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Bachelor's degree in sciences of Chemistry and Biochemistry

Development of a New Post-treatment Drying Method in Organic Solvent Nanofiltration for Poly(ether ether ketone) Nanofiltration Membranes

Chemical and Biochemical Engineering Master's Degree

NOVA University of Lisbon
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Resumo

A Nanofiltração com Solventes Orgânicos OSN, é uma das tecnologias de maior interesse, em processos de separação, de um ponto de vista sustentável, quando comparada com processos como a destilação e a evaporação. A maioria das investigações relacionadas com esta tecnologia, estão direcionadas para a estabilidade química de membranas poliméricas, estabilidade essa que é obtida através de técnicas, que utilizam reagentes tóxicos, e alguns químicos que podem causar um enorme desperdício orgânico, durante o processo de fabricação destas membranas. É, por isso, controverso afirmar, que a Nanofiltração com Solventes Orgânicos OSN é uma tecnologia desenhada para resolver problemas relacionados com a sustentabilidade, uma vez que a própria fabricação de membranas através desta tecnologia, está longe de ser sustentável.

Para melhorar a sustentabilidade desta tecnologia, foi investigado e desenvolvido, durante a fabricação de membranas PEEK, um novo método de secagem, mais eficiente que os convencionais métodos, tornando o processo de secagem mais rápido, e com um consumo energético menor. Foram ainda investigados, durante o passo de troca de solvente, diversos solventes, de forma a encontrar um solvente economicamente acessível e menos tóxico, capaz de otimizar o desempenho da membrana, e tornar o processo mais verde.

A metodologia usada neste estudo baseou-se na comparação de membranas PEEK, que foram sujeitas a diferentes temperaturas (30ºC, 50 ºC, 80 ºC, 100 ºC, 120 ºC, 140 ºC, 160 ºC), diferentes pressões (10, 30, 50, 100 bar), e tempo de 15 segundos, através de uma prensa quente. Foi feita ainda a comparação entre dois equipamentos de secagem diferentes (O Forno Convencional e a Prensa Quente). Por fim, foi investigado o efeito de dois solventes (Água Desionizada e Acetona), na etapa de troca de solvente.

Os resultados mostraram que, ao aplicar pressão e aumentar a temperatura, ao mesmo tempo, o limite de peso molecular MWCO tendeu a diminuir, criando membranas mais apertadas. Essa diminuição foi mais pronunciada, usando a água desionizada como solvente. Foi possível obter membranas mais uniformes, uma vez que a prensa quente, é constituída por 2 placas de metal que aplicam o calor diretamente na membrana e portanto, tem a capacidade de (após serem aquecidas à mesma temperatura), distribuírem o calor uniformemente pela membrana. Por meio desse método, foi ainda possível reduzir o tempo de secagem, de 1 hora, para 15 segundos, diminuindo o consumo energético. De uma forma geral, foi possível tornar a Nanofiltração com Solventes Orgânicos OSN, uma tecnologia mais sustentável.

Palavras-chave: Nanofiltração com Solventes Orgânicos OSN, membranas PEEK, prensa quente, método de secagem, etapa de troca de solvente, sustentabilidade.

Abstract

Organic Solvent Nanofiltration OSN, is considered as one of the most attractive technologies in membrane separation processes, mainly, due to its reputation as sustainable process, comparing with distillation or evaporation processes. Curiously, the main research made in OSN, is dedicated on improving chemical stability of polymeric membranes, and this chemical stability is obtained by several techniques (during membrane fabrication process), which use toxic reagents, and some chemicals can cause huge amounts of organic waste as well. So ironically, although OSN technology being designed to overcome problems related to sustainability, the fabrication of OSN membranes, is far from being sustainable.

In order to improve the sustainability of this technology, it was investigated and developed, during the fabrication of OSN membranes, a new drying method, applied to PEEK membranes, more efficient than conventional drying methods, and capable of making the drying process faster, with less energy consumption. It was Investigated, as well, during the solvent exchange step, a cheaper and less pollutant solvent, capable of, making the process greener, and optimizing the membrane performance.

The methodology used in this study was based on the comparison of PEEK membranes dried at different temperatures (30ºC, 50 ºC, 80 ºC, 100 ºC,120 ºC,140 ºC,160 ºC) pressures (10, 30, 50, 100 bar), and time of 15s, using a Hot Press Machine. It was made the comparison as well between two different drying equipment (Conventional Oven and Hot Press Machine), and finally it was investigated the effect of two different solvents (Deionized water and Acetone) in the solvent exchange step.

The results showed that, by applying pressure and increasing the temperature, at the same time, the MWCO tended to decrease, creating tighter membranes. This decrease was more pronounced, in membranes previously immersed in deionized water. Also, more uniform membranes were achieved, as the hot press equipment, applied the heat directly into the membrane, through their heated metal plates, that distributed heat evenly across the membrane. Through this method, it was possible to decrease the drying time during the drying process, from 1 hour to 15 seconds, decreasing the energy consumption. It was possible to make the Organic Solvent Nanofiltration OSN a more sustainable technology.

Key-words: Organic Solvent Nanofiltration (OSN), PEEK membranes, hot press, drying method, solvent exchange step, sustainability.

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List of abbreviations

Abbreviation	Description
BPR	Back Pressure Regulator
DIW	Deionized Water
ELSD	Evaporative Light Scattering Detector
HP	Hot Press
HPLC	High Performance Liquid Chromatography
ISA	Integrally Skinned Asymmetric
MeCN	Acetonitrile
MeOH	Methanol
MF	Microfiltration
MSA	Methane sulphonic Acid
MW	Molecular Weight
MWCO	Molecular Weight Cut-off
NF	Nanofiltration
OSN	Organic Solvent Nanofiltration
PA	Polyamide
PEEK	Poly (ether ether ketone)
PEG	Polyethylene Glycol
PEEK-WC	Poly(oxa-p-phenylene-3,3-phtalido-p-phenylenxoxa-p-phenylenoxoxy-p-phenylene) with Cardo group
PI	Polyimide
PPS	Polyphenylene Sulphide
PTFE	Polytetrafluoroethylene
RO	Reverse Osmosis
SA	Sulphuric Acid
SEM	Scanning Electron Microscope
S-PEEK	Sulphonated Poly(ether ether ketone)
S-PEEK-WC	Sulphonated Poly(oxa-p-phenylene-3,3-phtalido-p-phenylenxoxa-p-phenylenoxoxyp-phenylene) with Cardo group
UF	Ultrafiltration

Chapter 1. Introduction

1.1. Research Motivation

Pharmaceutical, Chemical, and Oil industries account with thermal processes such as, distillation, evaporation, and drying processes to manufacture their drugs, chemical products, or edible oils, (White & Nitsch, 2000; Constable, Jimenez-Gonzalez & Henderson, 2007; Darvishmanesh et al., 2011) using organic solvents. However, these thermal processes, consume a huge amount of energy (Sholl & Lively, 2016), cause fire hazards, and increase environmental emission. In addition, at elevated temperatures they degrade heat-sensitive products. Therefore, the demand for a technology capable of overcoming these problems has become imperative. Organic Solvent Nanofiltration (OSN) has emerged as the answer (Shi et al., 2021).

OSN is an energy efficient alternative to thermal processes (Rundquist, Pink & Livingston, 2012; Cheng et al., 2014), it is a pressure-driven and non-thermal method, in which separation is achieved mainly by size exclusion, at room temperature with minimal solvent loss and fire hazard and has the potential to decrease energy consumption by 90% compared with distillation or evaporation (Koutsou & Karabelas, 2012). By those reasons, OSN is considered one of the most attractive technologies to improve sustainability of separation processes.

Interestingly, most research efforts on OSN, have been dedicated on improving the chemical stability of polymeric membranes, to perform separation in organic media. For that, membranes needed to be stable over a wide range of pH and resistant to aggressive solvents (Koutsou & Karabelas, 2012). This was accomplished by techniques using toxic reagents (crosslinking), and some chemicals generate considerable amount of organic waste. So curiously, although OSN technology has developed to improve the process sustainability, the fabrication of OSN membranes has been far from sustainable (Kim et al., 2016).

Currently, the most common polymers used for OSN membranes are, Polyimide or Polyamide, but they are not considered green materials for OSN membranes, once they need crosslinking to increase their low resistance at high temperatures due to the lack of thermal stability.(Tsuru et al., 2000) In addition, their poor stability and performance in polar aprotic solvents and instability in some amines make them not a so good option for OSN process (Vanherck, Koeckelberghs & Vankelecom, 2013; See Toh et al., 2007; See Toh, Lim & Livingston, 2007). For that reason, an alternative polymer, poly (ether ether ketone) (PEEK), can be used, due to its strong chemical resistance in harsh solvents, doesn’t require crosslinking (da Silva Burgal et al., 2015), being considered a greener option, by other others, capable of making the OSN technology a more sustainable process.

However, to achieve this “sustainability” goal, OSN membranes fabrication by phase inversion method, need to be considered, as well, as it accounts with many steps (phase inversion step or post-treatment step, for example), that are related to several sustainable issues in OSN manufacture such as, the solvent and general waste generated, or even the chemicals chosen to use in a specific treatment.

Therefore, the focus of this project will be improving the sustainability of OSN, by finding greener solutions for the membrane fabrication. Starting with, the polymer used as membrane material for OSN, and ending up in the phase inversion method, where the focus will be, finding a suitable and greener solvent to immerse the polymer membrane, (solvent exchange step), and finding a novel drying equipment, more efficient than the conventional ones.

1.2. Project Objectives

The overall objectives of this research project are: Investigate and develop a new post-treatment method (drying method) applied to PEEK membranes, through a new equipment (Mini Hot Press Machine) and prove this method is equally or even more efficient than conventional post-treatment drying methods, since it will be capable of making the drying process faster, with less energy consumption; Investigate, during the solvent exchange step, a cheaper and less pollutant solvent, capable of making the process greener and optimizing the membrane performance; Finally, from a sustainability perspective, this work is focused on making OSN a more sustainable, and therefore, valuable technology, through optimization of different steps during the membrane fabrication process.

1.3. Thesis Structure

This Thesis is constituted by 5 main chapters. It starts with an introductory chapter (Chapter 1. Introduction), where it is explained the research motivation, project objectives and the thesis Structure. The following chapter (Chapter 2. Literature Review), is subdivided in three main parts: First one, gives a membrane overview, were membrane morphology, and its separation processes are the main notions; Second one, more detailed and focused on Organic Solvent Nanofiltration (OSN), the membrane separation process, used in this work. It drives from history and applications, common OSN membrane materials, and membrane manufacture, to membrane characterization, membrane configurations and transport models; Finally, the third one, is focused on the polymer used, in this work, Poly (ether ether ketone) (PEEK), as membrane material for OSN, and it gives brief notions about, its morphology, mechanical and thermal properties and some history and applications.

The third chapter (Chapter 3. Material and Methods) is focused on the experimental work. It is subdivided in two parts: Material, where can be found all the chemicals, equipment (HP and Oven) and analytical equipment (HPLC and SEM) used; Methods, which account with topics such as, the membrane preparation procedure, conditions used, solutions prepared, membrane performance and analysis, experimental set up used during the investigation.

In Fourth chapter, (Chapter 4. Results and Discussion) are presented and discussed the experimental results. In this chapter it will be used, discussed the different solvents used during the solvent exchange step (acetone and deionized water), the different drying equipment (HP and Oven) used during the drying step, the comparison between the two solvents used, and between the two drying methods used, and finding the greener option.

The last chapter, (Chapter 5. Conclusion) is focused on the Overall Conclusions where it is explained the new findings regarding the results obtained.

Chapter 2. Literature Review

2.1. Membrane Overview

2.1.1. Definition of membrane

In a simple way, a membrane is a thin barrier between two bulk phases, that permits transport of some components but retains others (Beerlage, 1994).

However, it is difficult to give an exact definition of a membrane, once should be considered different points of view, as its structure or morphology (homogeneous or heterogeneous), membrane transport (active or passive), or its nature (Synthetic or Biological) which is the clearest distinction possible, as these two types of membranes (Synthetic or Biological) differ completely in structure and functionality (Mulder, 1997).

Regarding its nature, Synthetic membranes can be divided into three main groups: Polymeric (Organic) membranes, which are the focus on this project, and include a wide variety of membranes (Baker, 2004), Ceramic (Inorganic) membranes, and Mixed matrix membranes, which are the set of the previous two (Mulder, 1997).

Polymeric membranes can be symmetric (isotropic) and asymmetric (anisotropic). Symmetric membranes can be further categorize in, porous membranes and nonporous membranes. Symmetric porous membranes have a rigid, highly voided structure with randomly distributed pores, interconnected, and the pore size diameter is in a range of (0.01-10) µm (UF and NF range). Nonporous membranes (dense membranes) are constituted by a dense film and are used in different separation processes, such as, pervaporation and reverse osmosis. Regarding asymmetric porous membranes, or integrally skinned asymmetric membranes, they have a very thin and dense skin layer in a range of (0.1-1) µm on the top of a thick and very porous sub-layer of (100-200) µm with an average void size between 0.01 µm and 1 µm. Both layers have the same material and are created in a simple operation. (Baker, 2004)

2.1.2. Membrane Separation Processes

Membrane separation processes, an emerging technology, has undergone rapid growth during the past few decades. Membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impact (Nath, 2017). In an industrial point of view, membranes separation processes can be classified into the following groups, according to the driving force that causes the flow of the permeant through the membrane (Matsuura, 2020): As Pressure difference across the membrane, which are the most widely used membrane separation technologies (Wang & Zhou, 2013). Reverse Osmosis (RO), Ultrafiltration (UF), Microfiltration (MF) and Nanofiltration (NF) are some examples; As Concentration difference across the membrane (Dialysis, Membrane Extraction); and as Electric potential difference across the membrane (Electrodialysis) (Matsuura, 2020).

However, membrane technologies are typically classified according to their effective pore size and separation mechanism (Hampu et al., 2020). Reverse Osmosis (RO) membranes that employs the tightest membranes for liquid separation, is used as barrier to salts, inorganic solutes, and organic solutes (Wang & Zhou, 2013). Their membrane pore radius is less than 1 nanometer (nm). Water is the usually solvent, however it is not necessarily restricted to water. While solvent water molecules, whose radius is about one tenth of 1 nm, can pass through the membrane freely, electrolyte solutes, such as sodium chloride and organic solutes that contain more than one hydrophilic functional group in the molecule (sucrose, for example), cannot pass through the membrane (Matsuura, 2020).

Ultrafiltration membranes (UF) is a process based on the same principle as that of reverse osmosis. The main difference between reverse osmosis and ultrafiltration is that ultrafiltration membranes have larger pore sizes than reverse osmosis membranes, ranging from 1 to 100 nm (Matsuura, 2020). Those membranes are of particular interest for drinking water and wastewater treatment, and ideal for rejecting wastewater contaminants, such as viruses, microbes, colloidal particles, and natural organic matter, according to their hydrodynamic size. Additionally, UF membranes are critical tools in certain industrial processes (e.g., bioprocessing, dairy processing), enabling low cost and highly efficient separations (Hampu et al., 2020).

Nanofiltration (NF) membranes, with properties between those of ultrafiltration (UF) and reverse osmosis (RO) membranes, removes multivalent ions and small molecules in the nanometer range (e.g., sulphate ions, sugars) (Oatley-Radcliffe et al., 2017). They can fractionate small compounds, such as salts and small organic molecules, and are commonly used to permeate monovalent ions while retaining divalent ions (Wang & Zhou, 2013). This membrane technology continues to see increasing interest due to their versatility as a separation tool, have a pore size typically of the order of 1 nm, which corresponds to a molecular weight cut-off (MWCO) in the range of 100–5000 Da (Oatley-Radcliffe et al., 2017).

2.2. Organic Solvent Nanofiltration

2.2.1. History and applications

Starting in the late 1960s, membrane processes have been gradually used for Industrial applications. They have provided feasible alternatives for, and have been combined with, more traditional purification and separation processes (distillation, evaporation, adsorption, extraction, and chromatography). This has been motivated by the benefits that membrane technology offers over conventional techniques, in terms of economy, environment and safety.(Vandezande, Gevers & Vankelecom, 2008; Geens, de Witte & van der Bruggen, 2007; Lin & Livingston, 2007; Rickerby, 2013)

Organic Solvent Nanofiltration, amongst all the other membrane processes appears in 1964, appears as technology capable of going beyond the aqueous applications to which these processes were limited.

Its first application in nonaqueous systems was reported in 1964 and consisted of the separation of hydrocarbon solvents using a cellulose acetate (CA) membrane. Later, these membranes were used to separate OS mixtures and organic and inorganic solutes (Sourirajan, 1964; Kopecek & Sourirajan, 1970; Farnand et al., 1983; Sourirajan & Takeshi, 1985). From 1980 onward, polymeric membranes started to be used to separate molecules present in organic solutions, with the main goal of, oil recovery (Shuey & Wankei, 1985; Anderson, 1990; Gould & Nitsch, 1996), enrichment of aromatics (Black & Boucher, 1986; Black, Peter G. & Georges, 1985; Black & Sarnia, 1992; Bitter & Haan, 1989), and homogeneous catalyst recycle (Miller et al., 1997). In the mid-1990s, products started appearing in the market, by the hands of Important names in membrane manufacture, such as Grace Davison (White, I-Fan Wang & Bhupender S. Minhas, 1993; Gould, White & Wildemuth, 2001; White & Nitsch, 2000; Kong et al., 2006) and Koch (Linder et al., 1993). Later, ExxonMobil Beaumont Refinery was responsible for one of the largest successful processes in industry, Max-Dewax™ process, responsible for the recovery of dewaxing solvent from lube oil filtrates (Gould, White & Wildemuth, 2001). Finally, in 2008 was launched the DuraMem™ series of highly solvent-stable OSN membranes, for the separation of organic solutes from various Organic Solvents, by membrane extraction technology (MET), that in 2010 was acquired by Evonik Industries as Evonik-membrane extraction technology (Peeva, Marchetti & Livingston, 2018). From 2010 until today, OSN was further investigated, in terms of sustainability, and it is now known by its potential on improving the sustainability of separation processes. Considerable efforts were made in terms of membrane fabrication, such as: replacing membrane materials by biodegradable alternatives, replacing toxic solvents for greener solvents, and minimizing waste generation with material recycling (Song et al., 2018).

2.2.2. Membrane Material

The membrane material play an important role in the development of membrane processes for OSN, once some of the main issues related to this development are the robustness of the membrane materials: in organic solvents, in harsh acid and basic conditions, and during module preparation; toward swelling and leaching, and the membrane selectivity for challenging molecular separations, as in the case of mixtures of main products and impurities with similar molecular size or for mixtures of isomers. (Marchetti et al., 2014)

These membranes materials can be either ceramic or polymeric, as long as they have mechanical, chemical and thermal stability (Marchetti et al., 2014). Ceramic membranes are superior considering mechanical, thermal, and chemical stability. They do not compact under pressure, do not swell in organic solvents, and can be easily cleaned, but their up-scaling is more difficult, there is less variety in materials compared to polymers, and they are more brittle than polymeric membranes (Marchetti et al., 2014), and less suitable for more apolar solvents. The lowest MWCO is at present significantly larger than that of polymeric membranes. For polymeric membranes is important to considering the type of polymer, since its structure, hydrophilicity or hydrophobicity, and charge density influence the membrane performance. The polymer structure by being linear or non-linear, has an impact on the flux. Non-linear polymers, possess higher interchain-distance which means higher fluxes. The hydrophilicity or hydrophobicity balance can give or not, water permeable membranes, and the charge density have influence in the rejection (Vandezande, Gevers & Vankelecom, 2008; Vankelecom et al., 2005). ISA membranes, used in NF operations, are made by stable polymeric materials (Vankelecom et al., 2005; Gevers et al., 2006a; Cuperus, 2005), and fabricated by phase inversion. Several examples of this type of membranes are, Polyimide (PI), (Matrimid), polyimide (PI) (P84), and Polyacrylonitrile (PAN), applicable as NF supports (Linder et al., 1991; Peeva, Marchetti & Livingston, 2018), polysulfone (PSf)/sulfonated poly(ether ether ketone) mixtures, polybenzimidazole(PBI) (Livingston & Bhole, 2013) , and Polyaniline(PANI) (Sairam et al., 2010; Loh et al., 2009), used in NF operations, and Poly(ether ether ketone) (PEEK) (Peeva, Marchetti & Livingston, 2018), can be either a UF support.

