UNIVERSITI PUTRA MALAYSIA

EFFECT OF ADDITIVES ON THE PERFORMANCE AND MORPHOLOGY OF POLYETHERSULFONE (PES) BLEND ULTRAFILTRATION MEMBRANE

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APPROVAL

This project entitled "Effect of Additives on the Performance and Morphology of Polyethersulfone (PES) Blend Ultrafiltration Membrane" prepared and submitted by Putri Arina Binti Rohman in partial fulfilment of the requirement for the degree of Bachelor of Engineering (Process and Food) is hereby accepted and approved.

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ABSTRACT

A membrane separation process has becomes one of emerging technologies that have gained an important place in separation technology and are used in a broad range of applications. However, there are few limitations such as membrane fouling and economic competitive that prevent the membrane technology to expand further. Thus, this project is aimed to seek alternatives in order to improve the membrane performance and reducing the fouling effects. The effect of additives on the Polyethersulfone (PES) membrane performance and also morphology is being investigated throughout this study. Aside from that, the effect of additives on the ability of the membrane to recover from the fouling is also determined in this project. The flat membranes were formulated from casting solution of PES polymer, N-methyl-2-pyrrolidone (NMP) solvent, Polyethylene glycol (PEG) and Pluronic F127 additives by immersing them in water as coagulant medium. All the membranes will be tested with analyses in order to determine their performances which are pure water permeation (PWP), filtration of apple juice and tap water with rejection, flux recovery and reduction, tensile strength and also the morphological structures by using scanning electron microscope (SEM). The experiment shows that the membranes prepared with additives contributed to the high flux value during PWP analysis and also high rejection value during the apple juice and tap water filtration. Furthermore, it was found that the additives also able to increase the membrane resistance towards fouling and also the ability of the membrane to recover from the fouling. In summary, it can be concluded that the performance of the membranes could be improved by the addition of polymeric additives.

ABSTRAK

Proses penapisan membran merupakan salah satu teknologi membangun dan telah mendapat tempat yang penting dalam teknologi penapisan. Walau bagaimanapun, terdapat beberapa masalah seperti mendapan kotoran pada membran yang telah menjadi penghalang kepada teknologi ini untuk berkembang. Sehubungan dengan itu, projek ini adalah bertujuan mencari alternatif bagi penambahbaikkan membran dan mengurangkan kesan mendapan kotoran terhadap membran. Keberkesanan penambahan aditif terhadap prestasi dan struktur morfologi membran Polyethersulfone (PES) telah disiasat sepanjang kajian ini. Selain itu, kesan penambahan aditif terhadap keupayaan membran untuk pulih daripada mendapan kotoran yang juga ditentukan dalam projek ini. Membran telah disediakan daripada satu larutan pemutus daripada polimer PES, pelarut N-metil-2-pyrrolidone (NMP), aditif polietilena glikol (PEG) dan Pluronic F127 dengan merendamkannya di dalam air sebagai medium koagulan. Semua membran akan diuji dengan beberapa analisis seperti keupayaan penyerapan air, penapisan jus epal dan air paip, pemulihan dan pengurangan fluks, kekuatan tegangan dan juga struktur morfologi dengan menggunakan imbasan elektron mikroskop (SEM) untuk menentukan prestasi membran tersebut. Eksperimen ini menunjukkan bahawa penambahan aditif di dalam membran menyumbang kepada nilai fluks yang tinggi ketika analisis PWP dan juga mendapat nilai penolakan yang agak tinggi untuk penapisan jus epal dan juga air paip. Selain itu, aditif juga berupaya meningkatkan rintangan membran terhadap mendapan kotoran dan keupayaan untuk pulih. Pada akhir kajian ini, dapat disimpulkan bahawa prestasi membran dapat diperbaiki dengan penambahan bahan aditif.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

The membrane separation process has become one of the emerging technologies where it has gained an important place in chemical technology and also used in many applications. It has undergone a rapid growth and development in the past few decades. Many articles and reviews have been written about the membrane development and it shows that remarkable progress has been achieved in the last years of membrane development. Membrane industry has been performing an excellent research and development (R&D) work on membrane materials in order to produce membrane that is suitable for a wide variety of applications with extended life. Although the membrane processes are a relatively new type of separation technology, several membrane processes such as particularly pressure-driven membrane processes that including Reverse Osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF), and Microfiltration (MF), are already being applied on an industrial scale to food and bio-product processing (Cui et al., 2010).

Membrane technology is known as the most important separation process due to its high efficiency and low separation cost. Ultrafiltration (UF) membrane has received huge attention in certain field application such as concentration or purification of protein solutions, pharmaceutical industry, dairy industry, biotechnology, and water treatments. The distinct advantages of ultrafiltration include no phase change involved, low operating pressure, and ambient or relatively low operating temperature. The desirable ultrafiltration membranes should be of high selectivity, high flux, and excellent antifouling property (Peyravi et al., 2012).

