

FABRICATION OF POLYETHERSULFONE HOLLOW FIBERS FOR
ULTRAFILTRATION

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GÜLÇİN KALTALI

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ULTRAFILTRATION**

submitted by **GÜLÇİN KALTALI** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Halil Kalıpçılar
Head of Department, **Chemical Engineering**

Asst. Prof. Dr. P. Zeynep Çulfaz Emecen
Supervisor, **Chemical Engineering Dept., METU**

Prof. Dr. Halil Kalıpçılar
Co-Supervisor, **Chemical Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. Ülkü Yetiş
Environmental Engineering Dept., METU

Asst. Prof. Dr. P. Zeynep Çulfaz Emecen
Chemical Engineering Dept., METU

Prof. Dr. Halil Kalıpçılar
Chemical Engineering Dept., METU

Prof. Dr. Suna Balcı
Chemical Engineering Dept., Gazi University

Assoc. Prof. Dr. Çerağ Dilek Hacıhabiboğlu
Chemical Engineering Dept., METU

Date: 29.08.2014

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Gülçin KALTALI

Signature :

ABSTRACT

FABRICATION OF POLYETHERSULFONE HOLLOW FIBERS FOR ULTRAFILTRATION

Kaltalı, Gülçin

M. S. Department of Chemical Engineering

Supervisor: Asst. Prof. Dr. P. Zeynep Çulfaz Emecen

Co-supervisor: Prof. Dr. Halil Kalıpçılar

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Hollow fiber membranes take an important part in membrane separation processes. They are used in many areas like gas separation, pervaporation, ultrafiltration and microfiltration processes due to their advantages like high membrane area per volume and easy backwashability.

Poly(ethersulfone) (PES) is one of the most commonly used polymers in preparing hollow fiber ultrafiltration membranes. Due to its hydrophobic character, use of hydrophilic additives is usually necessary to make membranes resistant to fouling. In this study, poly(ethylene oxide) PEO based additives (Pluronic F-127, PEG 10k and Triton X100) were used for preparing PES based hollow fiber membranes.

It was observed that adding water to polymer dope delays macrovoid formation in the hollow fibers. Pure water permeance of membranes decreased by adding water to polymer dope and all membranes retention values for bovine serum albumin (BSA, 66 kDa) were above 90%. By using water in polymer dope together with 50 °C

coagulation bath, pore sizes became larger and prepared membranes were nearly in microfiltration range.

The stability of the additives in the membrane matrix was examined via FTIR to estimate the anti-fouling performance of membranes in long-term. According to ratio of characteristic peak intensities of additives and PES; it was observed that all additives remained in the membrane matrix after coagulation.

Fouling characterizations were done by dead-end constant flux filtrations of BSA with intermediate backwashing. Among tight ultrafiltration membranes, Triton X100 showed lowest fouling resistances among additives. After Triton X100 additive, Pluronic F-127 showed second lowest fouling results. It was found that reversibility of fouling was highest in membranes with Pluronic F-127 additive. In loose ultrafiltration group; membrane with Pluronic F-127 additive showed the best fouling characteristics.

Between these three additives; Pluronic F-127 and Triton X100 additives can be more preferable in use than PEG 10k additive according to their stability and better anti-fouling properties.

Keywords: Membrane, hollow fiber, ultrafiltration, phase inversion, membrane fouling.

ÖZ

ULTRAFİLTRASYON İÇİN POLİETERSÜLFON KOVUKLU ELYAF ÜRETİMİ

Kaltalı, Gülçin

Yüksek Lisans, Kimya Mühendisliği Bölümü

Tez Yöneticisi: Yrd. Doç. Dr. P. Zeynep Çulfaz Emecen

Ortak Tez Yöneticisi: Prof. Dr. Halil Kalıpçılar

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Kovuklu elyaf membranlar, membranla ayırma proseslerinde önemli bir yere sahiptir. Birim hacimde yüksek membran alanı ve tersten kolay temizlenebilirlikleri gibi avantajlarından dolayı; gaz ayırma, pervaporasyon, ultrafiltrasyon ve mikrofiltrasyon proseslerinde kullanılmaktadırlar.

Poli(etersülfon) (PES), kovuklu elyaf ultrafiltrasyon membranları üretiminde sıklıkla kullanılan polimerlerden biridir. Hidrofobik karakterinden dolayı; polimer çözeltisinde hidrofilik katkı maddesi kullanımı, membranları kirlenmeye karşı dirençli yapmak için etkili ve kolay bir methodtur. Bu çalışmada; PES bazlı kovuklu elyaf membranların hazırlanması için poli(etilen oksit) PEO bazlı katkı maddeleri (Pluronic F-127, PEG 10k ve Triton X100) kullanılmıştır.

Polimer çözeltisine su eklemenin, kovuklu elyaflarda makroboşluk oluşumunu geciktirdiği bulunmuştur. Polimer çözeltisine su eklenerek, su geçirgenliği değerleri azalmıştır ve bütün membranların bovin serum albümin (BSA, 66 kDa) için tutma değerleri %90'ın üzerindedir. 50 °C koagülasyon banyosu ile birlikte polimer

çözeltisine su eklenerek; gözenek boyutu büyümüştür ve hazırlanan membranlar neredeyse mikrofiltrasyon aralığındadır.

Membranların uzun süreli kirlenme karşıtı performansını belirlemek için FTIR yolu ile katkı maddelerinin membran matrisi içinde stabilitesi incelenmiştir. Katkı maddeleri ve PES pik şiddeti oranlarına göre; koagülasyondan sonra bütün katkı maddeleri membran matrisi içerisinde kalmıştır.

Kirlenme karakterizasyonları, sabit akıda kapalı sonlu arada geri yıkama yapılarak BSA filtrasyonu ile gerçekleştirilmiştir. Sıkı ultrafiltrasyon membranları arasında; Triton X100, katkı maddeleri arasında en düşük kirlenme direncini göstermiştir. Triton X100 katkı maddesinden sonra, Pluronic F-127 ikinci en düşük kirlenme sonuçlarını göstermiştir. En yüksek kirlenme geri döndürülebilirliği, Pluronic F-127 katkı maddesi içeren membranlarda bulunmuştur. Gevşek ultrafiltrasyon membran gurubunda; Pluronic F-127 katkı maddeli membran en iyi kirlenme karakteristiğini göstermiştir.

Bu üç katkı maddesi arasında; Pluronic F-127 ve Triton X100 katkı maddeleri; PEG 10k katkı maddesine göre stabilite ve daha iyi kirlenme karşıtı özellikleri açısından kullanımda daha tercih edilebilirdir.

Anahtar kelimeler: Membran, kovuklu elyaf, ultrafiltrasyon, faz değişimi, membran kirlenmesi.

To my family

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

A	area of the hollow fiber membrane, m ²
C _p	permeate concentration
C _f	feed concentration
I _r	ratio of peak intensities
J	permeation flux, L/h. m ²
Q	permeate collected over a duration of time, L/h
R	retention
R _{mem}	membrane resistance
R _{total}	total membrane resistance
R _{fouling}	membrane fouling resistance
TMP	transmembrane pressure
ΔP	pressure difference between feed and permeate side , bar

Abbreviations

NMP	N-methyl pyrrolidone
PEG	Polyethylene glycol
PES	Polyethersulfone

Greek Letters

μ	viscosity
---	-----------

CHAPTER 1

INTRODUCTION

Ultrafiltration membranes have many application areas like waste water treatment, drinking water production, food and biotechnology. Ultrafiltration is a separation process for separating particles in liquid with membranes that have pore sizes between 1-100 nm. They are used for filtering dissolved macro molecules and colloidal matter from solutions and microfiltration is used for suspended matter and bacteria.

One of the most commonly used membrane preparation methods is phase inversion. It can be done by precipitation by NIPS (nonsolvent in vapor or liquid phase separation) or TIPS (thermally induced phase separation) method. Ultrafiltration membranes are usually made of polymeric materials and fabricated with NIPS method. In this method; a polymer solution is immersed in a coagulation bath which contains a non-solvent. Precipitation of the membrane occurs by exchange of solvent and non-solvent. In this method; properties of membranes are dependent on thermodynamic properties of the system and phase inversion kinetics [1-3]. Microfiltration membranes can be made by track-etching, stretching, TIPS or NIPS. For preparing microfiltration membranes via phase separation; addition of solvent in the coagulation bath and VIPS (vapor induced phase separation) are usually necessary [4].

Modules of polymeric membranes are of two types which are hollow fiber modules and spiral-wound modules. Spiral-wound modules consist of flat membranes wrapped as “membrane envelopes”. Hollow fiber membranes have many advantages like high membrane area within a given volume and easy module fabrication compared to flat sheet membranes [5]. Figure 1.1 shows an example of the structure of hollow fiber membrane. Typically at the outer or inner side, there is a skin layer which is the selective layer. Under that layer, a porous support layer is formed. The fiber bore is formed by the help of bore liquid during fiber spinning process.

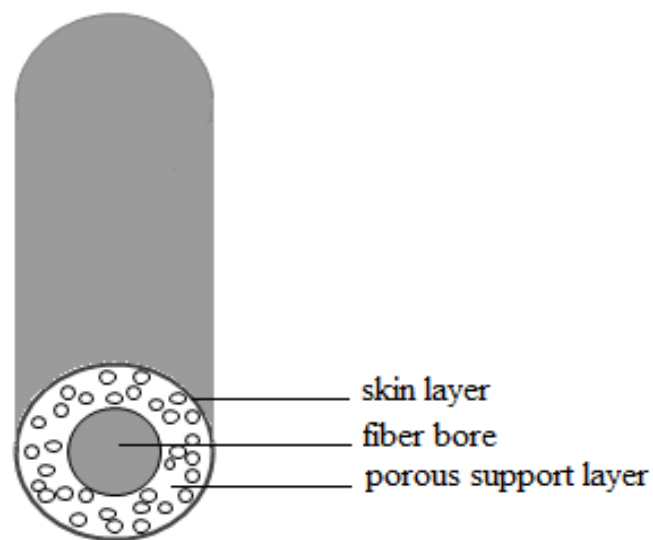


Figure 1.1. The structure of hollow fiber membrane

Polyethersulfone (PES) is one of the most commonly used polymers in preparing hollow fiber ultrafiltration membranes. It is preferred due to its advantages like high thermal, chemical and mechanical strength. On the other hand, the disadvantage of PES is its hydrophobic character which makes it prone to membrane fouling, which is deposition of materials on membrane surface or pores [6,7]. Fouling is the most serious problem in most membrane separation processes. It can be defined as the deposition of material retained by the membrane on the membrane surface or in the pores. Membrane fouling results in an increase in flow resistance (decrease in flux or an increase in pressure). Moreover, it reduces production rate and membrane life time and increases complexity of membrane operations [8]. For this reason, surface grafting, surface coating or adding additives to the polymer solution are used for

making membrane surfaces resistant to fouling [9-12]. Additive usage in polymer solution is an effective and easy method among them.

Hydrophilic additives usually make membranes resistant to fouling and poly (ethylene oxide) (PEO) based additives are one of them. PEO is a widely used polymer for preventing protein adsorption in marine, medical and membrane industry [13]. Pluronic[®] F-127 (PEO-PPO-PEO), Triton[®] X100 (surfactant) and Polyethylene (PEG) 10k are investigated as PEO based additives in this study. In literature studies, it is observed that these additives act like pore-forming agent which enhances porosity and interconnectivity and make membrane surfaces hydrophilic and make them resistant to fouling [9,10,14].

In this study, tight and loose ultrafiltration membranes were prepared in hollow fiber geometry using three additives containing PEO groups. Fouling behavior was characterized in dead-end constant flux filtrations of model foulant Bovine Serum Albumin (BSA) with intermediate backwashing. The degree and reversibility of fouling was investigated and compared. The stability of the additives in the matrix was also examined via FTIR to estimate the anti-fouling performance of membranes in long-term.

CHAPTER 2

LITERATURE SURVEY

2.1. Phase Inversion for Membrane Fabrication

Phase inversion method is used in many membrane fabrication applications. NIPS method is one of the commonly used phase inversion process. In NIPS method, phase exchange occurs by immersion of polymer solution in coagulation bath (non-solvent) which does not dissolve polymer but is fully miscible with the solvent. By the phase exchange between solvent and non-solvent solid membranes are formed finally [2,3,15]. Upon phase separation, the solution separates into two phases: a polymer-rich phase that turns into the matrix of membranes after the precipitation of the solution, and a polymer-poor phase that forms membrane pores after it is removed from the precipitated solution [16].

Membranes that prepared with NIPS method generally have asymmetric structure. There is a thin skin layer on one of the membrane surface which has high selectivity with relatively small pores. Under this skin layer, there is a support layer which is thick and has larger pores. With this structure, high selectivity and mechanical strength can be achieved together. The selectivity of the membrane related to the pore size distribution. On the other hand, permeance depends on pore size, porosity, thickness of the skin layer and pore connectivity. In NIPS method, these properties are related with chosen polymer, type and concentration of solvent and non-solvent in solution and coagulation bath, additives and other conditions in membrane preparation [1,7].

2.2 Hollow Fiber Membranes

In NIPS method, membranes can be formed in flat sheet and hollow fiber geometries. Hollow fiber membranes are prepared by pumping bore liquid which forms the hollow part of the membrane and polymer solution one within the other through a spinneret in non-solvent coagulation bath. There are many parameters that determine properties of hollow fiber membranes. Some of them are composition of polymer solution and bore liquid, temperature, spinning rate of polymer solution and bore liquid and air gap between the spinneret and the coagulation bath. Figure 2.1 shows a schematic presentation of spinning apparatus [17].

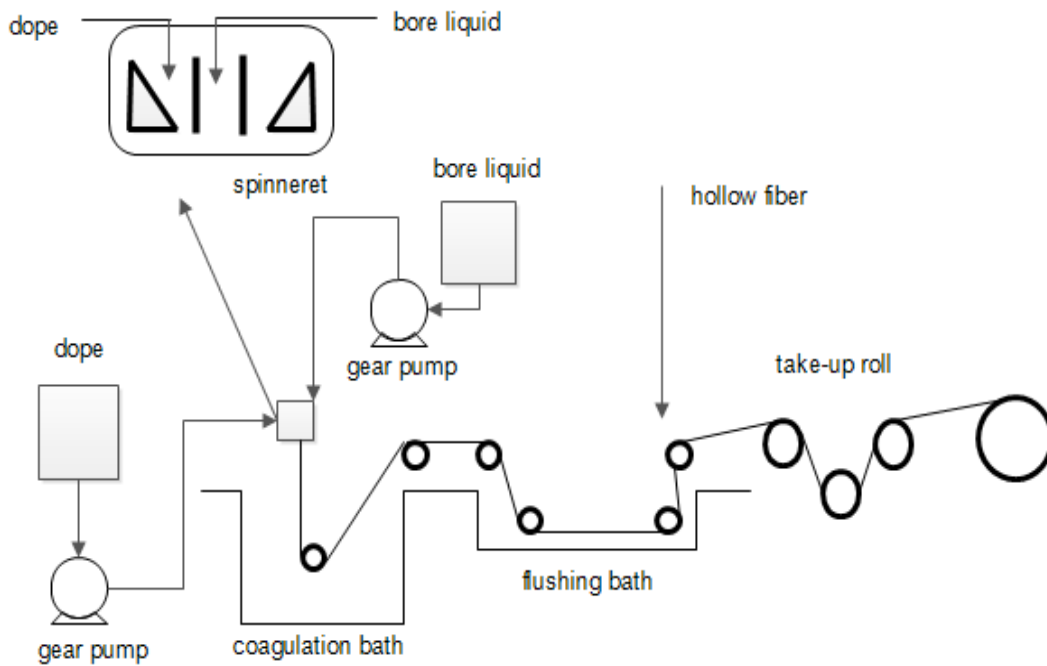


Figure 2.1. Schematic diagram of hollow fiber spinning set up

PES (Polyethersulfone) is one of the commonly used polymers in fabrication of ultrafiltration and microfiltration membranes. Advantages of this polymer are high mechanical, chemical and thermal stability. However, PES is a hydrophobic polymer which reduces its resistance to fouling [6,7]. Substances that can not pass through the membrane can easily adsorb on hydrophobic membrane surface and this cause low permeability and selectivity which can not be reversed easily. At this point there are some methods to make membrane resistant to fouling.

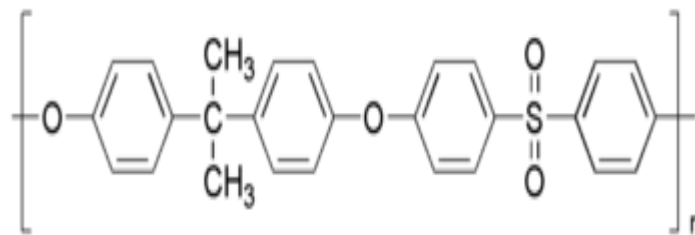


Figure 2.2. Chemical structure of PES

Membrane fouling can occur in different forms. Basic forms are the following ones;

- Pore restriction: a reduction in pore diameter occurs due to adsorption or deposition of molecules on the membrane surface
- Pore plugging/ blocking: a loss of pore density or blocking of pores due to retained molecules
- Cake formation: deposition of retained molecules on membrane surface [18].

Schematic presentations of these three fouling forms are given in Figure 2.3.

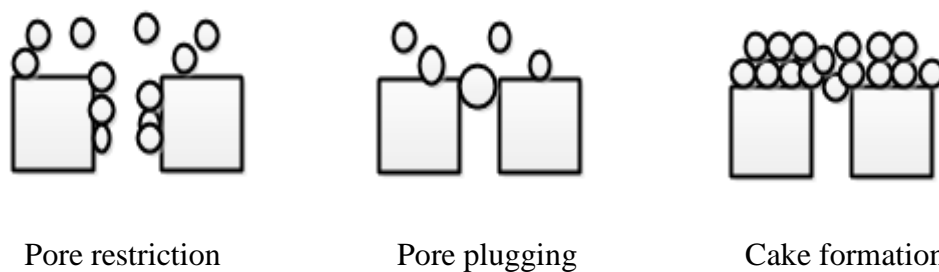


Figure 2.3. Schematic presentation of fouling mechanisms

For examining anti-fouling properties of membranes experiments can be done in two different operation modes which are cross-flow operation and dead-end operation. In these operations; filtration experiments are done by using either constant permeate flux or constant pressure [18].

In this study, dead-end constant flux filtration was carried out. In this operation, the permeate flux is fixed and the transmembrane pressure difference varies [19]. In constant flux; same flow rate towards membrane surface is applied. Same amount of material deposits on the membrane in all filtrations at constant flux by assuming 100% retention. This results in a more comparison of different membranes or feeds. Moreover, constant flux operations results are more realistic for membrane filtration applications because in industrial applications filtrations analysis are done at constant flux. At constant transmembrane pressure operations; as flux decreases, permeate drag decreases and fouling behavior depends strongly on membranes permeance [20].

In each filtration cycle, backwash is applied to membranes for cleaning membranes. By doing backwash reversible fouling on membrane is cleaned. Backwash is applied by pushing reversed flow from permeate side to feed side. In filtration applications in industry, backwashing process is applied automatically when the transmembrane pressure increases in the system [21].

Miller et al. compared constant flux and constant transmembrane pressure fouling experiments. Experiments were done by using soybean oil emulsion as foulant by using commercial flat sheet PS-20 polysulfone ultrafiltration membranes. In constant TMP experiments, organic rejection decreased with increasing transmembrane pressures. Similar behavior was found in constant flux experiments below threshold flux which can be defined as the flux that divides a low fouling region from a high fouling region. Above the threshold flux, it was observed that rejection increased because of the foulant accumulation on the membrane surface [22].

Grafting or coating of hydrophilic polymers, monomers or surface-active substances on membrane surface is one of the methods to prevent fouling. Belfort et al. used graft polymerization method on membrane surface with different monomers including N-vinylformamide (NVF), N-vinylacetamide (NVA) or N-methyl-N-

vinylacetamide (MVA). Lower fouling values were observed with mixed monomer compared to single ones. All graftings performed better than the control membrane according to fouling resistances [11].

Ulbricht et al. grafted poly(ethylene glycol) methacrylate (PEGMA) on PES membrane surface by using UV light. The surface modified membranes showed more resistance to fouling and higher rejection than unmodified membranes. Flux, rejection and fouling experiments showed that grafting PEGMA is a good alternative for the development of low-fouling ultrafiltration membranes [12].

2.2.1. Additives

Another alternative method to prevent fouling is adding polymeric or inorganic additives in membrane forming. The most common additives are poli(vinyl pyrrolidon) (PVP), poli(ethylene glycol) (PEG), Pluronic[®] and TiO₂.

Many additives used for anti-fouling behavior are hydrophilic materials and they move through the membrane surface during phase inversion and make the surface of the membrane more hydrophilic. In many researches it was found that adding a hydrophilic polymer as additive in polymer dope produces membranes with higher porosity, well interconnected pores and surface properties which are different from the pure membrane-forming polymer [9,10].

Kim et al. studied the effect of PEG additive on membrane formation by phase inversion. Membranes were prepared with Psf/NMP/PEG solutions by changing molecular weight of PEG additive. Instantaneous demixing was observed in membranes when PEG additive was used according to light transmittance analysis that was made. As the molecular weight and ratio of PEG additive in polymer solution increased, membranes top layer porosity also increased. This situation caused an increase in pure water flux and decrease in solute rejection values [14].

Ma et al. made a study about effect of PEG additive on the morphology and performance of polysulfone ultrafiltration membranes. PEG with different molecular weights (400 Da, 800 Da, 1500 Da, 4000 Da, 10,000 Da, and 20,000 Da) and different dosage (0-10%) was used as additives in 18% PSf and 82% DMAc system.

When the molecular weight of PEG and dosage of PEG 400 in polymer solution increased, large finger-like structures under the top surface layer of membranes were observed. According to contact angle analysis; it was concluded that as the PEG molecular weight increased, PEG molecules were trapped more in membrane matrix. With increase in molecular weight of PEG from 400 to 20.000, the pure water flux increased from 340 L/m² h to 1390 L/m² h. Moreover, mechanical strength of membrane also became higher. But if the molecular weight of PEG was too high, rapid increase of porosity reduced membranes strength. PEG 1500 was found to be the suitable additive in this study [10].

Ohya et al. examined polysulfone hollow fiber microfiltration membranes by using different molecular weights PEG additives which were raised from 6000 to 20000 Da. As the molecular weight of PEG increases, water flux of the membranes increased from 185 to 77.000 L / m² h. This was because of the increase in porosity and mean pore size of the membranes. This was explained with the high degree nucleation and growth of the polymer lean phase which occurs more when the molecular weight of PEG additive increases [17]. Chakrabarty et al. also found similar behavior that when the molecular weight of PEG additive increased, membranes porosity increased [23].

Another common additive is Pluronic which is a block copolymer of poly (ethylene oxide) (PEO) and poly (propylene oxide) groups which can be PEO-PPO-PEO or PPO-PEO-PPO configuration. Pluronic additive acts like pore forming agent and surface modifier. During the phase inversion process, PPO group which is the hydrophobic part of the copolymer mainly stays in polymer matrix and the hydrophilic part of the copolymer moves towards polymer/water interphase. By this situation, a hydrophilic fouling resistant layer is usually formed on the membrane surface by using Pluronic as additive.

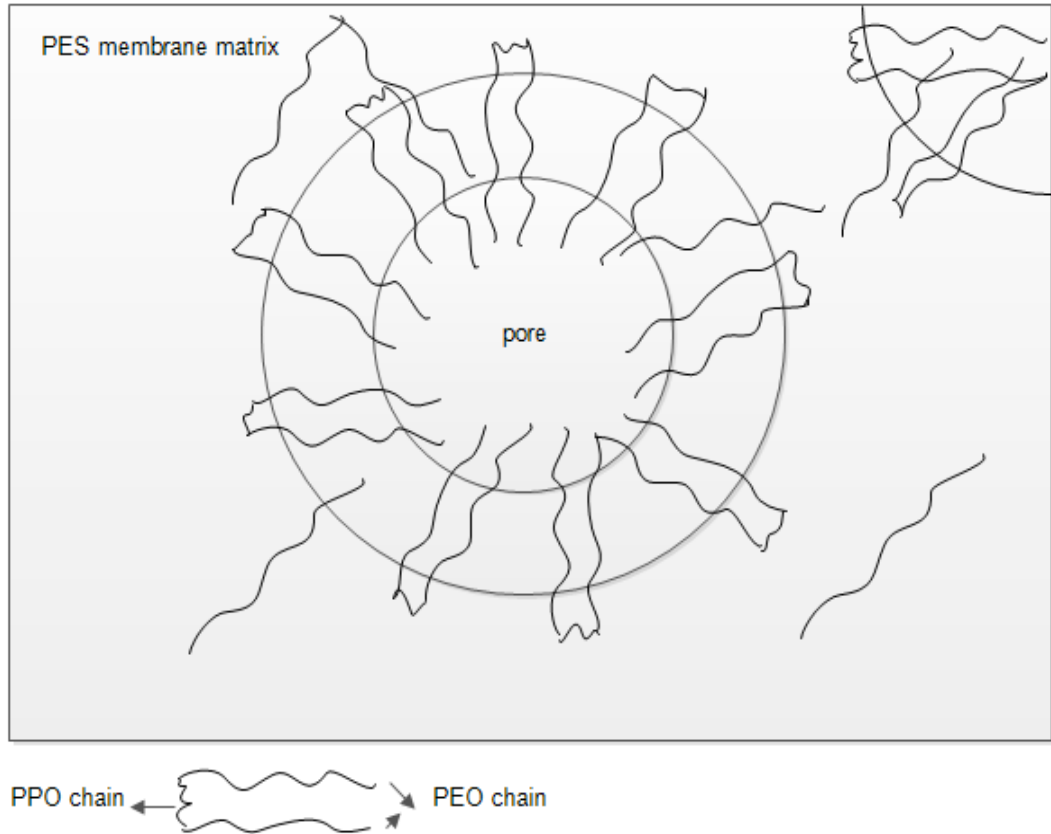


Figure 2.4. Illustration of PEO brush layer formation on the surface of membrane internal pores due to the surface segregation of Pluronic

Fane et al. made a research about fabrication of polyethersulfone ultrafiltration hollow fiber membranes using Pluronic block copolymers as additives. Different types of Pluronics (F127, F108, L64, and 17R4) and PEG 10k were used in this study as additive. Polymer dope solution consisted of %18 PES, %0-15 additive and rest was N-methyl-2-pyrrolidone (NMP). PEG is very water soluble and it was concluded that it was hard for it to stay in membrane matrix during phase inversion process with the absence of hydrophobic PPO block. Pluronic F127 and F108 were the most promising additives according to their permeances. They had both long PEO chains which improved solute rejection. The optimum Pluronic F127 concentration was found as 10 wt% with the highest PWP of 113.8 L/m² h bar [9].

Beside the performance of membrane, additive stability in membrane is also an important parameter. Susanto et al. made a research about performance and stability of ultrafiltration membranes by using PVP, PEG 10k and Pluronic F-127 as additives. Membranes were made by using 15% PES, 75%NMP and 10% additive. Stability of additives was examined by keeping membranes in water and sodium hypochlorite solutions. It was found that stability of PEG and PVP in membrane matrix was much lower than Pluronic [7].

Amirilargani et al. made a research about effects of Tween 80 as a surfactant additive on morphology and performance of polyethersulfone membranes. Effect of Tween 80 additive on PES/polyethylene glycol (PEG)/n-methyl-2-pyrrolidone (NMP) system was investigated. SEM images showed that larger pores formed under skin layer of membranes by addition of Tween 80 which is a hydrophilic surfactant additive. It was attributed to the high miscibility of Tween 80 with the coagulant and porosity of the membrane increased with it. Pure water permeability of the membrane increased with the addition of Tween 80 from 54.2 to 203.4 L/h m² bar [24].

Rahimpour et al. worked on the effect of surfactants on performance of polyethersulfone ultrafiltration membranes. Sodium dodecyl sulphate (SDS) as anionic surfactant, cetyl trimethyl ammonium bromide (CTAB) as cationic surfactant and Triton X-100 as non-ionic surfactant was used in this study. These surfactants were added in different ratios to PES/PVP/DMAC system. With the use of surfactants, porosity of the support layer increased. By using Triton X-100 as additive, formation of large-finger like macrovoids were seen under skin layer of membranes. It was found that porosity of membranes with Triton X-100 additive was higher than others. This porous structure made water permeation of prepared membrane higher than others [25].

