [10].**

In figure 4, one can see that the three membranes (a), (b), and (c) are allowing the green particles to pass so they are selective for the green particles. In (a) and (b), the size of the green particles allow them to pass as they are small. For the red particles in (a) they are blocked in so-called depth filtration which means that the particles can be stopped and not permeate to the end in a somewhere within the membrane because of the general homogeneous distribution in size, where in (b) the red particles are blocked at the surface of the membrane in which called a surface or screen filtration. In (c) the green molecules have been absorbed by the polymer after it pass and diffuse within the yellow dense selective layer, but for the red molecules they are not passed even that they are equal in size with the green ones because they are incompatible with the yellow dense selective layer.

The good values of selectivity referred to the membrane structure especially the selective layer, it may decrease or increase the selectivity. Also, one should know that the selective layer may also allow some red molecules to pass through it, which means that it could be just less compatible with red molecules compared to the green ones and this is the concept of Pebax®-Copolymer coating layer which had been investigated in this work.

### *2.3 Characteristics of membrane separation process*

Membranes are thin permeable and selective layers that control the permeability of chemical molecules come in touch with it, as represented in figure 5.

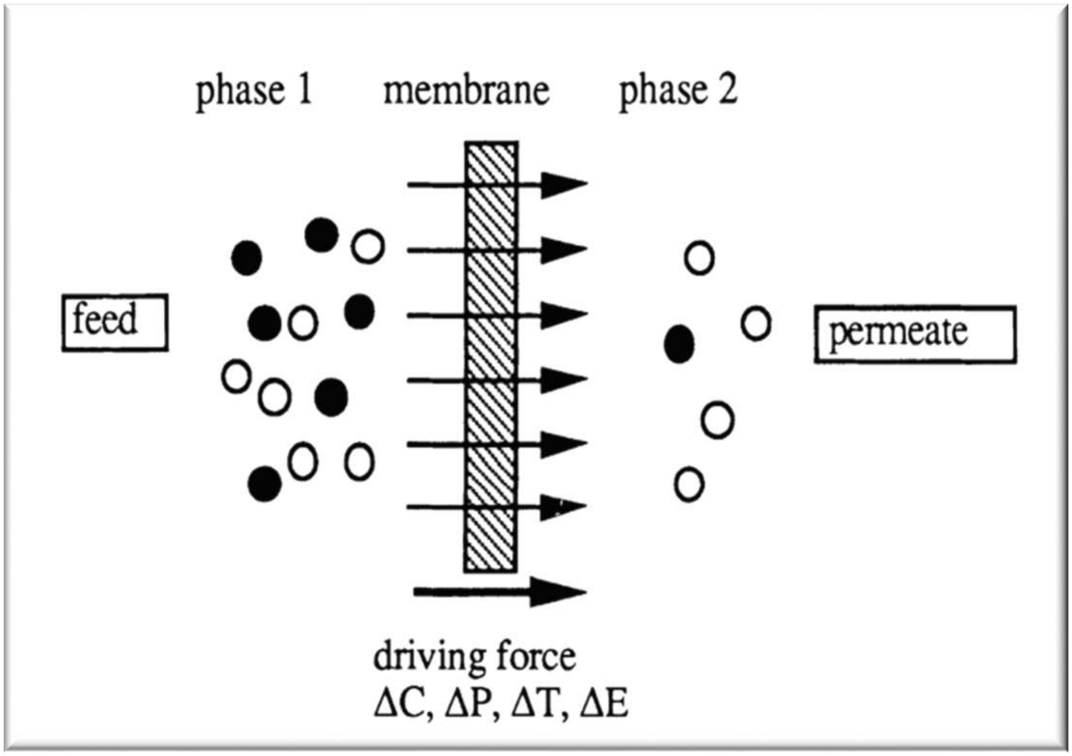


**Figure 5: Selective permeation of penetrants through a membrane [30].**

Many membrane separation technologies in this time are used in different applications in the industry world, such like pervaporation (PV), gas permeation (GP), membrane extraction, membrane absorption, and electrodialysis.

Each membrane separation process is connected to a specific separation. The main idea of separation is that the produced membrane has the ability to allow one particle to pass through it faster than other due to the differences between the membrane and particles contact the membrane in chemical properties, physical properties. or both of them [15].

The membrane transportation concept is that there is a driving force act on a specific component in the feed components, the driven force could be a concentration(ΔC), pressure(ΔP), electric potential gradient (ΔE) or temperature(ΔT) across the membrane. It is possible in some membranes to have more than one of driving force, in this case the total driving force is described by the chemical potential (μ). When the membrane allowing one component from the feed components to pass more faster than the other components then separation is achieved [16].

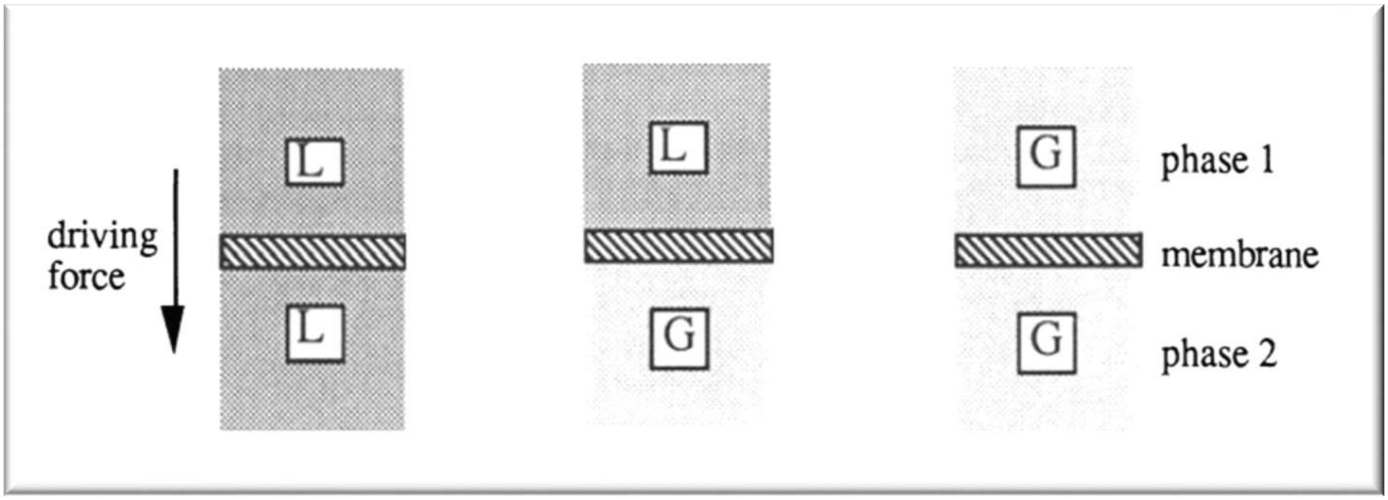


Figure 6: Schematic representation of phases divided by a membrane [16].

The structure of the membrane and the materials of it is also main factors beside the driving force that determining the flow rate and the selectivity. Thus, the membranes nature specify the application type, starting from the separation of microscopic particles to separation of an identical shape or size molecules.

When the diameter is larger than 100 nm of the particles, the particles should be retained, but one can use an open membrane structure. These membranes have a very low hydrodynamic resistance hence low hydrostatic pressure (small driving force) which are suitable to get high flow rates [17].

**Table 1. Some membrane processes and driving forces L,Liquid_G,Gas.**

| Membrane process | Phase 1 | Phase 2 | Driving force |
|---|---|---|---|
| Microfiltration | L | L | ΔP |
| Ultrafiltration | L | L | ΔP |
| Hyperfiltration | L | L | ΔP |
| Piezodialysis | L | L | ΔP |
| Gas separation | G | G | ΔP |
| Electrodialysis | L | L | ΔE |
| Pervaporation | L | G | ΔP |
| Osmosis | L | L | ΔC |

Lastly, based on the application of the membranes, membranes can be classified, two generations processes are there in the membrane separation, the early generation was handled many of separation processes like ultrafiltration, nanofiltration, microfiltration, electrodialysis and reverse osmosis. The next generation ($2^{nd}$ generation) many new separation processes have been obtained such as pervaporation, membrane distillation and gas separation. Gas separation was well established from (Mulder, 1991) [16]. Gas Separation which is relevant to the present study, is the focus of my thesis and it will be discussed in more details in the following sections.

## *2.4 Principle of gas separation and permeation*

### 2.4.1 Gas separation

Gas separation is a very popular industrial process in a lot of applications. Gas separation processes like absorption, pressure swing adsorption, and cryogenic distillation, need large amounts of energy and they are cost a lot to create and work. However, an alternative to these processes which consume a less energy, reduce the cost, simpler in work and operation and give a huge versatility in use is the membrane gas separation processes [3].

Organic or inorganic materials can create the gas separation membranes. However, because the solubility of gases are low in the inorganic materials and through liquid membranes there is a low gas diffusivity, then the major gas separation membranes are built from polymers [18]. Polymers can also be adjusted for a specific application.

It should be mentioned that gas separation membrane is much more sensitive to some defect factors, like holes in the layer which is suppose as the selective layer than other processes of separation.

Table 2 illustrates the main industrial applications of membrane gas separation and common membrane materials used are summarized.

**Table 2. Main industrial applications for membrane gas separation.**

| Separation | Process | Membrane materials |
|---|---|---|
| $H_2/N_2$ | Ammonia purge gas | Polysulfone, Polyaramids |
| $H_2/CO_2$ | Syngas ratio adjustment | Polyimide |
| $H_2$/hydrocarbons | Hydrogen recovery in refineries | Cellulous acetate |
| $O_2/N_2$ | Nitrogen generation, oxygen enriched air | Polyimide |
| $CO_2$/hydrocarbons ($CH_4$) | Natural gas sweetening, landfill gas upgrading | Nafion –Ethylenediamine (EDAH) |
| $H_2O$/hydrocarbons ($CH_4$) | Natural gas dehydration | Cactus membrane air dryer (Permea) |
| $He/N_2$ | Helium recovery | Polyimide |
| $H_2O$/air | Air dehumidification | Cactus membrane air dryer (Permea) |

A review of the main gas separation applications can be found in references [18] and [19].

### 2.4.2 Gas permeation

Partial pressure gradient (ΔP) is the driving force in gas separation processes, and it is yield from the product of mole friction and total pressure. Dense membranes are the major type of membranes that used for gas separation (non-porous) [2].

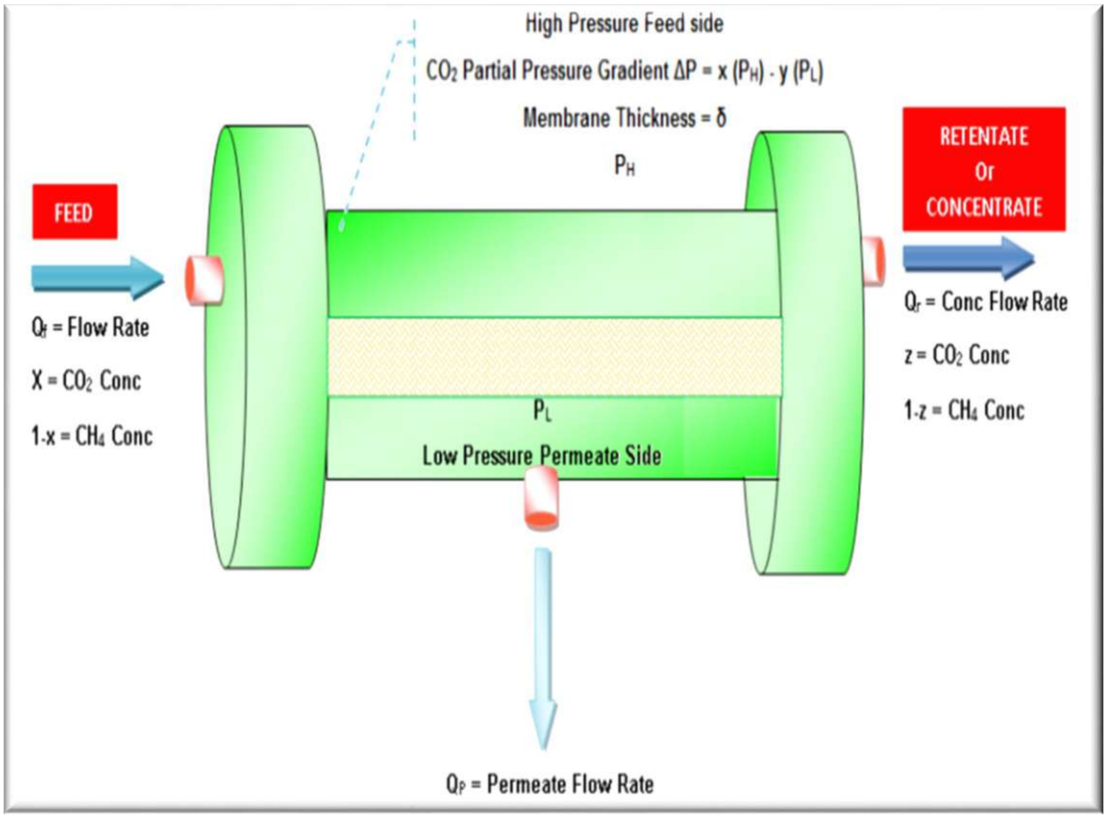


**Figure 7:Principle of Gas Permeation and Separation [2].**

The morphology of the membrane determine the permeation of gases through it, it is based on the mechanism of transportation. The pore size of a Porous membranes built from polymer is ranging from 0.5 to 10 µm, while in the non-porous ones the chain gap of the polymer is ranging 10.3 to 10.4 µm driven by thermal variation [20].

Figure 8 bellow illustrates two known mechanisms of the permeation process, which are the pore flow model on the left of the figure, and the solution-diffusion model which based on Fick's Law on the right of the figure [2]. There is a main difference between them, the solution-diffusion model produces thermally induced movement of the polymer chain which lead to random pores with different sizes to close and open and the feed molecules diffuse and jump from pore to another to pass the membrane, while pore flow model take as a permanent pore any size free-volume elements which is in the membrane [21].

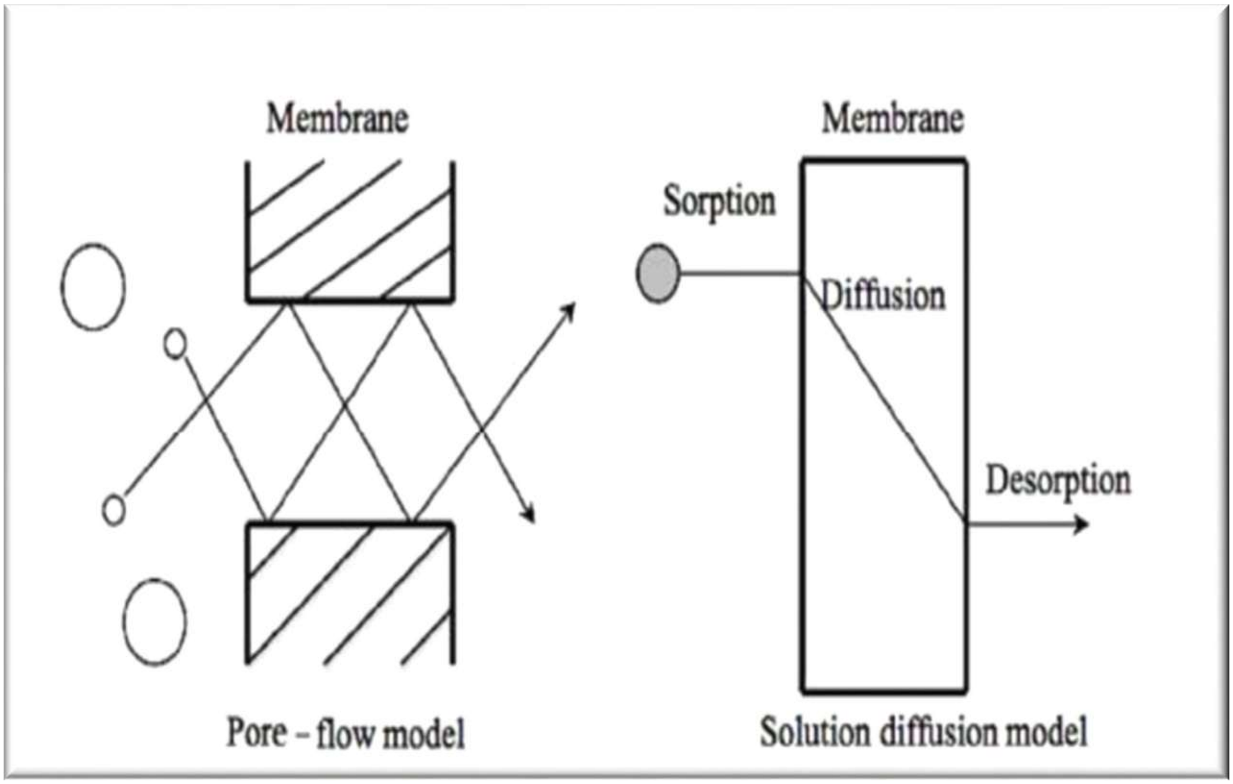


**Figure 8: Two main types of mass transport through porous and dense membranes [16].**

## *2.5 Mass transport mechanisms*

### 2.5.1 Transport through porous membranes

The pore flow model in general is classified to three groups: convective flow, Knudsen diffusion, and molecular sieving.

#### *2.5.1.1 Convective flow model*

In this model the transport mechanism occurs due to convective flow when the molecules are much smaller than the pores [2].

#### *2.5.1.2 Knudsen's diffusion model*

When the mean free path of the gases are larger than the pore sizes of the membrane, the transport may occur by Knudsen's diffusion mechanism. Figure 9-a illustrates the Knudsen's diffusion mechanism and shows how the gases transport through the porous membrane. Pore walls in the membrane interact with the molecules of gas much more than colliding each other, this lead the lighter molecules to diffuse and pass through the pores in a good way [20].

### *2.5.1.3 Molecular sieving model*

Figure 9-b illustrates the molecular sieving mechanism, simply when the molecules are enough smaller than the pore size, the larger molecules will be excluded [2].

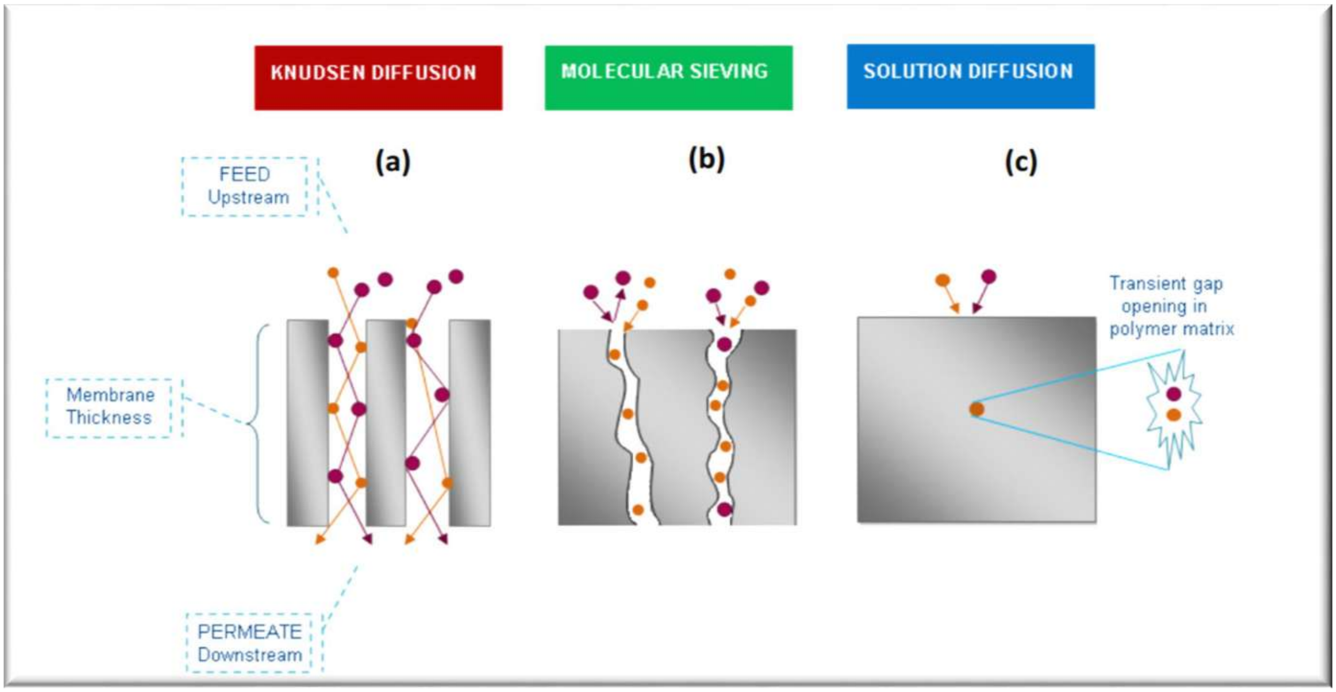


**Figure 9: Mechanisms of Gas Permeation : (a) Knudsen's Diffusion, (b) Molecular Sieving, (c) Solution-Diffusion [2].**

## 2.5.2 Transport through dense membranes

In nonporous polymeric membranes, solution-diffusion mechanism (figure 9-c) describes the transport of gases through the membrane. Until 1940s the popular model was the pore-flow model because of its closing to the physical experience [22]. However, the pore-flow model broke down at the pore diameter below 5m, thus it became insufficient and unattractive for pervaporation and gas separation [22]. Therefore, the separations through dense (nonporous) polymer membranes which are the basic to all current gas separation membranes are described by the solution-diffusion model [19].

### *2.5.2.1 Solution-diffusion model*

The solution-diffusion model in general follow a three-step process, start with dissolution and adsorption at the feed interface of the membrane, then the penetrant diffuse through the polymer matrix, and finally into the other side of the membrane the desorption occur.

To define the solution-diffusion model basically two main assumptions are needed. The 1st assumption is that the membrane material which is at the interface is at equilibrium with the fluids in contact, thus the sorption and desorption rates are faster than the diffusion rate because the gradient across the membrane of the chemical potential is continuous. The 2nd assumption is that across the membrane the potential gradient is presented as the gradient of the penetrant concentration, because within the membrane the pressure is uniform, figure 10 give a detailed overview of solution-diffusion model [22].

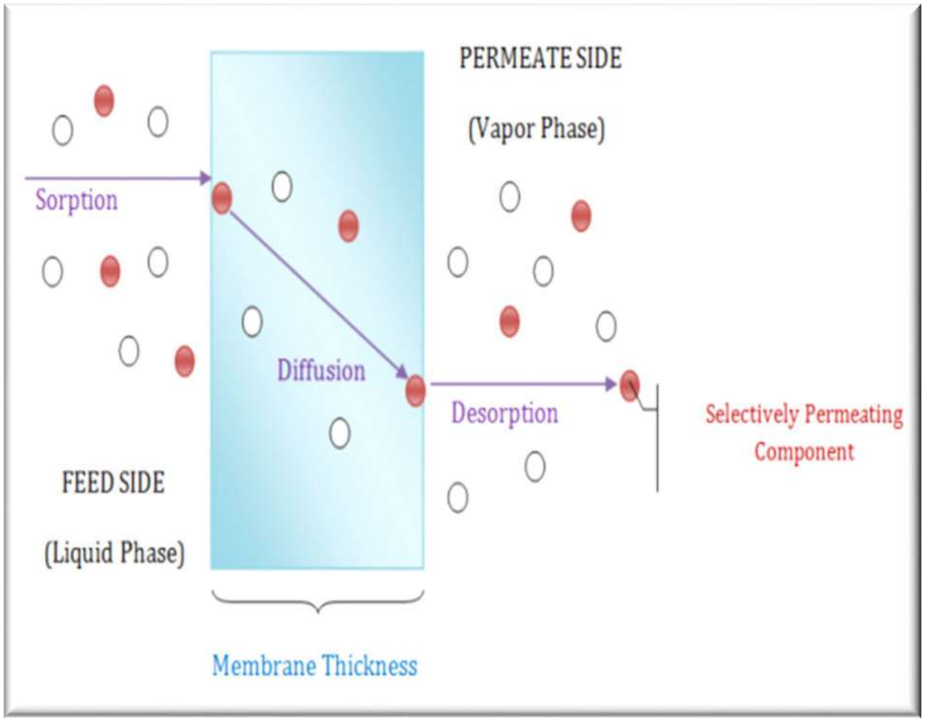


Figure 10: Detailed Overview of Mass Transfer by Solution-Diffusion [2].

In solution-diffusion model at the maximum value the pressure is constant, which means that the pressure which transmit across the membrane is same as incompressible liquids. Thus, the difference of the chemical potential can be represented only by the gradient of concentration [19].

During the steps of the solution-diffusion model, the diffusion rate is the slowest rate. The equation that connect the permeation flux (J) with the gradient of concentration is as the following equation (2.1):

$$J = -D\frac{dC}{dX} \qquad (2.1)$$

knowing that the penetrant diffusion coefficient is the *D* symbol in the equation. The Permeation process has a quantitative measurement coefficient called the permeability coefficient, and the derivation of this coefficient can be found in Wijmans and Baker [22].

The permeability coefficient(P), through a film of thickness(l) is defined as:

$$Permeability\ (P) = \frac{J}{\Delta p/l} = \frac{J}{(p2-p1)/l} \qquad (2.2)$$

Knowing that the steady state flux is J symbol in the equation, the feed pressure is p2 and the permeate pressure is p1. Gas permeation rate had been measured in a first scientific method by Richard Barrer, and related to his name, the common unit for gas permeability coefficient called Barrer. Such permeability may include a resistance of transport on the feed side and permeate side of the membrane. At a given rate of flow there is a need for a high flux to make the productivity of the process increase and the area of the membrane decrease trying to reduce the capital cost of the system. Alternatively, to determine the permeation capability of a membrane without normalizing the thickness of it the permeance (Q) can be used [23].

$$Permeance\ (Q) = \frac{J}{\Delta p} \qquad (2.3)$$

Diffusivity coefficient (D) multiplied by solubility coefficient (S) are resulting the permeability coefficient (P).

$$P = D\,.\,S \qquad (2.4)$$

Now to determine the preference of a membrane for a certain species enter the feed side of the membrane over another species, the ideal selectivity ($\alpha_{AB}$) is indicating that preference, and a high value for this selectivity are required in order to get a good separation from the membrane. For components A and B in a feed mixture, a diffusivity selectivity ($D_A/D_B$) and a solubility selectivity ($S_A/S_B$) are indicating the ideal selectivity also [24].

The following equation (2.5) shows how to calculate the overall selectivity:

$$\alpha AB = \frac{PA}{PB} = \left(\frac{DA}{DB}\right) = \left(\frac{SA}{SB}\right) \qquad (2.5)$$

Even that the permeability ratio of two species determined the selectivity $\alpha_{AB}$ of that species, there is a trade-off relation between permeability and selectivity, so that when the permeability increase the selectivity decrease and vice versa.

It should be mentioned that there are other factors affecting the goodness of the membrane separation process other than the high selectivity and the high flux, like stability under the temperature variations, mechanical stability, low manufacturing cost, ability of manufacturing reproducibility and to be packaged into modules of high surface area [24].

During pervaporation the membrane undergo swelling or plasticization, so solution-diffusion model is inadequate and there is a need to modify it.

When a large amount of molecules dissolve in the matrix of the polymer membrane, the plasticization occurs, which force the segments of the chain to swell leading to increase (FFV) fractional free volume, increase in segmental motion, which result in decrease of diffusivity selectivity and an increase in the permeability [25]. In the matrix of the membrane the plasticizes are working in the mass transport as a fixed carrier [26]. Therefore, the plasticising concentrations is affecting the diffusion coefficient. More than one of modified models of solution-diffusion mechanism were proposed to develop the concept of mass transport in the membranes, some examples of the most popular ones are: “six-coefficients” model [27], a simplified Brun’s model [28], and total solvent volume fraction model [29].

## *2.6 Preparation of synthetic and composite membranes*

In membranes preparation there are many kinds of synthetic materials can be used. Therefore, the material could be organic material which include polymers with any type or could be inorganic material like metal, ceramic, and glass. The main idea in membrane preparation is to develop the material properties in a way with a certain technique to get a suitable structure and morphology of a membrane which are suitable to do a certain kind of separation. The kind of the selected material specify the techniques of preparation that affect the morphology of the obtained membrane, hence, specify the allowed principle of separation. On the other hand not every problem of separation are back to the material type and not all the problems could be solved with every type of materials [1].

In order to prepare a synthetic membrane, there are many of available techniques, which could be involved to prepare polymeric (organic) membranes and inorganic membranes. Examples of the most common and used techniques are track-etching, stretching, sintering, coating and phase inversion [30].

**Track-etching:-**
Within a membrane the pore geometry in its simple type is a kind of cylindrical with uniform dimension pores which are located parallel to each other. These structures can be achieved using the technique of track-etching. The concept of this technique is that there is a polycarbonate foil which is projected to a perpendicular particle radiation of a very high energy. The radiation’s particles make tracks by break the matrix of the polymer. Then in an alkaline or acid bath the film is submerged so that the material of the polymer is etched along the obtained tracks and give a cylindrical uniform pore with a distribution of a limited size of the pore. The thickness of the available film and the particle’s energy which is applied (normally = 1 Me V), is specify the chosen material. The maximum penetration thickness of particles with this energy have a maximum thickness penetration equal about 20 J/m. the film thickness could be increased by increasing the particle’s energy. The radiation time is defining the porosity, while the etching time is determine the pore diameter [30].

**Stretching:-**
In Stretching technique a film which is built from a polymeric material which crystalline partially such as polyethylene, polytetrafluoroethylene, and polypropylene, is perpendicularly stretched to the extrusion direction, hence the crystalline parts parallelly located to the direction of extrusion. Small cracks is obtained while applying a mechanical stress, then pores is obtained. The membrane’s porosity which obtained from this method is higher than that of the membranes obtained by sintering [30].

**Sintering:-**

Sintering is a simple method that employs organic or non-organic materials to build a porous membrane. The main concept of the method is depending on particles with a certain size The method involves pushing a powder contains these particles and sintering them at increasing degrees of temperatures. The used material determines the needed temperature. The boundary between the particles which are on contact to each other are disappears during the sintering process [30].

**Coating:-**

The fluxes which are obtained from diffusion mechanism in dense membranes are generally low. The coating process can be used to increase that fluxes by the mean of reduce the effective thickness of the membrane as much as possible, this could be obtained by having a composite membrane which have an effective and suitable coating layer that covering these membranes, hence the flux through these membranes will increase [30].

**Phase-Inversion:-**

Phase inversion is the used process to make the majority of the available commercial membranes. It is a very adaptable process which allow to obtain all kind of morphologies [30]. This preparation technique will be described in detail later in this chapter.

Two different materials build the composite membranes, the base material is the sublayer material and upon it is the second material which called the selective layer (see figure-11). The main selectivity is referred to the top thin layer, whereas the base layer (porous sublayer) act as a support layer. Coating mechanism can be done using different procedures like in-situ polymerisation, plasma polymerisation, interfacial polymerisation, and dip coating [30].

More details about these techniques will be clarified later in this chapter. Another procedure of coating technique is available, where the pores of the sublayer had been sealed by the coating layer. In this procedure of coating the properties of the sublayer material are determining the overall membrane properties more than those properties of the coating layer [30].

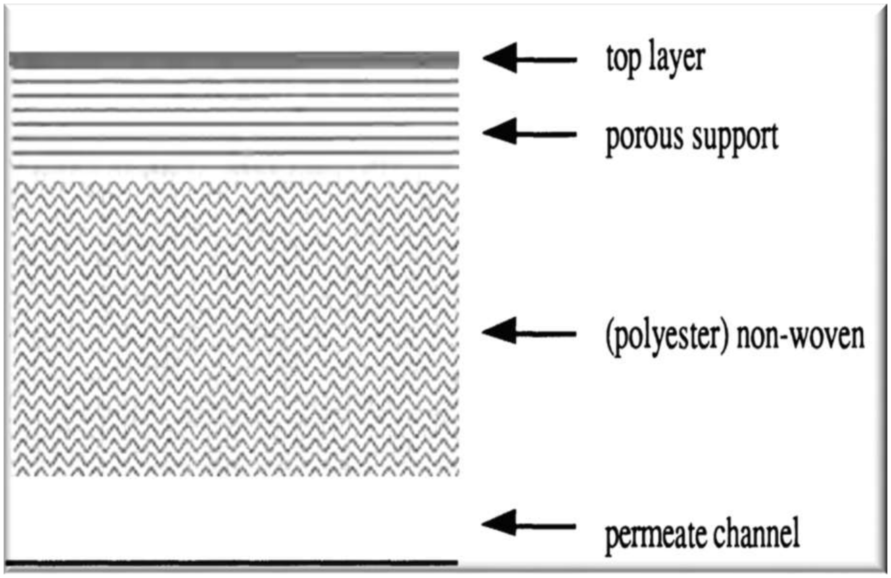


**Figure 11: Schematic drawing of a composite membrane [30].**

Only porous membranes are found when using stretching, sintering, track-etching, and leaching out techniques. In Composite membranes these membranes could use as a sublayer of the membranes, therefore they can be applied in other aspects. Open and dense membranes structures can be obtained from phase inversion techniques. Generally Coating procedures are used to obtain a thin-dense structures, that having a high flux and intrinsic selectivity. Also, by phase inversion, most of the support asymmetric layers of the composite membranes are obtained [30].

