

RAPHAEL RODRIGUES

Synthesis and characterization of polysulfone/nanoclay/polyethylene  
oxide composite ultrafiltration membranes

São Paulo

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We ourselves feel that what we are doing is just a drop in the ocean. But the ocean would be less because of that missing drop.

Mother Teresa



## RESUMO

A modificação da estrutura de membranas é uma abordagem utilizada para melhorar as propriedades de membranas e desempenho de um sistema. Por exemplo, a adição de dopantes na solução de síntese da membrana permite aumentar a hidrofiliabilidade, alterar a estrutura de poros superficiais e internos e conferir propriedades anti-depósitos. Neste estudo, foi avaliada como a adição de óxido de polietileno e de nano-argila afetam a estrutura e desempenho de membranas de ultrafiltração de polisulfona (PSU). O desempenho da membrana foi avaliado na configuração de fluxo paralelo (*cross-flow*). A permeabilidade média à água pura da membrana de PSU pura foi de 15 L/m<sup>2</sup>.h.bar. As dosagem ótimas das membranas dopadas individualmente foram de 1,5% em massa de PSU para nano-argila e 5% em massa de PSU para PEO, resultando em permeabilidades médias de 56 e 237 L/m<sup>2</sup>.h.bar, respectivamente. A dopagem simultânea usando ambas as percentagens individuais ótimas teve um efeito menor do que o esperado, resultando em uma permeabilidade média de 192 L/m<sup>2</sup>.h.bar. Em contraste, verificou-se que a adição simultânea de 4,5% de nano-argila combinada com 5% de PEO teve um efeito maior do que o uso isolado dos aditivos, resultando em uma permeabilidade média de 319 L/m<sup>2</sup>.h.bar. Desta forma, a membrana de controle foi comparada com as referidas membranas e com membranas compostas somente por nano-argila a 4,5. Estas membranas foram ainda examinadas em detalhes para determinar os efeitos dos dopantes na microestrutura dos poros, cargas superficiais, desempenho da separação, sensibilidade à formação de depósitos, rugosidade superficial e propriedades térmicas e mecânicas. Verificou-se que a dopagem com nano-argila melhora a resistência térmica e mecânica e a permeabilidade das membranas, com uma perda mínima na rejeição. A dopagem com PEO resultou em um aumento notável de permeabilidade em comparação com a adição individual de nano-argila. No entanto, a capacidade de rejeição e resistência térmica e mecânica destas membranas diminuem e a formação de depósitos irreversíveis aumenta. Desta forma, avalia-se que para a utilização de mais de um tipo de dopante os efeitos vantajosos e desvantajosos devem ser considerados individualmente e em conjunto no esforço de se otimizar o desempenho de sistemas de membranas.

**Palavras-chave:** membranas de polisulfona, modificação de estrutura, nano-argila, PEO



## ABSTRACT

Membrane structure modification is a common approach to enhance membrane properties and performance. For example, the addition of dopants to the membrane casting solution has been observed to increase hydrophilicity, alter surface and internal pore structure, increase thermal and mechanical resistance, and impart anti-fouling properties. In this study, it was evaluated how the addition of individual and simultaneous nanoclay and polyethylene oxide (PEO) dopants affected the structure and performance of polysulfone (PSU) ultrafiltration membranes. Membrane performance was evaluated in the cross-flow configuration. The pure water permeability of the neat PSU membrane was 15 L/m<sup>2</sup>.h.bar and at the optimal dosage of the individually doped membranes was 1.5% weight nanoclay to PSU and 5% weight PEO to PSU resulting in permeability of 56 and 237 L/m<sup>2</sup>.h.bar, respectively. Simultaneous doping using the optimal individual weight percentages had a lower effect resulting in a permeability of 192 L/m<sup>2</sup>.h.bar, in contrast the simultaneous addition of 4.5% nanoclay and 5% PEO had a higher effect resulting in a permeability of 319 L/m<sup>2</sup>.h.bar. The control membrane was compared to the referred membranes and with the 4.5% nanoclay membrane (best permeability only when combined with PEO). These membranes were further examined to determine dopant effects on pore microstructure, superficial charge, separation performance, and fouling susceptibility. In general, doping with nanoclay improved membrane thermal/mechanical resistance and permeability with minimal loss in rejection. Doping with PEO resulted in a greater permeability as compared to nanoclay; however, PEO doping decreased rejection, mechanical resistance, and increased irreversible fouling. Thus, both advantageous and disadvantageous effects should be considered when selecting a dopant to optimize membrane performance.

**Key words:** polysulfone membranes, structure modification, nanoclay, PEO



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## LIST OF ABBREVIATIONS

(in alphabetical order)

AFM	Atomic Force Microscopy
BOD	Biological Oxygen Demand
CAS	Chemical Abstract Service
CNT	Carbon Nanotubes
COD	Chemical Oxygen Demand
DCM	Dichloromethane
DMAc	Dimethylacetamide
DMSO	Dimethyl Sulfoxide
DMF	Dimethylformamide
EPS	Extracelullar Polymeric Substances
MBR	Membrane Bioreactor
MF	Microfiltration
MP	Morpholine
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
PAC	Powdered Activated Carbon
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PES	Polyethersulfone
PF	Formylpiperidine
PSU	Polysulfone
PVDF	Polyvinylfluoridine
RO	Reverse Osmosis
SEM	Scanning Electronic Microscopy
TCE	Trichloroethylene
UF	Ultrafiltration
US	United States
USD	United States Dollar
UV	Ultraviolet



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## 1. INTRODUCTION

Access to water in adequate quantity and quality features, among other factors, represents an essential condition for survival during human evolution history. Although being essential, according the World Health Organization (WHO; UNICEF, 2014), more than 700 million people still lack access to improved sources of drinking water. Considering the projections for world population growth, it is estimated that to achieve an adequate coverage on sanitation services to the entire world population by 2025, almost 3 billion people will need to be served with water supply and more than 4 billion with sanitation (LEIKNES, 2006) . These figures help to illustrate the awareness of what will be needed to be done in the near future in the field of water and wastewater engineering to provide adequate life conditions to people worldwide.

The increasing demand for water allied to the degradation of water sources caused by the lack of sanitation and the ever growing number of pollutants present in the wastewater compromise the access to reliable water sources, making this an even greater challenge to be faced by the water sector in this new century.

According to the database of the Chemical Abstracts Service (CAS), currently there are approximately 103 million organic and inorganic substances registered (AMERICAN CHEMICAL SOCIETY, 2015). To have an idea how fast the number grows, in the year of 2014 there were more new chemical substances entries than the whole interlude from 1965 to 1990. The main environmental concern regarding those compounds is their indiscriminate use in industrial processes, agriculture, personal care, among others, causes their release in the environment, affecting directly water sources used for supply. Such occurrences lead us to question if the existing treatment systems have the technical and economic ability to deal with this potential threat to human health and wellbeing.

As an example, research developed by Stackelberg and coworkers (2007) evaluated the removal efficiency of some contaminants such as pharmaceuticals, flavorizers, flame retardants, plasticizers, fertilizers, detergents, personal care products and pesticides, among others, by direct filtration (in a bed of granular activated carbon). The results showed that some organic compounds were in fact removed, most by the activated carbon. However, many of them still were detected in the final effluent. Some

of the persistent compounds were evaluated through bioassay tests and were detected in samples of animal's blood, milk and urine, indicating that perhaps the main exposure path (if not the only) was the ingested water.

Considering these results, it is necessary to consider the use of advanced technologies for wastewater and water treatment in order to minimize pollution of water bodies and minimize risks of human exposure to recalcitrant components.

An alternative to conventional treatment systems, for both water and wastewater, which presents notable efficiency is the membrane separation technology. Basically, the process consists on forcing water to pass through semipermeable membranes, which physically retain contaminants, by applying a driving force.

According to the report issued by the US market trend research company, BCC Research Llc (2015), the combined US market for membranes used in gas and liquid applications is expected to grow to \$3.5 billion by 2019. This number implies a compound annual growth rate of 7.9% during the period 2014-2019. This increase in demand is forecasted based on the adoption of more stringent water quality legislation, interest in waste minimization, and water reuse for industrial processes. Thus, it is possible to envisage an increasing in the use of this technology by many industries such as pharmaceutical, food and electronics, in order to concentrate components for reuse in the production system (avoiding their release into water bodies) and/or obtaining water with high purity (NICOLAISEN, 2003).

Despite the early use of membrane separation processes date from the mid-1960s, this technology is still considered emerging. That is because until the early 1990s, the use of membranes had technical restrictions, such as reduced lifespan and high energy consumption due to the fouling phenomena. Membrane fouling consists in the formation of a film containing salts, organic compounds, and/or biological matter on the surface or in the pores of the membranes, making difficult for water to permeate through this extra layer. Therefore, minimizing membrane fouling is important to upgrade membrane system's performance.

To illustrate the relevance of studies in this field, a comparison using the Science Direct® (Elsevier) database shows that the number of published papers discussing the fouling phenomena increased significantly in the last 20 years. The number of

published articles about membrane fouling between 2005 and 2015 was more than three times higher than the total number of papers about the same topics published between 1995 and 2005. This number shows that the problems caused by fouling are currently the major challenges to be overcome for implementing more efficient membrane systems (VROUWENVELDER; VAN LOOSDRECHT; KRUIHOF, 2011)

In order to solve the fouling problem and improve the use of membranes in several areas, many research lines aim to reduce the fouling on membranes surface involving physical mechanisms (backwashing, discharges, changing operating conditions), chemical (cleaning, use of biocides) and more recently modification of membranes' surface and internal structure.

Initially, the approach of surface modification consisted in promoting the adhesion of a layer with higher hydrophilicity to the base membrane (mechanisms called coating and grafting), resulting in lower adherence of compounds. Currently the most efficient and practical method to modify the structure and surface of the membrane is the addition of hydrophilic components in the polymer solution preparation (blending).

The addition of organic or inorganic components in the polymer solution influences pore formation, which significantly change the membranes' properties, such as permeability, resistance (thermal, chemical and mechanical) rejection capability, hydrophilicity and biocompatibility (ZHAO et al., 2013b). Moreover, this method has the advantage of being performed in only one step during membrane production and can be easily applied on a commercial scale.

There are also organic components used as pore forming agents, like polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and its form with higher molecular weight, the polyethylene oxide (PEO), glycerol, alcohols or di-alcohols. These components can be used as additives in the membrane dope solution or used in the coagulation bath, lowering the chemical potential of the bath and changing the inflow of water on the wet phase inversion step.

Beside these components, with the progress in the field of nanotechnology, the main researches related to manufacturing of modified membranes also include the use of nanoparticles such as titanium oxide, alumina, silica, silver, clay and others, thereby contributing for the improvement of membranes performance (KIM; BRUGGEN, 2010;

SITTER et al., 2014; YONG et al., 2013). Those surface and internal changes in the membranes structure make the use of membranes more competitive, reducing their limitations and improving their performance for many uses.

Despite the potential of researches in the production and modification of membrane structure and uses in more efficient systems, there are few studies focus on a multi-variable approach to characterize the membranes in terms of solute rejection, surface properties, mechanical properties, internal structure and fouling formation. Usually they focus on one of those topics to complement and justify the increments in permeability.

When this research proposed to focus on membrane synthesis and modification, it was defined that the characterization would embrace multiple parameters correlated to the membrane performance and membrane fouling, focusing the use of membranes for water treatment. Besides having a multi-parameter approach on membrane characterization, this study is relevant for the membrane field because it evaluated the association of two different additives (nanoclay and the pore former PEO).

Pore formers are known for increasing membrane permeability, but lowering membrane rejection by widening the pores on the internal structure. On the other hand, studies with nanoclay as additive show that the membrane rejection ability can be increased without compromising permeability (most of the times, except when clay aggregation). This research hypothesizes that the evaluation of these two additives could result on a synergistic effect of increased permeability without compromising membrane rejection. Both of those effects are desirable for ultrafiltration membranes for water treatment.

Thus, conducting research in the area of membranes is of great importance to dissemination of knowledge in this area, elucidating mechanisms involved in the formation of membranes, assisting in the determination of parameters that enable the production of membranes with improved efficiency and reduced costs of usage, and encouraging membrane applications in new processes.

## 2. OBJECTIVES

This research project has as main objective the modification of polysulfone membranes using clay nanoparticles, the pore forming agent polyethylene oxide (PEO), and combinations of different proportions of these additives, to evaluate their influence on physical properties and operational performance of membranes for water treatment.

In order to meet the proposed objective, a brief literature review related to the synthesis and structure modification of membranes is presented and results of experiments performed with membranes synthesized and modified in the laboratory are discussed.

Stand out as goals to be achieved:

- Determination of parameters for synthesis of polysulfone ultrafiltration membranes by phase inversion method;
- Synthesis of polysulfone membranes with the addition of clay nanoparticles in the polymer solution;
- Synthesis of polysulfone membranes with addition of PEO in molecular weights of 100,000 g/mol in the dope solution, as pore forming agent
- Membrane Fouling evaluation;
- Evaluation of membranes performance for water treatment.

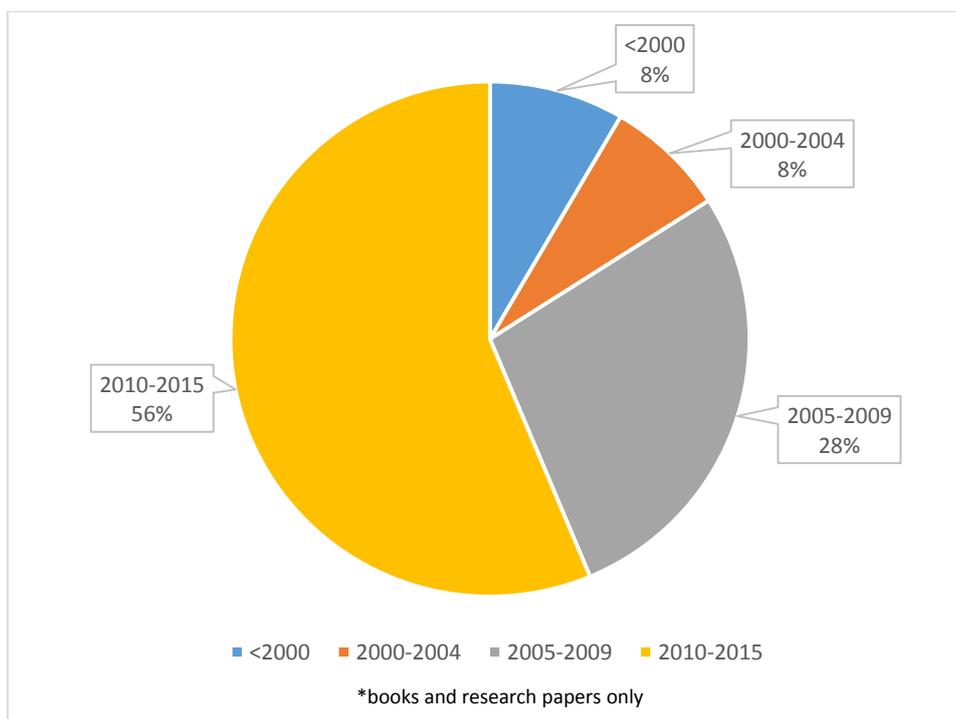


### 3. LITERATURE REVIEW

In this section, it is presented a brief overview of topics relevant for this research. By undertaking the literature review, it is possible to critically summarize the current knowledge in the membrane field and identifying strengths and weaknesses in previous works.

This review focus in both consolidated references and research papers. Figure 1 shows the time distribution analysis of the data considered for this review. Recent research papers (< 5 years) are equally important in the composition of this review, considering the membrane field has had important contribution in the recent years in fouling and membrane modification studies. The research papers reviewed focus on membrane fouling, use of different types of nanoparticles in polysulfone membranes, with special attention to clay nanoparticles and polyethylene glycol/oxide.

Figure 1 – References' (\*) Time Distribution



Consolidated references and papers published in the last 10 years are equally important as the state of art of the research, being important to mention the historic background of membrane sciences, membrane uses and material properties, which do not change over time, such as polymer and solvent properties, method for membrane synthesis, and thermodynamics behind the phase inversion.

After the presentation of the references, a brief discussion summarizes the relevance of the topics presented to the discussion of the results of the experiments.

### **3.1 Membrane Definition**

A precise and complete definition of membrane, covering all its aspects, is relatively complex. After all, membranes may be homogeneous or heterogeneous, can have symmetrical or asymmetrical structure, can be positively or negatively charged, neutral, or bipolar, with variable thicknesses and different separation mechanisms (PORTER, 1990).

Therefore, the term "membrane" encompasses a variety of materials and structures that make it easier to define a membrane based on processes in which it is used instead on their properties or appearance constitution (PORTER, 1990). An appropriate definition for membrane is "a selective barrier to a flow containing suspended matter, colloidal or dissolved that is able to control the concentrations of components, retaining certain species and allowing the flow of others, by applying an external force (pressure, chemical potential, the electric potential or temperature variation)" (MULDER, 1996)

### **3.2 Historic Background**

Membrane separation processes originated to solve different kinds of demands for separation of colloidal and dissolved species in industrial processes in the chemical, petrochemical, metallurgy, food, pharmaceutical and electronics industries, also presenting important contribution in the field of sanitation in water and wastewater treatment.

In terms of history, there are two branches on membrane usage history: the scientific and the commercial development.

In scientific terms, the first studies with membranes date from the mid-eighteenth century, with the aim of clarifying barrier properties and transport phenomena through them. At that time, the lines of study included chemists, physicists, biologists, biochemists and zoologists. They made use of membranes of animal origin, such as pig bladder skin and guts of other animals, to observe transportation phenomena for liquids and gases (MULDER, 1996)

From those experiments with membranes, laws such as the Law of Diffusion of Graham and the definition of Van't Hoff osmotic pressure emerged. Van't Hoff also found a similarity between the gas pressure and the osmotic pressure of dilute solutions based on Pfeffer's studies of osmotic pressure (MASON, 1991).

The development of membranes for commercial purposes began in lab scale experiments from Zsigmondy Sartorius at the end of World War I with membranes of cellulose nitrate and later with the production of membranes composed of asymmetric structure by Loeb and Sourirajan (in the 1960s) (MULDER, 1996).

Thereafter, membrane technology had been initially commercialized for sea water desalination through reverse osmosis systems in small scale. The advancement of membranes technology occurred with greater intensity in the early 1990s, with the popularization of the use of micro-and ultrafiltration systems already in commercial scale (SCHNEIDER; TSUTIYA, 2001).

In the meantime of those 30 years, many studies had been conducted in this area aiming to improve the characteristics of membrane systems regarding five key variables: reliability , speed , selectivity, costs and durability (BAKER, 2012), making the technology more competitive compared to other separation technologies.

### **3.3 Membrane Processes Types**

The four most common types of membranes used in water treatment are applied in systems which use hydraulic pressure as the separation driving force, namely microfiltration (MF) , ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). It should be noted that there are still other membrane processes that will not be addressed in this work, including dialysis, electrodialysis and pervaporation.

There are several factors that differ one process from another, such as the membrane pore diameter, system's operating pressure and membrane rejection capability (based on molecular weight cutoff).

### **3.4 Membrane Synthesis Materials**

#### *3.4.1 Polymer*

Any material that allows the synthesis of a porous film can be used for membrane manufacturing. A literary survey reported by Cheryan (1998) points out that more than 130 different materials have been studied for the production of membranes. Considering this data is from 1998 and considering all the advances in material sciences in the last 18 years, many other unique new materials and compositions have been studied, significantly increasing this number. Despite the variety of materials available, only a few are able to be featured for commercial use and are approved to be used in pharmaceutical and food industries. In the sanitation sector, the use of polymeric membranes is more common compared to inorganic membranes. However, inorganic membrane applications are also growing in numbers, mainly because of the use of ceramic membranes.

The most common polymers used for membrane synthesis are cellulose acetate, polysulfone, polyethersulfone, polyacrylonitrile, polyamide and polyvinylidene fluoride (PVDF). Each of them has its advantages and disadvantages for specific uses (LALIA et al., 2013). For example, cellulose acetate membranes are low cost and more hydrophilic compared to polysulfone and polyethersulfone membranes. However, cellulose acetate membranes have a low thermal and chemical resistance, being easily degraded by the use of chlorine or sodium hydroxide.

Apart from the chemical nature of a casting polymer, the polymer concentration also plays an important role on the membrane synthesis. The higher the polymer concentration in the casting solution the denser is the cast membrane. Membranes cast with more concentrated polymeric solution will effectively suppress macrovoids, resulting more likely in membranes with a sponge-like structure. For ultrafiltration membranes, the range of polymer concentration range from 12 to 20 wt.%, while for Reverse Osmosis membranes the polymer concentration in the casting solution should be higher than 20 wt.% (LALIA et al., 2013). Maximous et al. (2009) also report that as

the polymer concentration increases the water permeation decreases, increasing transmembrane pressure. This suggests that increasing polymer concentration a denser and thicker skin layer is formed, reducing membrane permeability.

### 3.4.2 Solvent

The correct choice of the pair solvent/non- solvent is essential for membrane synthesis by the method of phase inversion. The properties of the solvent used during the membrane-casting process can impact the membrane morphology and separation performance. The use of a volatile solvent can change the liquid–liquid interactions and result in different morphological structures (ADAMS et al., 2013).

A good water-miscible solvent has a high degree of polarity and hydrogen bonding ability which is able to suppress the solvent volatility (ADAMS et al., 2013). At the same time, it is important that the miscibility between solvent and polymer is high in order to obtain a porous membrane structure. (LALIA et al., 2013)

Among the most widely used solvents for fabrication of membranes, the most used are aprotic polar solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), formylpiperidine (PF), morpholine (MP) and N-methyl -2-pyrrolidone. Other solvents such as trichloroethylene (TCE), chloroform and dichloromethane(DCM) have been used in the past, but are currently out of use due to their carcinogenic potential and environmental persistence.

## 3.5 Methods of Synthesis

There are different methods for membranes synthesis. The most consolidated are sintering, stretching, track-etching and phase inversion. This research's focus is the phase inversion method. The phase inversion method was chosen considering it is a method suitable for synthesis of asymmetric membranes in large scale.

The phase inversion process consists in a controlled transition from a polymer solution from liquid to solid state. This transition can occur in different ways: (MULDER, 1996)

a) Precipitation by evaporation: the polymer is dissolved in a solvent, dispersed in a suitable support and stored in a controlled atmosphere. The porous membrane is formed when the solvent evaporates.

b) Precipitation by vapor phase: the polymeric film is placed in an atmosphere of non-solvent vapor saturated with solvent. The solvent high concentration in the vapor phase prevents evaporation of the solvent in the film. Thus, the membrane porous structure is formed by non-solvent diffusion into the film.

c) Precipitation by controlled evaporation: in this method the polymer is dissolved in a mixture of solvent and non-solvent. As the solvent is more volatile than the non-solvent, the solution composition changes during the evaporation process, increasing polymer concentration, resulting in its precipitation and formation of asymmetric membranes.

d) Thermal Precipitation: the polymer solution is cooled, so the solubility is decreased and hence there is the phase separation.

e) Precipitation by Immersion: method chosen for membrane synthesis on this research. It consists in the application of the polymer solution in a support which is immersed in a coagulation bath containing the non-solvent. The precipitation occurs due to solvent replacement by non-solvent, resulting in an asymmetric membrane structure.

### *3.5.1 Thermodynamics of the process of Phase Inversion*

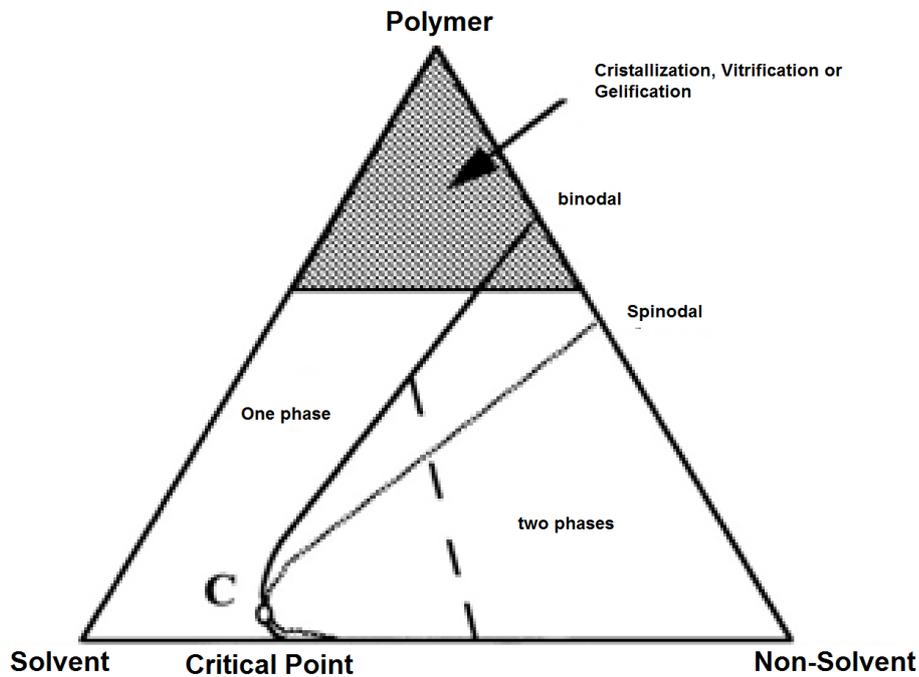
In the phase inversion processes, there are diffusive processes between various components due to exchange of solvent and non-solvent from the polymer solution and coagulation bath. These exchanges modify the film composition, creating conditions for solidification. In the case of semi-crystalline polymers, such as polysulfone, changing the film composition can lead to vitrification or crystallization.

Before being immersed in the nonsolvent, the system contains only polymer and solvent in equilibrium. Suddenly, a third element is introduced, causing thermodynamic instability to the system, resulting in a phase separation. This can happen in many different ways, according to the nonsolvent diffusion (as described in the previous section).

The simplest way to describe the many different ways this diffusion can happen into the system is through the relationship between the three components involved:

polymer, solvent and non-solvent, which may be represented in a ternary diagram as shown in Figure 2.

Figure 2 – Ternary Phase Diagram



Source: MACHADO; HABERT; BORGES, 1999

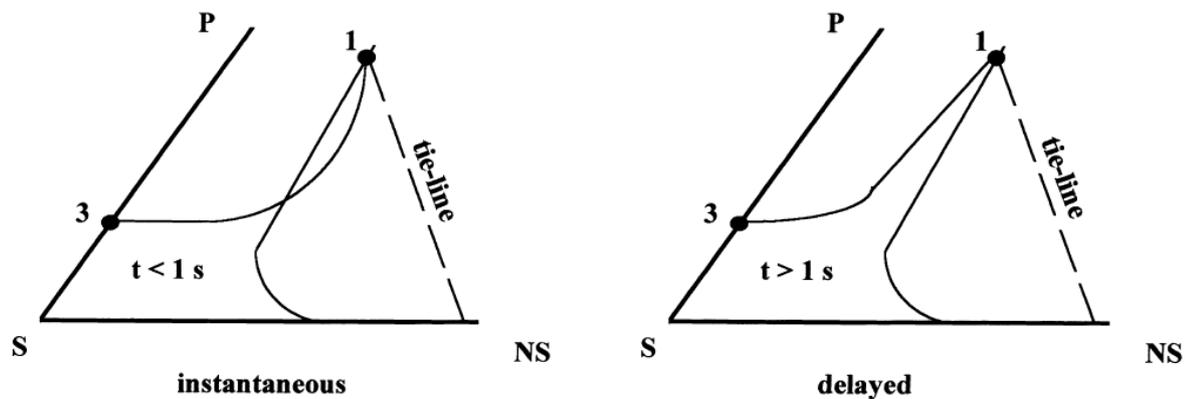
The ternary diagram representation is related to each component's concentrations in the regions bounded by the binodal and spinodal lines. The binodal line delimits the rich and poor regions in the polymer composition. The spinodal line represents a region where any disruption would lead to system instability. The region between these curves represents conditions at which there is a partial stability where phase separation occurs. The intercept of these two lines is the critical point of the system, which means that the equilibrium phases are identical in composition and volume.

The regions of high polymer concentration crystallization, gelification or vitrification, which are different ways of solidification of the polymer can occur, can be seen in the phase diagram.

Depending on the path that follows the inversion process, two different mechanisms might occur: the instantaneous or the delayed inversion. The instantaneous phase separation begins immediately after the immersion, crossing the binodal line. In delayed inversion, the path of precipitation does not cross the binodal line for a certain

period of time after the bath. (MACHADO; HABERT; BORGES, 1999). Figure 3 shows a comparison between the two situations.

Figure 3 – Precipitation in instantaneous and delayed separation



Source: MACHADO; HABERT; BORGES, 1999

In structural terms, the instantaneous separation forms a superficial porous layer, typical of ultrafiltration and microfiltration membranes. The delayed separation makes dense layers, being more suitable for reverse osmosis, gas separation and pervaporation (MACHADO; HABERT; BORGES, 1999).

Since an asymmetric membrane's porosity is determined by the concentration of polymer in solution and by the rates of exchange between the solvent by non-solvent, the phase diagram, theoretically, helps to highlight the preferred ways for this to happen.

The ternary phase diagram may be used as an effort to describe the phenomenon that occurs with the addition of non-solvent into a homogeneous solution of polymer and how added particles may influence in the formation of pores and permeability. Nevertheless, it is a limited tool, since it does not provide direct information about the size of pores and the porous layer structure. It can only be used as an auxiliary tool for analysis. (PORTER, 1990)

In thermodynamic terms, the membrane formation process considers the Flory-Huggins theory of polymer solutions extended to a ternary polymer/solvent/non-solvent diagram. The system is described by the binary interactions between components: non-solvent/polymer, solvent/polymer and solvent/non-solvent. The concentration and dependence of these interactions among themselves are binary parameters that affect

the positions of the binodal points, and spinodal critical point in the phase diagram curves.

According to the Flory-Huggins theory, the free energy of mixing,  $\Delta G_m$  to a ternary diagram can be described according to Eq. 1.

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12} n_1 \phi_2 + g_{13} n_1 \phi_3 + g_{23} n_2 \quad (1)$$

In which,

$n_i$  = number of moles of component i

$\Phi_i$  = volumetric fraction of component i

$g_{ij}$  = binary interaction parameter dependent of concentration of components i and j

Study by Barzin and Sadatnia (2008) evaluated the thermodynamic behavior of water/NMP/polyethersulfone and water/DMAc/polyethersulfone systems. Some simplifications have been considered in the interaction parameters defined by Eq. 1, i.e., the relations of interdependence between polymer/solvent and polymer/non-solvent were not considered. They compared cross sections images by scanning electron microscopy and noticed that at low polymer concentrations (5%), the structures were predominantly characterized by a finger-like structure (DMAc were narrower), for both solvents.

Considering the affinity between the solvent and non-solvent ( $g_{12}$  on Eq. 1) changes the dynamic water inflow and formation of the internal structure and the theoretical values of the coefficient  $g_{12}$  for the NMP/water system is higher than the DMAc/water system, it was expected that DMAc membranes had a finger-like structure with increasing concentrations of polymer. In practice, the opposite result was observed: the structures of the membrane became largely sponge-like with DMAc, while NMP remained finger-like even with increasing polymer concentration. The authors explain this occurrence because the polymer is amorphous, which contributes to the occurrence of early vitrification in the DMAc/water system, suppressing the formation of finger channels throughout the structure.

Another research conducted by the same authors in 2008 tried to correlate the large voids formation in the membrane structure (macrovoids) with the ternary diagram

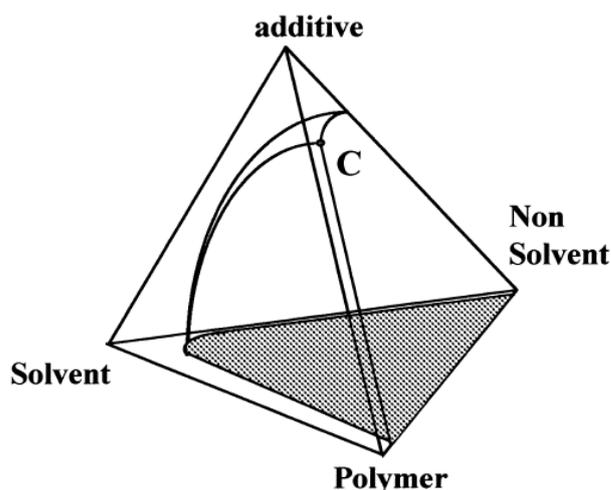
results, comparing the effects of DMAc and NMP solvent in polyethersulfone membranes. Some of the parameters, like the affinity between solvent and non-solvent, were defined in the previous study.

It was demonstrated again that membranes produced with DMAc showed sponge-like structure, justified by phenomena of early vitrification system, diverging from the theoretical expectation based on the affinity of the solvent with nonsolvent. The authors emphasize that the affinity should not be considered in isolation, but together with other curves of gelification and vitrification in explaining the phenomena of structure formation and macrovoids.

Divergent results from the theoretical expectation show that attempts to predict and characterize the behavior of a system through the ternary diagram, even under extremely controlled conditions, might not be such an effective tool as it is for the evaluation of binary cases.

In the case of experiments that take into account four components: solvent, non-solvent, polymer and an additive, the prediction of the final behavior tends to become more complex by 6 degrees of combination of the elements in a tetrahedral quaternary diagram format as shown in Figure 4.

Figure 4 – Quaternary Phase Diagram



Source: MACHADO; HABERT; BORGES, 1999

Instead of a binodal curve there is the presence of a plan. According to the research made by Kools (1998), no satisfactory assessment of quaternary diagrams are possible to be made since there are a wide variety of states of equilibrium between the

interface of the polymer solution and coagulation bath, making the definition of the boundary conditions for setting more complex calculations.

Moreover, the addition of extra additives would create new pairs of interactions with every other component, creating a number of binary interaction parameter in the order of a base 2 binomial (i.e. for 4 components, Eq.1 would be represented by  $\binom{4}{2} = 6$  interaction parameters and for 5 components,  $\binom{5}{2} = 10$  interaction parameters).