The additives used in membrane fabrication can also prevent irreversible adsorption of retained material on the membrane surface. Ma et al. examined protein resistant polyethersulfone flat sheet ultrafiltration membranes. For this purpose, membranes were made by using 18 wt% PES and 15 wt% PEG2000 in DMF solution and

various amounts of PS-b-PEG as membrane-modifying agent. Ultrafiltration experiments were done at constant pressure (100 kPa) with 1.0 mg/ml BSA PBS solution (pH 7.0) at a dead-end filtration system. In fouling test, firstly pure water flux of membranes were measured then BSA filtration occurred for 1 hour and membrane were cleaned. At last pure water flux of membranes was measured again. It was observed that PEO layer that was formed on membrane surface gave good anti-fouling properties to membranes. Moreover, flux recovery ratios of membranes were also investigated. It was observed that the flux recovery of membranes became higher when comparing to control PES membrane. When the PS-b-PEG content was 4.5%, flux recovery ratio became nearly 90% [26].

Wang et al. made a research about ultrafiltration performance of polyethersulfone membranes by using various types of Pluronic additives. In fouling experiments BSA concentration which was 1.0 mg/ml in PBS solution was used. These experiments were took place in four steps. Firstly pure water flux of membranes was measured then filtration of BSA solution occurred. After that water washing step was applied and pure water flux was measured again. It was found that membranes with additives showed better anti-fouling characteristics than PES membrane with respect to flux decline during filtration. It was observed that total and irreversible membrane fouling decreased when PEO chain length and density increased in Pluronic-PES blend membranes. Moreover, flux recovery ratios of membranes were examined by three repetitive ultrafiltration operations. It was observed that pure water flux of PES membrane went nearly zero at the end of second filtration cycle. Flux recovery ratios were found above 80% for membranes with Pluronic additives [27].

Zhao et al. investigated fabrication of PES ultrafiltration membranes by using Pluronic F-127 as additive. PES/Pluronic F-127 membranes were prepared in different ratios and compared with PES/PEG 2000 membrane. Due to the fouling experiments, it was found that Pluronic showed better antifouling properties. After three BSA solution filtrations, flux decline in Pluronic membranes were very low. Through the fouling analysis; the flux recovery ratio of Pluronic was above 90% while PEG was nearly 60%. It was attributed with the PPO group in Pluronic which make it stay in membrane matrix. Moreover, possible micelle formation and aggregation behavior may also affect the pore size of the skin layer which effects

fouling positively. These micelles can be extracted into the coagulation bath during the coagulation process and the spaces they once occupied may turn into the pores of the membranes [28].

In this study, PEO based additives (Pluronic F-127, PEG 10k and Triton X100) were used for preparing PES based hollow fiber membranes. The effect of additives and fabrication parameters such as water presence in polymer dope and temperature of coagulation bath on membrane morphologies was investigated. Then the fouling behavior of membranes prepared with different additives and without additive was compared in dead-end constant flux filtrations. The anti-fouling performance of a low molecular weight surfactant Triton was shown for the first time in literature. Also PEG and Pluronic additives, which have been used in several studies for anti-fouling have been compared for the first time in constant flux filtrations.

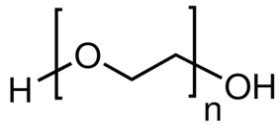
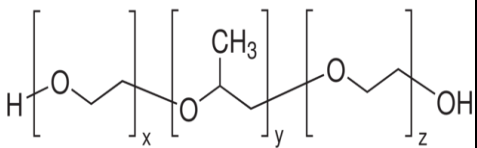
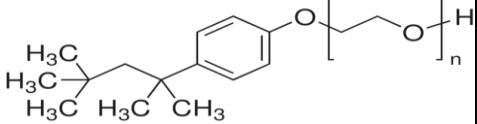
CHAPTER 3

EXPERIMENTAL METHODS

3.1. Materials

PES (Ultrason E6020P) was provided by BASF. N-methyl pyrrolidone (NMP, %99) was purchased from Sigma-Aldrich which was used as solvent. Ultrapure water was used as non-solvent in solution and tap water purified by Watermill Elegant 102 under bench water purifying device was used as coagulant. Additives which are Pluronic F-127 and Triton X100 were purchased from Sigma and PEG 10k was purchased from Fluka. Before use, PES was put in 80 °C vacuum oven for one night at atmospheric pressure. Pluronic F-127 and PEG 10k was also kept overnight in vacuum oven at room temperature.

Table 3.1. PEO based additives used in this study

additive	chemical formula	molecular weight	weight of PEO
Polyethylene glycol (PEG 10k)		10000 g/mol	100%
Pluronic F-127 (PEO-PPO-PEO)		12600 g/mol	67%
Triton X100		625 g/mol	65%

3.1.1. Cloud point experiments

Cloud point experiments were done to determine phase equilibrium for the polymer-additive-solvent-nonsolvent systems. For this purpose; part of the polymer-solvent-non-solvent phase diagrams were determined by titration.

Polymer solutions that were used in these experiments were prepared by dissolving fixed PES-additive ratio (3:1) in NMP. After preparing polymer solutions, 75% water- 25% NMP mixture added to solutions drop by drop. The reason of adding this mixture instead of only water is the local coagulation that takes place in polymer solution and the late homogenization of polymer solution after adding pure water. The average of the point that polymer solution become cloudy and the last point that clear solution is seen is defined as cloud point of polymer solution. Polymer solutions that have water as much as cloud point is defined as 100 % coagulation value and those that have less water was characterized by the coagulation value as follows [29];

$$\text{Coagulation value} = \frac{H_2O \text{ in polymer dope}}{H_2O \text{ at cloud point}}$$

Cloud point experiments were done two times for each additive and the given results were average of these experiments.

3.1.2. Light transmission experiments

Light transmission experiments were done to measure phase inversion rates of prepared polymer solutions. The setup that was used for this analysis is given in Figure 3.1. Similar setups were used in some researches for light transmission measurements [1,30]. In this system, a 42 W halogen lamp was used as light source and to spread the light white paper was put in front of the lamp. Light transmission was measured by Extech Instruments HD450 model light meter and recorded in computer every second.

For measuring light transmissions of polymer solutions; firstly polymer solutions were casted on a glass plate with 250 μm thickness. After that glass plate was immersed in coagulating bath which consisted of tap water (non-solvent). Light transmissions of polymer solutions were measured by time after they entered the water until membranes were formed completely. By these experiments, the starting point of phase inversion and average rate of phase inversion after starting were observed.

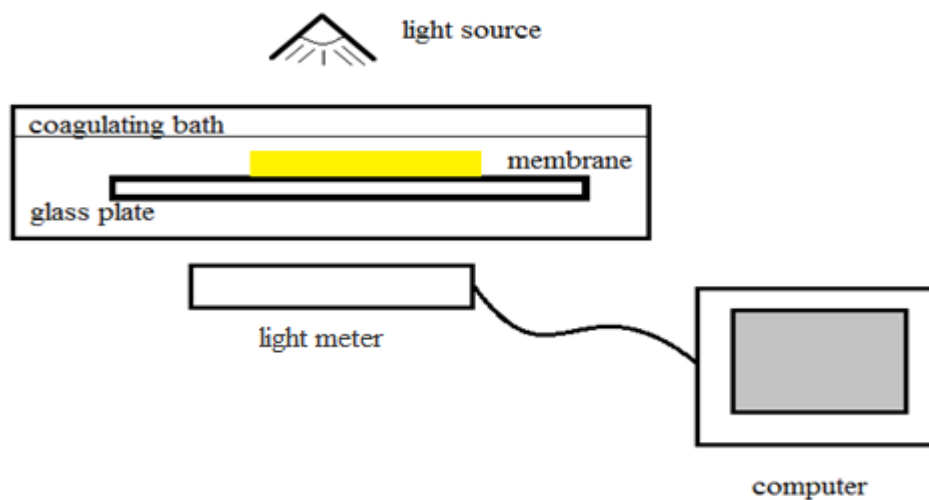


Figure 3.1. Equipment of light transmission experiments setup

Light transmission of each polymer solution was measured twice. The results were given with the standard deviation values. Polymer solutions were prepared with the same PES-additive ratio of 3:1. Moreover, PES-additive-water system was also examined by using 95% of coagulation values with again 3:1 PES additive ratio.

3.2 Membrane Preparation

3.2.1. Hollow fiber membranes

Hollow fiber membranes were prepared with a PES-additive ratio of 3:1. Membranes were prepared by using Pluronic F-127, PEG 10k and Triton X100 as additives. Spinning set up of tight ultrafiltration hollow fiber membranes were given in Figure 3.2. In this system, polymer solution was pumped by setting take-up speed (spinning rate) and pressure of gas together. Spinning rate was fixed and the nitrogen gas flow rate to the polymer tank was adjusted such that the fiber experienced no stretching. Bore liquid rate is fixed with the peristaltic pump which consist of NMP and water.

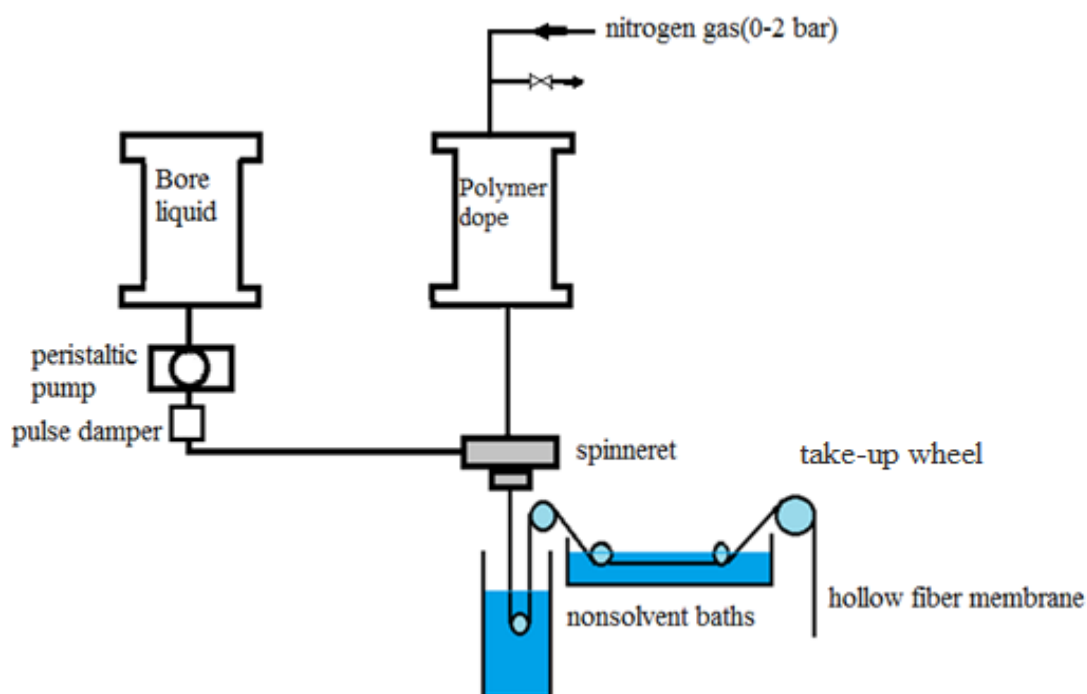


Figure 3.2. Hollow fiber spinning set up

The spinneret was made by FAYMER Makina, OSTİM, ANKARA. Internal diameter of spinneret orifice is 1.3 mm and outer diameter is 3 mm. In Figure 3.3, schematic presentation (a) and picture (b) of spinneret is seen. The bore liquid enters the spinneret through the inner hole and forms the bore part of the hollow fiber membrane. Polymer dope enters the spinneret through the annulus and they do not mixed or touch each other before leaving the spinneret.

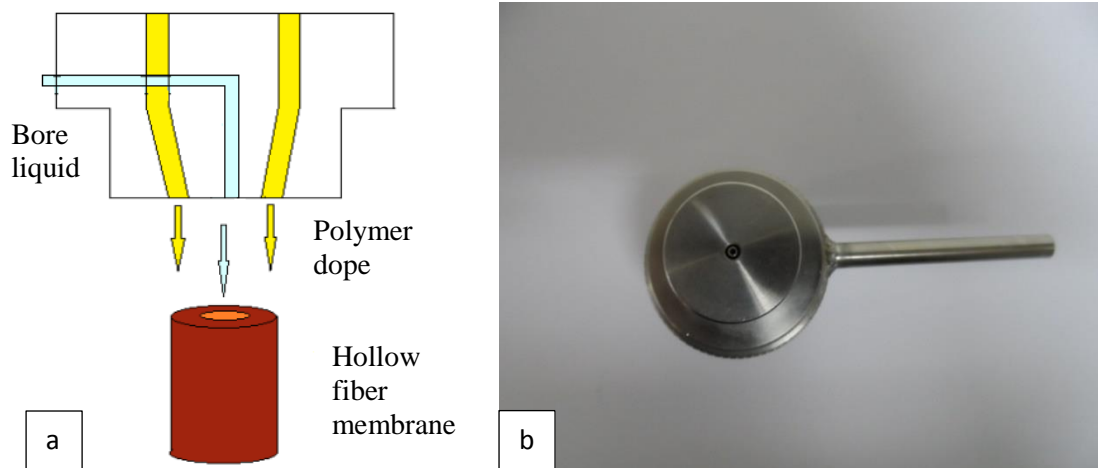


Figure 3.3. Spinneret (a,b)

There are two non-solvent baths in the spinning system. First bath has 270 L and second bath has 100 L volume. The first spinning wheel is in this bath and it can move for making easier the spinning of hollow fiber membranes. Other spinning wheels are fixed except the last one. This last spinning wheel has 16.5 cm diameter and can rotate 3-19 m/s rate by control. After passing the last spinning wheel, hollow fiber membranes enter a bucket which is 55 L volume and has water in it. When the hollow fiber spinning procedure is completed, membranes are washed with renewed tap water for one day. At last, hollow fiber membranes stay in 10% glycerol- 90% pure water solution one day. The purpose of this is to prevent collapsing of pores when they dried.

Loose ultrafiltration hollow fiber membranes were prepared with the new system. In this system gear pumps were used to pump the polymer dope and bore liquid. The picture of this part is given in Figure 3.4. There is no change in the rest of the system. Polymer dope and bore liquid rates were controlled via the electric panel.

In both spinning systems, circulation water baths are used for heating water in coagulation bath. JSR JSIB-50T circulation water bath is used for heating water up to 55 °C. Coagulation bath water temperatures can be achieved maximum 5 °C lower than circulation bath temperature. All parts of hollow fiber spinning systems were made in METU Chemical Engineering Department Workshop except spinneret, pumps and circulation water bath.



Figure 3.4. Hollow fiber spinning system with polymer dope and bore liquid pumps

In hollow fiber membranes, several parameters effect on membrane morphology and performance were examined. Firstly membranes were prepared with different polymer dope and spinning rates. Then these two parameters were fixed and bore liquid composition effect on membrane structure and performance was examined. Then water content effect in polymer dope was examined at 18 - 50 °C coagulation bath temperature. These parameters effect and additives effect on hollow fiber membrane performance were considered.

3.3 Characterization of Membranes

3.3.1 Pure Water Permeance

Pure water permeance of hollow fiber membranes were measured at two different pressures which were 0.5 and 1 bar. Several data were taken according to time at each pressure and when the measured value was fixed, it was taken as pure water flux of membrane at that pressure. Pure water permeance of membranes was calculated according to the following equation.

$$\text{Pure water permeance} = \frac{Q}{\Delta P \times A} \quad [9]$$

Q: permeate collected over a duration of time (L/h)

ΔP : pressure difference between feed and permeate side (bar)

A : area of the hollow fiber membrane (m²)

In each hollow fiber membrane set, measurements were done two or three times in different membrane modules and results are given as the average values of these measurements.

The schematic presentation and picture of the pure water permeance system are given in Figure 3.5 and Figure 3.6 respectively. The system is made to have a constant pressure between membranes feed and permeate side by dead-end set up. The permeate side of the membrane is open to atmospheric pressure and feed part is open to gas where the pressure is arranged.

Hollow fiber membranes were used in membrane modules in all filtration systems which separate feed and permeate parts of membranes. Membrane modules were prepared by putting hollow fiber membranes in plastic tubes which has 6 mm outer diameter and 4 mm inner diameter. The space between feed and permeate of membranes were filled with a two component transparent epoxy which is Bison[®]. When the epoxy solidified, there is no leak between feed and permeate part.

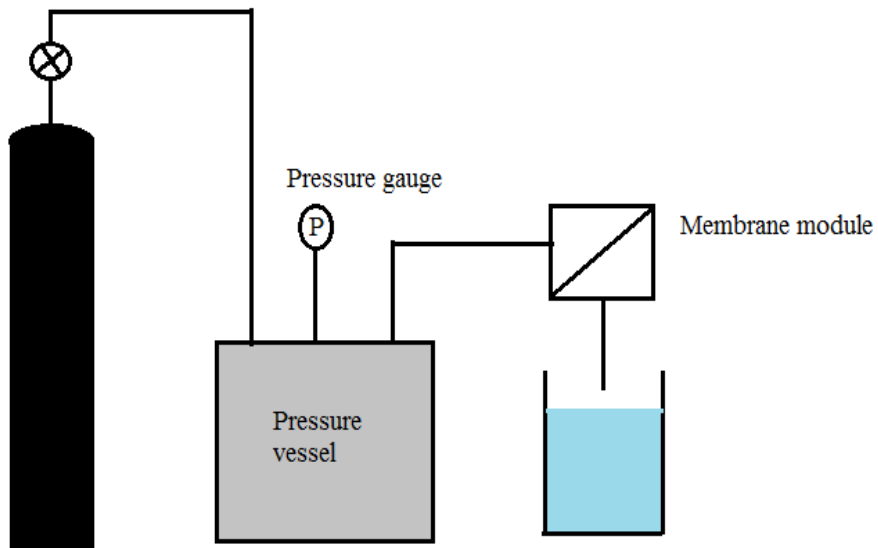


Figure 3.5. Schematic presentation of pure water permeance set up for hollow fiber membranes

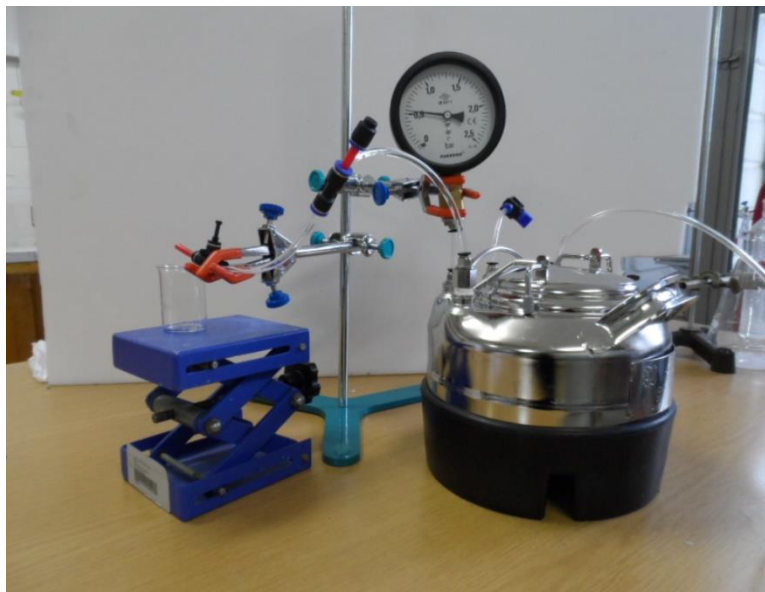


Figure 3.6. Pure water permeance set up picture of hollow fiber membranes

3.3.2 Retention test

Bovine serum albumin (BSA) which is a globular protein (~66,000 Da) purchased from Sigma-Aldrich is a commonly used model protein in membrane filtration applications for observing separation performances [7,10,28]. Feed that was used in this system is 1 g/L BSA solution which was dissolved in buffered solution (PBS, Phosphate Buffered Saline) with pH=7.4. Retention tests were done in cross-flow at 360 ml/min feed flow rate using a peristaltic pump with a pulse dampener. Tests were done at 0.2 or 0.5 bar pressure and measured for two or three times for each hollow fiber membrane set. The results are given by taking average values of these measurements.

During the filtration, samples were taken from feed, permeate and retentate lines. BSA concentrations in these solutions were measured by using UV absorbance (Shimadzu UV-255 UV-VIS Spectrophotometer) at 280 nm. Retention of membranes were calculated by the following equation [28].

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

C_p = permeate BSA concentration

C_f = feed BSA concentration

The schematic presentation (a) and picture (b) of retention test set up are given in Figure 3.7 and Figure 3.8. In this system, fixed pressure is obtained between feed and permeate. The permeate part of membrane module is open to atmospheric pressure. In the feed and retentate part, the pressure is kept constant by a controllable valve which is on retentate line and keeps the pressure higher than atmospheric pressure. For having cross flow in the system, a peristaltic pump is used. A pulse damper is used for preventing pulses that comes from peristaltic pump.

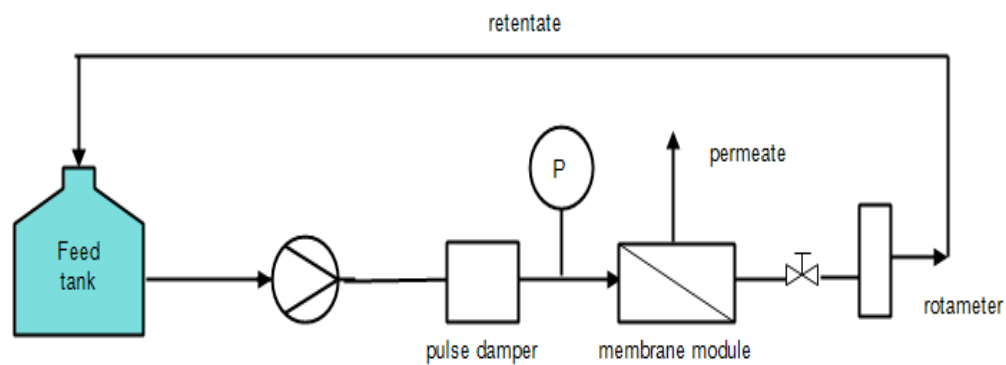


Figure 3.7. Schematic presentation of retention test set up for hollow fiber membranes



Figure 3.8. Retention test set up picture of hollow fiber membranes

3.3.3 Membrane Morphology Analysis

The connectivity between pores, porosity of membrane skin layer and pore sizes of membranes are important parameters that determine membranes performances. For examining these properties; membrane morphologies were determined by scanning electron microscopy (SEM) analysis (FEI Quanta-400 F).

Membranes were broken in liquid nitrogen and were placed vertically on carbon tape for cross section analysis. Moreover, surface analysis also done by placing membranes horizontally. Before SEM, membranes were coated by gold/palladium to have an electrically conductive layer. Images were taken between 200x to 100000x magnifications.

3.3.4 Additive Stability Measurements

Additives were used to enhance hollow fiber membranes performance and anti-fouling properties. During the membrane formation process; some part of additives stay in membrane matrix and some of them are leached due to the interaction of additives with PES and water (non-solvent) [7,9]. Surface chemistry and stability of additives in membrane matrix was examined by Fourier transform infrared spectroscopy (FTIR) analysis. For FTIR analysis, IR-PRESTIGE-21 SCHIMADZU device is used. The resolution of the device is 1 cm^{-1} and the spectra of hollow fiber membranes were taken between 698 to 4000 cm^{-1} wavenumber.

For stability analysis, prepared hollow fiber membranes were kept in two different solutions for 60 days. First solution is pure water which has 0.25 % weight sodium bisulfite to prevent microbial growth. Sodium bisulfite was purchased from Sigma-Aldrich (purum-40%). Second solution is 400 mg/L sodium hypochlorite solution in pure water. Sodium hypochlorite solution is commonly used as chemical cleaning agent to remove fouling of membranes [7]. It is purchased from Merck (16-14% active chlorine). Stability of additives in PF, PT, P and PP (tight ultrafiltration group) and PFWH, PTWH, PWH and PPWH (loose ultrafiltration group) were examined by FTIR. For each membrane, samples were taken every 15 days. As such, there have been five samples for each membrane (0th day, 15th day, 30th day, 45th day and 60th day). In both water and sodium hypochlorite solutions, solutions were refreshed in every 3 or 4 days. Taken samples were washed with water and dried in vacuum before FTIR measurements. By analyzing these samples, stability of additives in hollow fiber membranes was examined in physical (water) and chemical cleaning agent (sodium hypochlorite) as a function of time. Moreover, pure additives and pure PES FTIR spectra were also examined.

FTIR measurement results in membranes were given by using I_r (relative peak increase). From FTIR measurements, three peak values were taken which are 1105, 1578 and 2865 cm^{-1} which refer to the bonds in PES (1578) and additives. $I_{x/y}$ can be defined as the ratios of these peaks ($x/y=1105/1578$ or $2865 /1578$) in the spectra of a membrane with or without additive. For calculating I_r values; the $I_{x/y}$ ratio of membrane with additive to that of pure PES membrane was determined as follows;

$$I_r(1105/1578) = \frac{(I_{1105/1578})_{\text{membrane with additive}}}{(I_{1105/1578})_{\text{pure PES membrane}}}$$

3.3.5 Burst Pressure Measurements

Mechanical strength is another important parameter in hollow fiber membrane applications. For this purpose, burst pressure test were done. The schematic presentation of burst pressure test system is given in Figure 3.9. In this system membranes are placed in modules. The upper part of module is filled with epoxy and the other end of fiber is closed with silicon glue. A little part of module is cut in the upper part to have the hollow fiber membranes bore part open. At last this upper part is connected to a gas tube. The pressure of the gas was increased gradually. When the pressure fell down suddenly which means membrane is exploded the pressure was defined as burst pressure of hollow fiber membrane. For each membrane group, burst pressure measurements were done two or three times. Results are given as the average value of these measurements. By burst pressure results, the maximum pressure the fibers can be used was determined.

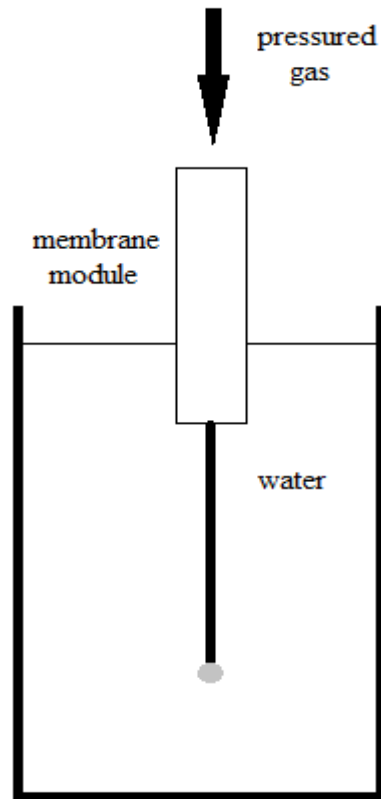


Figure 3.9. Schematic presentation of burst pressure analysis set up

3.4.Membrane Fouling

A dead-end filtration set up was used for fouling analysis of hollow fiber membranes. Schematic presentation of fouling test system is given in Figure 3.10 and picture of fouling test system is given in Figure 3.11. Before starting filtration analyses, pressure transmitters were connected to computer and comparison tests were made with analog pressure gauges. Peristaltic pumps which are in feed and backwash line were connected with the mass flow controller devices and these systems were tested. By the usage of mass flow controller, the desired flux can be reached in 20-30 seconds and become stable at that value.