### 2.6.1 Membrane spinning-phase inversion

Polymer used in Phase inversion is changed under a controlled way from liquid phase to a solid phase. This process of transition, usually start by the polymer transform from one liquid phase to two liquids (liquid-liquid demixing). Through demixing and at a certain point, the high concentrated of polymer phase will become solid and form a solid matrix. The morphology of the membrane can be utilized by controlling the starting point of phase modification, hence non-porous and porous membranes can be obtained [31].

The phase inversion process includes many several procedures like immersion precipitation, solvent evaporation, precipitation from the vapour phase, thermal precipitation, and precipitation by controlled evaporation. Immersion precipitation is using to make the bulk of the phase inversion membranes [30].

In immersion precipitation Process, a solution which consist of the polymer and the solvent is casting on a specific support and then submerged in coagulation bath which contain non-solvent. Due to the trade of solvent and non-solvent, the precipitation start. The final structure of the obtained membrane results from both phase separation and mass transfer [30].

A lot of polymers could be used in preparing phase inversion membranes. The only need is that the polymer will dissolve in the solvent or a mixture of solvents. Typically, the preparation procedure does not limit by the chosen polymer. Basically, two patterns can obtained for the membranes: flat membrane and tubular membrane [30].

#### *2.6.1.1 Flat membranes*

In spiral-wound and plate-frame systems, flat membranes are used. While in capillary, tubular, and hollow fibre, tubular membranes are used [30].

The process of preparing flat membranes technically is clarified in figure-12. The formulation procedure is as follows. At first in a suitable solvent the polymer is dissolved. The polymer concentration, the solvent type, and the polymer's molecular weight is defined the solution's viscosity [30].

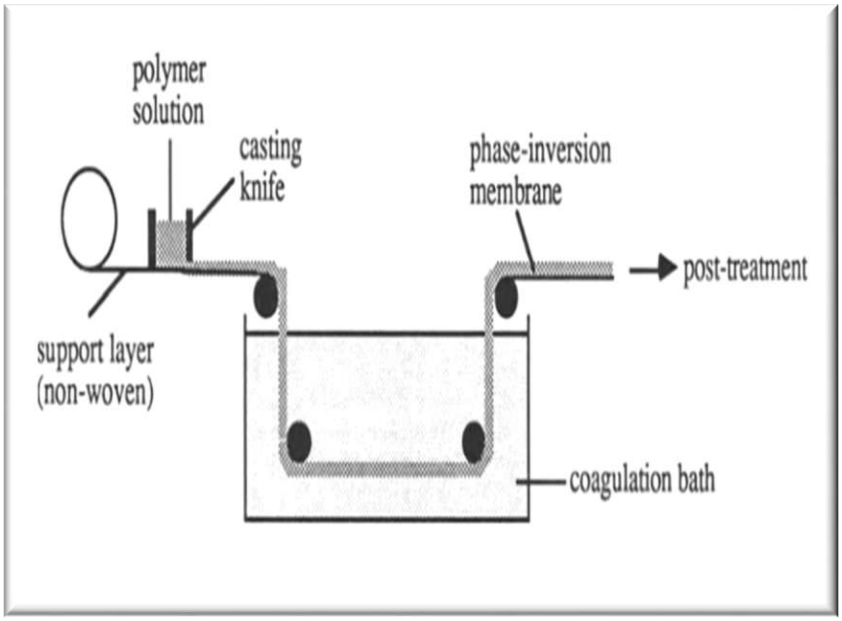


**Figure 12: Schematic drawing depicting the preparation of flat membranes [30].**

In figure 12, directly the casting solution (polymer solution) is casting on a supporting layer by the help of a casting knife. The thickness of  casting is in the range of 50-500 µm. Then in a non-solvent path the film is submerged and exchange between the solvent and non-solvent start and the polymer finally precipitates. As a non-solvent, water is usually the choice, but also there are other non-solvents can be used, hence determining the solvent and non-solvent pair is essential [30].

There is other parameters of preparation can affect the process, such like temperature, humidity, polymer concentration, composition of the casting solution, and evaporation time. These parameters are mostly reliable for the best membrane performing in selectivity and flux, hence for the membrane application [30].

By casting the solution on a metal, a flat membrane can be achieved. After clotting and during wash, one can gather the flat sheet [30].

Because the simplicity of preparing flat membranes, they are very excellent for checking on a laboratory scale. For membrane surface areas which is less than 1000 $cm^2$, the process of casting are done semi-automatically or manually by hand, usually on a flat glass plate or metals. Also, polymers like Polymethylmethacrylate can be used [30].

### *2.6.1.2 Tubular membranes*

The other pattern that the prepared membrane can formed with is the tubular form. According to the dimensions especially the diameter, tubular membranes can be classified to the following types: hollow fibre membranes (diameter: <0.5 mm), capillary membranes (diameter: 0.5-5 mm), and tubular membranes (diameter: > 5 mm) [30].

The size of the tubular membranes is too big to hold up on their own and require support, while hollow fibres and capillaries are strong enough to stand on their own. Three different techniques can be used to make hollow fibres and capillaries: wet spinning, dry spinning, and melt spinning [32].

Despite having similar performance, the methods for producing flat and hollow fibres membranes are distinct. Because hollow fibres are able to support themselves, the size of the fibres is crucial. Additionally, mixing occurs from both the inner bore and outer shell in hollow fibres preparation, while in flat membrane preparation, mixing takes place only from one side. During the production of hollow fibres, spinning parameters also play a significant role in determining the membrane's performance [31]. A schematic drawing of the dry-wet spinning process in shown in figure 13.

Hollow fibre membranes are a preferred choice for membrane modules due to several advantages they offer, such as their self-supporting nature, flexibility, and large surface area. Flat sheet membrane modules, on the other hand, require additional hardware, such as porous supports and spacers, for their use in filtration processes. The self-supporting and flexible properties of hollow fibre membranes simplify the hardware fabrication process during module assembly and operation. There are mainly two forms of hollow fibre membrane modules: cylinder modules and flat-plate modules made up of a bundle of many hollow fibre membranes [32].

A polymer solution composed of a polymer, solvent, and occasionally other components such as a secondary polymer or non-solvent, is forced through a spinneret after being filtered. The polymer solution must have a high viscosity (usually over 100 Poise). The inner tube of the spinneret is used to pump a bore injection fluid. After a brief period in air or a controlled environment (this step is called "drying"), the fibre is immersed in a bath of non-solvent, causing coagulation to occur. The fibre is then wound onto a godet [32].

The crucial spinning parameters include the flow rate of the polymer solution, the rate of the bore fluid, the "tearing rate," the time spent in the air gap, and the size of the spinneret. These parameters affect the formation of the membrane, which is influenced by factors such as the composition of the polymer solution, the composition of the coagulation bath, and its temperature [30]. Figure 14 shows a photograph of a fibre being spun in the air gap.

Figure 15 displays cross-sections of two types of spinnerets. In dry-wet spinning, the size of the spinneret is crucial because it largely determines the fibre’s dimensions. These dimensions become fixed once the fibre is placed in the coagulation bath [30].

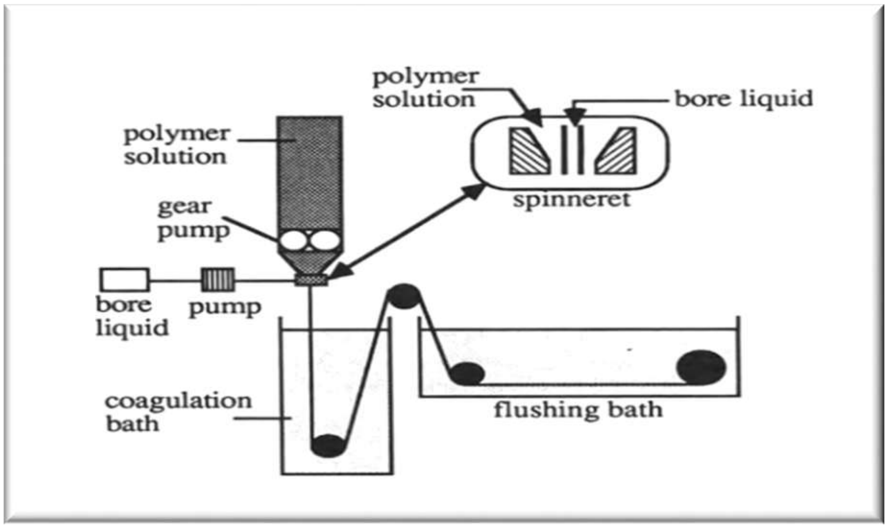


Figure 13: Schematic drawing of a dry-wet spinning process [31].

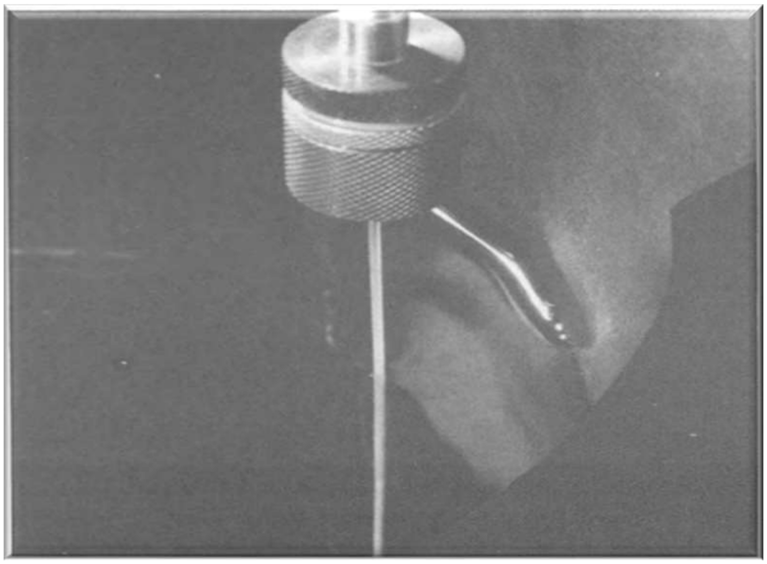


Figure 14: Photograph of a fiber in the air gap [30].

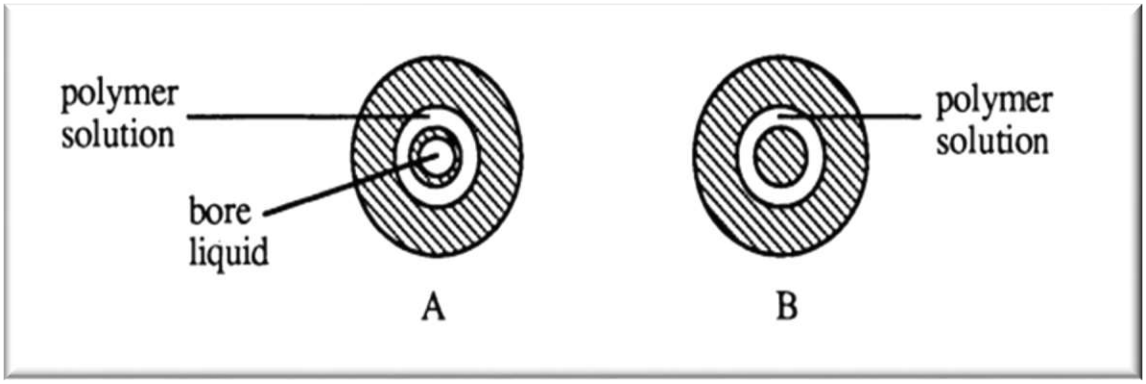


Figure 15: Cross-section of two types of spinnerets; (A) used for wet spinning and dry-wet spinning; and (B) used for melt spinning and dry-spinning [30].

### 2.6.2 Membrane coating

The initial methods for creating composite membranes involved spreading a diluted polymer solution on a liquid (such as water or mercury), and allowing the solvent to evaporate, leaving behind a thin film of polymer. The resulting membrane was supported by a porous substrate but was limited by poor mechanical stability and limitations in large-scale production [12].

There are various methods to apply a top layer onto a support, including dip-coating, interfacial polymerization, in-situ polymerization, plasma polymerization, and grafting. All of these methods, excluding dip-coating, involve polymerization reactions that produce a new polymer layer [30].

In this work dip coating technique is the using technique in coating the PP hollow fibres, so it will be described in detail in the following sections.

#### *2.6.2.1 Dip coating*

Dip-coating is an easy and effective method for creating composite membranes with a thin, dense top layer. These membranes are commonly used in reverse osmosis, gas separation, and pervaporation. The process is depicted in Figure-16 and involves immersing an asymmetric membrane (such as a hollow fibre or flat sheet typically used in ultrafiltration) into a solution containing the polymer, prepolymer, or monomer, with a low concentration of solute (usually less than 1%). After removing the membrane from the solution, a thin layer of the coating material adheres to it. The film is then dried in an oven where the solvent evaporates and crosslinking occurs, resulting in the top layer being firmly attached to the porous support [12].

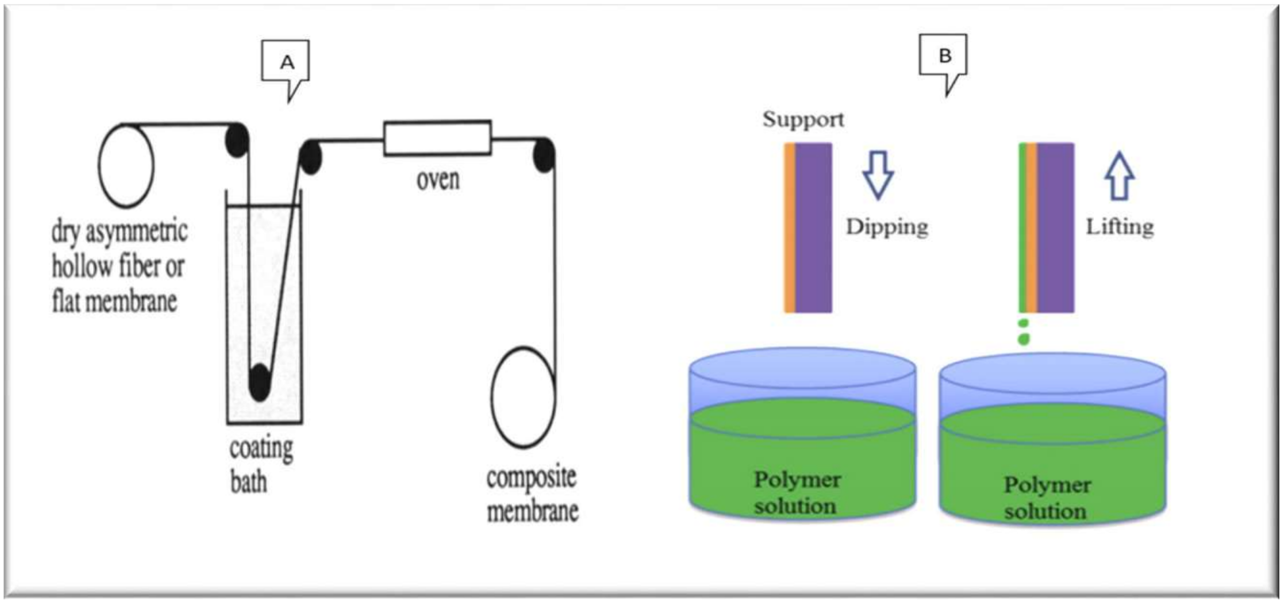


**Figure 16: Two Schematic illustration of dip-coating , A-[30] , B-[12].**

## 2.6.3 Polymer selection

Polymers can be classified into two categories based on their glass transition temperature (Tg): glassy and rubbery. Polymers with a Tg above their temperature are considered rubbery, while those with a Tg below their temperature are considered glassy [33].

Polymers with a rubbery texture have features like unsaturation, segmental mobility, and ample amounts of free space between molecules. This allows for small molecules to diffuse easily through the rubbery polymer [20].

Rubbery polymers often have a large amount of free volume because of gaps between highly mobile polymer chain segments. Free volume refers to the part of a polymer's volume not filled by the electronic clouds of the polymer and affects the diffusivity of penetrants. The distribution of free volume elements also plays a role in mass transport. Because of the high free volume fraction in rubbery polymers, their permeability is high, and selectivity is largely determined by the solubility of the penetrants. On the other hand, glassy polymers are rigid and have a lower free volume fraction, providing high mechanical stability. The separation in glassy polymers is based on differences in penetrant size. The sizes of free volume elements can be stabilized by cooling or through rapid solvent removal [33].

### *2.6.3.1 Pebax® copolymer*

Pebax® is a series of thermoplastic elastomers made by combining polyether (PE) blocks, which are flexible, and linear polyamide blocks (PA6, PA11, PA12, or a mix of PA6/PA12), which are rigid [33].

Pebax®, which stands for Poly (ether block amide), is a category of copolymers that are made up of both hard polyamide segments and soft polyether segments in their long polymer chains [34]. The hard amide blocks contribute to the material's mechanical stability, while the soft polyether segments play a major role in the separation process. Thanks to these special structures, Pebax® has good resistance to acid, bases, organic solvents, and has high thermal and mechanical stability. In several studies, Pebax® has proven to be a great choice for $CO_2$ separation, as its polar ether oxygen interacts well with $CO_2$ and other non-polar gases [35].

The majority of diffusion takes place in the PE (polyether) phase, with the PA (polyamide) phase offering the required mechanical support for the membrane [33].

Poly (ether-block-amide) copolymers, commercially known as Pebax®, offer a highly potential approach for producing high-performing $CO_2$ capture membranes from process streams with $CH_4$ and $N_2$. The combination of a flexible polyether segment and a hard polyamide block in Pebax® results in both high $CO_2$ affinity and desired mechanical strength in polymeric membranes. Additionally, researchers have been enhancing the performance of these membranes by creating a thin Pebax® selective layer on top of porous supports and incorporating inorganic and organic nanofillers into the Pebax® matrix to surpass the permeance-selectivity limit [6].

General formula of Pebax® shown in figure 17, where PA is the polyamide segment and PE is the polyether segment.

$$\mathrm{H}\left[\mathrm{O\text{-}PE\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}PA\text{-}\overset{\overset{\displaystyle O}{\|}}{C}}\right]_n\mathrm{OH}$$

**Figure 17: General formula of Pebax® [5].**

Pebax® copolymers can be found in the market and are known for their high mechanical strength and chemical stability. The physical properties of different grades of Pebax copolymers used as gas separation membranes are listed in Table 3. These grades consist of PEO (polyethylene oxide) and PTMO (polytetramethylene oxide) [6].

**Table 3: Physical properties of several grades of Pebax® copolymers [6].**

| Pebax® grade | PE | PA | PE:PA (wt. %) | Density (g/cm³) | Melting point(°C) | Ref |
|---|---|---|---|---|---|---|
| Pebax®-1657 | PEO | PA6 | 60:40 | 1.14 | 204 | [57] |
| Pebax®-5513 | PTMEO | PA6 | 33:67 | 1.01 | 159 | [39] |
| Pebax®-1074 | PEO | PA12 | 55:45 | 1.09 | 158 | [58] |
| Pebax®-4033 | PTMEO | PA12 | 53:47 | 1.01 | 160 | [58] |
| Pebax®-6333 | PTMEO | PA12 | 24:76 | 1.01 | 169 | [59] |
| Pebax®-3533 | PTMEO | PA12 | 70:30 | 1.01 | 144 | [60] |

The PE (polyether) segment in Pebax can be made up of either polyethylene oxide (PEO) or polytetramethylene oxide (PTMO). Similarly, the PA (polyamide) segment can be composed of 5 methyl units (PA6) or 11 methyl units (PA12) [6]. The chemical structures of PEO, PTMO, PA6, and PA12 are shown in figure 18.

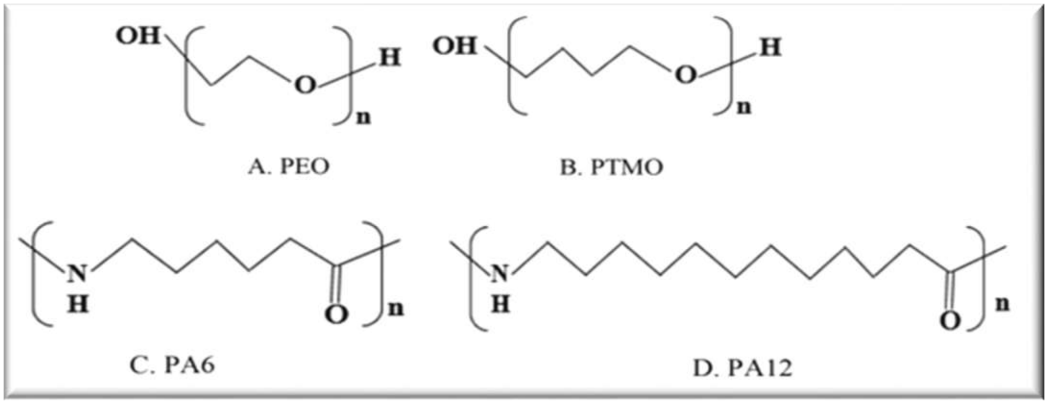


**Figure 18: (A) Poly(ethylene oxide),PEO; (B) polytetramethylene oxide,PTMO; (C) polyamide 6,PA6; and (D) polyamide 12,PA12 [6].**

When Pebax® is used as a coating on a polymer substrate, it is important for the selective layer to be as thin as possible. This is because gas permeance is inversely proportional to the thickness of the selective layer. However, if the membrane is too thin, there may be defects in the selective layer that significantly decrease gas selectivity [34].

### *2.6.3.1.1 Pebax®-1657*

Pebax®-1657 is a thermoplastic elastomer that consists of linear chains of rigid polyamide segments alternating with flexible polyether segments. It is made up of 60 wt.% polyethylene oxide (PEO) and 40 wt.% polyamide 6 (PA-6) [34]. The chemical structure of Pebax-1657 is displayed in figure 19 [36]. The composition of it is shown in figure 20 [34].

**Figure 19: Chemical structure of Pebax-1657 [36].**

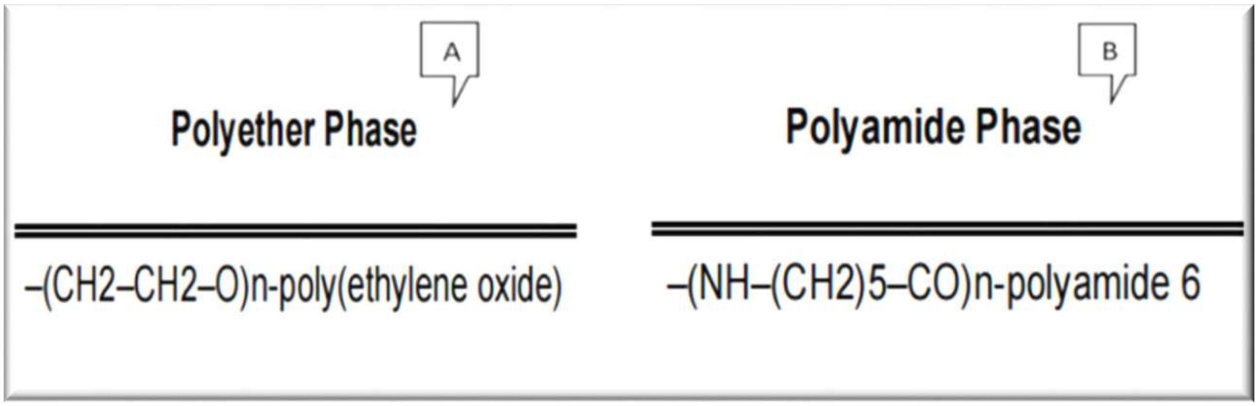


**Figure 20: composition of Pebax-1657 [34].**

Pebax®-1657 is a desirable material for membrane production due to its desirable characteristics, such as high durability, flexibility, and favourable selectivity for acid gas treatment, and polar-nonpolar gases like $CO_2/CH_4$. This is because of its mechanical strength and thermal resistance [37],[38].

### *2.6.3.1.2 Pebax®-5513*

Pebax®-5513 is a thermoplastic elastomer made up of 33 wt.% polytetramethylene oxide (PTMEO) and 67 wt.% polyamide 6 (PA-6) [6]. The chemical composition of Pebax-5513 is illustrated in figure 21.

Pebax®-5513, when combined with PA-6, improves the properties of PA-6, particularly at low temperatures and low humidity levels, while preserving the transparency of the nylon film and improving its soft feel. It has been engineered to be heat and UV resistant [39].

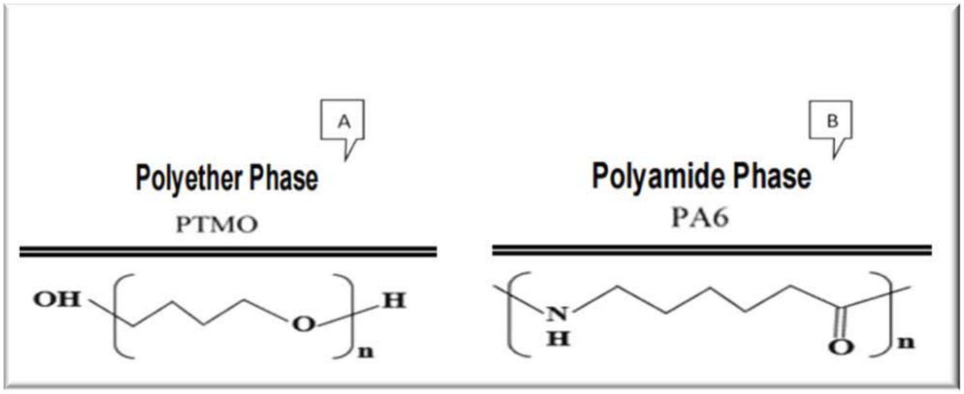
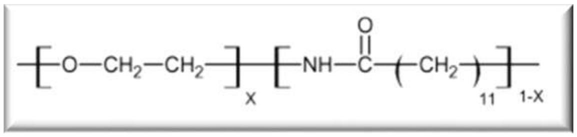


Figure 21: composition of Pebax-5513 [6].

### *2.6.3.1.3 Pebax®-1074*

Pebax®-1074 has a distinct composition of 55 wt.% soft polyethylene oxide (PEO) and 45 wt.% rigid polyamide 12 (PA12). Its glass transition temperature (Tg) is -55°C, making it rubbery at room temperature and slightly hydrophilic with a contact angle of 70°[40]. The chemical structure of Pebax®-1074 is shown in figure-22.

Compared to Pebax®-1657, Pebax®-1074 reached  a faster solution to gel process due to its relatively longer PA12 chain [40].



$$\left[ O-CH_2-CH_2 \right]_x \left[ NH-\overset{O}{\overset{\|}{C}}-\left(CH_2\right)_{11} \right]_{1-x}$$

Figure 22: Chemical structure of Pebax-1074 [40].

## 2.6.4 Pebax® solvents

Composite Pebax® membranes can be made through the direct mixing of two solutions (Pebax® and another polymer), or by coating Pebax® onto a polymer substrate. However, the selection of solvent to dissolve Pebax® must be carefully considered, as an incorrect combination of solvents can negatively impact the properties of Pebax® [34].

In various studies, a 70/30 weight percent mixture of ethanol (EtOH) and water ($H_2O$) has been found to be the most favourable solvent for the preparation of Pebax®-1657 and Pebax®-5513 membranes. The choice of this solvent is based on factors such as affordability, low toxicity, accessibility, and reduced environmental risk during evaporation when compared to alternative solvents [41],[42]. The combination of ethanol and water as a solvent for preparing Pebax® membranes has become popular due to its low cost, lower toxicity, and lower environmental hazard compared to other solvents. Additionally, the low reflux temperature and mild operational conditions make $H_2O$/EtOH a reasonable choice for this application despite its relatively undesirable solubility parameter [31],[32].

In addition, there have been a few uncommon instances of alternative solvents such as formic acid, n-butanol, and a blend of 1-propanol and n-butanol being utilized [37],[43]. These solvents can dissolve Pebax®-1657 Pebax®-5513 equally well, however, the resulting solution has a tendency to form a gel when cooled to room temperature [31],[32]. While formic acid is capable of preventing gelation of the solution, its use in large-scale membrane preparation is impractical as it is expensive, making it an unfavourable choice for the production of low-cost polymeric membrane separation [44].

Researchers typically use a single organic solvent, such as N-butanol or N-methyl-2-pyrrolidone (NMP), when working with Pebax®-1074. The most widely employed liquid for making it was 2-butanol, signifying a greater inclination towards cross-linking in its mixture than with Pebax®-1657 and Pebax®-5513 polymers. It underwent a quicker solution-to-gel transformation due to its comparatively longer PA12 chain [7],[8].

In conclusion, the choice of solvent suitable for Pebax® segments is based on their chemical makeup and polarity. For example, solvents such as DMAc, DMF, NMP, formic acid, and a water/ethanol mixture can effectively dissolve Pebax®-1657. However, only a limited number of solvents (formic acid and water/ethanol mixture) can form a solution without causing gelation at room temperature or above a certain concentration. This is due to the presence of a highly polar PA6 group in Pebax®-1657. However, because formic acid is expensive and toxic, the water/ethanol mixture is the most frequently used solvent for making solutions of Pebax®-1657 [45]. In contrast, Pebax®-1074, which features a long PA12 segment, dissolves more effectively in single organic solvents like DMF, NMP, or N-butanol [7].

# 3.Experimental equipment and procedure

## *3.1 Materials and chemicals*

### 3.1.1 Fibres

In this work Polypropylene (PP) fibres were used as the support layer of the separation membrane which will coated with different types of Pebax® . The fibres was purchased from 3M-Membrana company.

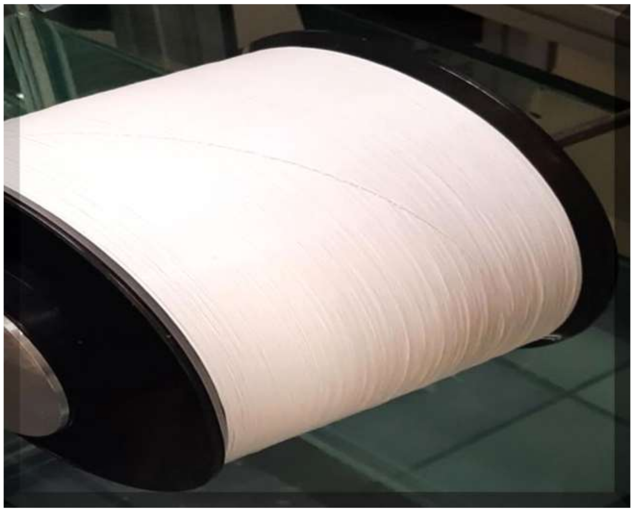


**Figure 23:Polypropylen (PP) fibers from 3M-Membrana.**

### 3.1.2 Polymers

The three polymers used in this work for coating PP Hollow fibres were Pebax®-1657, Pebax®-5513 and Pebax®-1074 which were provided from TU Wien. A detailed description for each type were mentioned above in sections (2.6.3.1.1, 2.6.3.1.2 and 2.6.3.1.3).