### **3.6 Mechanisms that influence membrane formation**

Various methods have been applied for adjusting rates of water inflow and solvent removal, including the use of additives in the casting solution, additives in the phase inversion bath, and temperature adjustment in the solution, in the bath or in both (PORTER, 1990).

Mulder (1996) cites a number of variables in the phase inversion that can cause a change in the final membrane produced: polymer choice, choice of the pair solvent/non-solvent, composition, temperature, humidity and speed during solution casting and coagulation bath conditions.

By changing one or more of these independent parameters it is possible to obtain membranes with different structures. For example, increasing polymer concentration can result in membranes more suitable for gas separation or pervaporation, while lowering the concentration and/or adding a solvent to the coagulation bath can result in more porous membranes for ultra or even microfiltration. (LALIA et al., 2013)

#### *Polymer Concentration*

Increasing the polymer concentration in the casting solution also increases polymer concentration at the interface during the coagulation bath, resulting in membranes with less porous surface and lower flow. Increasing polymer concentration from 12 to 17% in a polysulfone DMAc system can reduce the flow in 10 times (from 200 to 20 L/h.m<sup>2</sup>) (MULDER, 1996)

#### *Use of additives in the casting solution*

The addition of components in the casting solution results in an increase in the water inflow speed, resulting in more porous membranes. This happens because the use of

additives reduces the chemical potential of the solution. By reducing the chemical potential, the water inflow rate increases and the internal structure formation is modified. (PORTER, 1990).

#### *Use of additives on the coagulation bath*

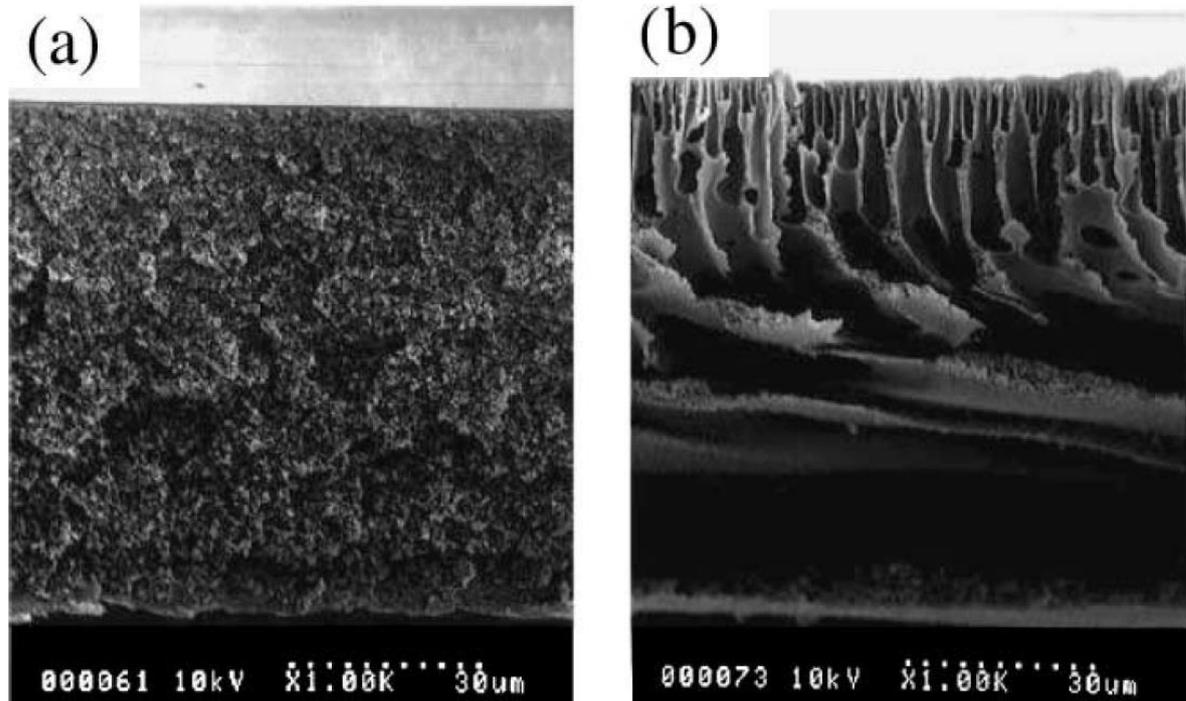
The use of additives in the coagulation bath slows the water inflow speed into the polymer film, since the chemical potential of the bath has been reduced compared to a bath of pure non-solvent. The results are less porous membranes. If the additive is the own solvent, the rate of solvent removal is delayed and produces membranes with larger pores with more homogenous distribution. (PORTER, 1990). By adding ethanol in the coagulation bath, PVDF membranes had their porosity decreased compared to control. As the chemical potential of the coagulation bath was reduced for adding ethanol, the precipitation rate was reduced and the final membranes had a spongelike structure. (DESHMUKH; LI, 1998; THÜRMER et al., 2012)

#### *3.6.1 Structures Obtained in the phase inversion process*

The membrane structure produced by the method of phase inversion may vary considering all the factors involved in pore formation process. Figure 5 shows two cross sections of polyimide membranes prepared by precipitation in an immersion bath with water at 8°C. The only difference in the synthesis process was that the membrane (a) used Dimethylsulfoxide (DMSO) as solvent, while the membrane (b) was synthesized using NMP.

It is observed that the use of different solvents implies in membranes with different structures. Figure 5a shows a “sponge-like” structure, while Figure 5b shows a structure with “finger-like” channels. This difference in morphology can be explained by the duration of the contact time during the immersion. For Polyimide/DMSO/water systems, the phase inversion process occurs slowly, being stopped before the inversion with NMP.

Figure 5 – Scanning Electronic Micrographs from membranes cross sections. (a) Asymmetric membrane with sponge-like structure; (b) Asymmetric membrane with “finger-like” structure.



Source: KIM et al., 2001

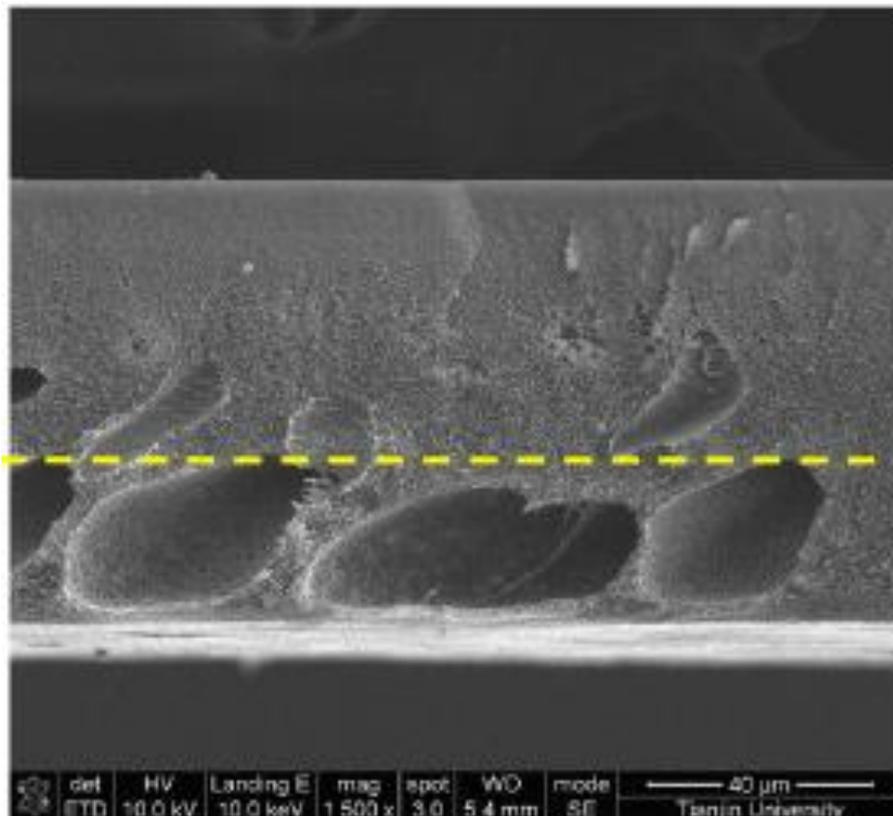
The terms “finger-like” and “sponge-like” structure are commonly used to describe membrane structure. Work of YOUNG and CHEN (1995) is a good example of paper that explain the formation mechanisms of membrane internal structure in finger-like and sponge-like types. They explain a two-step mechanism model. It has this name because it separates the membrane into two areas: the top layer and the sublayer. It explains that when the diffusion of solvent from the surface of casting solution occurs rapidly, a dense top layer is formed, and this influences the dynamics of solvent diffusion on bottom sublayer.

The polymer concentration is further important to model the membrane regarding their structural properties and separation parameter. By increasing the polymer concentration, the structure changes from finger-like structure to sponge-like structure (PORTER, 1990)

In terms of performance, the increase in polymer concentration (sponge-like) causes a decreased porosity, increased gelification time, higher retention capability and a remarkable decrease in membrane flux.

Some studies show the formation of macrovoids below the surface layer, as illustrated in Figure 6. The macrovoid formation mechanisms have been extensively investigated by theoretical analysis, mathematical calculations and computer simulations during the past decades (KOSMA; BELTSIOS, 2012). The nature and structure of these large voids significantly affect the mechanical properties of the membranes, making them less resistant. These voids can form under conditions of instantaneous inversion, so they can be suppressed by a delayed inversion, under the possibility of changing the membrane structure into a sponge-like profile. This inversion time is related to the affinity between the solvent and non-solvent: the higher the affinity, the faster the inversion (BARZIN; SADATNIA, 2008). As asymmetric membranes are commonly used as pressure-driven membranes, macrovoids are not desirable since they distress the membrane structural integrity, resulting a bad membrane performance.

Figure 6 – Macrovoids in membranes



Source: (TIAN et al., 2014)

By knowing the main factors that can induce one or another type of membrane structure it was possible to understand how some of the input conditions for membrane synthesis can affect the final structure. Comparing the polymer concentration in

previous works and the final membrane structures obtained helped to design the experimental conditions for the present work, aiming to produce membranes with fingerlike structure with reduced macrovoids.

### **3.7 Membrane uses**

Membrane separation processes have diverse uses nowadays, being considered methods of high performance separation not only in laboratory experiments and in the industrial sector, but also in the sanitation sector. Examples of membrane uses in industry include dairy, ethanol, textile, paper, leather, sugar, soybean and electronic industries, industrial laundry, slaughterhouses and the pharmaceutical sector (CHERYAN, 1998; PORTER, 1990). Other examples of membrane uses include petrochemical area (TAKHT RAVANCHI; KAGHAZCHI; KARGARI, 2009), medical area (STAMATIALIS et al., 2008), fuel cells (ZHAO et al., 2011), pesticide removal from water (PLAKAS; KARABELAS, 2012) and emerging pollutants treatment (KAYA et al., 2013; SECONDES et al., 2014).

#### Water Treatment

One of the first ways of using membranes, dating from the mid-1960s, was the treatment of seawater to obtain pure water through reverse osmosis.

Besides the remarkable contribution of membranes for desalination, considering the need for development of drinking water production on a large scale, hollow fiber (BENTAMA et al., 2004) and spiral-wound (MIERZWA et al., 2008) ultrafiltration membrane also came to be used for purification of surface water and groundwater for domestic consumption.

Data collected by the market trending company Freedonia Group, shows that the demand for membrane technologies for water treatment in the world between 2007 and 2016 will grow 99%, whereas in Brazil this growth is estimated at 118% (THE FREEDONIA GROUP, 2009). Micro and ultrafiltration membranes may be used as water treatment systems and as pre-treatment for reverse osmosis and nanofiltration.

Low-pressure membrane systems are having their use increased for drinking water treatment. The global installed volume of low-pressure membranes had grown at an impressive rate during the last 10 years and 60% of applications are for drinking water.

Compared to microfiltration, ultrafiltration technology is able to remove viruses due to its low cut-off and thus it can take the place of the disinfection step. In addition to concerns over microbial contaminants, low-pressure membranes are becoming more attractive for the drinking water industry due to some other reasons, such as stricter regulatory requirements, easier operational conditions, minimum staffing requirements, competitive cost and independence of water source quality. (GUO et al., 2010)

Ultrafiltration membranes can also be used as a pre-treatment for reverse osmosis systems, helping to remove components in particulate form that otherwise would damage the reverse osmosis membranes. Table 1 summarizes the pre-treatment needed to remove some contaminants by specific micro-and ultrafiltration membranes.

Table 1 – Pre-treatment required to remove specific contaminants

<b>Parameter</b>		<b>MF</b>	<b>UF</b>
Particulate	Turbidity	None	None
	Protozoa	None	None
	Bacteria	None	None
	Virus	Coagulation	None
Organics	Total Organic Carbon	Coagulation / PAC*	Coagulation / PAC*
	Precursors of Disinfection	Coagulation / PAC*	Coagulation / PAC*
	Color	Coagulation / PAC*	Coagulation / PAC*
	Taste and Odor	Coagulation / PAC*	Coagulation / PAC*
	Pesticides	PAC*	PAC*
Inorganics	Iron and Manganese	Oxidation	Oxidation
	Arsenic	Coagulation	Coagulation
	Hydrogen Sulfide	Oxidation	Oxidation

Source: AWWA (2011)

\*PAC: Powdered Activated Carbon

There are many examples of case studies using ultrafiltration membranes in large scale for water treatment with different results. The project AQUAPOT, developed by the Polytechnic School of Valencia, operates since 1996 on the effort to establish low-cost drinking water systems, which included the evaluation of membrane technologies in ultrafiltration. The main results in 10 years of operation showed that ultrafiltration membranes were effective on removal of total coliforms and thermotolerant coliforms, while providing quality water to villages in Ecuador and Mozambique. (ARNAL et al., 2009)

From 1996 to now, membrane technology has had a huge development in terms of technological applicability, innovation and decrease of costs, being commercially available by many companies around the world.

Study by Mierzwa and colleagues (2012) presents the results of the evaluation of operating performance of an ultrafiltration pilot plant for treating water at the Guarapiranga Reservoir, in the metropolitan region of São Paulo. The research objective was to evaluate different approaches as pretreatment, addition of chemicals, activated carbon, backwash and chemical cleaning in the final performance of the system, as attempts to minimize the problems caused by loss of flow through fouling. The research results show that it is possible to use the spiral-wound membranes for water treatment modules with removal of natural organic matter, turbidity and pathogens, considering additional procedures to minimize the effects caused by fouling.

In terms of costs, study by Chew and coworkers (2015b) compared the costs of an ultrafiltration unit with conventional systems (aeration, coagulation, flocculation, sedimentation, filtration and disinfection) in terms of capital expenditure, operational expenditure, maintenance cost, treated water quality and water losses for a water treatment plant in Kelatan, Malaysia. Considering the parameters evaluated for the country economic conditions, the conclusion was the conventional treatment had advantages in terms of costs. In terms of capital expenditure, the estimated cost for the conventional system was USD 251/m<sup>3</sup> of capacity, while for ultrafiltration it was 5.6% higher (USD 265/m<sup>3</sup>). In addition, considering the price of land in some places is a restrictive factor to build a water treatment plant, the cost of an Ultrafiltration plant may be lower compared to conventional. The operational costs for ultrafiltration are lower considering the use of chemicals, but are higher when considering the energy consumption to operate the facility. The maintenance is also another factor that put ultrafiltration behind the conventional systems because of the high costs to replace membranes and mechanical equipment. This research also shows an outcome expected for ultrafiltration systems: the water has elevated quality, regardless of the fluctuations of the feed.

Chun and coworkers (2015) analyzed the performance of the same ultrafiltration water treatment plant in Malaysia. The ultrafiltration unit is in operation since 2013 and has

a capacity of 14 million liters per day. The system consists in collecting water from the riverbank, aerating to oxidize iron and manganese and then ultrafiltration followed by disinfection. In this case, the lack of experience in operating the system and lack of resources resulted an energy increase of 60% due to membrane fouling and 35% increase in water pressure. Membrane chemical cleaning and backwash were not efficient to reestablish the initial operational conditions.

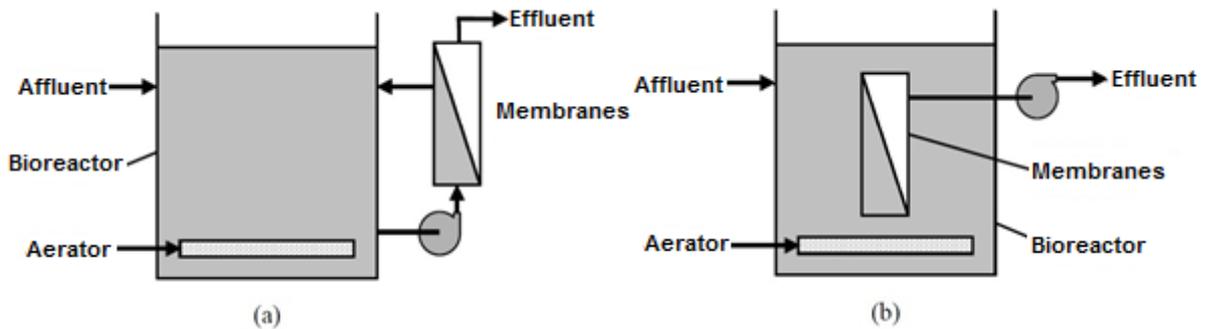
Besides operational problems, membrane fouling represents a significant limitation for the use of membranes in water treatment. Decreases in the flow rate can reach up to 80 % in a few days or sometimes in a few minutes of operation, depending on the membrane permeability, its surface and the concentration and nature of the solid phase present in the water (SINGH, 2005).

#### Membrane Bioreactors (MBR)

Membrane bioreactors combine biological treatment and membrane separation in a single process. The first reported use of this combination dates from 1969, when ultrafiltration membranes were used to separate activated sludge final effluent from a sewage treatment plant, and the sludge recirculated to the aeration tank.

There are two possible configurations for an MBR operation. The first operates with membranes outside the aeration tank, while the second have the membranes submerged. In the configuration with external membrane, the reactor influent is pumped into the membranes module. The system pressure determines the separation of water and sludge, which is recirculated to the reactor. In the case of submerged membrane reactors, a suction force is applied to remove the water through the membrane, while the sludge is retained on the membrane surface. The reactors may have aerators at the bottom, producing air bubbles to keep the environment under aerobic conditions and remove material attached to the membrane surface due to shear force. Figure 7 shows a simplified scheme of operation of these types of MBR. (NG; KIM, 2007)

Figure 7 – MBRs Configurations (a) external membrane (b) submersed membrane



Source: NG; KIM, 2007

The use of submerged reactors is more frequent than the external membrane, since it operates with lower energy consumption and the bubbles formed by the aerators help to clean membrane surface, serving as antifouling agent (NG; KIM, 2007).

Membrane Bioreactors exhibit high removal efficiency of COD, BOD and suspended solids. Because of the biomass separation from the effluent is carried out by membranes and not by gravity, MBRs operate with a higher sludge age and higher loads. This results in lower production of sludge and reduced hydraulic detention time. Another advantage of using membranes is that there is no need for effluent clarification, which makes the system more compact. (NG; KIM, 2007)

A study made by Gómez et al. (2012) presents the results of a monitoring in a municipal wastewater treatment station in the Czech Republic with operating capacity of up to 60 m<sup>3</sup>/day using a system of MBRs for a period of 2 years. The section of the membranes was characterized by submerged flat polyethersulfone membranes working in aerobic conditions at pressures of 50-80 mbar.

The result of monitoring showed a significant flow decreasing during operation ranging from 71 to 90%. It was found that the flow sharply fell until it achieved stabilization: in a first stage of operation this flow decrease took 80 days, whereas in the latter only 32 days.

The effluent quality had an average removal of 99% BOD, 93.5% dissolved organic carbon, 78.5 % nitrogen and 40.5 % phosphorus. The removals were lower in the second stage than the first. Moreover, there was an increase in concentration of

pathogens from one stage to another. These results were due to changes in operating membrane integrity over the long term.

Thus, MBR systems present some limitations that deserve attention regarding operational terms, such as the occurrence of fouling and loss of membrane integrity, as well as the transport of the final biosolids (LE-CLECH et al., 2005). In comparison to the conventional activated sludge processes, MBRs demand a high amount of energy, directed mostly for fouling mitigation by air scouring (JUDD, 2010)

Due to those high costs associated to fouling, a considerable number of studies have focused on the causes and how to control fouling in MBRs systems. According to Bohm et al. (2012) approximately 30% of all MBR publications between 2002 and 2012 was focused on fouling

Membrane fouling on MBR systems occurs due to the adsorption of solutes or colloids within or on membranes; by the deposition of sludge flocs onto surface; by the formation of a cake layer on the membrane surface and/or by the detachment of foulants attributed mainly to shear forces. (MENG et al., 2009).

Fouling behavior in MBRs is more complicated than that most membrane applications because of the variability of sludge quality inside the reactors and the extrapolymeric substances (EPS) which often play an important role on defining the fouling degree. Therefore for specific MBR systems it is important to identify and characterize membrane foulants and how the cake formation, pore blocking, and EPS/SMP adsorption within membranes occur. (MENG et al., 2009)

### **3.8 Fouling Incidence**

As mentioned in previous sections, the use of membranes in industry (mainly in the food sector) and for water or wastewater applications have limitations due to the formation of deposits on the membrane surface, resulting in decreased production of permeate, increased operating pressure, energy consumption, and operating costs.

This loss of flow due to deposits in the surface is called *fouling*. Membrane fouling results in an increase at the transmembrane pressure in an effort to maintain a constant flow. If the pressure is kept constant, then there is an undesired flow decrease. Fouling

can be classified as reversible or irreversible and is associated with the use of membranes and their conditions of operation and cleaning.

The definitions of reversible fouling and irreversible fouling change based on the evaluation of certain authors. Considering different definitions proposed in publications, generally, the irreversible fouling is defined as the fouling that cannot be removed by any means, including chemical cleaning. However, some studies define irreversible fouling as the fouling that can be removed by chemical cleaning but not by physical cleaning. (MENG et al., 2009).

The most common methods to recover membrane conditions are physical cleaning procedures, such as backwashing or scouring the surface, and chemical cleaning, using alkaline compounds to solubilize and detach components weakly adsorbed to the membrane surface. (GUO; NGO; LI, 2012)

In some cases, it is not possible to recover the loss of flow by hydrodynamic procedures or chemical cleaning. The mechanisms involved in the deposit layer are strong adsorption forces and sometimes pore clogging. In this case, the membrane should be replaced by a new one.

The fouling phenomenon is caused by different physicochemical interactions between the constituent components of feeding (concentration, pH, ionic strength), the material of the membrane surface (morphology, hydrophobicity, charge and molecular weight cut-off) and operational conditions. The mass transport can lead to adhesion, adsorption or accumulation of these components in the membrane, both on its surface and inside the pores. Thus, the change of one or several of these factors simultaneously allow the operator to have control over the performance of the membrane, decreasing the particles adhesion and controlling the time frame between cleaning or the eventual replacement of the membrane (GUO; NGO; LI, 2012).

Briefly, the causative agents of deposit are classified into four categories: (GUO; NGO; LI, 2012)

- Particulates: particulate or colloidal organic and inorganic matter that due to their size cause partial or total pore blocking, forming a layer hard to remove. Sometimes, layers

are formed upon other layers of matter. These layers create hydraulic resistance to flow, making it necessary to increase the operation pressure.

- Organic: natural dissolved organic matter, such as humic and fulvic acids, proteins and amino acids that adhere to the membrane surface by adsorption. Fouling like this affects a greater extent the hydrophobic membranes, compared to the hydrophilic ones.

- Inorganic: dissolved ionic components as iron, manganese and silica or residual coagulation and flocculation agents tend to precipitate on the membrane surface due to changes in pH or oxidation (manganese or iron oxides) in high hardness waters. They can cause fouling in the membrane pores, implying sometimes in an irreversible flow reduction.

- Microbiological: the phenomenon known as biofouling, is the adhesion of vegetable matter such as algae and/or bacteria (called pioneer organisms) using the membrane surface and support to adhesion and reproduction. These organisms are known to secrete extracellular polymers, which, besides easing their accession to the surface, also damage sensitive membranes.

Among all these types of fouling, biofouling is considered the worst regarding membranes application for water treatment. Autopsy studies of ultrafiltration membranes, nanofiltration, and reverse osmosis used for treatment of surface water showed that 50% of the dry weight of the adhered layer on the membrane had biological origin (MANSOURI; HARRISSON; CHEN, 2010)

Thus, the fouling phenomenon is considered one of major obstacles for the deployment of more efficient membrane systems. In case of membrane use for water treatment, most of water sources have all of those potential fouling agents (organic, microbiological, inorganic and particulate), which increases the complexity of the approaches to solve this problem.

### **3.9 Alternatives to minimize fouling**

Regarding organic, inorganic and particulate types of fouling, a pretreatment of the feed stream is a good alternative to minimize the flow decrease on membranes. It is known, for example, that reverse osmosis systems have thin and sensitive

membranes. Therefore, undesirable materials such as suspended solids, immiscible liquids and low solubility salts must be removed to ensure proper system operation without causing damage to membranes. Settable solids may be removed by gravity and non-settable solids, organic matter, immiscible liquids and low solubility salts can be removed by coagulation, filtration granular matrix, pH adjustment or addition of scale inhibitors (PRIHASTO; LIU; KIM, 2009). Microfiltration can be used as a polishing step following a conventional treatment or as a pre-treatment before a more retentive membrane process such as nanofiltration (NF) or reverse osmosis (RO) (FABRIS et al., 2007)

With the increasing of the use of ultrafiltration membranes for water treatment, there was an expansion of the association of membranes with other treatment technologies, such as coagulation, flocculation, sedimentation and adsorption, in order to maximize the removal of contaminants and optimize the performance membranes (OLIVEIRA; MIERZWA, 2011). These treatment systems, called embedded systems, are useful when it is necessary to achieve better performance on the removal of dissolved organic compounds with higher molecular weight. (ARYAL et al., 2015)

Research conducted by Oliveira and Mierzwa (2011) compared the operational performance of two ultrafiltration pilot units for water treatment in São Paulo. One of them treated water collected directly from the Guarapiranga reservoir and the other one had a pre-treatment with ferric chloride coagulation, flocculation, sedimentation and filtration. The use of pre-treatment had better results compared to untreated raw water. The permeate was within the potable water standards for both cases. Thus, the adoption of pre-treatment should be evaluated case by case, since the costs of implementation and maintenance of a parallel system might not be justified by the small improvement in performance and production.

Aryal et al., (2015) studied an approach to pre-treat the effluent by filtering in a bed of biological activated carbon and exchange resin before a nanofiltration system. This association was chosen to removal of dissolved organic carbon and high molecular weight fractions with high efficiency. Results show the flux was kept consistent over 140 hours of operation.

In order to evaluate the effects of biofouling and choose a pretreatment, a common operation is the membrane autopsy. The autopsy consists in opening a fouled and thus inoperative, membrane and evaluate the characteristics of the fouling layer. A comparison between the components in feed water and the substances attached to the membrane can help to figure out which kind of contaminants is more likely to deposit on the membrane. Hence, proper pretreatment technologies for membrane processes can be adopted to remove the specific components in feed water to decrease the fouling. (TANG et al., 2014)

Other alternatives to control fouling include the control of operating conditions and periodic chemical cleanings. When operating under low flow conditions, the fouling tendency becomes smaller, requiring in return greater membrane area and increased operational costs. (GAO et al., 2011)

One operational condition that can help to minimize fouling effects is introducing a relaxation period during operation. During the relaxation period the shear stress is maintained, but the filtration strength on particles is stopped. The shear stresses is increased, but the fouling layer accumulated is not modified. (CHARFI et al., 2015). When the filtration stops, the shear forces act mainly on external particles from the deposit and induce a laminar moving of deposit. Therefore, relaxation is effective remove superficial cake, but it is not effective to effects caused by pore clogging. (CHARFI et al., 2015)

The adoption of periodic stops to backwash helps to avoid accumulation of particles on the membrane surface due to the association between high pressure applied in the opposite direction and shear provided by high-speed flushing. (GAO et al., 2011; MIERZWA et al., 2008). Besides deconstructing the cake layer formed, the backwashing operation is also important to re-open blocked pores.

Chemical cleaning is associated with the introduction of acidic or alkaline solutions and/or biocides into the system. The choice of the cleaning solution is based on the characteristics of the source and, therefore, of the potential contaminants. Acidic solutions are recommended for the control of inorganic fouling, while alkaline solutions have efficient control of organic fouling. (GAO et al., 2011)

Research by MIERZWA and colleagues (2012) considered the integrated application of methodologies to combat fouling aiming to improve the performance of a spiral wound ultrafiltration system. It has been found that adopting periodic stops of relaxation and discharge combined with chlorine addition increased production of permeate in approximately 50%.

In the case of MBR systems, the aeration intensity makes bubbles to shear on the surface, reducing fouling incidence. Operational regimes at a low controlled flow, while require larger membrane area (and therefore higher cost) also contribute to reduce fouling. (LE-CLECH et al., 2005)

When it comes to biofouling, control strategies become more complex. This is because the organic layer has capacity for adhesion, adaptation and reproduction on the surface. (MANSOURI; HARRISSON; CHEN, 2010)

To minimize biofouling three approaches are commonly used:

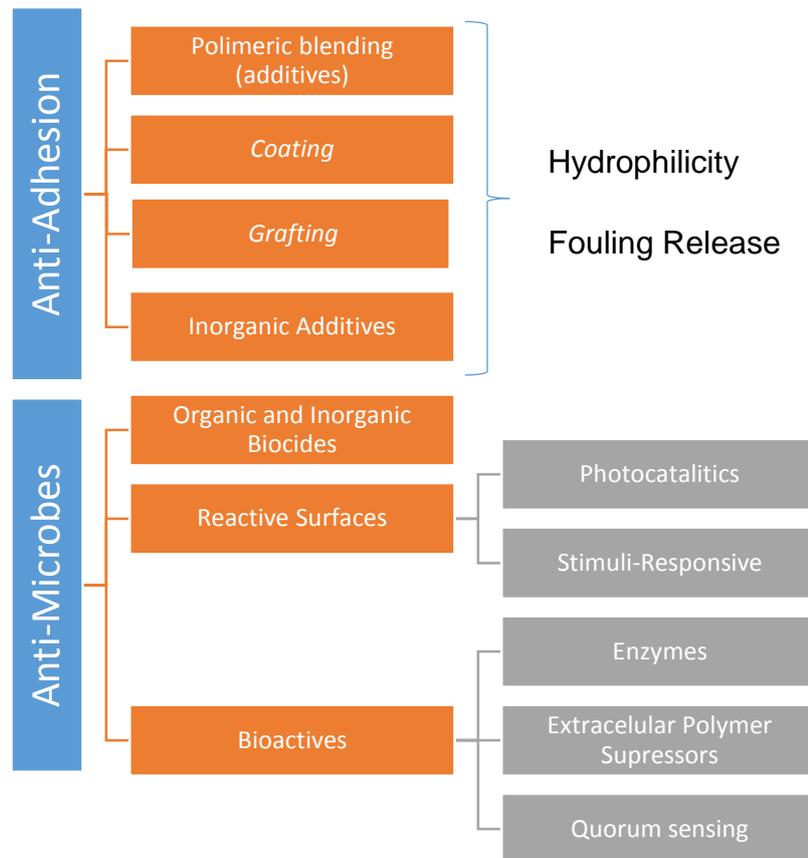
- Optimization of operating conditions, including pretreatment of the feed stream for nutrient reduction and changes in flow regime;
- Dosage of biocides - continuously or intermittently;
- Development of modified membranes or modification of existing membranes making them less prone to deposits;

It should be noted that there are also studies on surface modification of feed spacers. However, the use of spacers coated with copper or biocidal agents sold commercially lost their efficiency in the long term (ARAÚJO et al., 2012)

Figure 8 shows a diagram of the different strategies for controlling biofouling applicable to modified membranes. It is divided in two approaches: anti-adhesion and anti-microbial lines, noting that one approach does not necessarily eliminate another.

Among these methods, the focus of this research is on surface modification of membranes by the addition of nanoparticles in the polymer solution to increase its hydrophilicity and decrease the adhesion of organisms causing fouling, while allowing acceptable flow and selectivity.

Figure 8 – Mechanisms of biofouling control



Source: adapted from MANSOURI; HARRISSON; CHEN, 2010

### 3.10 Membrane Modification

Researches related to synthesis of membranes less prone to fouling have become increasingly representative in the field of membrane separation.

Initially, the first modification attempts involved coating with hydrophilic particles and grafting of layers with different properties in the membranes, giving them different properties.

In the coating process, the membrane receives a particle layer via a deposition bath. The layer deposited on the surface can be removable or permanent. The electrostatic interactions or affinity between the membrane and the surface determine the strength of these links. (BA; LADNER; ECONOMY, 2010)

The graft of hydrophilic layers in polysulfone membranes can be made via induction of reactions with low temperature plasma, gamma or ultraviolet radiation or induced

chemical reactions between the components of the hydrophilic layer and polysulfone (PARK et al., 2006). One of the most studied polymers for this type of modification is polyethylene glycol (PEG). Studies with membrane grafts showed reduction in fouling caused by proteins and increased permeability, despite the hydraulic resistance provided by the additional layer applied to the membrane. Both the coating process and the grafting have advantages, though small. Despite this, they add a new step in the membrane fabrication process: the post-treatment for adaptation. (LEO et al., 2012)

Through new understanding and manipulation of nanometer length scale compounds and the advancement of nanotechnology, researchers began to incorporate nanoparticles in polymer solutions for membrane synthesis. The addition of nanoparticles changes properties, particularly increasing flow and reducing occurrence of fouling.

The addition of inorganic particles make mixed matrix membranes. These membranes have specific properties inherently, which makes the synthesis more simple than grafting or coating.

Among the materials which can be added to polysulfone solutions for modification, there are researches on titanium oxide, silicon oxide, silver, zinc oxide, alumina, anionic dopants, carbon nanotubes and many others. The performance and structure of the final membranes will be briefly discussed.