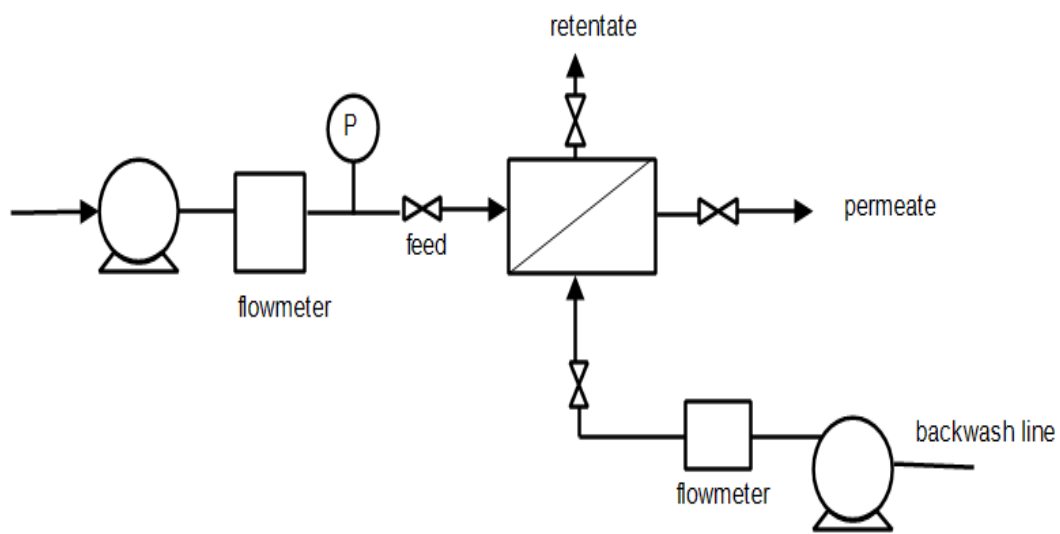


Figure 3.10. Schematic presentation of fouling test set up for hollow fiber membranes

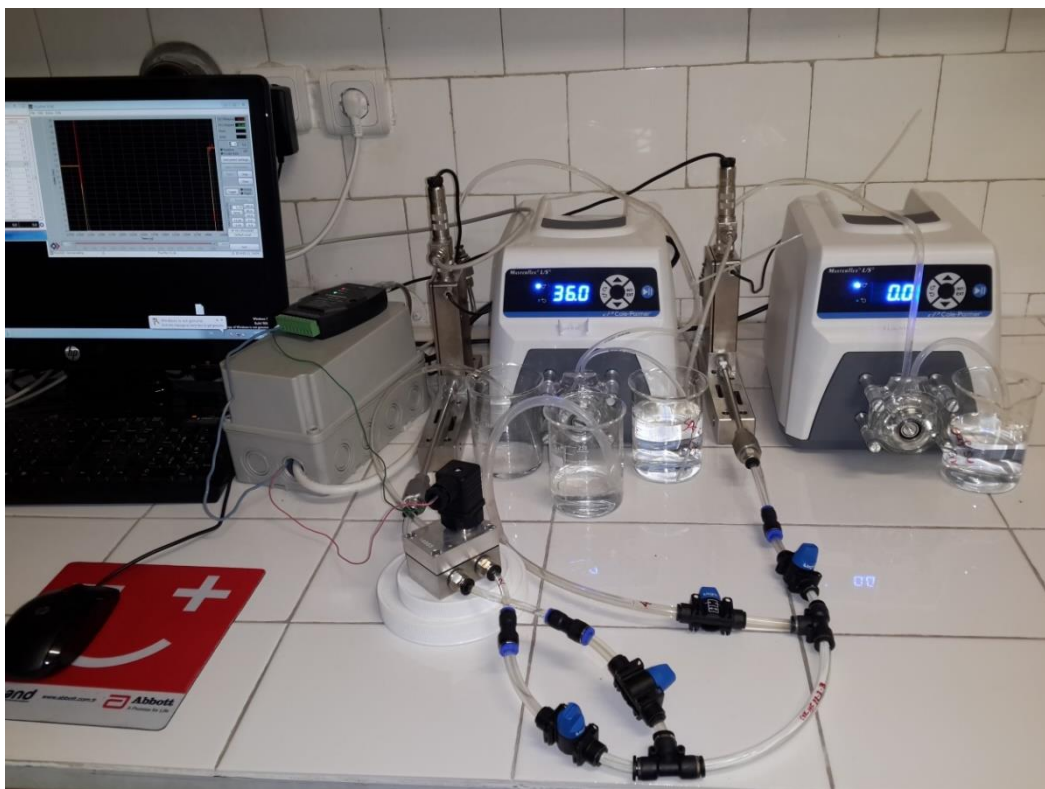


Figure 3.11. Fouling test set up picture of hollow fiber membranes

In fouling test experiments, firstly pure water permeance of membrane is measured. Then five filtration cycles at for 15 minutes (except for PES membrane where 45 minutes) takes place. Tests are done with 30 L/h. m² constant flux except for PES membrane (5 L/h.m²). In this membrane, the pure water permeance values are very low so high pressures are needed for having 30 L/h. m² constant flux which is not suitable for the fouling test system. For that reason, 5 L/h. m² constant flux is used for that membrane. At the end of each cycle, backwash with 60 L/h. m² for 3 minutes is applied to membranes except for PES membrane (10 L/h.m²). After physical cleaning by pure water, pure water permeance of membrane is measured again. Following the physical cleaning, chemical cleaning is applied to membranes. For chemical cleaning, alkali (NaOH -pH=13) and acid (HCl- pH=1) are used in turn. Membrane modules are kept in each solution for 20 minutes. Finally pure water permeance of membrane is measured again. The feed solution that is used in fouling tests is 1g /L BSA solution which is dissolved in Phosphate buffered saline (PBS) solution with pH=7.4. This fouling test procedure is applied for prepared tight ultrafiltration hollow fiber membrane group (PT, PP, PH and PFR) and given in APPENDIX C. Membrane modules are prepared from plastic tubes with 6 mm inner diameter by using 5 or 6 hollow fiber membranes from each set to have a membrane area between 3x10⁻³ to 5x10⁻³ m².

For loose ultrafiltration membrane set (PFWH, PTWH, PWH and PPWH), a different fouling test procedure is applied. No backwash is applied in this group. When the backwash applied, the silicon tube in backwash line start to expand. Because of these problems in the system, one filtration apply to membrane without backwash then pure water flush and pure water permeance is measured to compare the amount of material deposited in or on the membrane from the difference in resistance to pure water flow before and after BSA fouling. In this group, 30 L/h. m² constant flux is applied to all membranes.

In fouling tests, pressure change vs time data were taken and membrane fouling resistances were calculated for each membrane. The effect of physical and chemical cleaning on membrane performance was also observed and comparisons were done among additives. Fouling tests were done twice for each hollow fiber membrane set and results are given as average values of these analysis.

In fouling test experiments, following relationship is used for determining resistance values;

$$J = \frac{TMP}{\mu (R_{mem} + R_{fouling})}$$

J: permeation flux during BSA solution filtration,

TMP: transmembrane pressure during BSA solution filtration,

μ : viscosity of permeate,

R_{mem} : clean membrane resistance, $R_{mem} = \left(\frac{TMP}{J} \right)_{\text{pure water}} \times \frac{1}{\mu}$

$R_{fouling}$: membrane fouling resistance, [31].

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Phase inversion analysis

In NIPS method, resulting morphologies of membranes are related to thermodynamic properties of the polymer-solvent-nonsolvent system and phase inversion rates of the polymer solution that is used to prepare membranes [1,15,32]. To determine the phase equilibrium behavior of membranes cloud point measurements were done and light transmission analysis of polymer solutions during coagulation were made to determine coagulation kinetics of polymer solutions.

4.1.1. Cloud point experiments

Part of the binodal curve on the ternary phase diagram of polymer-solvent-nonsolvent system is formed with cloud point experiments. Cloud point measurements were done by using different PES-additive-NMP compositions all with 3:1 PES: additive ratio. In Figure 4.1, the cloud point measurements of PES-NMP-water system is shown. The measurements were done by using polymer contents between 10%-30%. The results show that the water content of polymer solutions at cloud points is nearly 10%. These values are similar to the data reported in literature [33]. In Figure 4.2; cloud point measurements of PES-NMP-additive-water systems are seen and it is also found that they also have cloud points near 10%.

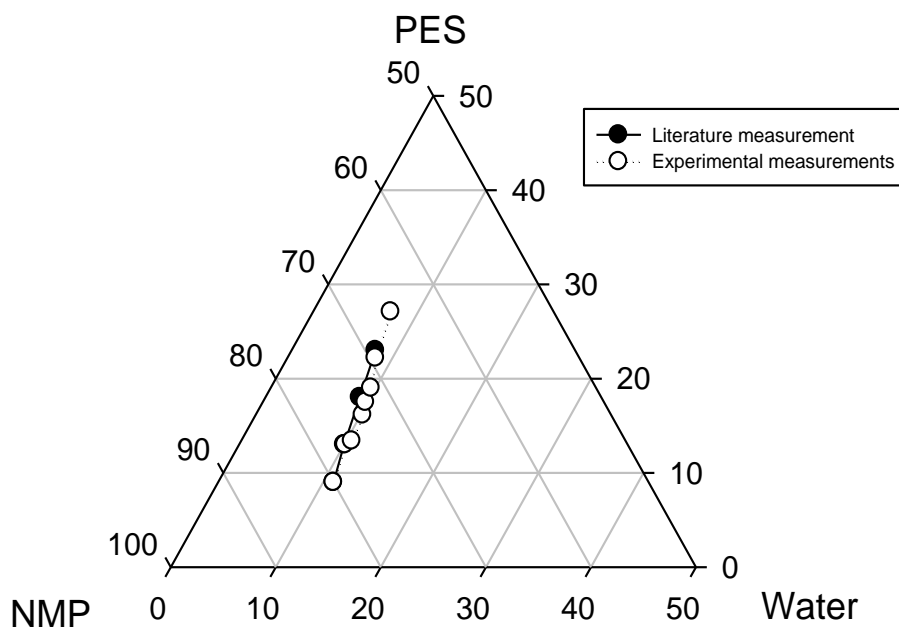


Figure 4.1. Cloud points of PES-NMP-water system

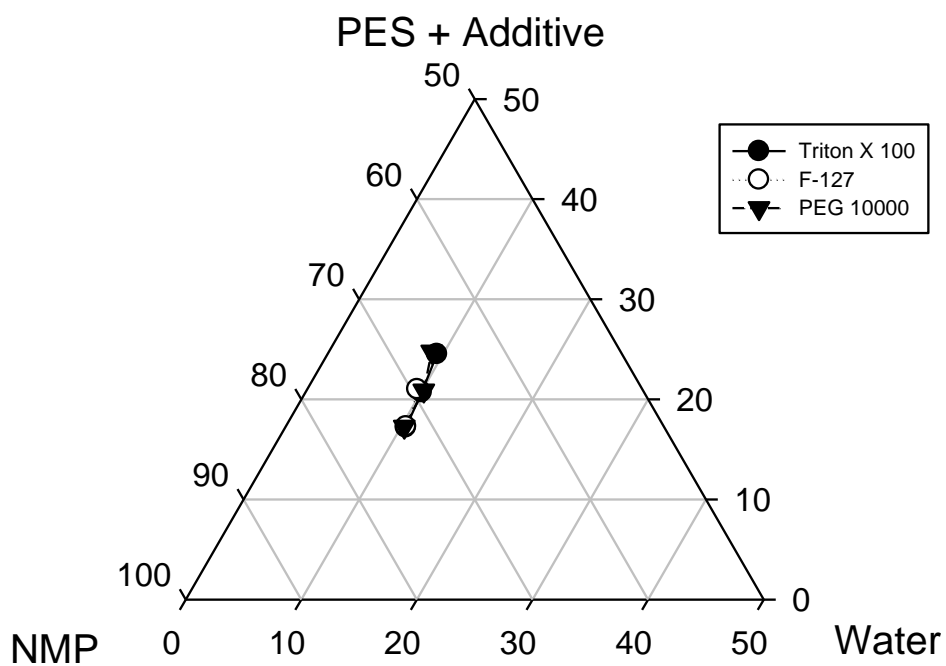


Figure 4.2. Cloud points of PES-NMP-additive-water system

4.1.2. Light transmission experiments

Light transmission experiments were done for observing phase inversion rates and precipitation kinetics of prepared membranes. In phase inversion rate analysis; some of the membranes were prepared by using water in polymer solution which is 95% of cloud point values. List of the polymer solutions that were examined in light transmission analysis are given in Table 4.1. These measurements were done for preparing hollow fiber membranes. The results of this analysis are given in Figure 4.3 and 4.4. In these figures; I represents the light transmission value at any time and I_0 represent the light transmission value at $t=0$ at which coagulant (water) was introduced. It is seen from figures that, there is a sharp decrease in light transmission values at the beginning of implying rapid phase inversion with no time delay. After that, light transmission values decrease much more slowly for each membrane which shows phase inversion of membrane is mostly completed. For examining the difference between only PES membrane and membranes with additives, the part that $I/I_0=1$ to $I/I_0=0.4$ of the figures where a sharp, nearly linear drop in light transmission are examined.

Initial phase inversion rate is compared using the slope between $I/I_0=1$ to $I/I_0=0.4$ in Figure 4.3 and Figure 4.4. In Figure 4.3, the change between $I/I_0=1$ to $I/I_0=0.4$ values exist in first 10 seconds of the light transmission analysis. The phase inversion rate order between these membranes are $P > PF > PP > PT$ ($0.9 \text{ s}^{-1} > 0.86 \text{ s}^{-1} > 0.84 \text{ s}^{-1} > 0.8 \text{ s}^{-1}$). In Figure 4.4, the change between $I/I_0=1$ to $I/I_0=0.4$ values exist in at first 5 seconds of the light transmission analysis. The phase inversion rate order between these membranes are $PW > PFW > PTW > PPW$ ($1 \text{ s}^{-1} > 0.95 \text{ s}^{-1} > 0.91 \text{ s}^{-1} > 0.9 \text{ s}^{-1}$). It is seen from Figure 4.3 and 4.4 that; membranes which have water in the polymer solution have higher phase inversion rates than membranes without having water in polymer solution. This can be due to the fact that; polymer solutions which have water in it start phase inversion earlier and since the light transmission is measured as a cumulative value from the whole cross-section of the polymer film they seem faster comparing to the other polymer solutions without water. Polymer solutions with and without additives have similar phase inversion rate. The initial rapid decrease observed in light transmission values in figures which is considered to be

related with the phase separation of the skin layer. After that point, a slower decrease took place which is probably related with phase separation of sublayer.

Table 4.1. Polymer solutions which are examined in light transmission measurements

Membrane name	PES	NMP	Additive	Water
P	%20	%80	-	-
PT	%15	%80	%5 Triton X100	-
PF	%15	%80	%5 Pluronic F-127	-
PP	%15	%80	%5 PEG 10000	-
PW	%15	%71.35	-	%8.65
PTW	%15	%70	%5 Triton X100	%10
PFW	%15	%70.52	%5 Pluronic F-127	%9.48
PPW	%15	%70.85	%5 PEG 10000	%9.15

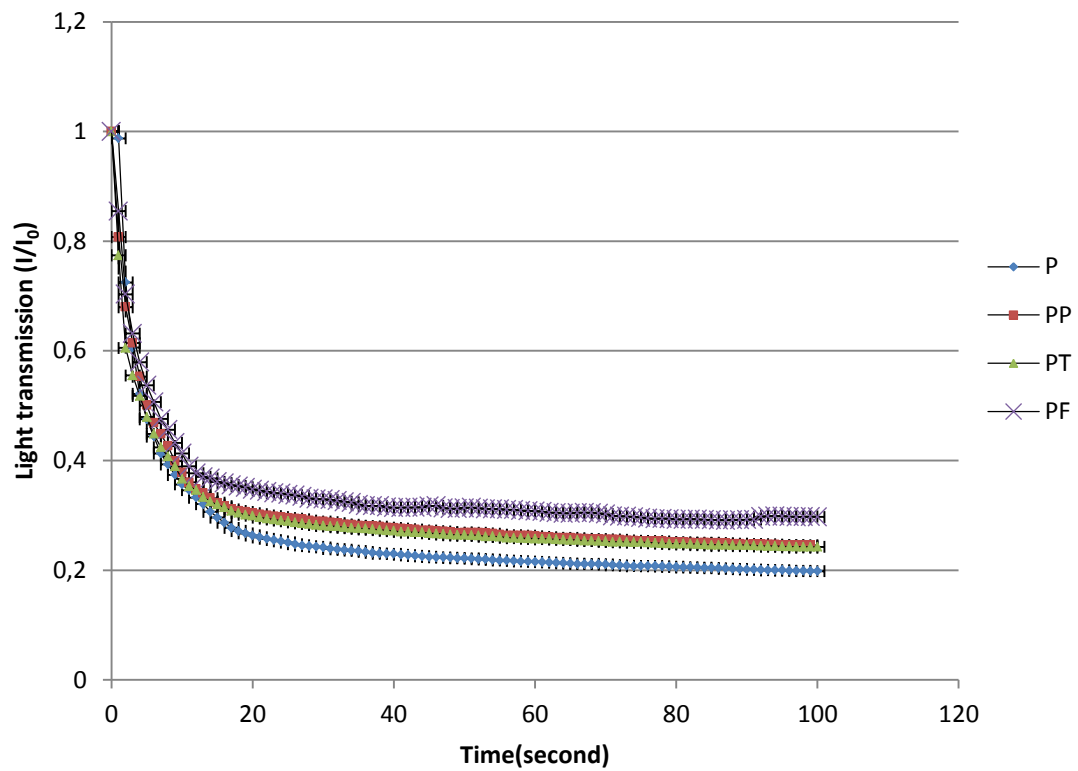


Figure 4.3. Light transmission measurement graphs of different polymer solutions

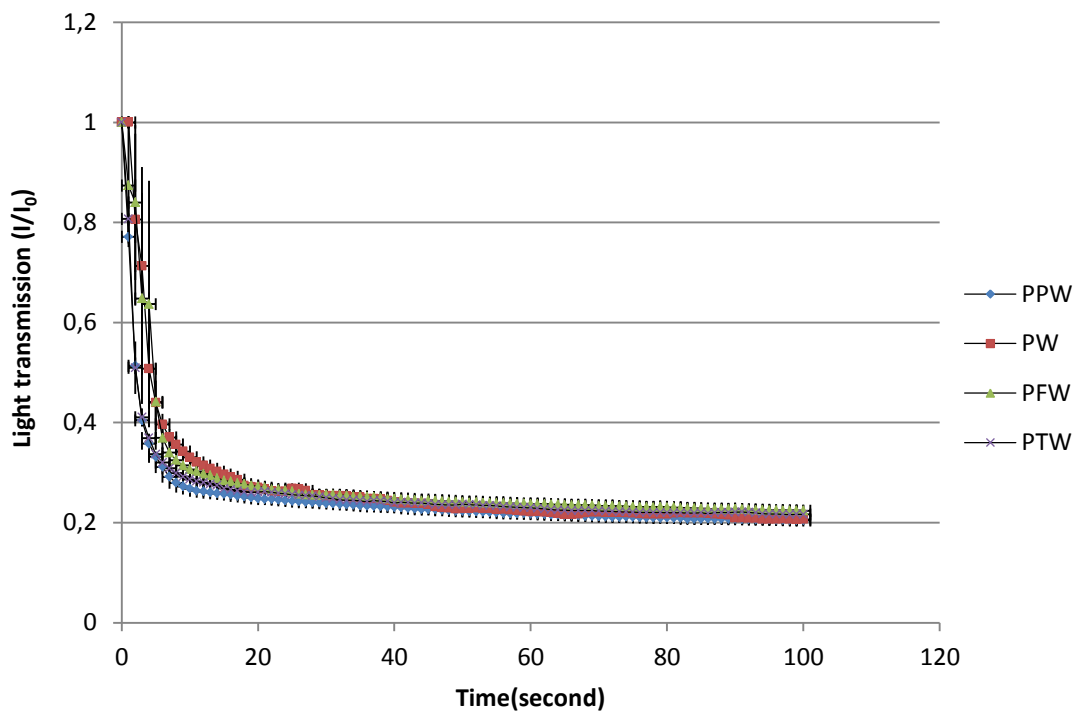


Figure 4.4. Light transmission measurement graphs of different polymer solutions

4.2.Hollow fiber membranes

PEG 10k, Pluronic F-127 and Triton X100 were used as additives in hollow fiber membrane preparation. Figure 4.5 shows the morphologic structure of the synthesized hollow fiber membranes on PPW membrane. It is observed that the membrane has an asymmetric structure with a selective skin layer at outside part of the membrane. In the inner part; macroporous structure is seen which acts as support layer. These similar structures were seen in all hollow fiber membranes. This structure is quite typical in hollow fiber membranes that are prepared with non-solvent induced phase separation method [9,34].

From most of the images; it is seen that the bore of the membrane is not centered; it is due to the spinneret bore not being exactly eccentric but it is not expected to have significant effect on membrane performance since it is the skin layer which determines the membranes separation behavior.

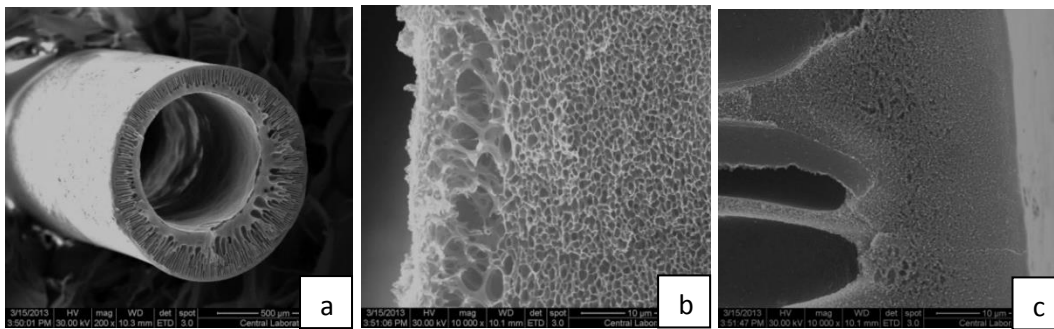


Figure 4.5. PPW (%15 PES-%5 PEG 10k- %80 NMP-water) a) cross section b) inner surface c) outer surface images

4.2.1. Effect of bore liquid flow rate and spinning rate

Before determining spinning conditions to use firstly, the effect of using different bore liquid flow rates and spinning rates were examined. To observe bore liquid and spinning rate effect PN and PNW membrane series were synthesized in different bore liquid and spinning rates which is given in Table 4.2. All membranes were prepared at 2 cm air gap at 20⁰C tap water coagulation bath and at 18⁰C room temperature.

Table 4.2. Effect of bore liquid rate and spinning rate

	Dope liquid	Spinning rate (m/min)	Bore liquid	Bore liquid flow rate (ml/min)
PN-1	%20 PES-%80 NMP	6.24	%80 NMP-%20 water	2.7
PN-2	%20 PES-%80 NMP	9.36	%80 NMP-%20 water	2.7
PN-3	%20 PES-%80 NMP	9.36	%80 NMP-%20 water	1.56
PN-4	%20 PES-%80 NMP	9.36	%80 NMP-%20 water	2.04
PN-5	%20 PES-%80 NMP	11.01	%80 NMP-%20 water	2.04
PNW-1	%20 PES- %71.35 NMP -%8.65 water	9.36	%80 NMP-%20 water	2.7
PNW-3	%20 PES- %71.35 NMP -%8.65 water	9.36	%80 NMP-%20 water	1.56

In PN series; in sample 2, 3 and 4 same spinning rates and different bore liquid rates were used. It is observed that bore diameter of membranes become a little smaller in PN-3 comparing to PN-2 and PN-4. Their morphological structures which include macrovoids and pores in membranes are nearly same. The bore liquid rates are same and spinning rates are different in sample 1-2 and sample 4-5 pairs. The wall of the membranes become thicker with increasing spinning rate and the bore of membrane becomes smaller. Cross section images of PN hollow fiber membrane series is given in Figure 4.6.

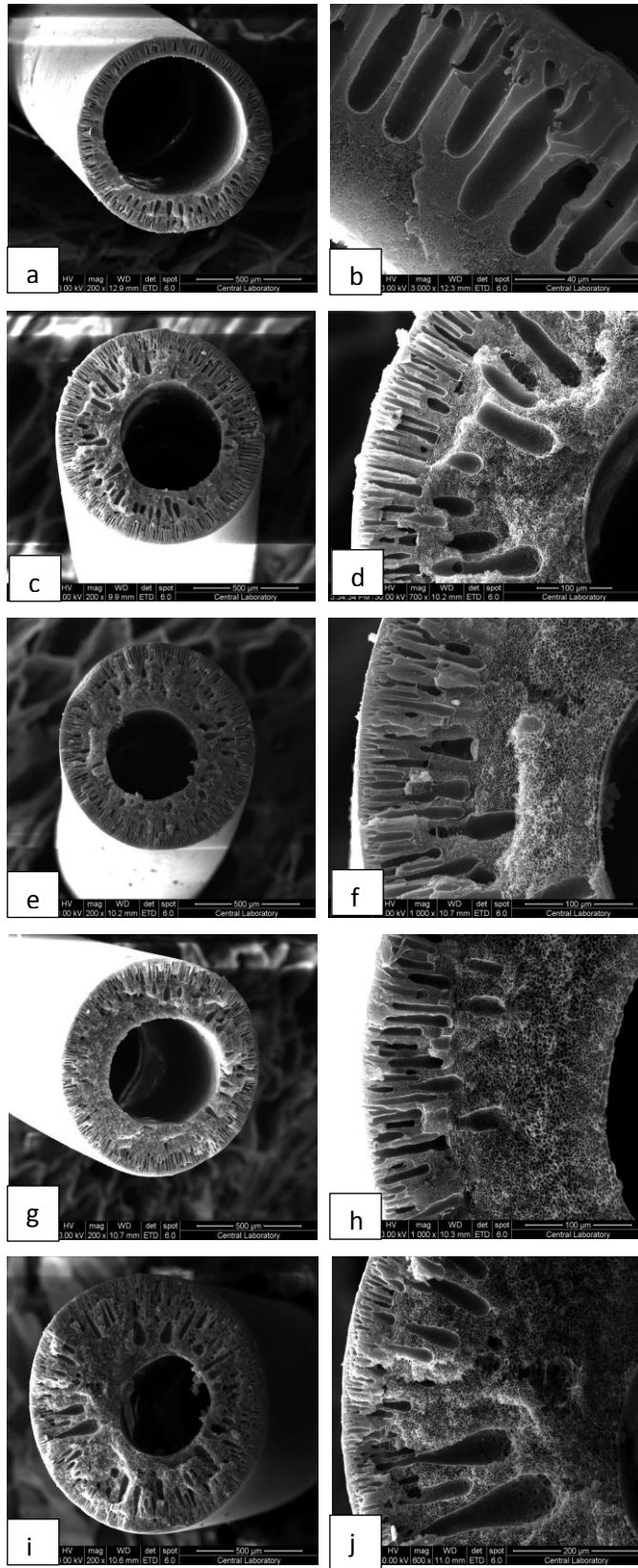


Figure 4.6. Cross section images of PN-1 (a,b), PN-2 (c,d), PN-3 (e,f), PN-4 (g,h), PN-5 (i,j) hollow fiber membranes. (The second column of images are in different magnifications)

In Figure 4.7, cross section images of PNW hollow fiber membrane series are given. In this membrane series, macrovoid formation becomes less comparing to PN hollow fiber series. This is attributed to the water that is used in polymer solution during membrane preparation. Water usage in polymer solution changes solvent-nonsolvent exchange rate and morphology of membranes. When the spinning conditions of PNW hollow fiber membrane series is examined, it is seen that at the same spinning rate, bore diameter of membranes are increasing due to the increase in bore liquid rate. This change was also seen in the PN series.