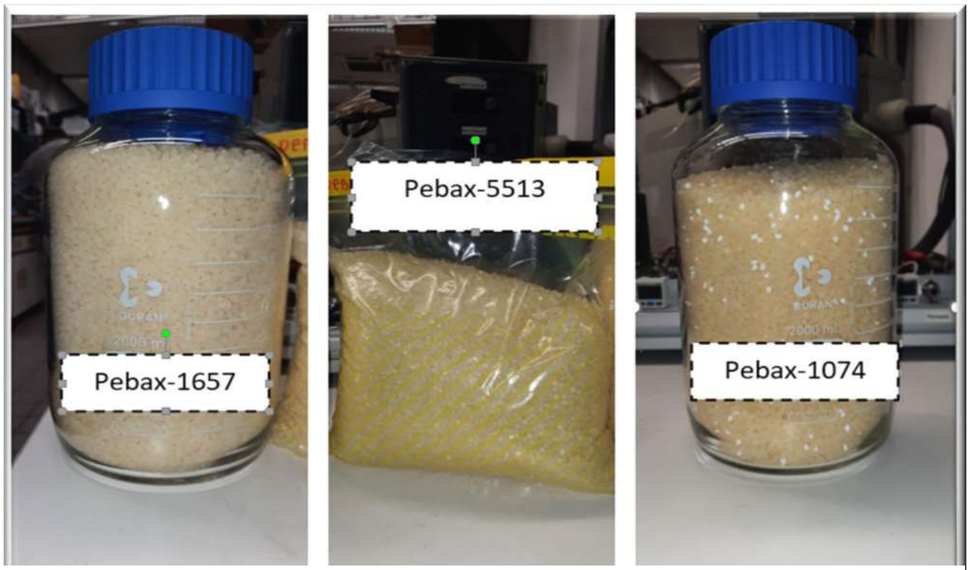


**Figure 24: Three different types of PEBAX® copolymer from TU Wien stores.**

### 3.1.3 Solvents

The solvents which were used in this work to dissolve the polymers are distilled water($H_2O$), Ethanol(EtOH) and 2-Butanol. Also, 1-Methyl-2pyrrolidinone (NMP) solvent was used in cleaning of the coating plant and in a small experiment at the beginning of my work to see the effect of different solvents in uncoated-PP fibres. All solvents except distilled $H_2O$ were purchased from VWR CHEMICALS company. Table 4 illustrates the specification test results of solvents from VWR CHEMICALS [46].

**Table 4: Specification test results of solvents from VWR CHEMICALS [46].**

| Solvent | Formula | Mol Wt. (g/mol) | Boiling point (°C) | Melting Point (°C) | Density (g/cm³) |
|---|---|---|---|---|---|
| EtOH | $H_3CCH_2OH$ | 46.07 | 77.5 - 78.5 | –117 | 0.7895 |
| 2-Butanol | $H_3CCH_2CH(OH)CH_3$ | 74.12 | 94 | –115 | 0.8534 |
| NMP | $C_5H_9NO$ | 99.13 | 202 | –24 | 1.033 |

### 3.1.4 Gases

The $CO_2$ and $N_2$ gases used for gas permeation experiments were obtained from MESSER Gases for Life, MESSER Austria GmbH. The purity of all gases used in this work was higher than 99.999%.
Table 5 illustrates the specifications for the Gases from MESSER [47].

**Table 5: Specifications for the gases from MESSER [47].**

| Gas ↓ /Components → | $H_2O$ | $O_2$ | Hydrocarbon (as $CH_4$) |
|---|---|---|---|
| $CO_2$ | < 5 ppmv | < 10 ppmv | < 1 ppmv |
| $N_2$ | ≤ 3 ppmv | ≤ 2 ppmv | ≤ 0.1ppmv |

## 3.2 Coating preparation

### 3.2.1 Coating solution (Polymer+Solvent)

In this work, three different types of Pebax®-copolymer (Pebax®-1657, Pebax®-5531, Pebax®-1074) with different concentrations were used to coat the substrate layer of commercial polypropylene hollow fibres. To Prepare the Pebax® coating solutions, 3 wt.%, 6 wt.% of each type were dissolved in a suitable solvent as described in section (2.4.6) in this work. As shown in Figure-25, the coating solution prepared in a 3-nickked glass flask connected with a condenser, thermometer and manual stirring device, all from IKA company.

Pebax®-1657 with concentrations of 9 wt.% and 15 wt.% were also prepared and tested, the solutions at these concentrations were very hard to deal with as they are high concentrations and the coating solutions transfer to gel form very fast when the temperature decrease, so for the other two types of Pebax® only 3 wt.% and 6 wt.% concentrations were prepared and tested. Table 6 illustrates the detailed preparation conditions of the polymeric solutions (Pebax®+solvent) that were used in this work.

After Pebax® pellets dissolve totally in the solvent, the mixtures was then stirred at 60°C for 24 hours before proceeding to the coating step. The hollow fibre membranes were dipped into the Pebax® solutions for 30 second then let them dry at room temperature for half an hour, the procedures were repeated five times in order to obtain good PEBAX® coating layer. It must be noted that this procedure was for dip-coating experiments while in machine coating the procedure will be clarified in the next sections as the goal of this coating was to study and compare the effect of different take-up speeds of the machine on the coating layer. Also, it is very important during the 5-times dip process to keep the PP hollow fibres that were dipped in Pebax-coating solution separate from each other to avoid them from sticking and damage the coating layer.

**Table 6: The different coating solutions were prepared and used in this work to Prepare different PP-Pebax® composite membranes.**

| Co-Polymer | PEBAX® Coating (wt.%) | Solvent | Temperature [°C] | r.p.m |
|---|---|---|---|---|
| Pebax®1657 | 3,6,9 and 15 | 30:70 Distilled H2O:EtoH | 75° | 150-200 |
| Pebax®5513 | 3,6 | 30:70 Distilled H2O:EtoH | 75°- 80° | 150-200 |
| Pebax®1074 | 3,6 | pure 2-butanol | 85°- 90° | 150-200 |

**Figure 25: (A) Equibments used in preparing Pebax® coating solutions, (B) The controller device of the white-manual Stirrer from IKA which control the RPM, (C) Thermometer device, (D) The heater device which control the temp of the solution, (E) A close Picture for the 3-nickked glass.**

## 3.2.2 Coating setup

### *3.2.2.1 Machine coating*

At the beginning of this work, experiments were conducted for coating PP hollow fibres with Pebax®-1657 using the coating machine which built by TU Wien. The machine illustrated in figure 25 below, the fibres in this procedure pass through a container filled with Pebax® coating solution, and it is possible to control and adjust the take up speed of the fibres when they are passing through this container hence control the residency time of the fibres in the coating solution. In this work, experiments at three different take up speeds 20-100-220 mm/s which are the lowest, mid, and higher speeds of the machine respectively, and at three different concentrations of Pebax-®1657 (3wt.% - 6wt.% - 9wt.%) to study the effect of different take up speeds and different concentrations of Pebax® on the coating layer.

As shown in figure 26, the machine have many parts which controlled the coating procedure, at the beginning of coating, the uncoated PP fibres took from their drum and pass through a certain glass-path (glass tube) which offer a controlled temperature then fibres are completing their way passing through the U-shaped container (the container filled with the coating solution) and then complete their way reaching a hexagonal rotator which keep rotating and the coated PP fibres wind on it and always the hexagonal adjust his position in a way that keep a distance between the fibres so they don’t stick to each other.

Also, to see if there's any effect of the solvents which used to dissolve Pebax® on the uncoated PP fibres themselves, the residency time for the fibres in the coating solution was calculated (the time that fibres took to pass the U-Shaped container which contain the coating solution). This time is differ depending on the chosen speed, then the uncoated PP fibres were dipped on each solvent for a times equal to these calculated times and let them dry then samples from each experiment were took and analysed under SEM microscope to see the effect of solvent on the uncoated PP fibres.

The distance of the U-shaped container 46.00 cm, and as mentioned above the experiments had been done at three different take up speeds (20-100-220 mm/s), and the residency time calculated from the following simple formula:

$$v = \frac{s}{t} \qquad (3.1)$$

Where: $v, s\ and\ t$ refer to the velocity, distance, and time respectively. Hence the residency times of the uncoated PP fibres in the coating solution are 23, 4.6 and 2.1 sec.

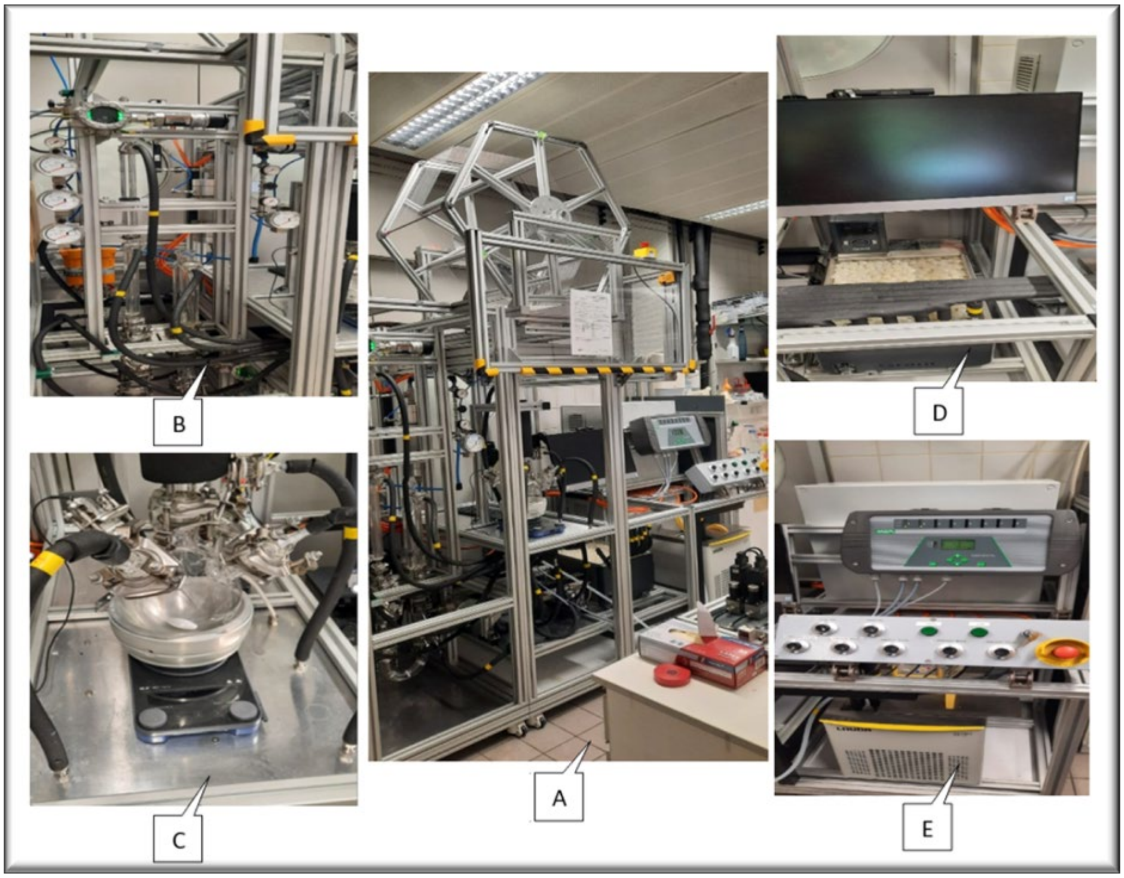


**Figure 26:** (A) Machine coating plant built by TUWien, (B) Sensors of tempreture and pressere in the fibres path, (C) The main container of the coating solution, (D) Display screen for programme related to the machine plant , (E) A close picture for a control unit of the machine which control the water flow.

### *3.2.2.2 Manual coating*

In the manual coating, the Coating procedure was different than the coating with machine, in this work, manual coating had been done to compare different three types of Pebax® (Pebax®-1657, Pebax®-5513 and Pebax®-1074) at different concentrations. Pebax®-1657 tested at 3 wt.%, 6 wt.%, 9 wt.% and 15 wt.% while Pebax®-5513 and Pebax®-1074 were tested at 3 wt.%, 6 wt.% only.

Figure 27 illustrates the equipments needed for coating the PP fibres with Pebax® manually. At the beginning, the uncoated PP fibres were winding in the black drum shown in figure 27-A under a controlled speed of winding (17.6 r.p.m) and controlled distance (2796 µm) between fibres, then the fibres transfer to aluminium frame and fix there tightly (fig 27-C), then the frame dipped in a stainless-steel container which contain the coating solution (the temp of the solution ~ 60-65°C) for 30 second then the frame lifted from the coating solution and the coated PP fibres are drying at room temperature for 15-20 minutes. The procedures were repeated five times in order to obtain a good Pebax® coating layer. Also, it is very important during the 5-times dip process to keep the PP hollow fibres that were dipped in Pebax®-coating solution separate from each other to avoid them from sticking and damage the coating layer.

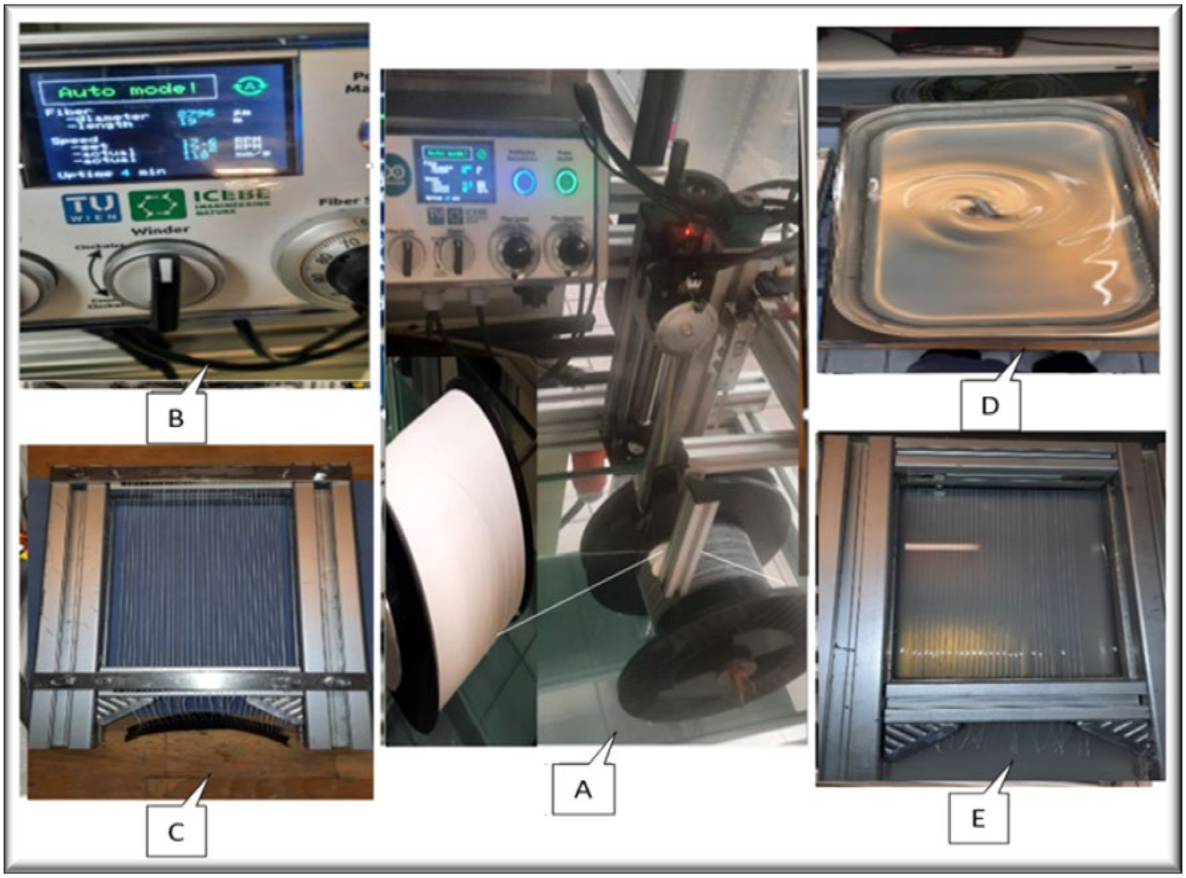


**Figure 27:** **(A) Uncoated PP fibers winding on a black drum, (B) The controller device of winding speed (RPM) and space between fibres, (C) Fibres-frame , (D) Stainless steel container, (E) The uncoated PP fibres on the frame dipped in the coating solution in the stainless steel container.**

## *3.3 Analytical methods for membrane characterization*

### 3.3.1 Scanning electron microscope (SEM)

The separation properties of the selective coated layer depend on the structure and morphology of that layer. Hence SEM images from cross-sectional view and longitudinal view of the prepared composite membranes were taken to investigate the effects of different Pebax types and different concentrations on the morphologies and structures of the fibres. Also, membrane-thickness and membrane-diameter were measured from the SEM pictures using NS 3.0.4 software.

Figure 28 illustrates the SEM from COXEM [48], the sputtering device, the connected software for the output picture NS 3.0.4 and the sample holder.

The samples for SEM study were cryogenically fractured in liquid nitrogen and then fixed on the sample-holder, then this sample-holder sputtered with gold inside the gold sputtering device under a current 50mA and time 100 sec. Figure 27-G shows the samples on the sample-holder after they sputtered, then the sample holder transfer to the SEM-drawer and waiting until the device be under vacuum then the samples will be shown on the connected software NS 3.0.4 to be analysed by the user.

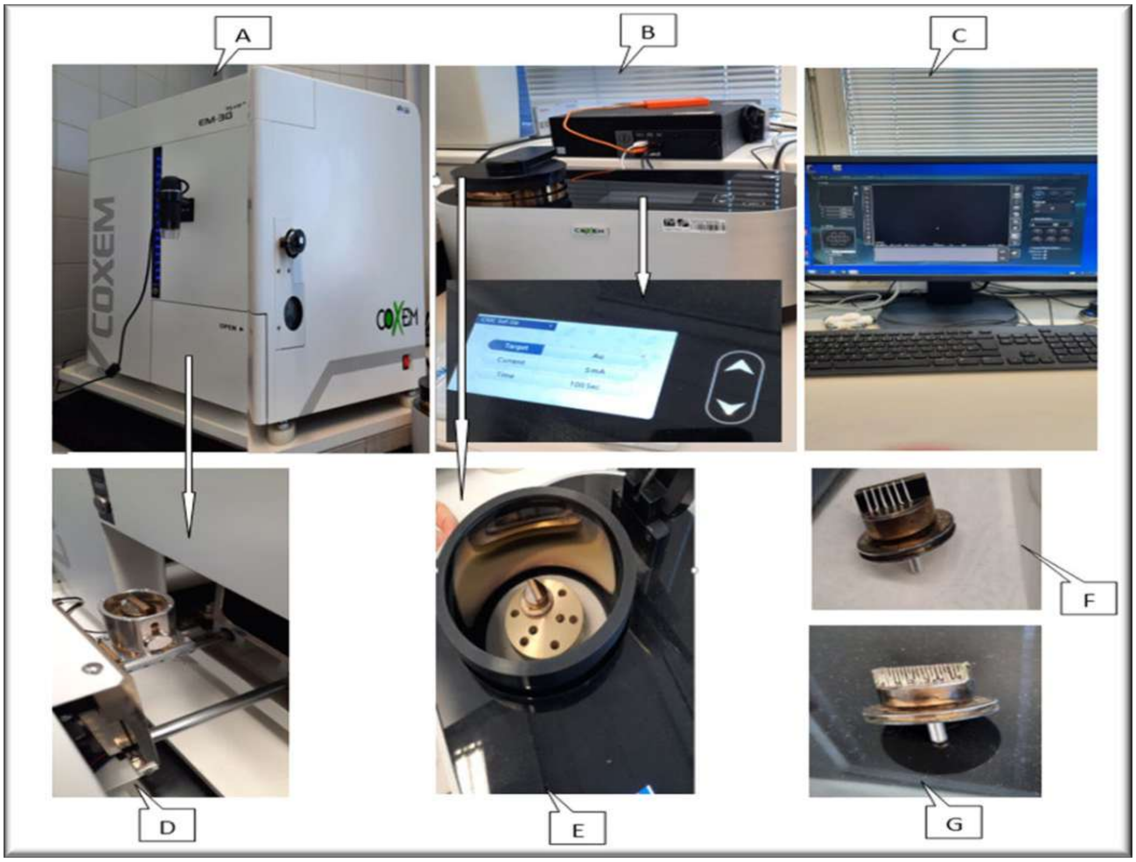


**Figure 28:** **(A) SEM device by COXEM, (B) Gold-sputtering device by COXEM, (C) NS 3.0.4 software, (D) SEM-drawer to recept the sample- holder, (E) The sample-holder in the sputtering device, (F) coated samples fractured cryogenically, (G) samples on the sample-holder after they sputtered with gold.**

### 3.3.2 Gas permeation unit (GP)

To test the separation properties of the membranes, an automated setup (GP Unit) was used. This setup was constructed by TU Wien.

The GP Unit allows the user to test the separation process under controlled conditions (pressure and flow). Gas flows were measured with flowmeter Definer 220H by Bios.

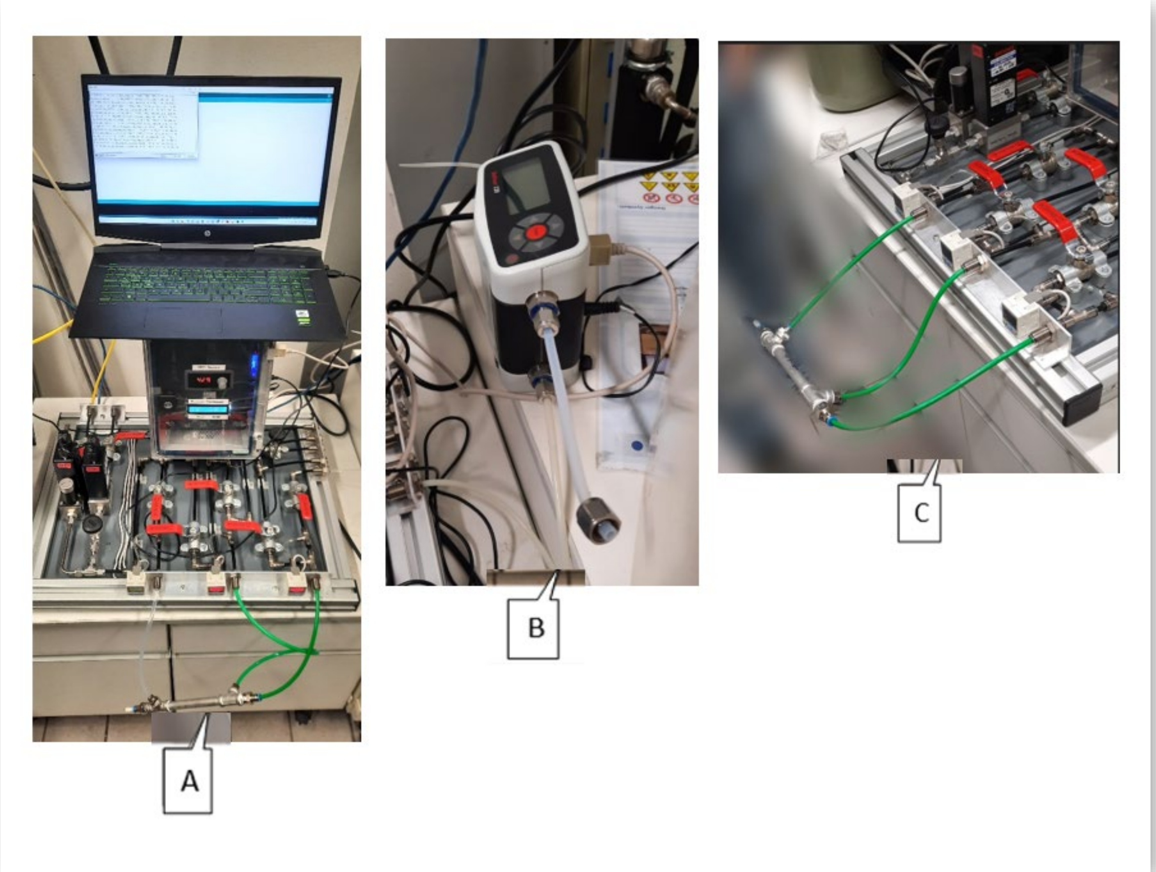


**Figure 29: (A) The GP unit with the arduino device and the mass flow controller (MFC), (B) The definer device by Bios, (C) The GP unit by TU Wien with a connected fibres module.**

### *3.3.2.1 Feed gas pressure*

Gases used for experiments were pure nitrogen ($N_2$) and carbon dioxide ($CO_2$) gas supplied by MESSER gases for life, MESSER Austria GmbH. The purity of all gases was higher than 99.999%.

Table 5 in section (3.1.4) above illustrates the specifications for the gases from MESSER.

The $N_2$ and $CO_2$ gases were connected via pipes to the feed-side of the GP-unit and the flow of gases controlled there via the MFC controller. The feed pressures applied to the modules which are related to machine coating experiments were equal 1, 1.5, 2, 2.5, and 3 Bar, whereas for the modules which are related to manual coating experiments the feed pressures were equal 3, 4, 5, 7, and 9 bar because under 3 bar the definer was out of range while the definer range is 5-500 mL/min.

**Figure 30: Pictorial Representation of The Laboratory Gas Manifold.**

### *3.3.2.2 Fibres modules for GP test*

The feed gas can be fed to the shell side or the lumen side of a hollow fibre membrane module. While the module design is generally simpler for shell side feed than the lumen side feed. For high stage cut applications, the pressure build-up in the fibre lumen can be substantial when a shell side feed configuration is used [49].

Figure 31 shows different configurations of membrane modules .

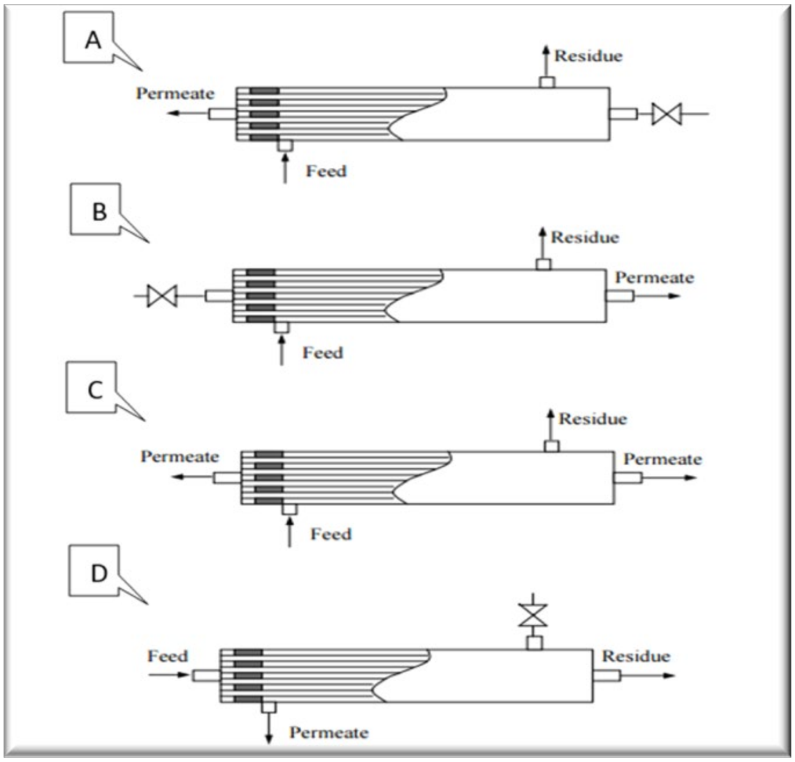


**Figure 31:** **Configurations of membrane modules: (A) shell side feed, counter-current flow; (B) shell side feed, co-current flow; (C) shell side feed, counter-co-current flow; (D) bore side feed, counter-current flow [49].**

Thirty-five units of hollow fibre membranes, 15 units for samples from machine coating at different speeds and concentrations while 20 units for samples from dip manual coating for three types of Pebax® at different concentrations) with effective length of 15.5 cm were bundled and placed within the stainless-steel membrane housing shown in figure 32-C. Table 8 and table 9 illustrate all the modules had been built in this research. The hollow fibre membranes were sealed with dead end manner using ”3M™ Scotch-Weld™, Epoxy Adhesive DP 100 Plus Clear Ent halt”. The flow way in this work was shell-side feed where the feed gas from the cylinder would diffuse through the outer surface of the hollow fibre membranes and the permeated gas will pass through the lumen of fibres.

**Figure 32:** **(A) 21 sample of coated PP fibers prepared to be bundeled, (B) a bundle of 21 sample of coated PP fibres , (C) stainless-steel membrane housing, (D) a view of the bundle of fibers after it enter the housing and sealed with resin, (E) The final look of the modules after attach the terminal connectors.**

The permeated gas from the module is connected to the definer in which the gas permeance could be determined as:

$$Q([ml/(min\,.\,bar.cm^2)]) = \frac{J\ \ ([ml/min])}{A\Delta P\ ([cm^2]*[bar])} \qquad (3.2)$$

where Q is the permeance([ml/(min.bar.cm²)], J is the definer flowrate[ml/min], A is the effective surface area of the Module[cm²] and ΔP is the pressure difference (Feed Pressure-Permeate pressure)[bar].

Effective surface area of the module (A):-

$$A = S.N \qquad (3.3)$$

Where N is the total number of fibres in the module and S is the surface area of a single fibre[cm²] and it is equal:-

$$S = \pi.D.L \qquad (3.4)$$

Where D is the diameter of coated fibre[cm] and it obtained from the SEM picture of the fibre, and L is the length of fibres in the module which is equal 15.5 in our work as mentioned in tables 8 and 9 below.

The permeance were presented in unit GPU (gas Permeation unit), in SI it is equal to $10^{-6}$cm$^3$STP/(cm$^2$.S.cmHg). A permeance of 1 GPU is when 1 µm thickness membrane has permeability of 1 Barrer [5]. By dividing the Permeance Q([ml/min.bar.cm^2] / (450.06*10^$^{-5}$) the result will be the permeance in GPU unit [50]. Strathmann clarify the conversion factors for gas Permeance, the following table (table 7) shows the conversion factors for different gas permeance units [50].

$$\frac{Q}{I}([GPU]) = \frac{Q}{4.5 \times 10^{-3}} \qquad (3.5)$$

**Table 7: Conversion factors for gas permeance [50].**

| | **Multiply by value below to convert to corresponding units** | | | | | |
|---|---|---|---|---|---|---|
| **Given a quantity in these units** | **1×$10^{-6}$ cm$^3$(STP)/ cm$^2$.s·cmHg (GPU)** | **L(STP)/m$^2$·h· bar** | **cm$^3$(STP)/cm$^2$· min·bar** | **scf/m$^2$·min ·bar** | **mol/m$^2$·s. Pa** | **mol/m$^2$·h· bar** |
| 1×$10^{-6}$ cm$^3$(STP)/cm$^2$·s· cmHg (GPU) | 1 | 2.7 | 4.5x$10^{-3}$ | 1.589x$10^{-3}$ | 3.348x$10^{-10}$ | 0.1205 |
| L(STP)/m$^2$.h· bar | 0.3703 | 1 | 1.645x$10^{-3}$ | 0.5808x$10^{-3}$ | 1.224x$10^{-10}$ | 4.404x$10^{-2}$ |
| cm$^3$(STP)/cm$^2$· min·bar | 0.2222x$10^3$ | 0.6079x$10^3$ | 1 | 0.3530 | 0.7439x$10^{-7}$ | 26.78 |
| scf/m$^2$·min ·bar | 6.293x$10^2$ | 1.722x$10^3$ | 2.832 | 1 | 2.107x$10^{-7}$ | 75.83 |
| mol/m$^2$.s.Pa | 0.2987x$10^{10}$ | 0.8172x$10^{10}$ | 1.344x$10^7$ | 0.4746x$10^7$ | 1 | 3.599x$10^8$ |
| mol/m$^2$.h. bar | 8.299 | 22.71 | 37.35x$10^{-3}$ | 13.19x$10^{-3}$ | 27.87x$10^{-10}$ | 1 |
| **A 1-µm-thick membrane having a permeability of 1 Barrer has a permeance of 1 GPU .** | | | | | | |

**Table 8: Modules overview for samples coated in the machine coating plant (machine coating).**

| Module number | Pebax® concentration [wt. %] | Pebax type | Solvent | Take-up speed [mm/s] | Fibres number | Effective Length [cm] | Test mode | Tested Gases | Fibre diameter (from SEM) [cm] | Total fibres surface area [$cm^2$] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 220 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.037 | 27.67 |
| 2 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 100 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 27.85 |
| 3 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 20 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.037 | 27.24 |
| 4 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 220 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.037 | 27.62 |
| 5 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 100 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 27.85 |
| 6 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 20 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.037 | 27.24 |
| 7 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 220 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.037 | 27.62 |
| 8 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 100 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 27.85 |
| 9 | 6 | 1657 | EtOH/$H_2O$ (70/30) | 20 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.037 | 27.24 |
| 10 | 9 | 1657 | EtOH/$H_2O$ (70/30) | 100 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 27.78 |
| 11 | 9 | 1657 | EtOH/$H_2O$ (70/30) | 100 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 27.78 |
| 12 | 9 | 1657 | EtOH/$H_2O$ (70/30) | 100 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 27.78 |
| 13 | 9 | 1657 | EtOH/$H_2O$ (70/30) | 20 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 28.00 |
| 14 | 9 | 1657 | EtOH/$H_2O$ (70/30) | 20 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 28.00 |
| 15 | 9 | 1657 | EtOH/$H_2O$ (70/30) | 20 | 15 | 15.5 | Shell-lumen | $N_2$,$CO_2$,$O_2$ | 0.038 | 28.00 |

**Table 9: Modules overview for samples coated manually (dip-coated).**

| Module number | Pebax® concentration [wt. %] | Pebax type | Solvent | Dipping's number | Fibres number | Effective Length [cm] | Test mode | Tested Gases | Fibre diameter (from SEM) [cm] | Total fibres surface area [$cm^2$] |
|---|---|---|---|---|---|---|---|---|---|---|
| A | 3 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.039 | 39.94 |
| B | 3 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.039 | 39.94 |
| C | 3 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.039 | 39.94 |
| D | 15 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.052 | 54.19 |
| E | 9 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.054 | 55.74 |
| F | 6 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.040 | 41.42 |
| G | 6 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.040 | 41.87 |
| H | 6 | 1657 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.039 | 40.69 |
| I | 3 | 5513 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.038 | 39.19 |
| J | 3 | 5513 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.038 | 39.19 |
| K | 3 | 5513 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.038 | 39.19 |
| L | 6 | 5513 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.041 | 42.02 |
| M | 6 | 5513 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.041 | 42.02 |
| N | 6 | 5513 | $EtOH/H_2O$ (70/30) | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.041 | 42.02 |
| O | 3 | 1074 | 2-Butanol | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.039 | 39.98 |
| P | 3 | 1074 | 2-Butanol | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.039 | 39.98 |
| Q | 3 | 1074 | 2-Butanol | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.039 | 39.98 |
| R | 6 | 1074 | 2-Butanol | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.040 | 40.90 |
| S | 6 | 1074 | 2-Butanol | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.040 | 40.90 |
| T | 6 | 1074 | 2-Butanol | 5 | 21 | 15.5 | Shell-lumen | $N_2$,$CO_2$ | 0.040 | 40.90 |

# 4. Results and discussion

## *4.1 Temperature of coating solutions (Pebax® and solvent) to become a homogenous solution*

The Pebax® pellets should dissolve totally in the solvent. The solvent had been heated gradually and the status of the solution had been remarked at each temperature until the solution become homogenous and the Pebax® pellets totally dissolve.