It should be noted that the use and handling of nanoparticle materials (alumina, silica, and titanium dioxide) deserves attention from the standpoint of human and environmental toxicity. The same properties that make it an attractive nanocomposite (size, shape, surface contact) can increase their toxicity. Few studies have been conducted in this direction, due to the difficulty in measuring concentrations of these compounds in the environment and lack of risk analysis tools. (THERON; WALKER; CLOETE, 2008)

#### *TiO<sub>2</sub> - Titanium Oxide*

In research by Bae and Tak (2005) results of modification using TiO<sub>2</sub> nanoparticles are shown on polysulfone, polyacrylonitrile and PVDF membranes by two different

approaches: coating an oxide layer by immersion and by trapping the particles in the polymer matrix. The results of the two approaches were similar: there was an increase in permeability and a further decrease as the concentration of nanoparticles increased, regardless of the polymer used. This experiment did fouling evaluation tests and it was found that membranes with a surface coated had shown lower propensity to fouling. Such occurrence is justified by the fact the nanoparticles were concentrated in the outer layer, minimizing the effects of surface phenomena.

In another study by Yang et al. (2007), titanium oxide nanoparticles were dispersed in a 18% polysulfone solution. It has been found that the addition of TiO<sub>2</sub> nanoparticles changed the solution viscosity proportionally to the added particles percentage. By observing the membrane structure in the scanning electron microscope, it was found that the membrane morphology showed alterations in the pores structure and, consequently, on its performance. In this case, the higher the percentage of particles became, less porous the membrane, resulting in lower flow. However, in a range between 1 and 2% of the particles, the membranes showed high hydrophilicity and increased rejection capability when treating an emulsion of water and kerosene.

In the case of reverse osmosis membranes with loads of titanium nanoparticles, research by Lee, Arnot and Mattia (2011) evaluated polyamide membranes with polyethersulfone support in DMF. As in previous studies, titanium oxide addition contributed to the increased water flow and the final membrane hydrophilicity. For this experiment, the optimal concentration of particles was about 5 wt%, which contributed to a significant increase in mechanical strength. Above this set point, however, the opposite effect was observed. The structure evaluation of these membranes revealed that the titanium oxide particles were homogeneously dispersed throughout the matrix, covered by a polyamide chain with stable nanoparticles. The authors state that the nanoparticle release after two days of continuous experiments was negligible.

The major difficulty in research with titanium oxide nanoparticles was to ensure adequate nanoparticles dispersion through the polymeric matrix, preventing agglomerations that could plug pores.

### *SiO<sub>2</sub> - Silicon Oxide*

The polymer matrices with silica nanoparticles addition, also called glassy matrices, exhibit improved performance characteristics for gas permeation. In studies by Aerts and coworkers (2000) fumed silica (Aerosil) was added to 18% polysulfone solutions in NMP. Aerosil addition influenced the solution viscosity and served as a barrier to the solvent/non-solvent substitution, delaying phase separation and generating irregular macropores. The increase in concentration up to 2 % caused an increase in pore size distribution for  $\mu\text{m}^2$  in a log-normal distribution, with an increased permeability without loss of rejection capability.

Another study by Ahn and coworkers (2008) with the addition of silica particles in the polymer solution resulted in polysulfone membranes with high CO<sub>2</sub>/CH<sub>4</sub> selectivity. The addition of silica nanoparticles in composite polyamide membranes with polysulfone support altered the structure of polyamide.

As in the case of titanium oxide nanoparticles, silica nanoparticles also show a tendency of agglomeration at high concentrations and decreased performance after achieving an optimal concentration (between 1 and 2%).

Research made by Song et al. (2014) consisted on synthesizing their own silica nanoparticles, ranging from 10 to 100 nm and then applying them on polysulfone membrane synthesis. The silica nanoparticles were grafted with a hydrophilic polymer (such as PVP or poly(vinyl)alcohol (PVA)) to minimize silica losses. The performance of the silica composite membranes was enhanced by reducing particle size. The polymer grafting the nanoparticles also represented a difference in terms of performance, although results of standard deviations are not shown (so the differences for some grafting polymers may not be significant). Also, there was no evaluation of a control membrane without silica to compare the effect versus a pure membrane.

### *Ag<sup>0</sup> - Silver*

The use of silver as the modifying agent has its reasons based on the bactericidal properties of the metal and its low toxicity to mammals. The bactericidal mechanism consists of interactions of silver ions with the amino acid cysteine, inhibiting the enzymatic activity of bacteria.

Study by Taurozzi et al. (2008) with polysulfone membranes prepared by phase inversion in N, N- dimethylacetilamide as solvent, involved modification with silver. Silver has been added as silver nitrate, which was reduced by dimethylformamide into silver. Three approaches to preparation of membranes were used: two involving other additives (polyethylene glycol and 2-propanol) and one without the use of additives. In this experiment, the amount of silver that came off the membrane was evaluated after 4 days of operation with ultrapure water. Silver addition (without additives) increased porosity in comparison to pure polysulfone membrane. There was a decrease on membrane's hydraulic resistance and a decrease on the rejection capability (35.1% to 32.1% of Dextran 150kDa).

Research conducted by Zhu et al. (2010) focused on the immobilization of ionic and reduced silver in chitosan membranes and fouling evaluation. The effects in the membrane internal structure and on its flow and rejection were evaluated. The results showed effective action to control *E. coli* and *Pseudomonas sp.* and inhibition of adhesion and surface growth.

The antibacterial ability occurs through gradual release of silver ions, reducing biofouling. In contrast, the adhesion of silver ion is not strong enough to withstand harsh operating conditions, releasing silver ions on the permeate. This phenomenon of silver loss was observed in both studies, whereas in the study by Zhu et al. (2010), results indicate that reduced silver is more stable than ionic silver.

Research made by Andrade et al. (2015) shows results of two different methods of applying silver nanoparticles in membrane synthesis: in situ (nanoparticles synthesized within the dope solution) and ex situ (nanoparticles already made introduced in the dope solution). There was a release from 1 up to 8 µg/L of silver on the permeate. This silver release can explain the efficiency on bacterial removal (*E. coli* and *P. aeruginosa*). Membranes made by the in situ method had a slightly higher permeability that can be attributed to the addition of PVP (also a pore former) used to synthesize the silver nanoparticles in the dope solution.

### *ZnO - Zinc Oxide*

Zinc oxide nanoparticles are used as antibacterial ingredient in creams, lotions, mouthwashes and as coating materials. In experiments conducted by Leo et al. (2012)

polysulfone membranes were modified with zinc oxide to reduce organic fouling (oleic acid). Zinc oxide nanoparticles yielded higher average pore diameters and at high concentrations (4%) led to decreased membrane resistance to pressure and tension, due to the agglomeration of the nanoparticles. It was observed that the contact angle decreased from 85° from the pure membrane to 62° to a concentration of 2% ZnO. Above this concentration value, the contact angle increased, indicating that the agglomeration of nanoparticles reduced the efficiency. In terms of fouling reduction, the addition of particles resulted in lower oleic acid adhesion (hydrophobic). For the 2% concentration, the flow decline was the lowest observed.

When using zinc oxide nanoparticles with PVDF membranes in NMP with polyvinylpyrrolidone (PVP) as a pore forming agent, Liang and coworkers (2012) concluded that the zinc oxide stayed stable in the form of cubes in the microstructure of the membrane. This contributed with membrane hydrophilicity and improved its permeability. However, as in Leo's experiment, after exceeding a certain zinc concentration, results showed worse performance.

#### *Al<sub>2</sub>O<sub>3</sub> - Aluminum Oxide*

In their research, Yan, Li and Xiang (2005) made 19% PVDF membranes modified with alumina in DMAc. The concentration of alumina in solution results in improved flow, but only up to a certain limit concentration around 3%. The membranes became more hydrophilic, had lower contact angles, reduced flow decay and higher mechanical strength. Nevertheless, the molecular weight cutoff and porosity of the membranes were slightly changed and the surface and cross section micrographs showed that alumina addition did not influence the process of forming the membrane structure. It was one of the few cases evaluated using an additive that was inert in terms of internal changes.

Studies by Mojtahedi, Mehnia and Homayoonfal (2013), complemented by Homayoonfal and collaborators (2015) evaluated the synthesis and use of nanoalumina in polysulfone membranes and their performance on membrane bioreactors. For this case, AFM images showed there was an increase on membrane roughness. The overall fouling was reduced in almost 83% (measured by the membrane hydraulic resistance by the adsorption of contaminants). Their first study

was very preliminary and authors attributes the performance changes exclusively to the enhanced hydrophilicity caused by the nanoalumina (trapped within or on the surface). The study lacks images of the membrane internal structure and a deeper morphology analysis. In their second paper, 2 years later, when the authors evaluate the effectiveness of those membranes on an MBR system, they work now with a deeper characterization of membrane properties, showing besides the AFM, SEM images and a Fourier Transform Infrared analysis to evaluate the presence of residual alumina on the final membrane.

### *Carbon nanotubes and Graphene Oxide*

Carbon nanotubes (CNTs) are graphene sheets shaped into a nanoscale diameter tube (or multi-walled tubes) and topped with spherical fullerenes (C<sub>60</sub>). CNTs are being considered as ideal model sorbent systems to investigate the effects of surface characteristics on the sorption and transport properties of porous solids (KIM; BRUGGEN, 2010; MAUTER; ELIMELECH, 2008). The smooth and hydrophobic inner core of the hollow CNTs can allow the uninterrupted and spontaneous passage of water molecules with very little absorption. (DAS et al., 2014)

Since the CNTs are intrinsically inert, agglomerated, and may contain impurities, a special treatment is needed to disperse the CNTs and order them into a film (KIM; BRUGGEN, 2010).

In order to use CNTs for water purification, CNT membranes have to be functionalized, since the CNT nanotubes are generally contaminated with metal catalysts, impurities and physical heterogeneities that agglomerate and reduce flux. (DAS et al., 2014). The functionalization makes CNT membranes selective for specific pollutants and increases water influx. Functionalized CNT membranes show good water permeability, mechanical and thermal stability, fouling resistance, pollutant degradation and self-cleaning functions. (DAS et al., 2014).

The main drawbacks of the CNTs currently consist on the synthesis of membranes with aligned CNTs with uniform pore size and distribution. The current methods for synthesis are also expensive and time consuming, making them inappropriate for industrial scale. (SCHNORR; SWAGER, 2011)

Another material that has been used for membrane synthesis, correlated to carbon nanotubes is Graphene Oxide (GO). This material has high surface area and electron transport properties. GO is hydrophilic and has a pH sensitive behavior. When GO is incorporated into a polymer matrix, it can also improve physical and mechanical properties of the main polymer, even at low dope concentration. (GANESH; ISLOOR; ISMAIL, 2013). Due to different types of hydrophilic functional groups present on the surface of GO, it can take up water very easily and it has also been well understood that the water uptake increases as the degree of oxidation increases (SZABÓ et al., 2006).

C. Zhao et al. (2013) reported the use of GO mixed in a PVDF matrix led to the development of finger-like voids and thin-walled sponge pores. Porosity and hydrophilicity were increased and the membranes had higher permeability and lower fouling compared to pure PVDF membranes

### **3.11 Use of clay for membrane modification**

Among various inorganic compounds for membrane modification, clay minerals have been used in studies thanks to their good dispersion in the polymer matrix and high hydrophilicity (GHAEMI et al., 2011).

The mixed polymer matrices and layered silicates exhibit improvements in physical properties such as higher tensile strength, heat resistance, lowest flammability and, in case of biodegradable polymers, most biodegradability (MONTICELLI et al., 2006). Despite the potential use of clay as a modifier, few studies have been conducted in this field.

Study by Monticelli et al. (2006) sought the modification of polysulfone membrane (25 wt%) in NMP prepared by phase inversion using clay. Two types of commercial clays, one with sodium and one without it in their compositions were evaluated, compared to pure polysulfone control membranes. This study suggests that NMP is a suitable solvent for solubilizing not only the polymer but also to disperse clay without sodium ions appropriately

Analysis by scanning electron microscopy further evidences this dispersion also evaluated changes in the structure caused by clay. Clay agglomeration reflected in

changes in the performance of the final membrane. The membrane containing 2% sodium clay showed slightly better flow than the pure membrane (1.07 and 0.58 L/h.m<sup>2</sup> respectively) and a dextran rejection capability of 92.2%. With the increase in clay concentration, the flux decreased compared to pure membrane (0.49 L / h.m<sup>2</sup>) and rejection capability was lower than the 2% clay membrane. This shows that increasing concentrations of clay resulted in decrease performance due to their agglomeration, as it was observed with inorganic nanoparticles in other studies.

The membranes modified with sodium- clay showed much higher flows compared to the pure membrane (192 L/h.m<sup>2</sup> at 2% and 226.71 L/h.m<sup>2</sup> at 5%), but their rejection to Dextran was much smaller (20.6% at 2 % clay and 0% at 5 % clay)

Thus, it was found that there was a tradeoff between flux and rejection: membranes with higher flow showed less rejection and membranes with greater rejection showed lower flows. The main focus of membrane modification is to reconcile the increase of both parameters.

Another study involved the addition of montmorillonite to polysulfone membranes was made by Anadão et al. (2010). In this study, 25 % polysulfone in NMP membranes were modified with sodium montmorillonite at 0.5 and 3.0% concentrations.

The authors noticed changes in the microstructure, thermal properties, tensile strength and hydrophilicity through analysis of contact angle. Hydrophilicity had small increments with the addition of clay nanoparticles. The pure membrane had average contact angle of 74.5° and 3% clay membranes had an average angle of 71.5°. The authors themselves note that only the evaluation of the contact angle is not sufficient to determine the hydrophilicity of a material and it should be complemented by studies of permeability and fouling.

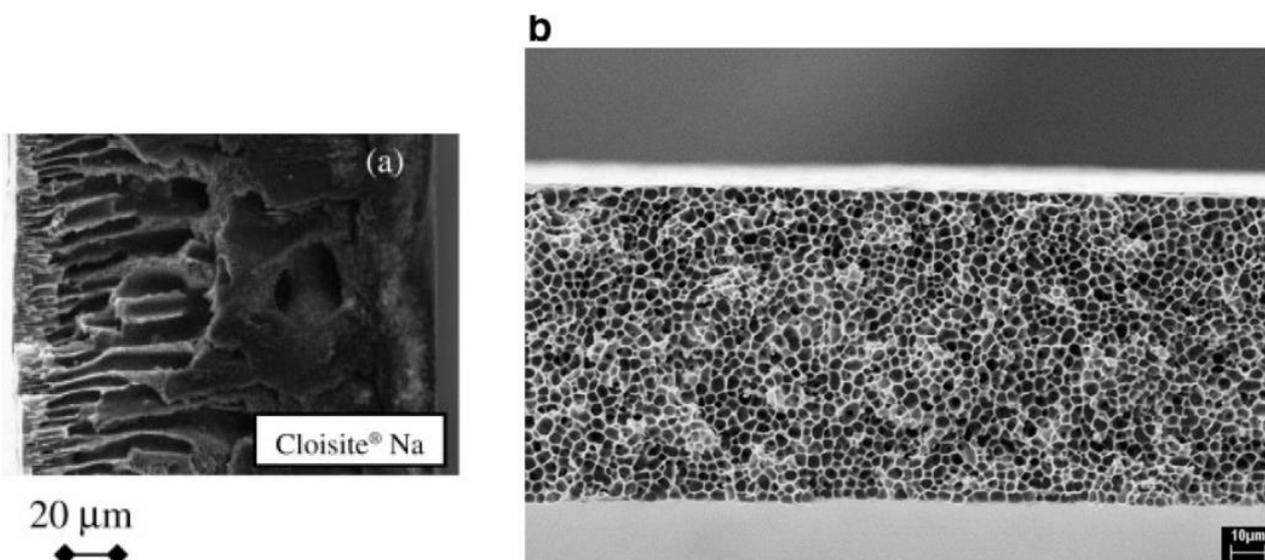
Apart from increases in hydrophobicity, the mechanical strength of the membrane, given by the tension of rupture at elongation and heat resistance were enhanced with the modification.

Microscopic cross section of the membrane showed a predominantly sponge-like structure, different from the membranes made by Monticelli et al. (2006), as compared in Figure 9.

Comparing both works, it appears that there were differences in the post-synthesis step. Monticelli et al. conducted the membrane immersion after an interval of 30 seconds after the casting (in controlled temperature and humidity environment) leaving the membranes in a coagulation bath for 5 minutes and then rinsing them in tap water for one night before characterization. In the experiment of Anadão et al, membranes were immersed in the bath of non-solvent for 1 minute immediately after the spreading, and then they were dried in a vacuum oven for 6 hours at 80°C.

Despite these differences, the step that determines the formation and distribution of pore membranes is the coagulation bath, step which the process of phase inversion occurs. Therefore, this difference in the post- synthesis process is not sufficient to explain the differences observed, since after the coagulation bath the membranes internal structures have been already consolidated.

Figure 9 – Comparison of the structures of PSU membranes (25%) with nanoclay a) Membrane with 2% sodium clay (Monticelli et al, 2006), b) Membrane 0.5% sodium montmorillonite (Anadão et al, 2010)



Anadão et al. made an update in their membrane research in 2014, evaluating membranes in the same conditions (25% Polysulfone in NMP and different contents of clay) using Small Angle X-ray diffraction and Transmission Electronic Microscopy. (ANADÃO et al., 2014)

In this work the addition of clay didn't promote changes in the cross section of the membranes, even for high contents of clay (5%). In this study, thermal and mechanical

resistance of the membranes increased with the clay content. However, no further studies of permeability and rejection were made.

A research study by Ma et al. (2011) presents modified polysulfone membranes with addition of montmorillonite and 400 g/mol polyethylene glycol (PEG) as a pore-forming additive. The difference compared to the other cited studies is the use of Dimethylacetilamide as solvent.

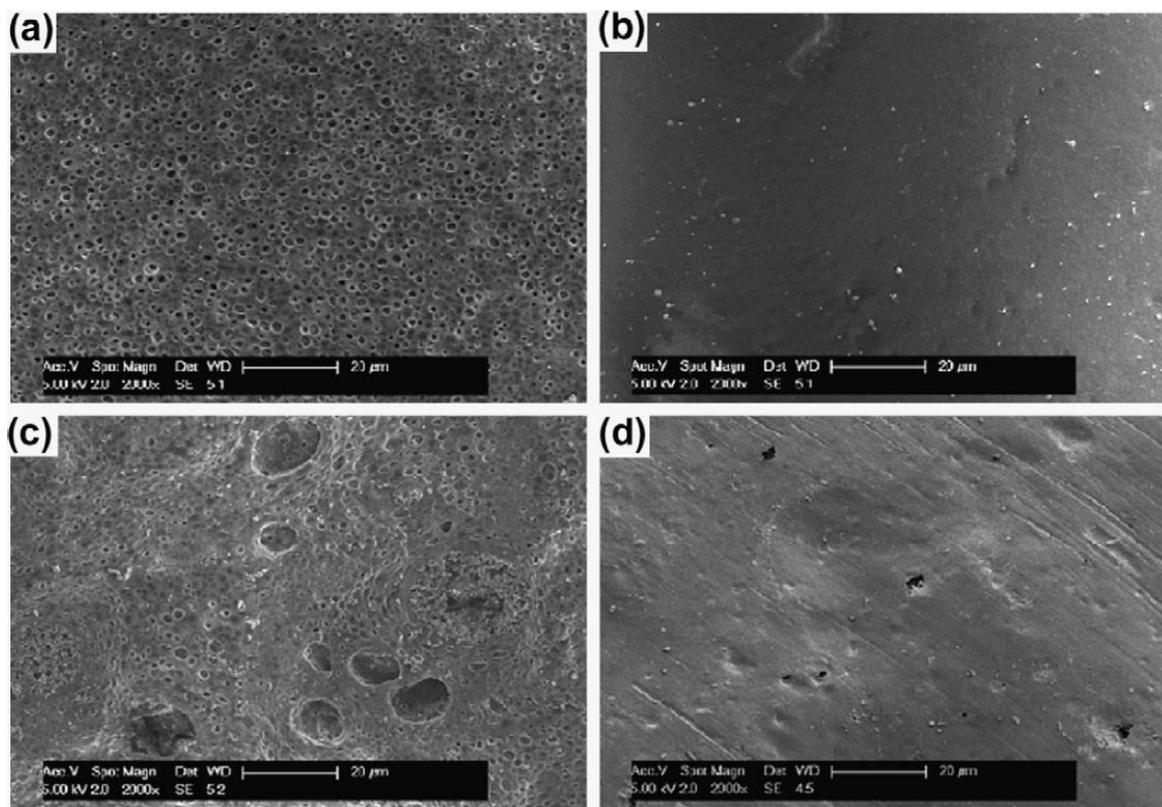
The percentage of polysulfone was fixed at 18 % and the clay was classified as clay modified by the addition of quaternary ammonium salts. The results of this study showed negligible change in hydrophilicity of the membrane, reduced tensile resistance and increased membrane porosity.

However, due to the fact there was no control membranes (without the addition of polyethylene glycol) it remains unclear whether the other contradictory properties observed in this study are due solely to the nanoparticles of clay or if there is any interaction of the PEG additive with the polymer and the clay used .

Another study, conducted by Tran, Patterson and James (2012), reports the changes of membrane performance in 10% polysulfone membranes in NMP 250  $\mu\text{m}$  thick challenged into adsorption of bovine serum proteins. The membranes produced had surface with a high pore density (even pure polysulfone membranes), as shown in Figure 10.

Incorporation of montmorillonite in the polymer matrix increased the hydrophilicity of the surface: the contact angle decreases in the order of  $89.5^\circ$  to about  $70^\circ$ . The modified membranes were more porous, and with improved flow and rejection capability decreased in comparison to the pure membranes.

Figure 10 – Top (a) and bottom (b) of pure membrane PSU 10% and top (c) and bottom (d) of modified membrane PSU 10% and montmorillonite 10



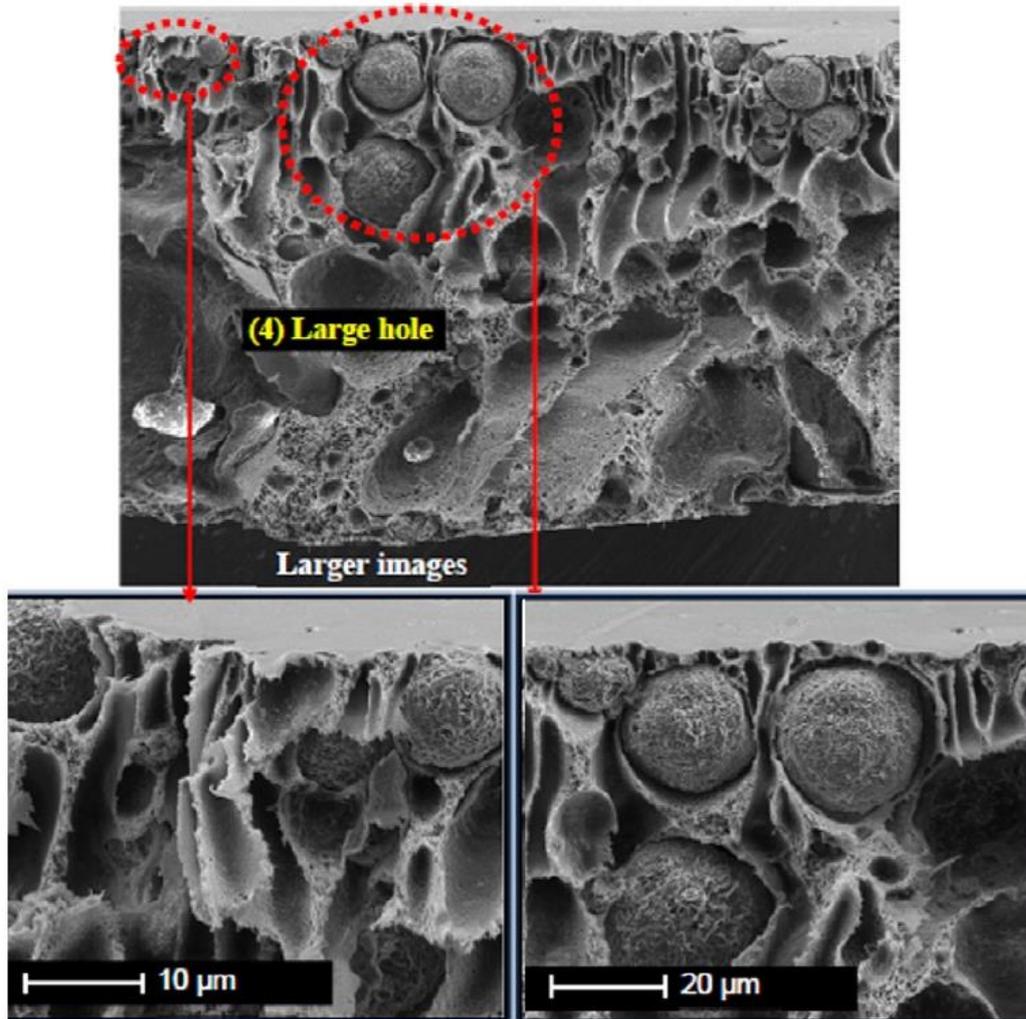
Source: TRAN; PATTERSON; JAMES, 2012

The authors came to the conclusion that the manufacturing process could be better if the solution was degassed and the adsorption capacity for bovine serum protein was slightly improved. However, they didn't consider that such phenomenon may have occurred due to the high porosity of the membrane (low polymer concentration) that would allow adsorption within the polymer matrix containing clay lumps of up to 20  $\mu\text{m}$  in diameter, as illustrated in Figure 11.

Comparing their cross section with those of other studies mentioned, it is possible to see clear differences by the presence of clumps of clay in the matrix and the membrane structure by itself, which presents a different pore distribution.

Thus, considering the variations of results observed in those experiments, the modification of polysulfone membranes made with clay, the mechanisms of formation of modified membranes need further study to clarify the influence of nanoparticles on the clay structure and consequently in membrane performance.

Figure 11 – Cross Section of membranes modified with clay (10% PSf, 10% Clay)



Source: TRAN; PATTERSON; JAMES, 2012

The contribution of this research will be synthesizing membranes with nanoclay in fixed conditions, compare the effects of nanoclay addition and the interaction of nanoclay and the pore former PEO on membrane structure and performance.

### 3.12 Properties of Clays

Among the phyllosilicates used for polymer composites, are clays. This subcategory includes kaolinite, montmorillonite, smectite, illite (mica) and chlorite groups. Clay minerals contain varying amounts of water, allowing cation substitution easily and allowing expansion of the silicate layers (GECKELER; NISHIDE, 2009)

Among the clay minerals used to change the properties of polymers, many studies have been conducted with montmorillonite aluminosilicate. According to this concept,

montmorillonite is composed by two silica tetrahedral sheets with a central alumina octahedral sheet. (aluminosilicate) or magnesia (magnesium silicate). The tetrahedral and octahedral sheets are combined, forming a common layer. There are exchangeable cations between the silicate layers, and depending on the cation size, the water layer can have different thickness when the montmorillonite is exposed to water (GRIM, 1968).

This research will use bentonite, which is the name to designate clays with high content of montmorillonite (55-70 %). Bentonite can be calcium, sodium or polycationic (DNMP, 2009). Bentonite is easily commercially available and can be found in nanoparticulate form.

Montmorillonite have irregular plate outline, are thin and tend to aggregate in the drying process. The stack of these plates is governed by relatively weak polar forces and Van der Waals forces. When the lamellae of montmorillonite are exposed to water, the water molecules are adsorbed on the surface of silica sheets, which are separated from each other. The more affinity for the cation has to water, the largest is the interlayer swelling.

Other interesting properties of bentonite include a moderate negative surface charge, with cation exchange capacity between 80 and 150 meq per 100g of smectite, high surface area (800 m<sup>2</sup>/g) and resistance to temperature and solvents (SILVA; FERREIRA, 2008)

### **3.13 Use of PEO/PEG for membrane modification**

Poly(ethylene glycol) (PEG), also known as poly(oxyethylene) or poly(ethylene oxide) (PEO), is a synthetic polyether available in the market in a wide range of molecular weights. Materials with average molecular weight lower than 100,000 are usually called PEGs, while higher molecular weight polymers are classified as PEOs. (BAILEY; KOLESKE, 1976)

These polymers are amphiphilic and soluble in water as well as in many organic solvents (methylene chloride, ethanol, toluene, acetone, and chloroform). Low molecular weight PEGs are viscous and colorless liquids, while higher molecular weight PEGs are waxy, white solids with melting points proportional to their molecular

weights (BAILEY; KOLESKE, 1976). PEG has been used in experiments of membrane modification in different ways: as additive in the dope solution, as additive in the coagulation bath and also used as polymer to evaluate molecular weight cut-off, since it's available in many molecular weights.

According to research by Kim and Lee (1998), the role of PEG is altering the behavior of the top layer formation. When a porous superficial layer is made, the macrovoids inside the membrane structure are suppressed, increasing water flux. In this study is also observed the hypothesis of the quick water influx is responsible for macrovoid formation.

Research developed by Idris and Yet (2006) reports the use of PEG as additive for synthesis of polyethersulfone (PES) membranes. In N-dimethylformamide as solvent. Different molecular weights were used in the experiment: 200, 400 and 600 Daltons and different concentrations of PEG were evaluated. The addition of PEG increase permeability of PES membranes. Also as the concentration of PEG 400 and PEG 600 in the dope solution increased, solute separation decreased while flux increased.

PEO has been reported as a weak polymer for membrane synthesis when used as component polymer. Even though it is very hydrophilic, with repeating oxygen units in its chain, it lacks the mechanical resistance needed by membranes submitted to high pressure conditions. It is very soluble and it can easily be dissolved in the phase inversion, which makes it a good additive for membrane synthesis instead of a membrane material. (CHO et al., 2011)

Cho et al. (2011) reported the use of PSF-PEO random copolymer used for membrane synthesis (not as additive), in order to immobilize the PEO in the membrane. Water flux was significantly improved as the PEO content in the random copolymer increased. The water flux and solute rejection also exhibited the same trade-off noticeable in other studies: in cases which permeability was increased, the rejection was decreased. Some membranes who had better permeability were challenged using bovine protein and emulsified oil solution.

### **3.14 Summary and Relevance of this Study**

The references analyzed show in common that membrane fouling is a complex phenomenon considered one of the most critical conditions for membrane applications

in large scale, such as water and wastewater treatment. Membrane fouling comprises interactions in superficial and structural level of membranes that result in significant losses of membrane performance. Therefore, the study of different approaches to minimize fouling has been targeted by many researchers on the membrane field.

Among those approaches, membrane modification studies have a significant relevance considering there are many possibilities of modifying a membrane by the use of nanoparticulated additives. The examples of nanoparticles evaluated in this review (alumina, titanium oxide, silicon oxide, ionic silver, zinc oxide, inorganic salts, carbon nanotubes, graphene oxide, and nanoclay – all on polysulfone membranes) are only a few of the possible materials to be used for membrane modification.

Despite the different compositions, all the additives show a common result: the internal structure changes and permeability enhancement. Another common result of the research with nanoparticulated materials is that the increment in permeability is significant until a certain concentration of additive. After reaching this optimal concentration the performance drops and the investment on using more additive becomes cost inefficient.

Membrane studies refer to the use of “additives” for membrane modification. However, there is no common sense on the literature about what percentage of the modification agent can be considered as an additive. In some studies, the concentration of the modification agent reached 10% in weight of the whole solution. That could be classified as a membrane component not as an additive. According to the IUPAC’s Compendium of Chemical Terminology (2007), the definition for additive in polymer chemistry is “usually a minor component of the mixture formed and usually modifies the properties of the polymer”. By referring to “minor component”, it is not specified an absolute threshold of what can be classified as an additive.

In this study it is clear and specified that the nanoclay and PEO concentration are ratios relative to the polymer weight, which represents a small fraction of the total solution. i.e., for a solution with base of 100 grams, 82 grams are solvent based, 18 grams polymer base. Over the 18 grams, 1% of nanoclay is used as additive (0.18 grams).

Most of the studies evaluated have an approach focusing on permeability. It is rare to find a research paper that focuses on a multi-variable approach to characterize the

membranes in terms of solute rejection, surface properties, mechanical properties, internal structure and fouling formation. Usually they focus on one of those topics to complement and justify the increments in permeability.

When this research proposed to focus on membrane synthesis and modification, it was defined that the characterization would embrace multiple parameters correlated to the membrane performance and membrane fouling, focusing the use of membranes for water treatment. Besides having a multi-parameter approach on membrane characterization, this study is relevant for the membrane field because it evaluated the association of two different additives (nanoclay and the pore former PEO).

Pore formers are known for increasing membrane permeability, but lowering membrane rejection by widening the pores on the internal structure. On the other hand, studies with nanoclay as additive show that the membrane rejection ability can be increased without compromising permeability (most of the times, except when clay aggregation). This research hypothesizes that the evaluation of these two additives could result on a synergistic effect of increased permeability without compromising membrane rejection. Both of those effects are desirable for ultrafiltration membranes for water treatment.

## 4. MATERIALS AND METHODS

### 4.1 Reagents

Table 2 shows the reagents used for the experiments of membrane synthesis and characterization.