The current trend nowadays is to develop the new membrane materials and structures specifically in view of reducing fouling effects, biocompatibility and function. Membrane structure and performance depends on polymer concentration, choice, solvent and non-solvent composition, evaporation time, elevation bath temperature and reaction time are among the parameters that play an important role to determine its final performance of the membrane (Bansod et al., 2012). The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. Most of the membrane experts have been investigating and synthesizing new polymers that are able to exhibit both higher permeability and selectivity. In particular, most emphasis has been given to the modification methods in order to improve the membrane process (Zhao et al., 2013).

Polyethersulfone (PES) is one of the most important polymeric materials and is widely used in separation fields. PES and PES-based membranes show outstanding oxidative, thermal and hydrolytic stability as well as good mechanical property. The membranes always show asymmetric structure, and are prepared by a phase inversion method. The membrane structure is influenced by few factors such as the compositions which are concentration, solvent, additives and temperature of PES solution, the non-solvent or the mixture of non-solvents. However, PES membrane consisting of high hydrophobicity properties can cause severe membrane fouling. Thus, PES membrane needs to be modified in order to overcome the limitation.

Modification of PES membranes to increase the hydrophilicity can be carried in several ways. Many kinds of modification methods have been used for the modification of PES membranes such as physical methods including blending and surface-coating methods and chemical methods including photo-induced grafting, and gamma ray (Zhao et al., 2013).

The physical blending is the most common method used where the technique is done usually by blending the modifying agents (additives) with the polymer as this technique is simple and practically feasible. In general, additives play a crucial role in modifying and adjusting the membrane properties as they contribute to the pore formation and can influence creation of either spongy, finger like or macrovoids containing cross-section morphology which they can also yield a hydrophilic character of the resulting membrane (Abdel-karim et al., 2017).

1.2 PROBLEM STATEMENT

Main drawbacks that prevent membrane technology from expanding further the current application often involve economic competitive of the existing membrane separation technologies and also the present challenge of membranes performance such as membrane fouling. Due to these problems, many applications are seeking for alternative in order to produce membranes with higher selectivity and permeability. Furthermore, membrane that has high ability to recover from fouling is also one of the desired characteristic for most applications. As the membrane can be recovered and reused thus it will help to reduce the economic costing.

Currently, the modification of PES membranes has been extensively investigated in order to enhance the membrane performance and also for improving the membrane anti-fouling property. It is impossible to produce zero-fouling membranes but the minimization of membrane fouling can be done efficiently (Malek et al., 2012). One of the modifications approaches of PES membrane is by blending the membrane together with the hydrophilic polymers (modified agent) which are also known as polymeric additives.

Therefore, this study is focused on the effect of adding two different additives with different concentrations to the PES ultrafiltration membrane in order to determine the membrane performance and also the anti-fouling property. The effect of adding two different additives on the membrane performances such as the permeability and recovery will be determined throughout this study.

1.2 OBJECTIVES

1. To fabricate Polyethersulfone (PES) ultrafiltration membrane with different kind of concentration additives (PEG/Plunoric F127) based on phase inversion process.
2. To study the effect of additives on the membrane performance such as flux, permeability and separation factor of PES-UF membrane.
3. To investigate the mechanical strength and the morphological structure of PES-UF membrane.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE TECHNOLOGY

Membrane is a thin layer or barrier that occupies through a selective separation wall and allows only certain substance to pass through it while the other substances are caught. In the most general sense, a membrane is a selective or contacting barrier that separates or contacts two different regions and controls the exchange of matter and energy between the regions. In the first case, it controls the exchange between the two regions adjacent to it in a very specific manner and for the latter case its function is mainly to contact the two regions between which the transport occurs (Strathmann, 2016). The principle of a membrane separation process is shown in Figure 2.1 below.

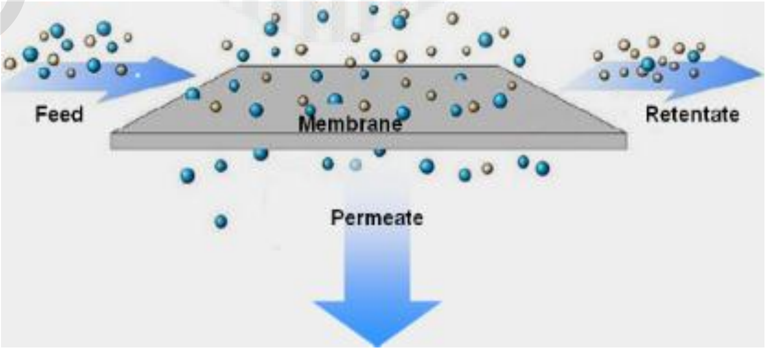


Figure 2.1 Membrane separation process (Schmeling et al., 2010).