The results of the suitable temperature for each solvent to dissolve the Polymer and the status of the polymer during heated are clarifying in the following tables, table 10, table 11, table 12, and table 13.

**Table 10: The status of 3 wt.% Pebax®-1657 polymer dissolved in 70/30 wt.% EtOH/$H_2O$.**

| Preparation Temp [°C] | Time of continuous stirring [r.p.m] | Solution Status |
|---|---|---|
| Room Temp (25°C) | 16 hours-750 | -polymer did not dissolve. |
| 35°C | 16 hours-750 | -polymer did not dissolve. |
| 45°C | 16 hours-750 | -polymer did not dissolve. |
| 50°C | 16 hours-750 | -polymer did not dissolve.<br>-The colour of the mixture change to white. |
| 55°C | 5 hours-750 | -polymer did not dissolve. |
| 60°C-65°C | 5 hours-750 | -polymer did not dissolve. |
| 70-75°C | 3 hours-750 | -polymer totally dissolved.<br>-solution became homogenous. |

From table 10, it observed that the polymer Pebax®-1657 did not dissolve in 70/30 wt.% EtOH/$H_2O$ at room temperature and low temperatures, the polymer started to dissolve from 70°C, and it is totally dissolved after 3 hours with continuous stirring at 750 r.p.m.

**Table 11: The status of 3 wt.% Pebax®-5513 polymer dissolved in 70/30 wt.% EtOH/$H_2O$.**

| Preparation Temp [°C] | Time of continuous stirring [r.p.m] | Solution Status |
|---|---|---|
| Room Temp (25°C) | 72 h / 750 | -polymer did not dissolve. |
| 40°C | 3 hours-750 | - polymer did not dissolve.<br>-the colour of the mixture changed to white.<br>- pellets of Pebax®- 5513 got larger |
| 50°C | 19 hours-750 | -polymer did not dissolve.<br>- pellets of Pebax®-5513 got larger |
| 60°C | 16 hours-750 | -polymer did not dissolve. |
| 70°C | 5 hours-750 | -polymer did not dissolve. |
| 75°C | 7 hours-750 | -polymer Totally dissolved.<br>-solution became homogenous. |

From table 11, it observed that the polymer Pebax®-5513 did not dissolve in 70/30 wt.% EtOH/$H_2O$ at room temperature and low temperatures, the polymer started to dissolve from 75°C, and it is totally dissolved after 7 hours with continuous stirring at 750 r.p.m.

**Table 12: The status of 3 wt.% Pebax®-1074 polymer dissolved in 100% 2-Butanol.**

| Preparation Temp [°C] | Time of continuous stirring [r.p.m] | Solution Status |
|---|---|---|
| Room Temp (25°C) | 3hours-750 | -polymer did not dissolve. |
| 40°C | 3 hours-750 | - polymer did not dissolve. |
| 50°C | 3 hours-750 | -polymer did not dissolve. |
| 60°C | 19 hours-750 | -polymer did not dissolve.<br>-the colour of the mixture changed to white. |
| 70°C | 5 hours-750 | -polymer did not dissolve.<br>- pellets of Pebax®-1074 got larger |
| 75°C-80°C | 8 hours-750 | -polymer totally dissolved.<br>-solution became homogenous. |

From table 12, it observed that the polymer Pebax®-1074 did not dissolve in 2-Butanol at low temperatures, the polymer started to dissolve from 75°C, and it is totally dissolved after 8 hours with continuous stirring at 750 r.p.m.

**Table 13: The status of 3 wt.% Pebax®-1074 polymer dissolve in 100% NMP.**

| Preparation Temp [°C] | Time of continuous stirring [r.p.m] | Solution Status |
|---|---|---|
| Room Temp (25°C) | 3 hours-750 | -polymer did not dissolve. |
| 60°C | 3 hours-750 | - polymer did not dissolve. |
| 70°C | 3 hours-750 | -polymer did not dissolve.<br>- pellets of Pebax®-1074 got larger |
| 80°C | 3 hours-750 | -polymer Totally dissolved.<br>-solution became homogenous. |

From table 13, one can noticed that the polymer Pebax®-1074 did not dissolve in NMP solvent at room temperature and low temperatures, the polymer started to dissolve from 80°C, and it is totally dissolved after 3 hours of continuous stirring at 750 r.p.m.

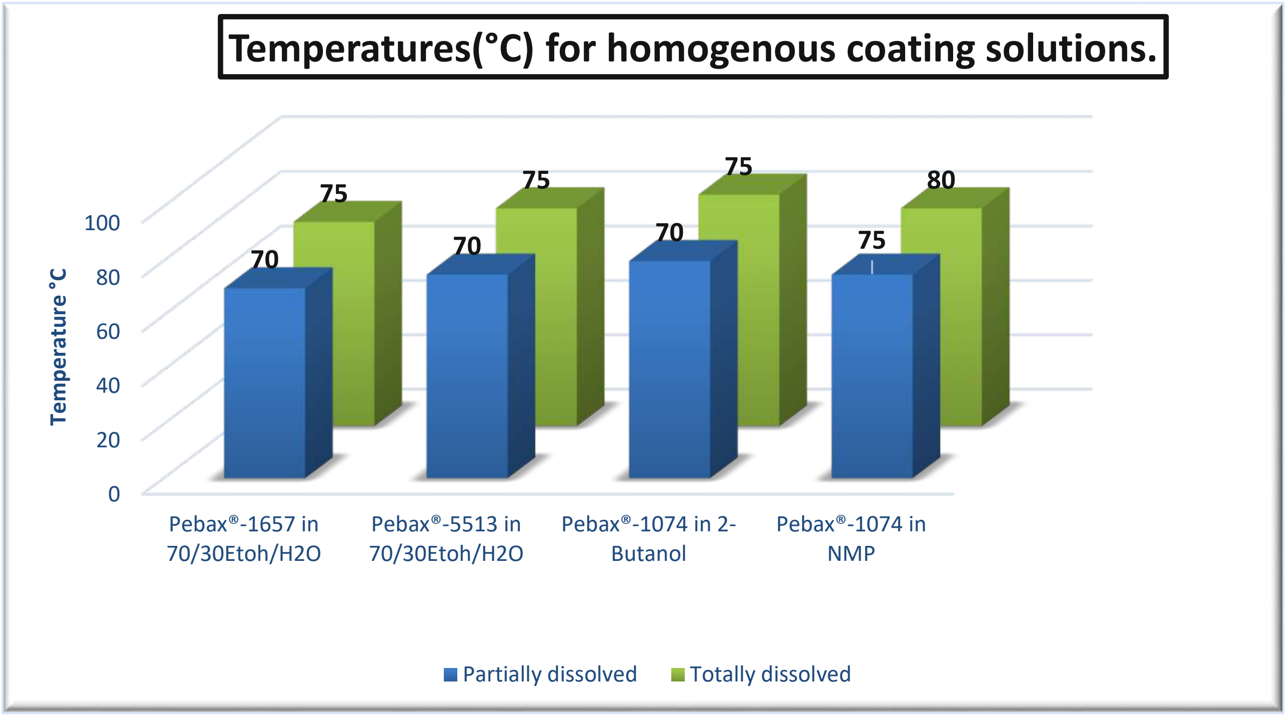


**Figure 33: The needed temperatures for the solvents to dissolve the Pebax® totally.**

Figure 33 illustrates the temperature where the polymer started to dissolve and change his status at it, and the temperature that the polymer totally dissolved at it.

From tables 10-13, one observed that for 70/30 wt.% EtOH/$H_2O$ solvent, the solution became a homogenous solution at a temperature ≥75°C, and for 2-butanol as a solvent, the solution became a homogenous solution at a temperature ≥75°C. Most of the research deal with these types of Pebax® which were used in this work, states that the combination to dissolve Pebax®-1657 and Pebax®-5513 can always be used as 70/30 wt.% ethanol/water and butanol solvent can always be used to dissolve Pebax®-1074 with heating these solvents to this range of temperature 75-80°C [28],[51],[9],[52],[53],[54].

For NMP solvent, the polymer totally dissolved at a temperature =80°C. But the used of this solvent in large scale membrane preparation is inconvenient as they are expensive for a low cost polymeric membrane separation [34]. So, NMP solvent was not used in this research experiments as the ethanol and butanol solvents can dissolve the needed polymers and they are cheaper.

After reaching a homogenous solution when the Pebax® pellets totally dissolved the solution still stirring in a rate of 750 r.p.m for at least 5 hours before starting the coating in order to degas any bubbles formed during the agitation.

All solutions became to be a gel-like at room temperature without heating even under continuous stirring. Also, when the concentration of the polymer in the solution increase, the solution becomes a gel-like solution faster. Figure 34 shows the gel-like form of the coating solution when it is at room temperature.

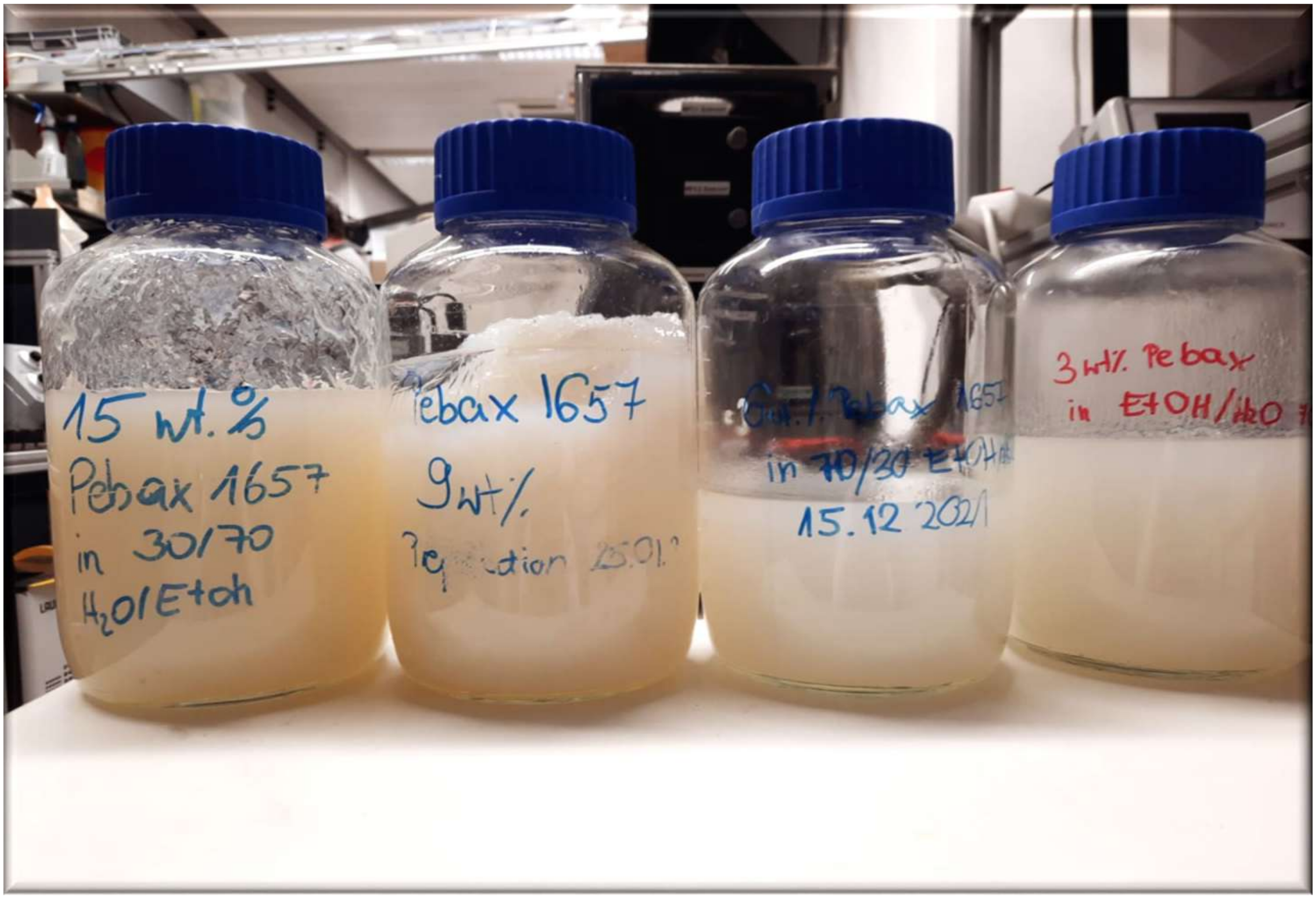


Figure 34: Gel form of the polymers at room temperature.

## *4.2 Membrane morphology*

### 4.2.1 Effects of solvents on uncoated PP fibres structures

The solvent used to dissolve the polymer may also affect the support layer morphology, in particular the formation of pores. If the solvent is very strong it may affect the uncoated PP fibre (the substrate layer) itself and it may dissolve it , depending on the residency time that the fibre will be in that solvent and the temperature of the solvent, in this research the maximum residency time of the fibre in the coating solution will not exceed 30s and always the temperature of the coating solution will be ~ 60-65°C. So, the effect of used solvents in this research was tested by dipping the uncoated PP fibres in each solvent for 30s at ~ 60-65°C, then longitudinal and cross-sectional SEM pictures for the samples were taking and the results clarified in the following pictures. Figure 35 illustrates longitudinal and cross-sectional SEM pictures for uncoated PP fibres.

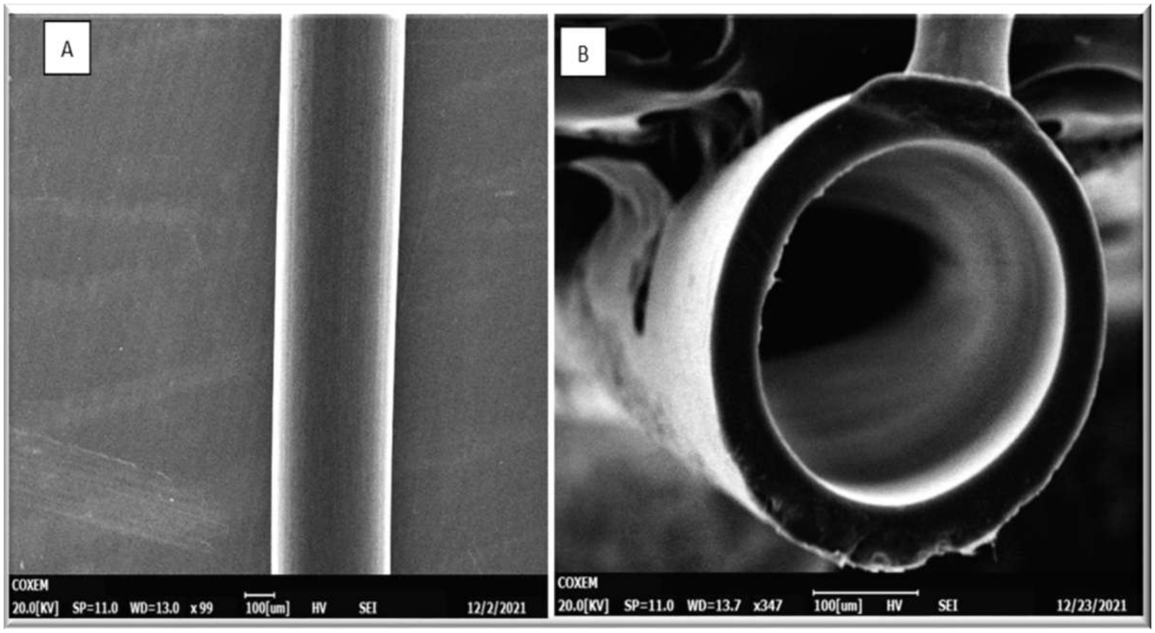


**Figure 35: A)Longitudinal B)Cross sectional - SEM pictures for uncoated PP fibers.**

The following figures 36-38 illustrate SEM pictures for the uncoated pp fibres after they were dipped in different solvents .

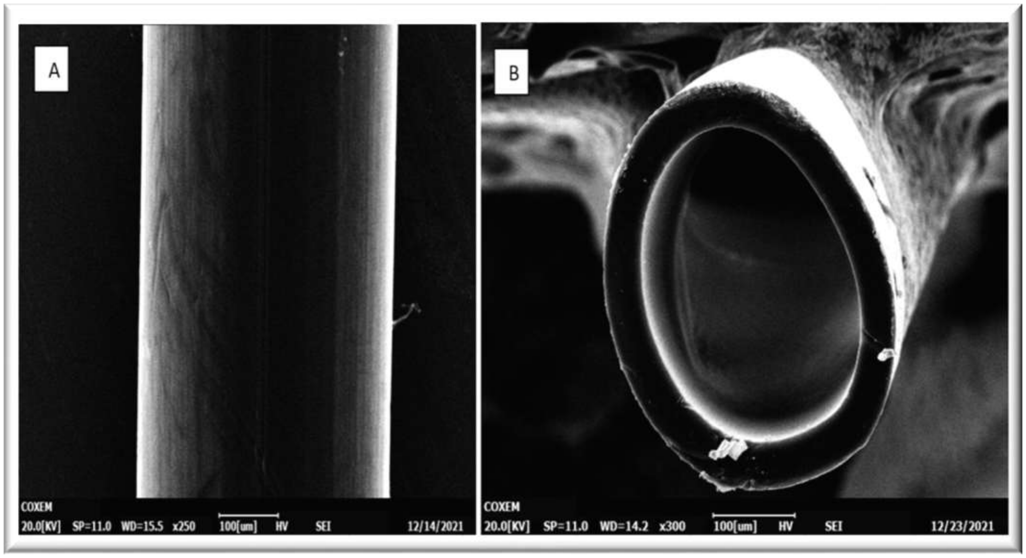


**Figure 36: A)Longitudinal B)Cross sectional - SEM pictures for uncoated PP fibres dipped in pure Ethanol for 30s at ˜ 60-65°C.**

The previous figure (figure 36), illustrates longitudinal and cross-sectional SEM pictures for uncoated PP fibres dipped in pure Ethanol for 30s at ˜ 60-65°C.

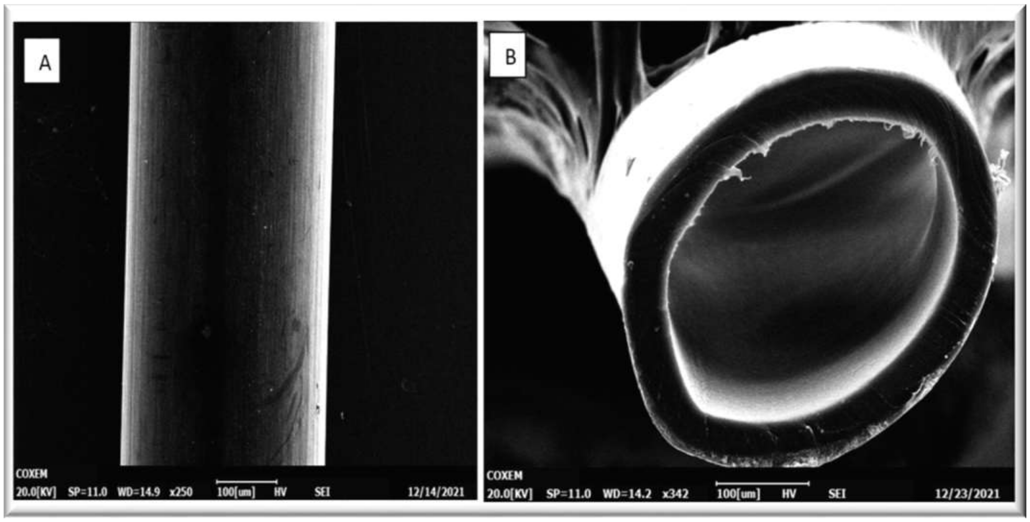


**Figure 37: A)Longitudinal B)Cross sectional - SEM pictures for uncoated PP fibres dipped in pure 2-Butanol for 30 sec at ˜ 60-65°C.**

Figure 37, illustrates longitudinal and cross-sectional SEM pictures for uncoated PP fibres dipped in pure 2-Butanol for 30s at ˜ 60-65°C.

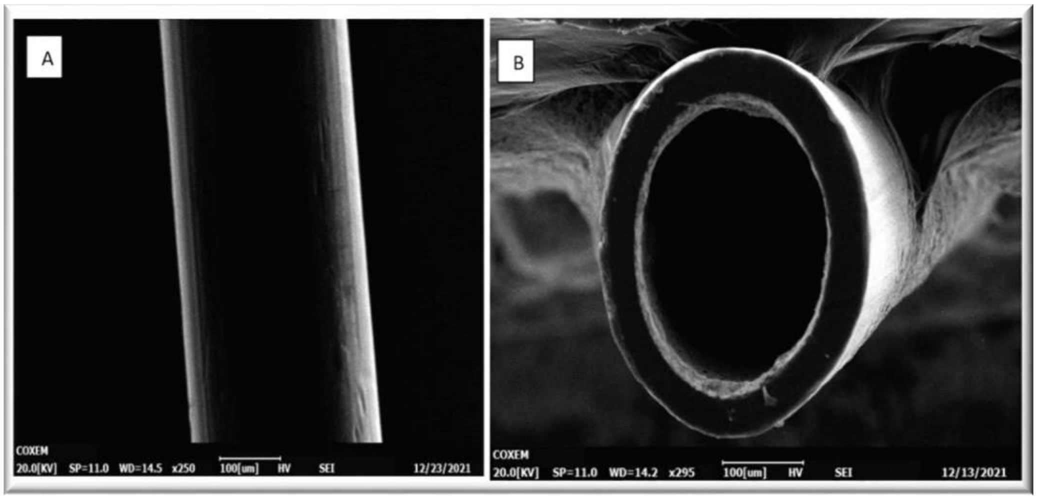


**Figure 38: A)Longitudinal B)Cross sectional - SEM pictures for uncoated PP fibres dipped in pure NMP for 30s at ˜ 60-65°C.**

Figure 38, illustrates longitudinal and cross-sectional SEM pictures for uncoated PP fibres dipped in pure NMP for 30 s at ˜ 60-65°C.

By analysing SEM pictures of the fibres after they were dipped in different solvents included that the Pure Ethanol, 2-Butanol, and NMP solvents do not affect the morphology of PP fibres. All of the SEM images revealed defect-free structures without any micropores inside.

### 4.2.2 SEM images for PP fibres coated with Pebax® [machine coating]

As mentioned in section (3.2.2.1), the coating experiments using the machine had been done for only one type of Pebax® which is Pebax®-1657 under different concentrations of polymer (3wt.%, 6wt.%, and 9wt.%) and different take up speeds of the machine (20mm/s, 100mm/s, and 220mm/s). The following figures (figure39 - figure41) are the results of SEM pictures for each experiment had been made with the machine, the conditions of coating (concentration and take up speed) were written under each figure.

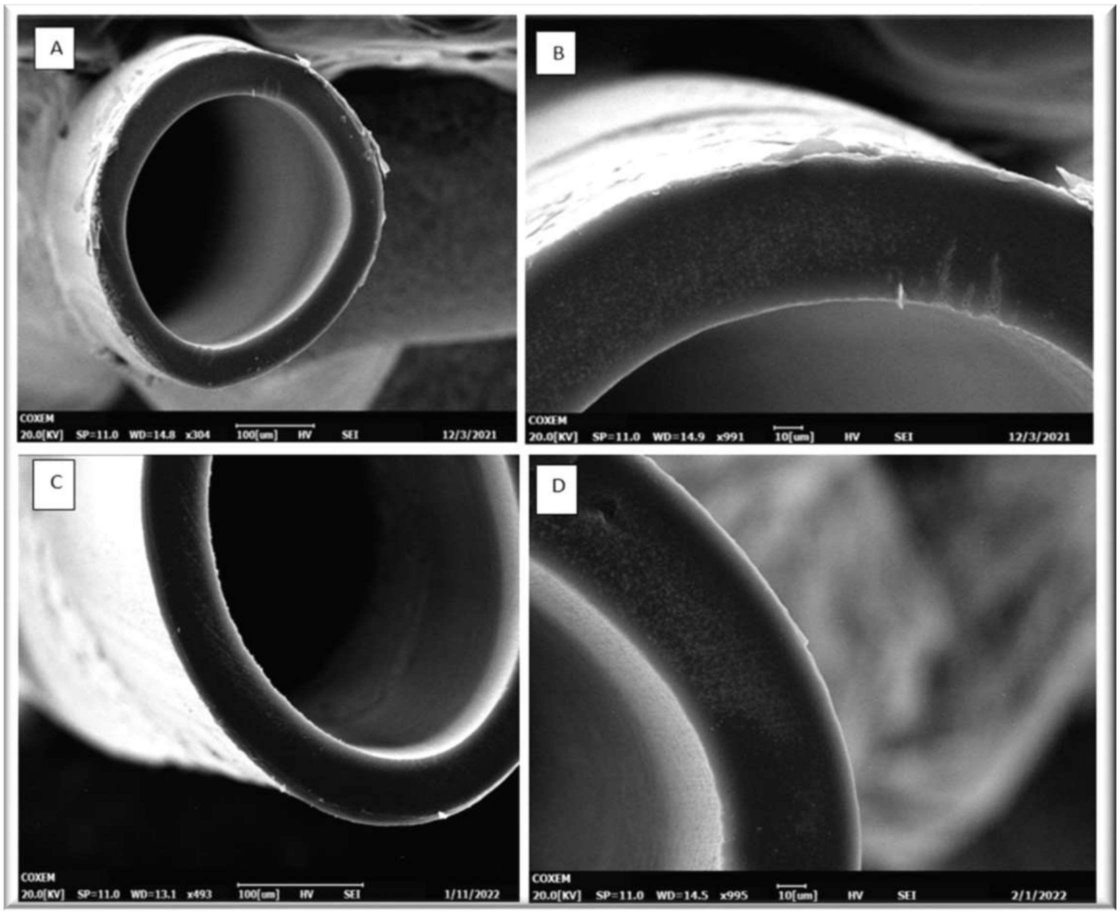


**Figure 39: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 3wt.% Pebax® 1657 with magnifications of x304, x991, x493, and x995 and take up speeds of 220, 220, 100, and 20 mm/s respectively.**

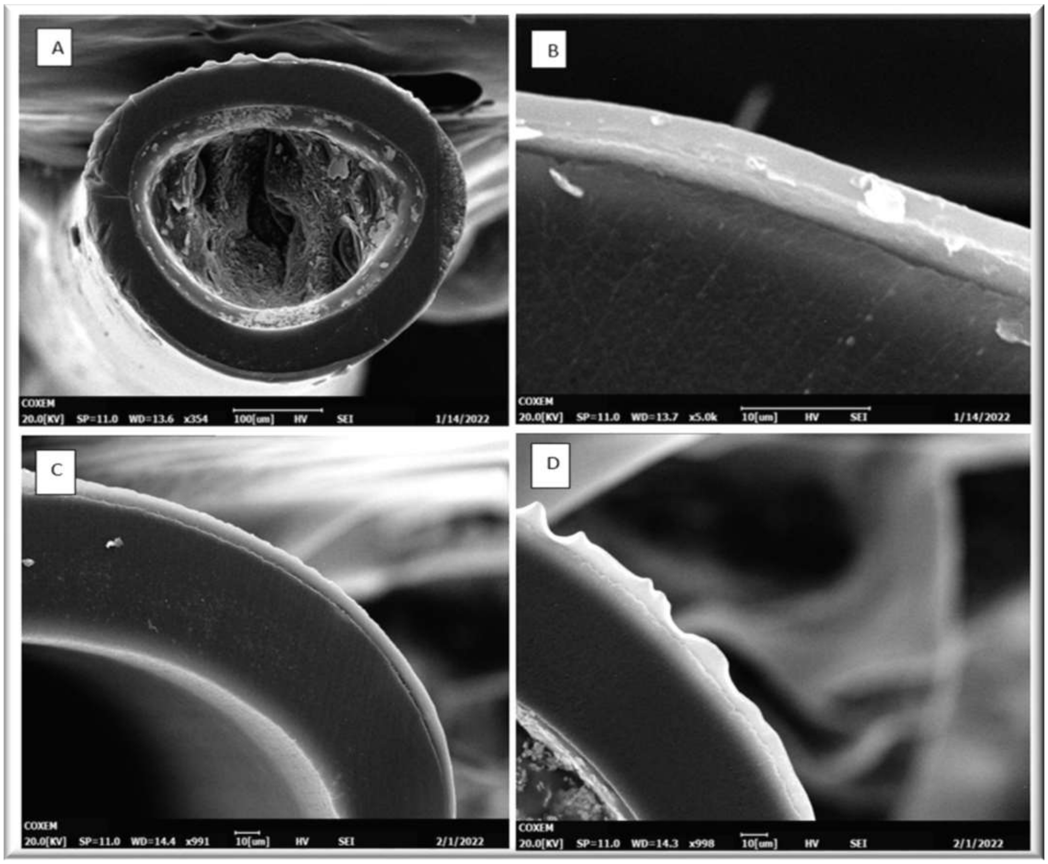


**Figure 40: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 6wt.% Pebax® 1657 with magnifications of x354, x5.0K, x991, and x998 and take up speeds of 220, 220, 100, and 20 mm/s respectively.**

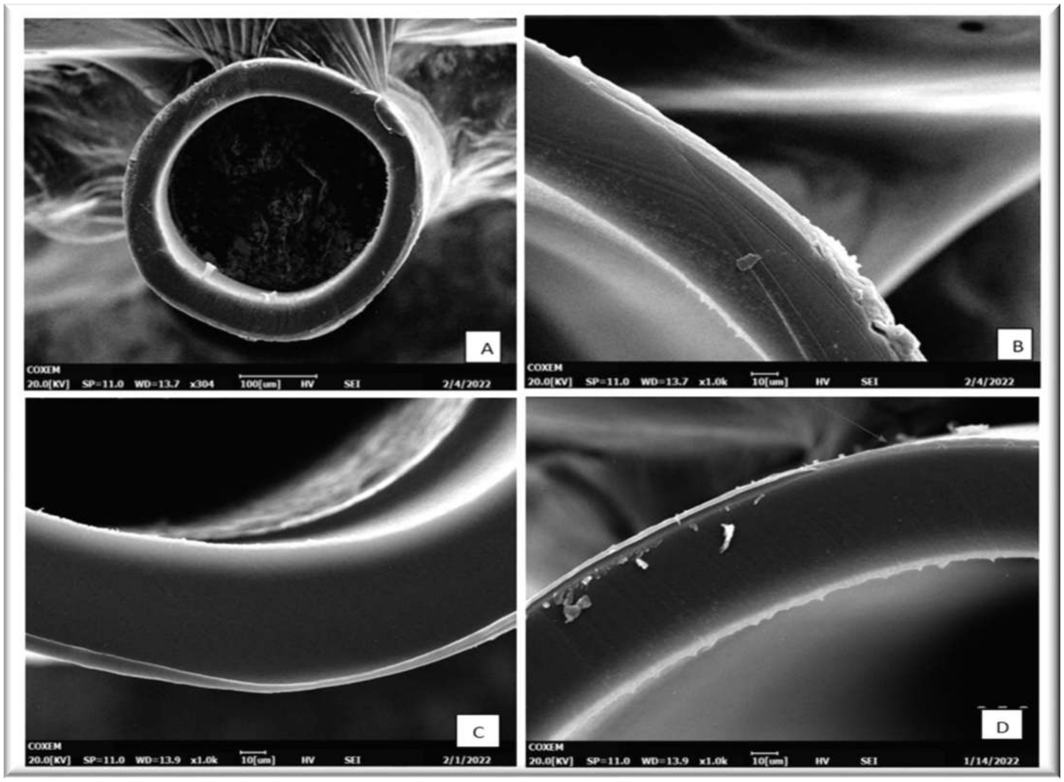


**Figure 41: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 9wt.% Pebax® 1657 with magnifications of x304, x1.0K, x1.0K, and x1.0K and take up speeds of 220, 220, 100, and 20 mm/s respectively.**

By analysing SEM pictures of the coated fibres, we can state that the obtained coating layer for 3wt.% concentration of Pebax®-1657 is very thin layer under the three take up speeds (220, 100, and 20 mm/s) , while for 6wt.% and 9wt.% concentrations the coating layer is thicker and clearer. The exact values for the thickness of the coating layers will clarify and discuss in the next section (4.2.3).