Table 2 – Reagents used

Reagent	Manufacturer	Composition	Use	Observation
<i>Synthesis</i>				
Polysulfone	Solvay	$(C_{27}H_{22}O_4S)_n$	Base Polymer	Polysulfone UDEL® P-3500, in pellets
N-metil-2-pirrolidone	SynthLab	$C_5H_9NO$	Solvent	---
Clay Nanometer PGV	Sigma-Aldrich	$H_2Al_2O_6Si$	Surface Modifier	Hydrophilic Bentonite
Polyethylene Oxide	Sigma-Aldrich	$C_{2n}H_{4n+2}O_{n+1}$	Additive	Molecular Weight of 100 kg/mol
Demineralized Water		$H_2O$	Non-Solvent in coagulation bath, washing, conservation and characterization	Double Step Reverse Osmosis Permeate. Conductivity < 1,0 $\mu S/cm$
Ethanol		$C_2H_5OH$	Glass Plate Drying	---
<i>Drying and Conservation</i>				
Sodium metabisulfite	SynthLab	$Na_2S_2O_5$	Conservation of wet membranes	---
Isopropilic Alcohol (Propan-2-ol)	SynthLab	$C_3H_7OH$	Membrane Drying	---
<i>Characterization</i>				
Sodium Alginate	Inlab	$NaC_6H_7O_6$	Tests for Fouling Evaluation	---
Toluidine Blue	Inlab	$C_{15}H_{16}N_3S^+$		---
Sodium Chloride	SynthLab	$NaCl$	Superficial Charge Evaluation	---
Sodium Hydroxide	SynthLab	$NaOH$		---
Chloridric Acid	SynthLab	$HCl$		---
Liquid Nitrogen	-	$N_2$	Scanning Electronic Microscopy. Membrane Breaking	---
Polyethylene Glycol	Polymer Source	$C_{2n}H_{4n+2}O_{n+1}$	Molecular Weight Cut-Off	Molecular Weights of 10, 20, 32, 90, 150 and 200 kg/mol

Polysulfone UDEL® P-3500 LCD pellets were kindly donated by Solvay Advanced Polymers. N-methyl-2-pyrrolidone (NMP; >99%; MW = 99.1 g/mol) was acquired from Alfa Aesar (Ward Hill, MA) and used as received. The nanoclay (Montmorillonite - Nanomer® PGV – Sigma Aldrich) is a single platelet montmorillonite of formula  $M^+_y(Al_{2-y}Mg_y)(Si_4)O_{10}(OH)_2 \cdot nH_2O$  where the M are lower valence cations yielding a cation exchange capacity 1.45 meq/g. The approximate dimensions of the individual

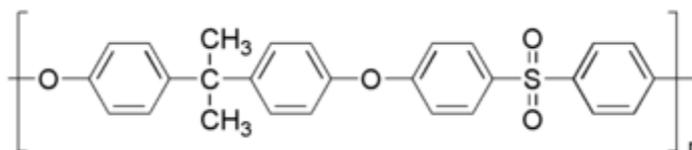
montmorillonite platelets are  $1 \times 150\text{--}200 \times 150\text{--}200$  nm. The PEO (MW = 100 kg/mol) was acquired from Sigma Aldrich (St. Louis, MO). Isopropyl alcohol ( $\geq 99.5\%$ ) was purchased from VWR International (West Chester, PA). Polyethylene glycol (PEG) samples of 10 kg/mol, 50 kg/mol, 90 kg/mol, and 203 kg/mol number average molecular weight were acquired from Polymer Source Inc. (Canada). The sodium alginate (SA) was acquired from MP Biomedicals, LLC. The natural surface water used for the fouling experiments was acquired from the Fresh Pond Reservoir at the Cambridge Drinking Water Treatment Plant. Deionized (DI) water ( $>18$  M $\Omega$ ) was produced by a Nanopure Infinity Ultrapure Water System (Barnstead/Thermolyne).

## 4.2 Membrane Materials

### 4.2.1 Polymer

The focus of this work is the use membranes made with the polymer polysulfone as base. The repetition unit structure of polysulfone is shown in Figure 12

Figure 12 – Polysulfone Repetition Unit



Polysulfone is characterized by the presence of sulfone group as part of its repeating unit. Evaluating the structure of the repetition unit, the  $\text{SO}_2$  group of the molecule is very stable, being allocated between aromatic groups. Oxygen molecules of this group have two pairs of free electrons each for donation, allowing the formation of hydrogen bonds with hydrogen molecules from the solvent (CHERYAN, 1998)

Phenylene rings repeated during this structure confers steric resistance<sup>1</sup> to rotation in the molecule implying a lower mobility and thus increases in stiffness, mechanical strength and dimensional stability<sup>2</sup> (CHERYAN, 1998)

<sup>1</sup> Steric resistance is a phenomenon that occurs when large groups repeated in a molecule prevent reactions that are usually seen in groups of shorter chain to occur

<sup>2</sup> Dimensional stability is the ability of a substance (or part) to conserve its shape when subjected to different conditions of temperature, humidity, pressure and other forms of stress

Polysulfones are rigid and tough, with practical engineering applications and have strength and stiffness properties even without reinforcement. The polymer exhibits ductile yielding over a wide range of temperatures and deformation rates. Also, polysulfone have inherit burning resistance characteristics compared with many engineering thermoplastics. (MARK, 2003)

Regarding health and safety, polysulfones are chemically inert and have no adverse effects known. It has approval from the U.S. Food and Drug Administration for direct food contact and it is used on food processing industry, plumbing and medical/prosthetic applications since 1960. (MARK, 2003)

Thus, polysulfone is considered a high-performance thermoplastic polymer to withstand varying temperatures, sanitizing agents, surfactants, mineral acids and alkalis. However, this polymer presents no resistance to polar organic solvents (such as ketones and chlorinated hydrocarbons), being soluble in solvents such as dichloromethane and N-methyl-2-pyrrolidone.

Table 3 presents the principal advantages and disadvantages in the use of polysulfone as a base polymer for membrane synthesis:

Table 3 – Advantages and disadvantages of using the polysulfone membrane synthesis

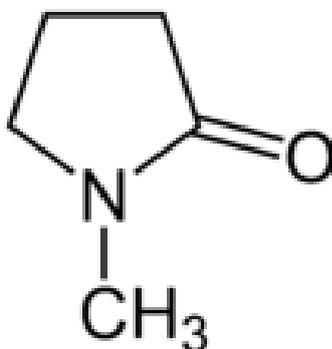
<b>Advantages</b>	<b>Disadvantages</b>
Resistance to halogenated aliphatic hydrocarbons, alcohols and acids	Low resistance to aromatic hydrocarbons, ketones, ethers and esters
Wide working temperature range (some cases up to 125 ° C)	Hydrophobicity
Moderate resistance to chlorine	High exposure to chlorine (> 200 ppm) damages the film
Low values of operating pressure of 7 bar flat and hollow fiber 1.7bar)	
Easy to manufacture in different arrangements	
Tolerance to variations in pH from 1 to 13 (advantages for cleaning)	

Source: CHERYAN, 1998

#### 4.2.2 Solvent

To carry out this study, the solvent used in the preparation of the membrane composition solution is N-methyl-2-pyrrolidone, known commercially as NMP or as pharماسolve. The NMP is a hygroscopic polar solvent and has varied uses in the chemical and petrochemical industry - being used as intermediate reactions with polymers agent - formulation of paints, dyes and pesticides and cleaning agent in the microelectronics industry (graphite remover) (BASF CORPORATION, 1999). The structural chemical formula of NMP is shown in Figure 13.

Figure 13 – Chemical Structure of N-methyl-2-pyrrolidone



Few studies involving toxicity of this solvent were performed in humans. Studies in animals show no evidence of carcinogenicity and mutagenicity (CARNERUP; SPANNE; JÖNSSON, 2006). Results of researches focusing in worker exposure to NMP found that there is no significant health effect detected among workers exposed to NMP at a maximum level of 0.8 ppm and below (NISHIMURA et al., 2009)

The risks of occupational exposure are associated to respiratory irritation, dermal absorption and irritability in the eyes. Therefore, it is recommended when handling this solvent are used appropriate protective equipment to avoid contact with these exposure pathways. (BASF CORPORATION, 1999)

The results of animal studies and human exposure to this solvent indicate risks of inhalation and dermal absorption. Despite these risks, when the NMP comes into contact with the blood undergoes rapid oxidation and hydroxylation into 5-hydroxy-Nmethyl-2-pyrrolidone (5-HNMP), N-methylsuccinimide (MSI), and 2-hydroxy-N-methylsuccinimide (2-HMSI), and excreted in urine as NMP itself and metabolites (NISHIMURA et al., 2009) in an average interval of 24 hours (HOWE; WOOD; KINGDOM, 2001).

Regarding to the environment, NMP is not toxic to aquatic life and is easily degraded by microorganisms in traditional wastewater treatment plants (BASF CORPORATION, 1999) When NMP evaporates, it is removed by the air humidity or by photochemical reactions with hydroxyl radicals. Because it is water miscible, NMP is hardly adsorbed on soil, sediment or suspended organic matter.

### 4.3 Membrane Synthesis

For this study, the membranes were synthesized via phase inversion (method described in details on section 3.5). The membrane casting solutions were produced by dissolving PSU (18% w/w) in NMP (82% w/w) with addition of nanoclay (1 to 5% w/w clay/PSU) and/or PEO (1 to 5% w/w PEO/PSU) when applicable. The polymer/solvent ratio was based on studies of Ma et al. (2011) and Chen et al. (2011).

Membranes with no clay or PEO were used as a control. The membrane compositions can be found in Table 4. For the study, membranes were classified as membranes with only nanoclay (C followed by the clay weight percentage to PSU), only PEO (P followed by the PEO weight percentage to PSU), and membranes with both clay and PEO (C followed by the clay percentage and P followed by the PEO percentage).

Table 4 – Membrane Casting Solution Composition.

<b>Name</b>	<b>Clay*</b>	<b>PEO**</b>	<b>Name</b>	<b>Clay*</b>	<b>PEO**</b>	<b>Name</b>	<b>Clay*</b>	<b>PEO**</b>
PS	0%	0%	C5	5.0%	0%	C3P1	3.0%	1.0%
C1	1.0%	0%	P1	0.0%	1.0%	C3P3	3.0%	3.0%
C1.5	1.5%	0%	P3	0.0%	3.0%	C3P5	3.0%	5.0%
C2	2.0%	0%	P5	0.0%	5.0%	C4.5P1	4.5%	1.0%
C3	3.0%	0%	C1.5P1	1.5%	1.0%	C4.5P3	4.5%	3.0%
C4	4.0%	0%	C1.5P3	1.5%	3.0%	C4.5P5	4.5%	5.0%
C4.5	4.5%	0%	C1.5P5	1.5%	5.0%			

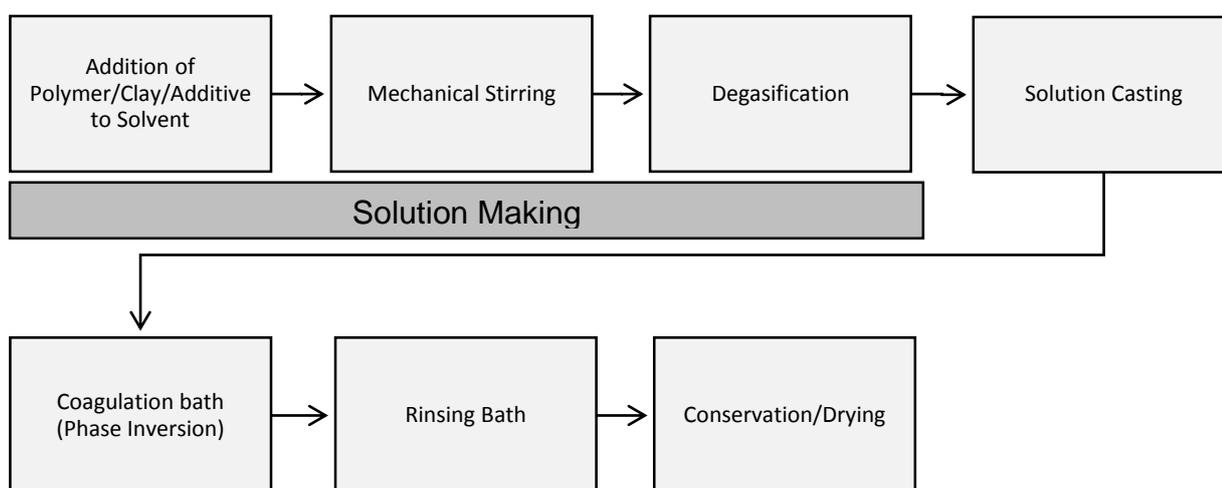
Variables that could cause interference in membrane structure were minimized. Those variables include changes in room temperature, casting solution temperature, coagulation bath conditions (temperature and presence of additives). Changing too many synthesis variables simultaneously could create at the end of the experiment uncertainty whether the changes in performance were caused by modification with nanoclay and PEO or by changing other casting variables (along with addition). Thus,

it was chosen to carry out the experimental work in a controlled room temperature of 25°C. The same temperature was used for the casting solution and coagulation bath.

The synthesis experiments were performed on the Vecitis Lab of Environmental Technology at Harvard University.

Figure 14 shows a flowchart of the manufacturing process and membranes, which will be described in sequence of synthesis:

Figure 14 – Steps on Membrane Synthesis



#### 4.3.1 Polymer Solution Preparation

To prepare the polymer solutions, polymer was dried at 180 °C during 4 hours, to minimize water interference. The solvent (99.9% purity) was used as received (without going through the drying process).

The solution preparation occurred in stages as follows:

- 1) Addition of PEO to solution (when applicable): PEO was added to the solvent until its full solubilization;
- 2) Addition of Clay to solutions (when applicable): before adding the polymer, clay was added to the solvent under stirring. Only after the dispersion of clay was added to polymer;
- 3) Addition of Polymer: polysulfone was added to the solvent under stirring. In order to prevent agglomeration of pellets in polysulfone solution, which would hinder the dissolution, the polymer was added in steps (a quarter every 30 minutes approximately);

- 4) Stirring: the solutions were left stirring at 120 rpm for 24 hours (mechanical stirrer) to ensure complete solubilization of the polymer and clay dispersion;
- 5) Degassing: prior to casting, the solutions were degassed in an ultrasonic bath (Branson 2100) for 30 minutes in order to eliminate air bubbles that could interfere with the final membrane structure

#### *4.3.2 Solution Casting*

After stirring and degassing, the solutions were ready to be cast on the automatic film applicator. In the procedure, the polymeric solution was carefully applied to a glass plate using an automatic film applicator (Elcometer 4340 Automatic Film Applicator) with a casting bar at a fixed height (100  $\mu\text{m}$ ) and application speed (1.0 cm/s). At the end of the casting, performed with a velocity of 1.0 cm/s, the polymeric film with desired thickness is adhered to the glass support, which is immediately immersed in a coagulation bath with demineralized water, so that the phase inversion phenomenon occurs and structures the membrane.

#### *4.3.3 Coagulation Bath*

The glass support containing the polymer film was immediately immersed on the non-solvent coagulation bath (deionized water) at room temperature, for membrane formation.

#### *4.3.4 Rinse Bath*

Once synthesized, the membranes were kept in deionized water bath at room temperature for 24 hours, to ensure total removal of the remaining solvent.

#### *4.3.5 Storage and Drying*

After the rinse bath, the membranes that were immediately tested in the test cell unit were kept in solution of demineralized water containing 1% sodium metabisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) to ensure their conservation and prevent bacterial growth.

Membranes which would be tested on equipment that requires dry samples (contact angle, scanning electron microscopy, tensile tests, thermogravimetric analysis and atomic force microscopy) were kept in propan-2-ol (isopropyl alcohol) for 24 hours and

dried in a controlled environment (fume-hood) for 24 h to ensure removal of water by natural propan-2-ol evaporation.

#### 4.4 Membrane Characterization

The purpose of the characterization of membranes is forecasting their performance, taking as references measurable characteristics. With the combination of knowledge about morphology, flow and rejection capability is possible to define the best choice of membranes for a particular operation.

Table 5 shows the characterization tests of the membranes produced in this study

Table 5 – Parameters evaluated in Membranes Characterization

<b>Physical Properties</b>	<b>Performance</b>
Polymer Solution Viscosity	Flow and Permeability Testing
Internal Structure (SEM)	Molecular Weight Cutoff
Hydrophilicity (Contact Angle )	Rejection Test
Porosity	Fouling Evaluation
Mechanical Strength	<i>E. coli</i> Removal
Thermal Stability	
Superficial Charges	
Surface Roughness	

##### 4.4.1 Physical Properties

###### Polymeric Solution Viscosity

The membranes produced were characterized in terms of dynamic viscosity of polymer solutions. The casting solution viscosity was measured to evaluate potential viscosity effects on the phase inversion process. Higher molecular weight additives such as PEO are expected to increase solution viscosity and in turn slow the diffusion of solvent out of the film during phase inversion leading to the formation of a denser skin layer (SADRZADEH; BHATTACHARJEE, 2013).

For the tests, the microprocessor rotary viscometer Brookfield RVDV-E was used and its calibration was performed with ultrapure water.

The casting solution was placed in a beaker and then the rotational spindle is slowly immersed to avoid bubble formation. The shear force is determined from the spindle geometry and the applied rotation rate according to Eq. 2:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (2)$$

where  $\eta$  is the viscosity in poise,  $\tau$  is the shear stress in dynes/cm<sup>2</sup>, and  $\dot{\gamma}$  is the rate of shear (sec<sup>-1</sup>). The viscosity was measured at a constant shear rate of 30 RPM and temperature of 25°C (same temperature as membrane casting). At least two different samples of different casting solutions were evaluated.

#### Structure (Scanning Electron Microscopy)

Analyses of Scanning Electron Microscopy have as main objectives to evaluate the porosity of the surface layer, membrane thickness and structure of the cross section.

The analyses were performed at the Laboratory of Technology Characterization (LCT) of the Department of Mines and Petroleum Engineering at Escola Politécnica da Universidade de São Paulo. The equipment used was a scanning electron microscope (SEM) with a field emission gun brand FEI QUANTA 600. Image acquisition was performed with the equipment operating in mode of secondary electrons detection and the accelerating voltage (HV) of 10 kV.

All membrane samples were coated with a modular high vacuum coating system (BAL-TEC MED 020) resulting in an ~10 nm platinum layer after 120-160 s of deposition at 43 mA current.

To evaluate the cross sections, the dried samples went through a pre-treatment with immersion in liquid nitrogen to ensure the breaking of the membranes while preserving the cross section. The use of conventional cutting tools can damage the sectional profile by the shear caused by the equipment.

#### Hydrophilicity Test (Contact Angle)

The contact angle test aims to determine the hydrophilicity of the membrane surface. The angle measured is the angle between the liquid–gas tangent and membrane–

liquid boundary. The smaller the angle between the droplet and the surface, more hydrophilic is the membrane and lower the tendency to fouling.

The methodology used for these trials was recommended by ISO 15989/2004 Plastics - Film and sheeting - Measurement of water- contact angle of corona -treated films. 20 to 30 measurements were performed on a minimum of three different samples of each membrane and the average and standard deviation of the samples were calculated.

Contact angle measurements were determined with a goniometer Ramé-Hart Instrument Co. Model 190 CA.

### Porosity

The porosity evaluation was performed by analyzing the difference between membranes wet and dry weight.

Another approach to evaluate porosity would be the evaluation of micrographs use the images obtained by scanning refined using a specific software electron microscopy, as described by Mierzwa and colleagues (2012). However, for this study the surface micrographs were not conclusive for an image refining to see surface pores.

Membrane porosity was determined following method described by Mierzwa et al. (2012) wet/dry weight methods. The wet weight was measured after removing the superficial water with two polyester/cellulose wipers (VWR International) and the dry weight was measured after drying the samples. The porosity was calculated using eq. 3:

$$\varepsilon (\%) = \frac{m_1 - m_2}{\rho_w V_m} \times 100 \quad (3)$$

where  $m_1$  and  $m_2$  (g) are the wet and dry weights,  $\rho_w$  ( $\text{g cm}^{-3}$ ) is the density of water,  $V_m$  ( $\text{cm}^3$ ) is the membrane volume, and  $\varepsilon$  (%) is the bulk porosity. The volume,  $V_m$ , was calculated by multiplying the sample area by its thickness, which was measured by a digital micrometer.

### Mechanical Strength

The mechanical resistance tests verify the influence of the deformation of the membrane stresses, being possible to determine the elastic modulus and rupture the membrane tension.

Standard Test Method for Tensile Properties of Thin Plastic Sheet - as a methodology for performing these tests to ASTM D 882 was used. At least three samples were evaluated for each membrane type being calculated the average modulus.

The test consists of applying tension in a specimen of defined dimensions until their elongation and subsequent rupture. The tension applied is plotted in the function of deformation, providing a curve whose linear coefficient provides the elastic modulus.

The mechanical resistance tests were completed on the Shimadzu Compact Table-top Universal Testing Machine EZTest EZ-LX at 25°C with a crosshead speed of 5 mm min<sup>-1</sup>. The dimensions of the samples used by this test was 5 x 15 mm x the membrane thickness. At least 3 samples were analyzed for average tensile strength, Young's modulus, and elongation at break.

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was completed using a TA Instruments Model TA 2950 TGA. The device consists on an association of a high precision scale and a furnace. Considering the samples are solid and non-volatile, the scale measures (with microgram precision) any change on weight of the sample while burned in a constant rate. After the combustion, it is possible to evaluate any residual weight from components that weren't burnt at the specified temperature range. So, it is possible to evaluate any residual clay on the samples and how the membranes resist to thermal degradation.

For the analyses, the scale is tarred with a platinum pan. Then, samples around 1 cm<sup>2</sup> are placed on the platinum pan and have their weight measured before being inserted in the furnace. The platinum pan is inserted in the furnace at a temperature increase rate of 10°C/min from 25 to 750°C under nitrogen and oxygen flows at 10 ml/min each.

### Superficial Electrical Charges

The electrostatic charge of membranes is an important property when evaluating fouling. When the surface and the fouling agent have similar charge, there are electrostatic repulsion forces between the foulant and the membrane. If the opposite charges, there are attraction forces that cause adherence of components at the membrane surface.

Evaluation of superficial electrical charge will follow the methodology proposed by Tiraferri and Elimelech (2012) using the cationic dye Toluidine Blue O. The method relies on the adhesion of the dye to the membrane at alkaline pH and its release at acidic pH.

The method consists in applying the dye solution 0.015 M sodium chloride at pH 11 on the active surface of the membrane ( $0.5 \text{ ml} / \text{cm}^2$ ) for varying periods. After the contact period the surface is washed with 0.015M NaCl solution (without dye) and soaked in this solution for 4 hours, ensuring the diffusion of the molecules not bonded to the membrane.

After this step, the samples are placed in 10 ml of 0.2 M NaCl solution at pH 2 for 30 minutes under stirring. Finally, the sample is analyzed in a spectrometer at a wavelength of 630 nm (using as a blank a solution with membrane without dye) and compared with calibration curves for various concentrations of dye, allowing to associate the functional density of charges in time.

### Surface Roughness

Surface roughness measurements were conducted using an Atomic Force Microscope Cypher (Asylum Research) operating in amplitude modulation with silicon tip (Bruker OTESPA) with resonance frequency of 340 kHz and nominal tip radius of 7nm. Images of  $10\mu\text{m} \times 10\mu\text{m}$  were acquired with 1V amplitude and 0.6 V set point amplitude in a scan rate of 1Hz.

Basically, in the AFM analysis, a probe scans the surface of a sample with a sharp tip, located at the free end of a cantilever. As the tip scans the surface of the sample, it moves up and down with the surface contour. The interaction forces between the tip and the surface makes the cantilever oscillates, causing a deflection detected by a

laser beam in the back of the cantilever. The laser beam is deflected off the cantilever into a dual element photodiode. This photodetector measures the difference in light intensities between the upper and lower photodiodes and then converts this signal into a voltage. This method enables a computer to generate a three-dimensional map of the surface topography. (BOUSSU et al., 2005)

The image refinement to create 3D surfaces was made using the software Argyle Light and the data extracted was analyzed with the R13.17.101 extension for IgorPro®. In this software, images were flattened with order 1 (minimize errors by curvature and slope) and the root mean squared (RMS) roughness was calculated by the deviation of data.

The RMS is defined by Eq. 4 as follows: (BOUSSU et al., 2005)

$$\sqrt{\frac{\sum_{n=1}^N (z_n - \bar{z})^2}{N-1}} \quad (4)$$

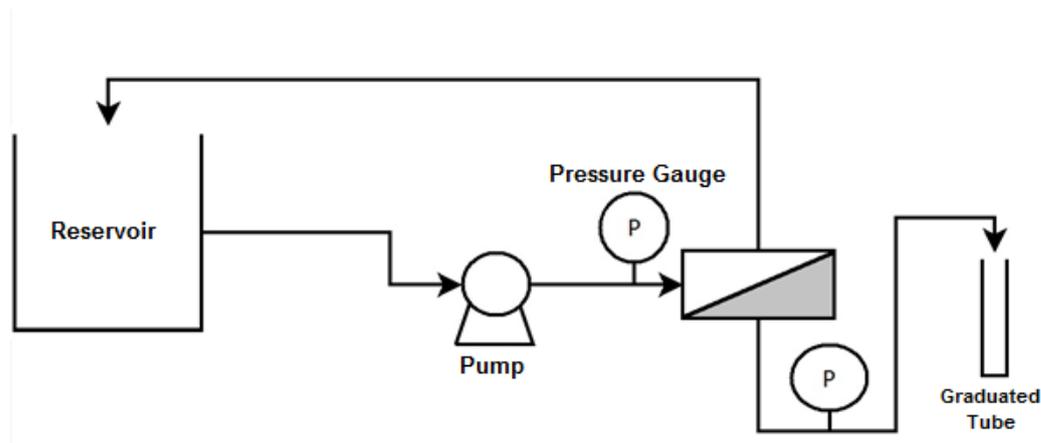
where  $\bar{z}$  is the average of the z values within the given area,  $z_n$  is the current z value, and N is the number of data points within the given area.

#### 4.4.2 Performance

##### Flow and Permeability

For evaluation of flux (flow per unit of membrane area), permeability (flux per unit of pressure applied) and hydraulic resistance of the membranes, it was developed a test station with a crossflow rectangular test cell. Pressure was adjusted to 1 bar during operation. Figure 15 shows a schematic representation of the testing system.

Figure 15 – Representation of the Flow Test Cell



The membranes produced were tested in deionized water for a period of 1 hour each. The flow was measured every 5 minute during the test and the average hourly flow was recorded. Known the useful area of the membrane (34 cm<sup>2</sup>), it was possible to determine the flux (J) according to Eq. 5.

$$J = \frac{Q}{A} \quad (5)$$

In which,

J = flux through the membrane (L/m<sup>2</sup>.h)

Q = Average flow measurement (L/h)

A = membrane area (m<sup>2</sup>)

Having the data of flow/flux, and the transmembrane pressure (the difference between the test cell pressure gauge inlet and outlet) it is possible to calculate membrane permeability and hydraulic resistance of the membrane were calculated according to Eq 6 to 8, described below:

$$P = \frac{J}{\Delta P} \quad (6)$$

In which,

P = membrane permeability (L/m<sup>2</sup>.h.bar)

J = flux through the membrane (L/m<sup>2</sup>.h)

$\Delta P$  = Transmembrane Pressure (bar)

$$J = \frac{\Delta P}{\mu_A \cdot R_M} \quad (7)$$

In which, (considering pressure and time units)

$J$  = flux through the membrane ( $L/m^2.s$ )

$\Delta P$  = Transmembrane Pressure (Pa)

$\mu_A$  = pure water viscosity (Pa.s)

$R_M$  = membrane hydraulic resistance ( $m^{-1}$ )

From equation 6 in 7

$$P \cdot \Delta P = \frac{\Delta P}{\mu_A \cdot R_M} \rightarrow P = \frac{1}{\mu_A \cdot R_M} \quad (8)$$

In which,

$P$  = membrane permeability ( $m^3/m^2.s.Pa$ )

The membrane permeability is inversely proportional to the hydraulic resistance of the membrane considering the viscosity of the fluid.

It is observed that in the presence of fluids other than pure water, the resistance is not only the membrane's, but a combination of flow resistances, resistance of the membrane itself, the resistance offered by fouling layer, the polarization caused by the gel layer and other factors hindering the flow through the membrane.

### Molecular Weight Cut-Off

By definition, the molecular weight cut-off of a membrane is defined as the molecular weight of the compound that is retained with an efficiency of 90%. (PORTER, 1990).

The molecular weight cutoff of the membranes was determined by conducting a test similar to the permeability test, but with the use of polyethylene glycol (PEG) with known molecular weights solution instead of demineralized water.

Solutions of approximately 20 mgC/L (NPOC equivalent) were made with PEG with average molecular weight of 10,000, 50,000, 90,000 and 203,000 g/mol. The feed and permeate collected after one hour of operation were analyzed in a total organic carbon analyzer (Shimadzu; TOC-VWS) to determine their concentration. The difference between them determined the membrane rejection ( $R$ ) to a particular molecular weight of PEG according to Eq. 9:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (9)$$

where  $C_p$  and  $C_f$  are the NPOC concentrations in the permeate and feed respectively

### Rejection to Sodium Alginate

Rejection to sodium alginate simulates a situation of natural organic matter and intends to assess the susceptibility of the membrane to fouling (MIERZWA et al, 2012).

The membranes were challenged with a solution of 10 mgC/L of sodium alginate. The performed procedure was similar to the determination of the molecular weight cut-off: feed and permeate samples were analyzed in a total organic carbon analyzer for determining concentrations and, consequently, the efficiency of rejection. Tests were performed within 2 hours of continuous operation with recirculation.

### Fouling Evaluation

In order to evaluate natural surface water treatment efficacy, the influent used was from Fresh Pond, a local drinking water reservoir in Cambridge, Massachusetts, United States. Effluent measurements were made after 2 hours of operation. NPOC, turbidity, and  $UV_{254}$  of the feed and permeate were measured to evaluate the treatment efficiency. The turbidity was measured using a portable turbidimeter (Hach; Model 2100Q). The  $UV_{254}$  absorption was measured using a UV–Visible spectrophotometer (Agilent; Model 8453).

For evaluation of natural surface water fouling potential, the membranes were challenged for 8 hours at 1 bar transmembrane pressure and the permeability decrease was compared to initial ultrapure water experiments. After fouling, the membranes were chemically cleaned using an alkaline (pH 11) feed solution for 30 minutes and subsequently rinsed with copious amounts of ultrapure water. After cleaning, the membranes were challenged again with ultrapure water to evaluate the flux recovery (as an estimative of irreversible fouling). At least three membrane samples were evaluated.

In order to evaluate the amount of organic matter adsorbed by the membrane surface, membrane samples were challenged with natural surface waters using the same conditions as the fouling potential measurement. After running for 8 hours, 9 cm<sup>2</sup>

squares were cut, immersed in solutions at pH 2, 7, and 11 and kept in in a rotating shaker (New Brunswick Scientific, E24) at 60 rpm for 6 hours. The NPOC of the solution containing these squares was measured to quantify the desorbed organic matter.

### *E.coli* Rejection

*Escherichia coli* is a type of fecal coliform bacteria commonly found in the intestines of animals and humans, indicating of recent sewage or animal waste contamination. Each bacterium measures approximately 0.5  $\mu\text{m}$  in width by 2  $\mu\text{m}$  in length. *E. coli* (w3110) was used to measure bacterial removal efficiency. *E. coli* Bacteria were harvested at mid-exponential phase and then centrifuged and resuspended in 0.9% NaCl saline solution twice prior to addition to the feed solution. The bacteria concentration in the feed and permeate was determined using fluorescence microscopy. Briefly, the solution (1 mL for the feed and 20 mL for the permeate) was vacuum filtered onto a polycarbonate membrane (Sterlitech PCTE), and the bacteria were stained with 4',6-diamidino-2-phenylindole (DAPI) for 5 minutes and then analyzed (excitation/emission of 358/461 nm). The prepared filter was transferred to the fluorescence microscope and imaged at 40x magnification. At least five random points on the filter were imaged (278 x 200  $\mu\text{m}$ ) and analyzed for cell enumeration.



## 5. RESULTS AND DISCUSSION

In terms of statistical analysis, the numerical data was submitted to Shapiro-Wilk Test to verify if the data came from a normally distributed population. In all cases, it was stated that the data is normally distributed with 95% confidence. Also, to reinforce the statistical relevance of the data, Analysis of Variance (ANOVA) was also applied to distinguish with at least 95% significance whether the changes were significant.

### 5.1 Membrane Synthesis

#### 5.1.1 Determination of Polysulfone Concentration

Before starting experiments using clay, it was conducted an experiment of membrane synthesis using different polysulfone concentrations and a casting thickness starting of 130  $\mu\text{m}$  (changed to 100  $\mu\text{m}$  for all the tested membranes produced after). Table 6 shows the results of viscosity, thickness and shrinkage. The samples are identified by the percentage of PSU in the membrane composition. i.e PSU-05% is a membrane with 5% PSU, 95% NMP.

Table 6 – Viscosity and Thickness of membranes at different polymer concentrations

Membrane	Viscosity (cP)	Thickness ( $\mu\text{m}$ )	Shrinkage (%)
PSU-05%	20.4	---	---
PSU-10%	111.2	83.2	36.0
PSU-15%	581.3	89.5	31.2
PSU-18%	1533.8	92.8	28.7
PSU-20%	5546.1	96.3	25.9

It was not possible to synthesize membranes with 5% PSU, since the polymer concentration was not enough to make a solid and stable membrane in the coagulation bath. The lower the polymer concentration, the thinnest was the membrane. It was also noticed that higher polymer concentrations (20%) resulted in membranes with holes distributed on the surface. Higher polymer concentrations implied in thick superficial layers, like the ones showed in Monticelli and Anadão's experiments. Considering that 18% membranes had shrinkage below 30% and didn't have as many holes as 20%, and also considering other researches use this concentration as reference (MA et al.,

2011; YOUNG; CHEN, 1995), 18% polymer was adopted for producing further membranes with clay nanoparticles and PEO.

### 5.1.2 *Casting Conditions*

During the initial attempts for casting membranes, different casting speeds were tested. Speeds greater than 3 cm/s generated non-uniform and discontinuous membranes. It was also found that reducing the casting speed to minimum (0.5 cm/s) resulted in early phase inversion process during the casting, probably due to exposure of the film to air humidity. Thus, based on these tests, the casting speed of 1.0 cm/s was adopted for all membranes.

Once defined the standard working conditions and the default rate of casting, a routine of solution preparation and casting activities was established to result in uniform surface membranes.

## 5.2 **Solution Viscosity**

Viscosity of the casting solution can hinder severely the exchange rate of solvent and nonsolvent during phase inversion process, and therefore, it can be used as an important parameter to influence the precipitation kinetics and thus, the formation of resulting membrane morphology (KIM; LEE, 1998). Higher molecular weight additives, such as PEO, are expected to increase solution viscosity and in turn slow the diffusion of solvent out of the film during phase inversion leading to the formation of a denser skin layer (SADRZADEH; BHATTACHARJEE, 2013).