Some types of polymeric membranes are made from glassy polymeric materials which age over time, and it influences the membrane performance in OSN, resulting in a decrease in the permeance of more than 30%, in the first 10 days of operation (Vandezande, Gevers & Vankelecom, 2008; Tang, Hu & Napolitano, 2014; Song et al., 2014; Sereewatthanawut et al., 2010). This ageing is explained by the re-arrangement of the polymer chains in the membrane by structural relaxation and depending on time, when at the membrane formation process, a non-equilibrium excess state move towards a stabilized equilibrim state (Hutchinson, 1995; Hodge, 1995; Murphy et al., 2011). The ageing can be noticed when there is a gradual decrease in the membrane volume (densification) that leads to a decrease in the permeability and entalphy, increase of the brittleness (Murphy et al., 2011).

For those reasons, a (PEEK) Poly ether ether ketone polymer, which do not suffer free volume collapse or become brittle when dried in air even at elevated temperature (120 °C) and in addition possess this inherent permeance (da Silva Burgal et al., 2015b, 2015a), was used in this research work, to produce OSN membranes, via immersion precipitation.

2.2.3. Membrane Manufacture

Phase inversion method is the method used for manufacturing ISA membranes in OSN, and consists in the precipitation of a casting solution by immersion in a nonsolvent (water) bath (Loeb & Sourirajan, 1963). This method involves four main steps: Dope solution; membrane casting; phase inversion, and membrane post-treatment (Strathmann & Kock, 1977). In these different steps, there are factors controlling the membrane formation process and the membrane performance (Peeva, Marchetti & Livingston, 2018). Evaporation time, casting temperature, (See-Toh, Ferreira & Livingston, 2007; Kim, Yoon & Lee, 2002; Leblanc et al., 2003; Ohya et al., 1997; Gupta, 1997; Jian et al., 1999), concentration of dope solution and volatile cosolvents addition (See-Toh, Ferreira & Livingston, 2007; Kim, Yoon & Lee, 2002; Vankelecom & Gevers, 2005; Bulut et al., 2006; Dai et al., 2001), are some of them.

By varying the composition of the dope solution, varying the conditions during the phase inversion step or via a post-treatment step (drying, conditioning or crosslinking) (See-Toh, Silva & Livingston, 2008; Soroko & Livingston, 2009), it is possible to manipulate the membrane performance.

The concentration of the dope solution strongly influences the selectivity and permeability (higher polymer concentrations, result in higher selectivities but lower permeabilities) (See-Toh, Ferreira & Livingston, 2007; Boussu, Vandecasteele & van der Bruggen, 2006; Ismail & Lai, 2003; Kim, Yoon & Lee, 2002; Hicke et al., 2002), and membrane structure (Li et al., 2008; Cadotte & Petersen, 1981; Marchetti et al., 2014).

Membrane structure can be influenced as well by the addition of cosolvents (Petersen, 1993; See-Toh, Ferreira & Livingston, 2007; Boussu, Vandecasteele & van der Bruggen, 2006; Marchetti et al., 2014), nonsolvents, and pore forming additives (Soroko & Livingston, 2009). The volatile cosolvents (e.g. ethyl ether (EE), tetrahydrofuran (THF) or dioxane) that are added to the dope solution, produce integrally skinned asymmetric membranes, where the evaporation step is essential (Bulut et al., 2006; See-Toh, Ferreira & Livingston, 2007) , since this partial evaporation will allow the formation of a skin-layer with high polymer concentration, between the casting and immersion step. Pore forming additives are used to increase permeability and porosity with or without compromising the selectivity, and they can be either inorganic, or organic (glycerol, polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP)); for example, by adding maleic acid (MA) to cellulose triacetate (CTA), the porosity and permeability are increased (Vandezande, Gevers & Vankelecom, 2008; Shimoda & Hiroshi, 1999).

The porosity of the membrane is also influenced by the rate of exchange between solvent and non-solvent. The higher the rate of exchange between solvent and non-solvent the higher the porosity of the membrane, it is the case for NMP/Water (solvent/non-solvent) pair. Alcohols and DMF are common additives used to vary exchange rates. In the coagulation bath, temperature is extremely important, since by increased, higher the exchange rate will be and therefore a more porous structure will be obtained. (Vankelecom et al., 2005; Shimoda & Hiroshi, 1999)

In the post-casting treatment, several factors can affect the membrane performance, and therefore need to be controlled. They are, temperature and time evaporation, air velocity (if it is a convective flow) and relative humidity. For PI membranes was discovered that the increase of evaporation time reduces the flux, but has no effect on rejection.(See-Toh, Ferreira & Livingston, 2007)

2.2.3.1. Post-treatments

There are considerable post-treatments that can be used to enhance the membrane performance: drying with the solvent exchange technique, treatment with conditioning agents, annealing the membrane in water or under dry conditions, exposure to concentrated mineral acids and plasma treatment are some of them. (Vandezande, Gevers & Vankelecom, 2008; Kim & Kim, 2006; Beerlage, 1994; Manos, 1978b; Kim, Yun & Lee, 2002)

In this work will be investigated the drying with the solvent exchange method, and the treatment with conditioning agents. When a nanofiltration membrane prepared by wet phase inversion is subjected to a drying process, its structure usually changes (“collapses”), once this drying process induces irreversible loss of solvent permeance, (related to the collapse of the nodular structure) so it is extremely important to the membrane, being stored under wet conditions (Beerlage, 1994). The nodule collapse upon drying can be either minimized by using a solvent exchange technique, where the residual non-solvent present in the membrane, after immersion, is replaced by a first solvent which is miscible with the non-solvent. This first solvent is replaced by a more volatile solvent, that will be removed by evaporation, and a dry membrane is obtained (Manos, 1978a; Macdonald & Chuen-yong, 1974; Tang et al., 1989).

Nodular collapse can be described by Brown Theory for polymer latex particles during film formation (Brown, 1956). This theory was used for PI ultrafiltration membranes (Beerlage, 1994), relating the capillary forces (Fc) with the resistance of the matrix to deformation (Fr)

$$F_c = \frac{2\gamma}{r_p}.cos\theta.A$$

Equation 2.1

$$F_r = 0.37\,E.A$$

Equation 2.2

γ (N.m^{-2}) - surface tension of the gas/liquid interface inside the pores

r_p (m) – pores radius

θ (°) – contact angle between the liquid and the membrane material

A (m^2) – pore cross sectional area

E (N.m^{-2}) – tensile modulus of the polymer material (measure of the pore wall elasticity)

If $F_c > F_r$ will occur nodular structure, so for any given pore size, the pore collapse if:

$$\frac{2\gamma.cos\theta}{r_p} > 0.37 \times E$$

Equation 2.3

If the strength of the matrix is high enough, the surface tension will decrease, minimizing the capillary force, and the pore structure of the membrane will be maintained. A good method to decrease the surface tension is the solvent exchange method (Beerlage, 1994; Macdonald & Chuen-yong, 1974; Tang et al., 1989; Brown, 1956) . Post-treatment of membranes using pore preserving agents is either important as necessary, to avoid pore collapse or aging of the membrane drying.

2.2.4 Membrane Characterization

In the nineteenth and twentieth centuries, membrane science has started as simple chemical/physical theories developed by philosopher scientists, without any commercial or industrial value. Today, membranes are of great value to almost every sector of chemical industry. (Baker, 2004)

Membranes need to be characterized to understand in which class of separations are they. Characterization relates membrane processes with structural membrane properties (pore size, pore size distribution, crystallinity, and free volume). Considering that membranes can have different morphology (porous and nonporous), characterization techniques are different depending on it. Porous membranes are the focus in this project. There are two types of characterization for porous membranes, Physico-chemical and Structural characterization, and functional characterization

2.2.4.1. Membrane Physicochemical and Structural Characterization

Physicochemical characterization is focused on parameters such as hydrophobicity, hydrophilicity, swelling, pore size, pore size distribution, surface porosity, skin layer thickness and charge, that can be determined by several techniques such as: atomic force microscopy (AFM) (Bottino et al., 1994), scanning electron microscopy (SEM) (Wu & Wu, 1995), transmission electron microscopy (TEM) (Sheldon, 1991), bubble point method and mercury intrusion method, amongst others.

AFM is used to measure pore and nodule sizes, and surface roughness (Otero et al., 2008; Hilal et al., 2003; Khulbe, Feng & Matsuura, 2008; Boussu et al., 2005; Stamatialis, Dias & Norberta De Pinho, 1999) , this Surface roughness is extremely important for OSN membranes, and it is understood as peak-to-valley height, root-mean-square (RMS) roughness, or average roughness. SEM and TEM are used to characterize the cross-section structures of NF membranes, which allows to image pores at the nanoscale and understand functional performance of NF membranes (Marchetti et al., 2014). The contact angle method (measure of membrane wettability), also known as a captive bubble method, is used to characterize the membrane surface properties, and to compare among different membranes, the hydrophobicity (Zhang & Hallström, 1990). Contact angle of zero degree corresponds to an ideal hydrophilic surface (considering water as the droplet). Mercury porosimetry method determine pore size and pore size distribution, and it is usually used to characterized porous materials, such as membranes (Mulder, van Voorthuizen & Peeters, 2005).

2.2.4.2. Membrane Functional Characterization and Performance

Membrane performance on OSN is usually influenced by the nature of the membrane and properties of solutes and solvents (size, structure, solubility parameter, concentration, dipole moment and dielectric constant) (Bhanushali et al., 2001; Gevers et al., 2006b; Kwiatkowski & Cheryan, 2005; Tsuru et al., 2001; Stafie, Stamatialis & Wessling, 2005; van der Bruggen et al., 1999; See Toh et al., 2007; Stamatialis et al., 2006; Zwijnenberg et al., 2005; Zheng et al., 2008; MacHado, Hasson & Semiat, 1999). It is characterized by the flux (or permeance), rejection (or selectivity) and also by the membrane nominal molecular weight cutoff (MWCO). (Marchetti et al., 2014)

Volumetric Flux *J* is defined as the rate of volume flow *V (L)* through the membrane per unit area *A* (m^2) per unit time *t (h)* and it is expressed as $L\ (m^{-2}\ h^{-1})$:

$$J[\ \mathrm{L}\, m^{-2}h^{-1}\ ] = \frac{V[L]}{A[m^2] \times t\ [h]}$$

Equation 2.4

Permeance *B* is normalized to the applied pressure ΔP *(bar)* (Marchetti et al., 2014), and it is expressed as $L\ (m^{-2}\ h^{-1}\ bar^{-1})$. *(Equation 2.5).* Equation 2.6 and 2.7 represent the dimensional equations for flux and permeance, respectively.

$$B[\mathrm{L}\, m^{-2} h^{-1} bar^{-1}] = \frac{V}{A \times t \times \Delta P}$$

Equation 2.5

$$J[L.T^{-1}] = \frac{\text{Flow rate } [L^3 T^{-1}]}{\text{Membrane area } [L^2]}$$

Equation 2.6

$$B[L^2.M^{-1}.T] = \frac{J[L.T^{-1}]}{\Delta p[M.L^{-1}.T^{-2}]}$$

Equation 2.7

Depending on the membrane and on the solvent, variations between Initial and steady fluxes can happen, resulting in membrane compaction/aging. This can be observed by the decrease on the initial flux. Solvent flux can be influenced by the rising of temperature, increase in solvent diffusion coefficients (Fritsch et al., 2012), and increase in polymer chain mobility (Uragami, Yono & Sugihara, 1979; Tamura, Uragami & Sugihara, 1978).

Rejection is expressed as function of the solute concentration in the permeate, $c_{i.l}$, and the solute concentration in the retentate (or feed) side, $c_{i.0.}$

$$Rej_i[\%] = \left(1 - \frac{c_{i,l}}{c_{i,0}}\right) \times 100$$

Equation 2.8

NF membranes can have different rejection profiles (Figure 2.1). Those rejection profiles can exhibit either a broad curve (the most common profile), with rejection rising slowly over a wide range of solute sizes (light blue line), or an ideal sharp separation curve, with rejection rising quickly with the solute size (dark blue line). An ideal sharp means that the separation between two solutes of different molecular sizes is perfect, by other words it represents a high separation selectivity.(Peeva, Marchetti & Livingston, 2018)

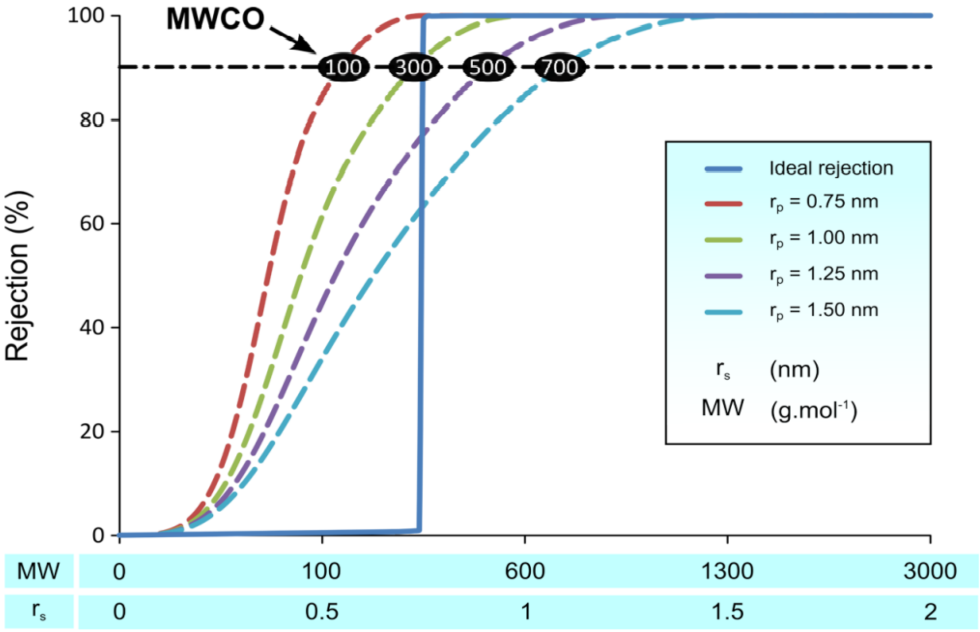


Figure 2.1 - Schematic representation of rejection profile for uncharged solutes by a membrane with uniform pore sizes (rp) between 0.75 and 1.5nm. The solid line represents the desired rejection profile, the other lines represent the common rejection profile. Illustration from: Peeva L. G. Marchetti P. Livingston A. G. Nanofiltration Operations in Nonaqueous Systems. (Kim et al., 2013; Peeva, Marchetti & Livingston, 2018)

The membrane nominal molecular weight cut off (MWCO), represents the smallest solute molecular weight for which the membrane has 90% rejection (Rej_i (%) ≥ 90) (Marchetti et al., 2014), obtained by plotting the percentage rejection of solutes versus their molecular weight (typically 200-2000 g mol^{-1}) and interpolating this data to find the molecular weight corresponding to 90% rejection. Should be noted that the MWCO often does not give sufficient information on the separation performance, and about the sharpness of the cut-off profile (the selectivity), by other others, the quality of the separation. (Marchetti et al., 2014; Peeva, Marchetti & Livingston, 2018)

The characterization of MWCO in OSN membranes can be made by several markers, such as: linear and branched n-alkanes (White, 2002); dyes (Bhanushali, Kloos & Bhattacharyya, 2002; Bhanushali et al., 2001; Vandezande et al., 2005; Gevers et al., 2006b); hexaphenyl benzene (HPB)(Bhanushali, Kloos & Bhattacharyya, 2002; Fritsch et al., 2012); polyethylene glycol (PEG) (Kwiatkowski & Cheryan, 2005; Tsuru et al., 2001; Rohani, Hyland & Patterson, 2011); poly-isobutylene(Stafie, Stamatialis & Wessling, 2005; van der Bruggen et al., 1999); oligostyrenes, (See Toh et al., 2007; Dutczak et al., 2011) .

2.2.5. Membrane Configurations

There are two types of configurations to manufacture membranes (flat sheet and tubular shape). Polymeric membranes are commonly produced as flat sheets. The equipment used in these different configurations are divided in dead-end and cross-flow modes. (Marchetti et al., 2014)

In the dead-flow filtration mode, the feed flow and permeate flux are in the same direction. The main drawback with this configuration it that the membrane performance can be affected by the concentration polarization, even at low solute concentration values. Cross-flow mode, on the other hand, reduces the extent of concentration polarization by increasing the shear rate over the membrane surface, resulting in better operation conditions. In this configuration, the feed flows tangentially over the membrane surface and perpendicularly to the membrane flux (Marchetti et al., 2014). The experimental results obtained with a cross-flow cell, are more useful for scaling up the process compared with the results with a dead-end cell, once the flow-direction in cross-flow cells is similar for spiral modules, or multi-channel tubes (used in large scale OSN processes)

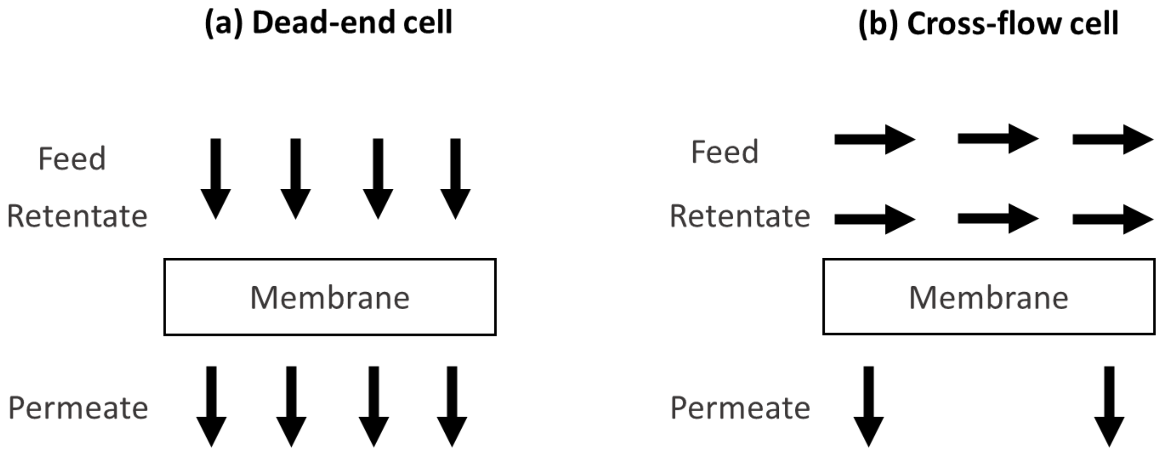


Figure 2.2 – Schematic representation of the two modes used in the different configurations, to manufacture polymeric membranes. (a) Dead-end cell, and (b) Cross-flow cell.

Those membranes can be packed, at an industrial scale, in different types of modules. They are the plate-and frame module (the first design, more expensive and less efficient), the hollow fiber, the tubular, and the spiral wound module. The spiral-wound module is the most attractive configuration at the industrial scale for polymeric membranes. In this type of module, the flat membrane sheets are wound around the central collection pipe. The membrane sheets glued along three sides and attached to the permeate channel along the unsealed edge of the leaf. A permeate spacer is positioned between the internal sides of the leaves, to give mechanical resistance, avoid collapse due to pressure, and guide the permeate to the permeate tube.

2.2.6. Membrane Transport Models

In the 1900s, membrane transport has gained lot of attention, starting with general theories, and ending up with questions such as, its potential practicality and benefits in the world (Mason & Lonsdale, 1990). Particularly for OSN, by understanding this mechanism, an advancement in OSN and in its applications, can be made (Wang et al., 2014).