Also, we can observe from the SEM pictures the distribution of the coating layer under each concentration and different take up speeds, the pictures shows that for the 3wt.% concentration the coating layer is distributed uniformly around the hollow pp fibre under the three take up speeds but the layer is very small (negligible) and so no modules for this concentration were built or tested because it is clear that the coating layer is not a good layer. For the 6wt% concentration the coating layer is distributed uniformly around the hollow pp fibre under the three take up speeds and the thickness of the coating layer is good. So, 9 modules for this concentration (three modules for each take up speed) were built and tested. For the 9wt% concentration the coating layer is distributed uniformly around the hollow PP fibre under the 20 mm/s and 100 mm/s take up speeds. So, as mentioned in table 8 which illustrates the modules built for the experiments had been done with the machine we can notice that three modules for each take up speed of these two take up speeds had been built and tested, while for the 3rd take up speed which is 220mm/s there is no any module built as the coating layer under this take up speed was not distributed uniformly and large droplets of the coating solution had been formed on the surface of the PP hollow fibre.

As mentioned in section (3.3.2.2), 15 modules were built, and the overview of these modules clarified in table 8 above. The results of GP test for these modules will be shown and discussed in the next sections of this chapter (4.3.1.1) and (4.3.1.2)

### 4.2.3 Thickness of coating layers done by machine coating

The thickness of the coating layer was measured at 10 different locations along the coated fibre two in each quadrant and two in the centre). All thicknesses measurements were made using SEM images.

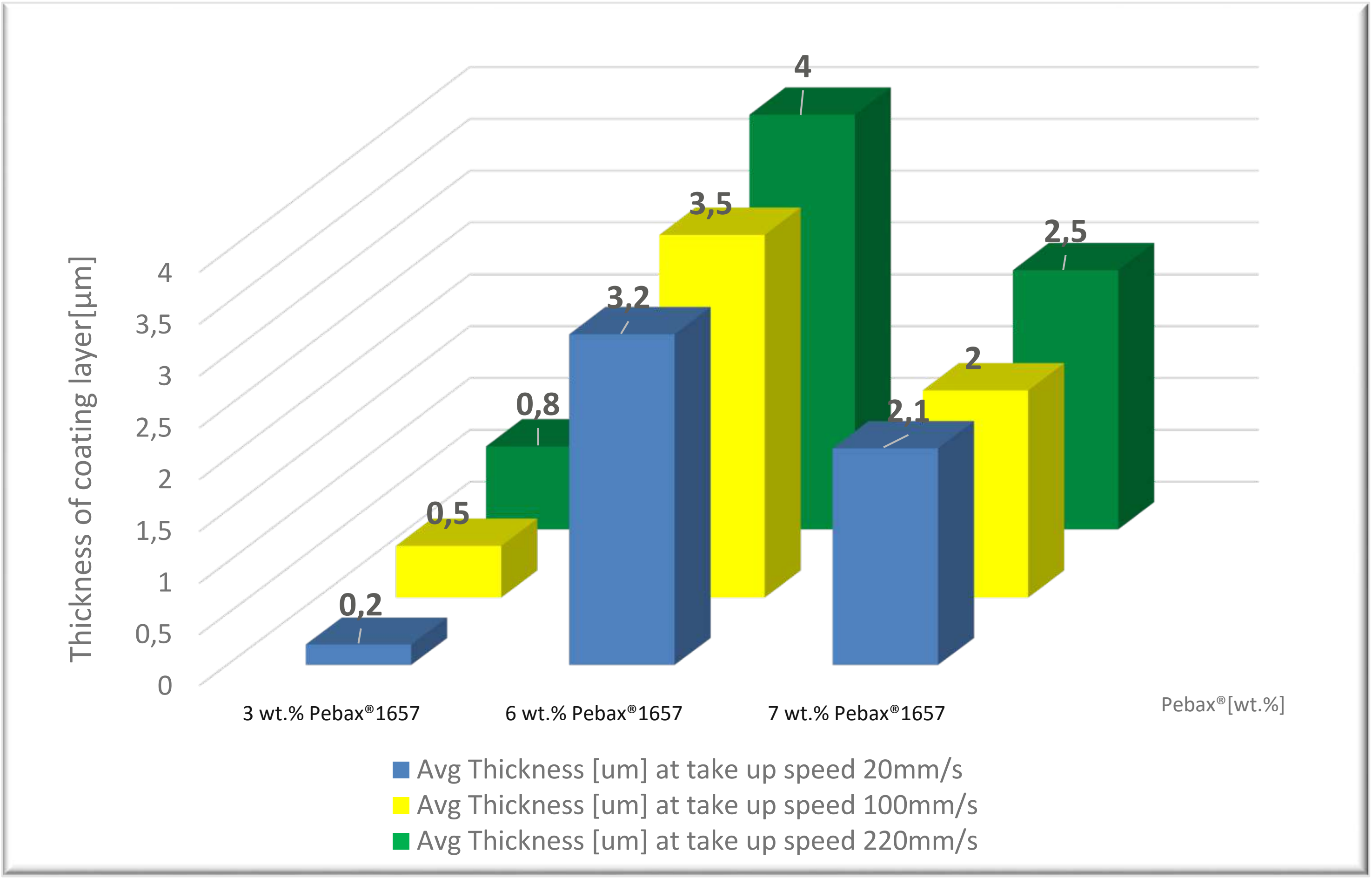


**Figure 42: Thickness values of different coating layers of Pebax-®1657 at different concentrations and different take up speeds.**

Thickness values of different coating layers of Pebax®-1657 at different concentrations and different take up speeds was shown in figure 42. For each concentration there is different values of thicknesses for each coating layer but always the lower take up speed at a certain concentration (20mm/s) has the lower thickness and the higher take up speed at the same concentration (220mm/s) has the highest thickness.

So, if the take up speed increase the thickness of coating layer increase and this may refer to the friction force, as under the higher speed the friction is higher than the friction at lower take up speed, so the coating layer applied on the fibres more effectively under high friction.

Noticed that when the concentration increase from 3wt.% to 6wt.% the thickness of coating layers for any of the three take up speeds was increased in general but when the concentration was increased to 9wt.%

the thickness of coating layers for any of the three take up speeds was reduced in general, thus may be because the density of the solution at higher concentration of the polymer is larger and the coating solution become to a gel form faster, then the coating layer not distributed in a very uniform way as in a lower concentrations.

### 4.2.4 SEM images for PP fibres coated with Pebax® [dip manual coating]

As mentioned in section (3.2.2.2), the dip manual coating experiments have been done for three types of Pebax® which are Pebax®-1657, Pebax®-5513, and Pebax®-1074 under different concentrations of polymers (3wt.% and 6wt.%). For Pebax®-1657, concentrations of 9wt.% and 15wt.% also were tested. The following figures (figure43 – figure50) are the results of SEM pictures for each experiment had been made with manual dip coating, the conditions of coating (which type of Pebax® and which concentration) were wrote below each figure.

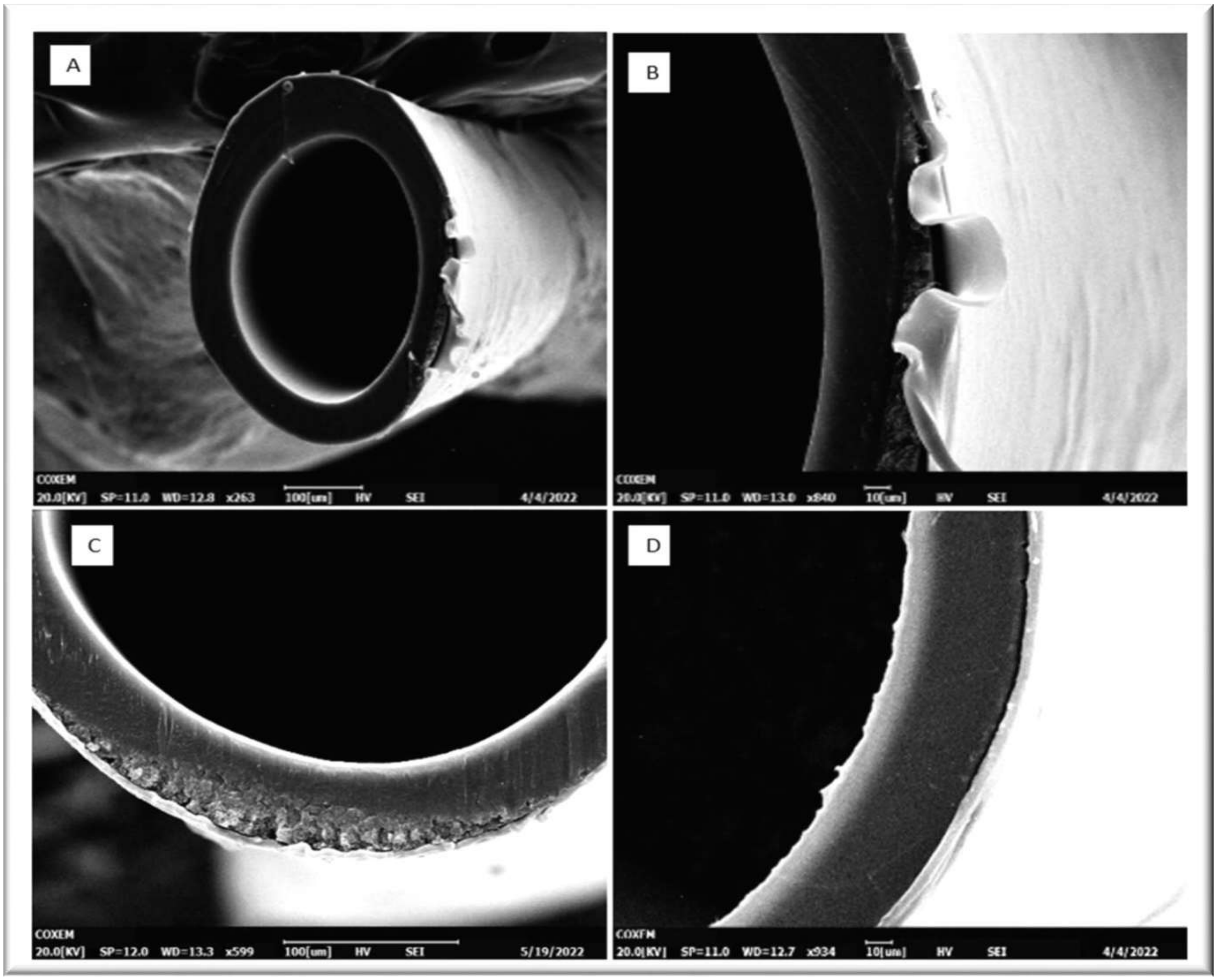


**Figure 43: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 3wt.% Pebax® 1657 with magnifications of x263, x840, x599, and x934 respectively.**

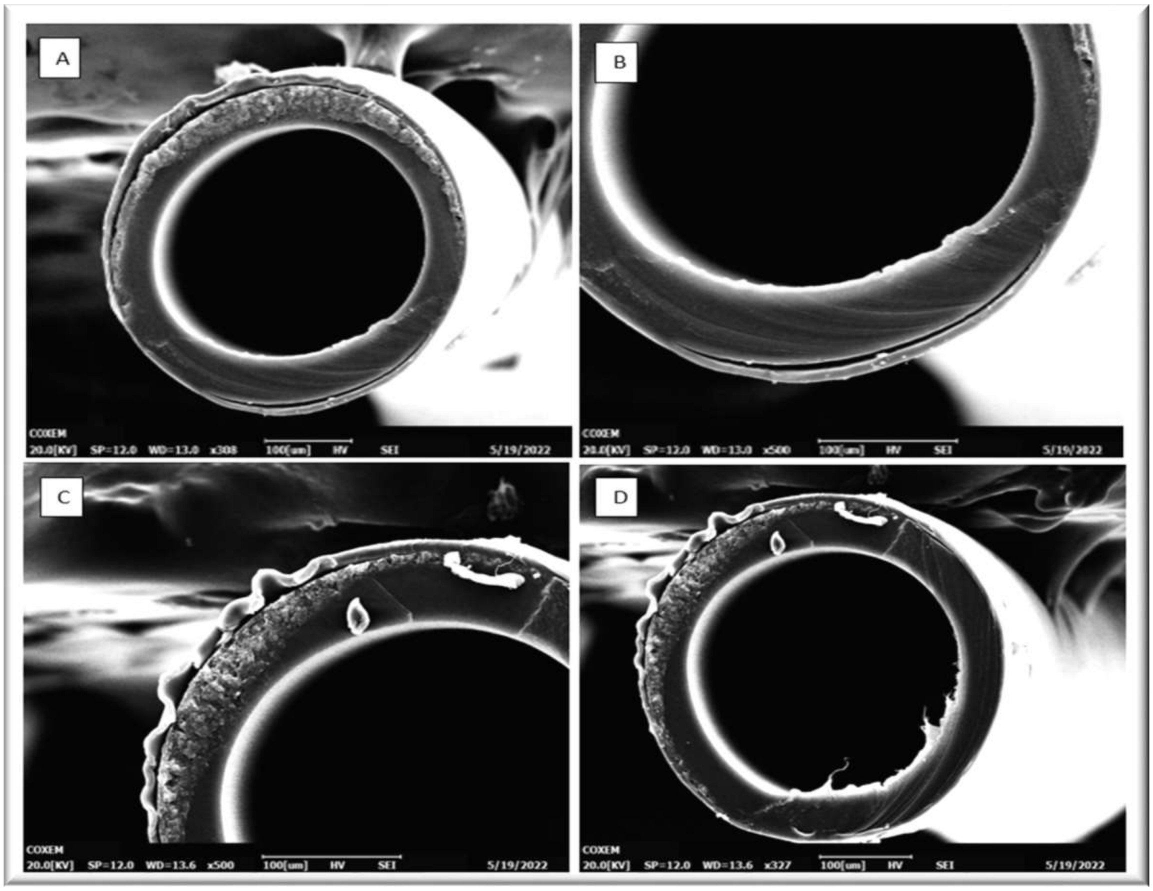


**Figure 44: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 6wt.% Pebax® 1657 with magnifications of x308, x540, x500, and x327 respectively.**

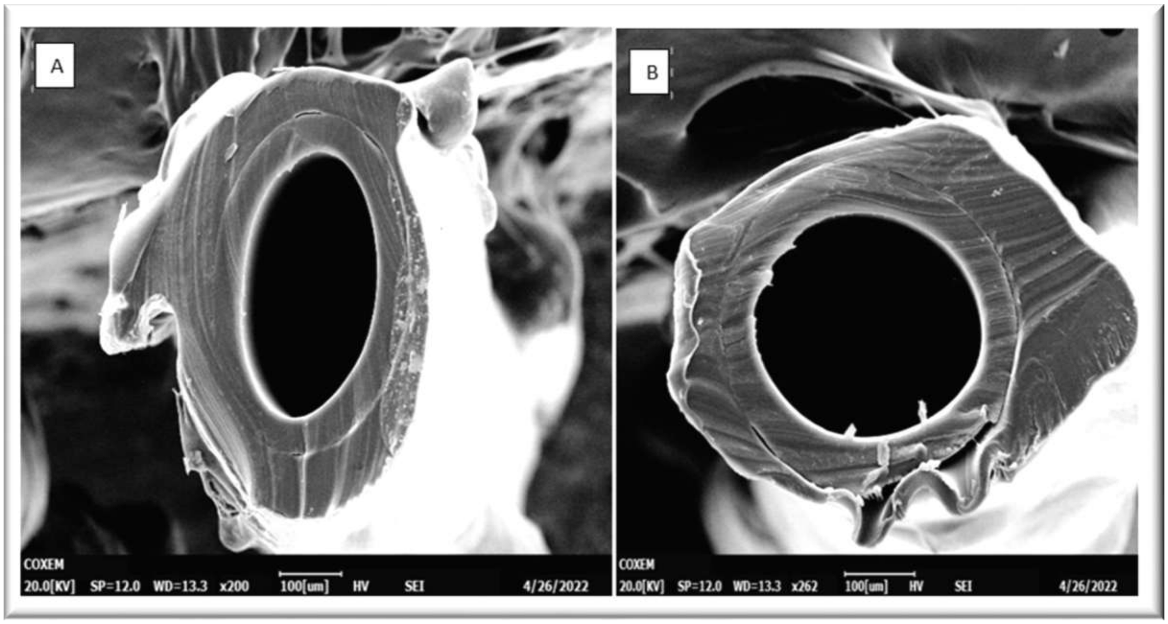


**Figure 45: A and B Cross sectional SEM pictures for PP fibers coated with 9wt.% Pebax® 1657 with magnifications of x200 and x262 respectively.**

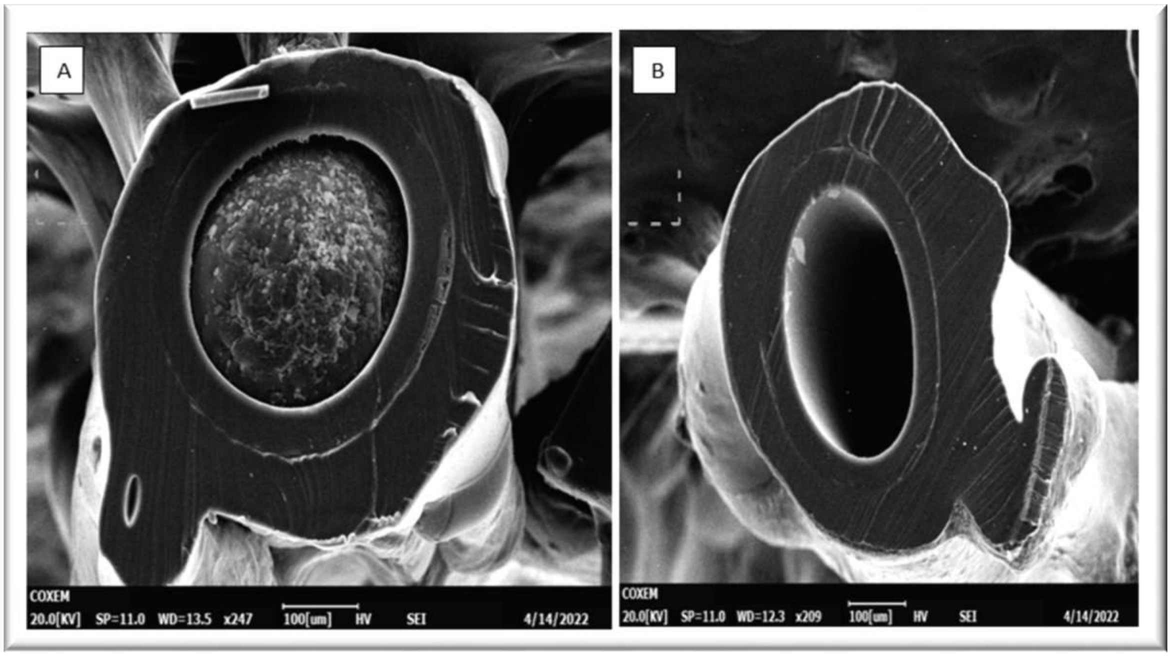


Figure 46: A and B Cross sectional SEM pictures for PP fibers coated with 15wt.% Pebax® 1657 with magnifications of x247and x209 respectively.

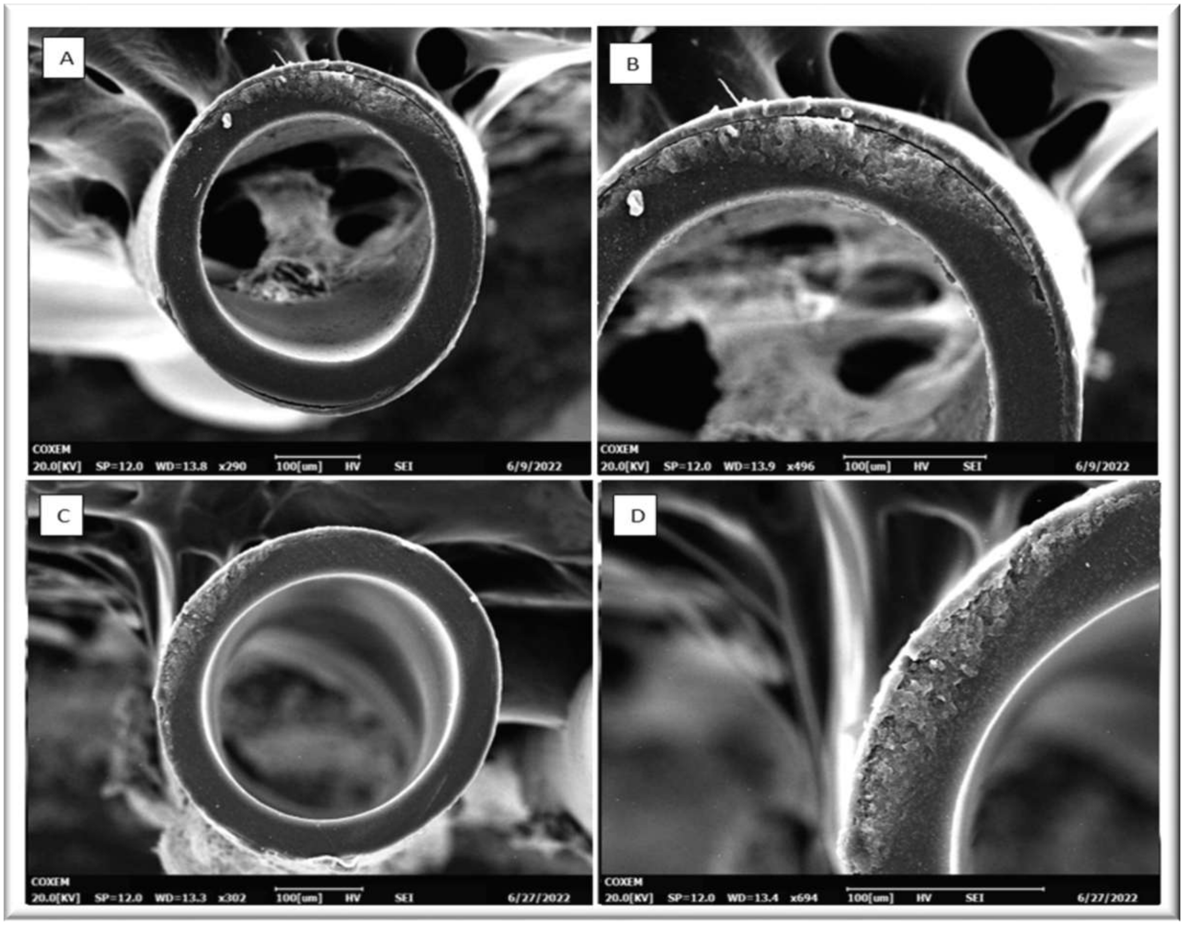


Figure 47: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 3wt.% Pebax® 5513 with magnifications of x290, x496, x302, and x694 respectively.

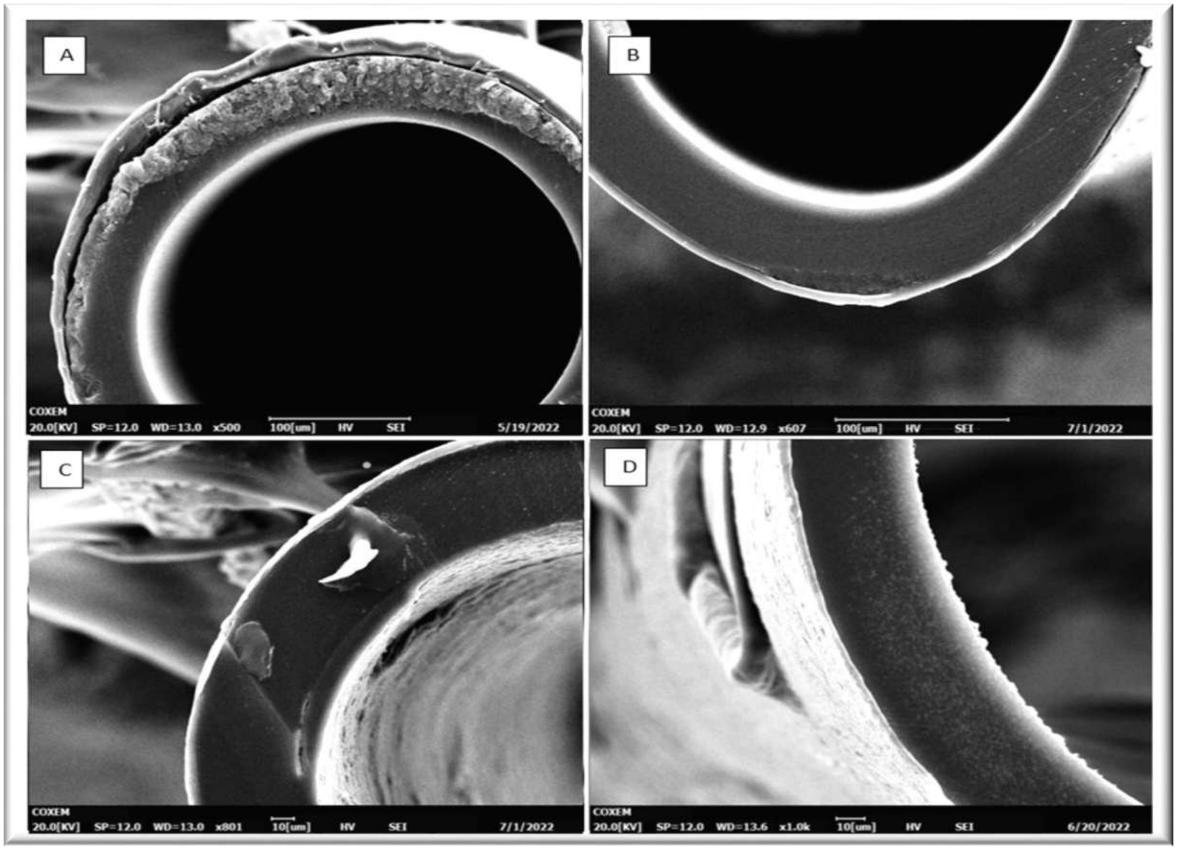


**Figure 48: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 6wt.% Pebax® 5513 with magnifications of x500, x607, x801, and x1.0K respectively.**

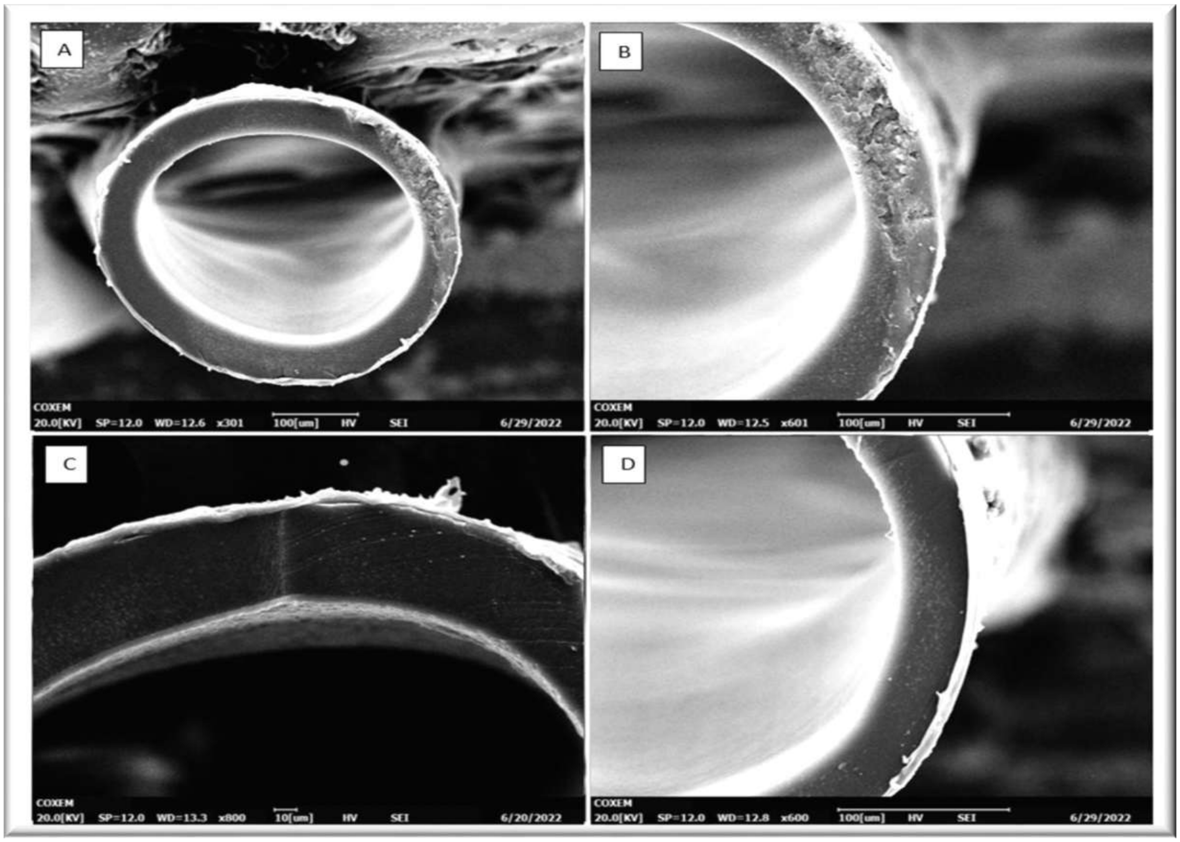


**Figure 49: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 3wt.% Pebax® 1074 with magnifications of x301, x601, x800, and x600 respectively.**

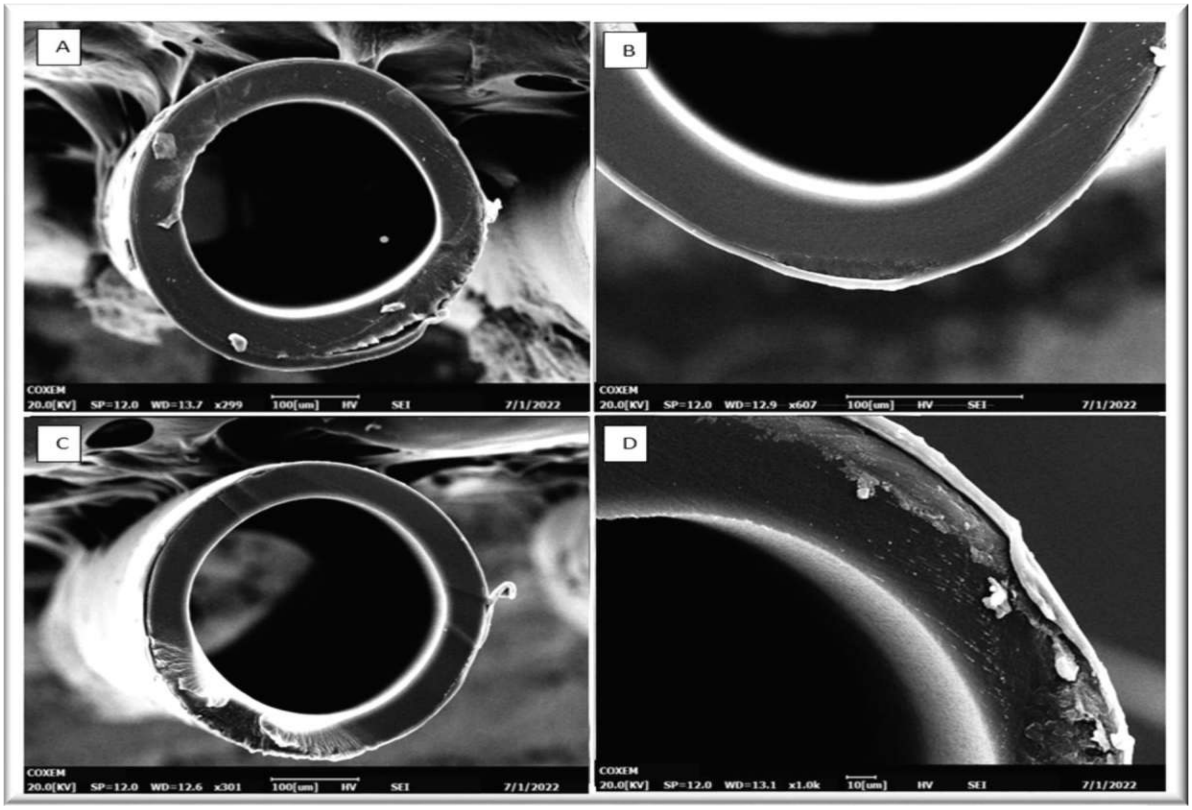


**Figure 50: A, B, C, and D Cross sectional SEM pictures for PP fibers coated with 6wt.% Pebax® 1074 with magnifications of x299, x607, x301, and x1.0K respectively.**

From the SEM pictures of the coated fibres, it observed that the obtained coating layers for 3wt.% and 6wt.% concentrations of the three types of Pebax® are good and clear layers which are also distributed in a uniform way around the PP hollow fibre. But for 9wt.% and 15wt.% concentrations which are prepared only from Pebax®-1657, it's observed that the coating layers are very bad layers and are not distributed uniformly around the PP hollow fibres as shown in figures 45 and 46, The 3wt.% and 6wt.% solutions were less viscous than the 9wt.% and 15wt.% solutions, thus when coat using the dip manual coating method, the solution quickly spread and distributed uniformly before the solvent evaporate making the thickness of the membrane uniform along the fibre [55]. However, the exact values for the thickness of the coating layers will be clarified and discussed in the next section (4.2.5). When the concentration of the polymer increase, the deal with the coating solution in our work become harder because the solution with high concentration become a gel like very fast [33], and it was very hard to control the temperature for the fibres themselves as the fibres in each coating experiment should dip in the coating solution more than one time and between each dip and another should dry at room temperature from 15-20 minutes and in this time the solvent evaporates fast and the polymer was distributed on the PP hollow fibre in a form of clots along the hollow fibre (as shown in figures 45 and 46). For that only one module was built up for these two concentrations (9wt.% and 15wt.%) to see how is that nonuniform layers behave during the GP test, and no solutions for the other two types of Pebax® which are Pebax®-5513 and Pebax®-1074 were prepared, only 3wt.% and 6wt.% concentration were tested. As mentioned in section (3.3.2.2), 20 modules were built for the manual dip coating experiments, for each experiment three modules were built to be test with GP unit and take the average of each three modules for the result, and the overview of these modules clarified in table 9 above. The results of GP test for these modules will be shown and discussed in the next sections of this chapter (4.3.2.1) and (4.3.2.2).