The casting solution viscosity for all membranes is displayed in Table 7. The addition of nanoclay had negligible effect on solution viscosity. The addition of 100 kg mol<sup>-1</sup> PEO made the solutions more viscous and viscosity increased as the PEO content increased. However, in comparison to Sadrzadeh and Bhattacharjee's study (2013), the difference (<10 %) in casting solution viscosities was not significant enough to state that viscosity was responsible for effects on the phase inversion process. For example, in their study the viscosity of the pure PES membrane (0.5 Pa.s) was increased to 12.8 Pa.s upon addition of 10% (wt%) 1,300 kDa PVP (additive with higher molecular weight compared to 100 kg.mol<sup>-1</sup> PEO).

Table 7 – Casting Solution Viscosity

Type	Viscosity (cP)	Type	Viscosity (cP)	Type	Viscosity (cP)
PS0	554 ± 7	C1.5P1	565 ± 3	C4.5P1	558 ± 3
C1.5	552 ± 3	C1.5P3	578 ± 4	C4.5P3	571 ± 5
C3	555 ± 5	C1.5P5	599 ± 2	C4.5P5	596 ± 3
C4.5	559 ± 3	C3P1	557 ± 4	P1	566 ± 4
C5	553 ± 5	C3P3	566 ± 3	P3	575 ± 7
		C3P5	588 ± 6	P5	601 ± 2

Kim and Lee (1998) discuss that the addition of a high molecular weight additive, in their case PEG, can result in inter and intra-molecular polymer aggregations in the casting solution, increasing the solution viscosity. This increase would hinder the diffusional exchange rate of solvent (NMP) and nonsolvent (water) in sublayer, making the precipitation rate of sublayer become slower and changing the internal structure.

In this study, however, the influence of viscosity was minimal with increase of PEO (with a higher molecular weight than PEG). Therefore, the influence of viscosity on final performance wasn't considered as a main driving agent to the observed membrane changes.

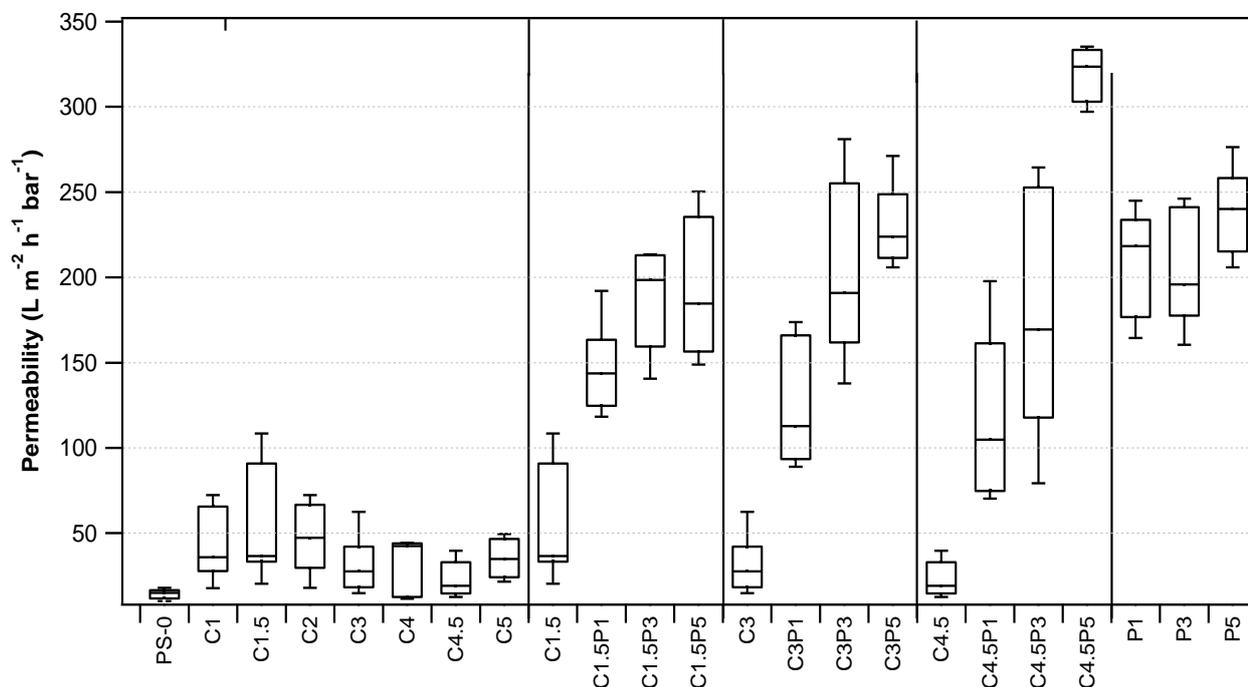
### 5.3 Membrane Permeability

Membrane water permeability was an initial analysis used to evaluate membranes' performance. Results from the ultrapure water cross-flow experiments are displayed on Table 8 and Figure 16.

Table 8 – Membrane Permeability

Type	Permeability (L/m <sup>2</sup> .h.bar)	Type	Permeability (L/m <sup>2</sup> .h.bar)	Type	Permeability (L/m <sup>2</sup> .h.bar)
PS0	15.4 ± 2.8	C1.5P1	146.4 ± 26.2	C4.5P1	115.5 ± 45.4
C1	42.1 ± 20.6	C1.5P3	188.7 ± 30.4	C4.5P3	182.2 ± 65.8
C1.5	56.2 ± 23.4	C1.5P5	192.1 ± 36.8	C4.5P5	319.3 ± 14.3
C2	48.1 ± 20.7	C3P1	126.4 ± 16.4	P1	207.0 ± 28.5
C3	31.5 ± 16.4	C3P3	205.0 ± 27.8	P3	206.7 ± 31.0
C4	36.1 ± 15.0	C3P5	228.8 ± 25.0	P5	237.4 ± 35.9
C4.5	25.9 ± 9.8				
C5	33.4 ± 9.1				

Figure 16 – Membranes permeability



All doped membranes had an increased permeability as compared to the pure PSU control. Membranes with only nanoclay had a similar permeability trend to that reported in previous studies (MIERZWA et al., 2013; MORIHAMA; MIERZWA, 2014) i.e., with increasing casting solution dopant the permeability increased to an optimal dopant concentration after which further increase results in permeability decrease. The best clay concentration range was between 1.5 and 2% nanoclay (56 vs. 15 L/m<sup>2</sup>.h.bar for the control).

After the pure clay dopants, membrane samples with fixed clay content (C1.5, C3, and C4.5) and increasing content of PEO (P1, P3, and P5) were examined. The best pure clay membrane C1.5 had a permeability of 56 vs. 192 L/m<sup>2</sup>.h.bar for the best mixed sample of C1.5P5 of the similar clay content. The C4.5 membrane had a lower permeability than C1.5 (26 vs. 56 L/m<sup>2</sup>.h.bar) but when combined with PEO (C4.5P5) it had the best permeability of all membranes examined (319 L/m<sup>2</sup>.h.bar).

Statistical analysis of variance (ANOVA) comparing the undoped membrane and clay and/or PEO doped membranes had a 95% confidence level of increased permeability.

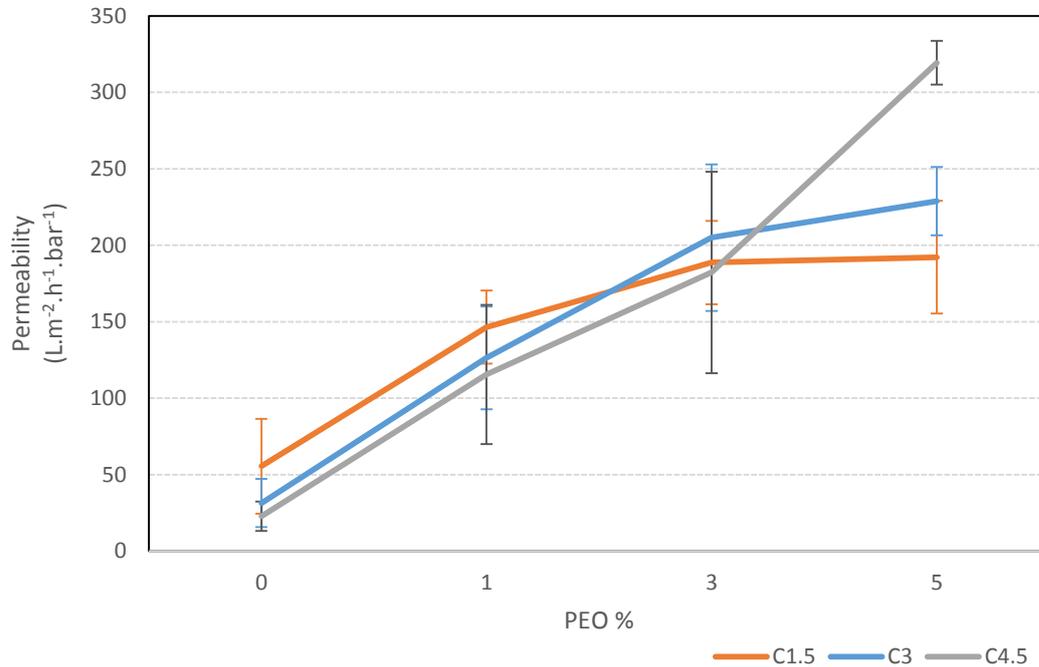
(Table 9). The most significant permeability difference was found for the membrane with 4.5% clay, 5% PEO.

Table 9 – ANOVA statistical analysis for membrane permeability (95%confidence)

Compared membranes	F	F crit	P-value	Compared membranes	F	F crit	P-value
PS0-C1	9.13	4.96	1.29E-02	PS0-C3P1	44.07	5.32	1.63E-04
PS0-C1.5	7.35	4.96	2.19E-02	PS0-C3P3	63.23	5.32	4.56E-05
PS0-C2	13.02	5.32	6.90E-03	PS0-C3P5	363.74	5.32	5.92E-08
PS0-C3	5.16	4.49	3.72E-02	PS0-C4.5P1	19.74	5.32	2.16E-03
PS0-C4	10.37	5.59	1.46E-02	PS0-C4.5P3	25.98	5.32	9.33E-04
PS0-C4.5	6.45	5.59	3.86E-02	PS0-C4.5P5	1752.17	5.32	1.17E-10
PS0-C5	20.43	5.59	2.73E-03	PS0-Z1	188.79	5.32	7.59E-07
PS0-C1.5P1	123.73	5.12	1.47E-06	PS0-Z3	152.37	5.32	1.73E-06
PS0-C1.5P3	163.10	5.32	1.33E-06	PS0-Z5	211.14	5.32	4.93E-07
PS0-C1.5P5	18.40	5.12	2.02E-03				

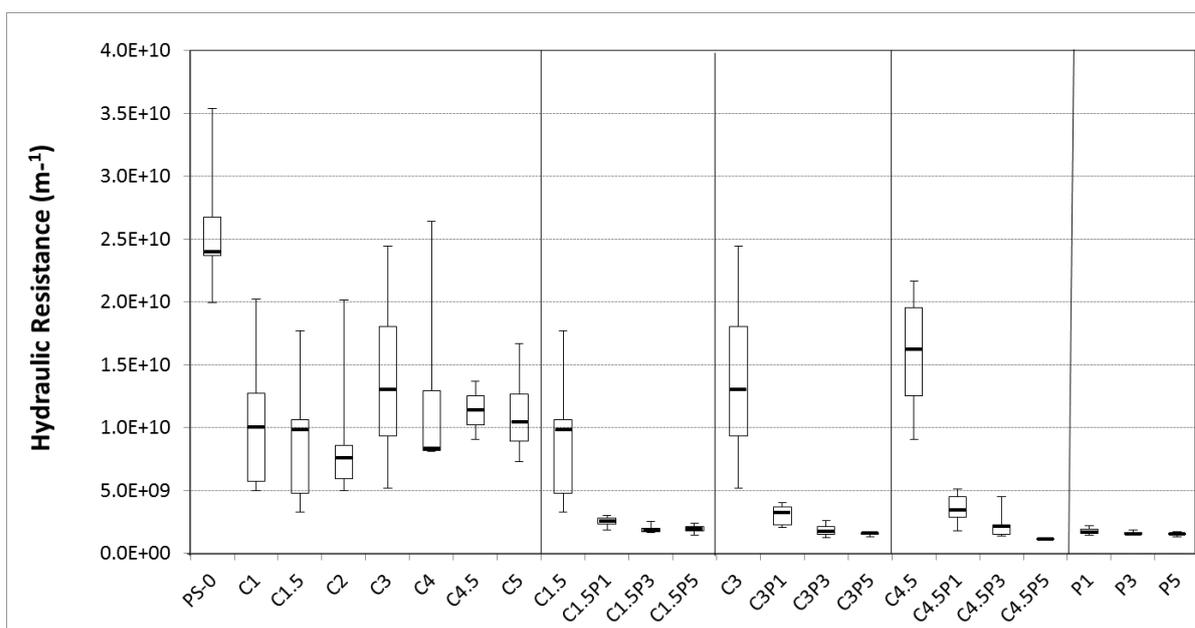
For membranes with 1.5% nanoclay (best flow performance among pure clay membranes), the addition of PEO had a lower increment effect compared to 4.5% nanoclay. i.e. C1.5 had better permeability results compared to C4.5, but C1.5P5 had lower permeability compared to C4.5P5. It was expected that adding PEO as pore former would increase permeability proportionally, regardless the nanoclay concentration. Thus, the pure control, PS0, the best individual dopants on permeability, C1.5 and P5, and their co-doped membrane, C1.5P5, and the best overall membrane permeability, C4.5P5, and its corresponding clay control, C4.5, were chosen for further rejection and performance analysis in order to verify dopant interaction effects on membrane properties. Figure 17 illustrates this observed effect.

Figure 17 – PEO effect on membrane permeability



Regarding the membrane hydraulic resistance, Figure 18 shows the data for all membranes. The higher the resistance, the more difficult was the water flow through the membrane. Nanoclay lowers the hydraulic resistance compared to pure polysulfone membranes. The addition of PEO (with and without nanoclay) significantly lowers the hydraulic resistance, improving membrane flow in all considered samples. Considering the magnitude of the numbers, a small increment in permeability represents a big change in membrane hydraulic resistance. Therefore, nanoclay membranes had a reduction of 50-60% in resistance while PEO membranes had nearly 90% reduction. The observed trend was expected considering PEO is a pore former agent and enhances membrane flow.

Figure 18 – Membrane Hydraulic Resistance

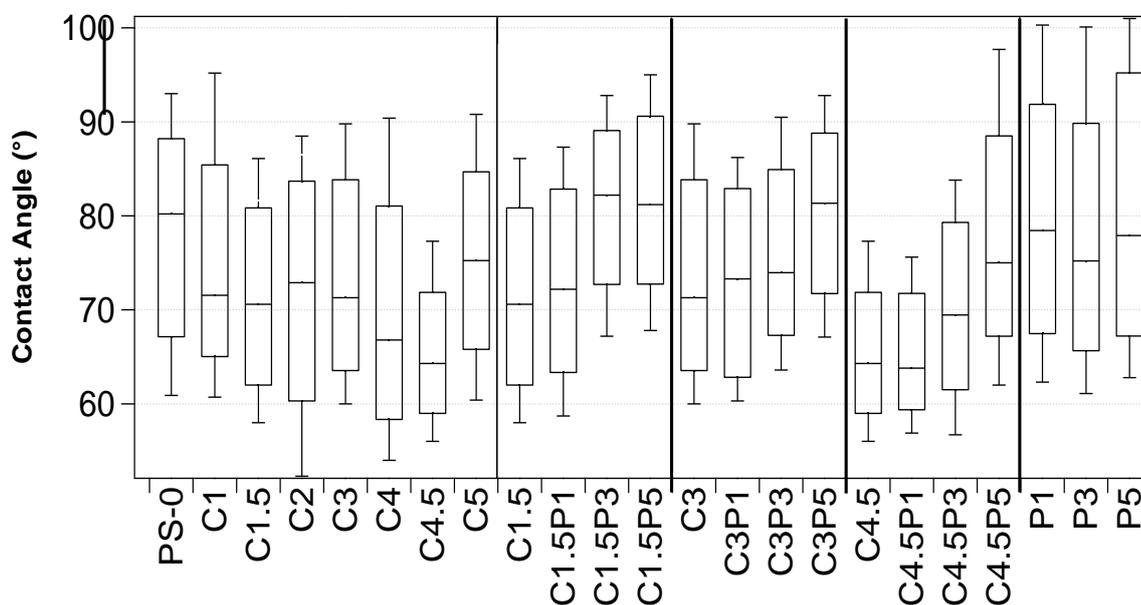


#### 5.4 Contact Angle and Surface Properties

The contact angle results are displayed in Figure 19. Analysis of variance (ANOVA) indicates that individual clay addition did not change the average contact angles ( $F$  1.61,  $F_{crit}$  2.57 and  $P$ -value 0.19), with exception of C4.5, which showed lower contact angles with a significant difference compared to control ( $F$  23.15,  $F_{crit}$  5.59 and  $P$ -value 0.002). ANOVA comparison of membranes with a similar clay concentration and increasing PEO indicated that there is a significant contact angle difference between the 0, 3% and 5% PEO membranes.

Comparing C1.5 to C1.5P5, the  $P$ -value was 0.0034, while comparing C4.5 to C4.5P5 resulted in a  $P$ -value of 0.01. According to Ghaemi et al. (2011) and Monticelli et al. (2006), nanoclay dopants tend to decrease contact angle by increasing membrane hydrophilicity. In this experiment, increasing the PEO content on nanoclay membranes ended up increasing the average contact angle. The change in membrane contact angle using additives may be better explained by alteration of membrane surface roughness.

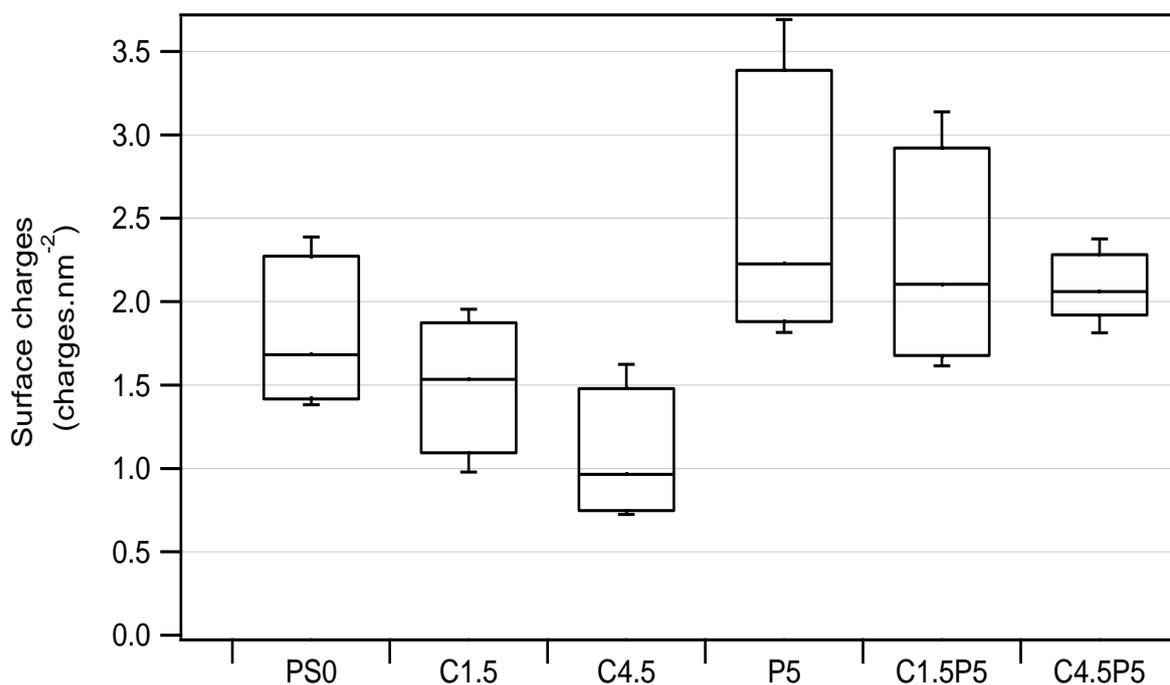
Figure 19 – Contact Angle



The selected membranes' negative surface charge is displayed in Figure 20 may explain the contact angle results since with increasing PEO concentration the negative surface charge increases. PEO is soluble in water and thus it is not likely for the PEO to remain in the membrane after phase inversion and change the surface charge. Even if the PEO remained at the surface, PEO has no properties that can change superficial charges, like the nanoclay was expected to.

One possible explanation for the observed phenomenon is that PEO doping may increase surface roughness and thus total membrane surface exposure, which could result in greater adsorption of dye. This explanation is reinforced by the high contact angles observed in the high PEO content membranes compared to their counterparts without PEO. The contact angles show that in this case the adsorption may be related to the surface roughness (higher contact angles). By increasing the clay content, the superficial charges decreased, similarly as reported previously (MIERZWA et al., 2013).

Figure 20 – Membrane surface charges



Membrane contact angle, surface charges and RMS surface roughness (nm) are listed in Table 10 and roughness profiles are presented on Figures 21 to 23. It was found a positive correlation between the surface charges and roughness and surface charges and contact angle by calculating the Pearson's correlation coefficient (0.868 and 0.872 respectively) while the correlation between roughness and contact angle was not as strong (0.636).

Table 10 – Contact Angle, Surface Roughness and Surface Charges average values

Membrane Type	Contact Angle (°)	Surface Charge ( $\text{charges.nm}^{-2}$ )	RMS Roughness (nm)
Control	$78 \pm 5$	1.79	50.4
P5	$80 \pm 6$	2.65	83.2
C1.5	$71 \pm 7$	1.50	35.3
C1.5P5	$81 \pm 6$	2.42	52.5
C4.5	$65 \pm 4$	1.30	40.7
C4.5P5	$76 \pm 5$	2.30	68.4



Figure 21 – Membranes' Surface Roughness (PS0 vs P5)

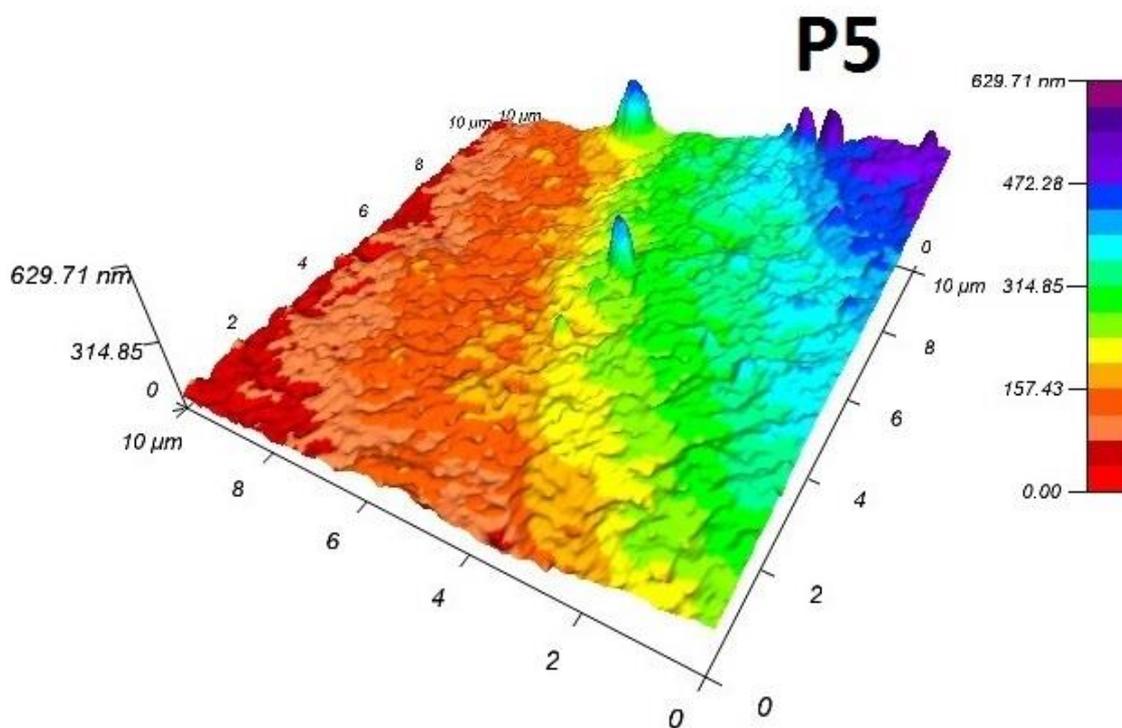
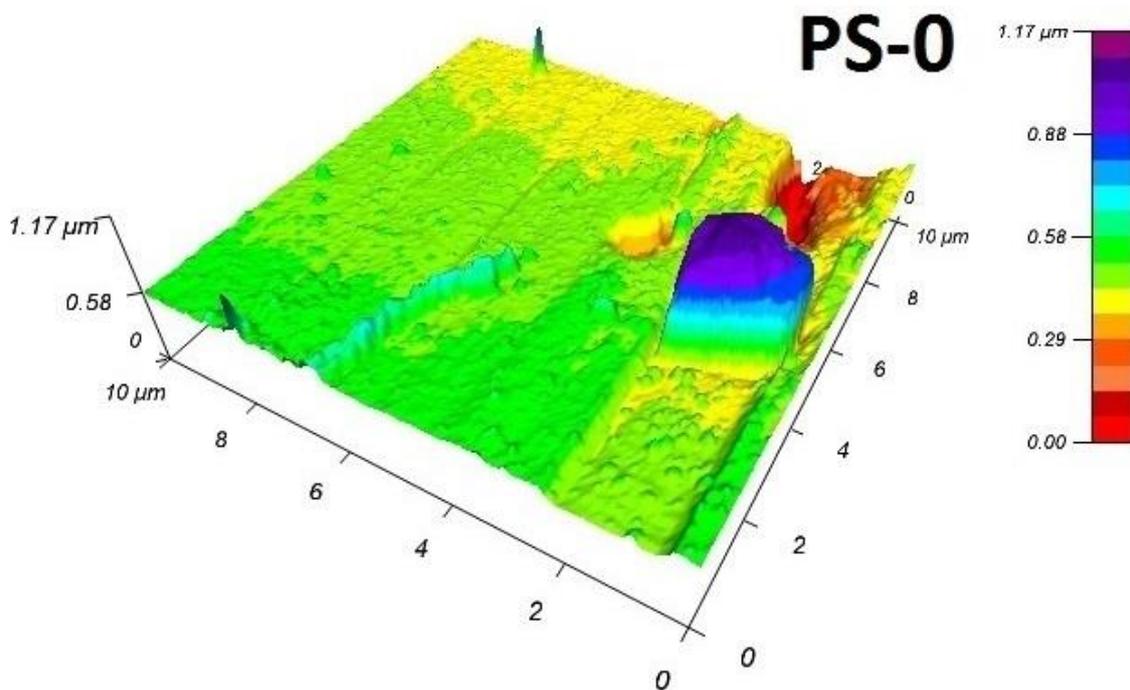




Figure 22 – Membranes' Surface Roughness (C1.5 vs C1.5P5)

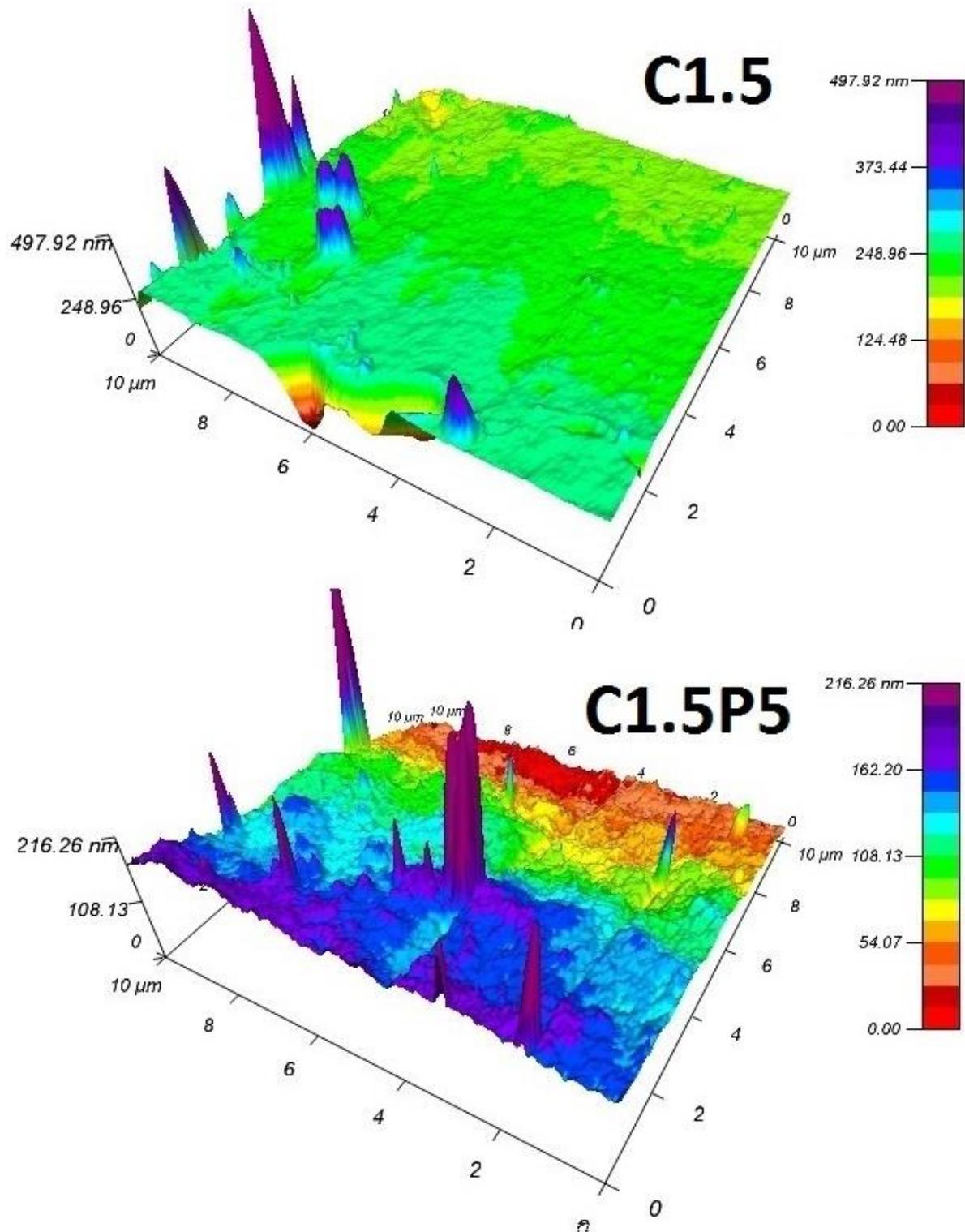
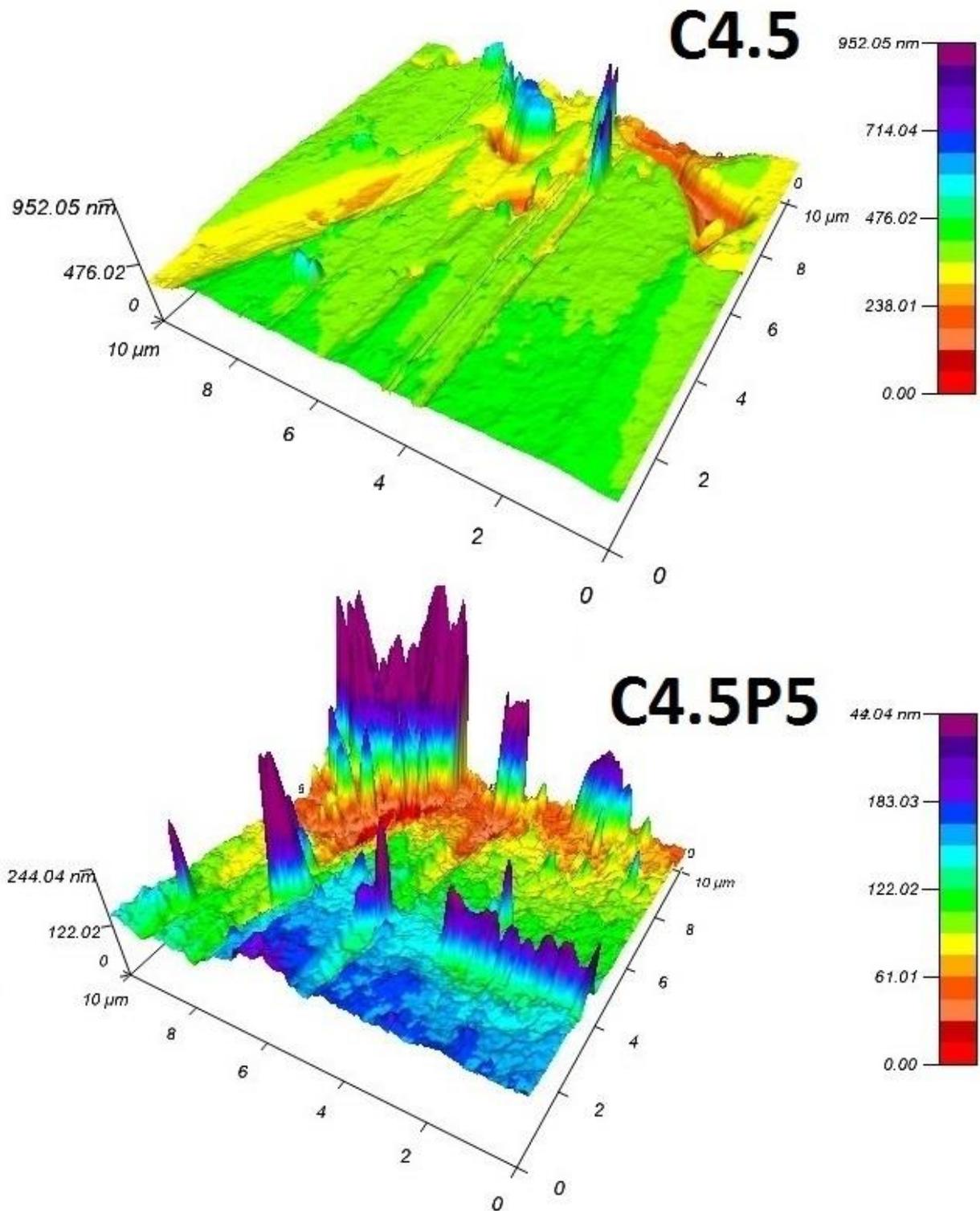




Figure 23 – Membranes' Surface Roughness (C4.5 vs C4.5P5)





The addition of PEO increased membrane surface roughness. Vrijenhoek et al. (VRIJENHOEK; HONG; ELIMELECH, 2001) reported the rate and extent of colloidal fouling is directly associated with surface roughness. Similarly, Woo et al. (WOO; PARK; MIN, 2015) reported that surface roughness and contact angle have greater correlation to membrane performance i.e., smooth membranes had greater flux as compared to rough membranes. Here, the PEO membrane surface roughness may play an important role toward adsorption of toluidine blue during the evaluation of superficial charges as well as the fouling behavior.