The membrane transport can be described by different transport models (Irreversible thermodynamics (Kedem & Katchalsky, 1958; Spiegler & Kedem, 1966), solution diffusion (Paul, 2004; Wijmans & Baker, 1995), and pore flow models (Ferry, 1936; Verniory et al., 1973; Nakao & Kimura, 1982; van der Bruggen et al., 2000; Matsuura & Sourlrajan, 1981; Mehdizadeh & Dickson, 1989; Wang et al., 1995). They are extremely important because allow to possible predict fluxes and rejections for a certain membrane (Vandezande, Gevers & Vankelecom, 2008).

Among the three different types of transport models, the most common models to describe the mechanism of OSN transport phenomena through a membrane is the solution diffusion model and the pore flow model.

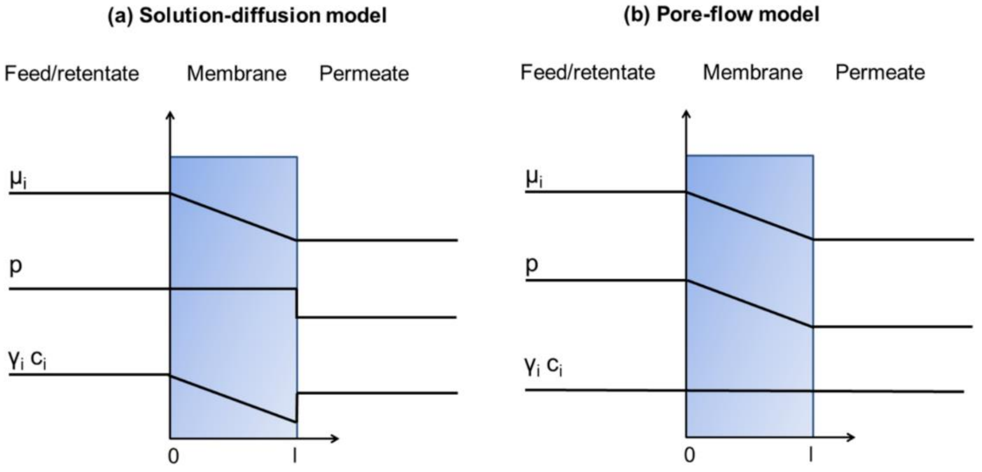


Figure 2.3 - Profiles of chemical potential, pressure, and solvent activity characteristic of pressure-driven filtration of a one-component solution through a membrane according to (a) solution-diffusion and (b) pore-flow transport models. (Marchetti et al., 2014)

These models consider membrane properties and describe the transport of solutes as a function of structural and physicochemical parameters. Differences in temperature, concentration, and pressure, can influence the chemical potential gradient. For the solution-diffusion model (figure 2.3.a) the chemical potential gradient is dependent of the concentration, while for the pore-flow model, the chemical potential gradient is dependent of the pressure (figure 2.3. b)

$$J_i = -L_i \frac{d\mu_i}{dx}$$

Equation 2.9

J_i – flux of species i

L_i – proportionality coefficient between flux J_i and driving force μ_i

μ_i– total chemical potential of species i

Considering only concentration and pressure gradients, the chemical potential is simplified in

$$d\mu_i = RT\, dln(\gamma_i x_i) + v_i dp$$

Equation 2.10

γ_i– activity coefficient

x_i – molar fraction of the species i

v_i– molar volume of the species i

p – pressure

R – universal gas constant

T – Temperature

This equation can be adapted for incompressible phases

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i x_i) + v_i(p - p_{i,sat})$$

Equation 2.11

μ_i^0 – chemical potential of pure species i

$p_{i,sat}$ – saturation vapor pressure

2.2.6.1. Solution-diffusion model

The solution-diffusion model is used for transport through dense membranes and assumes solute and solvent fluxes are independent from each other.

In these membranes, it is assumed that the statistical fluctuations of the free-volume elements (not fixed in time and space as the pores) occur at the same time scale as the motions of permeants through the membrane. When by across the membrane, there is no pressure gradient, the solute flux is expressed as the follow equation (same form as Fick's law), where the term RTL_i/c_i is replaced by the diffusion coefficient D_i.

$$J_I = -\frac{RTL_i}{c_i}\frac{dc_i}{dx} = -D_i\frac{dc_i}{dx}$$

Equation 2.12

When a pressure gradient exists across the membrane, the final equation for the "classical solution" model over the membrane thickness, after integration is.

$$J_i = \frac{D_i K_i}{l}\left(c_{i,0} - c_{i,l}e^{-\frac{v_i(p_0-p_l)}{RT}}\right) = p_i\left(c_{i,0} - c_{i,0}e^{-\frac{v_i(p_0-p_l)}{RT}}\right)$$

Equation 2.13

K_i – partitioning coefficient

$c_{i,0}$ – concentration of the component i in the feed solution

$c_{i,l}$ – concentration of the component i in the membrane

p_0 – pressure of on the feed side of the membrane

p_l – pressure within the membrane phase

This Equation is valid for both solvent and solute fluxes across the membrane as function of pressure and concentration. This model can be extended to multicomponent mixtures. (Marchetti et al., 2014)

2.2.6.2. Pore-Flow model

In the Pore flow model, the transport through the membrane is by pores, which are larger than the solute and solvent molecular diameters. The solute and solvent concentration within the pore of the membrane is uniform, and the chemical potential gradient across the membrane is expressed as pressure gradient. (Marchetti et al., 2014)

The following equation represents the Darcy's law, which is used to describe the transport through porous membranes in the absence of a concentration gradient.

$$J_i = k\frac{(p_0 - p_l)}{l}$$

Equation 2.14

k – permeability (function of membrane pore size r_p, surface porosity ε, and tortuosity τ)

l – membrane thickness

p_0 – pressure of on the feed side of the membrane

p_l – pressure within the membrane phase

In the pore flow model, the membrane pores are considered cylindrical, and the pure solvent flux through those uniform cylindrical pores (no concentration gradient present) is described by the Hagen-Poiseuille model, that derives from Darcy's law.

$$V = \frac{\varepsilon r_p^2}{8l\tau}\frac{\Delta p}{\eta} = K_{HP}\frac{\Delta p}{\eta}$$

Equation 2.15

η – viscosity

r_p – membrane pore size

ε – porosity

τ – tortuosity

According to this model, the viscosity η is the only solvent parameter affecting permeation. The membrane is represented by the pore size, r_p , the porosity, ε , the tortuosity, τ, and the membrane thickness, l.

2.3. PEEK membranes

2.3.1. Morphology

Polyaryletheretherketone, Poly(oxy-1,4-phenylene-oxy-1,4-phenylenecarbonyl-1,4-phenylene), referred as PEEK, is a member of PAEK polymer family. This polymer (plastic) is a linear chain of hundreds monomer units with an average molecular weight of 80 000 – 120 000 g mol $^{-1}$. (Kurtz, 2019; Rae, Brown & Orler, 2007)

PEEK (co polymer composed of ether and ketone) is synthesized from biphenyl (hy-droquinone) and fluorinated aromatic compound in a polar aprotic solvent (diphenyl sulfone). This fluorinated derivates are advantaged, comparing with chlorinated derivatives, due to its synthesis, better reactivity, and higher electronegativity. Its chemical reaction is a nucleophilic substitution obtained by polycondensation between 200°C and 400°C (Hallmann et al., 2012). The aromatic rings and saturated bonds within PEEKs structure provide good biocompatibility, high oxidation stability and chemical resistance at temperatures below T_g (Rusakov et al., 2022).

Its chemical structure confers stability at high temperatures (exceeding 300°C), resistance to chemical and radiation damage, compatibility with many reinforcing agents (such as glass and carbon fibers), greater strength (on a per mass basis) than many metals, making it highly attractive in industrial applications, such as aircraft and turbine blades. (Kurtz, 2019)

2.3.2. Mechanical and thermal properties

PEEK is an aromatic, high-performance, semi-crystalline linear, thermoplastic, with excellent mechanical and thermal properties, such as high strength-to-weight ratio, resistance to chemical and biological attack, excellent thermal stability, high glass transition, and melting temperatures (Yasin et al., 2019). This semi-crystalline linear polymer has a high elastic modulus of ($E = 3–4\ GP_a$), a high melt and glass transition temperatures of (T_m=343ºC, T_g=143ºC), tensile strength of ($\sigma \approx 100\ MP_a$) (Rusakov et al., 2022), high chemical resistance and it is melt processable (Rae, Brown & Orler, 2007).

At temperatures below T_g, PEEK can only be dissolved in concentrated sulfuric and methane sulphonic acid. At temperatures exceeding the glass transition temperature and getting close to the melting point, it is possible to dissolve PEEK in high boiling solvents (dichloroacetic acid, benzophenone, 4-phenylphenol, diphenyl sulfone, and chlorophenols) (Rusakov et al., 2022; Devaux et al., 1985). When the degree of sulphonation (DS) is low (DS around 4 mol %), this polymer is only resistant to strong polar organic solvents such as DMF, DMAc, DMSO and pyridine, therefore it is important to control the degree of sulphonation (DS) once it influences the stability of the membrane on those solvents (Jin et al., 1985).

PEEK is a promising material because of its inert response to chemical reagents and heat resistance, highly elastic modulus, and durability in thermo-oxidative conditions, even with their chemical resistance, reducing its processability (Hallmann et al., 2012; Jin et al., 1985), which make this polymer an excellent option for OSN membranes. Its stability, biocompatibility, radiolucency, and mechanical properties make PEEK a suitable biomaterial for a wide range of applications, mainly as a matrix in the growing thermoplastic composite industry, and as a biomaterial for orthopedic, trauma, and spinal implants (Kurtz, 2019; Rusakov et al., 2022).

PEEK membranes possess advantages over other polymeric membranes, and their manufacture is simple in terms of no need of crosslinking and conditioning agent decreasing its environmental burden.

2.3.3. History and applications

In the early 1960s, PEEK polymers were reported independently as novel materials (Rose, 1986). Later, in 1979, ICL's (Imperial Chemical Industries), have decided to launch this thermoplastic, because of its extending ICI's "VITREX" range of aromatic polymers with a crystalline material (Hallmann et al., 2012). Its first application area was as extruded insulation for high performance wires and cables, but there is now a wide spread of applications including injection molded parts, chemically resistant surface coatings, monofilament for industrial belts and filters and as the matrix in carbon fiber composites for aerospace components (Rose, 1986). They have been reported for other different applications as well, such as, continuous catalysis, gas separation, fuel cells, MF, UF, NF and RO (Jansen & Drioli, 2009).

PEEK membranes can be either non-sulphonated (PEEK), sulphonated (S-PEEK), and both can be modified. Which means that, by understanding all its structures, it is possible to understand its suitability for the wide range of applications that this polymer makes part of. Therefore, it is strictly important to know all its structures.

Non-sulphonated PEEK membranes have been mainly reported as supports for MF and UF (Shimoda & Hiroshi, 1999; Soroko et al., 2011; Yuan, 2005). Sulphonated PEEK (S-PEEK), that can be obtained via post-sulphonation, or via sulphonated monomers (Khan, Li & Vankelecom, 2011a), have been used for gas separation processes (Khan, Li & Vankelecom, 2011a, 2011b), polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) as an alternative to Nafion membranes (Li et al., 2010).

An example of a PEEK modified membrane is the PEEK-WC [poly(oxa-p-phenylene-3,3-phtalido-phenylene-oxa-p-phenylene-oxy-p-phenylene) with Cardo group], that is amorphous and soluble in many organic solvents with medium polarity such as, chloroform, dichloroform, dimethyl sulfoxide, dimethylacetamide (DMAc), dimethylformamide, 1- methyl-2-pyrrolidinone, and is not soluble in water and alcohols. Its applications are focused in gas separation, pervaporation and biomedical applications. It is possible to find PEEK WC in the sulphonated form, as well, and its applications are focused on the fuel cells. (Jansen & Drioli, 2009)

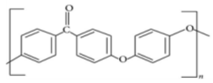
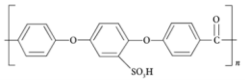
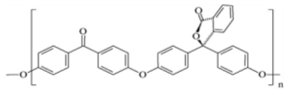
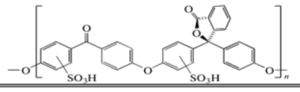
Polymer	Abbreviation	Molecular Structure	Modified
Poly(ether ether ketone)	PEEK		No
Sulphonated poly(ether ether ketone)	S-PEEK		Yes
Poly(oxa-p-phenylene-3,3-phtalido-phenylene-oxa-p-phenylene-oxy-p-phenylene) with Cardo group	PEEK-WC		Yes
Suplhonathed Poly(oxa-p-phenylene-3,3-phtalido-phenylene-oxa-p-phenylene-oxy-p-phenylene) with Cardo group	S-PEEK-WC		Yes

Figure 2.4 - Representation of the different molecular structures of PEEK. (Gujar et al., 2013; Xi et al., 2015; Najeeb et al., 2015; Jansen & Drioli, 2009)

Chapter 3. Material and Methods

3.1. Material

3.1.1. Chemicals

In the four tables below (Table 3.1, 3.2, 3.3 and 3.4) are presented all the chemicals used in this experimental work, and their suppliers. In Table 3.1, were presented the solvents (MSA and SA), and Polymer (PEEK) used, to create the dope solution. In Table 3.2, the solvents used to immerse the membrane, before the drying step. In Table 3.3, were presented the polymers used as support materials to PEEK membranes during the drying step, to avoid PEEK membranes of being damaged by the extreme conditions they were subjected to, during the drying process. Table 3.4 presented all the chemicals used to prepare the feed solution, used in the cross-flow rig system. All the solvents described below, were used, without being subjected to any purification process.

Table 3.1 - Chemicals used to prepare the Dope Solution.

Chemicals	Supplier
Methane sulphonic acid (MSA)	Sigma Aldrich
Sulphuric acid (SA) 95 vol%	Sigma Aldrich
VESTAKEEP® 400P	Evonik Industries

Table 3.2 - Solvents used to immerse the membranes pores, prior to the drying step.

Chemicals	Supplier
Propanone (acetone)	VWR Chemicals
Methanol (MeOH)	VWR Chemicals
Water	VWR Chemicals

Table 3.3 - Polymers used as support to the membrane (backing material), during the drying process.

Chemicals	Supplier
Poly(phenylene sulfide) (PPS)	Sigma Aldrich
Poly(tetrafluoroethylene) (PTFE)	Ebay

Table 3.4 - Chemicals used in the Feed Solution.

Chemicals	Supplier
Acetonitrile (MeCN)	VWR Chemicals
Poly(ethylene glycol) (PEG400)	Sigma Aldrich
Poly(ethylene glycol) (PEG1000)	Sigma Aldrich
Poly(ethylene glycol) (PEG2000)	Sigma Aldrich
Poly(ethylene glycol) (PEG8000)	Sigma Aldrich
Poly(ethylene glycol) (PEG35000)	Fluka Chemicals

3.1.2. Equipment

Different equipment was needed in this research work. During the drying step, a mini Hot Press machine (Novel technology) and a convective oven (Conventional technology), were used, and compared in terms of efficiency. Thereafter, analytical equipment such as, high performance liquid chromatography (HPLC) and Scanning electron Microscopy (SEM) were used to analyze the membrane performance by using different drying equipment.

3.1.2.1. Oven

The conventional oven is the common equipment used in the laboratory for drying and heating demands. It works with a mechanical convection (represented in figure 3.5) or forced air, in which, inside the chamber there is an integrated fan, that actively move the air, resulting in optimal temperature uniformity for reproducible results, for example for drying procedures, with very tight temperature requirements. Another advantage for this equipment is its fast temperature recovery when the door is opened. So far, this equipment was known, as well, by its faster drying process, comparing with other equipment. They are capable of completely drying out the solvent from the membrane, in 1 h. (Thermo Fisher Scientific, 2006)

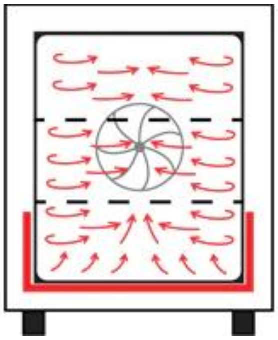


Figure 3.5 – Illustration of the mechanical Convection that happens inside the Convective Oven (Thermo Fisher Scientific, 2006).

In this work, several membranes, after immersed in different solvents (acetone and deionized water), were tested in this drying equipment, at several temperatures, for one hour, with the main goal of completely remove the solvent from the membrane pores. Table 3.5 and table 3.6, present all the membranes conditions tested in the convective oven, after being immersed in acetone (Table 3.5) and deionized water (Table 3.6).

Table 3.5 - membranes dried in the Oven, at different temperatures and with the same drying time (1 h), after being immersed in acetone.

	Acetone	
Membrane Code	Drying Temperature (ºC)	Drying Time (h)
PEEK.50T.AC.Ov	50	1
PEEK.80T.AC.Ov	80	1
PEEK.120T.AC.Ov	120	1
PEEK.140T.AC.Ov	140	1

Table 3.6 - membranes dried in the Oven, at different temperatures and with the same drying time (1 h), after being immersed in deionized water.

	Deionized Water	
Membrane Code	Drying Temperature (ºC)	Drying Time (h)
PEEK.50T.OVEN.DIW	50	1
PEEK.80T.OVEN.DIW	80	1
PEEK.100T.OVEN.DIW	100	1
PEEK.120T.OVEN.DIW	120	1

3.1.2.2. Hot Press Machine

A hot press machine, an equipment previously used to melt plastic or rubber resin to make laboratory specimens of sample sheets from high heat pressure (FMAM LAB, 2021), was never used by scientists in the membrane technology, as possible drying method. However, it brings considerable advantages comparing with the conventional methods (Convective Oven), since it can reduce the drying time, and confer uniformity to the membrane, since the heat is directly applied in the membrane by the two heated plates (Down and Up) showed in the figure 3.6

Figure 3.6 represent the mini hot press machine, used in this work, with dimensions of 500W x 400D x 750Hmm, constituted by two metal plates, with sizes of 200 x 200 mm each, those two plates are heated by the heater in the panel at the bottom of the equipment, and the temperatures are controlled (for each plate), through different temperature controllers, using a Digital P.I.D system. A pressure gauge, located in the panel at the bottom, is used to register the pressure that is applied to the membrane used (the membrane is inserted between the two metal plates), and this pressure is increased or decreased by the lever. The table below (table 3.7), present the specifications of the equipment.

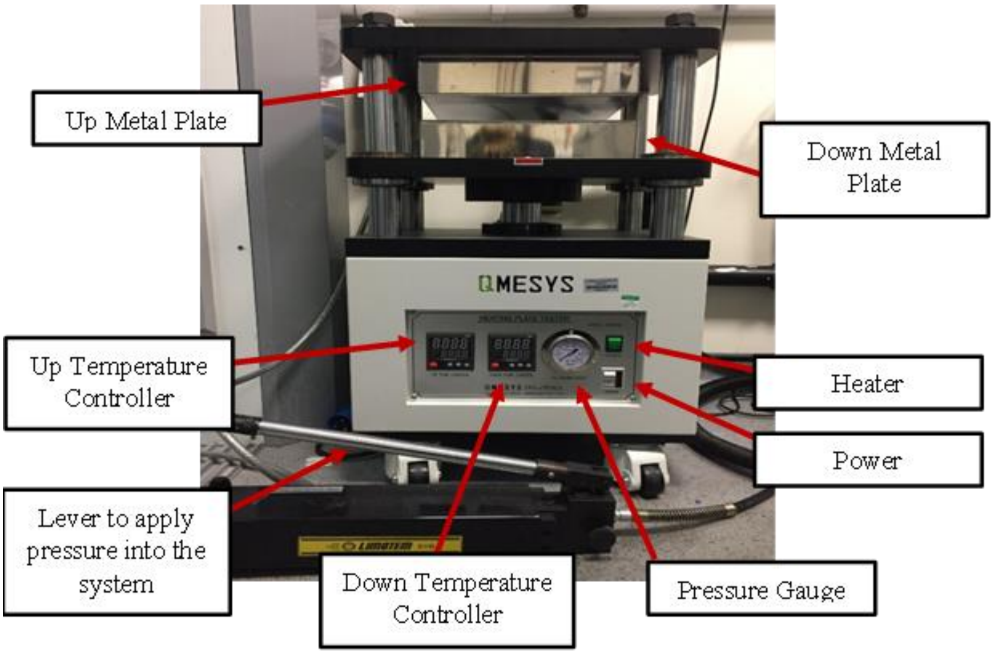


Figure 3.6 – Mini Hot Press Machine used in the investigation. Photography was taken with permission, in Imperial College London laboratories, Chemical Engineering Department.