Membrane technology is a term that refers to a number of different filtration processes that are used to separate substances (Lenntech, 2016). Membrane technology plays an important role with a wide range of applications for both in industrial and also scientific. They provide effective alternative to related technologies such as wastewater treatment and producing various quality of water from surface water, well water, brackish water and seawater (Nicolaisen, 2002). The membrane process nowadays are used in three main areas which are the area that includes the application such as seawater desalination or wastewater purifications, the area that includes applications such as the production of ultrapure water or the separation of molecular mixtures in the food and drug industry, and the last area where it is the membrane applications in artificial organs and therapeutic systems (Strathmann et al., 2016).

2.2 HISTORY OVERVIEW

Membrane technology has a relatively short but interesting history. Over the last three decades, the membrane based separation process has proved their potential as better alternatives to the traditional separation process (Boretos, 1973). The asymmetric membranes which are the foundation of most commercialized membrane nowadays were first synthesized in 1960s.

During that time, the membranes were not considered a good application but the membrane technology has developed and recognized for their potential to solve the separation process in 1970s and 1980s (Muralidhara, 2010). Other applications of membranes which were developed in recent years that have reached large technical and commercial significance include the controlled release of drugs in therapeutic devices and the storage and conversion of energy in fuel cells and batteries.

However, the most important application of membranes today is in reverse osmosis water desalination, hemodialysis and hemofiltration. The summary of membrane separation based development is shown in Table 2.1.

Table 2.1 Summary of membrane separation development

Name of Inventor	Year	Invention
J.K Mitchell	1831	First scientific observation related to gas separation
Thomas Graham	1850	Graham’s law of diffusion
J.S. Chiou and D.R. Paul	1987	Prove for two membranes as a function of CO2 conditioning and driving pressure
Stern et al.	1989	Development of nine types of polymide membranes
Suzuki et al.	1998	Fabricated dual-layer hollow fiber membranes composed of a dense polymide outer layer and a sponge like inner layer made of another polymide.
I.Cabasso	1979	Development of polyethyleneimine or polysulfone (PS) hollow fibers for reverse osmosis
Nitto Denko	1988	Develop first commercial vapors separation plants
Li et al.	2002	Conducted the first systematics study to investigate the effects of spinning conditions on dual-layer hollow fiber membranes.

2.3 MEMBRANE STRUCTURE

Membranes can be divided into two types according to their structures which are symmetric and asymmetric membranes (Cui et al., 2010). The classification of the structure is shown as in Figure 2.2 below.

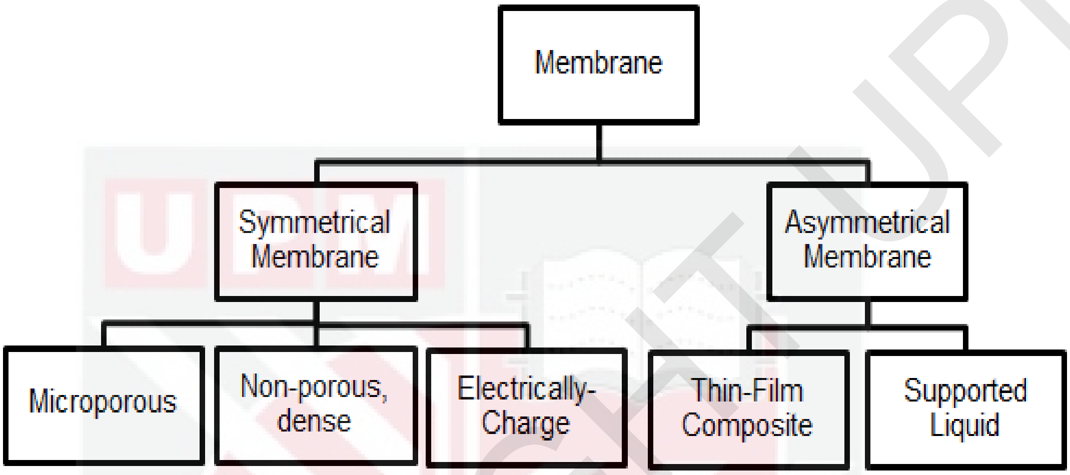


Figure 2.2 Membrane structure classification (Baker, 2011)

2.3.1 SYMMETRICAL MEMBRANE

Symmetrical membranes have a uniform composition and structure throughout the entire membrane thickness where the membranes can be porous or dense (Baker, 2011). Symmetric membranes are used mainly in dialysis, electro dialysis, and to some extent in microfiltration application. The range of symmetric membranes thickness is usually between 30 and 500 µm. The total of the mass transfer depends on the total thickness of the membranes. Thus, membrane thickness needs to be decreased in order to increase the permeation rate (Strathmann, 2011).