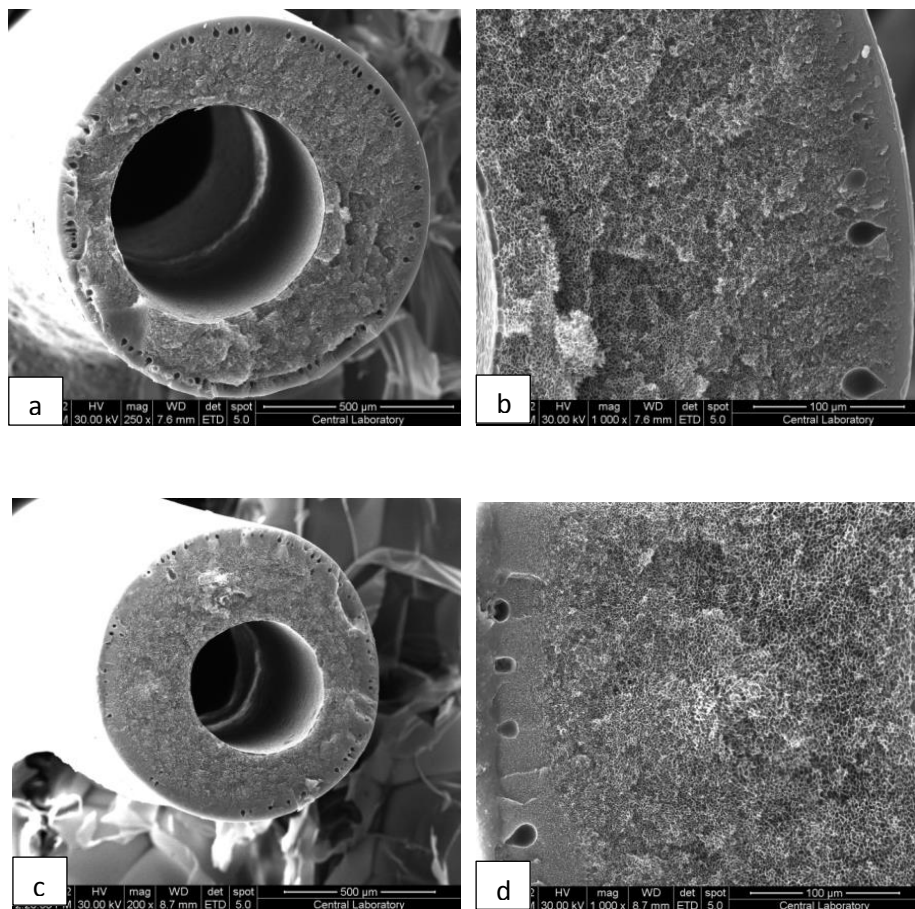


Figure 4.7. Cross section images of PNW-1 (a,b), PNW-3 (c,d) hollow fiber membranes (The first column of images are in different magnifications)

4.2.2. Effect of bore liquid composition

Another parameter that was examined is the bore liquid composition effect on membrane structure and performance. During hollow fiber membranes preparation, bore liquid composition was used which contains high percentage of solvent. This was done to have the selective skin layer at the outer surface of the membrane. Table 4.3 shows PF and PFW hollow fiber membranes which were prepared with three different bore liquid compositions. All membranes were prepared at 2 cm air gap with 9.36 m/min spinning rate and 2.7 ml/min bore liquid flow rates. Sample 3 in both sets which have 90% NMP- 10% water bore liquid composition is not very strong compared to others. It shows that when the NMP content in bore liquid is high, it may affect endurance of membrane badly. Performance analysis of sample 3 in both sets could not be done healthy, because some membranes burst during filtration analysis due to durability problems.

Table 4.3. Effect of different bore liquid composition

	Dope liquid	Bore liquid	Coagulation bath temperature (°C)	Room temperature (°C)
PF-1	% 15 PES- %5 F-127- %80 NMP	%70 NMP- %30 WATER	20.4	18
PF-2	% 15 PES- %5 F-127- %80 NMP	%80 NMP- %20 WATER	20.4	18
PF-3	% 15 PES- %5 F-127- %80 NMP	%90 NMP- %10 WATER	20.4	18
PFW-1	% 15 PES- %5 F-127- %70.8 NMP- %9.2 water	%70 NMP- %30 WATER	15.2	19
PFW-2	% 15 PES- %5 F-127- %70.8 NMP- %9.2 water	%80 NMP- %20 WATER	15.2	19
PFW-3	% 15 PES- %5 F-127- %70.8 NMP- %9.2 water	%90 NMP- %10 WATER	15.2	19

Morphology of PFW series is examined in Figure 4.8. In third row in Figure 4.8, inner part images of PFW set is seen. When non-solvent content increases, porosity in inner part of the membrane increases. Moreover, when the water content of bore liquid increases; there is another skin layer formed in inner surface of the membrane which may effects membrane performance. These similar morphologies are also seen in PF hollow fiber membrane series.

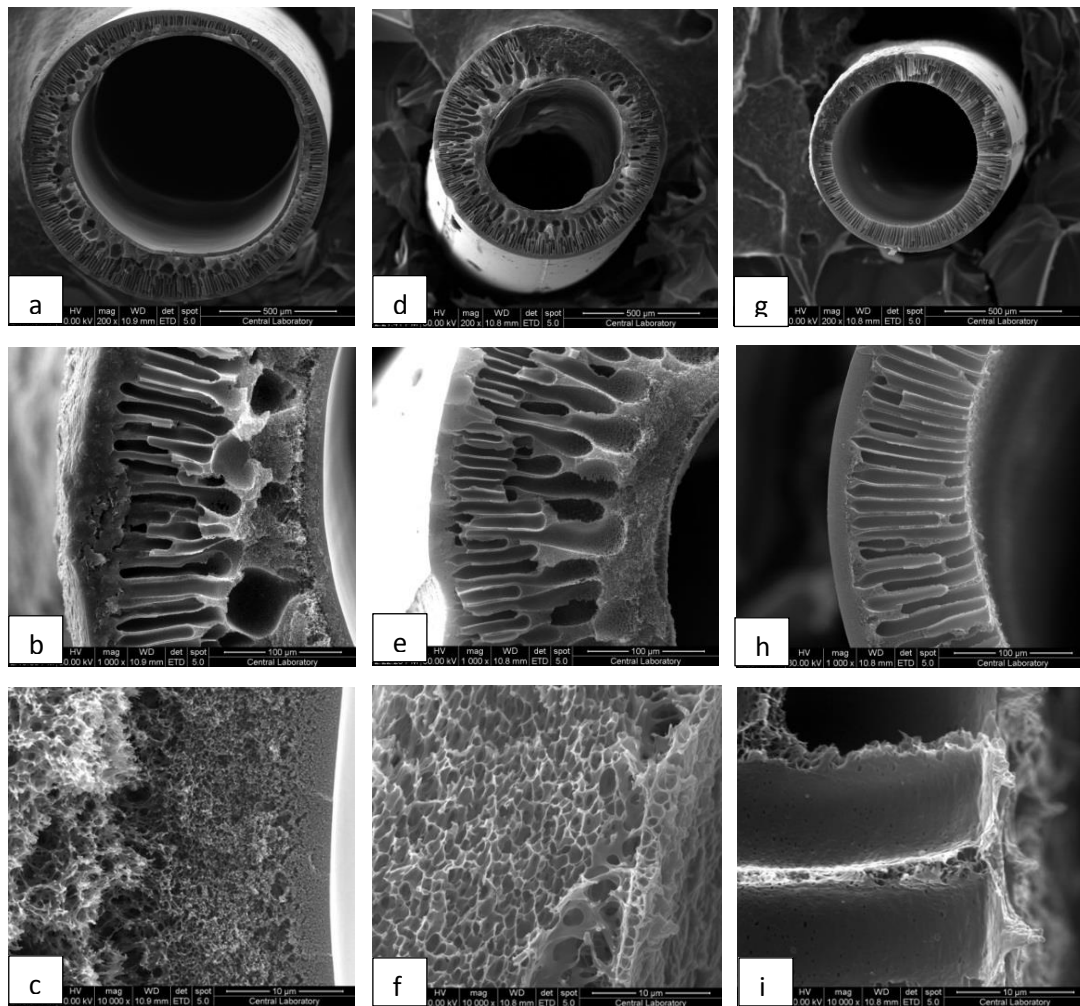


Figure 4.8. Cross section and inner part images of PFW membrane series, PFW-1 (a,b,c), PFW-2 (d,e,f), PFW-3 (g,h,i).

Pure water permeance and retention results of PF and PFW series are given in Table 4.4. In both sets permeance and retention tests of third series are hard because of the durability problem of membranes. It may due to the thinner membrane wall, permeance was not fixed easily and it was not possible to measure in PF-3 membranes. Between other two series, higher permeance and retention values are

seen in second sets which are PF-2 and PFW-2. It can be due to the low water content in bore liquids than PF-1 and PFW-1 sets. When 70wt %NMP solution was used as bore liquid, inner surface arrived to the coagulation composition sooner [17]. Due to that, there is a thin another skin layer formed which reduces membranes permeance values. On the other hand, it was observed that retention value of PF-1 membrane was lower than PF-2 membrane similarly for PFW-1 and PFW-2 membranes. This situation might be related with the pore size distributions in the skin layers. Moreover, when an inner skin forms, although the coagulant is same for the outer surface the coagulation conditions may be different which might effects retention of membranes.

Table 4.4. Pure water permeance and retention results of PF and PFW series

	Pure water permeance (L/m².h.bar)	Retention (%)
PF-1	55±3	79±1
PF-2	72±1	92
PF-3	-	-
PFW-1	39±8	79±1
PFW-2	66±7	90±2
PFW-3	77±7	94±1

4.2.3.Effect of water in polymer dope

Using a non-solvent (water) in polymer dope is another parameter that effect membranes morphology and performances. List of the synthesized membranes to investigate additive and water effect on hollow fiber membranes are given in Table 4.5. All membranes were prepared at 2 cm air gap with 9.36 m/min spinning rate and 2.7 ml/min bore liquid flow rates.

Table 4.5. Effect of water in dope liquid composition

	Dope liquid	Bore liquid	Coagulation bath temperature (°C)	Room temperature (°C)
P	%20 PES-%80 NMP	%80 NMP-%20 water	17	17
PW	%20 PES- %71.35 NMP - %8.65 water	%80 NMP-%20 water	17	17
PF	%15 PES- %5 F-127- %80 NMP	%80 NMP-%20 water	20.4	18
PFW	%15 PES- %5 F-127- %70.8 NMP-%9.2 water	%80 NMP-%20 water	15.2	19
PP	%15 PES- %5 PEG 10k- %80 NMP	%80 NMP-%20 water	18	17
PPW	%15 PES- %5 PEG 10k- %70.85 NMP- %9.15 water	%80 NMP-%20 water	14	12
PT	%15 PES- %5 TRITON X100- %80 NMP	%80 NMP-%20 water	16.3	20
PTW	%15 PES- %5 TRITON X100- %70.7 NMP- %9.3 water	%80 NMP-%20 water	18	19

Figure 4.9 and Figure 4.10 shows morphologies of these prepared membranes in Table 4.5. It is observed that there is not much structural difference between membranes which were made with different additives and only PES. Figure 4.9 consist of cross sectional and outer part (selective part) images of hollow fiber membranes with different additives and only PES. Figure 4.10, cross sectional and outer part (selective part) images of the same hollow fiber membranes with having water in polymer solution is considered (%95 coagulation value). It is seen from the outer surface images of membranes that having water in polymer solution delays macrovoid formation where macrovoids are further from the skin. Moreover, skin formation on outer surface is seen in all membranes. By using water (non-solvent) in

polymer solution, demixing rates were changed which effects macrovoid formation in membranes. Similar behavior in hollow fiber membrane synthesis was also seen in some studies [34,35].

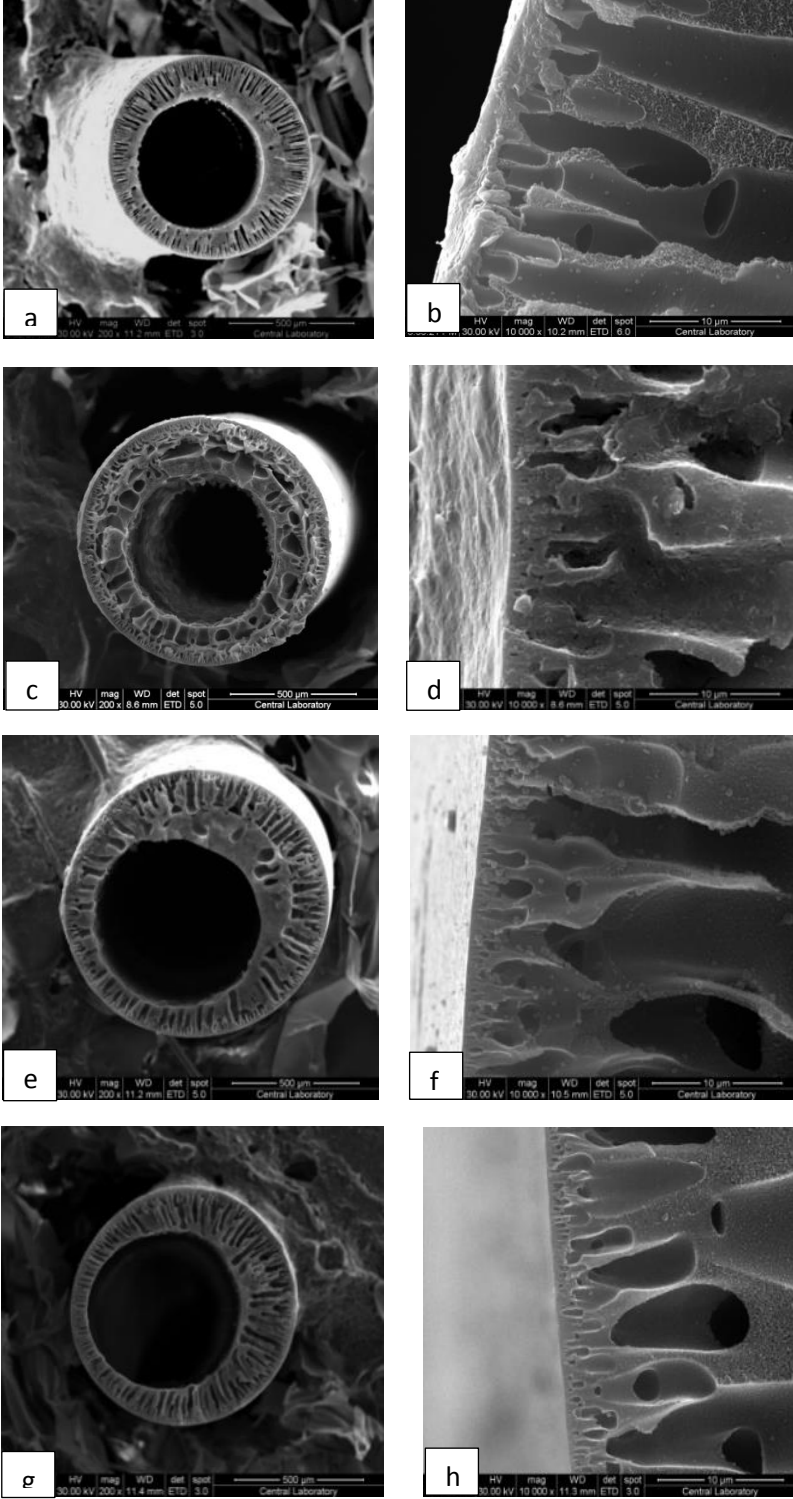


Figure 4.9. Cross section and skin layer (outer part) images of P (a,b), PF (c,d), PT (e,f), PP (g,h)

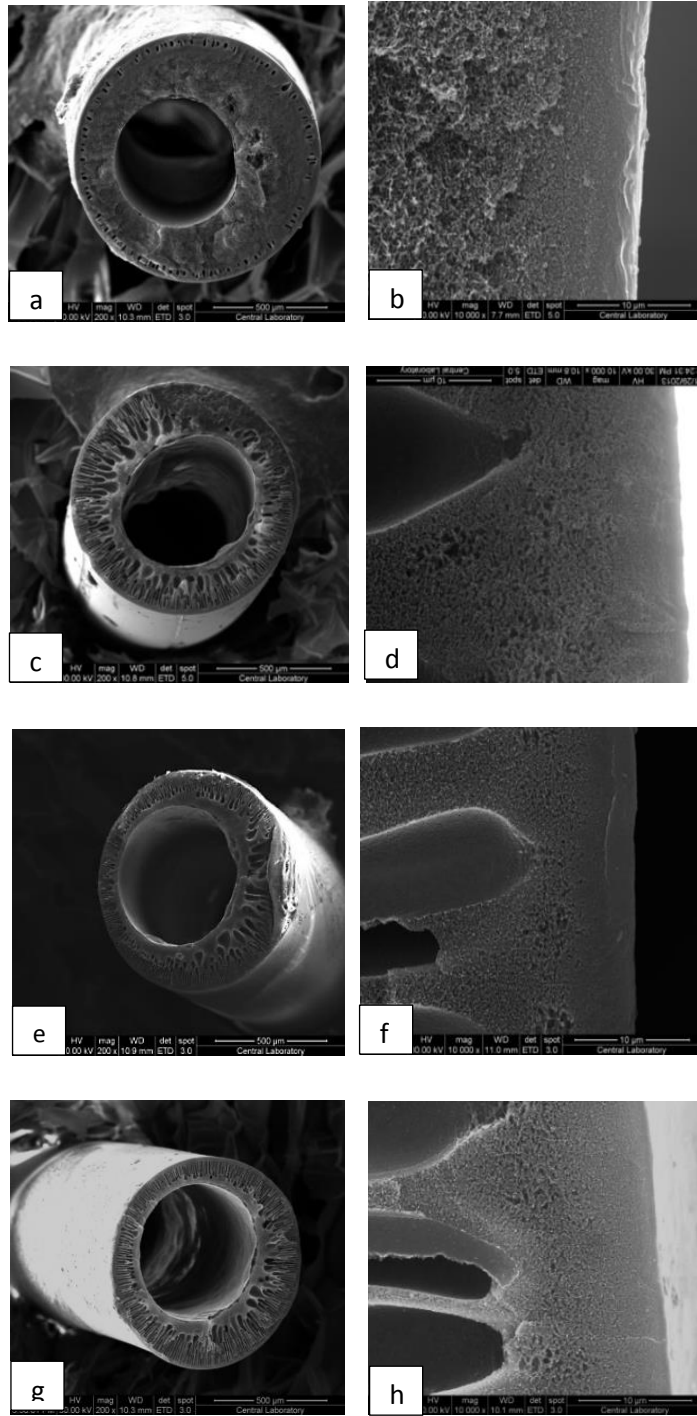


Figure 4.10. Cross section and skin layer (outer part) images of PW (a,b), PFW (c,d), PTW (e,f), PPW (g,h)

Pure water permeance and retention results of hollow fiber membranes coagulated in room temperature are given in Table 4.6. It was found that all membranes have retention values above 90%. According to pure water permeance results, only PES membranes (P and PW) have lower values comparing to membranes with additives.

Using additives enhances permeance in both cases [35]. According to both groups, there is a decrease seen in permeances of membranes when using water in polymer solutions. This decrease is also seen in Torrestiana-Sanchez et al. study [35]. Due to the delayed macrovoid formation skin layer appears to be thicker and this can decrease permeance of membranes (Figure 4.10).

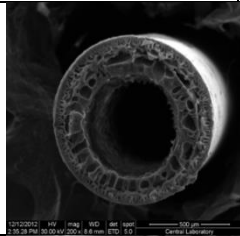
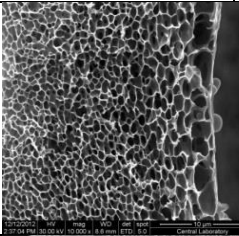
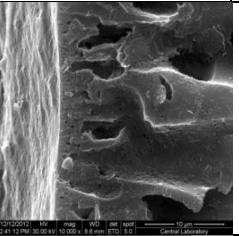
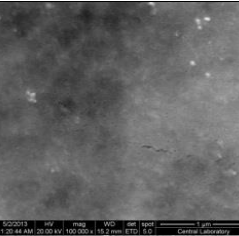
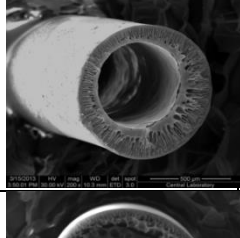
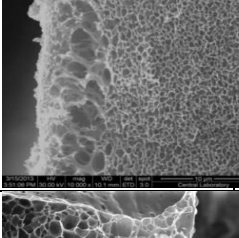
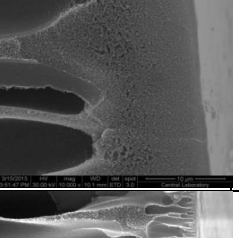
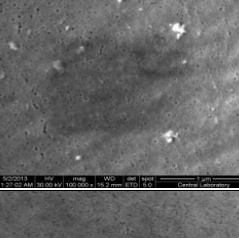
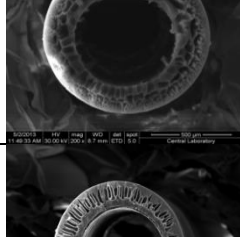
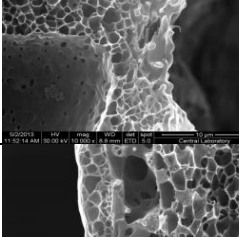
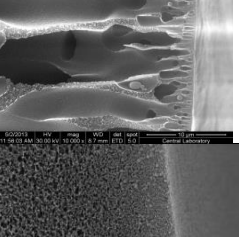
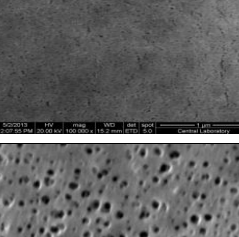
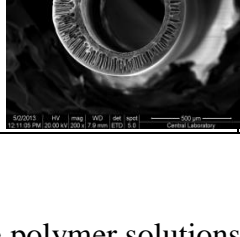
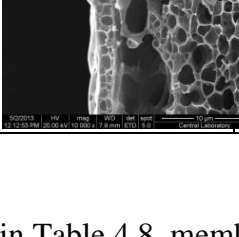
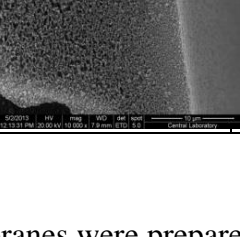
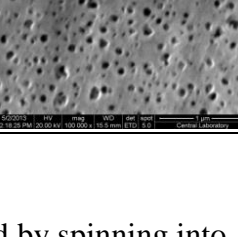
Table 4.6. Pure water permeance and retention results of membranes coagulated at room temperature

	Pure water permeance (L/m².h.bar)	Retention (%)
P	10±7	94±2
PW	15±1	99
PF	73±1	92
PFW	66±7	90±2
PP	230±31	99
PPW	13±8	91±5
PT	213±29	96±1
PTW	56±28	91±3

4.2.4. Effect of water in polymer dope together with 50 °C coagulation bath

Using water in polymer solution effects membrane morphology and performance because phase inversion of membranes takes place earlier and diffusion rates of non-solvent and water become faster. In Table 4.7, effect of using water in polymer solution is seen. When PF-2 and PFW-2 membranes are considered, it is seen that macrovoids in membrane cross section partially prevented and macrovoid formation occurs far from skin layer. At high coagulation bath temperatures, membranes start to form before entering coagulation bath due to the vapor that forms in air gap part.

Table 4.7. Effect of using water in polymer solution

	Cross section	Inner side	Outer side	Outer surface
PF-2				
PFW-2				
PFH				
PFWH				

Using the polymer solutions in Table 4.8, membranes were prepared by spinning into 50 °C coagulation bath temperature. 3.45 ml/min bore liquid flow rate and 8 ml/min dope flow rate was used. At these membranes which are PFH and PFWH; nearly the same morphologies were seen in cross sectional images like PF-2 and PFW-2 membranes. However; pores are much bigger in outer side of PFWH membrane which has water (95% coagulation value) in polymer solution and spin into hot coagulation bath. This group of hollow fiber membranes is characterized as loose ultrafiltration membranes. This situation is due to the water content in polymer solution together with high coagulation bath temperature. Due to the high temperature in coagulation bath, membrane probably starts to form with vapor before entering the coagulation bath. Because of the water in polymer solution, phase inversion of hollow fiber membranes start earlier with the effect of vapor from coagulation bath, compared to the polymer dope without water.

Table 4.8. Effect of water in dope liquid composition together with 50 °C coagulation bath

	Dope liquid	Spinning rate (m/min)	Bore liquid	Air gap (cm)
PWH	% 15 PES - %75.3 NMP- %9.7 water	15.2	%80 NMP-% 20 water	2
PFH	%15 PES-%5 Pluronic F-127 - %80 NMP	12.5	%80 NMP-% 20 water	2.2
PFWH	%15 PES-%5 Pluronic F-127 - %70.8 NMP- %9.2 water	14.2	%80 NMP-% 20 water	2
PPWH	%15 PES- %5 PEG 10000- %70.85 NMP- %9.15 water	15.2	%80 NMP-% 20 water	2
PTWH	%15 PES-%5 Triton X100 - %70.7 NMP- %9.3 water	15.2	%80 NMP-% 20 water	2

By changing coagulation bath temperature; there is high relative humidity occurs in the air gap part which may initiate VIPS before the membrane enters the coagulation bath. This situation changes the pore size of the membranes mainly in the outer surface. In Ohya et al. study, microfiltration membranes were synthesized in 80 °C coagulation bath with PEG additive with similar procedure [17]. In Figure 4.11, membranes with different additives and only PES membrane which are coagulated in 50 °C coagulation bath temperature are seen. It is observed that all membranes have large pores in outer surface of the membrane which is given in line two. PFWH pores at the outer surface of membrane are between 70-90 nm. Pore sizes at the outer surface is between 70-100 nm for PTWH membrane, 65-80 nm for PWH membrane and 60-70 nm for PPWH membrane as measured from SEM images by using Image J. The macrovoids and fingerlike structures are still present in all membranes cross sectional images.

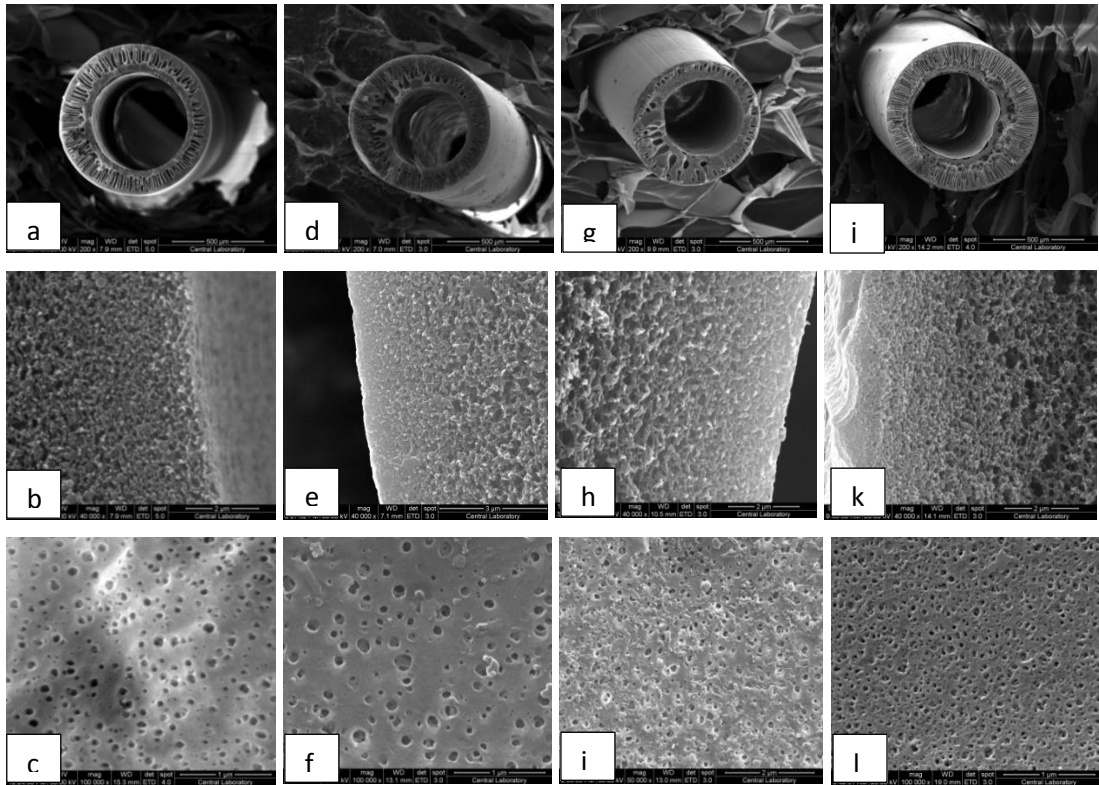


Figure 4.11. Cross section, skin layer(outer surface) and surface images of PFWH (a,b,c), PTWH (d,e,f), PWH (g,h,i), PPWH (j,k,l) (The surface magnification of PWH membrane is 50000x and others are 100000x.)