Table 3.7 - Specifications of Hot Press machine.(FMAM LAB, 2021; Jung, C. 2006)

HP machine Specifications	
HP model	QM900L (LIMOTEM)
Dimensions	500W x 400D x 750Hmm
Net weight	450 Kg
Main Body	SC45C Thermo powder coating and SKD
Plate size	200 x 200 mm
Temperature Range	RT ~ 350ºC (Max.320Cº)
Temperature Controller	Digital P.I.D System / Up, Down (1Ea/Each)
Pressure Max	350 bar
Power	220VAC, 60HZ, 4KW

The focus of this work was investigating the efficiency of this equipment, by exposing different PEEK membranes, to completely different temperature and pressure conditions in this equipment, after the solvent exchange step, where the membranes were immersed in different solvents for 24hours. In the tables bellow (Table 3.8 and 3.9), are presented all the conditions tested during this research.

Table 3.8 - Membranes tested with Hot Press machine, after being immersed in acetone.

Acetone		
Membrane Code	**Temperature in HP machine (°C)**	**Pressure in HP machine (bar)**
PEEK.30T10B	30	10
PEEK.50T10B	50	10
PEEK.80T10B	80	10
PEEK.120T10B	120	10
PEEK.140T10B	140	10
PEEK.160T10B	160	10
PEEK.30T30B	30	30
PEEK.50T30B	50	30
PEEK.80T30B	80	30
PEEK.120T30B	120	30
PEEK.140T30B	140	30
PEEK.160T30B	160	30
PEEK.30T50B	30	50
PEEK.50T50B	50	50
PEEK.80T50B	80	50
PEEK.120T50B	120	50
PEEK.140T50B	140	50
PEEK.160T50B	160	50
PEEK.30T.100B	30	100
PEEK.50T100B	50	100
PEEK.80T100B	80	100
PEEK.120T100B	120	100
PEEK.140T100B	140	100
PEEK.160T100B	160	100

Table 3.9 - Membranes tested with Hot Press machine, after being immersed in deionized water.

DIW		
Membrane Code	**Temperature in HP machine (°C)**	**Pressure in HP machine (bar)**
PEEK.DIW.30T10B	30	10
PEEK.DIW.50T10B	50	10
PEEK.DIW.80T10B	80	10
PEEK.DIW.100T10B	100	10
PEEK.DIW.120T10B	120	10
PEEK.DIW.160T10B	160	10
PEEK.DIW.30T30B	30	30
PEEK.DIW.50T30B	50	30
PEEK.DIW.80T30B	80	30
PEEK.DIW.100T30B	100	30
PEEK.DIW.120T30B	120	30
PEEK.DIW.160T30B	160	30
PEEK.DIW.30T50B	30	50
PEEK.DIW.50T50B	50	50
PEEK.DIW.80T50B	80	50
PEEK.DIW.100T50B	100	50
PEEK.DIW.120T50B	120	50
PEEK.DIW.160T50B	160	50
PEEK.DIW.30T100B	30	100
PEEK.DIW.50T100B	50	100
PEEK.DIW.80T100B	80	100
PEEK.DIW.100T100B	100	100
PEEK.DIW.120T100B	120	100
PEEK.DIW.160T100B	160	100

3.1.2.3. Analytical equipment

High Performance Liquid Chromatography (HPLC)

High performance Liquid Chromatography (HPLC) separation columns, usually work with an Evaporative Light Scattering Detector (ELSD), because of its capability of detecting samples that don't absorb UV light, as PEGs. Its principle is, the conversion of the eluents to a fine spray via a nebulized, using nitrogen has inert carrier gas, and its analysis comprises three stages: nebulization, mobile-phase evaporation, and detection. In the nebulization, the nitrogen flows through the effluent column to former an aerosol, then it is used in the mobile-phase evaporation which is heated allowing the evaporation of the mobile-phase. Finally, the detection is achieved by excitation of photons of the evaporated particles (Waters, 2021). The mobile phase A2 and B2 was prepared in 2.5L flasks, and it was used with the reverse phase column ACE 5-C18-300 column (Advanced Chromatography Technologies, ACT, UK). Phase A2 was prepared with 2.5L of water and 0,97g of ammonium acetate. Phase B2 was prepared with acetonitrile (MeCN) and methanol (MeOH) in a proportion of 80:20, respectively. The total flow was 1 ml.min^{-1}, with 0,1 ml.min^{-1} of A2, (10%) and 0.9 ml.min^{-1} of B2, (90%). The grade solvent used was acetonitrile (MeCN), since its lower absorbance of 190 nm, make it more suitable for molecules which don't absorb UV light, as PEGs (Troubleshooting, 2003). Each sample (approximately 30μL of eluted collected sample) was analyzed by the HPLC, for a period of 30 minutes. Chromatograms were obtained, where retention times of the PEGs standard solutions (1 g.L^{-1}), and their Signal area were observed.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM), give useful information about the functional performance of the membranes, as it allows their structural characterization. To obtain an image for surface imaging, small samples of a membranes were transferred to alumina supports, they were cut and placed horizontally onto SEM stubs and covered with carbon tape, at room temperature. Considering that polymeric membranes are non-conducting materials, the samples needed to be coated with a chromium-layer (15nm thickness), through a sputter coater Q150T S (Quorum Technologies Ltd.), under an argon atmosphere. This argon atmosphere was used to reduced sample charging under the electron beam. SEM pictures of the surface of membrane samples were recorded using a Field Scanning Electron Microscope with an acceleration voltage of 5 Kv. at room temperature and under dry conditions.

3.2. Methods

3.2.1. Membrane Preparation

PEEK membrane preparation involved five main steps: Dope preparation, Membrane casting, phase inversion in water bath, solvent exchange (it is optional) and ensuing drying. (Figure 3.7)

First, it was prepared the dope solution, in which, one grade of PEEK powder VESTAKEEP® 400P was dissolved, with a concentration of 12 wt. %, in a mixture of 3:1 wt. % methane sulphonic acid (MSA) and sulphuric acid (SA), using a mechanical stirring (IKA RW 20 digital), at room temperature (21ºC), until the polymer solution became homogeneous. After, the solution was left at room temperature for 72 to 96 hours, to prevent the solution of keeping any air bubbles (air bubbles can affect the membrane performance), in the moment of the membrane casting. During the membrane casting, the polymer dope solution previously left to dry, was spread across a blade, and cast on a polyphenylene Sulfide (PPS) support, with transverse speed of 0,5 cm.s^{-1}. Subsequently, the membrane was immersed in a precipitation bath with Deionized water (DIW), (phase inversion), at 20ºC, and it was washed with DIW several times, until it reaches a pH 6-7. After, it was cut into several batches, and each membrane batch was immersed in a different solvent (acetone and DIW) where remained for 24 hours, until the next membrane preparation step. Finally, the different membrane batches were submitted to two different drying equipment, the convective Oven method, where the membrane stayed for 1hour, with a specific temperature, and the Hot Press, where the membrane stayed for 15 seconds, and in which were played different conditions at same time, as temperature and pressure. The main goal for the Oven and Hot Press is to completely dry out, the solvent from the pores.

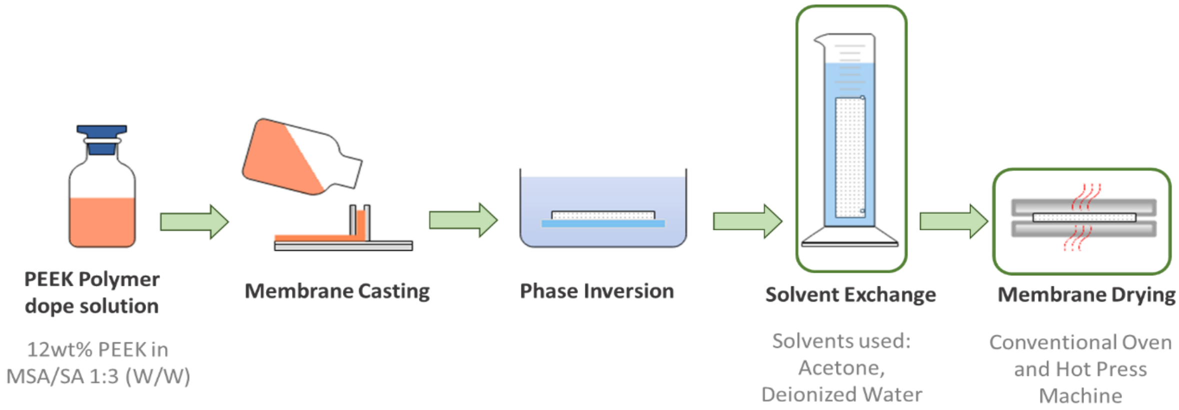


Figure 3.7 – Schematic representation of the membrane preparation steps, in the PEEK membrane via phase inversion method. Dope solution, Membrane casting, phase inversion in water bath, solvent exchange step (acetone and deionized water were used) and ensuing drying (Conventional Oven and Hot Press were used), are represented and are the main steps of phase inversion method.

3.2.2. Polyethylene Glycol Standard Solution Preparation

The Polyethylene glycol Standard Solution was prepared by dissolving five different Polyethylene glycols PEGs (PEG400, PEG1000, PEG2000, PEG8000, PEG35000) 2g.L^{-1} in a pure Acetonitrile (MeCN) solution of 2,5L.

3.2.3. Membrane Performance and Analysis

Ensuing the drying step, two small discs were cut from each membrane (from the two most distant points of the membrane), and 8 discs, with different conditions, were tested, into the cross flow filtration, where the fluid to be filtered, was pumped across the membrane parallel to its surface. Each membrane disc had 54mm in diameter and an active area of 18 cm^2.

Two solutions were created: the permeate (the filtrate) and the retentate (containing the retained particles of the solution). The system was initially running with pure solvent (MeCN), at 30 bar, room temperature of 21ºC, for 1 hour (to clean all the system from other possible chemicals residues), then an acetonitrile standard solution, described in section 3.2.2 (Chapter 3) was put into a 2L feed tank , and re-circulated at a flow rate of 30L.h^{-1}, using an HPLC pump, and the system was pressurized again, up to 30 bar, using a back pressure regulator located downstream of a pressure gauge. This cross-flow filtration was used to determine the long term performance of the membrane. At different time intervals (4h and 24h after the system was running) the permeate and retentate samples were collected, and the concentrations of PEGs presents in the permeate and retentate samples were analyzed in an Agilent HPLC system with UV/Vis detector (set at a wavelength of 264 nm). The flux (J), Permeance (B), and the Rejection (R_i) of PEGs were determined, and the MWCO curves, from the Rejection of PEGs results, were determined, by plot between Rejection of PEGS and their molecular weight.

Figure 3.8 represented the system configuration used in this work, for testing the membranes.

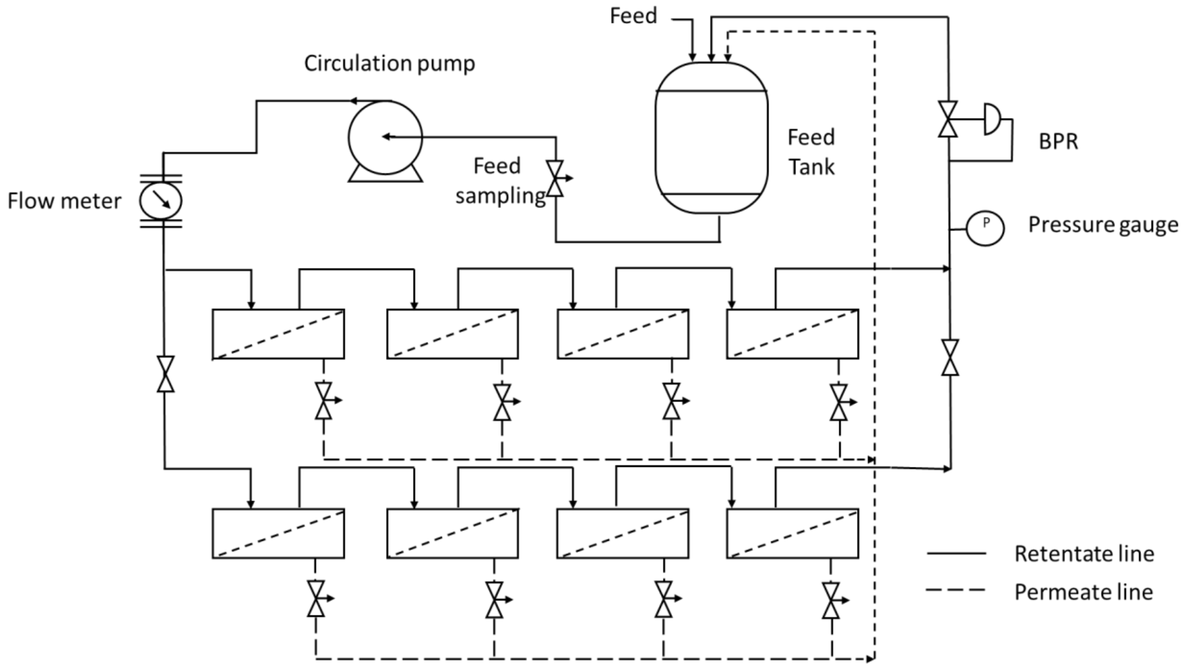


Figure 3.8 – Schematic representation of the configuration used (8 cells cross-flow rig configuration), for testing the membranes. Legend: BPR – back pressure regulator.

3.2.3.1. Experimental Setup

The system used in this research work, was represented in the figure 3.9. It was constituted by: One feed tank, localized above the other major units of the system, using a magnetic stirrer system to mix the feed tank solution, with the purpose of maintaining the homogeneity of the solution, since every time that were collected permeate samples, the permeate was recovered to the feed tank; two HPLC pumps, to re-circulate the feed solution; a flowmeter to measure the flow rate of the system; a back pressure regulator, to increase or decrease the pressure of the system; a pressure gauge to measure the pressure of the system; a membrane unit, with 8 cross-flow cells; nine different self-draining valves, for collect the permeate from each of the 8 cross-flow cells, and the other for collect the retentate samples in the retentate line (corresponding to the feed solution sample); two gate valves, that were always closed, to block the solution to go out of the system, while the system was working; and finally. a flexible tube, through which, Nitrogen gas passed, every time before the system was running, to clean all the system of possible undesirable chemicals.

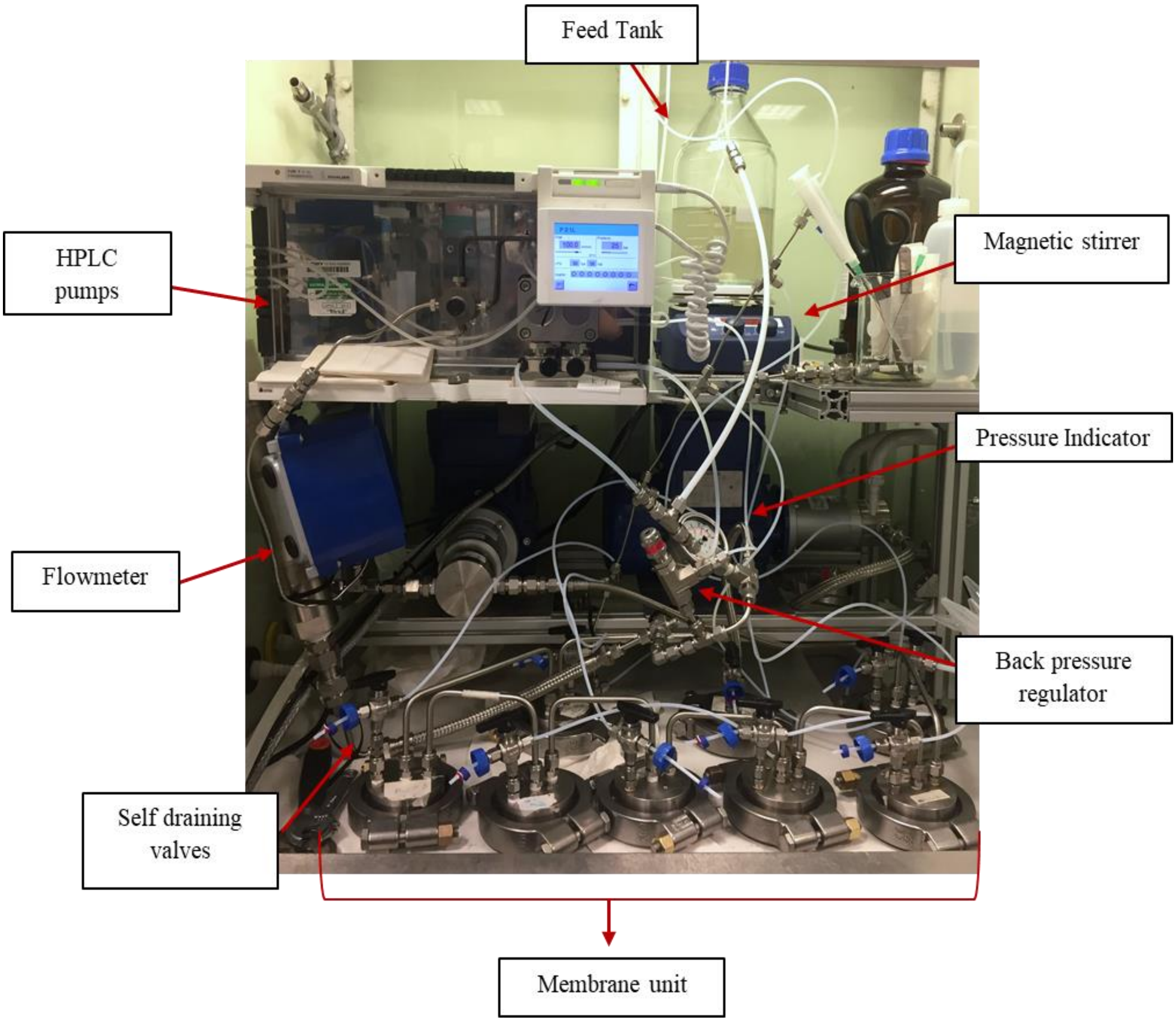


Figure 3.9 - Experimental Set-up used. 8 cell cross flow rig system. Photography was taken with permission, in Imperial College London laboratories, Chemical Engineering Department.

3.2.4. HPLC Calibration

HPLC is a very sensitive machine and one of the most common instruments in the quality control department, used for very precise analytical results. Therefore, it requires a good handling and regular calibration practice.

To calibrate a HPLC, it was prepared an acetonitrile solution with 2g.L^{-1} of PEG400, PEG1000, PEG2000, PEG8000 and PEG35000. Following this, the solution was diluted in 8 small flasks of 20mL each (small solutions), with concentrations of 0.001 g. L^{-1}, 0.01 g. L^{-1}, 0.1 g. L^{-1}, 0.2 g. L^{-1}, 0.25, g.L^{-1} 0.5 g. L^{-1}, 1 g.L^{-1}, and 2 g.L^{-1}. By calibrating the HPLC, it was possible to convert the HPLC peak areas to concentration and mass, and consequently calculate the purity and the yield.

The calibration curves, presented in figure 3.10, were considered linear with a square error of the regression line between 88-95%. However, a polynomial curve, would fit the data better, avoiding, or decreasing the errors of the regression line, resulting in experiments more reliable.