The roughness evaluation is important in order to understand surface adsorption phenomena. According to research by Vrijenhoek, Hong and Elimelech (2001) the rate and extend of colloidal fouling on membranes is directly associated with surface roughness. Particles preferentially accumulate in rough surface membranes, causing flux decline compared to smooth membranes.

For this study, the surface roughness for PEO membranes play an important role on explaining their higher adsorption of toluidine blue in the evaluation of superficial charges. PEO membranes had a rougher surface and higher adsorption of the dye. Membrane rejection and fouling behavior are also influenced by surface roughness, as it will be further discussed on sections 5.7 and 5.8 respectively.

## **5.5 Porosity, Thickness and Morphology**

The measured membrane thickness and porosity are presented in Table 11 (ANOVA on Table 12). PEO doping resulted in slight increases in thickness and porosity regardless the clay concentration. There was an average post-phase inversion shrinkage of 41% for clay membranes and 38% for PEO membranes considering all membranes were originally cast as 100  $\mu\text{m}$  films.

Table 11 – Effect of Casting Solution Additives on Membrane Thickness, Porosity, Contact Angle, and Permeability

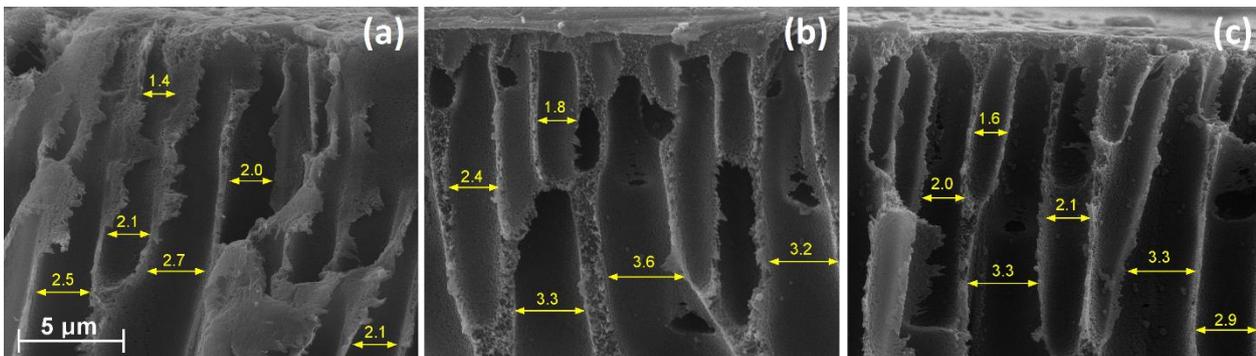
Membrane Type	Thickness ( $\mu\text{m}$ )	Porosity (%)	Permeability (L /m <sup>2</sup> .h.bar)
Control	59 $\pm$ 1	61 $\pm$ 2	15 $\pm$ 2
P5	61 $\pm$ 1	69 $\pm$ 1	237 $\pm$ 36
C1.5	58 $\pm$ 1	63 $\pm$ 2	56 $\pm$ 30
C1.5P5	62 $\pm$ 1	68 $\pm$ 2	192 $\pm$ 37
C4.5	59 $\pm$ 1	63 $\pm$ 1	23 $\pm$ 9
C4.5P5	63 $\pm$ 2	68 $\pm$ 2	319 $\pm$ 14

Table 12 – ANOVA (95% relevance) comparing membranes in terms of Porosity (Por) and Thickness (Thk)

Membranes Compared	Variable	F	Fcrit	P-Value
PS0-C1.5-C4.5	Por	1.4233	5.1432	0.3120
	Thk	1.3400	5.1432	0.3302
PS0-P5	Por	31.704	7.7086	0.0048
	Thk	10.596	7.7086	0.0312
C1.5-C1.5P5	Por	9.5951	7.7086	0.0363
	Thk	13.196	7.7086	0.0221
C4.5-C4.5P5	Por	12.988	7.7086	0.0227
	Thk	16.315	7.7086	0.0156

The cross section's top layer is detailed for pure and nanoclay membranes in Figure 24, while the internal morphology is displayed in Figure 25 and are in detail from Figure 26 to Figure 31. All membranes have an asymmetric structure with a thin separation layer at the surface followed by a sublayer containing finger-like structure and a bottom macrovoid layer.

Figure 24 – Top layer cross-section SEM images. (a) PS0 (b) C1.5, (c) C4.5



By increasing clay content, it was possible to notice changes in the pore formation and distribution on the top layer. These changes observed can be explained by the thermodynamics of the phase inversion. As the casting solution's chemical potential increases by the presence of additives, the water inflow into the film is slower. The top layer formation tends to become finger-like type, straightening the pore structure. However, when the additive concentration increases up to a higher level, the water inflow becomes too slow and the structure, that initially starts with finger-like pores, develops a denser spongelike region in the bottom with the formation of macrovoids throughout the bottom layer.

The structure evaluation helps to explain the permeability behavior observed by increasing nanoclay concentration. C1.5, membrane that had the best permeability among samples with just nanoclay, showed a fingerlike structure with pores wider than the control membrane and does not show macrovoid on its structure (despite showing a pore tortuosity, noticeable in all samples). For higher concentrations of nanoclay it is possible to see the presence of many small pores not connected to the other side of the membrane, being interrupted by a sponge layer with voids in the bottom.



Figure 25 – Cross-section SEM images of PSU, PSU/clay and PSU/clay/PEO membranes (a) Control (PS-0); (b) 5% PEO (PS-5); (c) 1.5% nanoclay (C1.5); (d) 1.5% nanoclay + 5% PEO (C15P5); (e) 4.5% nanoclay (C4.5); (f) 4.5% nanoclay + 5% PEO (C4.5P5)

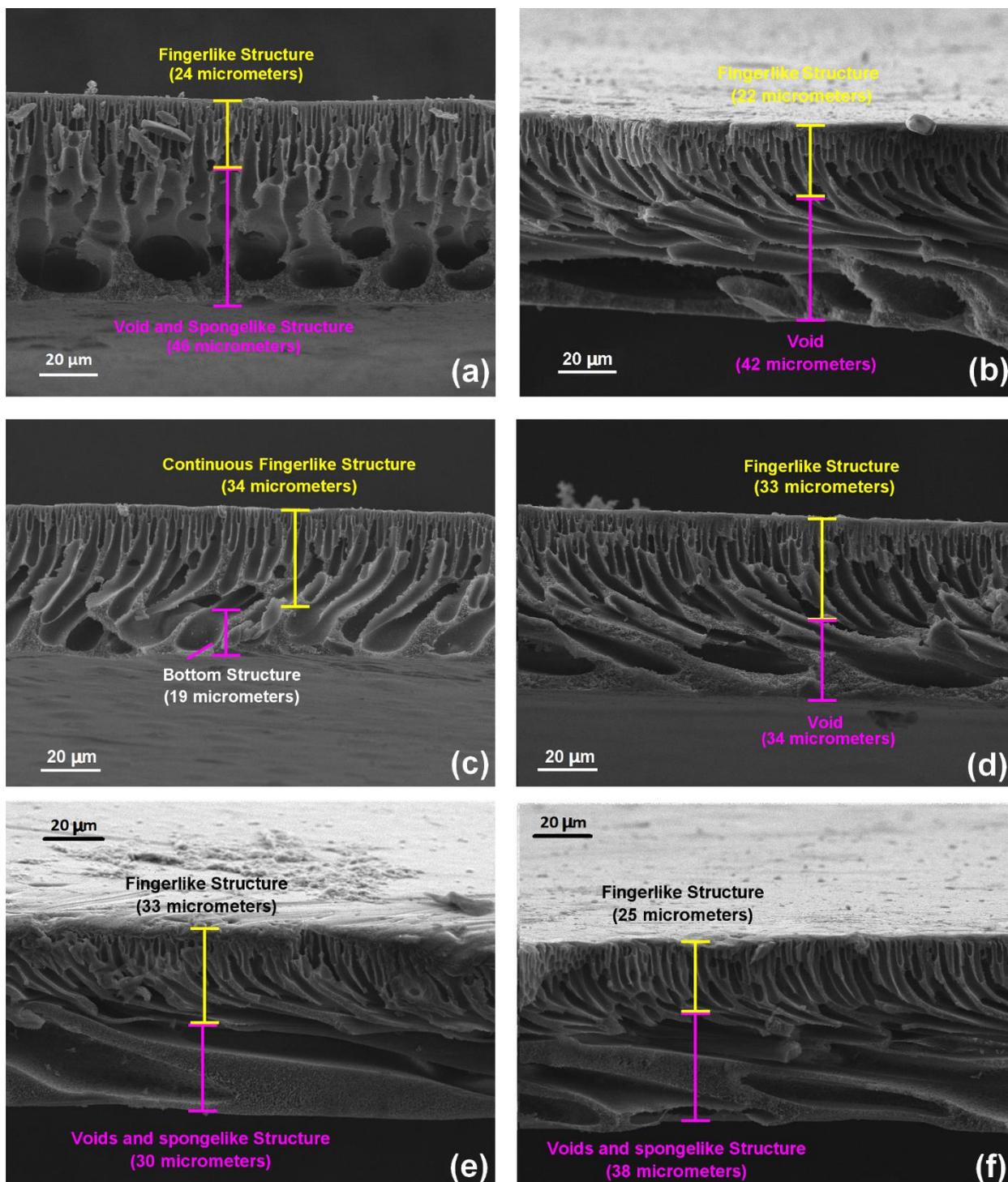




Figure 26 – Cross Section PS0

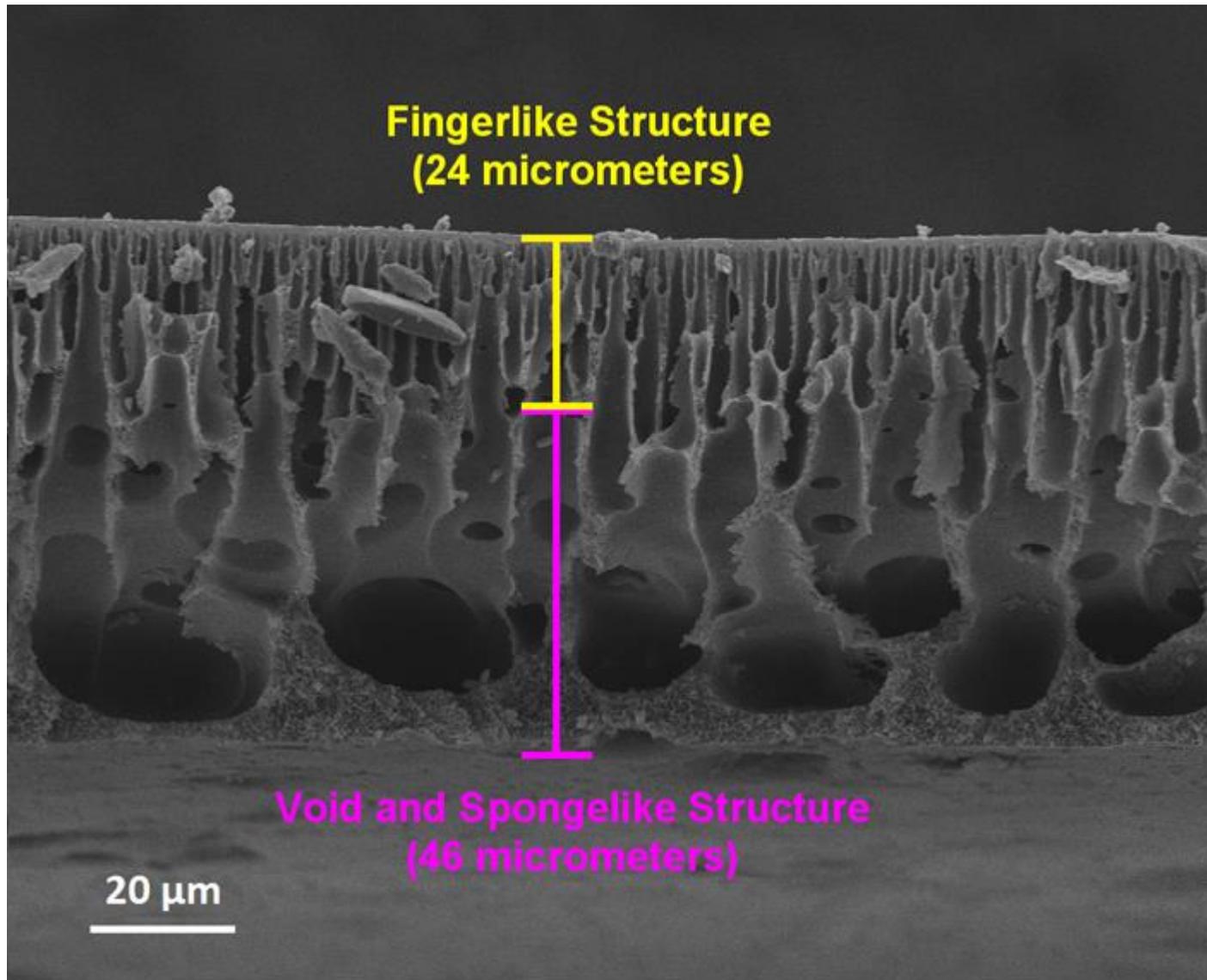




Figure 27 – Cross Section P5

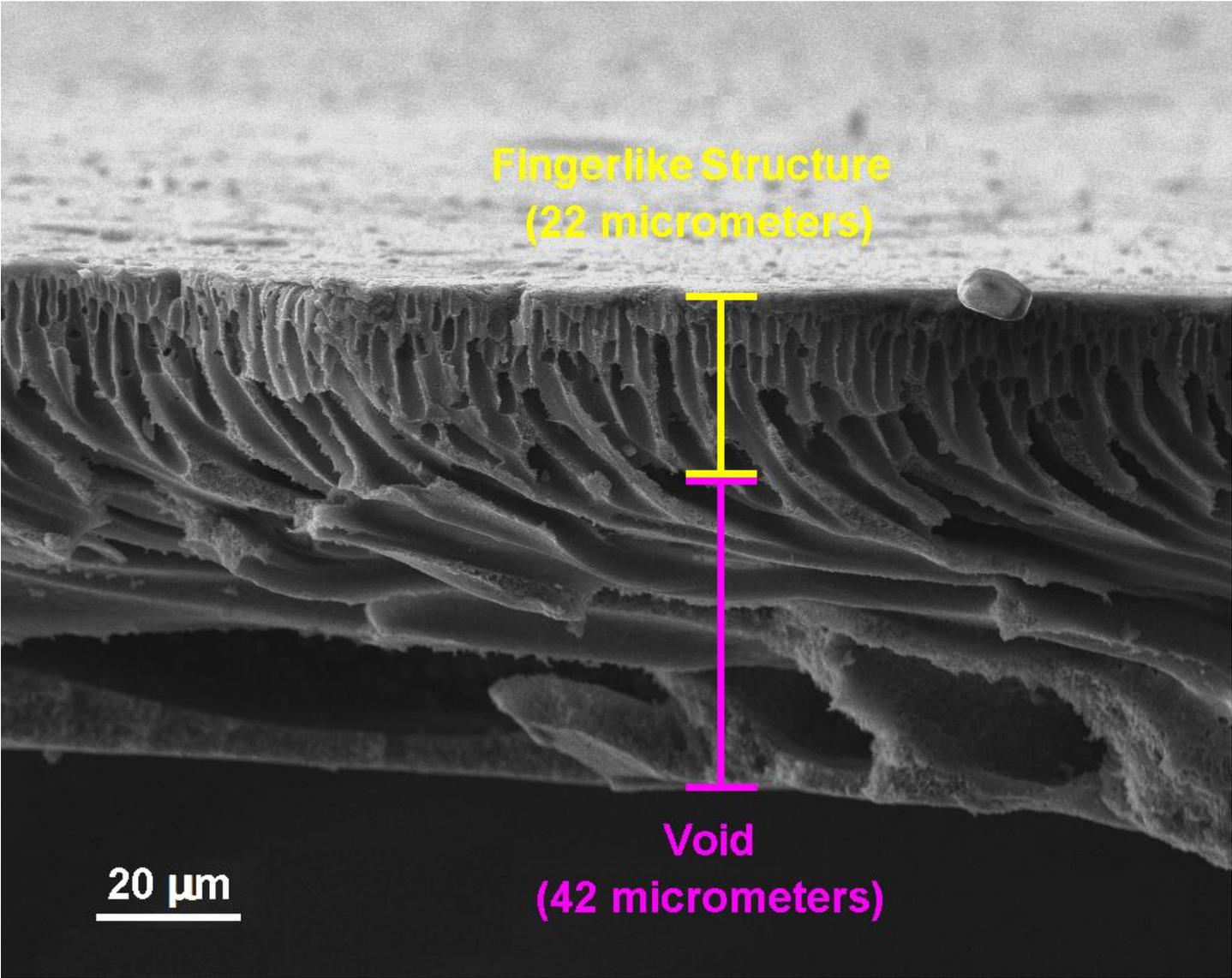




Figure 28 – Cross Section C1.5

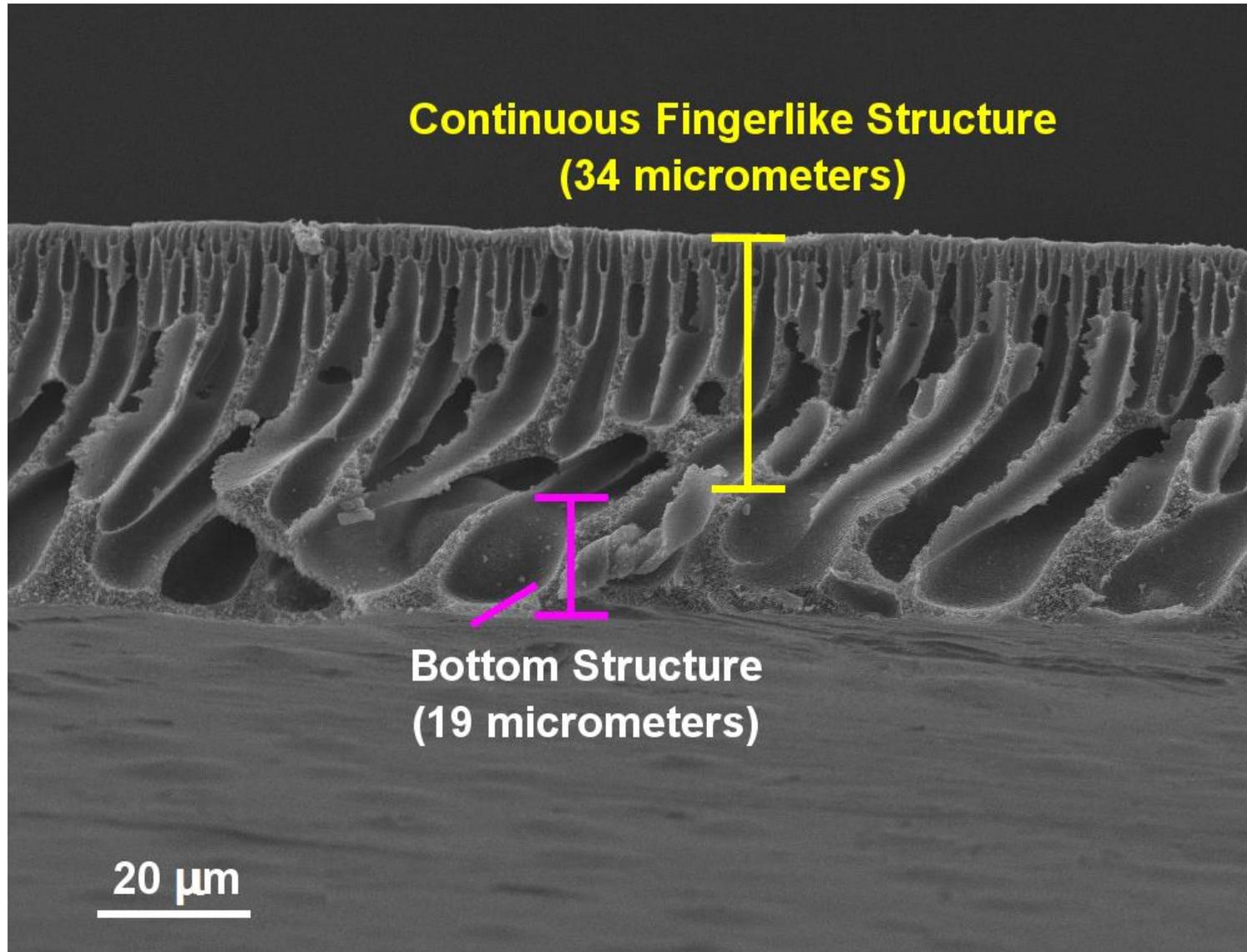




Figure 29 – Cross Section C1.5P5

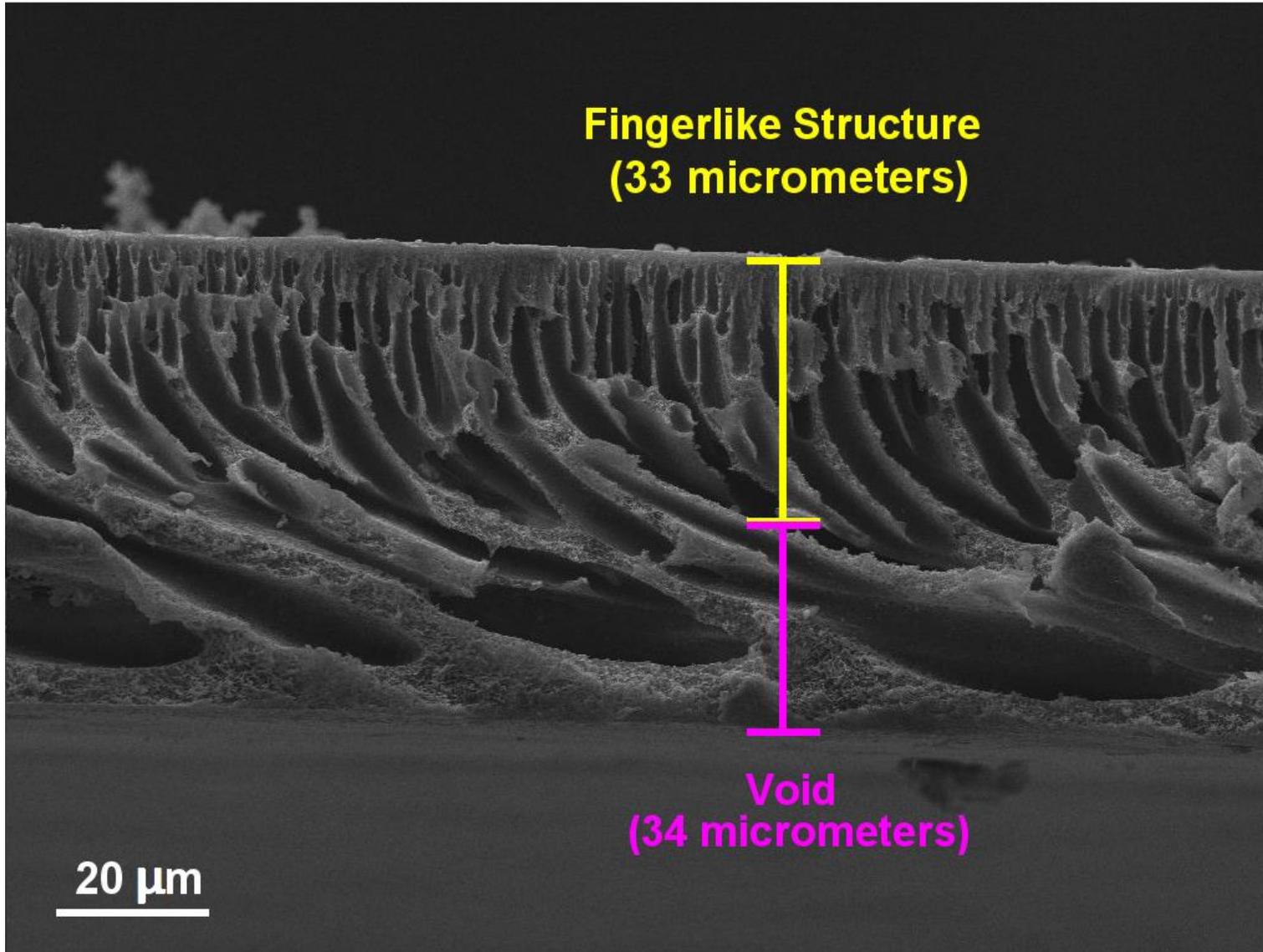




Figure 30 – Cross Section C4.5

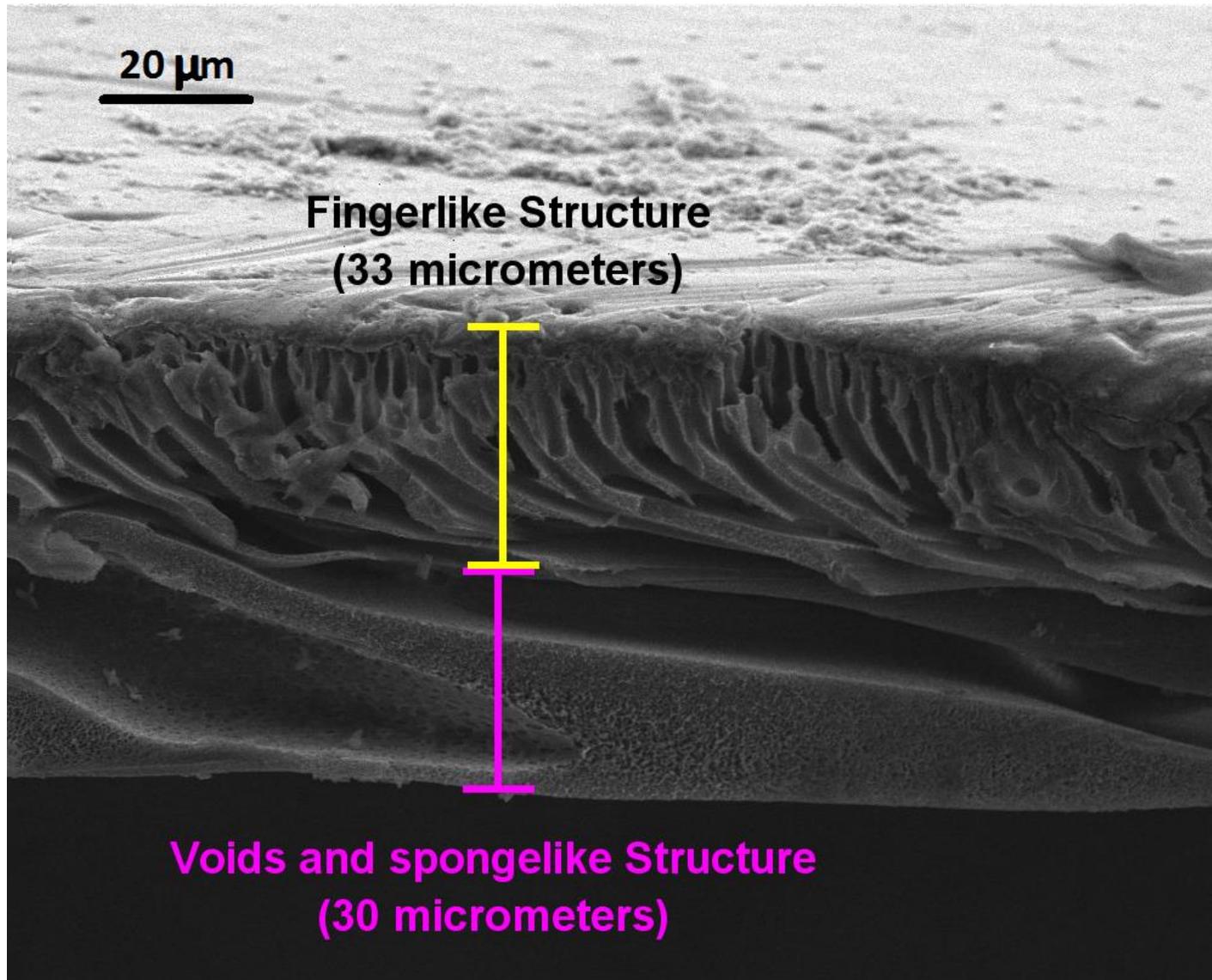
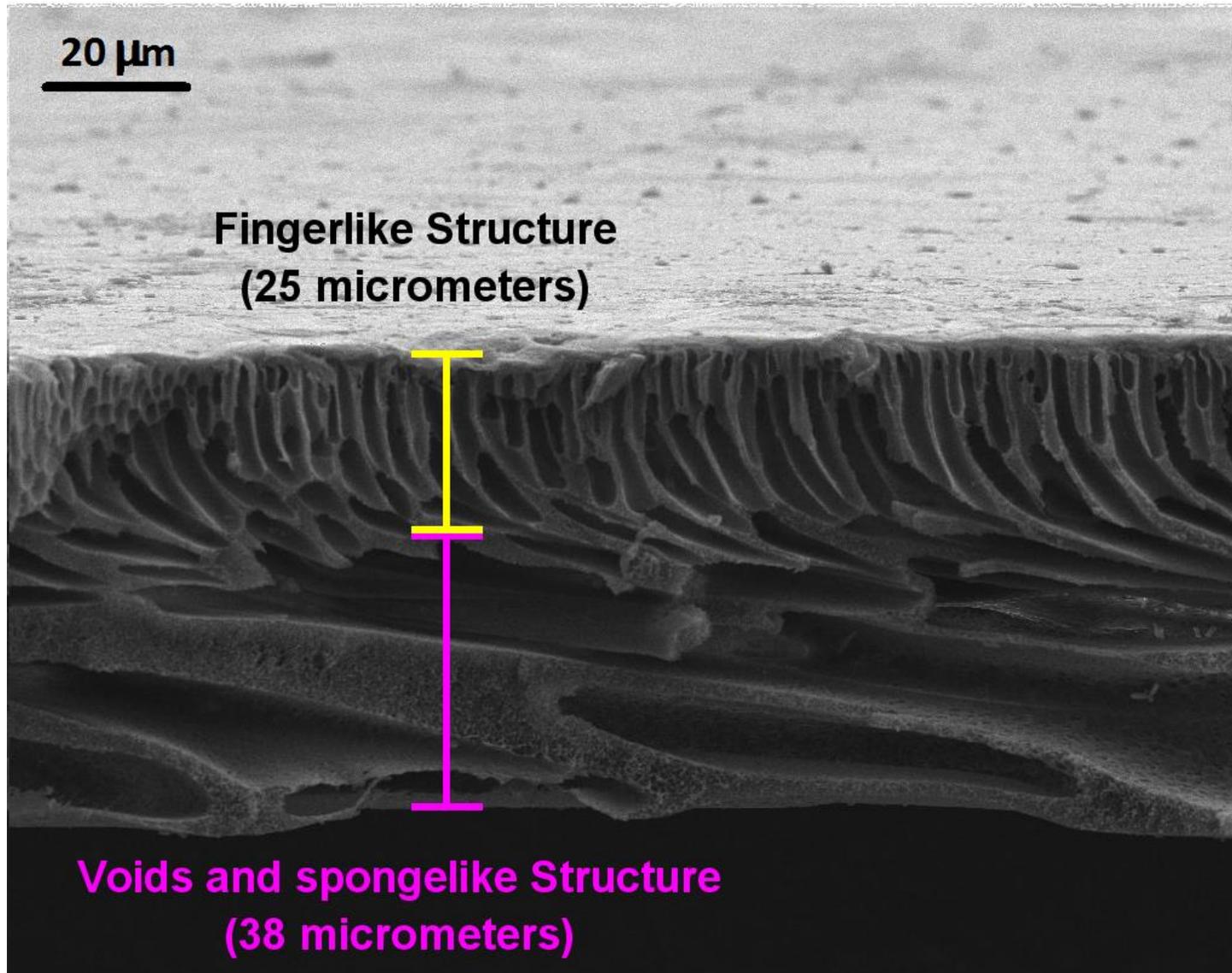




Figure 31 – Cross Section C4.5P5





PEO did not affect directly the superficial pore formation, showing top cross sectional structures similar to the pure nanoclay membranes. PEO, however, had a significant influence on the bottom layer. Comparing the samples C1.5 and C1.5P5, while the first shows a fingerlike structure followed by a small tortuous pore zone connecting both sides of the membrane, the latter shows a bottom structure consisting in a fingerlike structure until half of the cross section, followed by a macrovoid zone. The macrovoid presence implies in higher permeability, in detriment of reducing membrane rejection ability.

PEO is an amphiphilic polymer with an affinity for both organic solvents due to its long organic chain as well as water due to hydrogen bonding with PEO ether group oxygen atoms (HAMMOUDA; HO; KLINE, 2004). This mutual affinity affects the exchange rate of solvent and non-solvent during the phase inversion and influences in the precipitation kinetics and consequently in the membrane structure formation. Polyethylene glycol (PEG), which has a similar structure to PEO of  $(-\text{CH}_2\text{CH}_2\text{O}-)_n$  but a molecular weight of  $<20,000$  g/mol has been reported to influence membrane structure. For example Idris et al. (2007) reported that membranes doped with increasing molecular weight PEG (200, 400, and 600 g/mol) had increased macrovoids, surface roughness, and flux, but lower selectivity.