### 4.2.5 Thickness of coating layers done by dip manual coating

**Figure 51: Thickness values of different coating layers of Pebax®-1657, Pebax®-5513, and Pebax®-1074 at 3wt.% and 6wt.% concentrations .**

The thickness of the coating layer was measured at 10 different locations along the coated fibre two in each quadrant and two in the centre). All thicknesses measurements were done by using SEM images.

Figure 51, illustrates thickness values of different three types of Pebax® with a 3wt.% and 6wt.% concentrations for each type. From this figure it observed that in all of the three types of the polymer the thickness of the coating layer in 6wt.% concentration is higher than the thickness in 3wt.% concentration, so when the concentration of the polymer increase the thickness of the coating layer increase [3]. Most of the other researchers in this field were control the thickness of the coating layers exactly as they want under any concentration using wires of different diameters when coating or casting with the polymer solution, and then get the exact value they want [33].

The thickness of the coating layer at 3wt.% concentration for the Pebax®-5513 is the lowest thickness 1.7µm, and Pebax®-1657 is the higher thickness at the same concentration 3.5µm. For the 6wt.% concentration the Pebax®-5513 has the higher thickness of the coating layer 9.6µm and Pebax®-1074 has the lowest thickness of the coating layer 6.7µm. However, the three types of the polymer in both concentrations are close to each other in the three types of Pebax®, so the thickness values at 3wt.% is in the range of (1.5-3.5µm), and the thickness values at 6wt.% concentration is in the range of (6.5-9.5µm).

## *4.3 Membrane performance*

All the coating fibres experiments were repeated 3 times to yield the average results with standard deviation. After taking SEM Pictures of coated fibres to study the membrane morphology and examine the distribution of the coating layer, the coated samples placed in the fibre's modules to be test with GP unit and see their performance and permeabilities and selectivity of $CO_2$ and $N_2$ gases. Samples coated with machine were tested also with $O_2$ gas. The permeabilities for gases were measured from the definer which connected to the GP unit, and for the selectivity (αA/B) which describes the ratio of gas pair permeability it was calculated by took the ratio of measured permeabilities of high permeable gas over low permeable gas. The results of permeabilities and selectivity for samples coated with machine and samples coated manually will be shown and discussed in the following sections.

### 4.3.1 Results of gas permeation tests [machine coating]

In this section, the results of GP test for samples coated with the coating machine had been shown and discussed. As mentioned in the previous sections, three modules for each machine coating experiment at different concentration of Pebax®-1657 and different take up speeds were built to be tested with GP unit and then take the average of the results of the three modules.

The GP test was done for 6% concentration of Pebax®-1657 at three different take up speeds (20,100 and 220 mm/s), then the work of this thesis was transferred to the manual dip coating, the average results of GP for each experiment will clarify below, when the results were not consistent the results from module were not considered (possibility of having a broken / blocked module). The modules description and modules overview was discussed and clarified above in section (3.3.2.2 - fibres modules for GP test – table 8).

#### *4.3.1.1 Permeabilities of gases*

#### (Pebax®-1657)

#### (Take-up speed 20mm/s)

PP fibres samples coated with 6% concentration of Pebax®-1657 dissolved in EtOH/$H_2O$ (70/30) at take-up speed equal 20 mm/s were investigated using modules and GP unit to see their Permeance and selectivity for the three gases ($CO_2$ ,$N_2$, and $O_2$), the result showed that the samples had a high gas permeability for the three gases and with increasing the feed pressure from 1-3 bar, the value of the permeability was increased due to the plasticization of membrane caused by relatively high solubility of $CO_2$ in the membrane [4]. At ΔP=3 bar one can notice that permeance values of the three gases was the same which mean that the modules were broken, this is because of the small thickness of coating layer at this speed as mentioned before in section 4.2.3. Figure 52 illustrates the result of gases permeability through the modules.

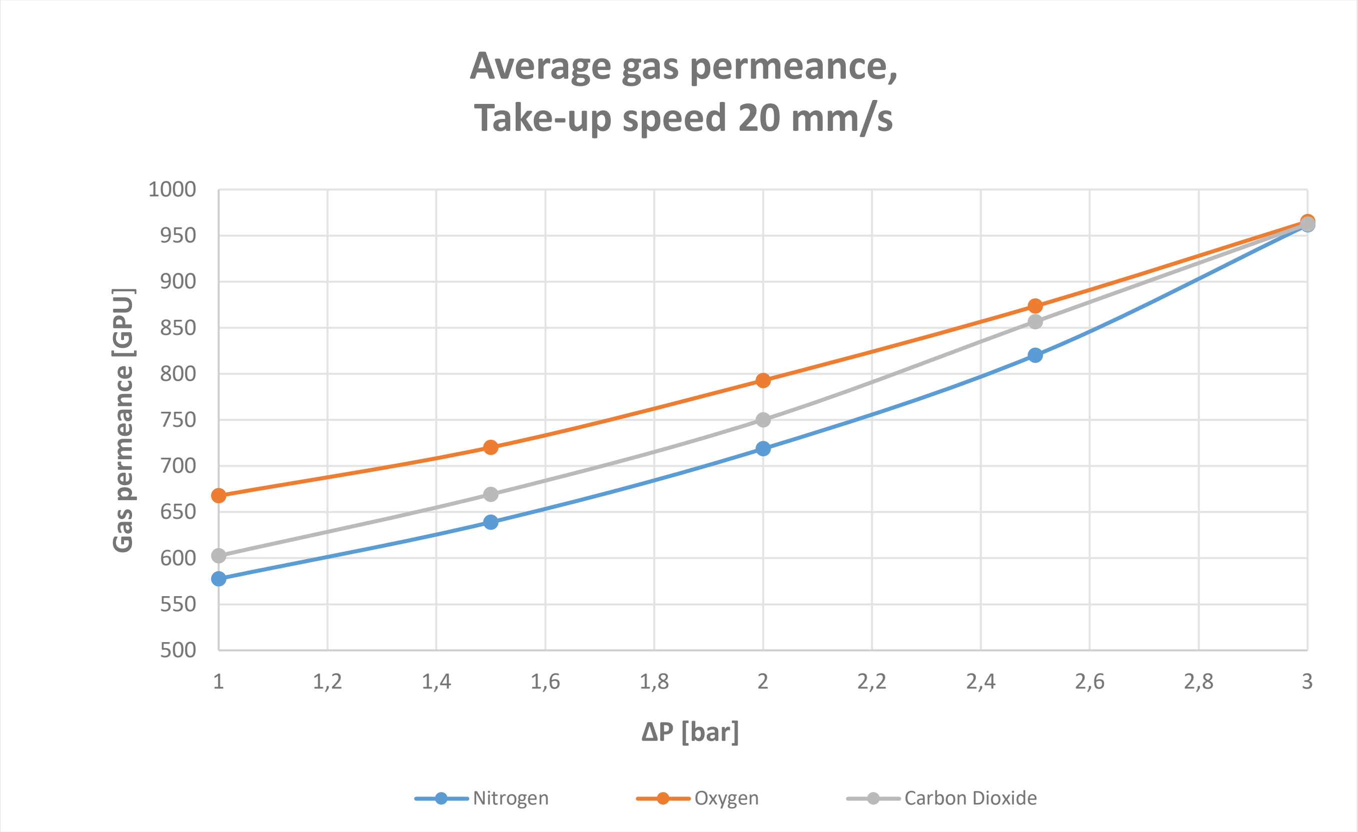


**Figure 52: $N_2$ ,$O_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 6% Pebax®-1657 at take-up speed=20 mm/s.**

**(Take-up speed 100mm/s)**

For PP fibres samples coated with 6% concentration of Pebax-1657 dissolved in EtOH/$H_2O$ (70/30) at take-up speed equal 100 mm/s, the result showed that the samples had a lower values of gas permeability for the three gases than the values of the same gases at take-up speed =20 mm/s, and with increasing the feed pressure from 1-3 bar, the value of the permeability was increased [4]. At ΔP=3 bar the modules were not broken as happened with the previous samples (samples coated at take-up speed=20 mm/s) because the thickness of the obtained coating layer was much higher under 100 mm/s take-up speed than 20 mm/s. Figure 53, illustrates the result of gases permeability through the modules.

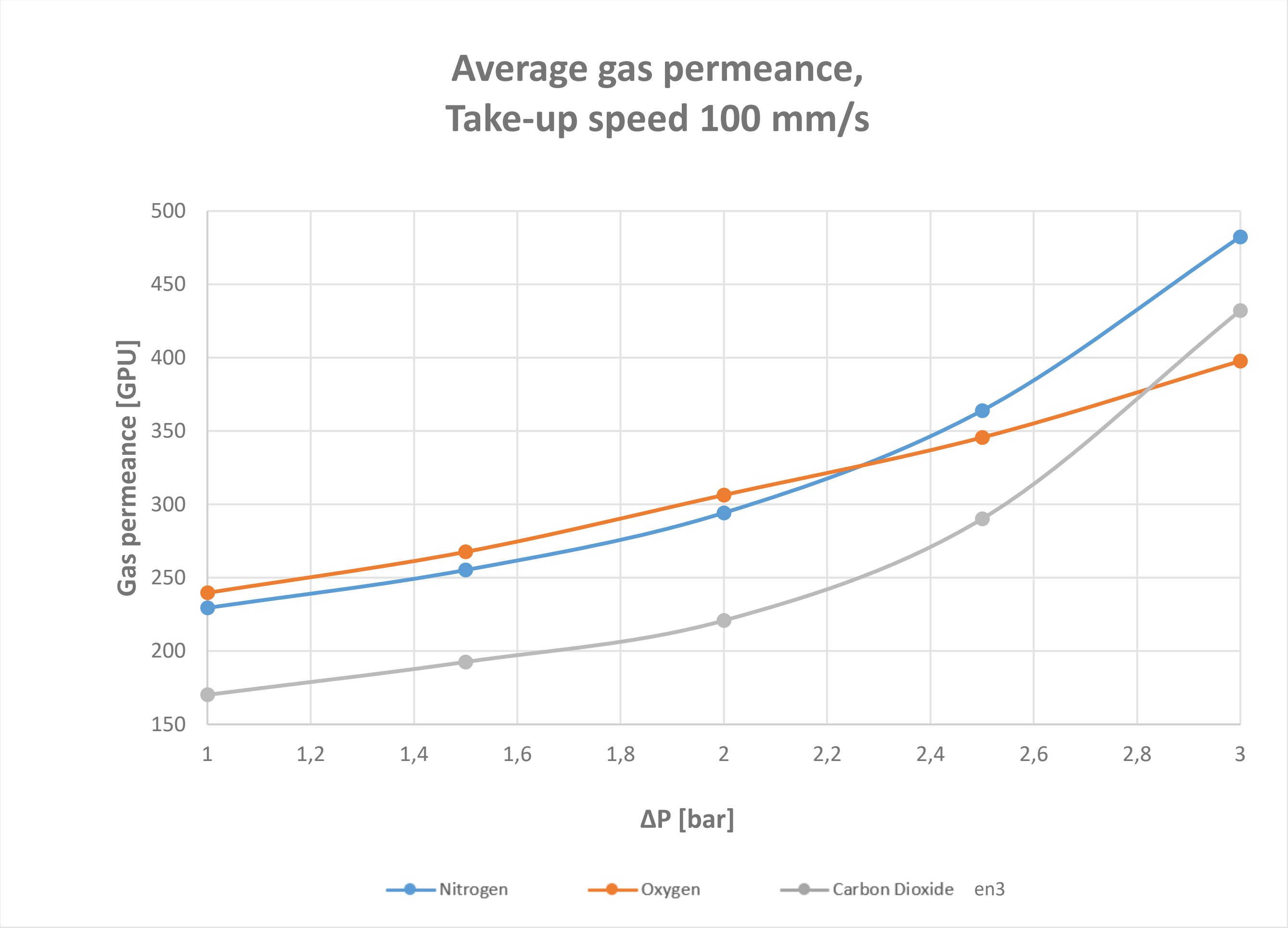


**Figure 53: $N_2$, $O_2$, and $CO_2$ average gas permeances of modules of PP fibres coated with 6% Pebax®-1657 at take-up speed=100 mm/s.**

### (Take-up speed 220mm/s)

PP fibres samples coated with 6% concentration of Pebax-1657 dissolved in EtOH/$H_2O$ (70/30) at take-up speed equal 220 mm/s showed that the samples had a lower gas permeability for the three gases than the previous take-up speeds (20 and 100 mm/s), the reason of the low permeability values is that the thickness is higher and increase with increasing the take-up speed, more details can be found in section (*4.2.3-Thickness of coating's layers done by machine coating*) and with increasing the feed pressure from 1-3 bar, the value of the permeability was increased [4]. At ΔP=3 bar the modules were working and referring to thickness section 4.2.3 one can see that 220 mm/s take-up speed has got the highest thickness value for the coating layer. Figure 54 illustrates the result of gases permeability through the modules.

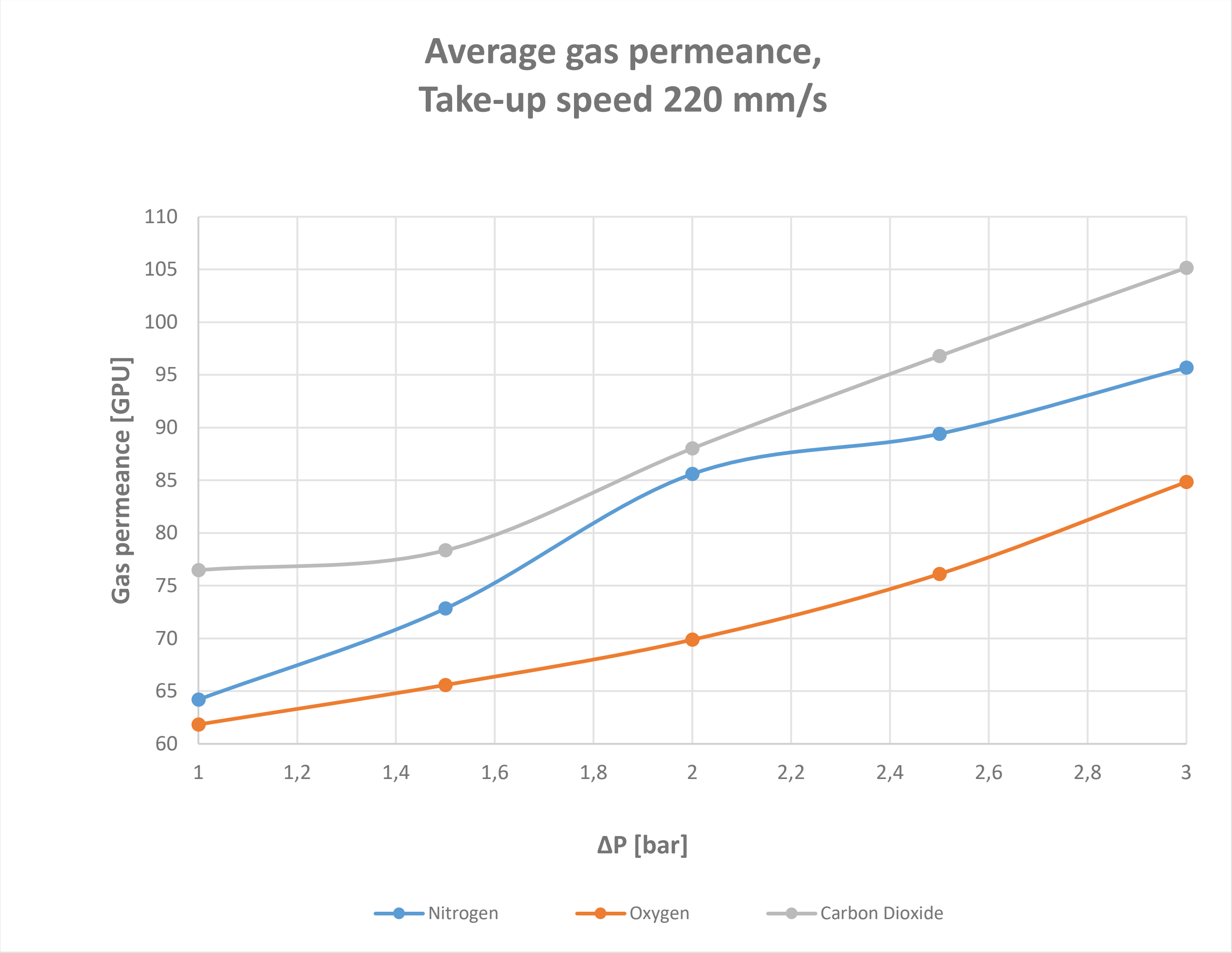


**Figure 54: $N_2$,$O_2$and $CO_2$ average gas permeances of modules of PP fibres coated with 6% Pebax-1657 at take-up speed=220 mm/s.**

For the chosen ΔP = 3 bar, average permeance of 3 gases values were plotted as function of the fibres take-up speeds (table 14 and figure 54).

**Table 14: Average gas permeance of different take-up speeds at ΔP = 3 bar**

| Average gas permeance at ΔP = 3 bar | | | |
|---|---|---|---|
| Take-up speed [mm/s] | $N_2$ | $O_2$ | $CO_2$ |
| 20 | 961,61 | 965,22 | 962,52 |
| 100 | 482,47 | 397,78 | 432,19 |
| 220 | 95,68 | 84,84 | 105,16 |

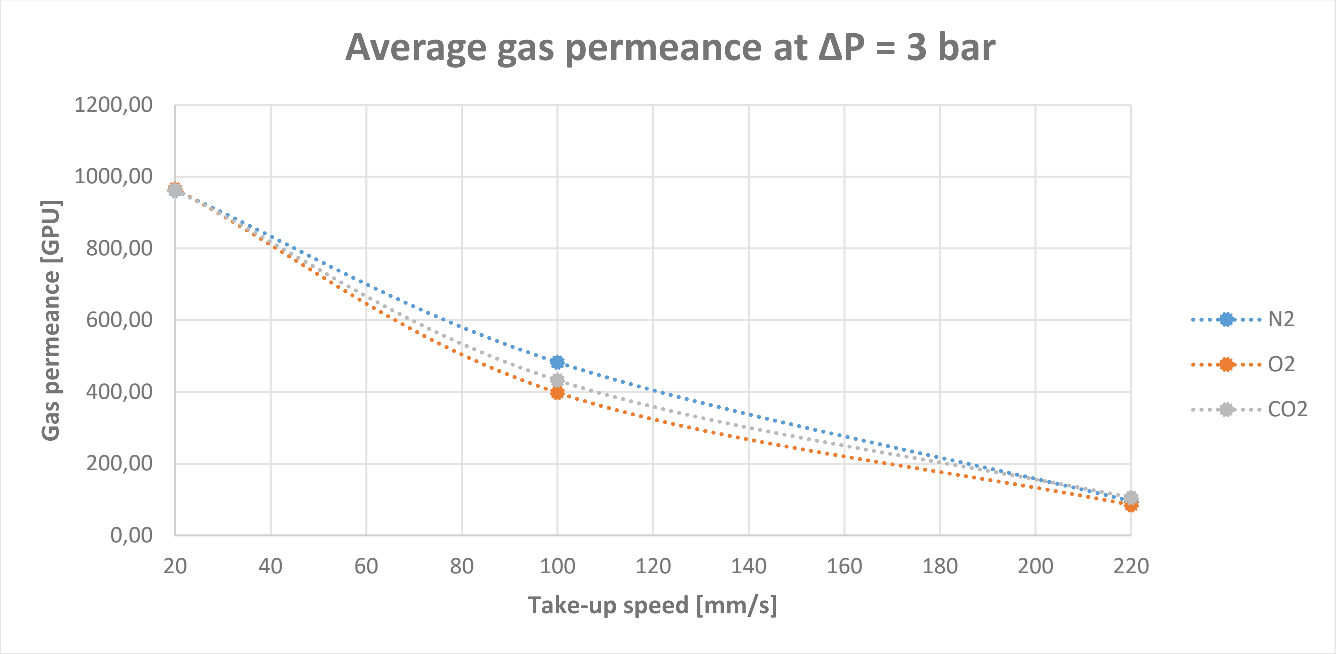


**Figure 55: $N_2$, $O_2$, and $CO_2$ average gas permeances of different take-up speeds at ΔP=3 bar.**

As mentioned before the permeability of the samples of PP coated fibres decrease with increasing the take up speed (see figure 55). The reason of this is that the thickness of the coating layer for PP fibres coated at higher take-up speeds was higher than the thickness of PP fibres coated under a lower take-up speed. More details can be found in section (4.2.3).

### *4.3.1.2 Selectivity of gases*

As discussed in section (2.5.2.1) the ideal selectivity of the membrane measured by the permeability ratio. Normally there exists a trade-off between permeability and selectivity, where an increase in permeability is often coupled with a decrease in selectivity [29],[24],[56].

This section is illustrated the calculated selectivity for the three gases $CO_2$,$N_2$ and $O_2$, (see figures 56,57 and 58). Although the values of selectivity were not exceed 1.5 which mean a very small selectivity but the results showed that the higher take up-speed (220m/s) has higher values of selectivity than the other lower speeds (100 and 20 mm/s) and this result is in agreement with the trade-off relation between selectivity and permeability [29],[24],[56]. as the higher speed (220mm/s) had the lower values of permeability than the other tested take-up speeds (100 and 20 mm/s).

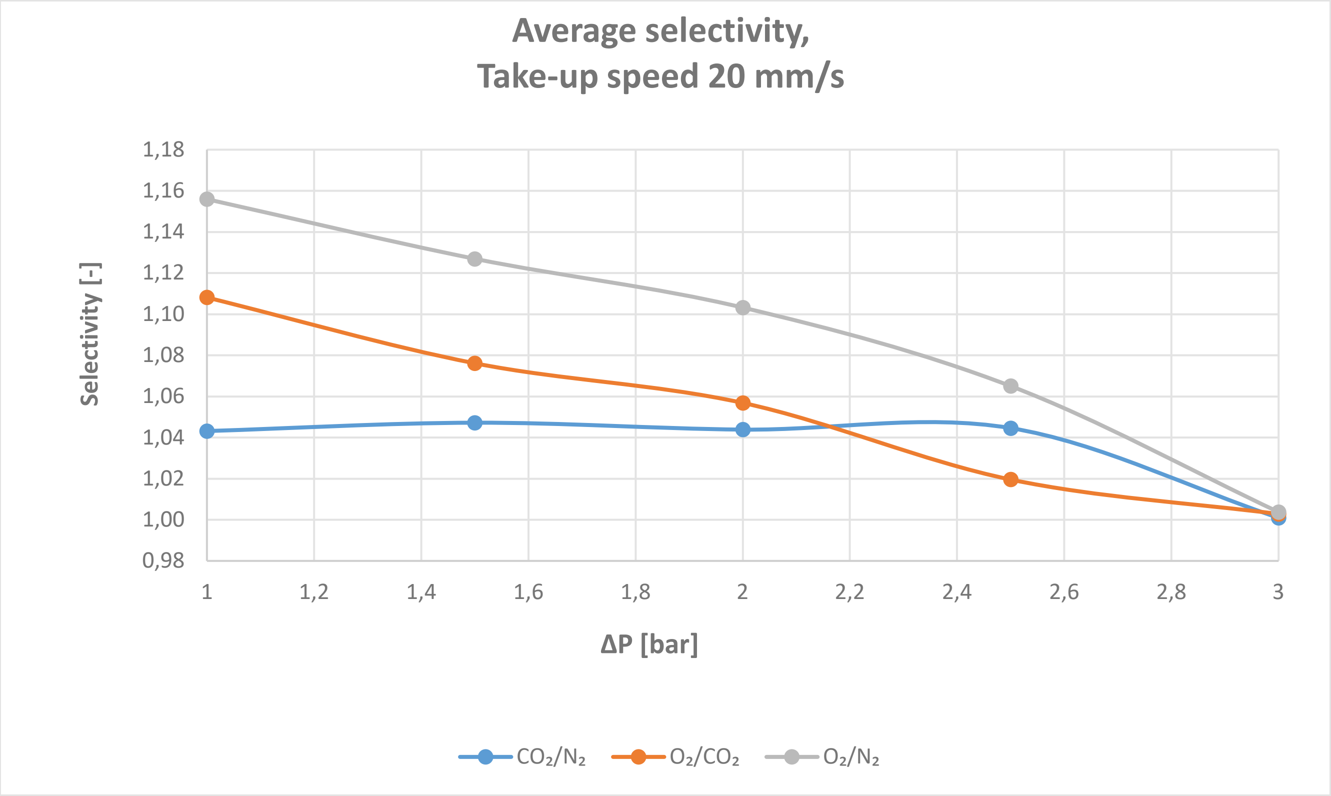


**Figure 56: $N_2$, $O_2$, and $CO_2$ average gas selectivities of modules of PP fibres coated with 6% Pebax-1657 at take-up speed=20 mm/s.**

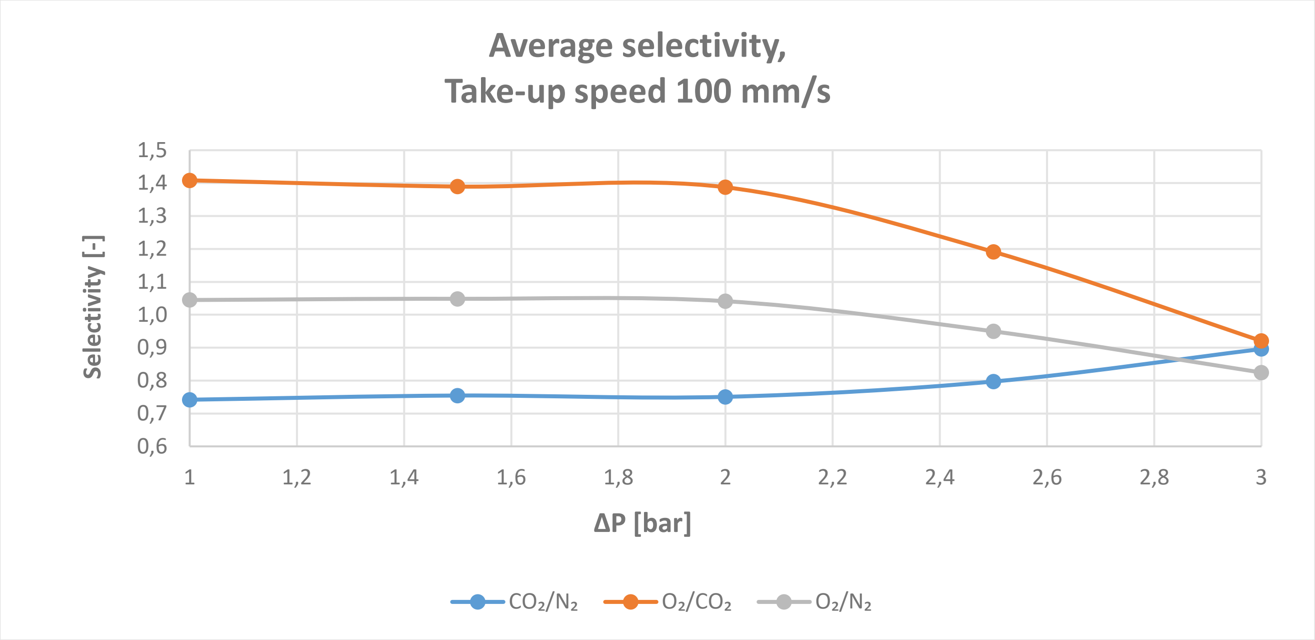


**Figure 57: $N_2$, $O_2$, and $CO_2$ average gas selectivities of modules of PP fibres coated with 6% Pebax-1657 at take-up speed=100 mm/s.**

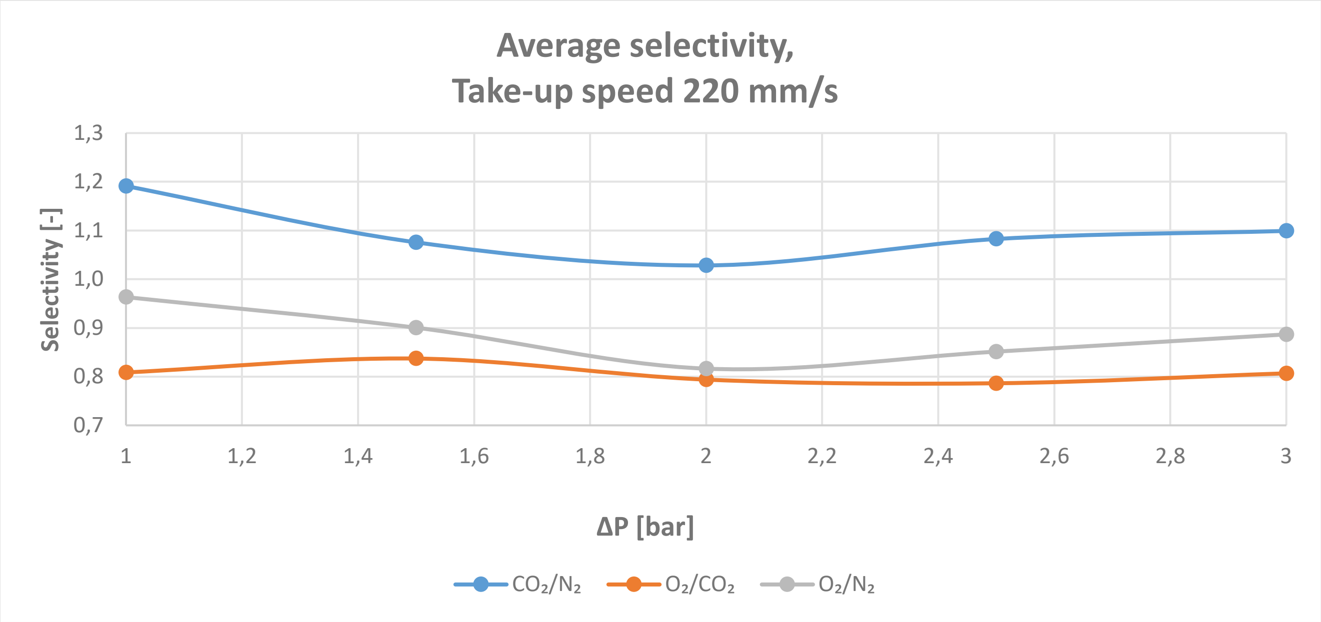


**Figure 58: $N_2$, $O_2$, and $CO_2$ average gas selectivities of modules of PP fibres coated with 6% Pebax-1657 at take-up speed=220 mm/s.**

All of the modules exhibited very high gas permeances, but poor selectivity.Observed tendency for higher take-up speeds → lower permeances → proof of the higher coating thickness (results in agreement with SEM images) → higher selectivity [29],[24],[56].