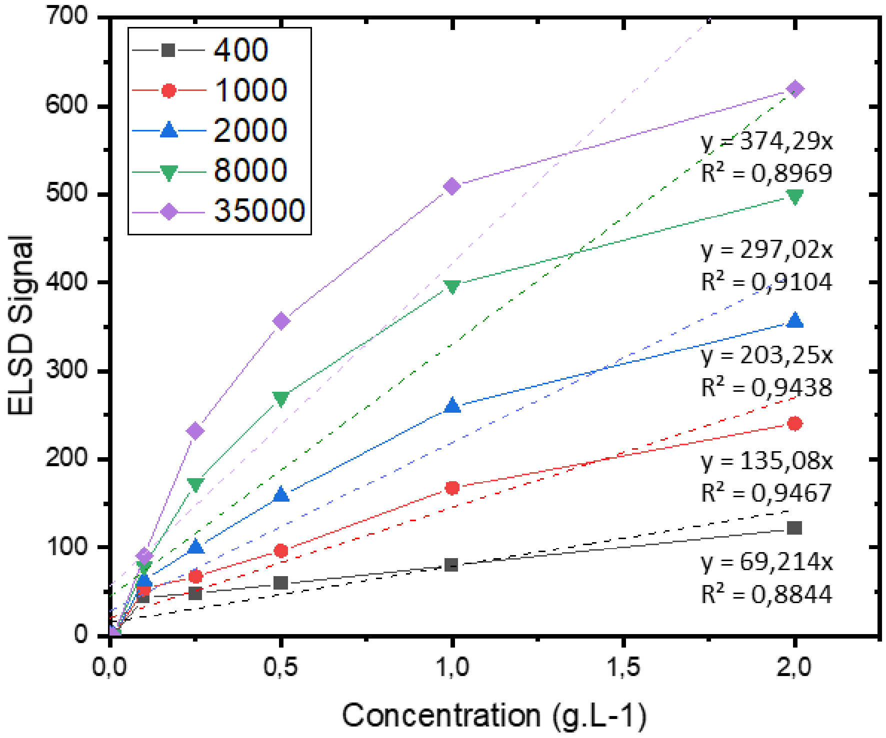


Figure 3.10 - HPLC calibration

Chapter 4. Results and Discussion

To improve and stabilize PEEK membrane performance, a study focused on the post treatment steps (solvent exchange and drying method) of its manufacture, was made. In the solvent exchange step, the membrane was immersed in two different solvents (Deionized water and Acetone). After, the membrane was subjected to different drying methods (Hot Press Machine, and Convective Oven), where different factors such as, temperature, pressure and time were studied.

4.1. Acetone

4.1.1. The effect of acetone as drying solvent with the Hot Press machine

It is known that is possible to influence the membrane performance by post-treatment steps, such as drying. The following table (table 4.10) presented all the conditions that the membranes were submitted at, with the Hot press machine, after the membranes being immersed in the solvent for 24 h. Table 4.11, presented the properties of the solvent used in the solvent exchange step (acetone).

Table 4.10 – Different temperature and pressure conditions, that several membranes were submitted at, with the Hot Press machine, after being immersed into acetone, at the solvent exchange step.

Membrane Code	**Temperature in the HP machine (°C)**	**Pressure in the HP machine (bar)**
PEEK.30T10B	30	10
PEEK.50T10B	50	10
PEEK.80T10B	80	10
PEEK.120T10B	120	10
PEEK.140T10B	140	10
PEEK.160T10B	160	10
PEEK.30T30B	30	30
PEEK.50T30B	50	30
PEEK.80T30B	80	30
PEEK.120T30B	120	30
PEEK.140T30B	140	30
PEEK.160T30B	160	30
PEEK.30T50B	30	50
PEEK.50T50B	50	50
PEEK.80T50B	80	50
PEEK.120T50B	120	50
PEEK.140T50B	140	50
PEEK.160T50B	160	50
PEEK.30T.100B	30	100
PEEK.50T100B	50	100
PEEK.80T100B	80	100
PEEK.120T100B	120	100
PEEK.140T100B	140	100
PEEK.160T100B	160	100

Table 4.11 – Acetone properties (Smallwood, 2012; See Toh, Lim & Livingston, 2007; Scheirs, 2000)

Solvent Properties (Acetone)	
Surface tension (mN.m^{-1})	**Heat of vaporization (cal.g^{-1})**
23,3	122
Boiling Point (°C)	**Molecular Volume (cm^{3}.mol^{-1})**
56,1	73,8

Solubility Parameter (cal.cm^{-3})	
PEEK at 20ºC	**Acetone**
9,5	10

Regarding Figure 4.11, the membranes dried at 30 ºC and 50ºC presented a higher MWCO in a range of 1888-5784 g.mol $^{-1}$, and higher permeance, in the range of 2.92-8.56. However, at these temperatures, just few of them, were in the NF range, such as PEEK.30T10B (MWCO = 1940 gmol^{-1}), PEEK.50T10B (MWCO = 1888 gmol^{-1}), PEEK30T30BAR (MWCO = 1994 gmol^{-1}), PEEK.50T30B (MWCO = 1940 gmol^{-1}), and PEEK50T50B (MWCO = 1992 gmol^{-1}).

Membranes dried at temperatures superior to the solvent boiling point (80ºC, 100ºC, 120ºC, 140ºC and 160ºC) presented lower permeance (0.07-2.99) L.h-1.m-2.bar^{-1}, and lower MWCO, in a range of 549-1835 g.mol $^{-1}$ (tightest membranes). There was a trend as function of the temperature, (the higher the temperature the lower the MWCO, and the tighter the membrane). In terms of pressure, there was no trend either for the rejection profiles, or for permeance. For all the membranes dried at different temperatures: at 10 bar, the permeance was in the range of 0.26-6.22 L.h^{-1}.m^{-2}.bar^{-1}, at 30 bar, of 0.06-6.17 L.h^{-1}.m^{-2}.bar^{-1}, at 50 bar, of 0.10-6.33 L.h^{-1}.m^{-2}.bar^{-1} and at 100 bar, of 0.11-7.11 L.h^{-1}.m^{-2}.bar^{-1}. By the results it was observed that, there was no sharp border line between MWCO of the different membrane separation processes. However, once nanofiltration separations of molecules are in a 200-2000 Da range, the membranes dried at 80ºC, 100ºC, 120ºC, 140ºC and 160ºC, were considered nanofiltration membranes, and the membranes dried at 30ºC and 50ºC were not considered as nanofiltration membranes.

For 10 Bar (Figure 4.11 R1), the tighter membranes were PEEK.140T10B, and PEEK.160T10B, both with a MWCO of 760.4 g.mol $^{-1}$, and with permeance values (Figure 4.11 P1) of 0.25 L.h^{-1}.m^{-2}.bar^{-1}, and 0.26 L.h^{-1}.m^{-2}.bar^{-1}, respectively. At 30 Bar, (Figure 4.11 R2), the tighter membrane was PEEK.140T30B (140ºC, 30 bar), with a MWCO of 682 g.mol $^{-1}$ approximately, and a permeance value (Figure 4.11 P2) of 0.26 L.h^{-1}.m^{-2}.bar^{-1}. At 100 bar, (Figure 4.11 R4), the tighter membrane was PEEK.140T100B (140ºC, 100bar), with a MWCO of 839 g.mol $^{-1}$ and permeance of 0.33 L.h^{-1}.m^{-2}.bar^{-1}. On Figure (4.11 R3), PEEK.140T50B (140ºC, 50 bar), was the tightest membrane, over all the membranes immersed in acetone prior to drying, with a MWCO of 549 g.mol $^{-1}$ and a permeance of 0.18

$L.h^{-1} m^{-2} bar^{-1}$. Followed by PEEK.120T50B, (120ºC, 50 bar) and PEEK.160T50B (160ºC, 50 bar), both with a MWCO of 668 $g.mol^{-1}$ approximately. Interestingly, PEEK.1400T50B, seemed to be greatly influenced by the pressure applied, once by increasing from 10bar to 30 bar, and from 30bar to 50bar, its MWCO decreased from 760 $g.mol^{-1}$, to 549 $g.mol^{-1}$, but it was the only example where this trend was verified.

The fact that was obtained tight membranes can be explained by the solvent used to fill the membrane pores (acetone), before the drying step. It is known by fact, that the final membrane pore size is influenced by the surface tension of the solvent filling the membrane pores, prior to drying, and according to Brown's Theory (Gevers et al., 2006a; Beerlage, 1994; Brown, 1956), which considers surface tension, as the only solvent property that influences membrane drying process, as it influences the pore collapse. It assumes, as well, that the solvent is completely evaporated of the membrane. According to this theory, the higher the surface tension the lower the MWCO and the tighter the membrane and also, though acetone would be expectable to obtain tighter membranes, as it has a surface tension of 23,3 $mN.m^{-1}$. Therefore, the results obtained were in accordance with Browns theory, since were obtained tighter membranes with acetone.

However, it is important to mention, the present theory, does not explain many of the results obtained, since it considers surface tension, as the only solvent property that influences membrane drying process. In the case of acetone, this theory could be easily considered, since its boiling point is considerably low, which allows its total removal from the membrane pores at a faster rate (solvent being completely removed from the membrane), by other words, could be easily assumed, the surface tension was the only solvent property that matter for this specific case. These results could be either explained, by other studies(Matsuyama, Kim & Lloyd, 2002) , that relate the membrane porosity, with the solvent surface tension and the boiling point of the solvent in a matter that, the membrane porosity is inversely proportional to the solvent surface tension and to the boiling point of the solvent.

According to these studies, pore collapse involves rearrangement of the amorphous polymer molecules within the matrix phase, which requires time. Assuming this, the longer the capillary force is in effect, the greater is the time for rearrangement of polymer chains in the matrix phase and the greater is the extent of pore collapse. For solvents with lower boiling points and higher vapour pressures, the solvent disappears much faster from the membrane pores, shortening the action time of the capillary force applied and the degree of pore collapse.

Few other studies, presented a correlation between the dried membrane properties, and the polymer-drying solvent affinity, expressed by the Hansen solubility parameter, in which solvents such as acetone, presented the highest affinity to PEEK, as presented in the table 4.11, and for this reason, this solvent should be more difficult to remove from the pores, being obtained more open pores.(Matsuyama et al., 2002; Jie et al., 2005; Philip, 1978) However, this theory didn't match with the results obtained, once tighter membranes were obtained instead.

Regarding Figure 4.12, the following SEM images corresponded to 4 different membranes, in which, were applied different temperatures, PEEK50T50BAR (Figure 4.12 S1) at 50ºC, PEEK80T50B (Figure 4.12 S2) at 80ºC, PEEK140T50BAR (Figure 4.12 S3) at 140ºC and PEEK160T50BAR (Figure 4.12 S4) at 160ºC, and the same pressure of 50 bar. Interestingly, it was noticed that, for PEEK140T50BAR, and for PEEK160T50BAR, the SEM images seemed similar in terms of pores size. The pores were noticeably smaller, comparing with PEEK50T50BAR and PEEK80T50B. This was explained by the fact that, when the temperature was increased, the solvent filling the pores was removed at a faster rate, and the pores became smaller. Therefore, it was observed a trend in which, the size of the membrane pores was reduced with the increasing of temperature. Which is in accordance with the previous results. It was expectable for the tightest membranes, having smaller pores, since, during the drying method, the usual phenomena is, decreasing the pore size with the quick remotion of the drying solvent of the membrane pores, and that was observed through the SEM images.

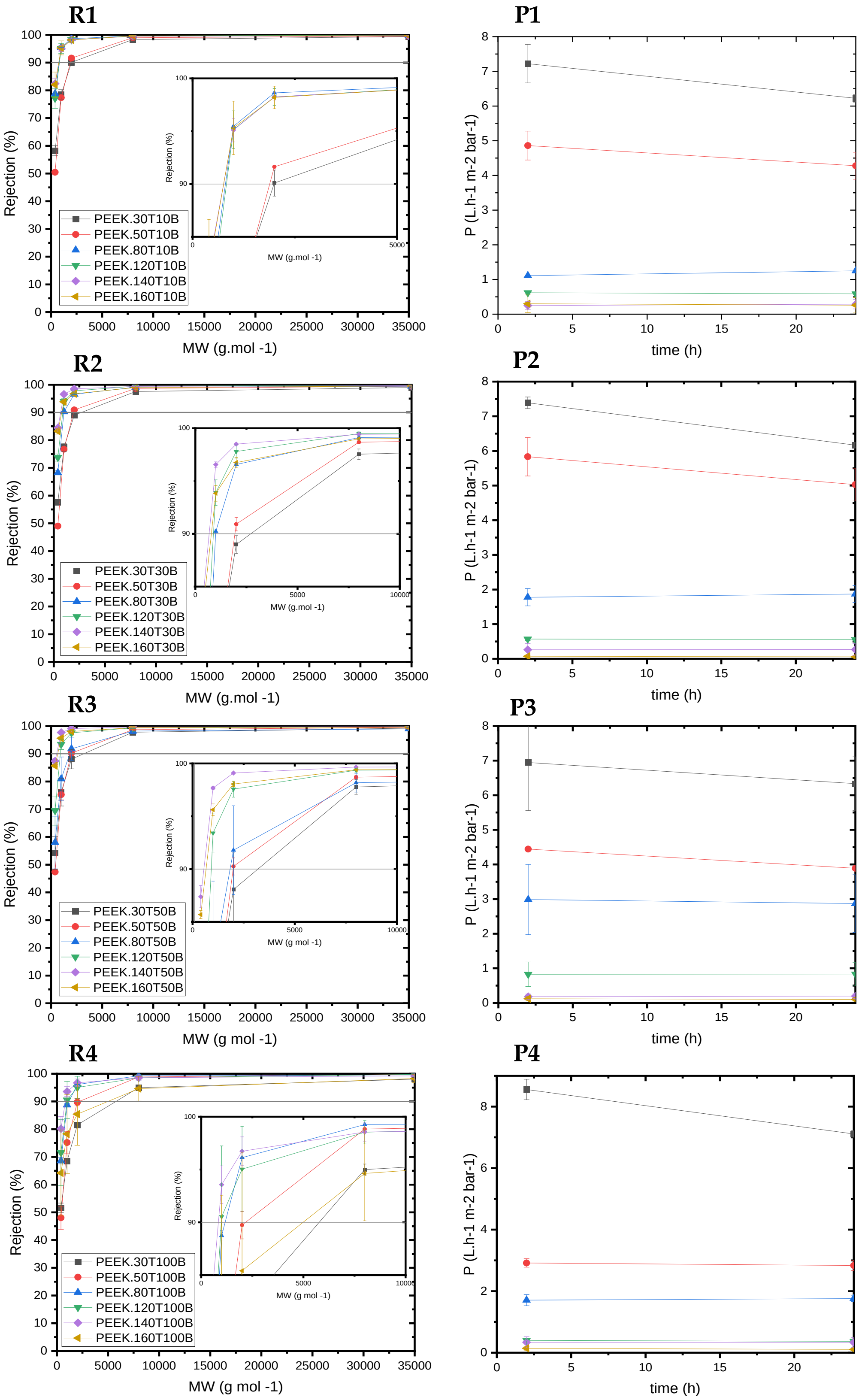


Figure 4.11 – R1, R2, R3 and R4 presented the Rejection values of the different PEEK membranes under study as a function of the molecular weight (MW, g.mol^{-1}) of different polyethylene glycols after 24 hours. P1, P2, P3 and P4 the Permeance values (L.h^{-1}.m^{-2}.bar^{-1}) over a period of 24 h for the different membranes under study. The membranes were dried from acetone, using a Hot press, as drying method, and these results were obtained after the membranes being inserted in the cross-flow cells system.

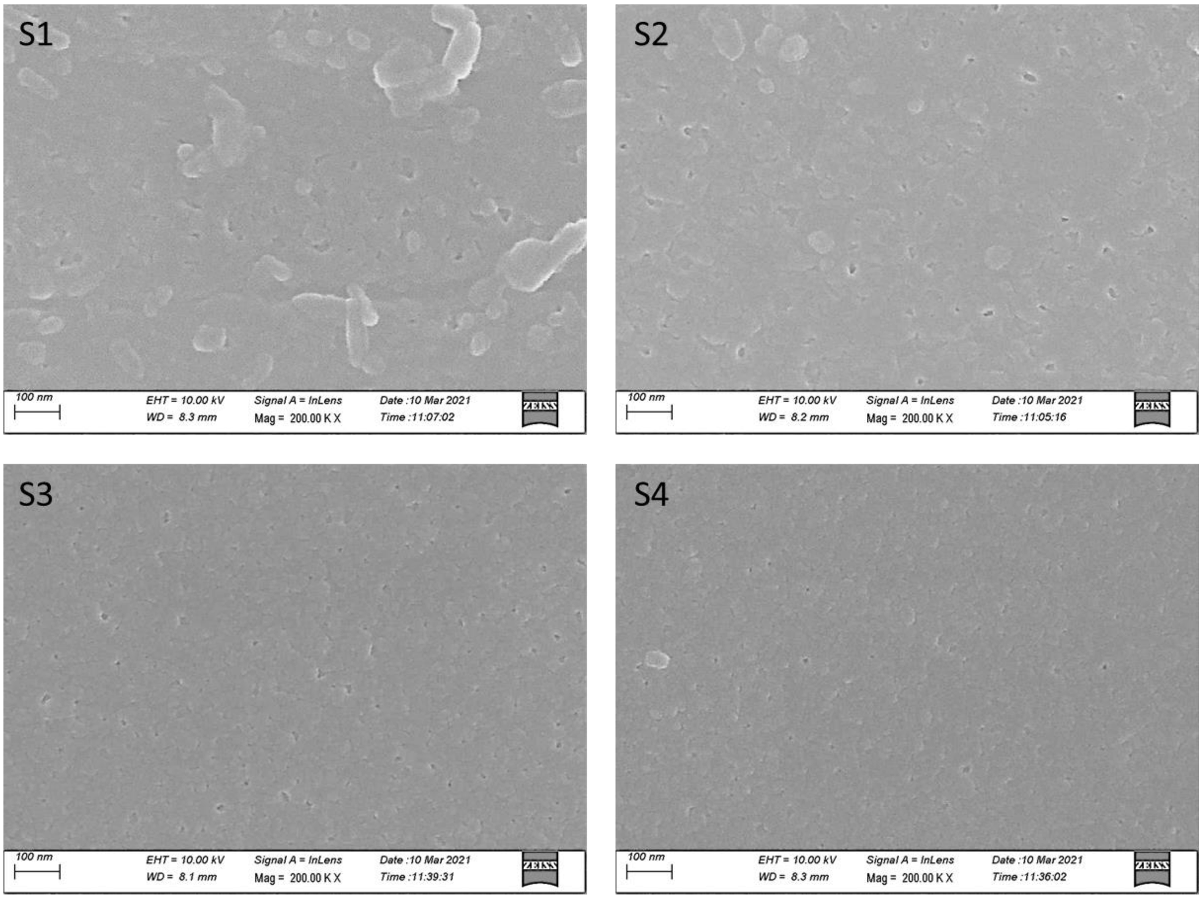


Figure 4.12 - Scanning electron microscopy (SEM) images of membranes dried at different temperatures, S1 - PEEK50T50B, 50ºC and 50 bar; S2 -PEEK80T50BAR, 80ºC and 50 bar; S3 -PEEK140T50BAR, 140ºC and 50 bar; S4 -PEEK160T50BAR, 160ºC and 50 bar.Figure 4.11 – R1, R2, R3 and R4 presented the Rejection values of the different PEEK membranes under study as a function of the molecular weight (MW, g.mol-1) of different polyethylene glycols after 24 hours. P1, P2, P3 and P4 the Permeance values (L.h-1.m-2.bar-1) over a period of 24 h for the different membranes under study. The membranes were dried from acetone, using a Hot press, as drying method, and these results were obtained after the membranes being inserted in the cross-flow cells system.

4.1.2. The effect of acetone as the drying solvent with the Conventional Oven

Four different temperatures were tested in the oven (50ºC, 80ºC, 120ºC and 140ºC). Table 4.12 presented all the membranes tested at these. The membranes were previously immersed in acetone and then left in the oven for 1 hour, until the solvent filling the pores being completely dry out.