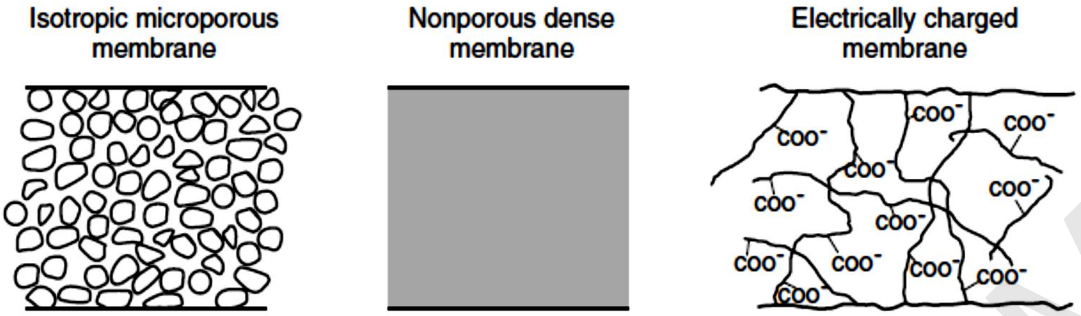


Figure 2.3 Types of symmetrical membrane structure

2.3.1.1 Isotropic Microporous Membrane

Microporous membrane is quite similar to conventional filter in terms of structure and function. The structure of the membrane is rigid, highly voided with randomly distributed and interconnected pores (Baker, 2011). Microporous membranes are designed to reject all particles above their rating and block any species that are similar sizes with the pores (Cui et al., 2010). In other words, any particles that are larger than the pores will be rejected by the membrane while the particles that are smaller than the pores are available to pass the membrane. The study also found that the microporous membranes able to separate the molecules that differ in size effectively (Baker, 2011).

2.3.1.2 Nonporous, Dense Membrane

Nonporous membrane is a dense film where permeate diffuse through by pressure, concentration, or electrical potential gradient. The separation process of the components occurs from their diffusivity and solubility in the membrane material. Hence, the nonporous membrane can separate particles that have similar size if their solubility is different. Non-porous membranes are mainly used for reverse osmosis, perfavoporation, or gas separation (Baker, 2011). However since the non-porous membranes have low flux, these membranes will have an anisotropic structure to improve the flux (Synder, 2016).

2.3.1.3 Electrically Charged Membrane

Electrically charged membranes can either be dense or microporous but the most common is microporous with the pore walls carrying fixed positive and negative charged ions. The membrane with positive ions is known as anion-exchange membrane where it binds anion in the surrounding fluid while for the negative ion the membrane is referred to cation-exchange membrane. Separation is achieved mainly by exclusion of ions of the same charge as the fixed ions on the membrane structure, and is affected by the charge and concentration of ions in the solution (Baker, 2011).

2.3.2 ASYMMETRICAL MEMBRANE

Asymmetric membrane consists of selective skin layer on the top of its membrane body. The thickness of the skin layer is range about 0.1–5 μm on a highly porous 100–300 μm thick membrane structure (Strathmann 2011). The skin layer functions as selective barrier of the asymmetric substructure and the separation properties are thoroughly determined by the nature of the material or the size of pores in the skin layer. The dense surface layer is considered to be responsible for the membrane selectivity while the top layer is mainly to determine the resistance to the mass transfer (Buonomenna et al., 2011). The membrane layers usually are made from different polymers (Baker, 2011). The separation properties and permeation rates of the membrane are determined exclusively by the surface layer while the membrane body which is usually void giving mechanical support to the skin layer (Strathmann, 2011).

Asymmetric membrane can be prepared using two procedures where the first method is based on phase inversion process which leads to integral structure (Kesting 1971) , and the second method resembles a composite structure in a two-step process in which a thin barrier layer is deposited on a microporous substructure (Strathmann, 2011). Compared to the microporous membranes, the asymmetric membranes rarely get blocked. Most ultrafiltration, nanofiltration, and reverse osmosis membranes are of asymmetric structure, while most polymeric microfiltration membrane of microporous structure.