It is seen from the Table 4.9 that permeance of membranes were very close at PFH and PFWH membranes which have Pluronic F-127 as additive. The difference between these two membranes was observed at retention values. PFWH membrane which has water in polymer solution had lower BSA retention value. This is due to high pore sizes in skin layer on membrane surface. Since it has big pores; it is expected to have higher permeance values in PFWH than PFH membrane. This can not be seen due to the thin skin layer formed in inner surface of the membrane which is given in Figure 4.12a which lowers permeance of PFWH membrane.

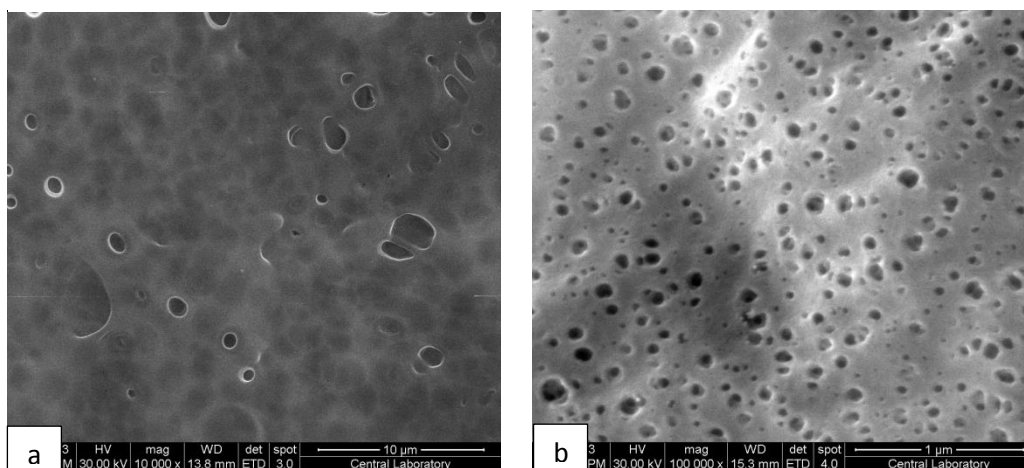


Figure 4.12. Inner surface image (a), skin layer (outer surface) images of PFWH (b)

Table 4.9. Pure water permeance and retention results of membranes coagulated in

50 °C temperature

	Pure water permeance (L/m².h.bar)	Retention (%)
PWH	64±11	23±2
PFH	270±81	96
PFWH	373±43	34±1
PPWH	43±23	25
PTWH	41±14	

At a total view, membranes which have additives had higher permeability values than membranes without additives. In addition to that, membranes which have water in their polymer solutions had lower permeability values than membranes without containing water in their polymer solutions when coagulated in water at room temperature. It was also found that for the membranes coagulated in water at room temperature, BSA retention results were found to be similar and above 90%. It can be said from these results that; the difference in pure water permeability results are not mainly due to pore size distribution, it is also effected by porosity of membranes on skin layer and connection between pores and thickness of membranes skin layer. According to the delay of macrovoids, this can be the most important reason for membranes performances.

The membranes which are synthesized by using water in polymer solution and 50 °C coagulation bath temperature had low BSA retention values comparing to those spun at room temperature. SEM images show that their pore sizes were nearly 75-80 nm which explains the low retention values. These membranes which are PWH, PFWH, PTWH and PPWH show these similar results.

4.2.5. Burst pressure analysis

For the usage of hollow fiber membranes in industrial applications, membranes mechanic properties are important. Burst pressure analyses were done to make predictions about in which pressure range the prepared hollow fiber membranes can be used. According to analysis, burst pressures of prepared hollow fiber membranes were all found to be higher than 5-6 bar pressure. This pressure is applicable for ultrafiltration usage areas of hollow fiber membranes.

4.2.6. Additive stability

Additive stability is another important factor that determines membranes performance. By using additives, an enhancement in membrane performance is expected. But using additives is not enough alone. The stability of the additives that are used in polymer matrix determines performance and anti-fouling properties of hollow fiber membranes. During the phase inversion process, due to the interaction between additives, base polymer and non-solvent, some of the additives might leave the membrane. The fraction that stays in the polymer matrix after membrane formation is a measure of additive stability.

For determining stability of additives, FTIR is used for surface analysis. By using FTIR analysis; it is expected to find which additive stay in membrane matrix more and its effect on membrane fouling is considered together.

PES is a hydrophobic polymer mainly consists of aromatic and sulfone groups. All additives that are used have hydrophilic character. When Pluronic is considered; it has both hydrophilic and hydrophobic groups together which may effects its stability

in membrane matrix. Triton X100 which is a surfactant also has aromatic groups and it has hydrophobic and hydrophilic character together like Pluronic F-127.

For examining long-term stability behavior, prepared hollow fiber membranes were kept in water and sodium hypochlorite (NaOCl) solutions for a period of 60 days. Sodium hypochlorite solution is one of the chemical cleaning agents which is commonly used in membrane applications. However it is a harsh chemical and may degrade polymeric materials. Figure 4.14 shows FTIR spectra of hollow fiber membranes before putting in these solutions which can be called zeroth day. At this figure; three peaks are used for analyzing FTIR spectra. These peaks are C-O bond of ethylene glycol at 1105 cm^{-1} , aromatic C-H bands at 1578 cm^{-1} and C-H band at 2865 cm^{-1} from CH_2 and CH_3 groups. By using ratio of peak intensities, presence of additives in membrane matrix is examined. Figure 4.13 shows FTIR spectra of pure polymer (PES) and pure additives (Pluronic F-127, Triton X100 and PEG 10k). PEG and Pluronic and Triton X100 can be characterized by the 1105 cm^{-1} peak which shows the C-O bond in ether groups of PPO and PEO blocks. However, PES also has a contribution to this peak as seen in Figure 4.13. Also, Triton X100 has an impact on 1578 cm^{-1} peak due to its aromatic groups. To determine presence of ethylene glycol groups, the ratio of $1105 / 1578$ is used which were also used in some studies [4,7,9]. Due to the contribution of Tritons aromatic groups to the peak at 1578 cm^{-1} , the peak ratio of $2865/1578$ was also considered for the stability of the additives.

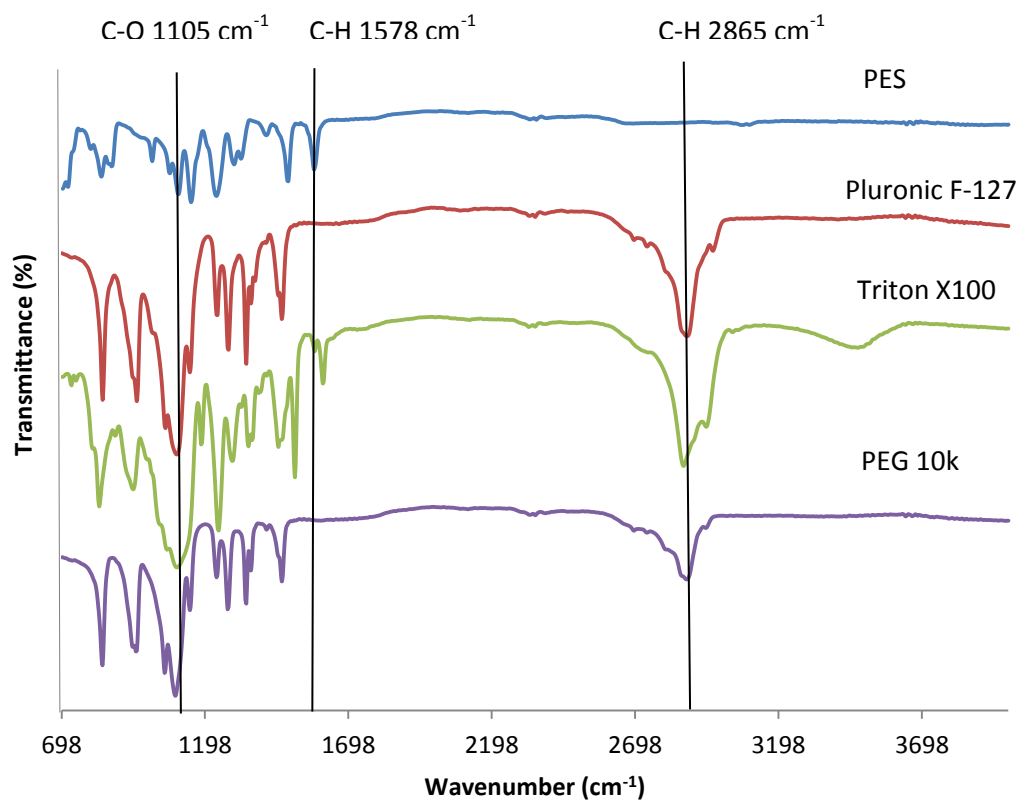


Figure 4.13. FTIR spectra of pure PES and pure additives

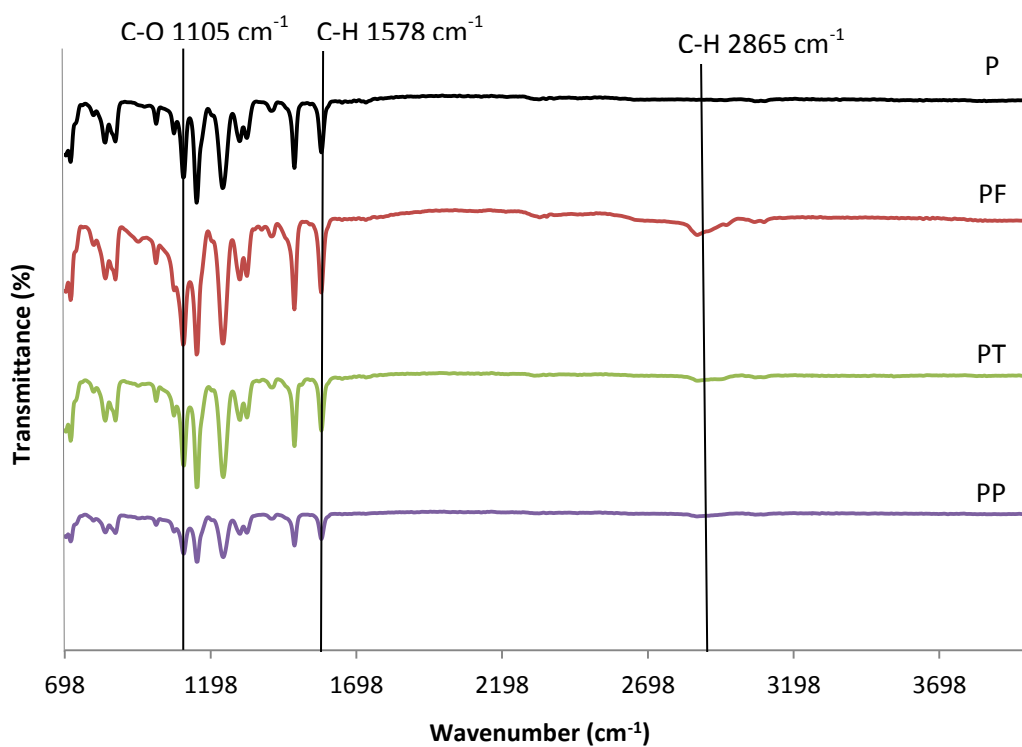


Figure 4.14. FTIR spectra of hollow fiber membranes (zeroth day)

From Figures 4.13 and 4.14; FTIR spectra of hollow fiber membranes at zeroth day, pure additives and PES were given. In Figures 4.15 to 4.21 the ratio of the peak ratio of the membranes containing the additives to the peak ratio of the pure PES membranes are shown. It was observed that all additives stayed in membrane matrix. Figure 4.15 is drawn according to results of $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ of pure additives. Figure 4.16 is drawn according to the results of $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ of prepared hollow fiber membranes at zeroth day. It was seen from Figure 4.16 that; $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio of prepared hollow fiber membranes are nearly same in tight ultrafiltration membranes. Membranes that contain Pluronic F-127 additive (PFWH) had the highest $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio in loose ultrafiltration membrane group (PFWH, PTWH and PWH). Loh. et al. also found that according to $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio in membranes, membranes with Pluronic (contains PPO groups) had higher ratio than PEG (PEO groups) [9].

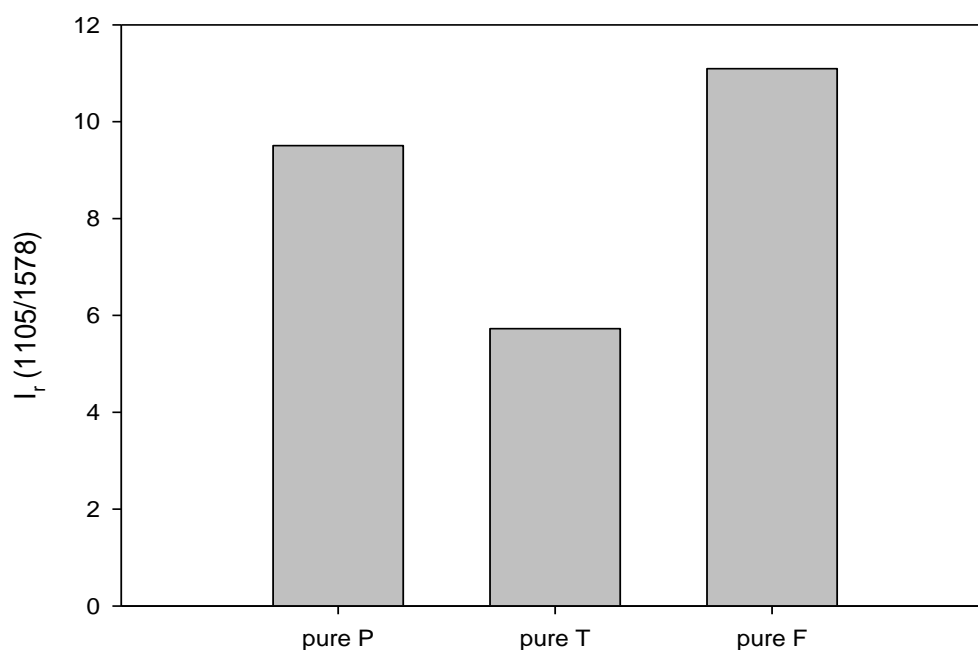


Figure 4.15. Ratio of peak intensities (1105/1578 peak ratio) of additives (pure P: Pure PEG 10k, pure F: Pure Pluronic F-127)

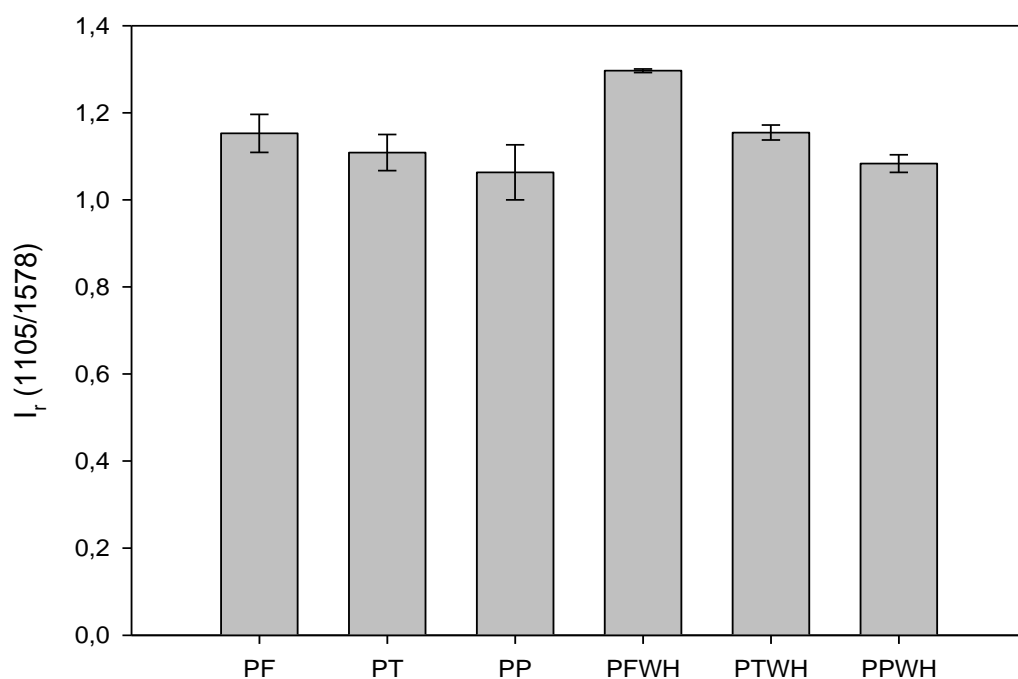


Figure 4.16. Ratio of peak intensities (1105/1578 peak ratio) of membranes at zeroth day.

In Figure 4.17, ratio of peak intensities of $2985\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio of pure additives are drawn. In Figure 4.18; ratio of peak intensities of $2985\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio of prepared hollow fiber membranes are seen. Among the three membranes; they show similar behavior according to $2985\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio in loose ultrafiltration membrane set and PP and PF membranes with PEG and Pluronic additive show the highest $2985\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratios in tight ultrafiltration membrane set.

In both ratios ($2985\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ and $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$), generally it can be said that hollow fiber membranes with Pluronic F-127 additive has higher ratios than other membranes. The interaction of additives with PES and solubility of additives in water (non-solvent) are two important parameters in the comparison of FTIR analysis results. Pluronic F-127 consists of PEO-PPO-PEO group together. This means that, it has a hydrophobic character that comes from PPO group which makes its interaction with PES better. By this reason; it can stay in polymer matrix more than other additives. Moreover, PEG 10k is more soluble in water than Pluronic F-127. It

consists of only PEO groups and it does not contain PPO hydrophobic groups. For that reasons it is easier for PEG 10k additive to dissolve into the coagulation bath during membrane fabrication [9]. Triton X100 is a nonionic surfactant which is soluble in water at 25 °C. Although it has a hydrophobic aromatic group, it is a smaller molecule and therefore can diffuse faster through the polymer solution during phase inversion. At Figure 4.15 and Figure 4.17, pure additive to pure PES ratio of peak intensities for 2985 cm⁻¹ / 1578 cm⁻¹ and 1105 cm⁻¹ / 1578 cm⁻¹ ratio is given. It is seen that there is a big difference seen in 2985 cm⁻¹ / 1578 cm⁻¹ ratio intensities which comes from C-H bonds in additives. Among these ratios, membranes with Pluronic F-127 additives have highest ratios. Molecular weights of additives should also be considered when comparing ratio of peak intensities for the membranes.

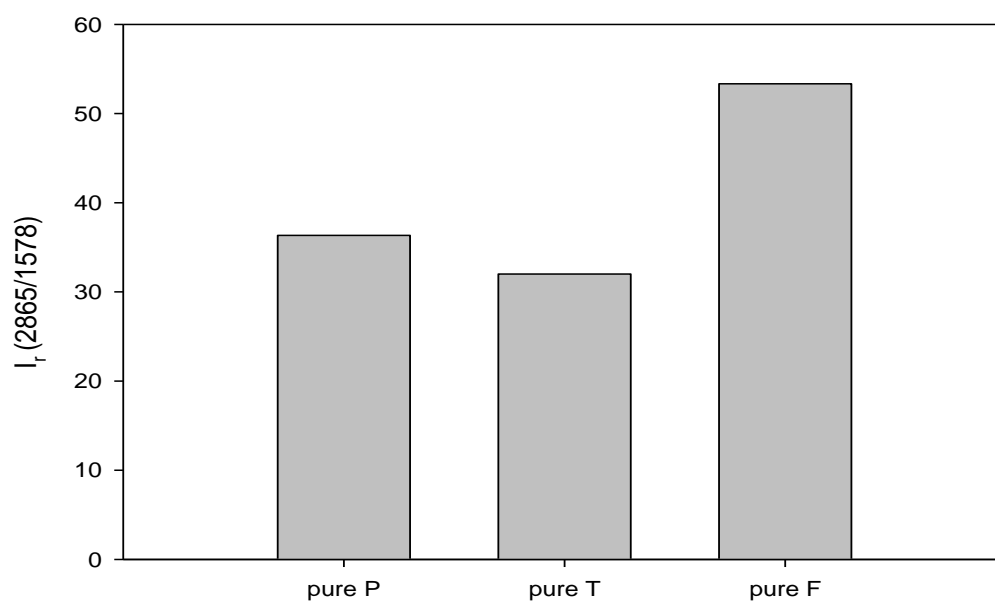


Figure 4.17. Ratio of peak intensities (2865 /1578 peak ratio) of additives (pure T: pure Triton X100, pure P: Pure PEG 10k, pure F: Pure Pluronic F-127)

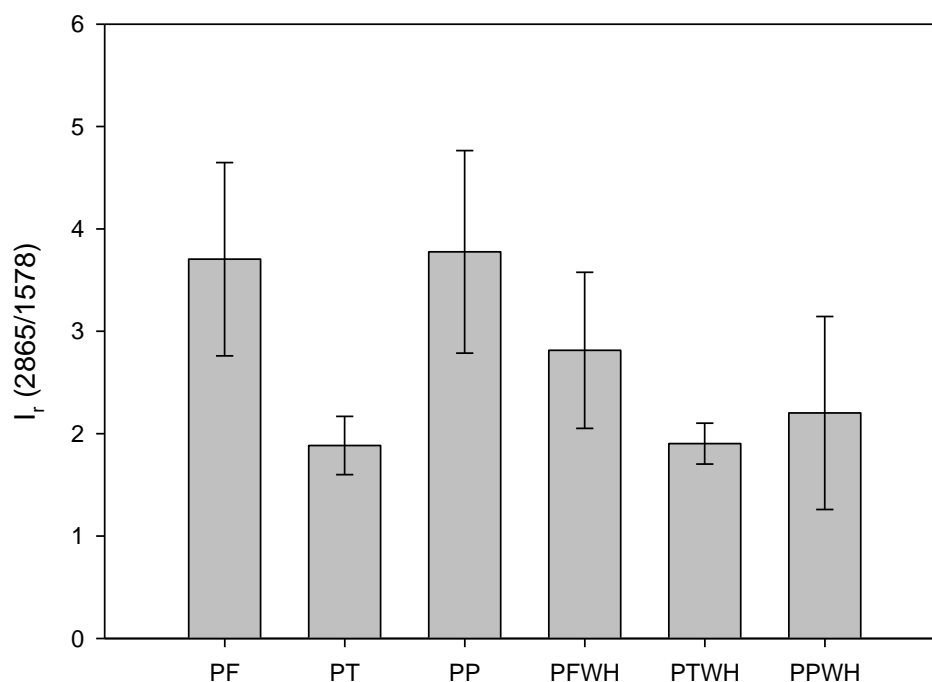


Figure 4.18. Ratio of peak intensities (2865 /1578 peak ratio) of membranes at zeroth day.

After analyzing prepared hollow fiber membranes zeroth day situations; membranes are kept in water and sodium hypochlorite solutions for 60 days. Samples were collected at each 15 days. The values of 2985 cm^{-1} , 1578 cm^{-1} and 1105 cm^{-1} peaks for all hollow fiber membranes according to the FTIR analysis of membranes for each 15th day samples are given in APPENDIX B.

Susanto et al. used the same procedure in flat sheet membranes for FTIR analysis. Membranes were also kept in water and NaOCl solutions and examined per time. It was found that $1105\text{ cm}^{-1}/1578\text{ cm}^{-1}$ ratio of membranes stay nearly same in water and decrease a little in NaOCl solution [7]. By using these two solutions, leaching (water) and chemical degradation (sodium hypochlorite solution) effect are considered.

Figure 4.19 and Figure 4.20 show the $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ peak ratios of membranes per days in water and sodium hypochlorite solutions. For the two groups of membranes (tight and loose ultrafiltration), there is a variation in FTIR results per day. But generally, there is not much difference in $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio in membranes that were kept in water solution. The variations at the results are more in $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ ratio in membranes that were stayed in sodium hypochlorite solutions and there is a little decrease is seen. It might be due to the chemical degradation of PEG groups by NaOCl.

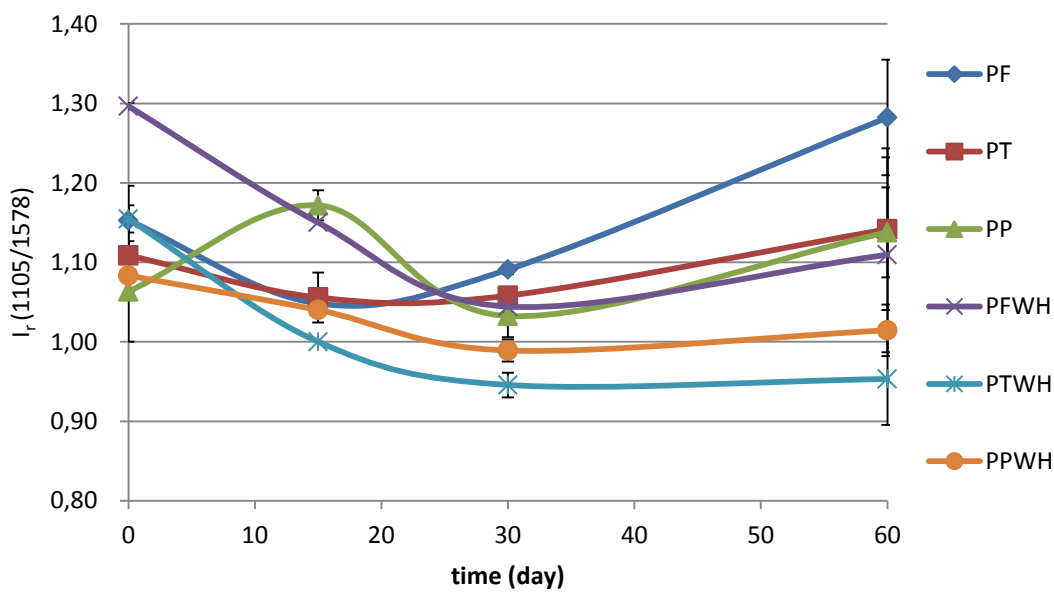


Figure 4.19. Ratio of peak intensities ($1105/1578$ peak ratio) of membranes per days in water

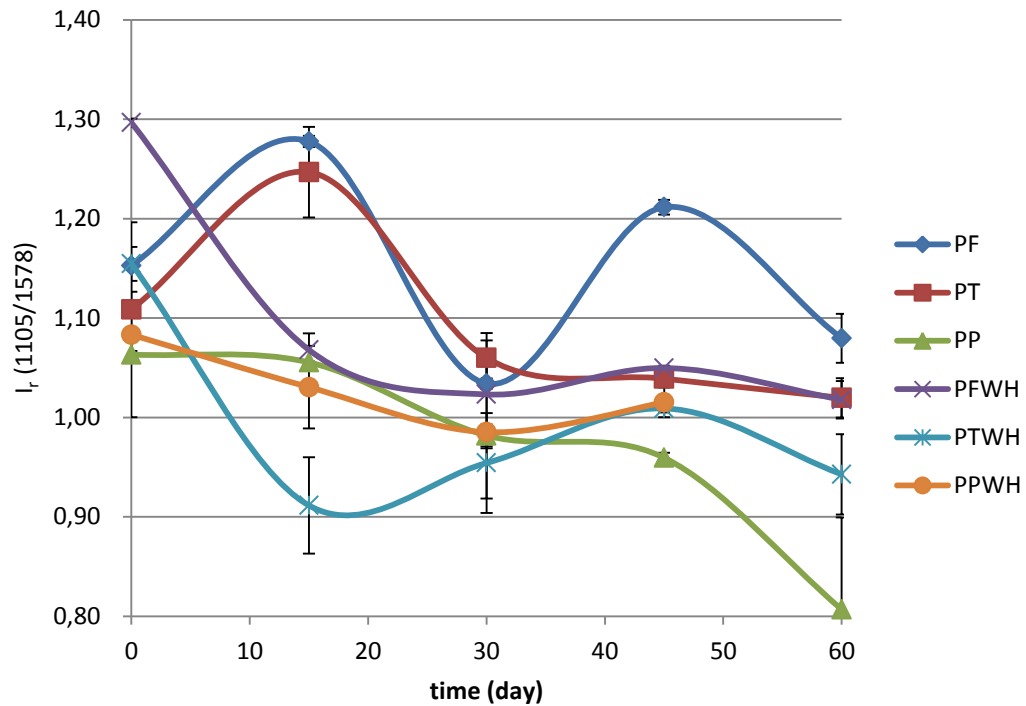


Figure 4.20. Ratio of peak intensities (1105/1578 peak ratio) of membranes per days in sodium hypochlorite solution

Figure 4.21 shows the $2985\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ peak ratio change of prepared hollow fiber membranes in water. It can be said from Figure 4.18 that 2985 cm^{-1} peak which refers to CH_2 and CH_3 bonds that come from additives stay in membrane matrix. According to both $2985\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ and $1105\text{ cm}^{-1} / 1578\text{ cm}^{-1}$ peak ratios, stability of additives in polymer matrix occurred in water and but some decrease is seen in sodium hypochlorite solutions per time. Both three additives (Pluronic F-127, PEG 10k and Triton X100) can be useful for membranes to prevent from fouling according to FTIR stability results.