Considering the results obtained, The MWCO was in the range of 853-1115 g.mol^{-1}. PEEK.80T.AC.Ov (red line) was not considered a nanofiltration membrane, since its MWCO was 8500 g.mol^{-1} (beyond the NF range), and once the standard deviation was not narrow enough, it was not possible to validate the result.

There was a trend as function of temperature for the rejection and for permeance. The higher the temperature the higher the rejection and the lower the MWCO (Figure 4.13 R5). PEEK.140T.AC.Ov (green line), presented the lowest MWCO of 853 g.mol^{-1} (tightest membrane), with a permeance of 1.39 L.h^{-1}.m^{-2}.bar^{-1}. PEEK.50T.AC.Ov (black line), with the highest MWCO of 1115 g.mol^{-1}, was the loosest membrane, with a permeance of 3.25 g.mol^{-1}. For permeance (Figure 4.13 P5), with the increasing of the temperature, the permeance of the membranes decreased. The permeance values were in the range of 1.39-3.25 L.h^{-1}.m^{-2}.bar^{-1}.

Regarding all the results, it was observed that by using the Oven as drying method, although the temperature had influence in the rejection profiles and in the permeance values, this effect was not very pronounced, which means this method probably is not the best option to manipulate the MWCO, and consequently the membrane performance, in the case of, considering temperature as the only variable in study.

Table 4.12 - Different temperature conditions, that several membranes were submitted at, with the Oven, after being immersed into acetone, at the solvent exchange step.

Membrane Code	Temperature in the Oven (°C)
PEEK.50T.AC.Ov	50
PEEK.80T.AC.Ov	80
PEEK.120T.AC.Ov	120
PEEK.140T.AC.Ov	140

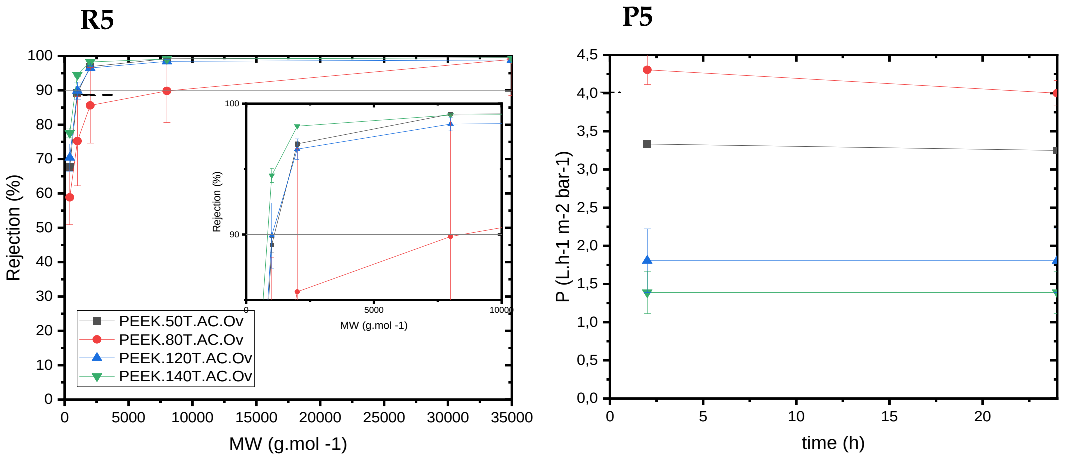


Figure 4.13 – R5 presented the Rejection values of the different PEEK membranes under study as a function of the molecular weight (MW, g.mol^{-1}) of different polyethylene glycols after 24 hours. P5 presented the Permeance values (L.h^{-1}.m^{-2}.bar^{-1}) over a period of 24 h for the different membranes under study. The membranes were dried from acetone, using the oven, as drying method. These results were obtained after the membranes being inserted in the cross flow cells system.

4.1.3. Comparison between HP machine and Conventional Oven

To prove the efficiency of a specific equipment, or to compare two different equipment, it is important to understand the notion of energy consumption. Energy consumption can be easily calculated by the product between, the working time of the equipment, and the power used to the equipment work. In table 4.13, were compared the different powers, drying times and energy consumed, to perform the drying work. It was observed that HP machine had lower energy consumption (even with a power of 4 kW), due to the fact, that it just needed 15 seconds to perform the same drying process, as the oven, that needed 1h.

Table 4.13 – Comparison in Energy Consumption, between Hot press machine and Convective Oven

HP machine		**Oven**
4	Power (kW)	1,6
15	Drying time (s)	3600
60	Energy (kJ)	5760

After investigated different conditions for each equipment, in sections 4.1.1 and 4.1.2., six membranes, (three, dried with HP and other with the oven), were chosen to compare and discussed in this section. The criteria chosen to select the best membranes, dried with HP, was selecting the ones with the lower MWCO (the tightest ones), therefore, membranes pressurized at 50 bar were the tightest ones, comparing with the other pressures. The membranes chosen were represented in figure 4.14 R6, representing their rejection profiles, and Figure 4.14 P6, their permeance values. PEEK.50T50B (black line), PEEK.80T50B (blue line) and PEEK.140T50B (purple line), were membranes dried from Hot press machine, at 50ºC, 80ºC, and 140ºC, respectively, all pressurized at 50 bar. PEEK.50T.AC.Ov (red line), PEEK.80T.AC.Ov (green line), and PEEK.140T.AC.Ov (dark yellow line), correspond to the membranes dried from oven, at 50ºC, 80ºC and 140ºC, respectively (same range of temperatures, to make a clear comparison).

Regarding the rejection profiles (Figure 4.14 R6), all the membranes presented a MWCO in the nanofiltration range, except for PEEK.80T.AC.Ov, as mentioned in section 4.1. 2.. For membranes dried with HP, the MWCO values were, for PEEK.50T50B, of 1993 g.mol^{-1}, for PEEK.80T50B, of 1836 g.mol^{-1}, for PEEK.120T50B, of 668 g.mol^{-1}, and for PEEK.140T50B, of 550 g.mol^{-1}, While, for membranes dried with the oven, the MWCO observed were, for PEEK.50T.AC.Ov, of 1115 g.mol^{-1} , for PEEK.120T.AC.Ov, of 1021 g.mol^{-1} , and for PEEK.140T.AC.Ov, of 853 g.mol^{-1}. According to these results, it was possible to affirm that was a clear overall trend, the higher the temperature, the lower the MWCO. In addition, pressure seemed to play an important role in the MWCO, as well. For instance, for PEEK.50T.AC.Ov at 50ºC, and dried with the oven, the MWCO was not that higher comparing with PEEK.140T.AC.Ov dried at 140ºC and note there was a significant rise of temperature. On the other hand, by using the Hot press, these differences in MWCO for each temperature was far more pronounced, for example, PEEK.140T50B, at 140ºC, 50 bar with a MWCO of 550 g.mol^{-1}, and PEEK.50T50B, at 50ºC, 50bar, with MWCO of 1993 g.mol^{-1}, almost four times higher than PEEK.140T.50B.

According to the results, it was concluded that pressure influenced in great matter the membrane MWCO, and consequently its performance (considering acetone as the solvent), probably due to the fact, that by applying pressure into the membrane, the solvent was more easily squeezed out of the membrane pores, and the drying process was faster. Hot press machine, proved to be more efficient than oven, so far, once it achieved better results in terms of, drying process efficiency, due to its reduction in the drying time for 15 seconds, and less energy consumption. In addition, it was obtained tighter membranes comparing with the Oven.

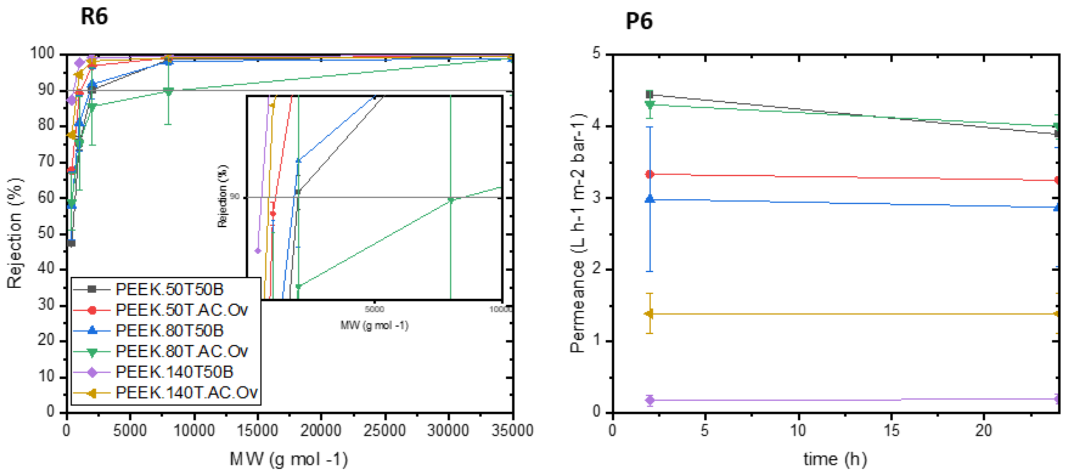


Figure 4.14 – R6 presented the Rejection values of 6 different PEEK membranes under study, as a function of the molecular weight (MW, g.mol^{-1}) of different polyethylene glycols after 24 hours. In R6, were presented 3 membranes dried with the Hot press machine (PEEK.50T50B, PEEK80T50B and PEEK.140T50B), and 3 membranes dried with the oven (PEEK.50T.AC.Ov, PEEK.80T.AC.Ov, and PEEK.140T.AC.Ov). In P6 are presented the Permeance values (L.h^{-1}.m^{-2}.bar^{-1}) over a period of 24 h for the corresponding to these different membranes. These results were obtained after the membranes being inserted in the cross flow cells system.

4.2. Deionized Water

4.2.1. The effect of DIW as drying solvent with the Hot Press machine

Membranes dried from water were investigated, at different temperatures: 30ºC, 50ºC, 80ºC, 100ºC, 120ºC and 160ºC, and different pressures: 10 bar, 30 bar, 50 bar, 100 bar, and they were presented in table 4.14. Deionized water properties were presented in table 4.15

Table 4.14 - Different temperature conditions and pressure conditions, that several membranes were submitted at, with the Hot press machine, after being immersed into deionized water, at the solvent exchange step.

Membrane Code	**Temperature in the HP machine (°C)**	**Pressure in the HP machine (bar)**
PEEK.DIW.30T10B	30	10
PEEK.DIW.50T10B	50	10
PEEK.DIW.80T10B	80	10
PEEK.DIW.100T10B	100	10
PEEK.DIW.120T10B	120	10
PEEK.DIW.160T10B	160	10
PEEK.DIW.30T30B	30	30
PEEK.DIW.50T30B	50	30
PEEK.DIW.80T30B	80	30
PEEK.DIW.100T30B	100	30
PEEK.DIW.120T30B	120	30
PEEK.DIW.160T30B	160	30
PEEK.DIW.30T50B	30	50
PEEK.DIW.50T50B	50	50
PEEK.DIW.80T50B	80	50
PEEK.DIW.100T50B	100	50
PEEK.DIW.120T50B	120	50
PEEK.DIW.160T50B	160	50
PEEK.DIW.30T100B	30	100
PEEK.DIW.50T100B	50	100
PEEK.DIW.80T100B	80	100
PEEK.DIW.100T100B	100	100
PEEK.DIW.120T100B	120	100
PEEK.DIW.160T100B	160	100

Table 4.15 – Deionized water properties (Smallwood, 2012; Scheirs, 2000; See Toh, Lim & Livingston, 2007)

Solvent Properties (DIW)	
Surface tension (nM.m^{-1})	**Heat of vaporization (cal.g^{-1})**
72,8	540
Boiling Point (°C)	**Molecular Volume (cm^{3}.mol^{-1})**
100	18

Solubility Parameter (cal.cm^{-3})	
PEEK at 20ºC	**Water**
9,5	25,5

The membranes dried at 30ºC and 50ºC, represented by the black line and red line, in all the graphics bellow (figure 4.15 - R8, R9, R10, R11), did not show the commonly rejection profile (broad curve) of the nanofiltration membranes, by other words, did not present a MWCO in the NF range. At 80ºC, the membranes, presented permeance values in a range of 0.42-5.03 L.h^{-1}.m^{-2}.bar^{-1} (annexe3). These membranes presented a MWCO in a range of 931-2238 g.mol $^{-1}$. PEEK.DIW.80.100BAR (Figure 4.15 R11) with a MWCO of 2230 g.mol^{-1}, was not in the NF range, and PEEK.DIW.80.30BAR (Figure 4.15 R9), has not showed the typical rejection profile to be in the NF range, as it was impossible to observe its MWCO, therefore, this membrane was not considered as a NF membrane either.

At 10 Bar (Figure 4.15 R8), the MWCO, at different temperatures, was in the range of 787-1961 g.mol $^{-1}$, and the permeance values, in the range of 0.06-5.03 L.h^{-1}.m^{-2}.bar^{-1}. The tightest membrane was PEEK.DIW.100T10B, with the lower MWCO, of 787 g mol $^{-1}$ approximately, and permeance of 1,14 L.h^{-1}.m^{-2}.bar^{-1}. The loosest membrane was PEEK.DIW.80T10B with a MWCO of 1961 g mol $^{-1}$ and a permeance of 5,03 L.h^{-1}.m^{-2}.bar^{-1}. At 30 Bar (Figure 4.15 R9), the MWCO was in the range of 426-931 g mol $^{-1}$, and the permeance in the range of 0.08-0.98 L.h^{-1}.m^{-2}.bar^{-1}. PEEK.DIW.160T30B, was the tightest membrane, with a MWCO of 426 g mol $^{-1}$ and permeance of 0.08 g mol^{-1}, and PEEK.DIW.100T30BAR was the loosest membrane with a MWCO of 931.37 g mol^{-1}, and a permeance value of 0.98 L.h^{-1}.m^{-2}.bar^{-1}. At 50 Bar (Figure 4.15 R10), the MWCO ranged between 870 g mol^{-1}, and 26717 g mol^{-1}. However, 26717 g.mol^{-1} is not in the NF range. Therefore, the membrane PEEK.DIW.160T50B was not a NF membrane. PEEK.DIW.80T50B, PEEK.DIW.100T50B and PEEK.DIW.120T50B, presented the same MWCO of 870 g mol^{-1}, with permeance values of 2.87 L.h^{-1}.m^{-2}.bar^{-1}, 0.84 L.h^{-1}.m^{-2}.bar^{-1}, and 0.36 L.h^{-1}.m^{-2}.bar^{-1}, respectively. Thus, in figure 4.15 R10, the temperature had no significant effect on the MWCO, however, it had in the permeance (the higher the temperature the lower the permeance). At 100 bar, (Figure 4.15 R11), the MWCO was in the range of 397-2238 g mol^{-1} and the permeance values, between 0.11 L.h^{-1}.m^{-2}.bar^{-1}, and 1.76 L.h^{-1}.m^{-2}.bar^{-1}. PEEK.DIW.100T100B had the lowest MWCO, of 397 g.mol^{-1}, and a permeance of 0.84 L.h^{-1}.m^{-2}.bar^{-}

^{1}. PEEK.DIW.80T100B, with the MWCO value of 2238 g mol^{-1} was not in the NF range. In figure 4.15 R11, PEEK.DIW.100T100B at 100ºC and with a pressure of 100 bar, was the tightest membrane (MWCO of 397.29 g.mol^{-1}), comparing with all the other membranes used. Interestingly, when the membrane was subjected to 100ºC, and different pressure conditions, (30bar, 50 bar and 100 bar), its MWCO decreased significantly. It was assumed that, by applying pressure into the membrane, the solvent filling the membrane pores, was completely squeezed out, allowing its drying at a faster rate, therefore, it was concluded that higher pressures leaded to a faster drying process.

Regarding the permeance values, they were presented in figure 4.16, but only two different pressures were considered, due to the fact, the pressure seemed to have no significant effect on the membrane. For 10 bar and 100 bar, which are clearly disparate pressures, the permeance values were in a range of 0.06-9.67 L.h^{-1}.m^{-2}.bar^{-1}, and 0.07-6.39 L.h^{-1}.m^{-2}.bar^{-1}, respectively. For that reason, would not be relevant to show any other results. Regarding this, were then selected membranes subjected at 10 bar (Figure 4.16 R8) and membranes subjected at 100 bar (Figure 4.16 R11). It was observed for the lowest temperatures (30ºC, 50ºC and 80ºC) that by increasing the pressure, the permeance values decreased significantly, PEEK.DIW.30T10B (30ºC, 10 bar), had a permeance value of 9.67 L.h^{-1}.m^{-2}.bar^{-1} and PEEK.DIW.30T100B (30ºC, 100 bar), had a permeance value of 6.39 L.h^{-1}.m^{-2}.bar^{-1}. PEEK.DIW.50T10B (50ºC,10 bar), had a permeance value of 4,19 L.h^{-1}.m^{-2}.bar^{-1} , and PEEK.DIW.50T100BAR (50ºC, 100 bar), had a permeance value of 2.83 L.h^{-1}.m^{-2}.bar^{-1}. PEEK.DIW.80T10BAR (80ºC, 10 bar), had a permeance value of 5.03 L.h^{-1}.m^{-2}.bar^{-1}, and PEEK.DIW.80T100BAR (80ºC, 100 bar), had a permeance value of 0.43 L.h^{-1}.m^{-2}.bar^{-1}. On the other hand, for the highest temperatures (100ºC, 120ºC and 160ºC) the membranes subjected to 10 bar or to 100 bar, presented similar permeance values of, 0.22 L.h^{-1}.m^{-2}.bar^{-1} for PEEK.DIW.100T100BAR (100ºC, 100 bar), and 1.14 L.h^{-1}.m^{-2}.bar^{-1} for PEEK.DIW100T10BAR (100ºC, 10 bar). For PEEK.DIW120T10B (120ºC, 10 bar) the permeance was 0.63 L.h-1.m-2.bar^{-1}, and for PEEK.DIW120T100B (120ºC, 100 bar) the permeance was 0.24 L.h-1.m-2.bar^{-1}. Finally for PEEK.DIW160T10B (160ºC, 10 bar) the permeance was 0.07 L.h-1.m-2.bar^{-1}, and PEEK.DIW160T10B (160ºC, 100 bar) the permeance was 0.06 L.h-1.m-2.bar^{-1}.

Regarding all the results, it was concluded for figure 4.5 that, there was no trend as function of the temperature (with the increasing of the drying temperature some membranes MWCO increased and some decreased), and although pressure had a significant effect on the membrane, it was not possible to finding a trend. For the highest temperatures (160ºC, 120ºC, 100ºC), there were big fluctuations in the MWCO values, between the pressures applied. For figure 4.6, the pressure had no significant effect on the permeance values of the membranes dried at higher temperatures but had significant effect on the lowest temperatures, and the decreasing in permeance, was more pronounced for membranes dried at 80ºC.

For solvents, such as deionized water, some residual water could be retained in the smallest pores of the membrane, because of its higher boiling point 100ºC (higher temperatures would be needed, to completely remove the solvent from the pores), and for that reason, surface tension could not be the only property to be considered, as for example, in the case of acetone (mentioned in the subsection 4.1.1).

In this case, other solvent properties such as boiling point, vapor pressure, viscosity, molar volume, heat of vaporization, and Hansen solubility parameter can have a significant weight in the membrane drying method, and therefore need to be considered.(Beerlage, 1994; Gevers et al., 2006a) For the lowest temperatures, the fact they were below to Deionized water boiling point, meant the solvent was not removed from the pores. Therefore, the results obtained could not be validated, since the membranes were not dried, and the objective of this drying method was to completely remove the solvent from the pores. To the highest temperatures, the inconsistency in the results could be explained by the heat of vaporization of water (around 540 $cal.g^{-1}$ at 100 °C), that refers to the energy necessary to convert liquid into gas, that for water is high, which means by other words, that is necessary more energy, comparing with other solvents, to convert liquid into gas, consequently, the evaporation rate, is slower, and 15 seconds (the drying time for Hot press), was not probably enough, for the solvent on the surface, being completely removed from the pores, in some membranes.