### 4.3.2 Results of gas permeation tests [dip manual coating]

In this section the results of GP test for samples coated manually will be shown and discussed. As mentioned in the previous sections, three modules for each manual dip experiment with different concentration of Pebax®(3% and 6%) and different types of Pebax®(Pebax®-1657,Pebax®-5513 and Pebax®-1074) were built to be tested with GP unit and then take the average of the results of the three modules, the average results of GP for each experiment will clarify below, when the results were not consistent the results from module were not considered (possibility of having a broken / blocked module). In manual coating part $CO_2$ and $N_2$ gases were tested with the GP unit. The modules description and modules overview was discussed and clarified above in section (3.3.2.2 - Fibres Modules for GP test – table 9).

#### *4.3.2.1 Permeabilities of gases*

**(Pebax®-1657):**

Samples of PP fibres coated manually with 3% concentration of Pebax®-1657 dissolved in EtOH/$H_2O$ (70/30) showed a gas permeability of (99.5 - 118.3)GPU for $CO_2$ and (84.7-99.0)GPU for $N_2$ at ΔP=(4-9)bar, the reason of high permeability of $CO_2$ was probably due to the plasticization of membrane caused by relatively high solubility of $CO_2$ in the membrane. Also, the permeability of both gases increase with increasing the feed pressure [4]. Figure 59 below shows the results of permeability in details.

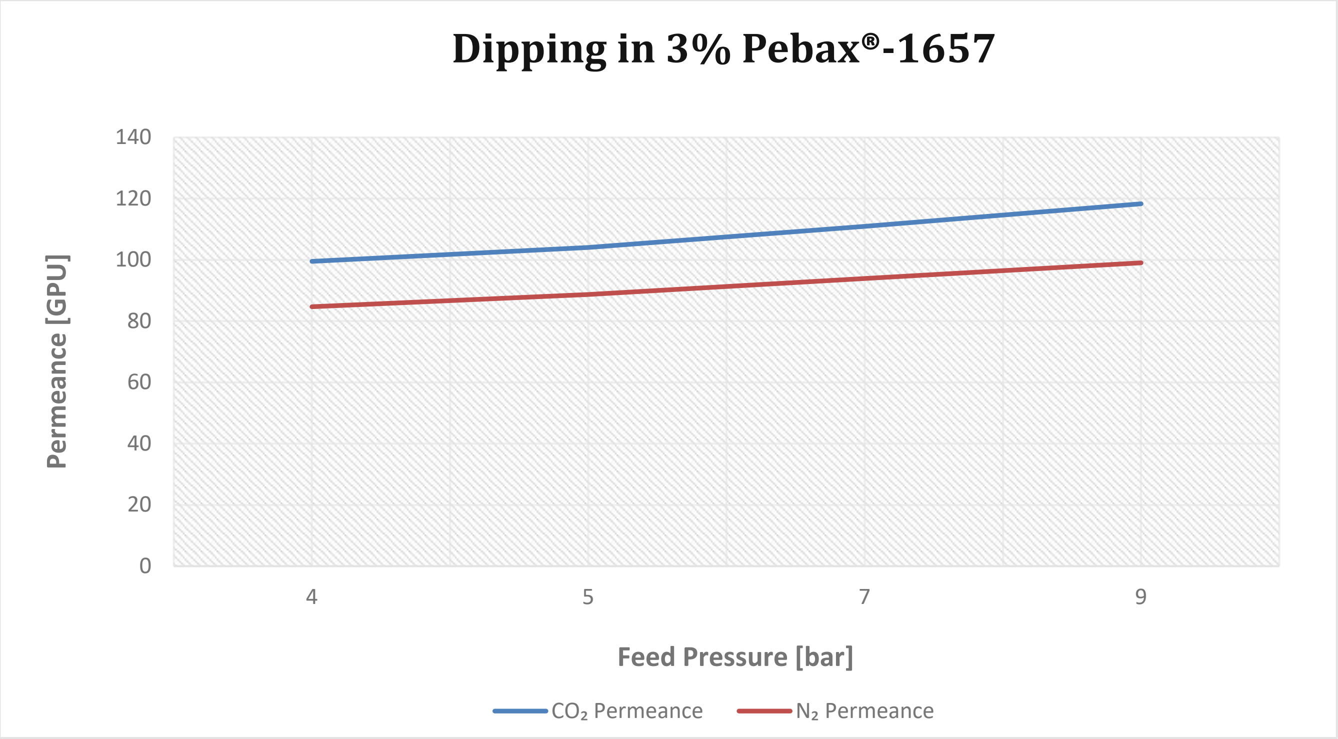


**Figure 59: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 3% Pebax®-1657 manually.**

Now for samples of PP fibres coated manually with 6% concentration of Pebax-1657 dissolved in EtOH/$H_2O$ (70/30) a gas permeability of (66.0 – 68.2)GPU for $CO_2$ and (17.8-23.1)GPU for N2 at ΔP=(4-9)bar had been got. The gases permeance decreases with increasing concentration of the coating solution [56]. Figure 60 below shows the results of permeability in details.

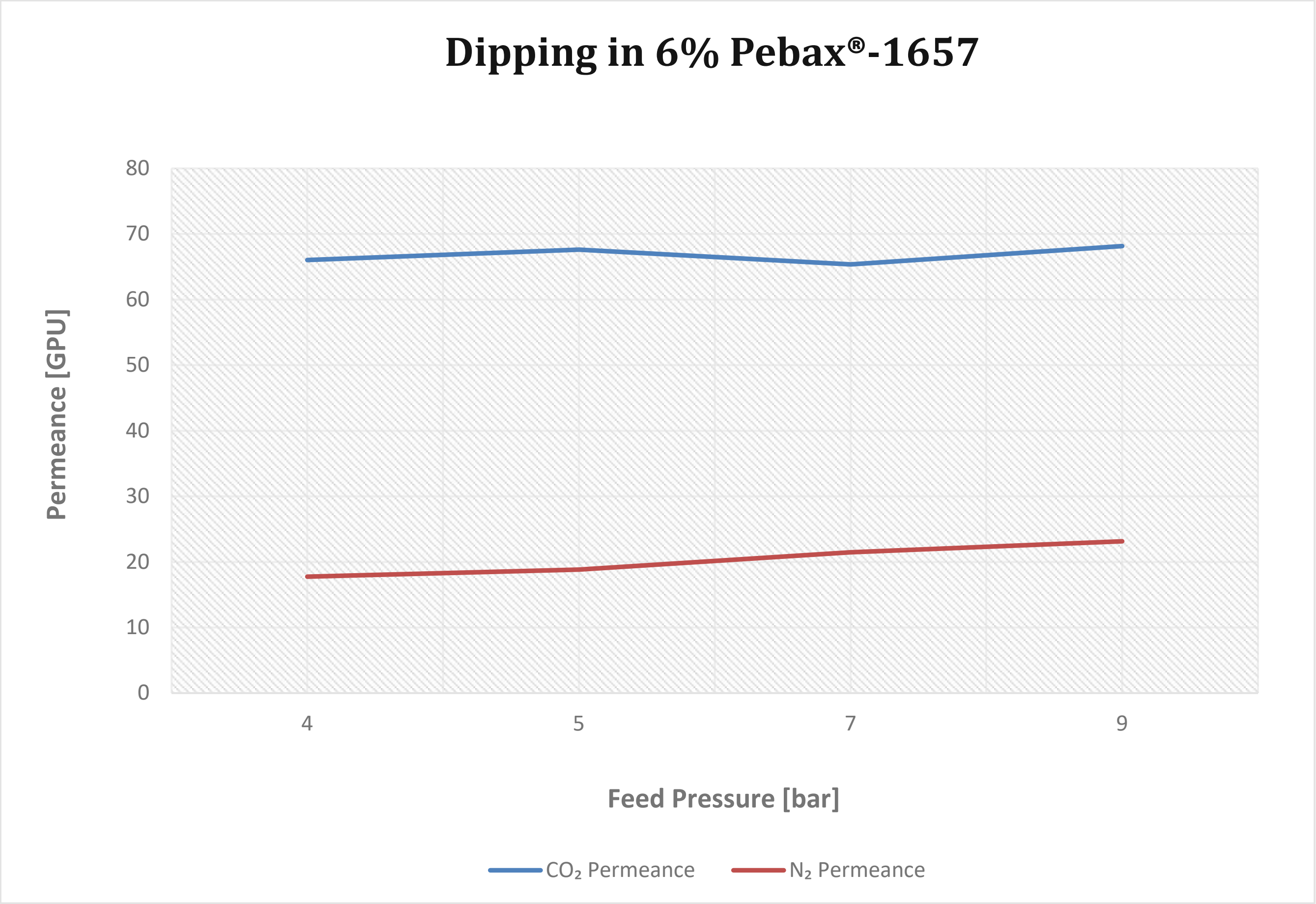


**Figure 60: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 6% Pebax®-1657 manually.**

For 9% and 15% concentration of Pebax®-1657 as mentioned before that the solution was very bad for coating, random distribution of the coating layer on the PP fibres and therefore the thickness was differed along the fibre and not uniformly distributed. Experiments under these concentrations was not repeated so only one module for these experiments were built and the results of permeability are shown in the following two figures (figure 61 for 9% concentration and figure 62 for 15% concentration).

The following figure (figure 61) shows $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 9% Pebax®-1657 manually. It noticed that at 4 bar the permeance was 174.99 GPU and 150.08 GPU for $N_2$ and $CO_2$ respectively and then with increasing the feed pressure the permeance values were dropped and became approximately similar for both gases so there was no selectivity.

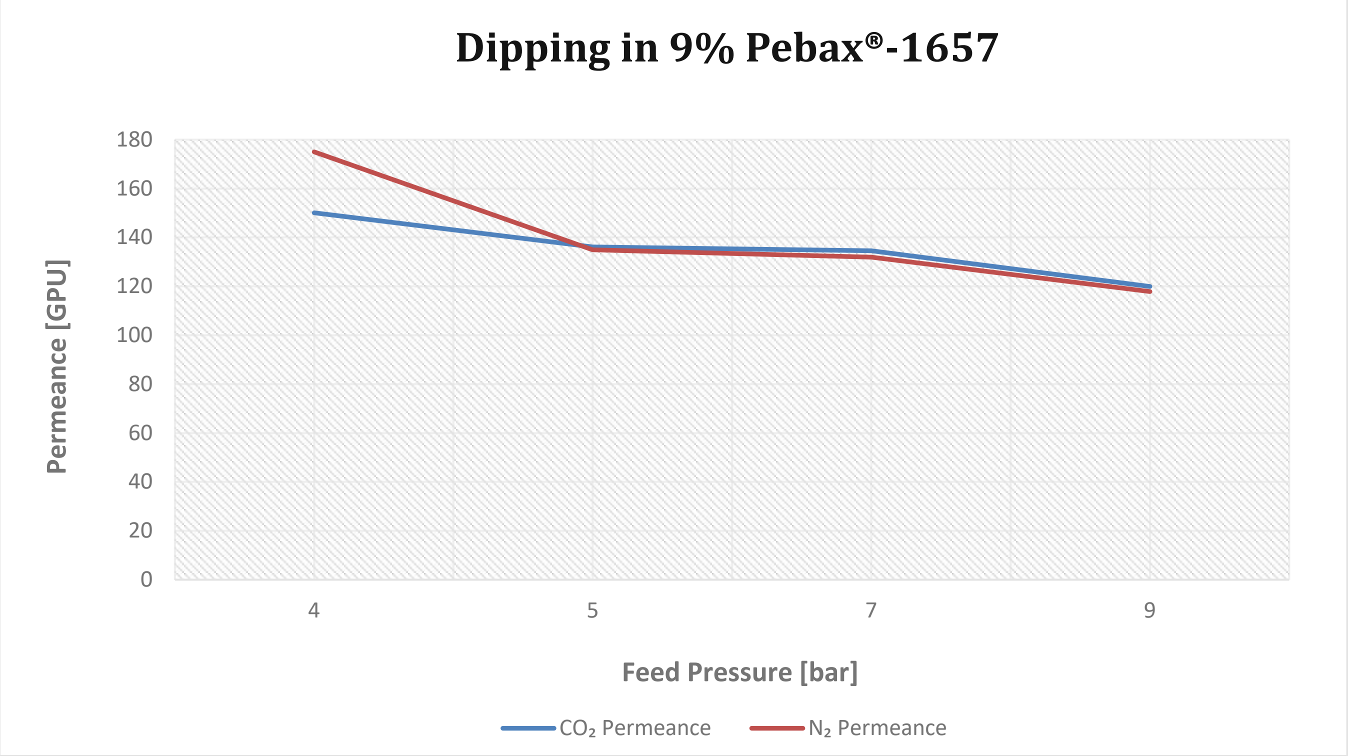


Figure 61: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 9% Pebax®-1657 manually.

The following figure (figure 62) shows $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 15% Pebax®-1657 manually.

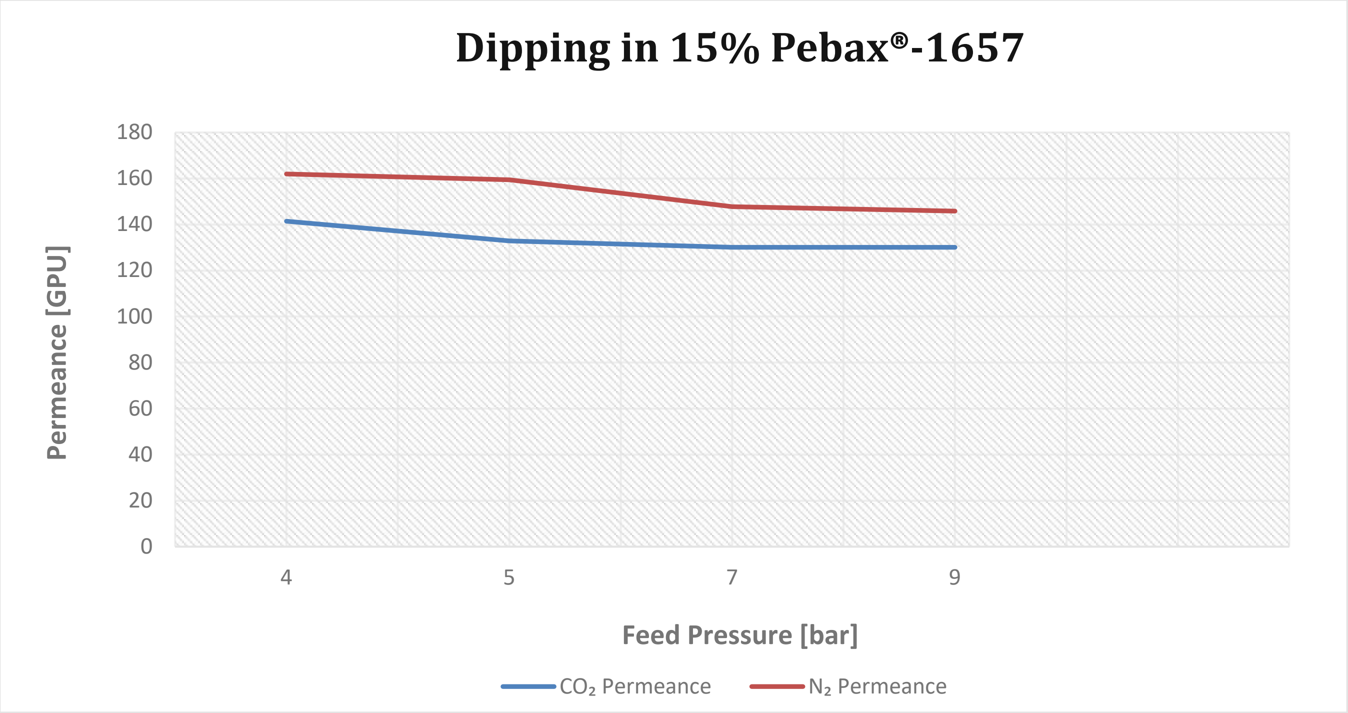


Figure 62: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 15% Pebax®-1657 manually.

From the previous two figures (61 and 62) it noticed that the permeability values for 9% concentration were higher than the permeability values for 15% concentration for both gases $CO_2$ and $N_2$, the results agreed with the previous results at 3% and 6% concentrations, the gases permeance decreases with increasing concentration of the coating solution [56].

The next two types of Pebax (Pebax®-5531 and Pebax®-1074) were prepared with concentrations of 3% and 6% of Pebax® in the solution.

**(Pebax®-5513):**

Samples of PP fibres coated manually with 3% concentration of Pebax®-5513 dissolved in EtOH/$H_2O$ (70/30) showed a gas permeability of (43.4-76.7)GPU for $CO_2$ and (34.8-55.7)GPU for $N_2$ at ΔP=(2-7)bar. The permeability of both gases increase with increasing the feed pressure , the values of permeability at 3% concentration of this type of Pebax® (Pebax®-5513) is lower than the permeability values under 3% concentration of the previous type of Pebax (Pebax®-1657). Also it noticed that after 5 bar the permeability increased for both gases and this is maybe because the porosity of fibres increase when increasing the feed pressure [5]. Figure 63 below shows the results of permeability in details.

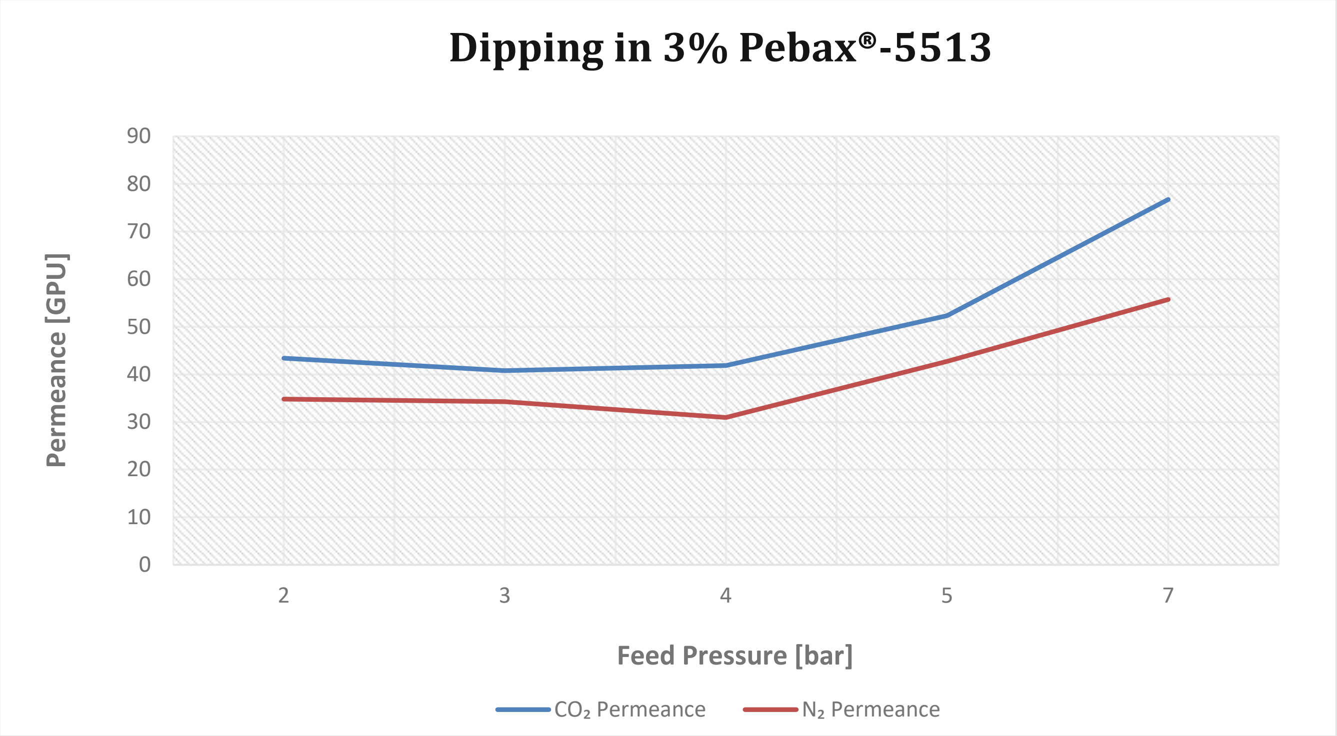


**Figure 63: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 3% Pebax®-5513 manually.**

Now for samples of PP fibres coated manually with 6% concentration of Pebax®-5513 dissolved in EtOH/$H_2O$ (70/30) a gas permeability of (40.9 – 54.4)GPU for $CO_2$ and (14.3 – 18.0)GPU for $N_2$ at ΔP=(2-7)bar had been got from the GP unit, the values of permeability at 6% concentration of this type of Pebax® (Pebax®-5513) are lower than the permeability values under 6% concentration of the previous type of Pebax® (Pebax®-1657). The gases permeance decreases with increasing concentration of the coating solution [56]. Also, it worth noticing that also here the permeability for both gases increased after 5 bar and this is probably due to increasing in porosity of the membrane with increasing the feed pressure [5]. Figure 64 below shows the results of permeability in details.

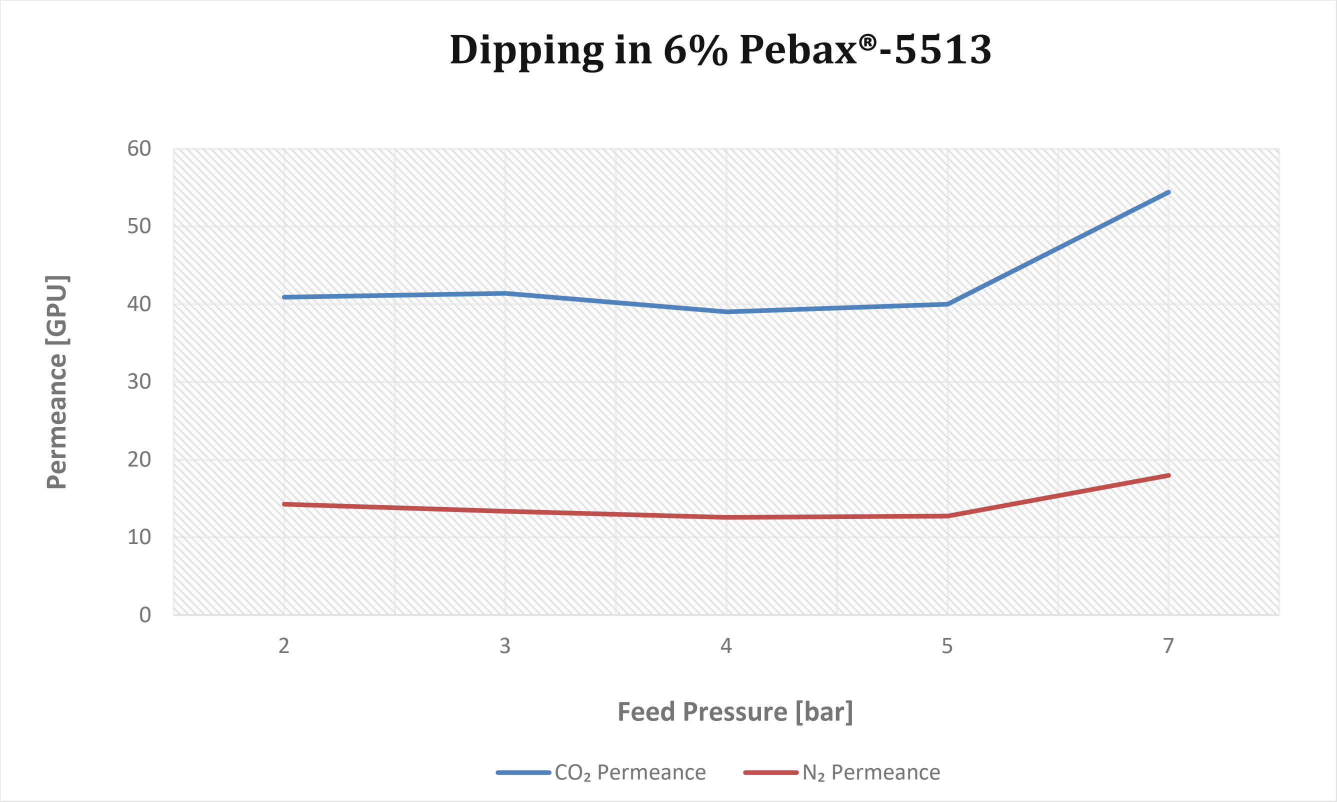


**Figure 64: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 6% Pebax®-5513 manually.**

By comparing the previous two types of Pebax® (Pebax®-1657 and Pebax®-5513) one can notice that under both concentrations of 3% and 6% of Pebax® in the coating solution; type 1657 had higher values of gas permeability than type 5513. The selectivity of both types will be shown and discussed in a coming section.

**(Pebax®-1074):**

Samples of PP fibres coated manually with 3% concentration of Pebax-1074 dissolved in $EtOH/H_2O$ (70/30) showed a gas permeability of (521.4 – 500.1)GPU for $CO_2$ and (469 – 461.4)GPU for $N_2$ at $\Delta P$=(2-7)bar. The permeability of both gases increase with increasing the feed pressure [4]. Noticed that the values of permeability at 3% concentration of this type of Pebax® (Pebax®-1074) is much higher than the permeability values under 3% concentration of the previous types of Pebax (Pebax®-1657 and Pebax®-5513) [33]. Figure 65 below shows the results of permeability in details.

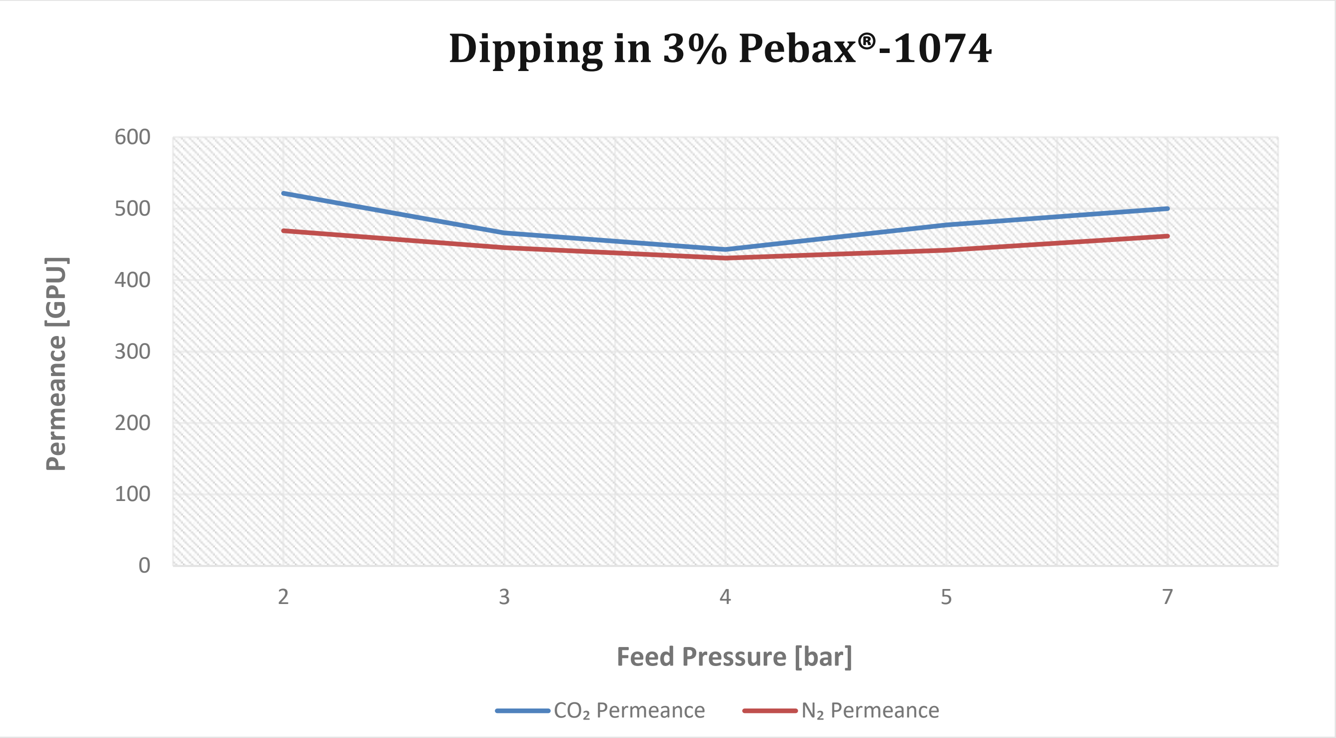


**Figure 65: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 3% Pebax®-1074 manually.**

For samples of PP fibres coated manually with 6% concentration of Pebax®-1074 dissolved in $EtOH/H_2O$ (70/30) a gas permeability of (251.7 – 232.2)GPU for $CO_2$ and (163.0 – 127.9)GPU for $N_2$ at $\Delta P$=(2-7)bar had been got from the GP unit, the values of permeability at 6% concentration of this type of Pebax® (Pebax®-1074) are much higher than the permeability values under 6% concentration of the previous types of Pebax® (Pebax®-1657 and Pebax®-5513). The gases permeance decreases with increasing concentration of the coating solution [56]. Figure 66 below shows the results of permeability in details.