Chakrabarty et al. (2008) also reported that membranes doped with increasing MW PEG (400 to 20000 Da) had a decreased sublayer finger-like structure and increased macrovoids. Ma et al. (2011) reported that membranes co-doped with a constant PEG 400 concentration and increasing organically-modified nanoclay resulted in a bottom layer with crescent macrovoids and sponge-like characteristics. However, no control membranes (with only clay or without any additive) were evaluated to compare the effect on macrovoid formation. They hypothesized that since the clay was hydrophilic, it would enhance water permeability, however, the organic nanoclay had an affinity for the solvent and restrained the solvent-non solvent exchange.

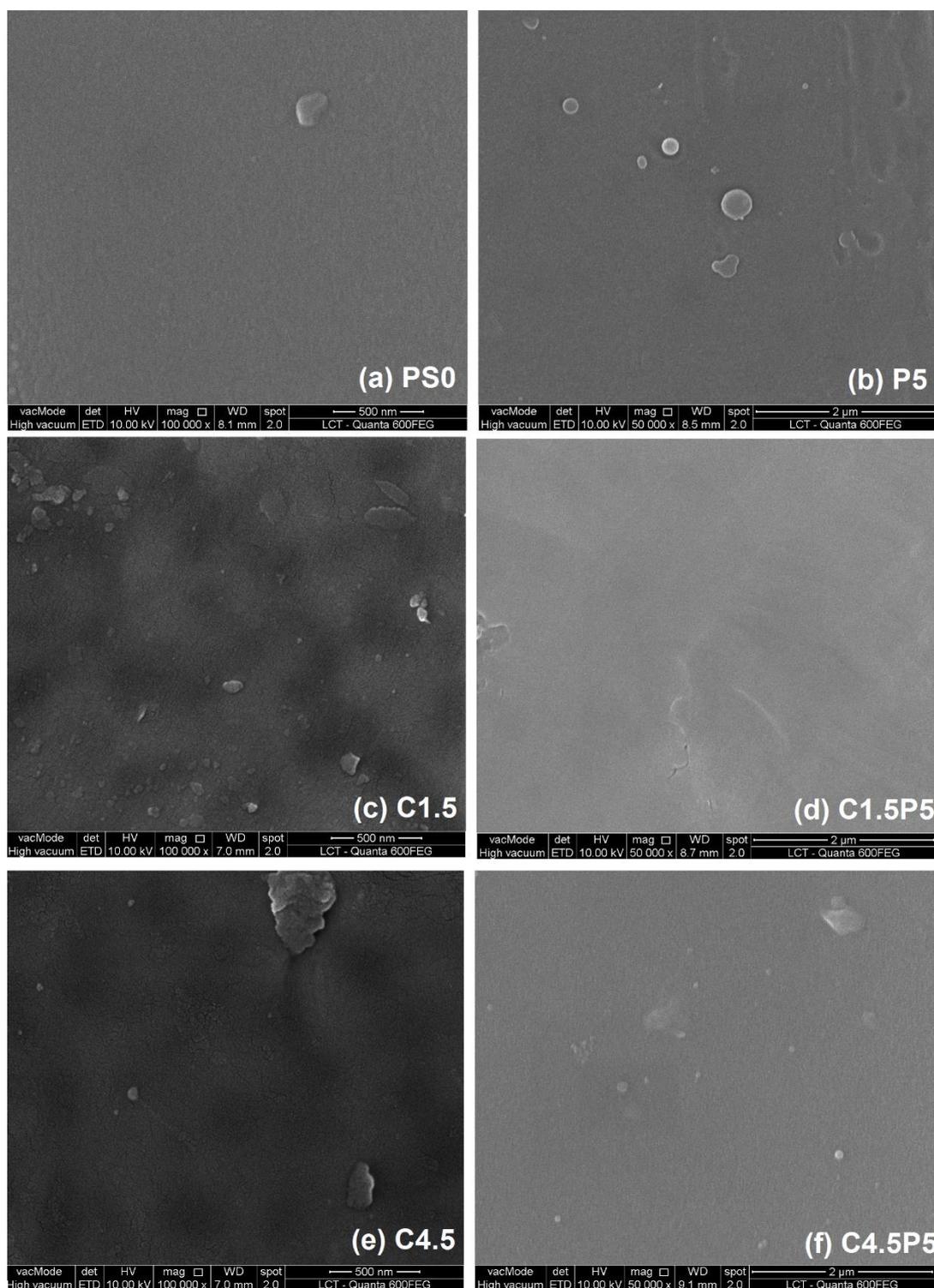
In the present study, the PEO concentration was low (maximum of 5% of polymer weight) and PEO clusters were not seen in the final membranes. According to Sadrzadeh and Bhattacharjee (2013), enhanced casting solution viscosity hinders the solvent and additive leaching rate out of the casting solution. Thus, the delayed demixing was responsible for the growth of macrovoids (i.e., the more the PEO added,

the larger the macrovoids) and the growth of a sponge-like structure in the bottom layer.

Regarding the surface SEM analysis, which could lead to a better understanding of the surface pore formation and distribution, the efforts to characterize samples were inconclusive. Changing the magnification, focus and operation energy of the SEM were not enough to capture images of the pores, as it can be seen on Figure 32. It is possible to see some surface defects caused by the phase inversion when solvent migrates to the surface very fast and makes the polymer crystallize.

The superficial structure, in different magnifications in micrometric scale, do not show the pore structure as it can be seen on other research paper (MIERZWA et al., 2013; MORIHAMA; MIERZWA, 2014). Therefore, the image refinement for pore distribution was not possible to be completed and compared to the membrane calculated porosity. Since the calculated porosity (eq 3) has a relevant degree of similarity to the measured porosity, it will be used as reference.

Figure 32 – Surface SEM images of PSU, PSU/clay and PSU/clay/PEO membranes (a) Control (PS-0); (b) 5% PEO (P5); (c) 1.5% nanoclay (C1.5); (d) 1.5% nanoclay + 5% PEO (C1.5P5); (e) 4.5% nanoclay (C4.5); (f) 4.5% nanoclay + 5% PEO (C4.5P5).

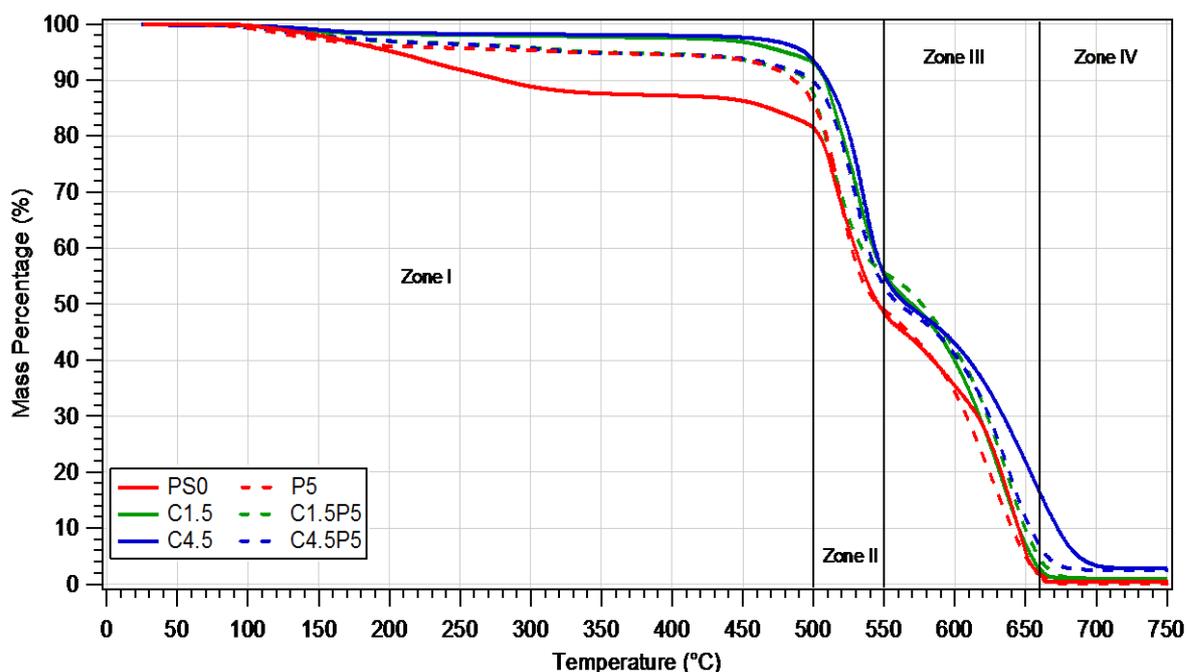




## 5.6 Thermal and Mechanical Analysis

TGA was used to evaluate the thermal resistance of the membranes as displayed in Figure 33. All nanocomposite membranes had better thermal resistance than control membranes.

Figure 33 – Thermogravimetric Curves



There are four stages of degradation in all TGA curves: the first one from 25 to 500°C, the second from 500 and 550°C, the third from 550 and 660-700°C, and the final where there is minimal degradation. In the first stage, samples with nanoclay displayed better thermal stability, with small mass losses compared to PEO and control membranes. In the first stage of decomposition, the control and P5 membranes lost 18.5% and 14.6% of their weight, respectively. For the same stage, membrane C1.5 lost 6.9% of its weight versus 12.3% of C1.5P5, while C4.5 lost 6.5% versus 10.2% loss of C4.5P5.

Analyzing the second stage, there is a prominent weight loss, indicated by the slope of the curve. In this stage, the weight loss reaches a total of 52% for the control and P5, 45% for C1.5, C1.5P5 and C4.5 and 47% for C4.5P5.

The third stage represents a slower thermal decomposition, leading to the final residue after combustion. The third stage temperature range was slightly dependent on the

nanoclay content. Membranes with 4.5% clay had a greater final degradation temperature (>95% combusted; 700 vs. 660°C for the other samples).

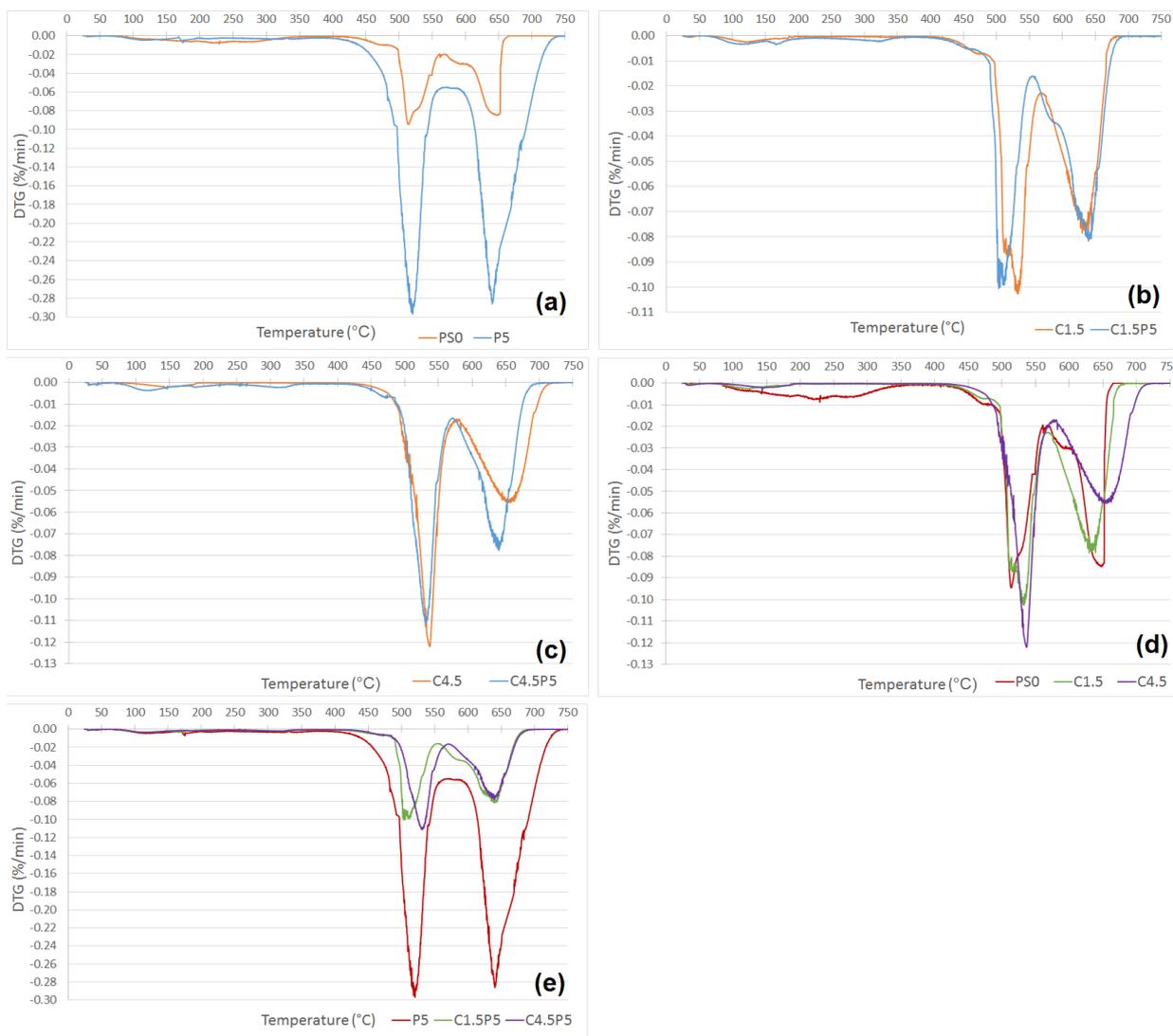
Comparing the control membrane and pure PEO (P5) samples, PEO had influence in the first stage of decomposition, but then the degradation was similar to other samples without nanoclay. For higher clay contents, PEO addition lessened clay effects on thermal stability. For example, C4.5P5 had a greater weight loss until the third stage (93%) and lower final decomposition temperature (660°) as compared to C4.5 (84% and 700°C). According to Anadão et al. (ANADÃO et al., 2010), the increasing clay content decreases oxygen diffusion into the polymeric matrix retarding combustion.

The residual weight after TGA analysis is attributed to the incombustible (mostly inorganic) components of the membranes i.e., residual nanoclay. Pure polysulfone membranes had a residual weight of 0.52%, while membranes with 1.5% and 4.5% nanoclay had 1.00% and 2.83% respectively and mixed nanoclay-PEO membranes had residues of 0.98% (C1.5P5) and 2.49% (C4.5P5)

In order to help analyze the thermal degradation conditions, Figure 34 shows the differential thermogravimetric curves. The curves show how many grams are lost per minute in function of temperature. It is another approach to analyze the data Figure 33. The valleys on Figure 34 (different scales on Y axis) shows the transition between Zones II and III and between Zones III and IV on Figure 33 as well as the intensity of the weight loss in that temperature.

Comparing membranes with and without PEO, Figure 34 (a) show that the mass loss with PEO is more prominent, but around the same temperature range as pure polysulfone. Figure (b) and (c) compares nanoclay membranes versus nanoclay+PEO membranes. The peaks of thermal degradation sometimes are in higher temperatures for pure nanoclay membranes. i.e. 503°C for the first stage C1.5P5 versus 532° for the same stage C1.5 or 638°C for the second degradation of C4.5P5 versus 653°C for C4.5. Therefore, PEO is slightly reducing the temperature thermal resistance whether in the first or second decomposition stages.

Figure 34 – Differential Thermogravimetric Analysis (a) PS0 x P5; (b) C1.5 x C1.5P5; (c) C4.5 x C4.5P5; (d) PS0 x C1.5 x C4.5; (e) P5 x C1.5P5 x C4.5P5



Comparing the membranes without PEO (d), the nanoclay addition changed the temperature decomposition for 4.5% nanoclay in the latter stage of decomposition, while the first stage was slightly improved for both membranes. Membranes with PEO and nanoclay (e) do not show significant changes in the peaks of decomposition. However, the differential loss for nanoclay membranes was lower compared to pure PEO.

The membrane mechanical properties are displayed in Table 13. Results show that increasing the clay content increased membrane stiffness (i.e., increased Young modulus and stress at rupture) as a result of an increased sponge-like structure (14  $\mu\text{m}$  thick on PS-0 and 25 $\mu\text{m}$  thick on C4.5) and absence of voids (C1.5). The results

are in agreement with previous reports (ANADÃO et al., 2010; LAI et al., 2014) that increasing the clay content increased membrane tensile strength.

Table 13 – Membrane mechanical properties

Membrane Type	Young Modulus (MPa)	Tensile Strength (MPa)	Elongation at rupture (%)
PS0	58.3 ± 3.2	3.80 ± 0.2	11.4 ± 1.1
P5	38.7 ± 2.3	3.72 ± 0.1	15.6 ± 2.1
C1.5	63.1 ± 1.2	3.50 ± 0.2	9.6 ± 1.4
C1.5P5	59.4 ± 1.9	3.28 ± 0.2	16.3 ± 1.7
C4.5	73.1 ± 3.5	3.97 ± 0.3	8.5 ± 0.9
C4.5P5	63.8 ± 2.7	3.44 ± 0.2	10.7 ± 1.2

Figures 35-37 (and a general comparison on Figure 38) show a median distribution for membrane elongation and Young Modulus. Comparing the membranes PS0 and P5 it is possible to see that PEO has a strong influence increasing membrane elasticity, lowering the Young Modulus from 60.01 to 37.40. By adding nanoclay the membranes' elasticity decreases even considering the presence of PEO. Regarding the tensile strength, the difference between 1.5% nanoclay and 0% nanoclay was not significant, sometimes being lower for 1.5% nanoclay. However, for 4.5% nanoclay the Tensile Strength was higher than their respective controls.

In contrast to these results, Ma et al. (2012) reported that nanoclay weakens membranes mechanical properties, due to an increase on membrane porosity (from 45.2% to 48.1%). However, on their experiments, all membranes were synthesized with nanoclay and PEO (no pure nanoclay membranes). Hence, it remains unclear if the porosity change and tensile strength decrease was caused effectively by the nanoclay as the authors want to prove. Their nanoclay concentrations vary from 0 to up to 6% in total solution percentage, which are effectively high concentrations for nanoclay.

Figure 35 – Stress-Strain curves for membranes PS0 and P5

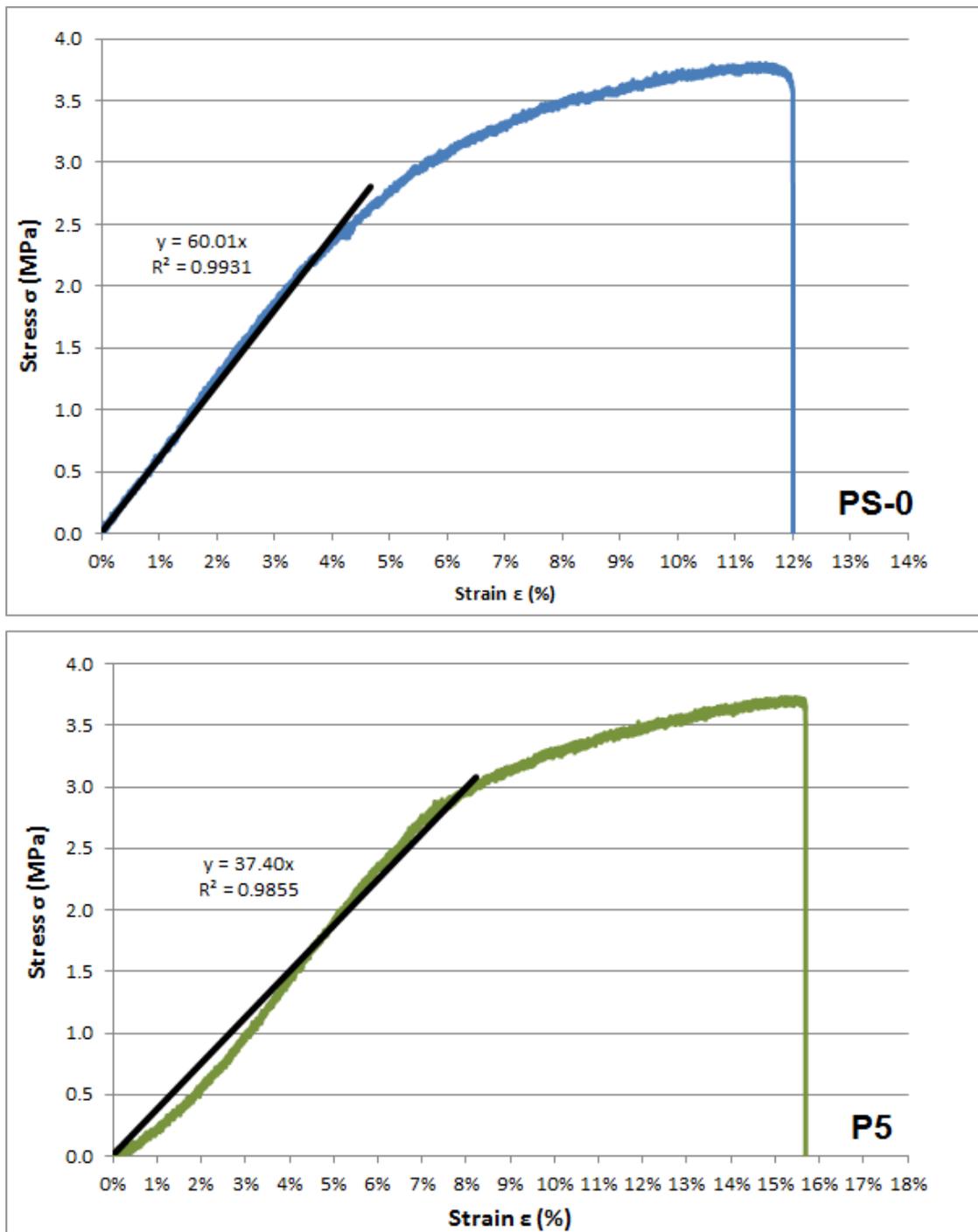




Figure 36 – Stress-Strain curves for membranes C1.5 and C1.5P5

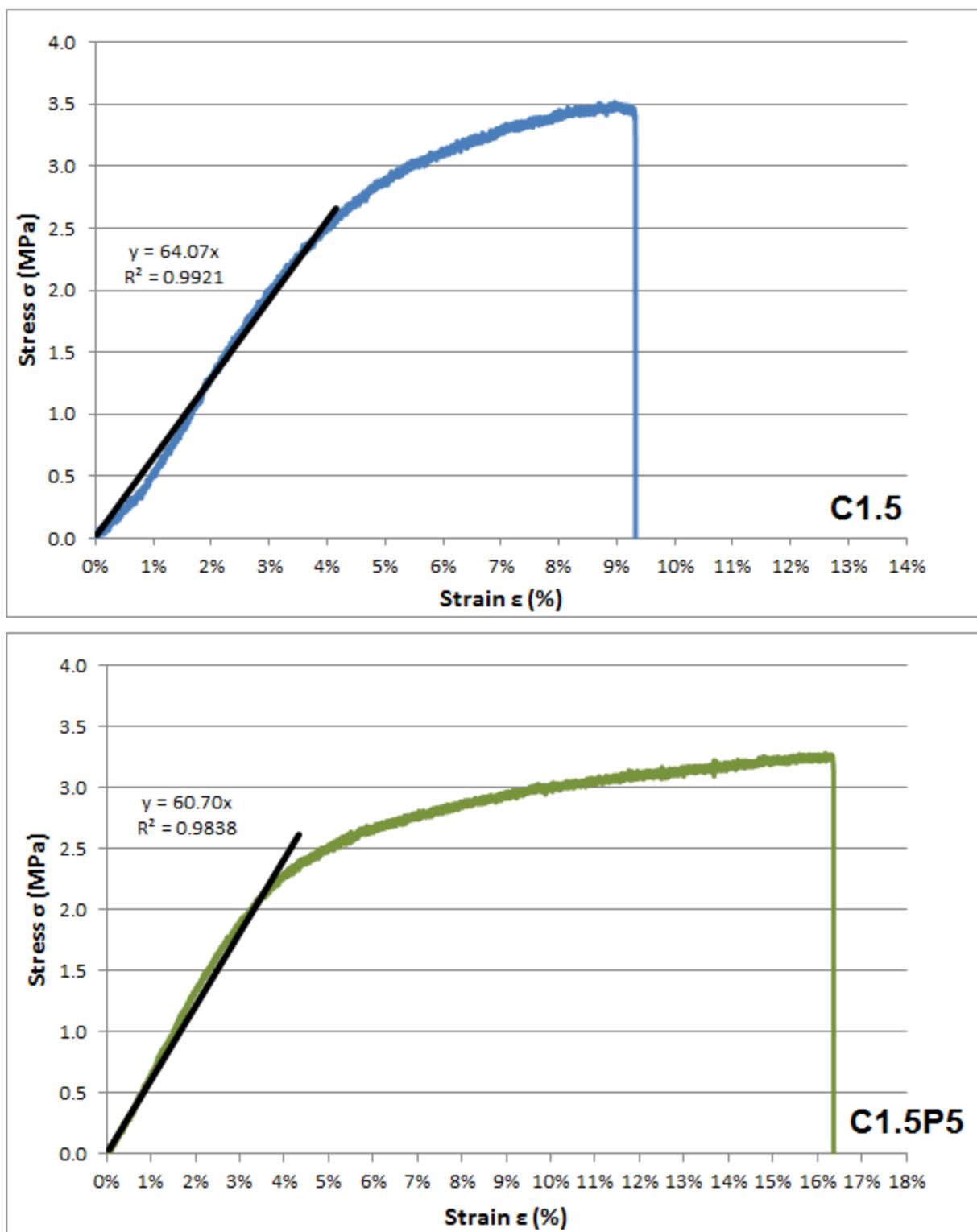




Figure 37 – Stress-Strain curves for membranes C4.5 and C4.5P5

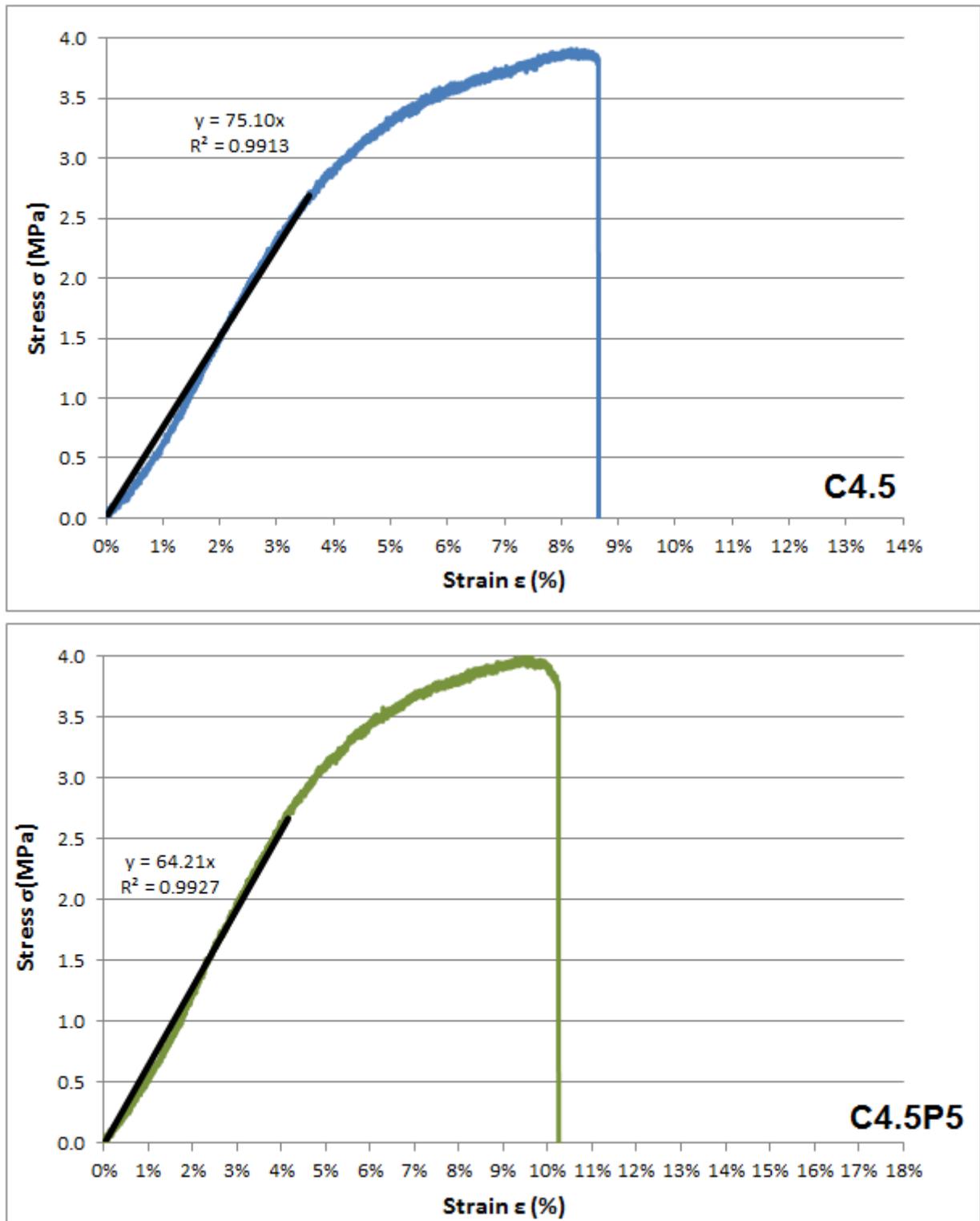
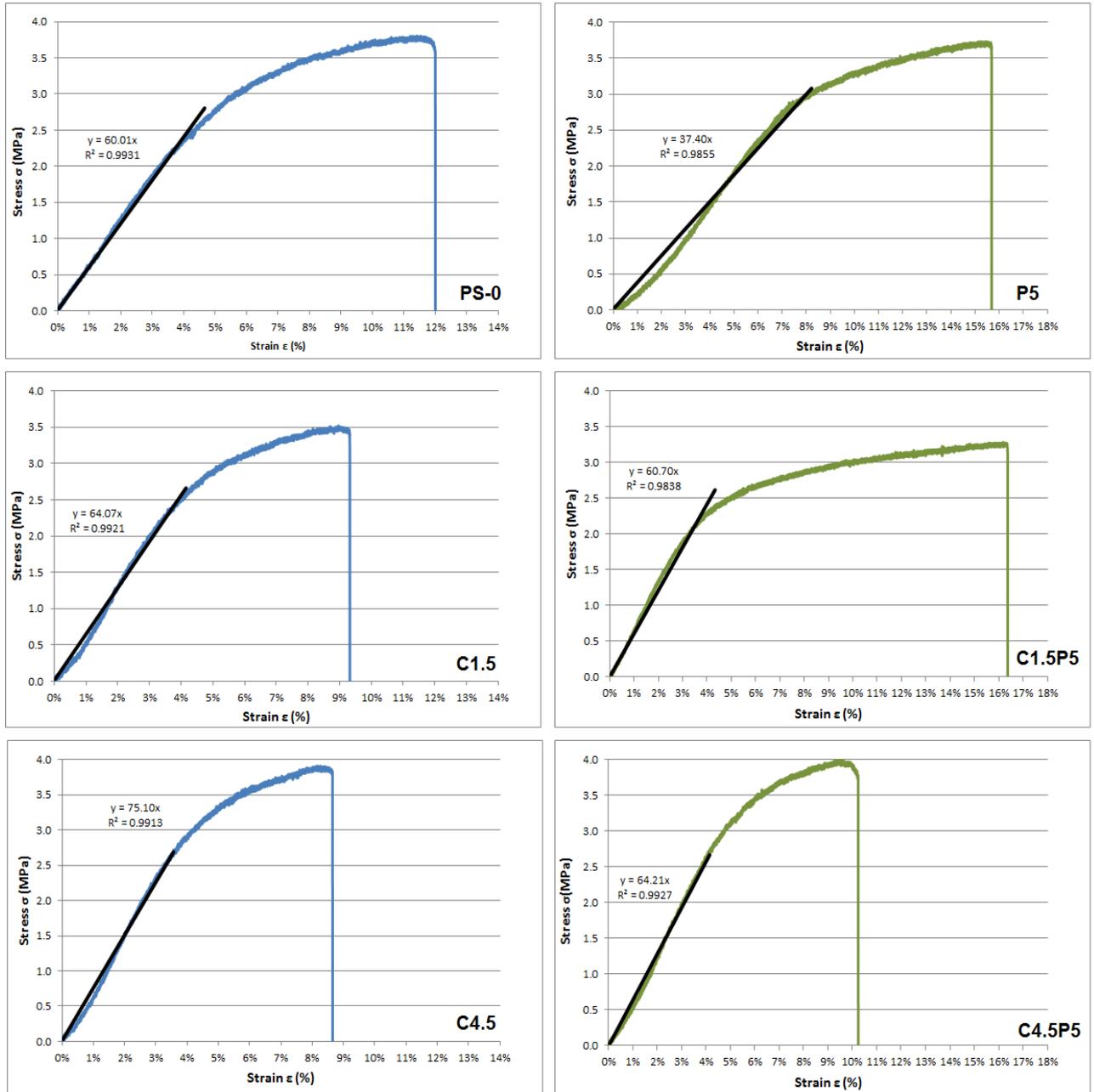




Figure 38 – Stress-Strain curves comparing all evaluated membranes





Liu et al. (2014) reported that this unexpected behavior seen by Ma et al. may be caused by poor clay dispersion i.e., if the nanoclay and polymer are uniformly dispersed the ionic bonds and thus high interfacial interaction between the polymer and nanoclay enhances the membrane tensile properties. They also point that nanoclay can act as a temporary crosslinker to the polymer chain (in their case, PVDF) due to its mobility and provide regions of increased strength.