These conclusions were based in a limited number of experiments, so would be recommended to investigate this process in more detail. Although, the standard error in all these experiments was considerable low. All the standard errors can be found in the annexes.

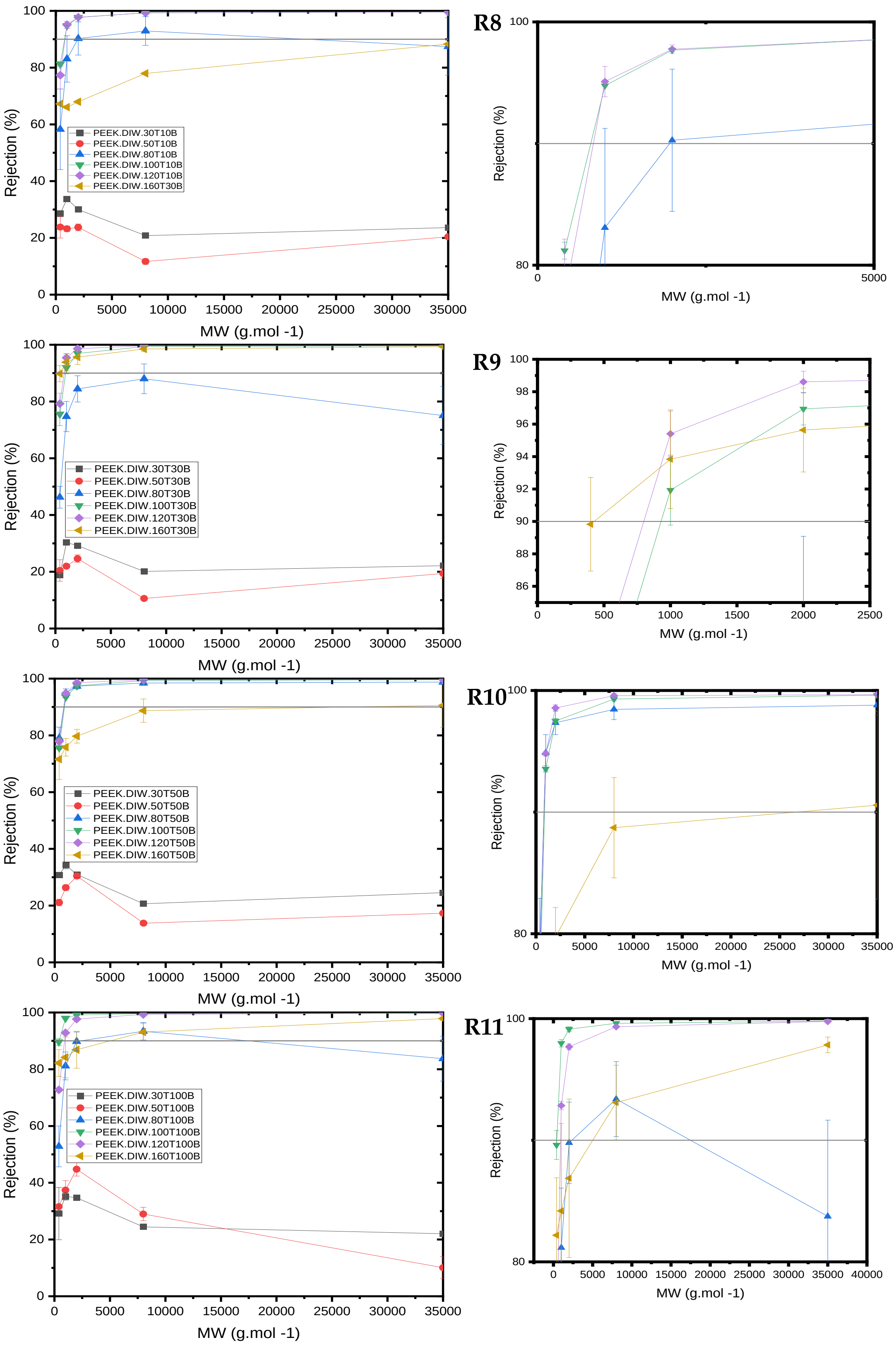


Figure 4.15 – R8, R9, R10 and R11 presented the Rejection values of the different PEEK membranes under study as a function of the molecular weight (MW, g.mol^{-1}) of different polyethylene glycols after 24 hours. The membranes were dried with DIW, and these results were obtained after the membranes being inserted into the cross-flow cells system.

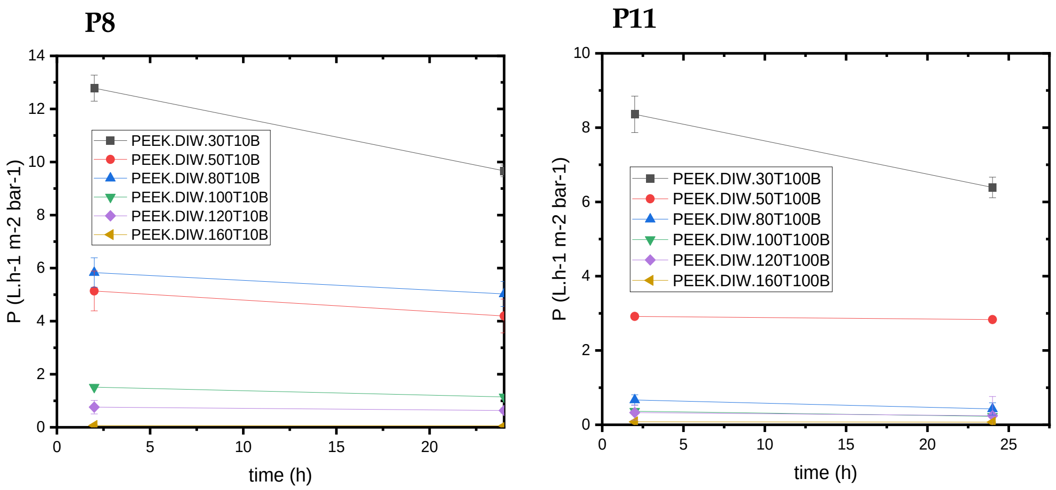


Figure 4.16 - P8 and P11 presented the Permeance values (L.h^{-1}.m^{-2}.bar^{-1}) over a period of 24 h, for the membranes presented in R8 and R11 respectively. These results were obtained after the membranes being inserted in the cross flow cells system. The membranes were dried with DIW.

4.2.2. The effect of DIW as drying solvent with the Conventional Oven

Four different temperatures were tested in the oven (50ºC, 80ºC, 100ºC and 120ºC). In table 4.16 were presented all the conditions tested. The membranes were previously immersed in deionized water and then left in the oven for 1 hour, until the solvent filling the pores being completely dry out (or at least, this would be the expected scenario).

Considering the results obtained, there was no trend as function of temperature for the rejection and for permeance. Permeance values (Figure 4.17 P12), were in a range of 0.06-0.08 L.h^{-1}.m^{-2}.bar^{-1}. PEEK.80T.OVEN.DIW present the highest permeance, and PEEK50T.OVEN.DIW the lowest one. Regarding the MWCO (Figure 4.17 R12), for all the membranes, the MWCO was not in the NF range, and a change in all the membrane rejection profiles was observed, comparing with the other membranes tested (in the previous subsections), presumably due to the fact the solvent filling the pores was not completely drying out. This can be explained by two phenomena, the evaporation and boiling. Evaporation is the process where liquid get converted into vapor at a slow rate, and occurs in the surface, and the boiling means rapid evaporation of any liquid. For temperatures as 50ºC, or 80ºC, as they were lower than the DIW boiling point, it was easily assumed the solvent filling the pores was not evaporated at all. For the highest temperatures, this cannot be assumed as 100ºC and 120ºC, are equal and higher than the DIW boiling point, respectively. Interestingly, the water has the highest heat of vaporization, by other words, the amount of energy needed, to change one gram of liquid into gas (540 cal. g^{-1}), is higher, and for that reason, it was assumed that the water was more difficult to remove from the pores in the membrane surface, even at the highest temperatures.

Table 4.16 - Different temperature conditions, that several membranes were submitted at, with the Oven, after being immersed into deionized water, at the solvent exchange step.

Membrane Code	Temperature in the Oven (°C)
PEEK.50T.OVEN.DIW	50
PEEK.80T.OVEN.DIW	80
PEEK.100T.OVEN.DIW	100
PEEK.120T.OVEN.DIW	120

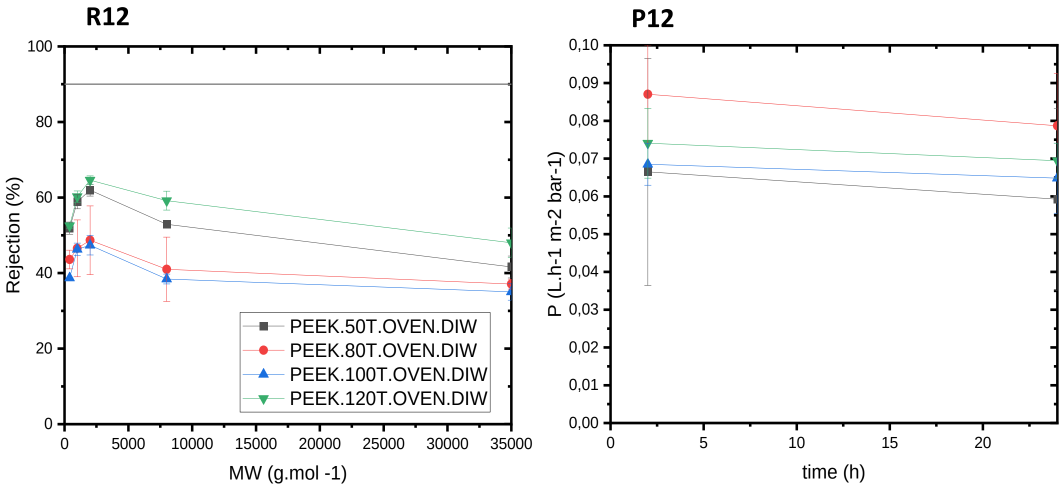


Figure 4.17 - R12 presents the Rejection values of the different PEEK membranes under study as a function of the molecular weight (MW, g.mol^{-1}) of different polyethylene glycols after 24 hours, P5 the Permeance values (L.h^{-1}.m^{-2}.bar^{-1}) over a period of 24 h for the different membranes under study. The membranes were dried from DIW, using the oven, as drying method. These results were obtained after the membranes being inserted in the cross-flow cells system.

4.2.3. Comparison between HP machine and the Conventional Oven

In order to investigate and compare, which drying equipment (Hot Press and Oven) was more effective, different conditions were tested (in the previous subsections of this chapter), and compiled in one figure (Figure 4.18), to be easier to analyze the main differences in the rejection profiles.

In figure 4.18, were presented eight different membranes tested, four with the HP machine (PEEK.DIW.50T30B, PEEK.DIW.80T30B, PEEK.DIW.100T30B, PEEK.DIW.120T30B), and other four, with the conventional oven (PEEK.50T.OVEN.DIW, PEEK.80T.OVEN.DIW, PEEK.100T.OVEN.DIW, PEEK.120T.OVEN.DIW). From the results obtained, it was possible to observe completely different trends, depending on the equipment. Regarding the results with the Hot press machine, the membranes presented, were subjected to 30 bar pressure. For PEEK.DIW.50T30B (black line), at 50ºC, and PEEK.DIW.80T30B (red line) at 80ºC, the membranes were not in the NF range.

In terms of direct comparison between these two equipment, it was noticed, that by using the oven, PEEK.50T.OVEN.DIW (purple line) and PEEK.80T.OVEN.DIW (dark orange line), had similar rejection profiles, in a range of (40-60) %, while, with the HP, PEEK.50T30B (50ºC, 30 bar) presented a rejection in a range of (10-20) %, and PEEK.80T30B (80ºC,30bar) in a range of (45-89) %. Therefore, pressure had a great influence in the rejection profile of the membrane, once, by applying pressure in the membrane surface, the rejection values increased significantly. For the highest temperatures, this contrast, between membranes dried from the HP and the oven, was even higher. PEEK.DIW.100T30B (blue line), at 100ºC and, PEEK.DIW.120T30B (green line), at 120ºC, presented rejection profiles in the NF range, with MWCO of 932 g.mol^{-1}, and 803 g.mol^{-1}, respectively, whereas PEEK.100T.OVEN.DIW (light blue line), at 100ºC, and PEEK.120T.OVEN.DIW (brown line), at 120ºC, were not in the NF range, and had rejection profiles in the range of (35-50) % and (50-65) %, respectively.

According to the results: First, pressure had a great effect in the membrane performance, once by applying pressure, in a membrane the rejection profiles were increasing; and Second, HP proved to be a more efficient, drying method, since it operated in just 15 seconds, to achieve tighter membranes than with the conventional oven, and as previously discussed, consume much less energy.

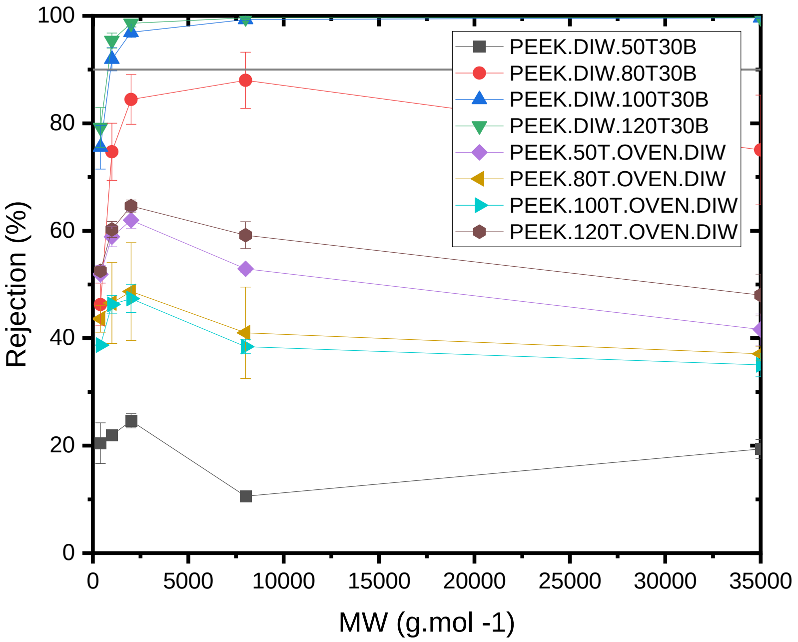


Figure 4.18 - Comparison of 8 different membranes, dried with different drying equipment: (PEEK.DIW.50T30B, PEEK.DIW.80T30B, PEEK.DIW.100T30B, PEEK.DIW.120T30B) dried with Hot Press machine; (PEEK.50T.OVEN.DIW, PEEK80T.OVEN.DIW, PEEK.100T.OVEN.DIW, PEEK.120T.OVEN.DIW) dried with the oven. The membranes were dried at the same temperatures for Hot press machine and Oven to make easier the comparison between these two methods

4.3. Acetone vs Deionized Water

This section was focused, in the comparison between two solvents (acetone and deionized water), used to filling the membrane pores, prior the drying process, with the purpose of avoiding pore collapse, once in the drying process, this phenomena is common. The figure 4.19 R14 and figure 4.19 R15 represented some of the conditions used in this work, for acetone and deionized water, respectively. For acetone, the membranes used for this comparison were, PEEK.30T50B (30ºC, 50 bar), PEEK.50T50B (50ºC, 50 bar), PEEK.80T50B (80ºC, 50 bar), PEEK.120T50B (120ºC, 50 bar), PEEK.140T50B (140ºC, 50 bar) and PEEK.160T50B (160ºC, 50 bar). Regarding, deionized water, PEEK.DIW.30T30B (30ºC, 30 bar), PEEK.DIW.50T30B, (50ºC, 30 bar), PEEK.DIW.80T30B (80ºC, 30 bar), PEEK.DIW.100T30B (100ºC, 30 bar), PEEK.DIW.120T30B (120ºC, 30 bar) and PEEK.DIW.160T30B (160ºC, 30 bar).

According to the figures 4.19 R14, and 4.9 R15, there was a clear difference, between membranes dried from acetone (figure 4.19 R14) and dried from DIW (figure 4.19 R15). In figure 4.19 R14, all the membranes presented a nitid broad curve in the NF range, with exception of PEEK.30T50B (R14. black line) with a MWCO of 3199 g.mol^{-1}. In figure 4.19 R15, the scenario was different. Membranes dried at 30ºC, 50ºC and 80ºC, PEEK.DIW.30T30B (R15. Black line), PEEK.DIW.50T30B (R15. Red line) and PEEK.DIW.80T30B (R15 blue line) respectively, none of them, presented the typical broad curve, of a rejection profile in NF, or had the MWCO inside the nanofiltration range, so they were not considered NF membranes, as explained in the sections before.

For acetone, there was a nitid trend depending on temperature, where, by increasing it, the MWCO decreased (although this decreasing was not so significative), being achieved tighter membranes. In the case of deionized water, there was no trend as function of temperature, but curiously the tightest membrane over all the membranes investigated in this work, was PEEK.160T.30B, dried from deionized water at 160ºC, with a MWCO of 426 g.mol^{-1}, and with a standard error between 0.2-2.9. which is in accordance with Brown's Theory since, water has higher surface tension than acetone and higher boiling point so it has to produce tighter membranes, although at lower temperatures there may be a residual solvent (not all water is evaporated) and it keeps open pores hence lower rejections. In addition to this, there was an even tighter membrane (not mentioned in this section), dried from DIW as well, PEEK.100T.100T, with a MWCO of 397 g.mol^{-1} and as the standard error was in the range of 0.04-1.19, it was possible to prove the veracity of these results. These interesting results about the tightest membranes being dried from deionized water, even without a trend being observed, leaded to the following thoughts: First, Deionized water DIW must be further investigated as solvent, in the drying process with HP, to find a possible trend, once the results presented in this work showed its potential in the manufacture of tighter membranes, considering as well, the experiments made, were not enough.

Second, if deionized water can actually replace other solvents less green and sustainable and sustainable, and producing tightest PEEK membranes, further researchers should be considered, in order to prove the sustainability of the OSN fabrication process.

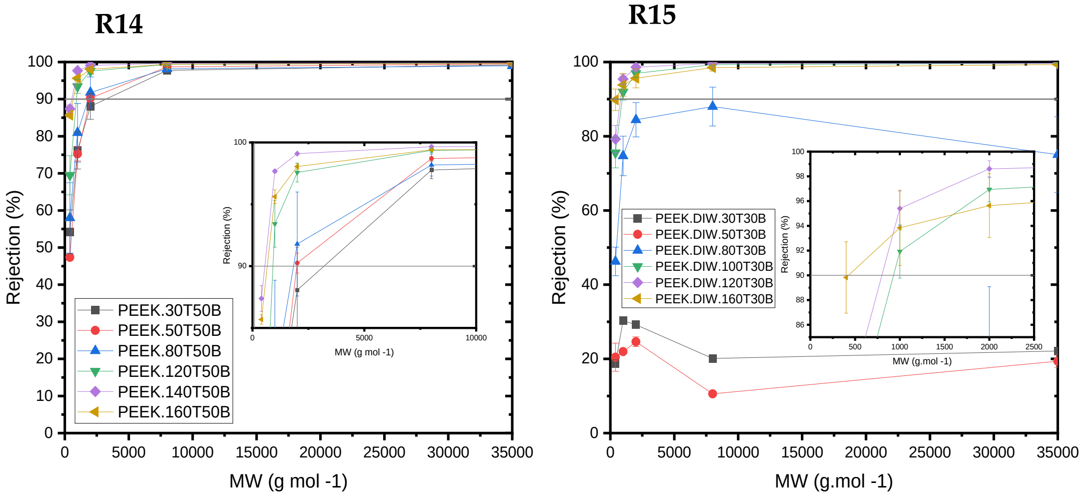


Figure 4.19 - Comparison between DIW and acetone, by analyzing the rejection profiles of the different membranes dried with each solvent. R14, presented all the membranes tested with acetone. R15, presented all the membranes dried with DIW. Were chosen, similar temperature conditions for each solvent, to do an easier comparison.