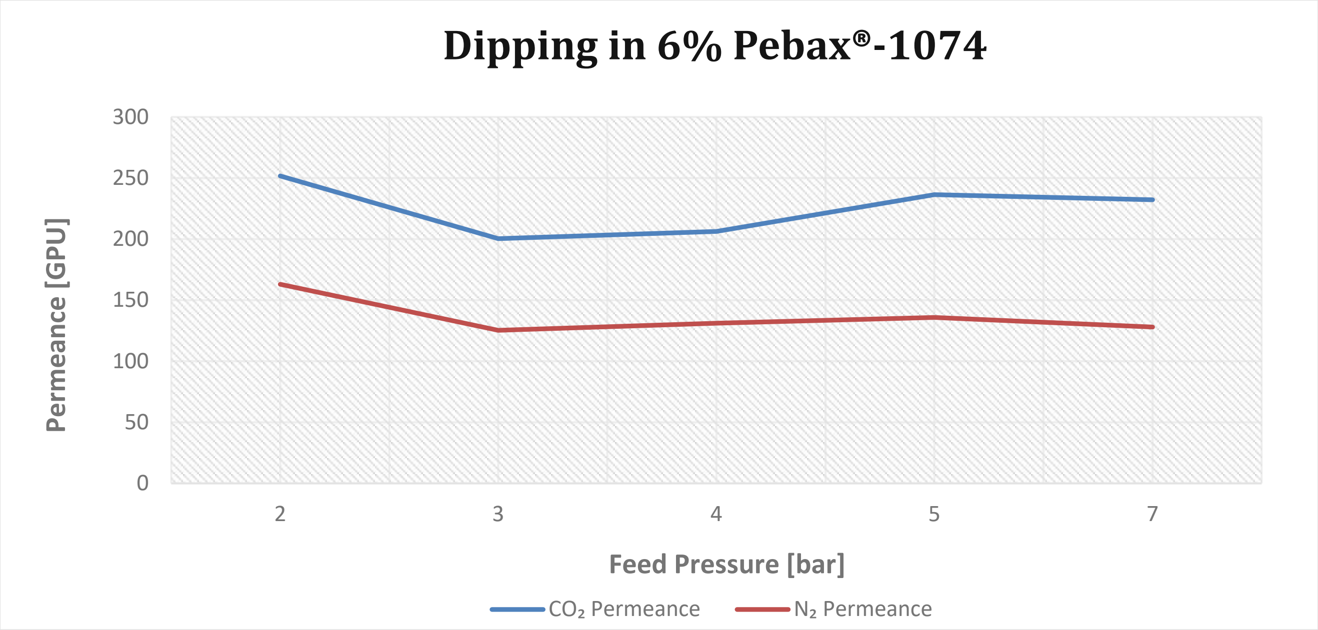


**Figure 66: $N_2$ and $CO_2$ average gas permeances of modules of PP fibres coated with 6% Pebax®-1074 manually.**

By comparing the previous results of the three types of Pebax® (Pebax®-1657,Pebax®-5513 and Pebax®-1074) one can notice that under both concentrations of 3% and 6% of Pebax® in the coating solution, Pebax®-1657 had higher values of gas permeability than Pebax®- 5513. Pebax®-1074 had the highest values of permeability between the three types [6],[33]. Also, in all experiments with the three types of Pebax and with all concentrations $CO_2$ gas had a higher permeability in the module than $N_2$ gas, and this was probably due to the plasticization of membrane caused by relatively high solubility of $CO_2$ in the membrane [4], and as mentioned before the soft segment in Pebax copolymer had a high affinity to $CO_2$ gas. The selectivity results of the three types will be calculated, shown, and discussed in the following section.

#### *4.3.2.2 Selectivity of gases*

As mentioned in section (2.5.2.1) the ideal selectivity of the membrane measured by the permeability ratio. Normally there exists a trade-off between permeability and selectivity, where an increase in permeability is often coupled with a decrease in selectivity [29],[24],[56].

The following section will illustrate the calculated selectivity of $CO_2/N_2$ gas. the values of selectivity were not high values which mean that coating PP fibres with these types of Pebax® under the used concentrations is not a promise application for $CO_2/N_2$ gas separation. the higher value of selectivity was 3.7 and it was for Pebax®1657 with 6% concentration of Pebax® in the coating solution, the value of selectivity here is much higher than the value of selectivity for samples had been coated using machine with this type of Pebax®-1657 and under the same concentration (6%).

The selectivity for each type had higher values in 6% concentration than 3% concentration of the same type, this result is in agreement with the trade-off relation between permeability and selectivity [29],[24],[56], as with increasing the concentration the permeability of gases decrease, then the selectivity increase [56], [57],[58],[59],[60].

The exact values of selectivity for the three types of Pebax® (Pebax-®1657, Pebax®-5513, and Pebax®-1074) are illustrated in the following figures (figure67 – figure72).

**(Pebax®-1657):**

The following figure (figure 67) shows the average selectivity of $CO_2/N_2$ for membranes coated with 3% of Pebax®-1657. It noticed that the highest value of selectivity (1.325) was at ΔP=9 bar feed pressure. This value of selectivity indicate that there was a separation between $CO_2$ gas and $N_2$ gas, but it was very small and not effective.

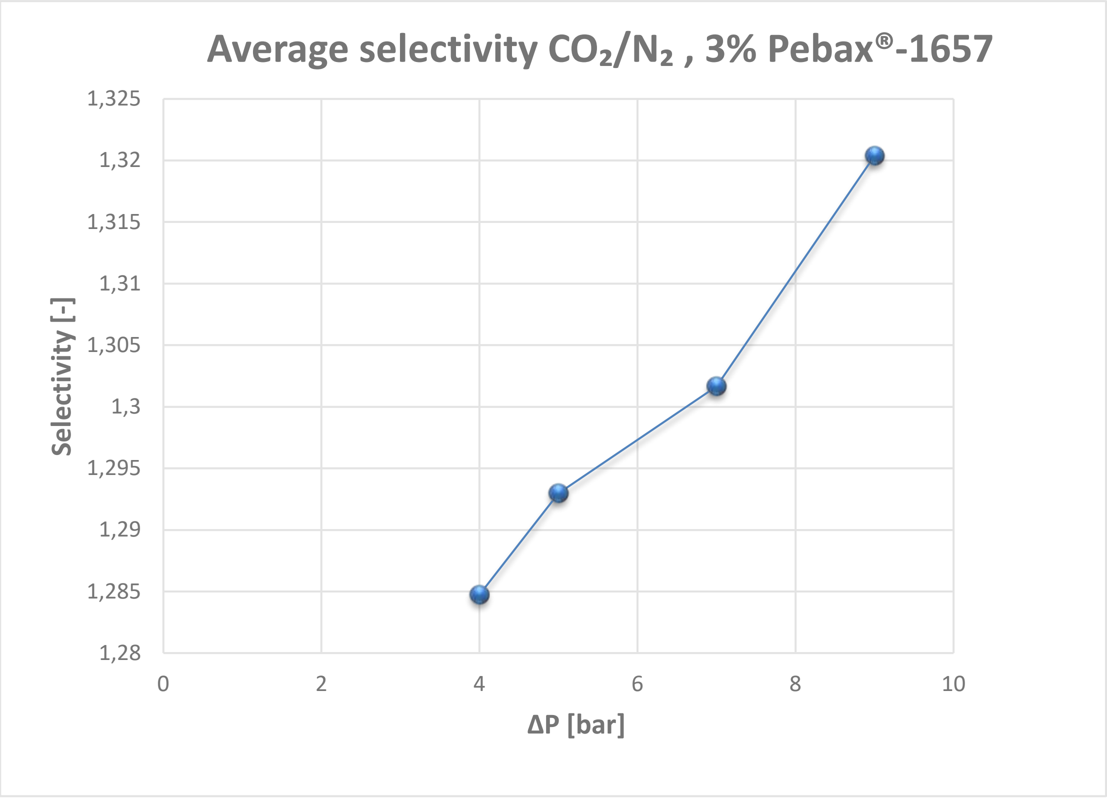


Figure 67: $CO_2/N_2$ average gas selectivity of PP fibres coated with 3% Pebax®-1657 manually.

The next figure (figure 68) shows the average selectivity of $CO_2/N_2$ for membranes coated with 6% of Pebax®-1657. It noticed that the highest value of selectivity (3.9) was at ΔP=9 bar feed pressure. The value of selectivity at this concentration (6%) is much better and effective than the value of selectivity for the same type of Pebax® which is Pebax®-1657 at a lower concentration equal 3%.

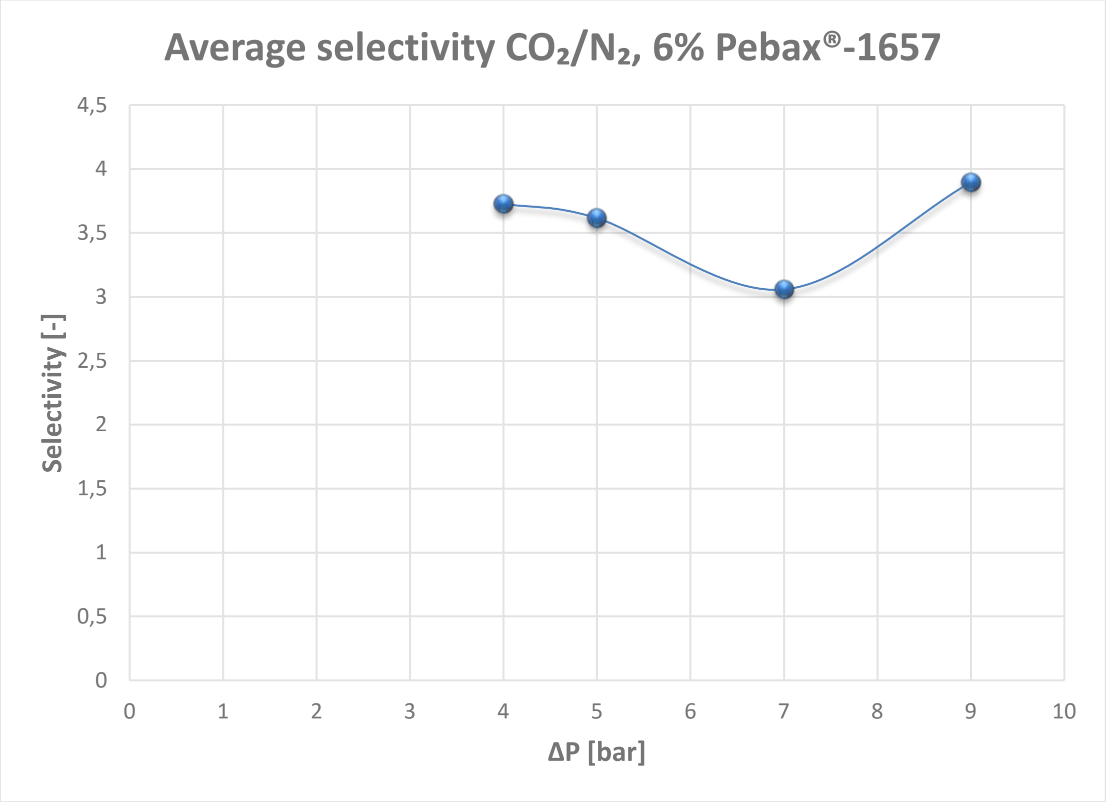


Figure 68: $CO_2/N_2$ average gas selectivity of PP fibres coated with 6% Pebax®-1657 manually.

Also, from figure 68, one can notice that the value of selectivity decrease slightly at ΔP=4-7 bar and the start to increase at ΔP=7-9 bar.

**(Pebax®-5513):**

For 3% concentration of Pebax®-5513, the following result of selectivity had been got (figure 69), from the figure one can observe that the value of selectivity was increase at ΔP=2-4 bar, then decrease at ΔP=4-5 bar, and then start increase again to reach the highest value of selectivity was equal 1.34 at ΔP=7 bar, this value of selectivity indicate that there was a separation between $CO_2$ gas and $N_2$ gas but it was very small and not effective.

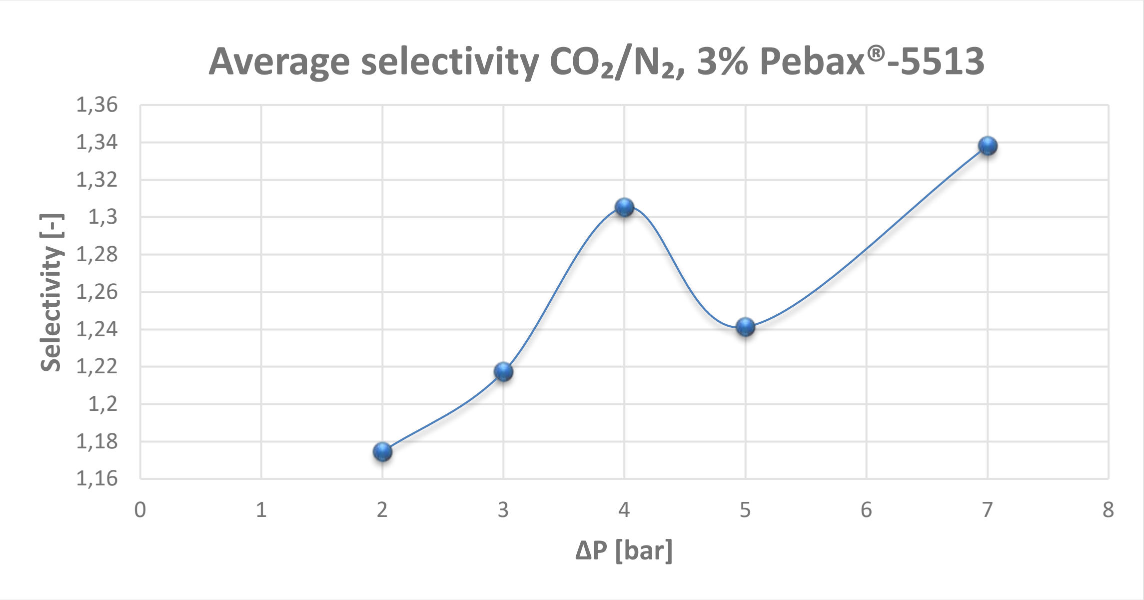


**Figure 69: $CO_2/N_2$ average gas selectivity of PP fibres coated with 3% Pebax®-5513 manually.**

Now when increasing the concentration of Pebax®-5513 from 3% to 6%, the following result of selectivity had been got (figure 70). The highest value of selectivity (3.2) was reached at ΔP=5 bar of feed pressure, this value of selectivity indicate that a higher concentration of Pebax®-5513 is much better and effective than the value of selectivity for the same type of Pebax® at a lower concentration equal 3%. In addition, comparing the selectivity result for 6% Pebax®-5513 with the selectivity result for 6% Pebax®-1657, one can observe that Pebax®-5167 has a higher selectivity (3.9) than selectivity of Pebax®-5513 (3.2).

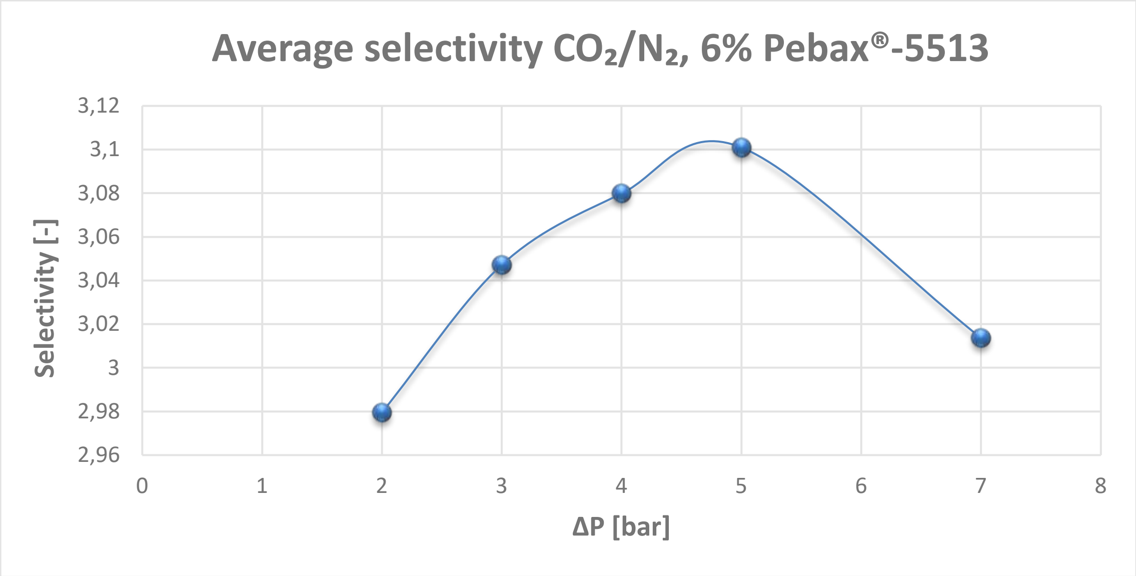


**Figure 70: $CO_2/N_2$ average gas selectivity of PP fibres coated with 6% Pebax®-5513 manually.**

Also, from figure 70 one can observe that the value of selectivity was increase from 2-5 Bar, then decrease from 5-7 Bar

**(Pebax®-1074):**

Finally, Pebax®-1074 is the third and the final type of Pebax which had been investigated in this work. For 3% concentration of Pebax®-1074 the following result of selectivity had been got (figure 71), from the figure it observed that the value of selectivity was decrease from 2-4 bar, then increase from 4-5 bar and stay at the same value from 5-7 bar. The highest value of selectivity was equal 1.13 at ΔP=2 bar, this value of selectivity indicate that there was a negligible and nor effective separation between $CO_2$ gas and $N_2$ gas.

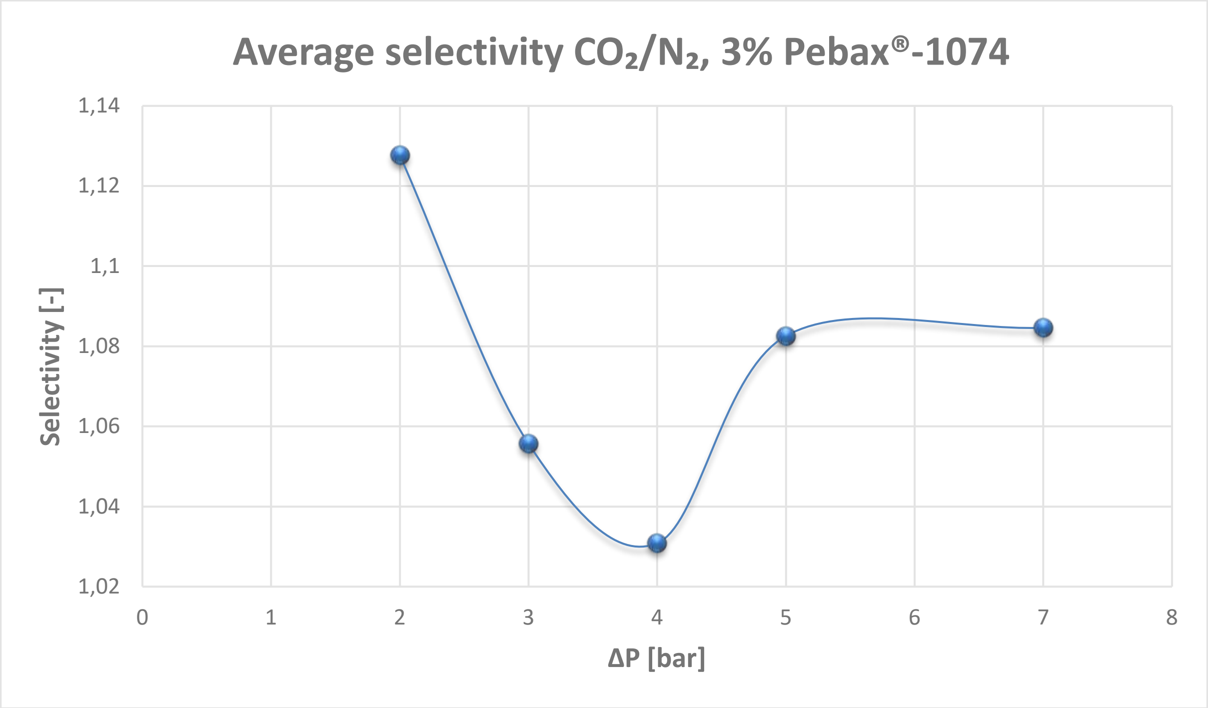


**Figure 71: $CO_2/N_2$ average gas selectivity of PP fibres coated with 3% Pebax®-1074 manually.**

Now when increasing the concentration of Pebax®-1074 from 3% to 6%, the following result of selectivity had been got (figure 72). The highest value of selectivity (1.9) was reached at ΔP=7 bar, this value of selectivity indicate that a higher concentration of Pebax®-5513 is better and slightly effective than the value of selectivity for the same type of Pebax® at a lower concentration equal 3%. In addition, comparing the selectivity result for 6% Pebax®-5513 with the selectivity results for 6% Pebax®-1657 and 6% Pebax®-5513, one can observe that Pebax®-1657 has a higher selectivity (3.9) of these three types and Pebax®-1074 has the lower selectivity (1.9).

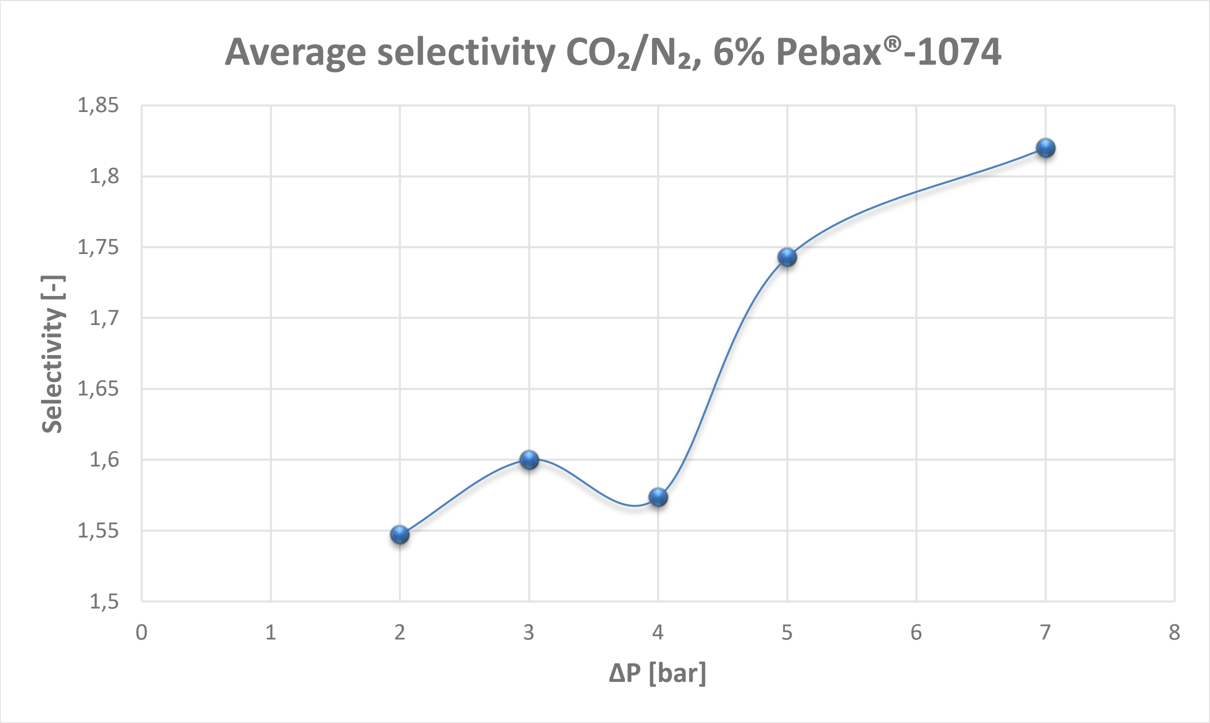


**Figure 72: $CO_2/N_2$ average gas selectivity of PP fibres coated with 6% Pebax®-1074 manually.**

Also, from figure 72 one can observe that the value of selectivity was decrease at ΔP=3-4 bar and then start increase at ΔP= 4-7 bar.

To summarise and referring to figure67 – figure72, it observed that the highest values for $CO_2/N_2$ selectivity had been got from Pebax®-1657 with 6% concentration, the selectivity was in the range of (3-3.9) at ΔP=(4 - 9)bar [6]. Also, Pebax®-5513 with 6 % concentration had the 2nd order of the high selectivity with a selectivity range of (2.8 – 3.2) at ΔP=(2 - 7)bar. Pebax®-1074 showed the lowest values of selectivity at both concentrations comparing to Pebax®-1657 and Pebax®-5513 [6].

Permeability and selectivity properties were dependent on the quantity and polarity of the PE component within the block copolymer, the polarity of the polymer increasing in presence of the segments of PEO or PA6 while maintaining the same concentration of both groups caused a decrease in the solubility of $N_2$, while carbon dioxide solubility remained unaffected. Therefore, higher $CO_2/N_2$ selectivity was obtained in Pebax®-1657 [6].

# 5. Summary and conclusions

In this study, the surface properties of the PP hollow fibre membranes were modified by coating process using a coating machine and by dip manual coating to be applied in $CO_2/N_2$ gas separation application. Three different types of Pebax® copolymer go under different concentrations, different coating speed, and different thickness had been investigated, the membrane characteristic and membrane performance was evaluated for each experiment using SEM pictures and GP unit test. At first, suitable solvent for each type of Pebax® had been tested to get a homogenous solution for coating. Machine coating procedure had been done using 6% of Pebax®-1657 in the coating solution at different take-up speeds. Then different three types of Pebax® (Pebax®-1657, Pebax®-5513, and Pebax®-1074) were compared, each type was prepared with 3% and 6% concentration dissolved in a suitable solvent and got a homogenous coating solution (Pebax®-1657 was prepared also with 9% and 15% concentration), the coating procedure of PP fibres which used with these coating solutions to compare the three types of Pebax® under different concentrations had been done manually by dip manual coating.

The results show that the solvent combination to dissolve Pebax®-1657 and Pebax®-5513 can always be used as 70/30 ethanol/water with heating these solvents in range of temperature of 75°-80°C. While Pebax®-1074, contains long polar PA12, is better dissolved in a single organic solvent such as butanol at a temperature ≥ 80°C. Also, the effect of these solvents on PP fibres was investigated using SEM pictures and the result showed that there was no effect of solvents on the PP fibres itself.

All coating solutions tend to be like a gel at room temperature without heating even under continuous stirring. Also, When the concentration of the polymer in the solution increase, the solution becomes like a gel solution faster. Compared to Pebax®-1657, Pebax®-1074 achieved a quicker solution to gel status because of its longer PA12 chain, faster solution to gel transition encourages random chain packing and this led to less regular microstructure and higher gas permeability than other two types of Pebax (Pebax®-1657 and Pebax®-5513).

Membranes which are coated with Pebax copolymer usually possess a high $CO_2$/nonpolar selectivity like $CO_2/N_2$ coupled with a higher $CO_2$ permeability due to the presence of polar ether oxygen atoms in the soft segment (PEO as in Pebax®-1657 and Pebax®-1074, or PTMO as in Pebax®-5513) that result in good $CO_2$ affinity.

Permeability properties were strongly dependent on the quantity and polarity of the PE component within the block copolymer. Gas permeability was increased as the percentage of polyether increased, Pebax®-1657 has the highest PE quantity compared to Pebax®5513 and Pebax®-1074, therefore, obtain a higher $CO_2/N_2$ selectivity, this is usually linked to the increased in consistent energy density that obstructs the diffusion and permeability of nonpolar gases such as $N_2$.

Coating of PP fibres with 3% and 6% Pebax®-1657 using the coating machine had been done under different take up speeds (20mm/s, 100mm/s, and 220mm/s). Thickness values of different coating layers of Pebax®1657 at different concentrations and different take up speeds were differ, the lower take up speed at a certain concentration (20mm/s) has the lower thickness and the higher take up speed at the same concentration (220mm/s) has the highest thickness, this may refer to the friction force, as under the higher speed the friction is higher than the friction at a lower take up speed, so the coating layer applied on the fibres more effectively under high friction.

The permeability of coated fibres which had been done using machine, as mentioned before, three modules for each machine coating experiment at different take up speeds (20,100 and 220 mm/s), were built to be tested with GP unit. The modules description and modules overview was discussed and clarified in section (3.3.2.2 - Fibres modules for GP test – table 8). The results showed that the permeability of PP coated fibres decrease with increasing the take up speed (figure 55). The reason of this is that the thickness of the coating layer for PP fibres coated at higher take-up speeds was higher than the thickness of PP fibres coated under a lower take-up speed. Therefore, the higher take up-speed (220m/s) has higher values of selectivity than the other lower speeds (100 and 20 mm/s) and this result is in agreement with the trade-off relation between selectivity and permeability [29],[24],[56], as the higher speed (220mm/s) had the lower values of permeability than the other tested take-up speeds (100 and 20 mm/s).

Coating of PP fibres manually with Pebax®-1657, Pebax®-5513, and Pebax®-1074 had been done under different concentration for each type (3% and 6%). The thickness of the coating layer was measured at 10 different locations along the coated fibres (two in each quadrant and two in the centre). All thicknesses measurements were done by SEM images. In all the three types of the polymer the thickness of the coating layer in 6wt.% concentration is higher than the thickness in 3wt.% concentration, so when the concentration of the polymer increase the thickness of the coating layer increase.

The thickness of the coating layer at 3wt.% concentration for the Pebax®-5513 is the lowest thickness 1.7µm, and Pebax®-1657 is the higher thickness at the same concentration 3.5µm. For the 6wt.% concentration the Pebax®-5513 has the higher thickness of the coating layer 9.6µm and Pebax®-1074 has the lowest thickness of the coating layer 6.7µm. However, the three types of the polymer in both concentrations are close to each other in the three types of Pebax®, so the thickness values at 3wt.% is in the range of (1.5-3.5µm), and the thickness values at 6wt.% concentration is in the range of (6.5-9.5µm).

On the other hand, the permeability of coated fibres which had been done manually, its observed that in the three tested types of Pebax (Pebax®1657, Pebax®5513, and Pebax®1074), the $CO_2$ permeance decreases with increasing concentration of the coating solution from 3% to 6%. The $CO_2$ permeability increased with increasing ΔP (feed pressure difference) and this is due to plasticization effect.

As a result of the trade-off between permeability and selectivity, the membrane coated with 6wt % concentration of Pebax®1657 was selected as the most appropriate for this application.

The best selectivity result of Pebax® coated membrane was for 6% Pebax®-1657, showed (66.0 – 68.2)GPU and (17.8-23.1)GPU at ΔP=(4-9)bar for $CO_2$ and $N_2$ gas, respectively with a selectivity of 3.9. The best second result was obtained in 6% Pebax®-5513, with (40.9 – 54.4)GPU and (14.3 – 18.0)GPU ΔP=(2-7)bar for $CO_2$ and $N_2$ gas, respectively with a selectivity of 3.2.

As a future recommendation for this work, changing the PP fibres and deal with other less permeable fibres to be the support layer for the coating layer of Pebax® may lead to better results of selectivity under the same conditions of coating. Also, using PDMS polymer in coating as a gutter layer between the fibres support layer and the coating layer of Pebax®, this will prevent any penetration of the coating solution to the support layer and may lead to a better result. Finally, using the heat treatment for the fibres after coating would be possible to study the effect of oven-drying and normal drying at room temperature.

# 6. Abbreviations and symbols

| | |
|---|---|
| $v$ | Velocity |
| $s$ | Distance |
| $t$ | Time |
| $\mu$ | Chemical potential |
| $L$ | liquid |
| $G$ | Gas |
| $S$ | Solid |
| $J$ | Permeation flux |
| $D$ | Diffusion coefficient of the penetrant in the membrane |
| $l$ | Film thickness |
| $A$ | Effective surface area of the module |
| $p2$ | Feed pressure |
| $p1$ | permeate pressure |
| *GP* | Gas Permeation |
| $\Delta P$ | Pressure gradient |
| $\Delta C$ | *Concentration gradient* |
| $\Delta T$ | Temperature gradient |
| $\Delta E$ | Electric potential gradient |
| PP | Polypropylene |
| Tg | Glass transition temperature |
| PEO | Polyethylene oxide |
| PTMO | Polytetramethylene Oxide |
| EtoH | Ethanol |
| PE | Flexible polyether blocks |
| PA | Rigid linear polyamide blocks |

MFC…………………………………………………………………………………………………………………….Mass Flow Controller

Q.…………………………Permeance (measure of permeability without normalizing the membrane thickness)

Q/l.……………………….Permeance (measure of permeability with normalizing the membrane thickness)

GPU.…………………………………………………………………………………………………………………..GAS Permeation Unit

TU.Wien.………………………………………………………………………………………….Vienna University of Technology

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