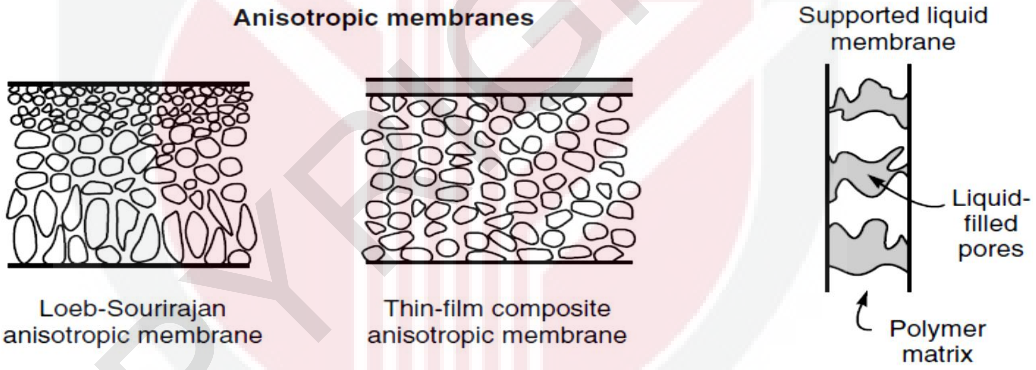


Figure 2.4 Types of asymmetrical membrane structure

2.4 MEMBRANE SEPARATION PROCESS

Membrane separation processes are one of the fastest growing and fascinating fields in separation technology. It has played an important role in developing more efficient and selective production with a minimization of wastewater and solid waste. Membrane processes have been introduced in industrial operations for wastewater treatment and also for the potential reuse and recovery of by-products. Different membrane separation processes are used in the treatment of water, sewer and industrial wastewater (A. Moura Bernardes et al., 2014). Even though membrane processes are a relatively new, several membrane processes, particularly pressure-driven membrane processes including reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), are already being applied on an industrial scale to food and bioproduct processing. The classification on the applicability of different membrane separation processes based on particle or molecular sizes is shown in Figure 2.5.

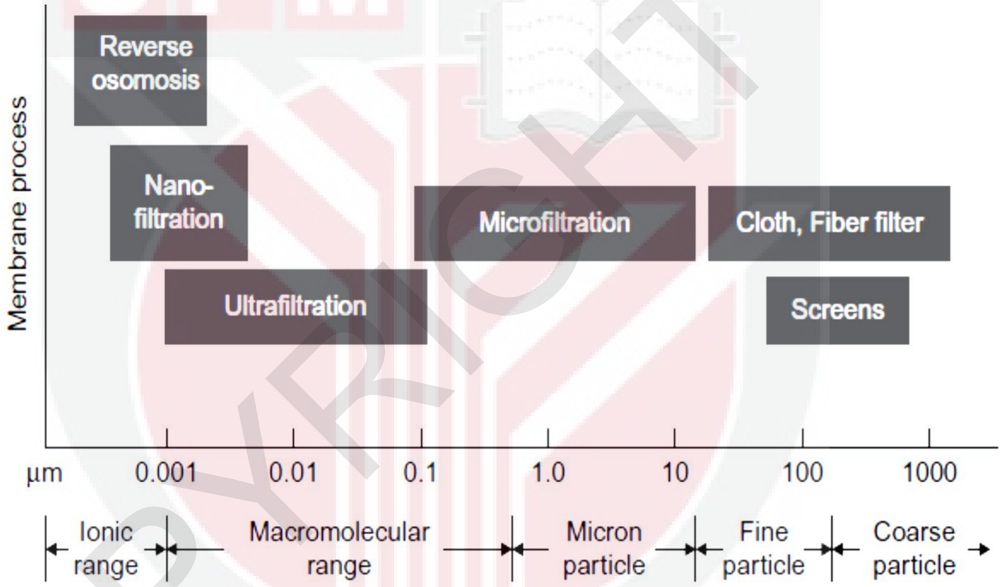


Figure 2.5 Classification of membrane separation process

2.4.1 ULTRAFILTRATION

Ultrafiltration (UF) is the process of separating extremely small particles and dissolved molecules from fluids (Munir, 2006). The pores of ultrafiltration membranes can remove particles of 0.005 – 0.01 µm from fluids. They have a finely porous surface layer or skin supported on a much more open microporous substrate. The finely porous surface layer performs the separation whereas the microporous substrate provides mechanical strength. The membranes discriminate between dissolved macromolecules of different sizes and are usually characterized by their molecular weight cut-off (Baker, 2011). Ultrafiltration can only separate molecules which differ in size where any molecules that are similar size with the pores can pass through the ultrafiltration membranes. Materials which are in size range from 1K to 1000K molecular weight (MW) will be retained by certain ultrafiltration membranes, while salts and water will pass through the membranes (Munir, 2006).

In other words, ultrafiltration membranes can be used both to refine material passing through the filter and also to collect material retained by the filter. The materials that is smaller than the pore size rating pass through the filter and can be dehydrogenated, clarified and separated from high molecular weight contaminants while the materials that larger than the pore size rating are retained by the filter and can be concentrated or separated from low molecular weight contaminants (Munir, 2006). Ultrafiltration can be used to filter dissolved macromolecules such as proteins from the solution (Koros, 1998). It is typically used to separate proteins from buffer components for buffer exchange, desalting, or concentration.

Ultrafiltration membranes are also ideal for removal or exchange of sugars, non-aqueous solvents, protein separation from protein-bound ligands, the removal of materials of low molecular weight, or the rapid change of ionic and/or pH environment. Ultrafiltration is far gentler to solutes other than processes such as precipitation. It does not require a phase change, which often denatures labile species, and UF can be performed either at room temperature or in a cold room (Munir, 2006).