Chapter 5. Conclusions and Future Work

In this work was demonstrated for the first time that it is possible, to replace the conventional oven, used as drying method, in PEEK membranes manufacture, on Organic Solvent Nanofiltration (OSN), by a much greener option, Hot press machine.

After investigated several conditions of temperature and pressure, applied to the membranes during the drying process, with the hot press, it was possible to conclude that pressure had a great influence in the membrane performance, and accelerate the drying process. By the experiments made, it was observed that, by increasing the temperature and applying pressure at the same time, the MWCO tended to decrease, creating tighter membranes. This decrease was more pronounced, with deionized water. Interestingly, the tightest membranes, correspond to the ones immersed in deionized water, instead of acetone, which means, that it was possible to achieve tight membranes, without a solvent exchange step needed, with other words, by keeping deionized water, and consequently make the process more sustainable.

Through this method, were achieved more uniform membranes, as this equipment applied the heat directly into the membrane, through their heated metal plates, that distributed heat evenly across the membrane. In addition, through this method it was possible to decrease the drying time during the drying process, from 1 hour, with the convective oven, to 15seconds, with the novel equipment, decreasing the energy consumption.

To outline everything, through this new drying method and by proving “no need” for a different solvent in the solvent exchange step, it was possible to achieve a more sustainable process.

Note that, there is still a lot of room, for improvement on membrane performance through this new equipment, as for the understanding of the complex relation between temperature and pressure, working together, during the drying process. One of the unsolved problems was understanding, why deionized water did not completely dry out from the membrane pores, at temperatures higher than its boiling point. Regarding this, further research should be done, as, continuing the experiments with deionized water, to clarify the conclusions made in this work, using other type of polymeric or ceramic membranes, and even testing different solvents, although the deionized water being the most interesting solvent to work with.

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Annexes

Table A.17 - MWCO for all the PEEK membranes tested, after using the Heat Press Machine

Acetone		**Deionized Water**	
Membrane Code	MWCO	**Membrane Code**	MWCO
PEEK.30T10B	1993,84	PEEK.DIW.30T10B	0,00
PEEK.50T10B	1888,39	PEEK.DIW.50T10B	0,00
PEEK.80T10B	809,96	PEEK.DIW.80T10B	1960,78
PEEK.120T10B	832,76	PEEK.DIW.100T10B	786,59
PEEK.140T10B	760,37	PEEK.DIW.120T10B	832,19
PEEK.160T10B	760,37	PEEK.DIW.160T10B	0,00
PEEK.30T30B	1940,26	PEEK.DIW.30T30B	0,00
PEEK.50T30B	1940,26	PEEK.DIW.50T30B	0,00
PEEK.80T30B	891,47	PEEK.DIW.80T30B	0,00
PEEK.120T30B	891,47	PEEK.DIW.100T30B	931,37
PEEK.140T30B	681,71	PEEK.DIW.120T30B	803,12
PEEK.160T30B	786,59	PEEK.DIW.160T30B	426,36
PEEK.30T50B	3198,81	PEEK.DIW.30T50B	0,00
PEEK.50T50B	1992,70	PEEK.DIW.50T50B	0,00
PEEK.80T50B	1835,39	PEEK.DIW.80T50B	869,81
PEEK.120T50B	668,03	PEEK.DIW.100T50B	869,81
PEEK.140T50B	549,48	PEEK.DIW.120T50B	869,81
PEEK.160T50B	668,03	PEEK.DIW.160T50B	26716,83
PEEK.30T.100B	5784,31	PEEK.DIW.30T100B	0,00
PEEK.50T100B	2177,38	PEEK.DIW.50T100B	0,00
PEEK.80T100B	1192,43	PEEK.DIW.80T100B	2238,37
PEEK.120T100B	982,67	PEEK.DIW.100T100B	397,29
PEEK.140T100B	839,03	PEEK.DIW.120T100B	949,61
PEEK.160T100B	5009,12	PEEK.DIW.160T100B	2238,37

Table A.18 - Permeance Values for PEEK membranes dried from acetone

Membrane Code	Permeance ($L.h^{-1}.m^{-2}.bar^{-1}$)	
	2h	24h
PEEK.30T10B	7,22	6,22
PEEK.50T10B	4,86	4,28
PEEK.80T10B	1,11	1,25
PEEK.120T10B	0,62	0,59
PEEK.140T10B	0,25	0,29
PEEK.160T10B	0,30	0,26
PEEK.30T30B	7,39	6,17
PEEK.50T30B	5,83	5,03
PEEK.80T30B	1,78	1,87
PEEK.120T30B	0,57	0,55
PEEK.140T30B	0,26	0,27
PEEK.160T30B	0,07	0,06
PEEK.30T50B	6,94	6,33
PEEK.50T50B	4,44	3,89
PEEK.80T50B	2,99	2,87
PEEK.120T50B	0,83	0,83
PEEK.140T50B	0,18	0,20
PEEK.160T50B	0,12	0,10
PEEK.30T.100B	8,56	7,11
PEEK.50T100B	2,92	2,83
PEEK.80T100B	1,71	1,76
PEEK.120T100B	0,40	0,37
PEEK.140T100B	0,34	0,33
PEEK.160T100B	0,14	0,11

Table A.19 - MWCO for all the PEEK membranes tested, after using the Convective Oven

Acetone		**Deionized Water**	
Membrane Code	MWCO	**Membrane Code**	MWCO
PEEK.50T.AC.Ov	1114,91108	PEEK.50T.OVEN.DIW	-
PEEK.80T.AC.Ov	8499,772	PEEK.80T.OVEN.DIW	-
PEEK.120T.AC.Ov	1021,43183	PEEK.100T.OVEN.DIW	-
PEEK.140T.AC.Ov	852,713178	PEEK.120T.OVEN.DIW	-

Table A.20 - Permeance values of PEEK membranes dried from deionized water

Membrane Code	Permeance	
	2h	24h
PEEK.DIW.30T10B	12,78	9,67
PEEK.DIW.50T10B	5,14	4,19
PEEK.DIW.80T10B	5,83	5,03
PEEK.DIW.100T10B	1,51	1,14
PEEK.DIW.120T10B	0,76	0,63
PEEK.DIW.160T10B	0,07	0,06
PEEK.DIW.30T30B	11,65	8,61
PEEK.DIW.50T30B	4,86	4,03
PEEK.DIW.80T30B	4,86	4,28
PEEK.DIW.100T30B	1,33	0,98
PEEK.DIW.120T30B	0,66	0,57
PEEK.DIW.160T30B	0,09	0,08
PEEK.DIW.30T50B	8,55	6,44
PEEK.DIW.50T50B	4,44	3,89
PEEK.DIW.80T50B	3,23	2,67
PEEK.DIW.100T50B	1,00	0,84
PEEK.DIW.120T50B	0,43	0,36
PEEK.DIW.160T50B	0,08	0,07

Table A.21 - Rejection values for every membrane tested with acetone, in each PEG and respective standard error.(For Hot Press machine)

PEEK(10BAR.AC)	**PEEK.30T10B**	STDEV	**PEEK.50T10B**	STDEV	**PEEK.80T10B**	STDEV	**PEEK.120T10B**	STDEV	**PEEK.140T10B**	STDEV	**PEEK.160T10B**	STDEV
PEG400	58,24	1,81	50,45	0,05	78,81	0,05	77,11	3,58	82,43	1,96	82,05	4,57
PEG1000	78,46	1,78	77,36	0,54	95,46	0,09	95,13	1,79	95,11	1,12	95,31	2,53
PEG2000	90,09	1,24	91,63	0,05	98,63	0,02	98,23	0,80	98,25	0,39	98,20	1,07
PEG8000	98,33	0,18	98,97	0,05	99,64	0,01	99,62	0,12	99,53	0,07	99,59	0,20
PEG35000	99,38	0,13	99,57	0,05	99,79	0,00	99,93	0,07	99,73	0,05	99,75	0,15

PEEK(30BAR.AC)	**PEEK.30T30B**	STDEV	**PEEK.50T30B**	STDEV	**PEEK.80T30B**	STDEV	**PEEK.120T30B**	STDEV	**PEEK.140T30B**	STDEV	**PEEK.160T30B**	STDEV
PEG400	57,56	0,77	49,02	0,19	68,24	0,73	73,73	1,28	84,45	0,28	83,23	1,05
PEG1000	77,39	1,45	76,73	0,47	90,24	0,22	93,90	1,21	96,55	0,26	93,83	0,75
PEG2000	88,98	0,85	90,91	0,64	96,56	0,12	97,79	0,62	98,49	0,03	96,75	0,50
PEG8000	97,54	0,49	98,68	0,12	99,12	0,15	99,49	0,23	99,42	0,05	98,99	0,10
PEG35000	98,97	0,15	99,45	0,06	99,47	0,06	99,79	0,12	99,70	0,06	99,54	0,06

PEEK(50BAR.AC)	**PEEK.30T50B**	STDEV	**PEEK.50T50B**	STDEV	**PEEK.80T50B**	STDEV	**PEEK.120T50B**	STDEV	**PEEK.140T50B**	STDEV	**PEEK.160T50B**	STDEV
PEG400	54,23	5,93	47,38	0,71	57,99	9,49	69,50	5,27	87,38	1,05	85,69	0,38
PEG1000	76,18	5,00	75,26	1,93	80,94	7,91	93,41	1,89	97,67	0,13	95,62	0,55
PEG2000	88,06	3,47	90,25	0,81	91,79	4,21	97,57	0,76	99,10	0,04	98,05	0,23
PEG8000	97,77	0,70	98,70	0,15	98,18	0,89	99,36	0,17	99,65	0,01	99,40	0,01
PEG35000	99,24	0,40	99,52	0,00	98,98	0,49	99,78	0,01	99,78	0,02	99,64	0,01

PEEK(100BAR.AC)	**PEEK.30T100B**	STDEV	**PEEK.50T100B**	STDEV	**PEEK.80T100B**	STDEV	**PEEK.120T100B**	STDEV	**PEEK.140T100B**	STDEV	**PEEK.160T100B**	STDEV
PEG400	51,64	1,70	48,04	4,16	68,62	1,13	71,55	11,91	80,16	4,40	64,22	15,49
PEG1000	68,55	0,72	75,17	4,04	88,74	0,51	90,53	6,71	93,57	1,78	78,30	14,26
PEG2000	81,54	0,73	89,74	1,31	96,12	0,07	95,04	4,04	96,73	1,36	85,42	11,23
PEG8000	95,00	0,52	98,83	0,05	99,26	0,05	98,53	1,11	98,55	0,87	94,63	4,49
PEG35000	98,04	0,59	99,75	0,01	99,62	0,00	99,76	0,24	99,23	0,31	98,27	1,40

Table A.22 - Rejection values for every membrane tested with DIW, in each PEG and respective standard error. (For Hot press machine)

PEEK(10BAR.DIW)	**PEEK.DIW.30T10B**	STDEV	**PEEK.DIW.50T10B**	STDEV	**PEEK.DIW.80T10B**	STDEV	**PEEK.DIW.100T10B**	STDEV	**PEEK.DIW.120T10B**	STDEV	**PEEK.DIW.160T10B**	STDEV
PEG400	28,56	1,10	23,81	3,86	58,28	14,19	81,20	0,70	77,33	4,82	67,24	0,00
PEG1000	33,73	0,41	23,21	0,99	83,08	8,17	94,75	0,03	95,09	1,25	66,07	0,00
PEG2000	30,00	0,17	23,71	1,20	90,27	5,85	97,68	0,14	97,76	0,35	67,98	0,00
PEG8000	20,79	0,68	11,69	0,98	92,92	5,08	99,34	0,13	99,30	0,04	77,95	0,00
PEG35000	23,62	0,95	20,36	0,24	87,42	10,14	99,60	0,13	99,59	0,08	88,32	0,00

PEEK(30BAR.DIW)	**PEEK.DIW.30T30B**	STDEV	**PEEK.DIW.50T30B**	STDEV	**PEEK.DIW.80T30B**	STDEV	**PEEK.DIW.100T30B**	STDEV	**PEEK.DIW.120T30B**	STDEV	**PEEK.DIW.160T30B**	STDEV
PEG400	18,77	0,97	20,46	3,80	46,26	3,85	75,54	4,07	79,23	3,71	89,83	2,89
PEG1000	30,31	0,19	21,95	0,47	74,71	5,32	91,93	2,16	95,40	1,40	93,84	3,04
PEG2000	29,19	0,48	24,63	1,31	84,45	4,63	96,94	0,99	98,61	0,66	95,64	2,59
PEG8000	20,10	0,27	10,60	0,54	88,01	5,23	99,33	0,18	99,64	0,12	98,51	0,94
PEG35000	22,14	0,52	19,38	1,75	75,04	10,23	99,64	0,12	99,65	0,00	99,33	0,32

PEEK(50BAR.DIW)	**PEEK.DIW.30T50B**	STDEV	**PEEK.DIW.50T50B**	STDEV	**PEEK.DIW.80T50B**	STDEV	**PEEK.DIW.100T50B**	STDEV	**PEEK.DIW.120T50B**	STDEV	**PEEK.DIW.160T50B**	STDEV
PEG400	30,86	0,87	21,08	1,16	79,02	3,89	75,62	0,31	77,85	1,04	71,59	7,15
PEG1000	34,25	1,29	26,33	0,99	94,87	1,49	93,55	0,27	94,81	0,19	75,83	3,13
PEG2000	30,94	1,01	30,43	0,98	97,35	0,98	97,49	0,22	98,56	0,27	79,71	2,45
PEG8000	20,66	0,82	13,81	0,65	98,45	0,84	99,30	0,17	99,58	0,18	88,72	4,12
PEG35000	24,56	0,44	17,32	0,04	98,80	0,84	99,61	0,04	99,66	0,14	90,57	7,74

PEEK(100BAR.DIW)	**PEEK.DIW.30T100B**	STDEV	**PEEK.DIW.50T100B**	STDEV	**PEEK.DIW.80T100B**	STDEV	**PEEK.DIW.100T100B**	STDEV	**PEEK.DIW.120T100B**	STDEV	**PEEK.DIW.160T100B**	STDEV
PEG400	29,14	9,23	31,57	0,58	52,82	7,21	89,61	1,19	72,76	0,67	82,19	4,72
PEG1000	35,24	1,33	37,41	3,36	81,17	4,90	97,97	0,31	92,85	0,35	84,19	7,19
PEG2000	34,72	1,00	44,76	2,41	89,79	3,34	99,14	0,20	97,68	0,26	86,88	6,52
PEG8000	24,46	0,31	28,98	2,36	93,38	3,08	99,62	0,05	99,33	0,01	93,10	3,08
PEG35000	22,05	0,95	10,09	3,92	83,74	7,91	99,80	0,00	99,77	0,08	97,84	0,64

Table A.23 - Permeance values and respective standard errors, for each membrane tested with acetone, after being in the cross-flow rig system. (For Hot press machine)

PEEK(10BAR.AC)	PEEK.30T.10B.AC	STDEV	PEEK.50T.10B.AC	STDEV	PEEK.80T.10B.AC	STDEV	PEEK.120T.10B.AC	STDEV	PEEK.140T.10B.AC	STDEV	PEEK.160T.10B.AC	STDEV
2h	7,22	0,56	4,86	0,42	1,11	0,00	0,62	0,01	0,25	0,11	0,30	0,25
24h	6,22	0,11	4,28	0,39	1,25	0,00	0,59	0,03	0,29	0,14	0,26	0,22

PEEK(30BAR.AC)	PEEK.30T.30B.AC	STDEV	PEEK.50T.30B.AC	STDEV	PEEK.80T.30B.AC	STDEV	PEEK.120T.30B.AC	STDEV	PEEK.140T.30B.AC	STDEV	PEEK.160T.30B.AC	STDEV
2h	7,39	0,17	5,83	0,56	1,78	0,25	0,57	0,04	0,26	0,18	0,07	0,03
24h	6,17	0,06	5,03	0,47	1,87	0,24	0,55	0,03	0,27	0,18	0,06	0,02

PEEK(50BAR.AC)	PEEK.30T.50B.AC	STDEV	PEEK.50T.50B.AC	STDEV	PEEK.80T.50B.AC	STDEV	PEEK.120T.50B.AC	STDEV	PEEK.140T.50B.AC	STDEV	PEEK.160T.50B.AC	STDEV
2h	6,94	1,39	4,44	0,00	2,99	1,01	0,83	0,35	0,18	0,08	0,12	0,06
24h	6,33	0,78	3,89	0,00	2,87	0,83	0,83	0,34	0,20	0,07	0,10	0,05

PEEK(100BAR.AC)	PEEK.30T.100B.AC	STDEV	PEEK.50T.100B.AC	STDEV	PEEK.80T.100B.AC	STDEV	PEEK.120T.100B.AC	STDEV	PEEK.140T.100B.AC	STDEV	PEEK.160T.100B.AC	STDEV
2h	8,56	0,33	2,92	0,14	1,71	0,18	0,40	0,02	0,34	0,18	0,14	0,06
24h	7,11	0,11	2,83	0,17	1,76	0,09	0,37	0,00	0,33	0,16	0,11	0,05

Table A.24 - Permeance values and respective standard errors, for each membrane tested with DIW, after being In the cross-flow rig system. (For Hot press machine)

PEEK(10BAR.DIW)	**PEEK.DIW.30T10B**	STDEV	**PEEK.DIW.50T10B**	STDEV	**PEEK.DIW.80T10B**	STDEV	**PEEK.DIW.100T10B**	STDEV	**PEEK.DIW.120T10B**	STDEV	**PEEK.DIW.160T10B**	STDEV
2h	12,78	0,49	5,14	0,75	5,83	0,56	1,51	0,01	0,76	0,26	0,07	0,03
24h	9,67	0,22	4,19	0,64	5,03	0,47	1,14	0,03	0,63	0,10	0,06	0,02

PEEK(30BAR.DIW)	**PEEK.DIW.30T30B**	STDEV	**PEEK.DIW.50T30B**	STDEV	**PEEK.DIW.80T30B**	STDEV	**PEEK.DIW.100T30B**	STDEV	**PEEK.DIW.120T30B**	STDEV	**PEEK.DIW.160T30B**	STDEV
2h	11,65	0,34	4,86	0,14	4,86	0,42	1,33	0,11	0,66	0,07	0,09	0,01
24h	8,61	0,28	4,03	0,14	4,28	0,39	0,98	0,07	0,57	0,00	0,08	0,01

PEEK(50BAR.DIW)	**PEEK.DIW.30T50B**	STDEV	**PEEK.DIW.50T50B**	STDEV	**PEEK.DIW.80T50B**	STDEV	**PEEK.DIW.100T50B**	STDEV	**PEEK.DIW.120T50B**	STDEV	**PEEK.DIW.160T50B**	STDEV
2h	8,55	0,79	4,44	3,16	3,23	0,00	1,00	0,11	0,43	0,14	0,08	0,01
24h	6,44	0,33	3,89	2,61	2,67	0,00	0,84	0,04	0,36	0,13	0,07	0,01

PEEK(100BAR.DIW)	**PEEK.DIW.30T100B**	STDEV	**PEEK.DIW.50T100B**	STDEV	**PEEK.DIW.80T100B**	STDEV	**PEEK.DIW.100T100B**	STDEV	**PEEK.DIW.120T100B**	STDEV	**PEEK.DIW.160T100B**	STDEV
2h	8,36	0,49	2,92	0,00	0,67	0,14	0,37	0,00	0,33	0,20	0,08	0,01
24h	6,39	0,28	2,83	0,00	0,43	0,17	0,23	0,00	0,24	0,52	0,07	0,00

2021

Mariana Inês Garcia Gentilhomem

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