### **5.7 Molecular Weight Cut-Off (MWCO)**

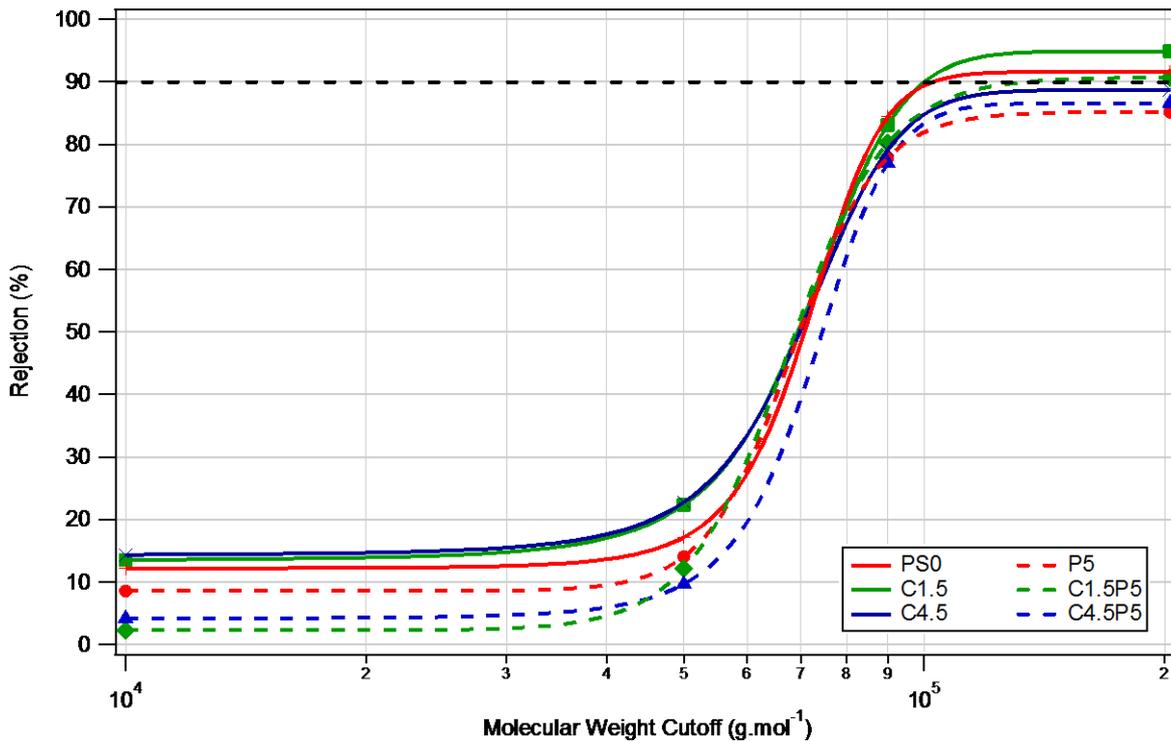
The selected membranes were challenged with PEG solutions (MW = 10.000, 50.000, 90.000, and 203.000 g/mol) to determine the membrane MWCO, which is the molecular weight when the rejection is >90%. The average percent retention vs. PEG molecular weight is presented in Figure 39. The purpose of this analysis was to verify how would be the decrease of rejection facing the overall increment in permeability.

Considering the curves obtained, the estimated MWCO for PS0 was between 110.000 and 120.000 g/mol, while C1.5 and C1.5P5 had MWCO between 120.000-130.000 and 190.000-200.000 g/mol respectively. All the other membranes were unable to achieve the minimum of 90% rejection for PEG of 203.000 g/mol. Further evaluation of other molecular weights were not interesting from this research's perspective, considering 203.000 g/mol is a big particle size and rejections of bigger molecules would apply for microfiltration systems.

The results show that in all cases doping with PEO increased the MWCO. This behavior was expected since PEO is a pore former and the PEO membrane permeability was significantly higher compared to PS0 membrane (15 x 237 L/m<sup>2</sup>.h.bar).

The simultaneous addition of clay and PEO increased membrane rejection as compared to pure PEO. Membrane C1.5 had a MWCO similar to the pure PSU membrane with a flow nearly 4 times greater. A previous study (MIERZWA et al., 2013) indicated that nanoclay improved membrane rejection at a concentration of 1%, but further increases decreased rejection (similar to results here) due to changes in internal pore structure.

Figure 39 – Molecular Weight Cutoff



## 5.8 Fouling Evaluation

Membranes were challenged by cross-flow filtration with a 10 mg/L of sodium alginate solution in order to evaluate membrane permeability, fouling potential, and colloidal natural organic matter (NOM) removal capacity as presented in Table 14 (1 h; constant  $P = 1$  bar). At least three different membranes were evaluated, first being challenged with DI water and then with sodium alginate solution.

Table 14 – Sodium Alginate Rejection and Permeability Decrease after 1 h

Membrane Type	Permeability (L/m <sup>2</sup> h.bar)		Relative Permeability (%)	Rejection (%)	ANOVA P-Value* (Rel. Perm./Rejection)
	Ultrapure Water	Sodium Alginate			
PS0	14 ± 4.4	9.5 ± 2.9	68.6 ± 1.3	94.5 ± 0.2	0.069/0.0188
P5	22.1 ± 6.6	13.5 ± 4.3	60.2 ± 2.7	92.0 ± 2.4	
C1.5	29 ± 6.8	21.5 ± 6	73.4 ± 4.9	95.0 ± 0.2	0.681/0.0044
C1.5P5	112.2 ± 16.2	77.9 ± 7.4	70.4 ± 8.8	91.5 ± 0.8	
C4.5	36.5 ± 7.1	24.8 ± 5.3	67.8 ± 4.6	94.7 ± 0.1	0.193/0.0183
C4.5P5	138.2 ± 19.8	80.8 ± 4.4	59.3 ± 6.1	93.1 ± 0.6	

\*95% Significance level

All membranes rejected >90% of the alginate. Similar to PEG rejection, the membranes with PEO had a lower rejection performance in a significant level. The average permeability over the experiment was compared to the DI water flow measured for the

same samples before starting the experiment, to estimate the extent of membrane fouling. For this scenario, clay-doped membranes had higher relative permeability as compared to the PEO membranes, but not statistically significant, considering the variance between samples with same nanoclay content.

PEO membranes did not have a statistically significant relative permeability difference compared to the control membrane (P-value 0.211). The average flow after alginate filtration decreased indicating all membranes were prone to fouling. However, it was not observed a statistical significant difference between nanoclay membranes and nanoclay-PEO membranes in terms of relative flow decreasing.

To examine potential for drinking water treatment, cross-flow experiments were completed using natural surface water (NSW) from Cambridge's Walter J. Sullivan Water Treatment Facility reservoir. Membranes were operated continuously for 8 hours and turbidity, total organic carbon, and UV254 from the feed and permeate during the final hour of treatment were measured and compared. (Table 15)

Figure 40 shows the removal efficiency for the referred parameters. Horizontal lines refer to effluent water of the Cambridge Treatment Facility (measured in lab).

Figure 40 – Relative decrease in NPOC, turbidity, and UV-254 of filtered Cambridge reservoir water

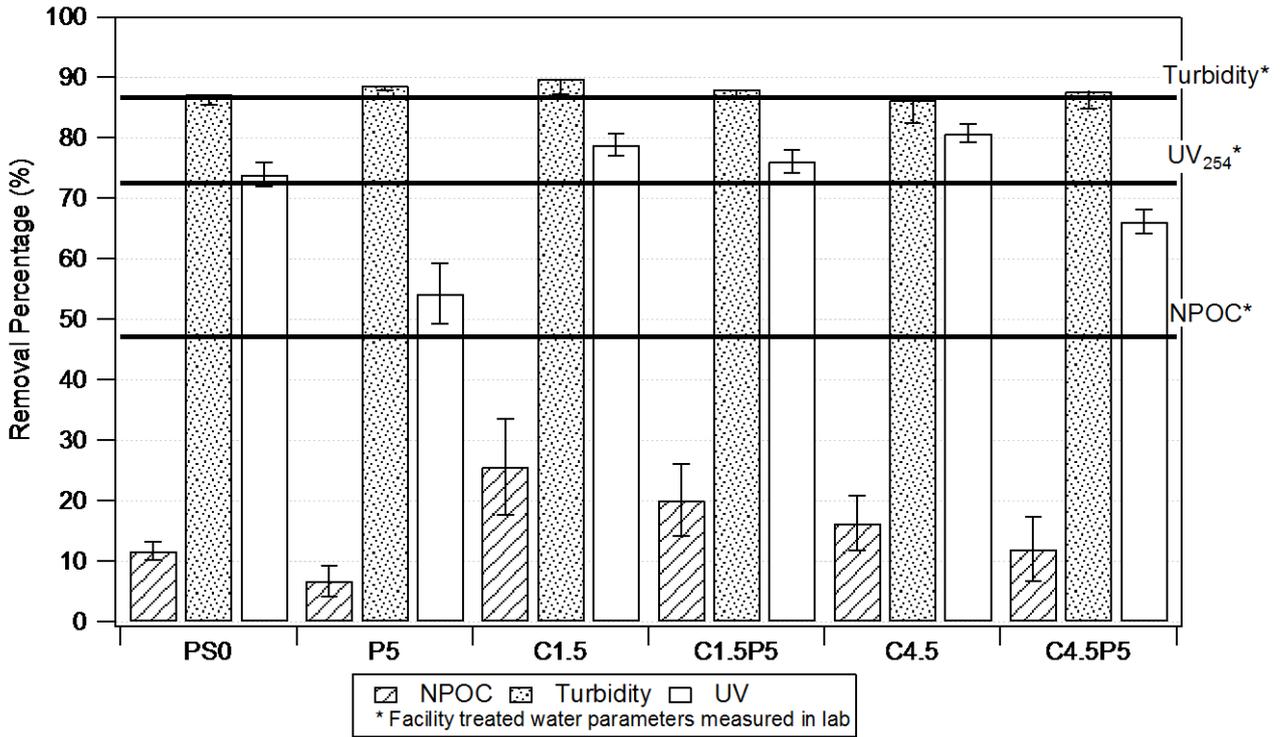


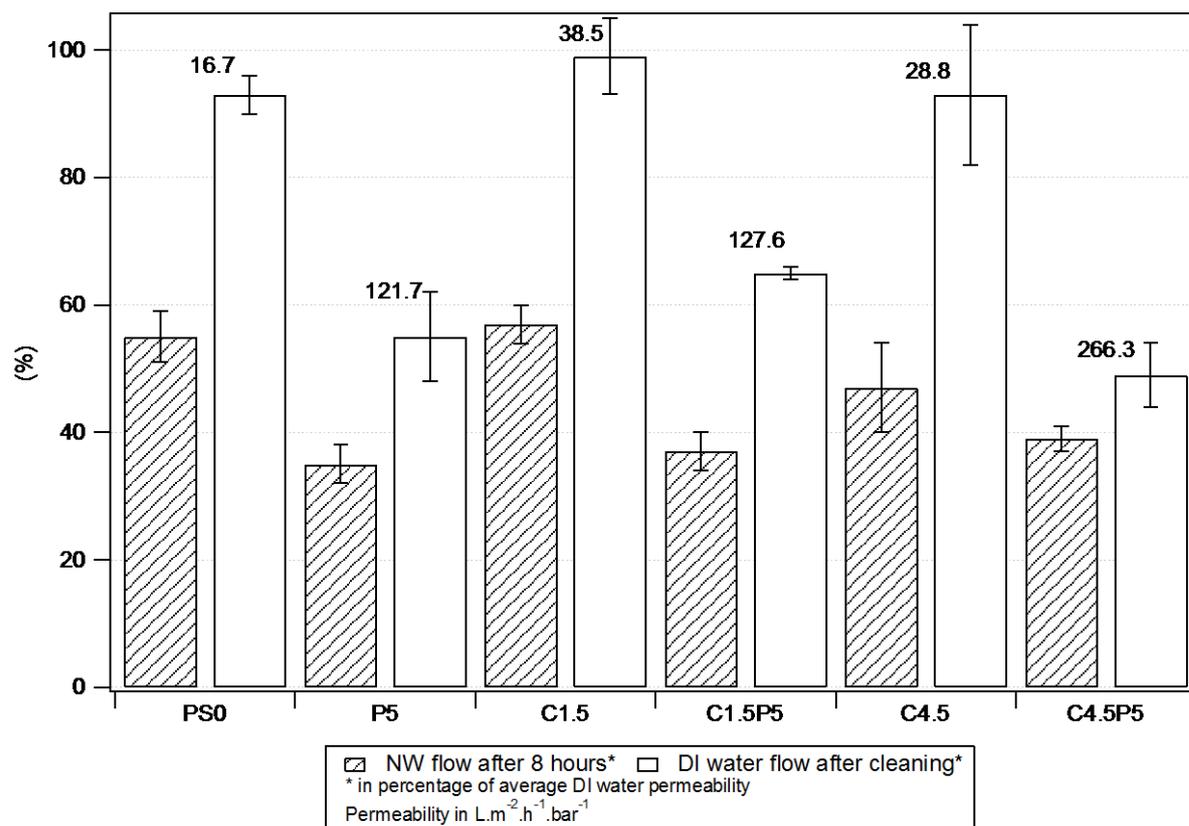
Table 15 – Turbidity, NPOC and UV<sub>254</sub> measurements

Membrane	Turbidity (NTU)	NPOC (ppm)	UV <sub>254</sub> (cm <sup>-1</sup> )
PS-0	0.22 ± 0.03	3.103 ± 0.053	0.0431 ± 0.003
P5	0.20 ± 0.02	3.277 ± 0.175	0.0760 ± 0.008
C1.5	0.18 ± 0.04	2.613 ± 0.281	0.0351 ± 0.003
C1.5P5	0.21 ± 0.03	2.808 ± 0.207	0.0397 ± 0.003
C4.5	0.24 ± 0.06	2.942 ± 0.160	0.0319 ± 0.002
C4.5P5	0.21 ± 0.05	3.093 ± 0.186	0.0561 ± 0.003
Treated Water*	0.23 ± 0.08	1.858 ± 0.144	0.0238 ± 0.004
EPA Standards	0.3 <sup>(1)</sup>	---	---

(1) For systems that use conventional or direct filtration, at no time can turbidity (cloudiness of water) go higher than 1 Nephelometric Turbidity Unit (NTU), and samples for turbidity must be less than or equal to 0.3 NTUs in at least 95 percent of the samples in any month

Figure 41 shows the relative flow decrease after challenging membranes for 8 hours with NSW and the recovery percentage after a manual chemical cleaning using alkaline solution at pH 11 and copious amounts of ultrapure water to eliminate residual alkaline solution.

Figure 41 – Flow decrease after 8 hours of operation and flow recovery after chemical cleaning



The percentages are related to the permeability to DI water, measured for each membrane before starting the fouling experiment. After cleaning, the PEO doped membranes had a lower permeability recovery as compared to the other membranes achieving at best (C1.5P5) 65% of the initial flow.

All the clay membranes without PEO had a high permeability recovery after cleaning of 99% for C1.5 and 93% for C4.5 as compared to 88% for the control membrane. The flow after running NSW for 8 hours was also higher for clay membranes: 57% of the DI average flow for C1.5 and 47% for C4.5 versus 37% for C1.5P5 and 39% for C4.5P5, which shows that the membranes with PEO were more prone to irreversible fouling. Even considering the irreversible fouling presence, the absolute permeability of PEO membranes was still higher than membranes without it.

After running NSW for 8 hours, a yellow layer was visually observed on some membrane samples (Figure 42). In order to evaluate the amount of adsorbed carbon, 4 cm<sup>2</sup> coupons were cut from the membranes and placed in aqueous solutions of pH 2, 7, and 11 (adjusted with HCl and NaOH).

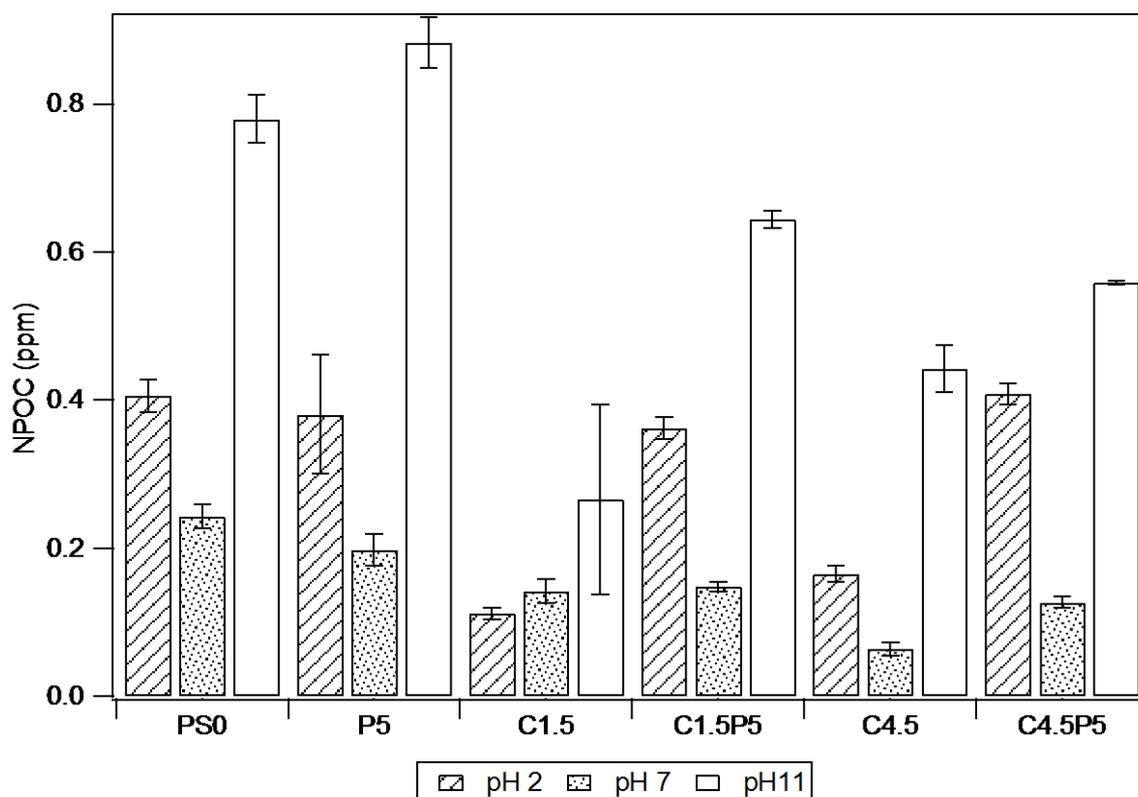
Figure 42 – Membranes after 8 running 8 hours with natural surface water: C1.5P5 (left), C1.5 (right)



The vials were kept in a shaker for 24 hours at 75 RPM and the extract's total organic carbon (desorbed from the membranes) was measured for organic matter adsorption evaluation (Figure 43). Membranes with nanoclay had concentrations of released organic matter 41% to 73% lower compared to the control. Adding PEO to nanoclay membranes made them more prone to surface fouling, since the adsorption of organic matter increased from 4% to 222% considering the different pH scenarios.

These results are correlated to the surface roughness and superficial charges analysis. Both indicated that PEO membranes surface were rougher and more prone to adsorption, which led to increased fouling. As pointed by Woo et al. (WOO; PARK; MIN, 2015) and Vrijenhock et al. (VRIJENHOEK; HONG; ELIMELECH, 2001) the use of additives that increase surface roughness (but keeping other properties such as contact angle) results in accumulation of particles in the rough surface and also imply in a flux declining.

Figure 43 – Carbon desorption at different pH values



Regarding membrane potential to remove bacteria, all membranes showed a removal from three to four logs (99.9% to 99.99%). Images showing the difference between membrane effluent and feed in terms of coliform for counting can be seen on Figure 44 to Figure 46. Images had originally 278 x 200  $\mu\text{m}$  and a 40 times magnification. Feed had 1 ml of *E. coli* concentrate solution and the membrane effluent had 20 ml. The measurements are taken into account to normalize the final bacteria count.

Considering the experiment used a concentrated *E. coli* culture and it used a single flat sheet membrane for separation, the results were showed a good potential for a physical separation method. The membrane separation potential can be enhanced by associating other membrane layers in serie and/or by associating a chemical disinfection methods. The formation of disinfection by-products can be minimized, once organic matter can be physically separated by the membranes.



Figure 44 – E coli removal (a) Feed (b) PS0 (c) C4.5P5

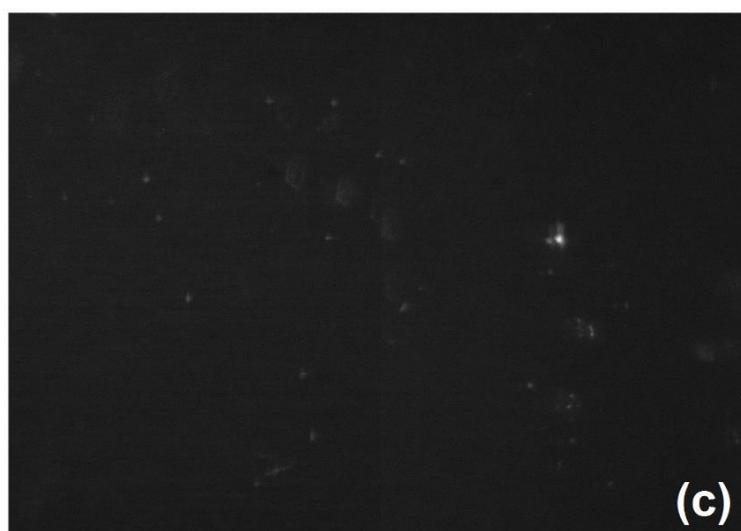
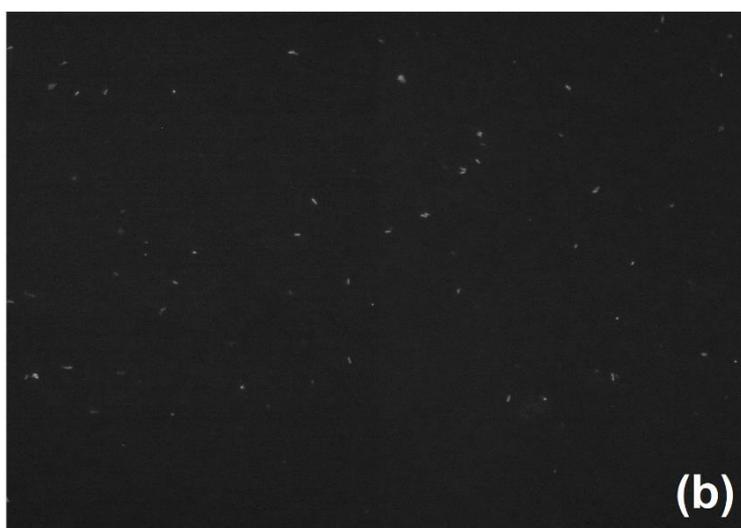
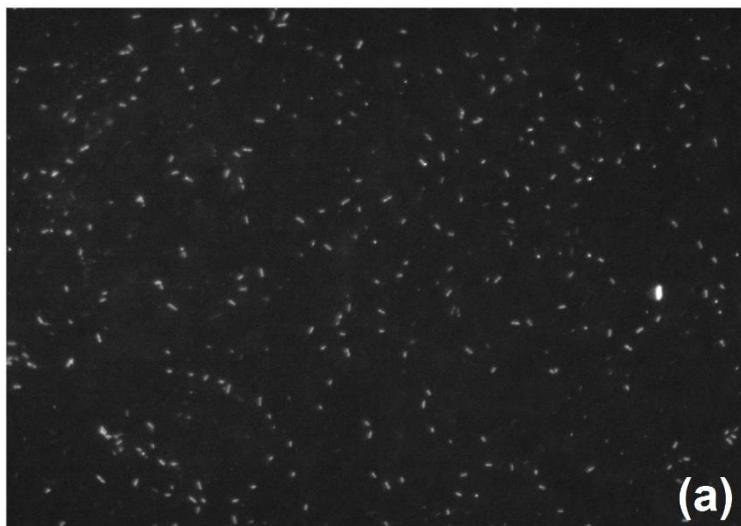




Figure 45 – *E. coli* removal (a) Feed (b) C1.5 (c) C4.5

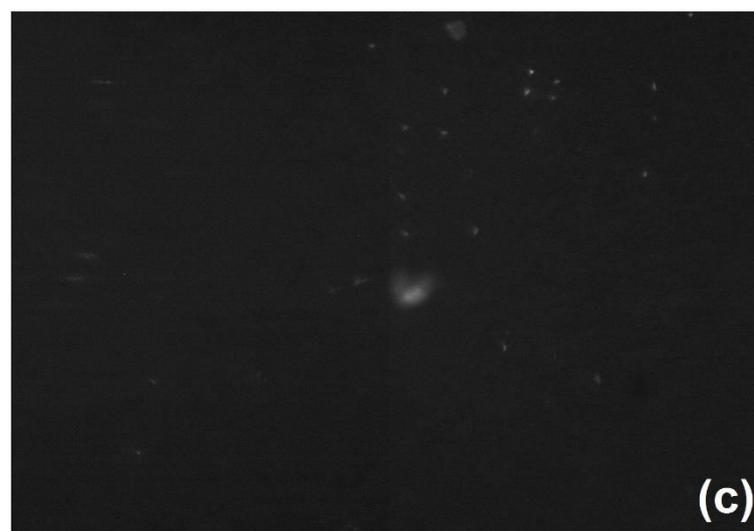
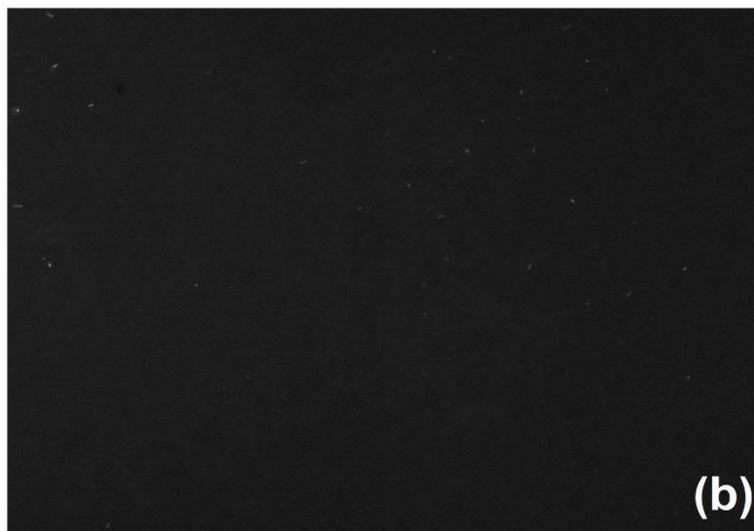
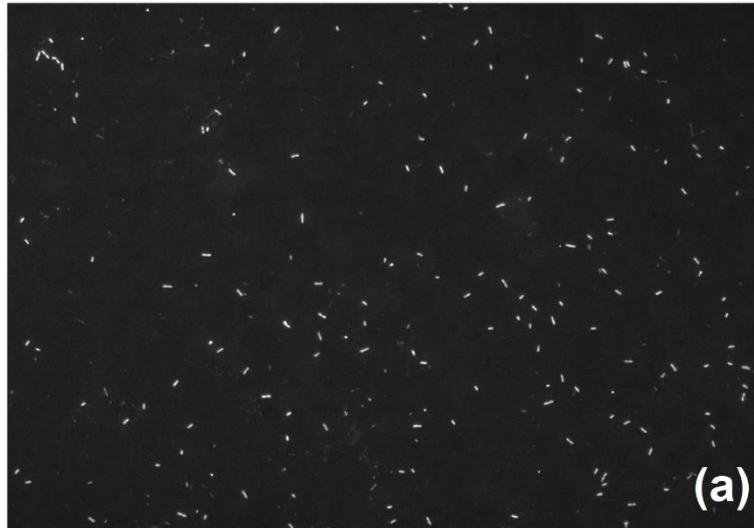
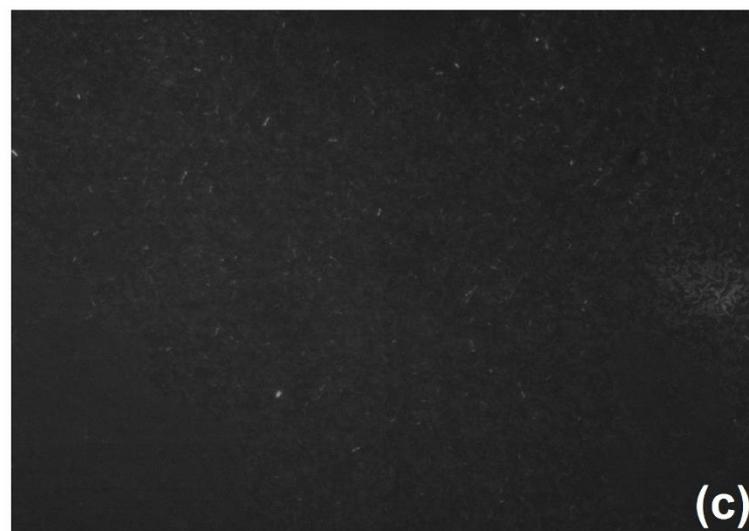
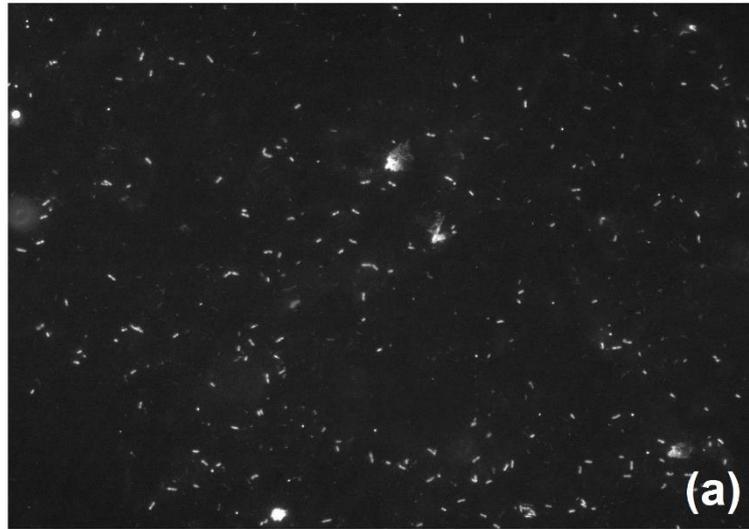




Figure 46 – *E. coli* removal (a) Feed (b) P5 (c) C1.5P5





## 6. CONCLUSION AND CONSIDERATIONS

### Conclusion

This research focused on the synthesis and structural modification of polysulfone membranes in the efforts of making them less prone to fouling. The fabrication of structure modified membranes is innovative because it can potentially result in cost effective and high-performance membranes with possible applications in many fields of water and wastewater treatment.

The structure modification was made by the addition of hydrophilic nanoclay in the membrane dope solution, facilitating the inflow of water in the phase inversion process and changing the internal structure (and therefore the performance, of the produced membranes) and association with a pore former, PEO, to increase membrane permeability.

Regarding the final results, the membranes made purely with nanoclay had the best relative performance in terms of permeability recovery, anti-fouling properties, and thermal and mechanical resistance. The addition of clay up to 4.5% revealed a membrane with a spongelike bottom structure, which, despite for being know to improve membrane retention, did not showed satisfactory performance in terms of MWCO. Despite that, all the membranes were successfully able to retain *E.coli*, but still needing a complementary disinfection method for reliability. The highlight among the synthesized membranes was 1.5% nanoclay. These membranes had a flow increment of 382% (from 14.4 to 55 L/m<sup>2</sup>.h.bar), without compromising their rejection (their MWCO is similar to pure polysulfone membranes)

The amphiphilic pore former PEO, also used as additive, was responsible for thicker membranes with higher absolute flux, higher porosity and lower rejection. In terms of structure, PEO resulted in thicker membranes with pronounced macrovoids structure in the bottom layer. The increase of the dope solution viscosity can be pointed as one of the factors that changed the membrane structure during the phase inversion. The delayed demixing was responsible for growth of macrovoids, which are pointed to weak the membranes mechanical resistance, counterbalancing the improvement caused by the nanoclay. Membranes with PEO also showed higher contact angles and higher

superficial adsorption capability, which points for a rougher surface. The rough surface, along with the larger pore size, led those membranes to a faster (superficial) and irreversible (internal) fouling.

Considering the results, nanoclay membranes are potential alternatives to complement standard polysulfone membranes applications, since for a nanoclay concentration around 1.5%, the membranes had an overall improved flow without compromising the rejection and flow recovery. The attempts of increasing membrane flow and hydrophilicity using a high molecular weight pore former as PEO showed that, although the absolute permeability of the PEO membranes was higher, their selectivity was compromised and they showed a higher fouling tendency compared to both, nanoclay and pure polysulfone membranes.

### Considerations

The experience of synthesis in laboratory allowed to observe in practice what has been observed by other researchers in the field working with different nanomaterials. The interactions between polymer, solvent, non-solvent and additives are very sensitive. Thus, changing concentrations of any of the casting solution components or even the indirect influence of uncontrolled room conditions may result in alterations on the final membrane's structure and performance.

Considering the 5 years of research, over 1200 flat sheet membranes, divided in 18 main categories, were synthesized. Considering some authors evaluate only a few parameters when analyzing membrane performance, this research's effort was to have a complete membrane characterization. The qualitative variables chosen for evaluation included material properties and relevant performance parameters for water treatment. Even though, some analysis were not possible to be applied, such as surface pore distribution (SEM surface images did not show pores for image refining, even in high magnification rates) and X-ray diffraction (which required a small angle X-Ray equipment and the samples were reflecting in an angle that could not be captured by the X-Ray device).

Besides further characterization via X-ray diffraction, as recommendations for future studies, the membrane synthesis could be made in a porous support media - so the membranes could be tested in flat sheet membrane reactors – the solution could be

cast into hollow fiber membranes - so a performance evaluation could be made for a different arrangement – and the membranes could be tested for gas separation.

Characterization of membrane's physical properties and performance are extremely necessary to guarantee the right choice when developing a membrane system for a given application. The association with pore formers agents must be evaluated based on his rejection needs, operational pressure and average flow after the membranes become fouled. As it was shown on this research, a pore former agent may enhance the membrane permeability, but when it changes membrane's surface properties it may make them more prone to fouling, due to surface adsorption and internal fouling.



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