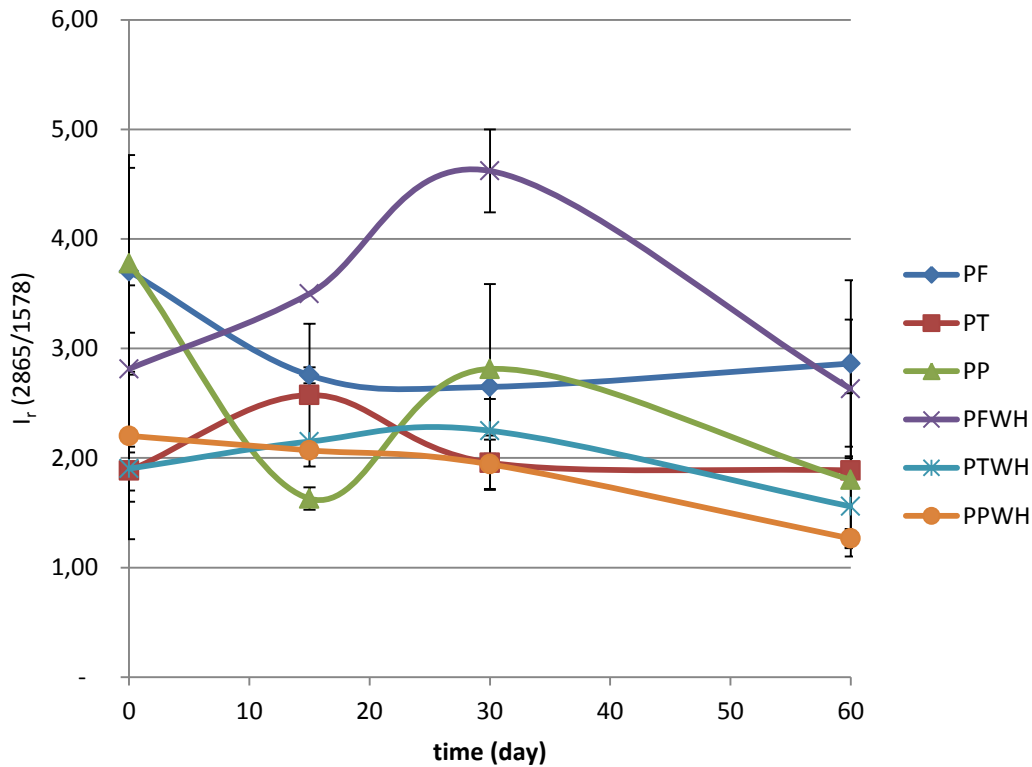


Figure 4.21. Ratio of peak intensities (2865/1578 peak ratio) of membranes per days in water

4.2.7. Membrane fouling

Membrane fouling is the most important problem in membrane filtration and determines membrane performance and membrane life time. In this study; fouling behaviors of prepared hollow fiber membranes were examined in dead end constant flux filtration system by using 1 g/L BSA solution. Different procedures were used for the tight and loose ultrafiltration group as explained in the experimental section. Fouling test analysis procedure and results are given in APPENDIX C and D. For using as control (PES) membrane, PH membrane was prepared. Other PES membranes could not be used in filtration experiments because they had very low permeance values which make them harder to study in filtration experiments due to high pressure required at 30 L/h.m².

Table 4.10. Hollow fiber membrane list for membrane fouling analysis (tight ultrafiltration group)

	Dope liquid	Spinning rate (m/min)	Bore liquid flow rate (ml/min)	Dope liquid (ml/min)	Coagulation bath temperature (°C)	Room temperature (°C)
PT	%15 PES- %5 TRITON X100- %80 NMP	9.36	2.7	-	16.3	20
PP	%15 PES- %5 PEG 10000- %80 NMP	9.36	2.7	-	18	17
PH	%20 PES - %80 NMP	15.2	3.45	8	50	25
PFR	%80 NMP-%15 PES-%5 Pluronic F-127	9.36	2.7	8	20	21

Figure 4.22 show a sample membrane fouling test analysis result of PT membrane (with Triton X100 additive) according to pressure change in constant flux dead end filtration. Pressure change per time of other prepared hollow fiber membranes are given in APPENDIX D. From this figure, it was observed that membrane resistances were getting higher per each cycle. By backwashing with pure water after each cycle, PT membrane cleaned a little but it had still irreversible membrane resistance that could not turn back to original resistance of membrane.

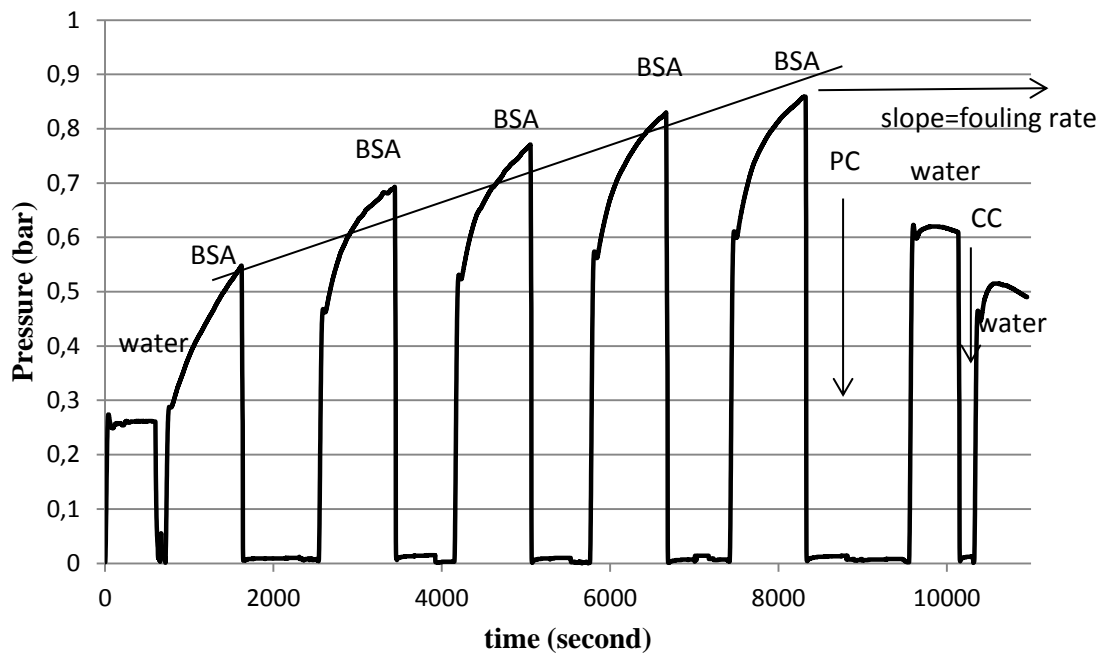


Figure 4.22. Fouling test result of PT membrane change with pressure

Before filtration with BSA solutions, permeances of membranes and membrane resistance before fouling test were determined. According to the pressure values at the end of each cycle; membrane fouling resistances of hollow fiber membranes were calculated. At the end of 5 cycles, pure water permeances of membranes were measured after physical and chemical cleaning and reversible and irreversible fouling resistances was calculated. According to pressure values at the end of each cycle; fouling rate of membranes were determined by the slope of 5 cycles which is also shown in Figure 4.22.

Membrane resistance of hollow fiber membranes per cycles is given in Figure 4.23. It is seen that, fouling of membranes increased in each filtration cycle for all membranes. Backwashing of membranes cleaned membranes a little at each cycle but irreversible fouling in membranes were exist. Membranes prepared by using additives show lower fouling behaviors than PES membrane (PH). Between the additives, the lowest membrane fouling resistances were found in PT membrane with Triton X100 additive.

The non-ionic Triton X100 additive has both hydrophobic and hydrophilic groups in it. Although it has shorter PEO groups and lower stability than Pluronic F-127 additive in membrane matrix, it has the best fouling characteristics between additives. This can be attributed to the lower pressure during filtrations with this membrane which was a result of the higher permeance of this membrane. Because of the different pressures, which were all between approximately 1-2 bars, the cake layer that builds up on different membranes may have been compressed to different extents, in turn causing different resistances even though the amount of BSA in the cake is the same [36].

So the fact that the pressure during filtrations with the membrane containing Triton additive was lower by a factor of about two compared to those with Pluronic (due to the lower intrinsic membrane resistance) may also be contributing to the better fouling behaviour, although it is probably not the only explanation.

Between the Pluronic and PEG additives, PEG shows worst fouling behavior. Although it contains more hydrophilic groups than Pluronic, because of the stability problems fouling rates of PEG membrane is higher. But due to stability problems, PEG additive could not able to show good fouling resistance.

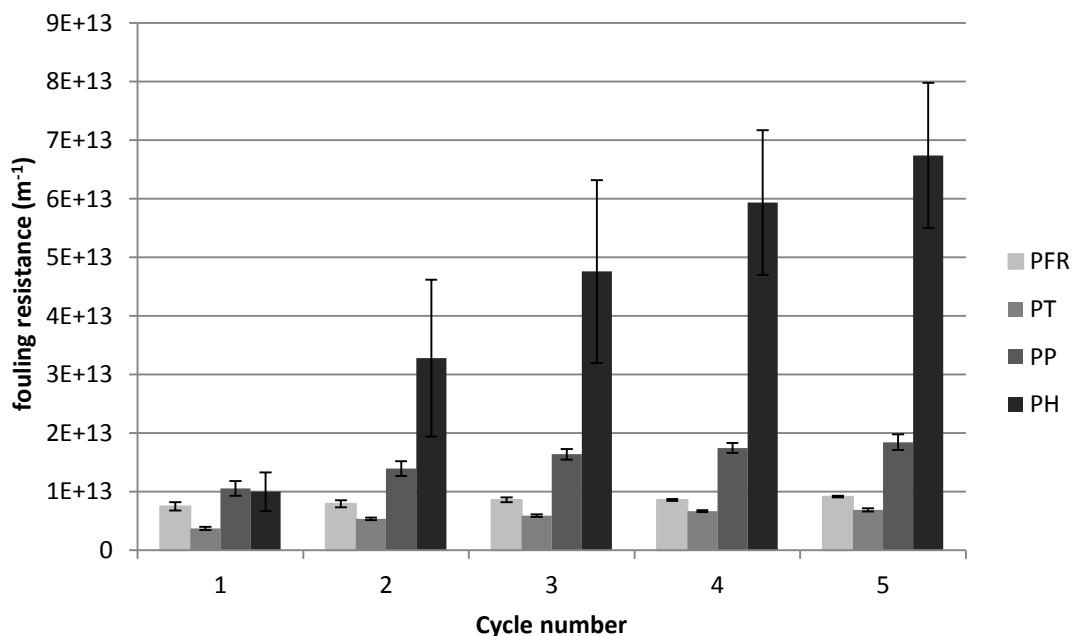


Figure 4.23. Membrane fouling resistances of hollow fiber membranes per cycle (tight ultrafiltration group)

Membrane resistances of hollow fiber membranes before fouling analysis and after physical and chemical cleaning are seen in Figure 4.24. Fouling resistances of PH (PES) membrane is almost seven times higher than hollow fiber membranes with additives. In fouling test experiments, pure water permeances of PES membranes without additives are measured very low comparing to others. Due to that the pressures that exists on membrane surface is high in fouling test system even though the flux was lowered to 5 L/h. m² in PES membranes. Filtration experiments were done in 30 L/h. m² flux for 15 minutes in 5 cycles for membranes with additives and 5 L/h. m² flux for 45 minutes in 5 cycles for PES membranes. At PES membranes foulant load was half of membranes with additives. It was measured that pressures were changed between 0.5-1.2 bar for membranes with additives and 1.6-2 bar for PES membranes in filtration experiments.

At PFR membrane, it can be cleaned mostly by chemical and physical cleaning. However, fouling on PT and PP membranes were not cleaned efficiently by physical and chemical cleaning.

In contrast to three additives; PH membranes results show that after physical and chemical cleaning, membrane resistances became higher which means the membranes fouled more with cleaning. This is not a commonly seen situation in fouling experiments. Shi et al. saw same behavior with trypsin on poly (methacrylic acid)-graft-polyethersulfone (PMAA-g-PES) membrane. When permeance of water was calculated after protein filtration and cleaning; it became lower due to the severe protein fouling of the prepared membrane [37].

In backwashing part during filtration experiments, the flux that was used was two times filtration flux. This situation also causes higher pressures than filtration parts which might cause compression of fouling layer of PES membranes during backwashing.

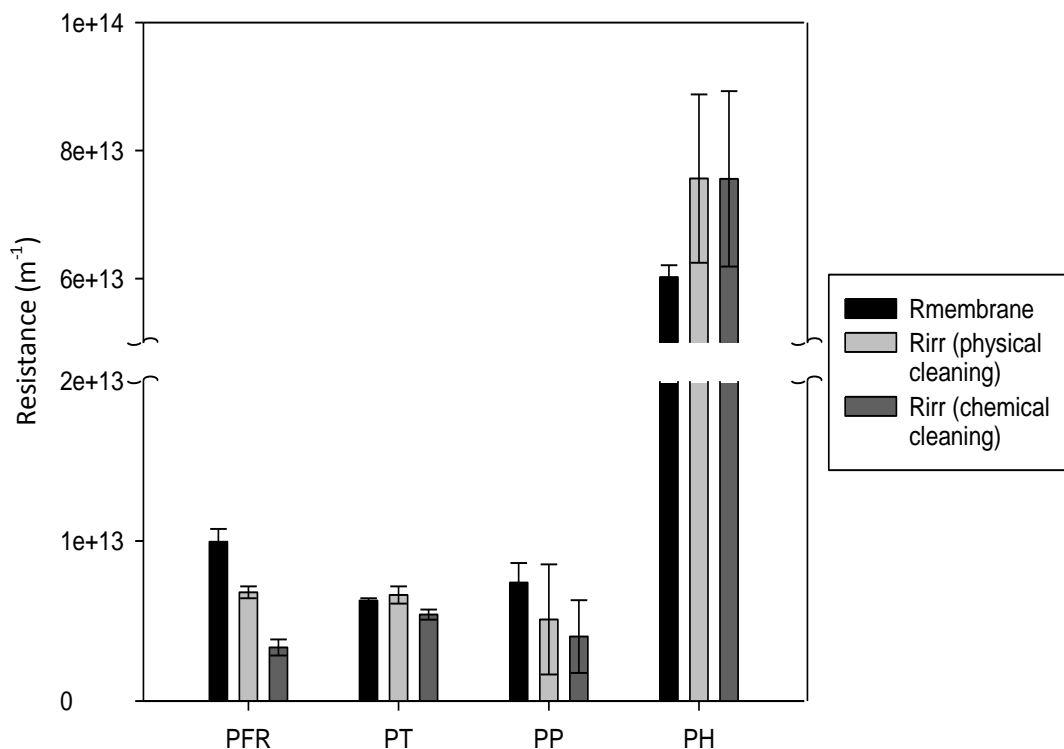


Figure 4.24. Membrane resistances after chemical and physical cleaning (tight ultrafiltration group)

Figure 4.25 shows the fouling rate results of hollow fiber membranes in tight ultrafiltration group. By taking pressures at the end of each BSA filtration in each cycle, membrane resistances are calculated. By taking the slope of these five membrane resistances at each cycle, fouling rates of prepared hollow fiber membranes are calculated. Fouling rate analysis through fouling experiments show that PES membrane (PH) not only had highest fouling resistance but also highest fouling rate comparing to other membranes with additive. Between additives PEG (PP) had the second highest fouling rate which is still far from PES hollow fiber membrane. According to the low stability of PEG additive in polymer matrix, fouling rate can be high. After PEG membrane (PP), membranes with Triton X100 (PT) and Pluronic F-127 (PFR) additives came for which fouling rates were similar, and somewhat lower in PFR.

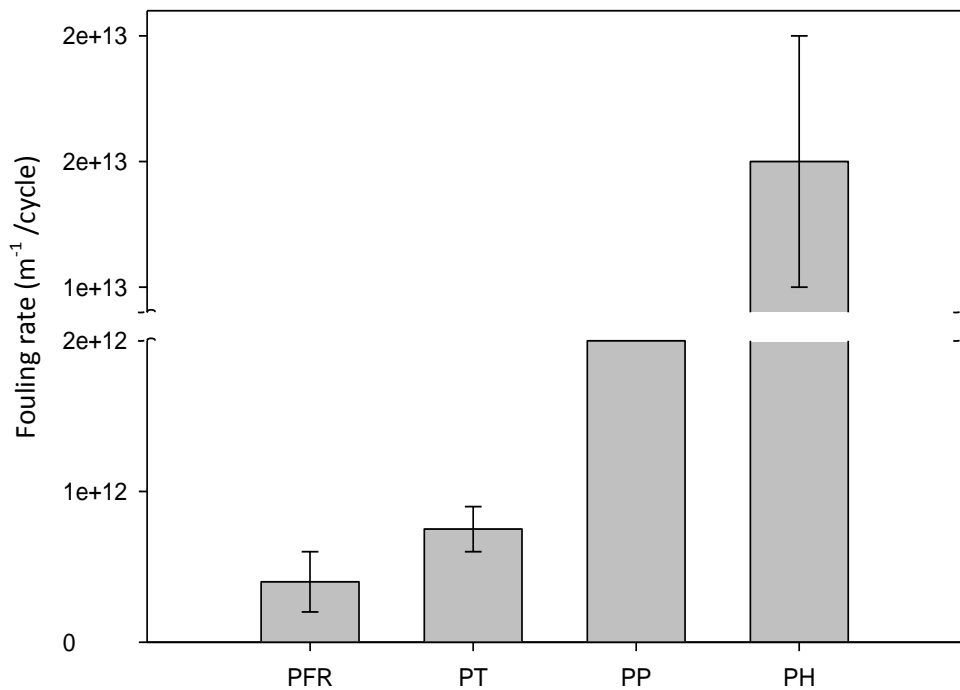


Figure 4.25. Fouling rate results of hollow fiber membranes

In fouling analysis; a different filtration procedure was applied for hollow fiber membranes which are in loose ultrafiltration range. These hollow fiber membranes are PFWH, PTWH, PWH and PPWH. This group of membranes were coagulated at 50 °C coagulation bath temperature using water in polymer solution (%95 of coagulation value). For this group, a different fouling test procedure is applied. Fouling test experiments were done with one filtration without backwash for these hollow fiber membranes. When the backwash applied, the silicon tube in backwash line start to expand. Because of these problems in the system, one filtration applied to membrane without backwash then pure water flush and pure water permeance was measured by applying 30 L/h. m² constant flux.

Membrane fouling resistance values of hollow fiber membranes (loose ultrafiltration group) are drawn in Figure 4.26. It was found that PFWH which has Pluronic F-127 additive in it showed the best fouling characteristics. From pure water permeance analysis; it was found that it had highest permeance value comparing to other three membranes. It might due to its high surface porosity, pore sizes and connectivity

between pores. Moreover, it has high stability percentages in hollow fiber membranes polymer matrix. Those reasons can cause better anti-fouling characteristics to PFWH membrane. BSA protein molecules can easily pass through membrane with large and good connected pores without plugging the pores.

Between three additives, PFWH membrane shows the lowest fouling characteristics. It is nearly 12 times lower than PTWH and PPWH membranes which have nearly same fouling resistances. PWH membrane shows worst fouling resistances but very close to PTWH and PPWH membranes. It is also found that physical and chemical cleaning made not much improvement on membrane performances. It can be due the internal fouling that happened to membranes which is irreversible and physical and chemical cleaning make no effect to that.

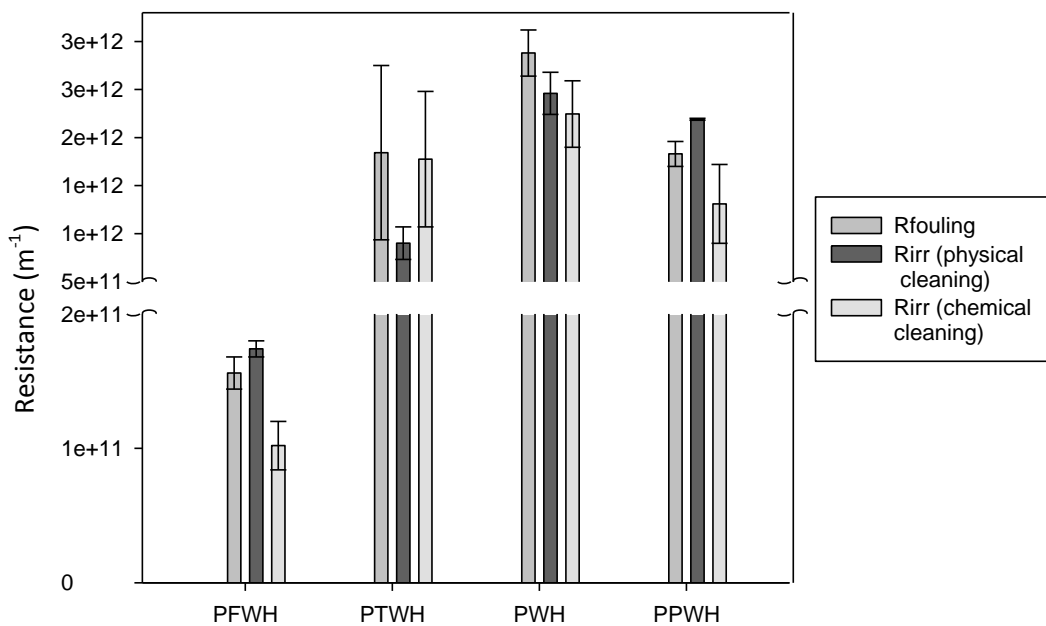


Figure 4.26. Membrane fouling resistances of hollow fiber membranes (loose ultrafiltration group)

CHAPTER 5

CONCLUSION

In this study, fabrication and characterization of fouling resistant Polyethersulfone (PES) hollow fiber ultrafiltration membranes by using Polyethylene oxide (PEO) based additives (PEG 10k, Triton X100 and Pluronic F-127) were done.

Before starting hollow fiber membrane preparation, phase equilibrium behavior of membranes and coagulation kinetics of polymer solutions were determined. After that hollow fiber spinning parameters on membrane performances were examined. It was found that bore liquid flow rate and spinning rate changed dimensions of membranes but did not make much effect on membrane morphology and performances. Different bore liquid compositions were also used. According to the morphologies observed optimum bore liquid composition was chosen as 80% NMP-20% water. 95% coagulation value in dope was also tested to observe its effects on membrane morphology. It was found that adding water to polymer dope delays macrovoid formation. Permeance values of membranes decreased by adding water to dope liquid. For all membranes spun into water at room temperature, retention values for BSA were above 90%. Moreover, membranes mechanic properties were tested and it was found that membranes can be used above 5-6 bar pressures.

Another parameter that was examined is using water in dope liquid together with 50 °C coagulation bath. At this group, phase separation started before entering the coagulation bath with the vapor in air gap region. It was observed that pore sizes become larger and fabricated membranes were loose ultrafiltration membranes.

Beside these spinning conditions, additive stability is another important factor that determines membranes performances. According to ratio of peak intensities for the

additives to PES; it was observed that generally membranes with Pluronic F-127 additive has high stability ratios than other additives. The hydrophobic part in the Pluronic F-127 additive makes its interaction with PES better and it can stay in membrane matrix more. It has also higher molecular weight than other additives which can affect its stability. Triton X100 additive also has hydrophobic part but it is smaller and may diffuse out of the polymer solution faster during coagulation. According to PEO contents; the most prone additive to get away from polymer matrix is PEG during phase inversion process. PEG additive consist of just hydrophilic groups. This makes it more soluble in water and high interaction with non-solvent. As PES has hydrophobic group, PEG has low interaction with it and it is hard for PEG to stay in membrane matrix. Stability of additives in polymer matrix in both water and sodium hypochlorite solutions per time was also examined. It was found that ratio of peak intensities not change much in water but a little decrease was observed in sodium hypochlorite solution due to degradation of PEG groups.

In this study, membrane fouling was examined which determines membrane performance and membrane life time by using model protein BSA as foulant. Fouling tests were done in constant flux set-up which is close to industrial applications. Fouling of membranes increased in each filtration cycle and by backwashing membranes cleaned a little but in all membranes irreversible fouling exists. PES membrane shows highest fouling and least reversibility comparing to membranes with additives. Between additives, Triton X100 shows the lowest membrane fouling resistances. After Triton X100 additive, Pluronic F-127 shows second lowest fouling results according to high stability values in membrane matrix. Although it has more hydrophilic groups in it, membranes with PEG additives show worst fouling resistances than other additives due to stability problems.

After filtration cycles, physical and chemical cleaning applied to membranes. It was found membranes with Pluronic F-127 additive can be cleaned mostly but cleaning ratio was very low in membranes with PEG 10k and Triton X100 additives.

In loose ultrafiltration group; PFWH (membrane with Pluronic F-127 additive) showed the best fouling characteristics. High stability, high permeance values with high surface porosity and connectivity between pores can give better anti-fouling characteristics. Membranes with PEG and Triton X100 additives showed higher fouling properties comparing to Pluronic F-127. Physical and chemical cleaning made not much effect on membrane performances. Internal fouling might be the reason of that which is irreversible.

At a general view, it was found that PES membrane had high fouling behavior due to its hydrophobic structure. Among the three additives; Pluronic F-127 and Triton X100 additives can be more preferable in use than PEG 10k additive according to their performance, stability and better anti-fouling properties.

REFERENCES

- [1] Machado, P.S.T., Habert, A.C., Borges, C.P., “Membrane formation mechanism based on precipitation kinetics and membrane morphology: Flat and hollow fiber polysulfone membranes”, *Journal of Membrane Science*, 155, 1999, p. 171-183.
- [2] Mulder, M., “Basic Principles of Membrane Technology”, Kluwer Academic Publishers, Second edition, 1997, Dordrecht.
- [3] Baker, R.W., “Membrane Technology and Applications”, WILEY, Second edition, 2004, John Wiley and Sons.
- [4] Susanto, H., Stahra, N., Ulbricht, M., “High performance polyethersulfone microfiltration membranes having high flux and stable hydrophilic property”, *Journal of Membrane Science*, 342, 2009, p. 153–164.
- [5] Wang, K.Y., Matsuura, T., Chung, T., Guo, W.F., “The effects of flow angle and shear rate within the spinneret on the separation performance of poly(ethersulfone) (PES) ultrafiltration hollow fiber membranes”, *Journal of Membrane Science*, 240, 2004, p. 67–79.
- [6] Xu, Z., Qusay, F.A., “Polyethersulfone (PES) hollow fiber ultrafiltration membranes prepared by PES/non-solvent/NMP solution”, *Journal of Membrane Science*, 233, 2004, p. 101–111.
- [7] Susanto, H., Ulbricht, M., “Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives”, *Journal of Membrane Science*, 327, 2009, p. 125-135.