Currently, ultrafiltration (UF) is considered as a very important and promising process in separation field and has been widely used in major industries such as food and beverage industry, biotechnology, chemical and pharmaceutical industry, and water treatments (Xu et al., 2016). As the demand increase, the effort to improve the ultrafiltration process performance becomes imperatives. Those efforts include feed pre-treatment, advanced membrane and module design, and process condition optimization. However, in many cases, the key for the performance of ultrafiltration process is the membrane itself. In this regard, three important characteristics for achieving high performance of ultrafiltration membrane are high flux as well as selectivity, low fouling and performance stability for long-term operation (Susanto et al., 2009).

2.5 MEMBRANE FOULING

Membrane fouling is a phenomenon that refers to the blockage of membrane pores during the filtration process by the combination of sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores. Pore blockage reduces the permeate production rate and increases the complexity of the membrane filtration operation (Abdelrasoul et al., 2013). In other words, it is generally defines as process that resulted in low performance of membrane due to deposition of suspended or dissolved solids in the feed on the external membrane surface, on the membrane pores, or within the membrane pores (Cui et al., 2010).

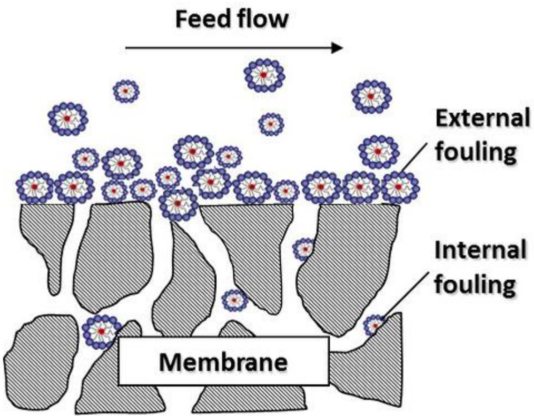


Figure 2.6 Membrane fouling mechanism

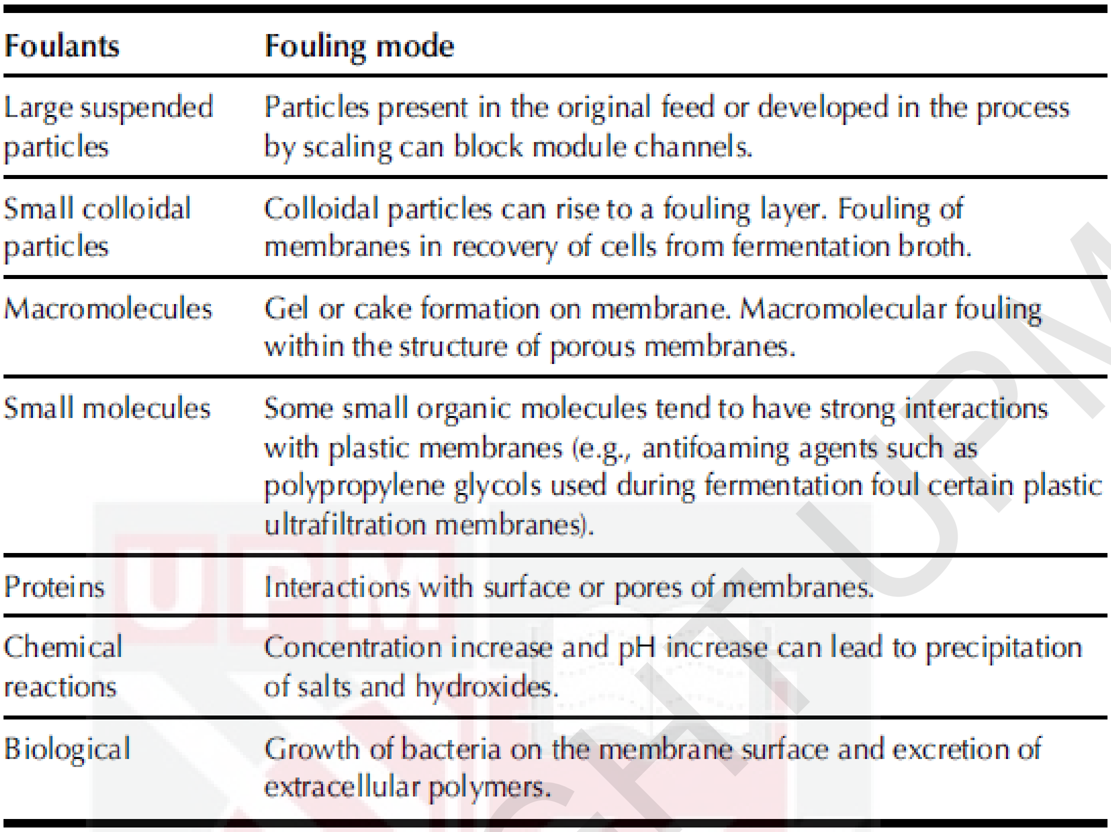
Membrane fouling is the main limitation to the successful membrane application of food and biotech industries as it can cause critical problems that reduces the permeate flux, requires periodic cleanings, and limits further membrane development due to the hindrance of wider application to various processes by fouling (Abdelrasoul et al., 2013). There are several parameters that influence the fouling rate such as:

a) Membrane properties such as pore size, hydrophobicity, pore size distribution and membrane material.

b) Solution properties such as solid (particle) concentration, particle size and nature of components.

c) Operating conditions such as pH, temperature, flow rate and pressure (Cui et al., 2010).

Fouling can be related to different modes such as adsorption, chemical interactions, cake formation, and pore blocking by particles. These modes can lead to blockage or partial blockage of the active membrane area or to deposition of a layer onto the membrane surface. The examples of foulants in membrane process are shown in Figure 2.7:



Foulants	Fouling mode
Large suspended particles	Particles present in the original feed or developed in the process by scaling can block module channels.
Small colloidal particles	Colloidal particles can rise to a fouling layer. Fouling of membranes in recovery of cells from fermentation broth.
Macromolecules	Gel or cake formation on membrane. Macromolecular fouling within the structure of porous membranes.
Small molecules	Some small organic molecules tend to have strong interactions with plastic membranes (e.g., antifoaming agents such as polypropylene glycols used during fermentation foul certain plastic ultrafiltration membranes).
Proteins	Interactions with surface or pores of membranes.
Chemical reactions	Concentration increase and pH increase can lead to precipitation of salts and hydroxides.
Biological	Growth of bacteria on the membrane surface and excretion of extracellular polymers.

Figure 2.7 Examples of foulant and fouling mode in membrane process (Cui et al., 2010)

2.5.1 FOULING MECHANISM

Generally, there are four fouling mechanisms for porous membranes can be observed which are complete pore blocking, internal pore blocking, partial pore blocking, and cake filtration (Cui et al., 2010). The examples of fouling mechanism are shown as Figure 2.8 below:

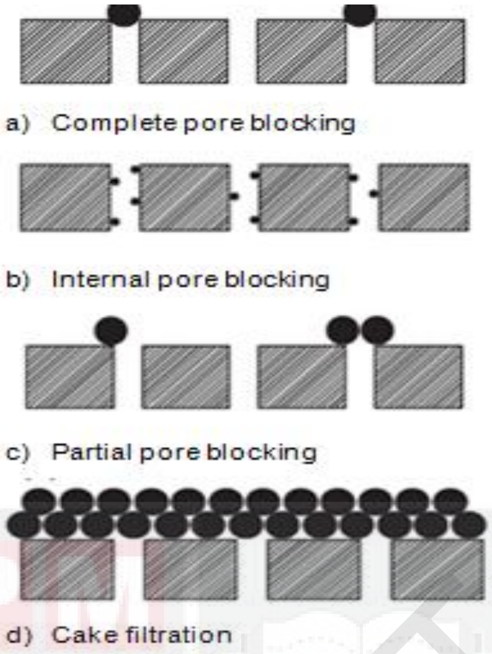


Figure 2.8 Fouling mechanism of porous membrane membranes

The pore blocking increases the membrane resistance while the cake formation creates an additional layer of resistance to the permeate flow. Pore blocking and cake formation can be considered as two essential mechanisms for membrane fouling. The rapid initial drop of the permeate flux can be attributed to quick blocking of membrane pores. The maximal permeate flux always occurs at the beginning of filtration because membrane pores are clean and opened at that moment.

Flux declines as membrane pores are being blocked by retained particles. Pores are more likely to be blocked partially and the degree of pore blockage depends on the shape and relative size of particles and pores. The blockage is generally more complete when the particles and pores are similar in both shape and size. Pore blocking is a quick process compared with cake formation since less than one layer of particles is sufficient to achieve the full blocking.

2.5.2 MEMBRANE PROPERTIES

Membrane properties are one of the factors that influence the fouling rate. Membrane can be attractive or repulsive to water in an aqueous environment. The interaction of membrane with water or its wettability is affected from the membrane composition and its corresponding surface chemistry. Hydrophilic membranes are characterized by the presence of active groups that have the ability to form hydrogen-bonds with water and so these membranes have wettability. Hydrophobic membranes have the opposite interaction to water compared to hydrophilic membranes as they have little or no tendency to adsorb water and water tends to bead on their surfaces thus it has high tendency to enhance fouling. Hydrophobic membranes possess low wettability due to the lack of active groups in their surface for the formation of hydrogen-bonds with water.

The particle which has hydrophobic characteristic tends to foul the membranes in aqueous media. They tend to agglomerate or group together to form colloidal particles because this process lowers the interfacial free energy. Usually, greater charge density on a membrane surface is associated with greater membrane hydrophilicity. Polymeric membrane such as polyethersulfone membranes used for water treatment and wastewater recovery typically carry some degree of negative surface charge and hydrophilic.

Thus, fouling can be reduced with use of membranes with surface chemistry which have been modified to render them hydrophilic. Membrane morphology also has a considerable effect on fouling as pore size, pore size distribution and pore geometry especially at the surface of the membrane. These determine the predominant fouling mechanisms such as pore blocking and cake formation as previously explained.