- [8] Pilutti, M., Nemeth, J.E., “Technical and cost review of commercially available MF/UF membrane products”, International Desalination Association, BAH03-029.
- [9] Loh, C.H., Wang, R., Shi, L., Fane, A.G., “Fabrication of high performance polyethersulfone UF hollow fiber membranes using amphiphilic Pluronic block copolymers as pore-forming additives”, *Journal of Membrane Science*, 380, 2011, p. 114-123.
- [10] Ma, Y., Shi, F., Ma, J., Wu, M., Zhang, J., Gao, J., “Effect of PEG additive on the morphology and performance of polysulfone ultrafiltration membranes”, *Journal of Membrane Science*, 272, 2011, p. 51-58.
- [11] June, P., Kilduff, J., Belfort, G., “Fouling-resistant properties of a surface-modified poly(ether sulfone) ultrafiltration membrane grafted with poly(ethylene glycol)-amide binary monomers”, *Journal of Membrane Science*, 377, 2011, p. 159–166.
- [12] Susanto, H., Balakrishnan, M., Ulbricht, M., “Via surface functionalization by photograft copolymerization to low-fouling polyethersulfone-based ultrafiltration membranes”, *Journal of Membrane Science*, 288, 2007, p. 157–167.
- [13] Gombotz, W.R., Guanghai, W., Horbett, T.A., Hoffman, A.S., “Protein adsorption to poly(ethylene oxide) surfaces”, *Journal of Biomedical Materials Research*, 25, 1991, p. 1547-1562.
- [14] Kim J., Lee, K., “Effect of PEG additive on membrane formation by phase inversion”, *Journal of Membrane Science*, 138, 1998, p. 153-163.
- [15] Witte, P., Dijkstra, P. J., Berg, J.W.A., Feijen, J., “Phase separation processes in polymer solutions in relation to membrane formation”, *Journal of Membrane Science*, 117, 1996, p. 1-31.
- [16] Wang, D., Lai, J., “Recent advances in preparation and morphology control of polymeric membranes formed by nonsolvent induced phase separation”, *Current Opinion in Chemical Engineering*, 2013, p. 229-237.

- [17] Ohya, H., Shiki, S., Kawakami, H., “Fabrication study of polysulfone hollow-fiber microfiltration membranes: Optimal dope viscosity for nucleation and growth”, *Journal of Membrane Science*, 326, 2009, p. 293–302.
- [18] Fane, A.G., Xi, W., Rong, W., “Chapter 7: Membrane filtration processes and fouling, *Interface Science in Drinking Water Treatment*”, *Interface Science in Drinking Water Treatment*, 2006, p. 109-132.
- [19] Bacchin, P., Aimar, P., Field, R.W., “Review Critical and sustainable fluxes: Theory, experiments and applications”, *Journal of Membrane Science*, 281, 2006, p. 42–69.
- [20] Miller, D.J., Paul, D.R., Freeman, B.D., “A crossflow filtration system for constant permeate flux membrane fouling characterization”, *Review of Scientific Instruments*, 84, 2013, p. 1-11.
- [21] Shi, X., Tal, G., Hankins, N.P., Gitis, V., “Fouling and cleaning of ultrafiltration membranes: A review”, *Journal of Water Process Engineering*, 1, 2014, p. 121–138.
- [22] Miller, D.J., Kasemset, S., Paul, D.R., Freeman, B.D., “Comparison of membrane fouling at constant flux and constant transmembrane pressure conditions”, *Journal of Membrane Science*, 454, 2014, p. 505–515.
- [23] Chakrabarty, B., Ghoshal, A.K., Purkait, M.K., “Effect of molecular weight of PEG on membrane morphology and transport properties”, *Journal of Membrane Science*, 309, 2008, p. 209–221.
- [24] Amirilargani, M., Saljoughi, E., Mohammadi, T., “Effects of Tween 80 concentration as a surfactant additive on morphology and permeability of flat sheet polyethersulfone (PES) membranes”, *Desalination*, 249, 2009, p. 837–842.
- [25] Rahimpour, A., Madaeni, S.S., Mansourpanah, Y., “The effect of anionic, non-ionic and cationic surfactants on morphology and performance of polyethersulfone ultrafiltration membranes for milk concentration”, *Journal of Membrane Science*, 296, 2007, p. 110–121.

- [26] Ma, X., Su, Y., Sun, Q., Wang, Y., Jiang, Z., “Preparation of protein-adsorption-resistant polyethersulfone ultrafiltration membranes through surface segregation of amphiphilic comb copolymer”, *Journal of Membrane Science*, 292, 2007, p. 116–124.
- [27] Wang, Y., Su, Y., Ma, X., Sun, Q., Jiang, Z., “Pluronic polymers and polyethersulfone blend membranes with improved fouling-resistant ability and ultrafiltration performance”, *Journal of Membrane Science*, 283, 2006, p. 440–447.
- [28] Zhao, W., Su, Y., Li, C., Shi, Q., Ning, X., Jiang, Z., “Fabrication of antifouling polyethersulfone ultrafiltration membranes using Pluronic F127 as both surface modifier and pore-forming agent”, *Journal of Membrane Science*, 318, 2008, p. 405–412.
- [29] Çulfaz, P.Z., Rolevink, E., Rijn, C., Lammertink, R.G.H., Wessling, M., “Microstructured hollow fibers for ultrafiltration”, *Journal of Membrane Science*, 347, 2010, p. 32–41.
- [30] Boom, R.M., Boomgaard, T., Smolders, C.A., “Mass transfer and thermodynamics during immersion precipitation for a two-polymer system Evaluation with the system PES-PVP-NMP-water”, *Journal of Membrane Science*, 90, 1994, p. 231-249.
- [31] Field, R. W., Wu, D., Howell, J. A., Gupta, B. B., “Critical flux concept for microfiltration”, *Journal of Membrane Science*, 100, 1995, p. 259-272.
- [32] Young, T., Chen, L., “Pore formation mechanism of membranes from phase inversion processes”, *Desalination*, 103, 1993, p. 233-247.
- [33] Barzin, J., Sadatnia, B., “Correlation between macrovoid formation and the ternary phase diagram for polyethersulfone membranes prepared from two nearly similar solvents”, *Journal of Membrane Science*, 325, 2008, p. 92–97.
- [34] Liu, Y., Koops, G., Strathmann, H., “Characterization of morphology controlled polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to

the dope and bore liquid solution”, *Journal of Membrane Science*, 223, 2003, p. 187–199.

[35] Torrestiana-Sanchez, B., Ortiz-Basurto, R.I., La Fuente, E., “Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes”, *Journal of Membrane Science*, 152, 1999, p. 19-28.

[36] Belfort, G., Davis, R.H., Zydney, A.L., “Review The behavior of suspensions and macromolecular solutions in crossflow microfiltration”, *Journal of Membrane Science*, 96, 1994, p. 1-58.

[37] Shi, Q., Su, Y., Ning, X., Chen, W., Peng, J., Jiang, Z., “Trypsin-enabled construction of anti-fouling and self-cleaning polyethersulfone membrane”, *Bioresource Technology*, 102, 2011, p. 647–651.

APPENDIX A

RETENTION ANALYSIS

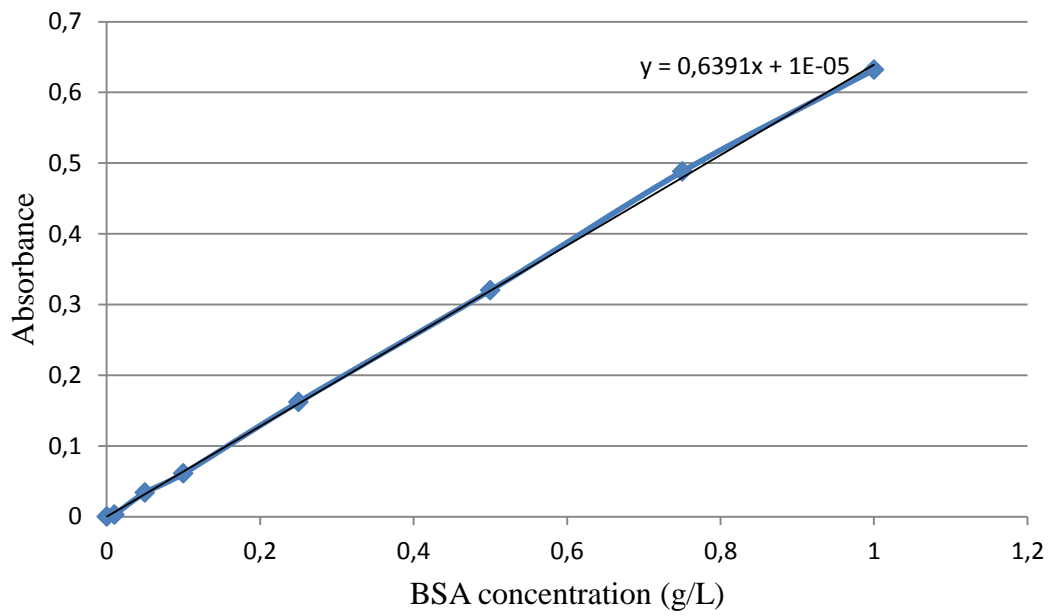


Figure A.1. BSA concentration vs. absorbance calibration curve

APPENDIX B

FTIR ANALYSIS

FTIR analysis results are presented in the following pages.

Table B.1. FTIR analysis results of hollow fiber membranes (tight ultrafiltration membranes) waited in water solution

	1105 cm⁻¹	1578 cm⁻¹	2865 cm⁻¹
PF (0 day)	28.7±6.3	17.5±4.9	5.1±2.5
PF (15 day)	28.2±1.4	19.4±1.1	5.1±0.4
PF (30 day)	27.3±0.3	17.6±0.3	3,8±0.1
PF (45 day)	30.5±2.9	18.5±2.4	4.8±1
PF (60 day)	25.9±1.4	14.2±0.6	3±0.1
PT (0 day)	19.9±2.3	12.4±1.3	1.7±0.1
PT (15 day)	31.1±7.6	21.4±5.8	5.4±2.4
PT (30 day)	20.9±1.8	13.9±1.3	2.3±0.6
PT (45 day)	31.8±0.5	20.8±0.6	4.1±0.4
PT (60 day)	23.9±4.6	14.9±3.5	2.2±0.8
P (0 day)	17.6±1.7	12.2±1.5	0.9±0.1
P (15 day)	11.1±1.4	8±1	0.7±0.1
P (30 day)	15.5±0.7	10.9±0.5	0.9
P (45 day)	17±0.6	11.3±0.5	0.6±0.1
P (60 day)	27.6±6.3	19.6±5.3	1.6±0.8
PP (0 day)	9±1.7	5.9±1.3	1.5±0.1
PP (15 day)	7.9±3.6	4.9±2.3	0,8±0.3
PP (30 day)	26.4±5.9	18.1±4.5	4.4±2
PP (45 day)	20.2±3.3	15.3±2.8	3.2±0.7
PP (60 day)	14.9±2.5	9.2±1.5	1.3±0.5

Table B.2. FTIR analysis results of hollow fiber membranes (loose ultrafiltration membranes) waited in water solution

	1105 cm⁻¹	1578 cm⁻¹	2865 cm⁻¹
PFWH (0 day)	18.1±1	9.3±0.7	1.9±0.1
PFWH (15 day)	26.7±0.3	15.2±0.1	3.2±0.1
PFWH (30 day)	21±3.9	11.9±2.5	2.9±0.7
PFWH (45 day)	11.2±2	5.3±1	0.9±0.1
PFWH (60 day)	15.8±2.7	8.3±1.9	2±0.7
PTWH (0 day)	11.1±0.6	6.4±0.4	0.9±0.2
PTWH (15 day)	15.7±2.5	10.8±2.6	1.9±0.8
PTWH (30 day)	15.9±0.2	9.9±0.1	1.2±0.1
PTWH (45 day)	14.9±1.9	8.6±1.1	0.8±0.1
PTWH (60 day)	13.3±0.2	8±0.1	1.1±0.2
PWH (0 day)	15.5±5.5	10.4±3.9	0.7±0.1
PWH (30 day)	9.5±0.5	5.6±0.4	0.3
PWH (45 day)	9.8±1.3	6.1±1	0.7±0.2
PWH (60 day)	8.3±1.5	4.8±1.1	0.5±0.1
PPWH (0 day)	18.4±0.9	11.3±0.5	1.7±0.2
PPWH (15 day)	16.9±1.7	10.1±0.9	1.5
PPWH (30 day)	16.1±5.3	9.6±3.2	0.9±0.2
PPWH (45 day)	15.6±0.2	9.4±0.4	1±0.1
PPWH (60 day)	15.4±0.6	8.7±0.5	1±0.1

Table B.3. FTIR analysis results of hollow fiber membranes (tight ultrafiltration membranes) waited in sodium hypochlorite solution

	1105 cm⁻¹	1578 cm⁻¹	2865 cm⁻¹
PF (15 day)	28.7±6.3	17.5±4.9	5.1±2.5
PF (30 day)	21.1±6.4	13.6±4.4	2.6±1
PF (45 day)	22.5±1.5	15.2±1.4	2.5±0.4
PF (60 day)	27.3±3.6	18.1±2.2	3.4±0.4
PT (0 day)	20.8±2.7	13.1±1.8	1.8±0.3
PT (15 day)	19.9±2.3	12.4±1.3	1.7±0.1
PT (30 day)	16.3±0.3	10.7±0.3	1.6±0.1
PT (45 day)	20.7±4.4	13.6±2.8	1.9±0.3
PT (60 day)	21.2±1.2	16.4±0.9	2.8±0.2
P (0 day)	12±2.2	8±1.5	1±0.3
P (15 day)	17.6±1.7	12.2±1.5	0.9±0.1
P (30 day)	37.7±2.4	30.8±2.8	4±1
P (45 day)	23.3±2.3	16.3±2.1	1.1
P (60 day)	26.1±2.5	21±2.1	1.9±0.1
PP (0 day)	15.3±0.8	10.4±0.7	0.5
PP (15 day)	9±1.7	5.9±1.3	1.5±0.1
PP (30 day)	27.4±0.6	21.3±1	5.2±0.5
PP (45 day)	18.2±1.9	12.9±1.1	2.4±0.1
PP (60 day)	15.5±1.2	12.9±0.1	2.4±0.6
PF (15 day)	13±2	10.9±0.6	1.9±0.2

Table B.4. FTIR analysis results of hollow fiber membranes (loose ultrafiltration membranes) waited in sodium hypochlorite solution

	1105 cm⁻¹	1578 cm⁻¹	2865 cm⁻¹
PFWH (0 day)	18.1±1	9.3±0.7	1.9±0.1
PFWH (15 day)	17.2±0.2	9.7±0.1	1.8±0.4
PFWH (30 day)	14.8±2.4	8.7±1.4	1.3±0.3
PFWH (45 day)	15.4±1.8	9.5±1.4	0.7±0.1
PFWH (60 day)	11.6±0.7	6.8±0.5	0.5±0.1
PTWH (0 day)	11.1±0.6	6.4±0.4	0.9±0.2
PTWH (15 day)	19.1±1.9	12.6±0.8	1.3
PTWH (30 day)	13.8±0.1	8.7±0.1	1.2
PTWH (45 day)	15±0.5	9.6±0.6	0.8
PTWH (60 day)	17.5±3.6	11.1±2.4	1.1±0.4
PWH (0 day)	15.5±5.5	10.4±3.9	0.7±0.1
PWH (30 day)	7.8±0.2	4.7±0.2	0.3±0.1
PWH (45 day)	10±0.5	6±0.1	0.2
PWH (60 day)	13.4±2.5	8.7±1.9	0.4±0.3
PPWH (0 day)	8.9±0.4	5.3±0.1	0.2±0.1
PPWH (15 day)	18.4±0.9	11.3±0.1	1.7±0.2
PPWH (30 day)	13.3±1.4	7.8±1	0.9±0.1
PPWH (45 day)	15.2±0.9	9.3±0.7	0.7
PPWH (60 day)	11±0.9	7±0.7	0.3

APPENDIX C

FOULING TEST

Fouling test analysis results are presented in the following pages.

Membrane area: $4.3 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $179 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $185 \text{ L/m}^2 \text{ h bar}$

Table C.1. Fouling test analysis of PT hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.286
Feed flush	10	-
Backwash flush	3	-
First filtration	15	0.620
Pressure relief	1	-
Backwash flush	3	-
First Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	15	0.752
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	15	0.761
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	15	0.830
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	15	0.836
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	3	-
Pressure relief	1	-
Pure water flush	10	-
Pure water permeation	10	0.546
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.462

Membrane area: $4.3 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $175 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $160 \text{ L/m}^2 \text{ h bar}$

Table C.2.Fouling test analysis of PT hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.261
Feed flush	10	-
Backwash flush	3	-
First filtration	15	0.548
Pressure relief	1	-
Backwash flush	3	-
First Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	15	0.692
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	15	0.771
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	15	0.829
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	15	0.859
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	3	-
Pressure relief	1	-
Pure water flush	10	-
Pure water permeation	10	0.610
Chemical cleaning (alkali acid)	20-20(outside system)	-
Pure water permeation	10	0.490

Membrane area: $3.6 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $107 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $99 \text{ L/m}^2 \text{ h bar}$

Table C.3.Fouling test analysis of PP hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.280
Feed flush	10	-
Backwash flush	3	-
First filtration	15	1.056
Pressure relief	1	-
Backwash flush	3	-
First Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	15	1.342
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	15	1.575
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	15	1.667
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	15	1.703
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	3	-
Pressure relief	1	-

Membrane area: $3.6 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $100 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $101 \text{ L/m}^2 \text{ h bar}$

Table C.4.Fouling test analysis of PP hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.482
Feed flush	10	-
Backwash flush	3	-
First filtration	15	1.464
Pressure relief	1	-
Backwash flush	3	-
First Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	15	1.745
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	15	1.922
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	15	2.004
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	15	2.131
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	3	-
Pressure relief	1	-
Pure water flush	10	-
Pure water permeation	10	1.294
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	1.018

Membrane area: $3.3 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $9 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $7.5 \text{ L/m}^2 \text{ h bar}$

Table C.5.Fouling test analysis of PH hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.675
Feed flush	10	-
Backwash flush	3	-
First filtration	45	0.860
Pressure relief	1	-
Backwash flush	3	-
First Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	45	1.317
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	45	1.553
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	45	1.671
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	45	1.784
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	9	-
Pressure relief	1	-
Pure water flush	10	-
Pure water permeation	10	1.961
Chemical cleaning (alkali-acid)	20-20 (outside system)	-
Pure water permeation	10	1.966

Membranearea: $3.2 \times 10^{-3} \text{ m}^2$

Membranepermeance (pressurevessel): $11 \text{ L/m}^2 \text{ h bar}$

Membranepermeance (system): $7 \text{ L/m}^2 \text{ h bar}$

Table C.6.Fouling test analysis of PH hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.727
Feed flush	10	-
Backwash flush	3	-
First filtration	45	0.820
Pressure relief	1	-
Backwash flush	3	-
First Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	45	0.996
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	45	1.171
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	45	1.380
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	9	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	45	1.491
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	9	-
Pressure relief	1	-
Pure water flush	10	-
Pure water permeation	10	1.648
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	1.638

Membrane area: $3.9 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $45 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $48 \text{ L/m}^2 \text{ h bar}$

Table C.7.Fouling test analysis of PFR hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.621
Feed flush	10	-
Backwash flush	3	-
First filtration	15	1.184
Pressure relief	1	-
Backwash flush	3	-
First Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	15	1.233
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	15	1.306
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	15	1.324
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	15	1.373
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	3	-
Pressure relief	1	-
Pure water flush	10	-
Pure water permeation	10	0.910
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.657

Membrane area: $3.9 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $43 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $40 \text{ L/m}^2 \text{ h bar}$

Table C.8.Fouling test analysis of PFR hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10	0.755
Feed flush	10	-
Backwash flush	3	-
First filtration	15	1.441
Pressure relief	1	-
Backwash flush	3	-
First Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Second filtration	15	1.467
Pressure relief	1	-
Backwash flush	3	-
Second Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Third filtration	15	1.505
Pressure relief	1	-
Backwash flush	3	-
Third Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fourth filtration	15	1.486
Pressure relief	1	-
Backwash flush	3	-
Fourth Backwash	3	-
Pressure relief	1	-
Feed flush	3	-
Fifth filtration	15	1.528
Pressure relief	1	-
Backwash flush	3	-
Fifth Backwash	3	-
Pressure relief	1	-
Pure water flush	10	-
Pure water permeation	10	1.107
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.875

Membrane area: $3.4 \times 10^{-3} \text{m}^2$

Membrane permeance (pressure vessel): $210 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $210 \text{ L/m}^2 \text{ h bar}$

Table C.9.Fouling test analysis of PFWH hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.138
Feed flush	10	-
Filtration	15	0,150
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	0.152
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.148

Membrane area: $3.4 \times 10^{-3} \text{m}^2$

Membrane permeance (pressure vessel): $325 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $271 \text{ L/m}^2 \text{ h bar}$

Table C.10.Fouling test analysis of PFWH hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.100
Feed flush	10	-
Filtration	15	0.114
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	0.115
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.107

Membrane area: $3 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $58 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $52 \text{ L/m}^2 \text{ h bar}$

Table C.11.Fouling test analysis of PTWH hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.575
Feed flush	10	-
Filtration	15	0.653
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	0.664
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.664

Membrane area: $3.2 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $37 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $32 \text{ L/m}^2 \text{ h bar}$

Table C.12.Fouling test analysis of PTWH hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.947
Feed flush	10	-
Filtration	15	1.176
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	1.008
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	1.154

Membrane area: $3.2 \times 10^{-3} \text{m}^2$

Membrane permeance (pressure vessel): $53 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $47 \text{ L/m}^2 \text{ h bar}$

Table C.13.Fouling test analysis of PWH hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.635
Feed flush	10	-
Filtration	15	0.855
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	0.822
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.793

Membrane area: $3.2 \times 10^{-3} \text{m}^2$

Membrane permeance (pressure vessel): $43 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $38 \text{ L/m}^2 \text{ h bar}$

Table C.14.Fouling test analysis of PWH hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.785
Feed flush	10	-
Filtration	15	1.045
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	1.008
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	1.001

Membrane area: $3.2 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $34 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $32 \text{ L/m}^2 \text{ h bar}$

Table C.15.Fouling test analysis of PPWH hollow fiber membrane (first experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.877
Feed flush	10	-
Filtration	15	1.040
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	1.060
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	1.020

Membrane area: $3.4 \times 10^{-3} \text{ m}^2$

Membrane permeance (pressure vessel): $80 \text{ L/m}^2 \text{ h bar}$

Membrane permeance (system): $75 \text{ L/m}^2 \text{ h bar}$

Table C.16.Fouling test analysis of PPWH hollow fiber membrane (second experiment)

Process	Time (min)	Final pressure (bar)
Pure water flush	10	-
Pure water permeation	10(stable)	0.401
Feed flush	10	-
Filtration	15	0.543
Pure water flush (500 g/h)	15	-
Pure water permeation	10 (stable)	0.583
Chemical cleaning (alkali-acid)	20-20(outside system)	-
Pure water permeation	10	0.476

APPENDIX D

FOULING TEST RESULTS

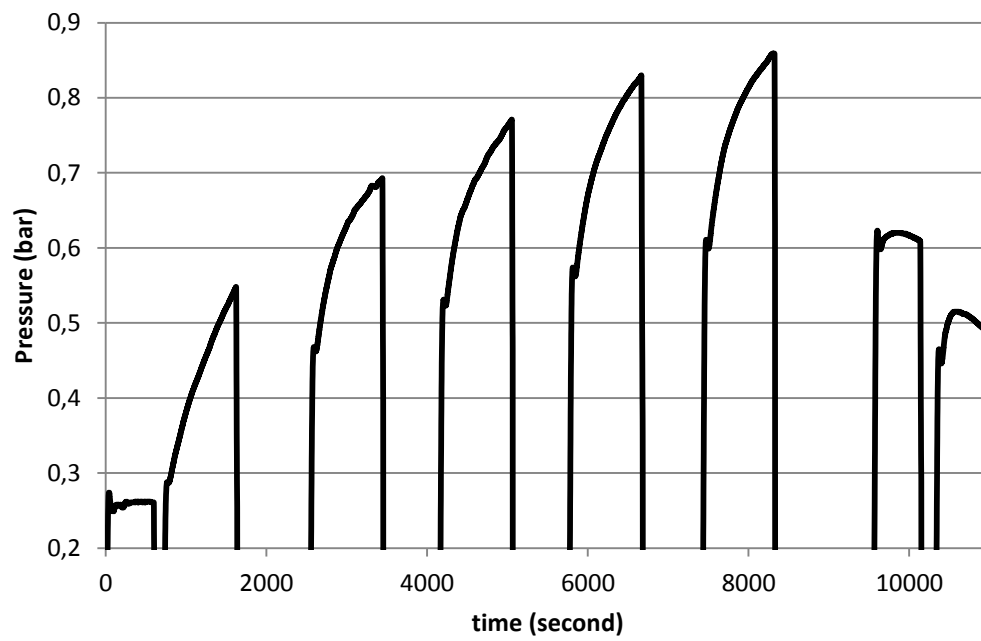


Figure D.1. Fouling test result of PT membrane (second experiment) change with pressure

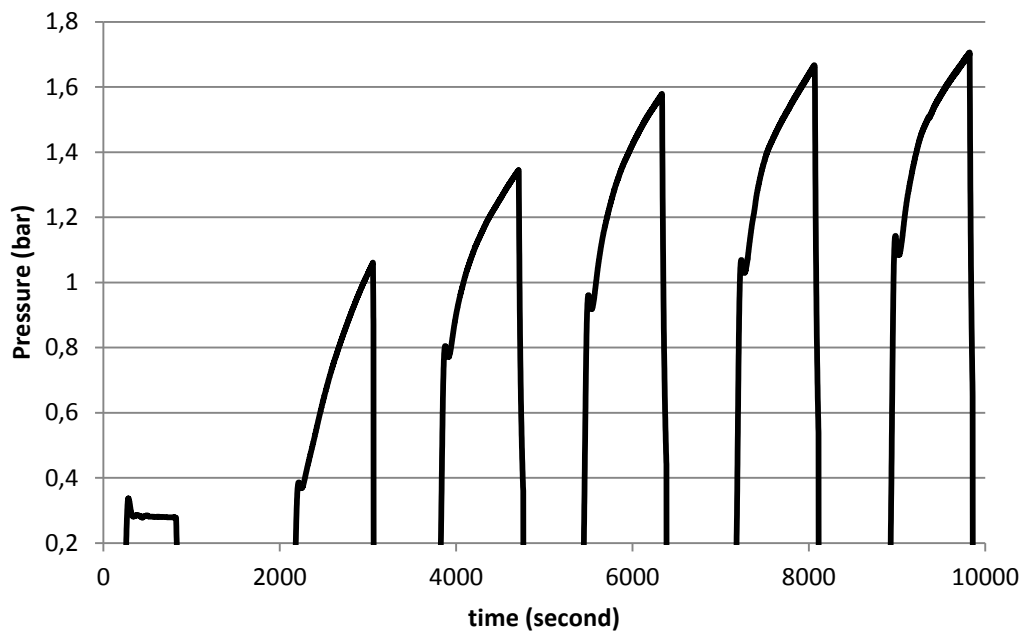


Figure D.2. Fouling test result of PP membrane (first experiment) change with pressure

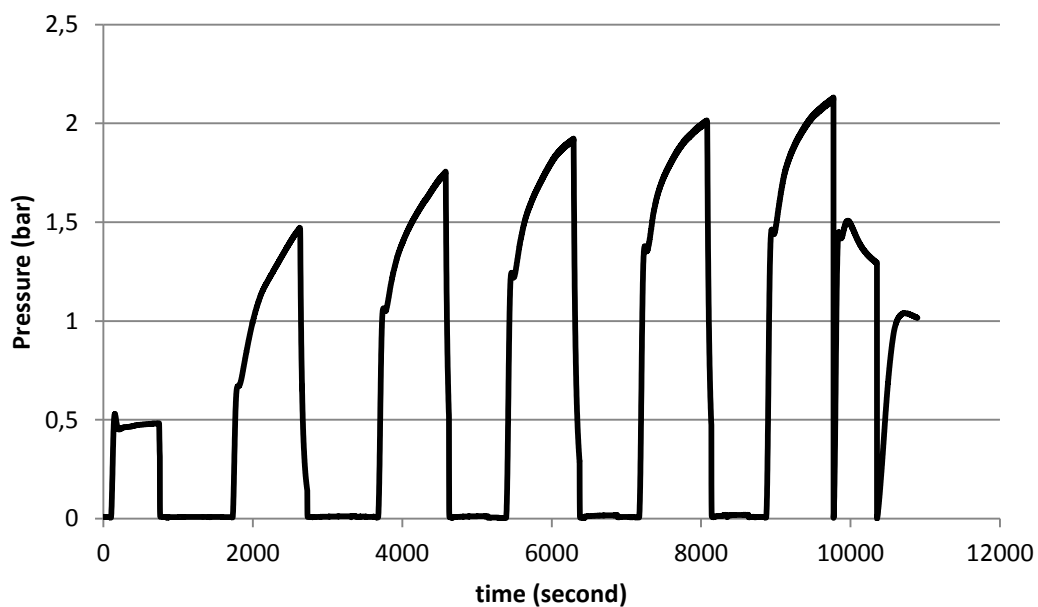


Figure D.3. Fouling test result of PP membrane (second experiment) change with pressure

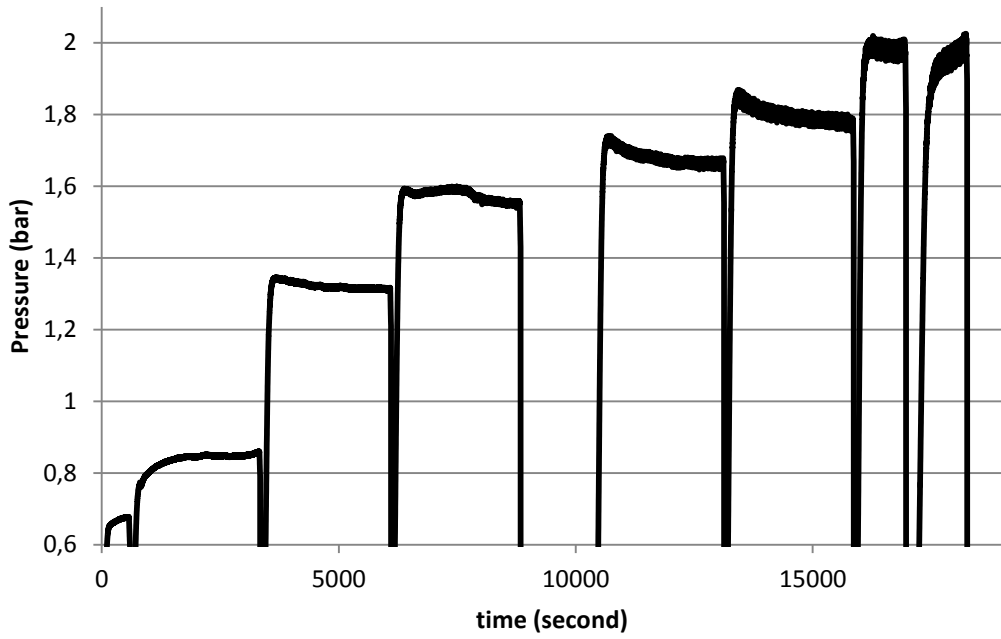


Figure D.4. Fouling test result of PH membrane (first experiment) change with pressure

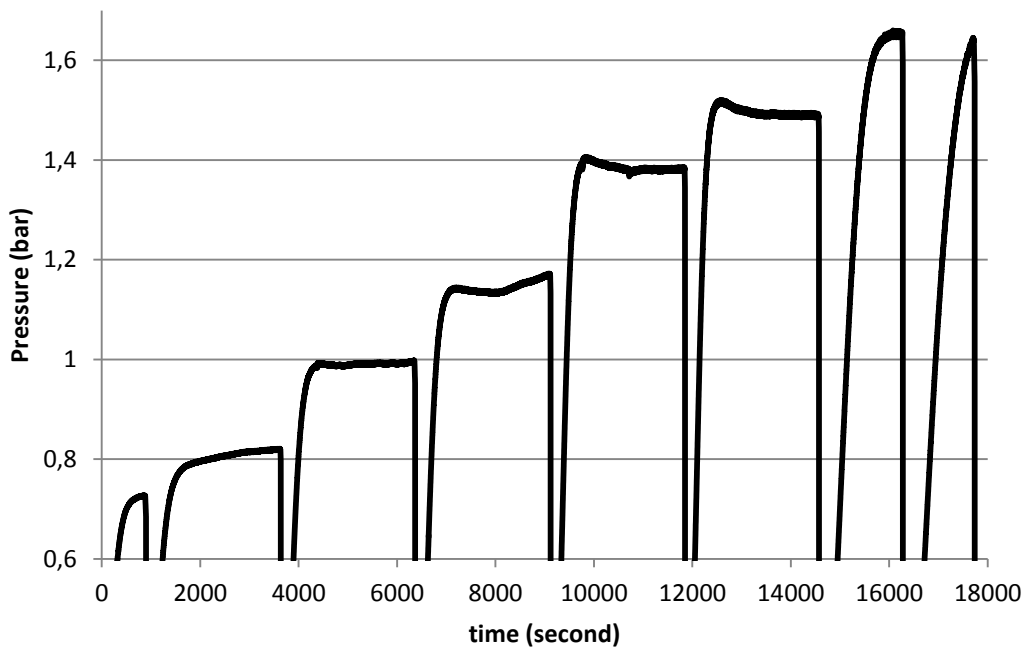


Figure D.5. Fouling test result of PH membrane (second experiment) change with pressure

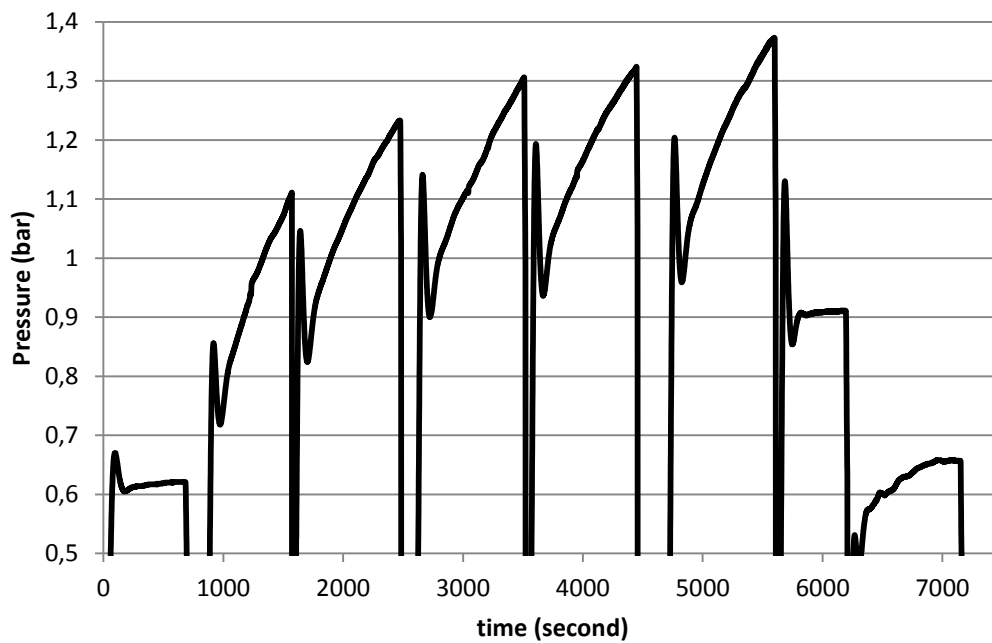


Figure D.6. Fouling test result of PFR membrane (first experiment) change with pressure

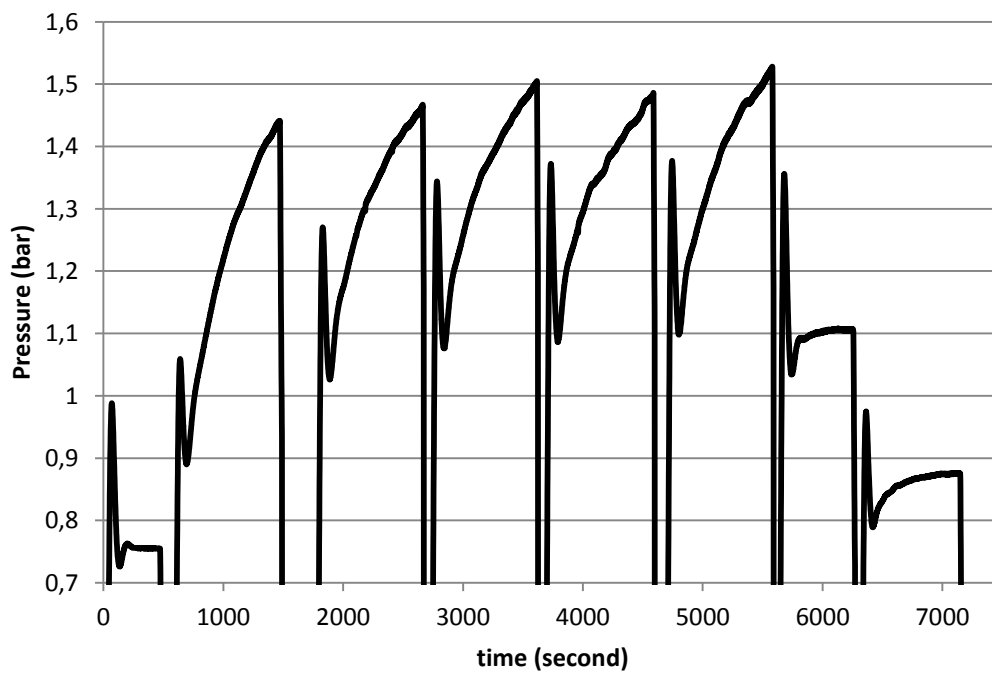


Figure D.7. Fouling test result of PFR membrane (second experiment) change with pressure

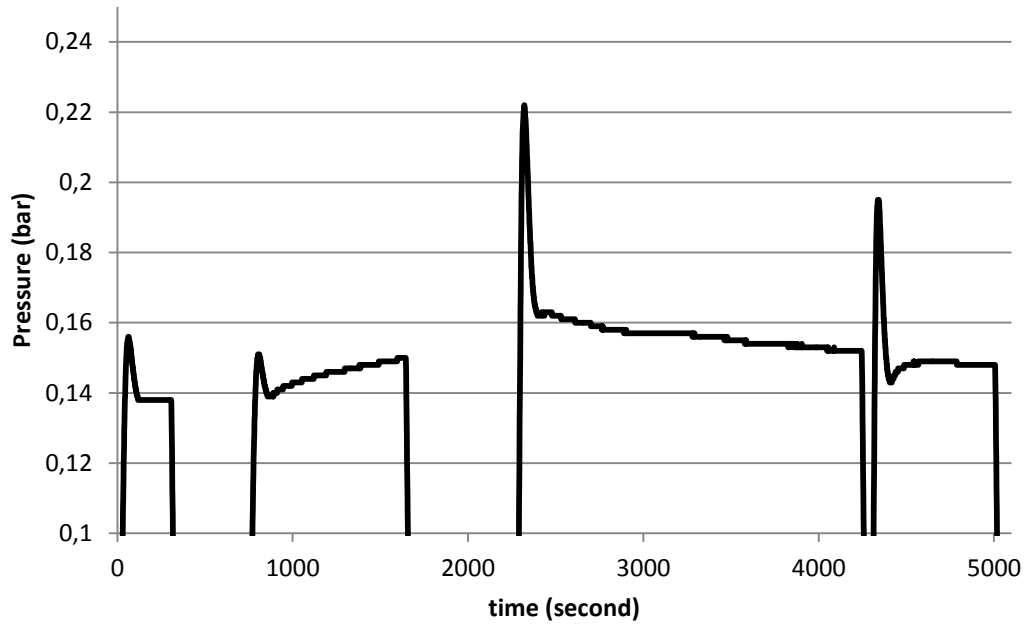


Figure D.8. Fouling test result of PFWH membrane (first experiment) change with pressure

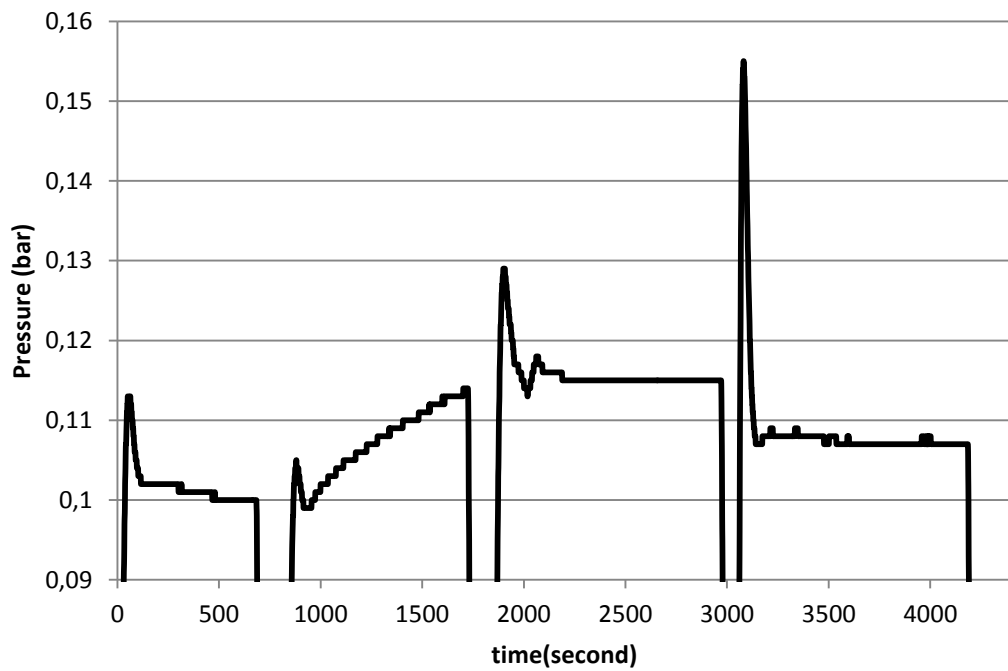


Figure D.9. Fouling test result of PFWH membrane (second experiment) change with pressure

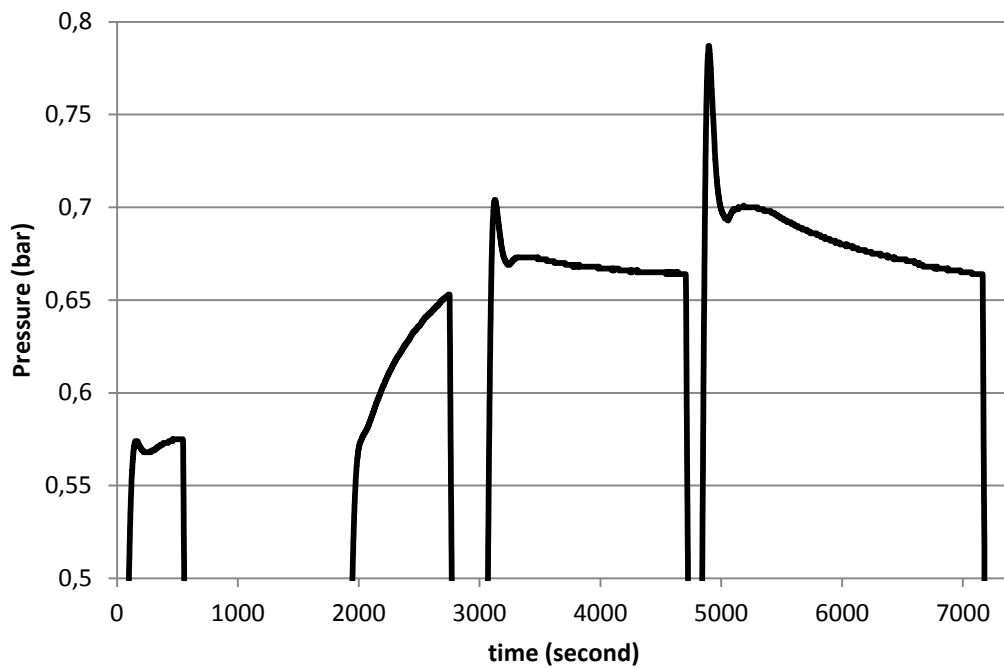


Figure D.10. Fouling test result of PTWH membrane (first experiment) change with pressure

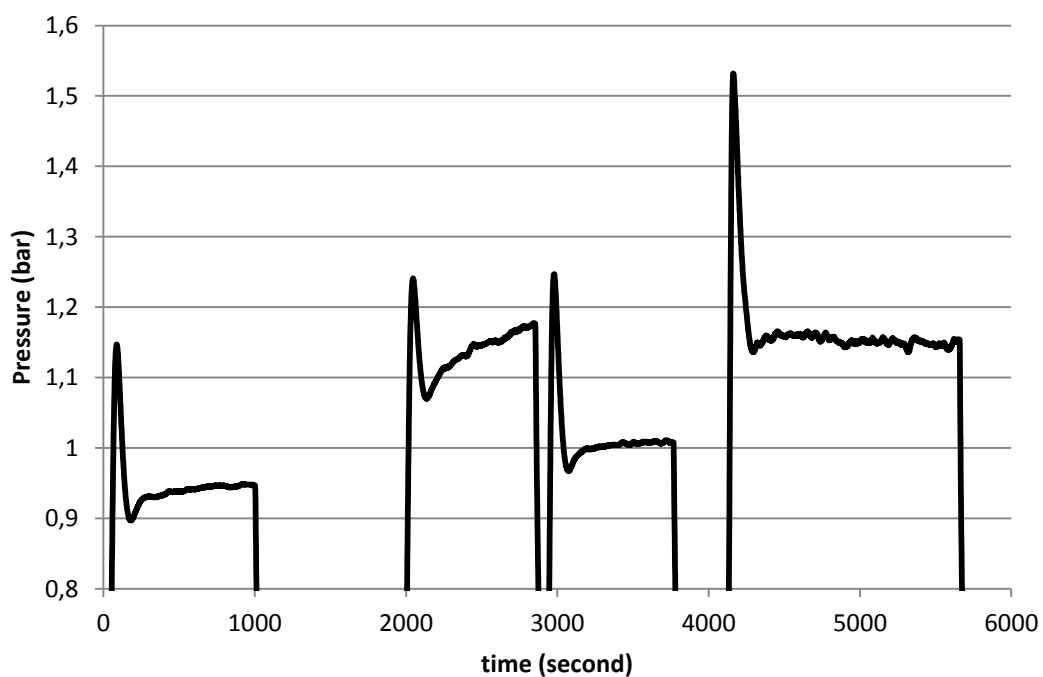


Figure D.11. Fouling test result of PTWH membrane (second experiment) change with pressure

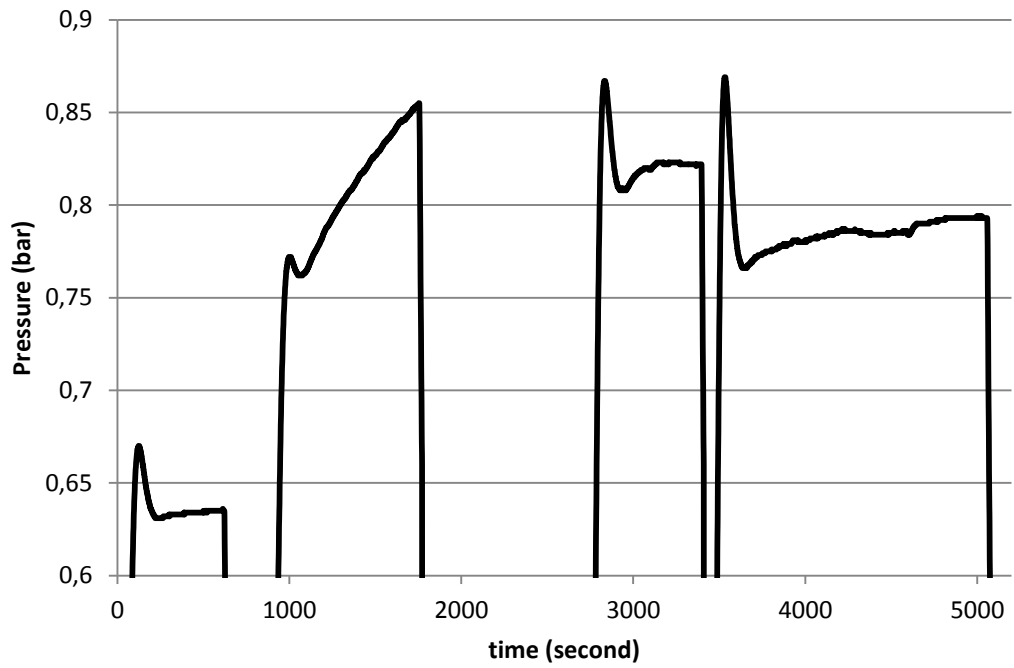


Figure D.12. Fouling test result of PWH membrane (first experiment) change with pressure

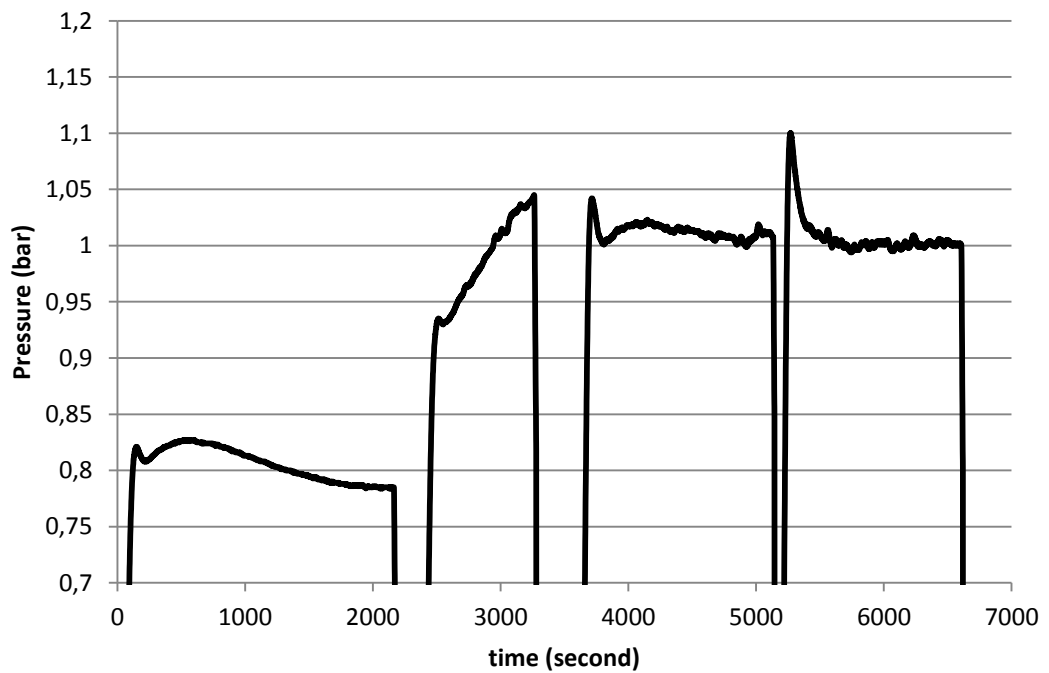


Figure D.13. Fouling test result of PWH membrane (second experiment) change with pressure

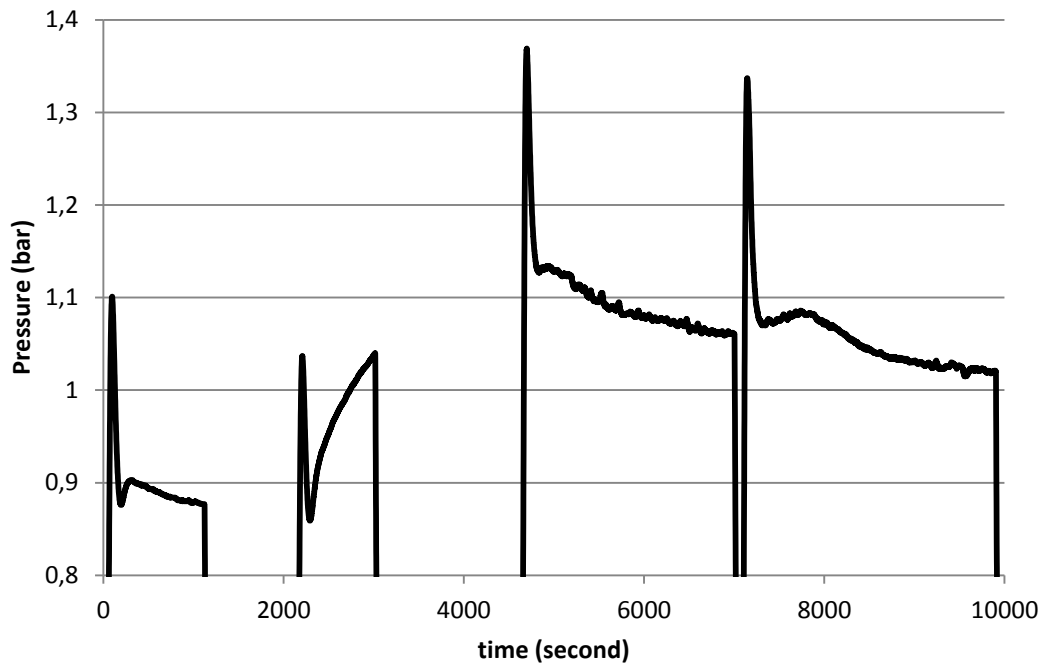


Figure D.14. Fouling test result of PPWH membrane (first experiment) change with pressure

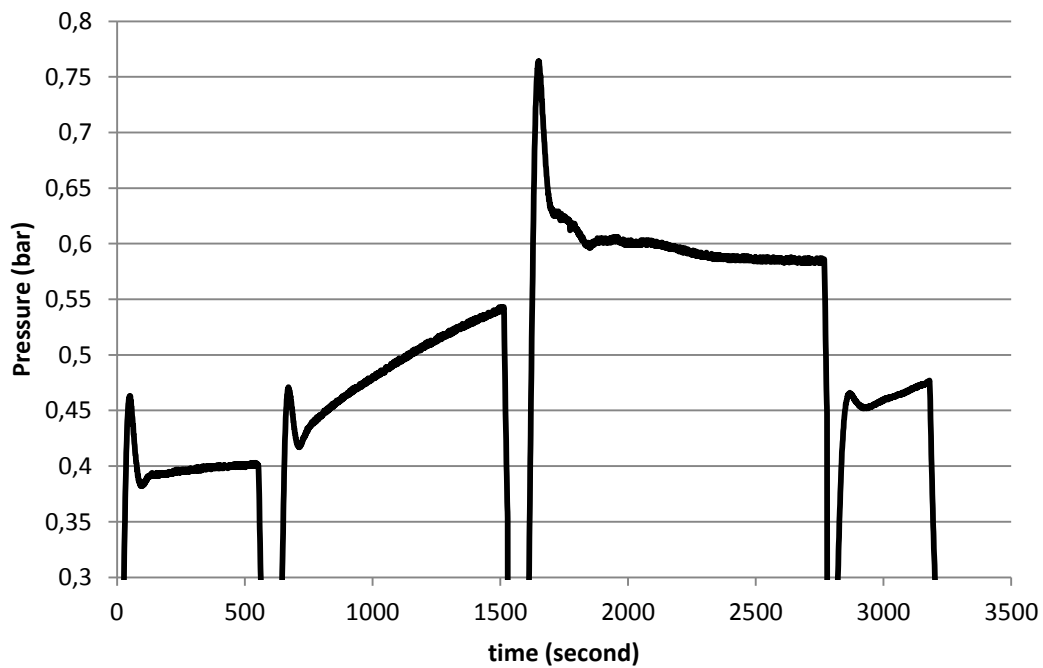


Figure D.15. Fouling test result of PPWH membrane (second experiment) change with pressure