2.6 MEMBRANE MODIFICATION

The most commonly used membrane material in the industry is an organic polymeric membrane that has chemical property of hydrophobicity. Thus, the membranes that are made from these materials are also strongly hydrophobic. In a practical application, the surface of hydrophobic membrane has no hydrogen-bond interaction with water which when the hydrophobic solutes approaching membrane surface have a spontaneous process of entropy increase, so they are easy to be absorbed and deposited on the membrane surface which then causing blockade of membrane holes. The blockage then can lead to severe membrane fouling which cause decrease in membrane performance and cut down on membrane life spans (Sun et al., 2013).

In contrast, the membrane with the hydrophilic layer possesses a high surface tension and is able to form the hydrogen bonds with surrounding water molecules to reconstruct a thin water boundary between the membrane and bulk solutions. It is therefore difficult for hydrophobic solutes to approach the water boundary and break the orderly structure because an increase of energy would be required to remove the water boundary and expose the membrane surface (Liu et al., 2011). Therefore, an increase in the hydrophilic of the membrane surface is often a key goal to reducing membrane fouling with colloids, microorganisms and organic pollutants.

The modification of membrane material or membrane surface is the common method to improve the membrane performance and increase the membrane resistance towards the fouling. There are three different approaches for the membrane modification which are membrane polymer modification (pre-modification), blending of the membrane polymer with a modifying agent (additive) and surface modification after membrane preparation (post-modification) (Susanto & Ulbricht, 2009).

The modification procedures allow finding a compromise between hydrophobicity and hydrophilicity, localize the hydrophilic material specifically in the membrane pores, where they have a positive effect on flux and fouling reduction, and endow functions of membranes such as good blood compatibility and stimuli-responsivity. Physical or chemical membrane modification processes after the formation of the membrane create more hydrophilic surfaces (Zhao et al., 2011)

2.7 POLYMERIC MEMBRANE

In terms of materials, membranes can be classified into polymeric or organic membranes ceramic or inorganic membranes. Organic membranes are usually made up of various polymers and among which the typical ones are Cellulose Acetate (CA), Polyamide (PA), Polysulfone (PS), Polyethersulfone (PES), Polyvinylidenefluoride (PVDF), Polypropylene (PP), and others.

Polymeric membranes are relatively cheap, easy to manufacture, available in a wide range of pore sizes, and they have been widely used in various industries (Cui et al., 2010). Polymeric membranes structures generally consist of a dense skin supported by a porous sub layer. These asymmetric morphologies can be produced by a phase separation process being a result of either a temperature or a non-solvent addition (Gao et al., 2008).

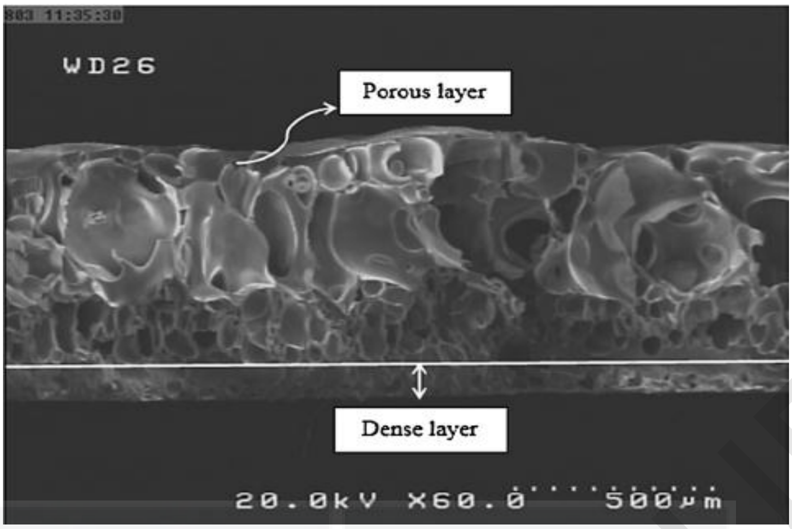


Figure 2.9 Example of SEM of Polymeric Membrane

2.7.1 POLYETHERSULFONE (PES) MEMBRANE

Polyethersulfone which is a polymeric membrane is a favorable material for membranes because it has resistance to oxidation, acid and alkalis and excellent bio-compatility. Polyethersulfone is an important engineering thermoplastic possess favorable mechanical properties and thermo oxidation stability where it is closely related derivatives of polysulfone which is totally devoid of aliphatic hydrocarbon groups and has a high glass transition temperature of 230°C.

Polyethersulfone (PES) contains repeated ether and sulfone linkage alternating between aromatic rings which provide high degree of molecular immovability creating creep resistance, high rigidity, superior strength, and dimensional stability. This polymer is widely used in membrane preparation for various applications. The employment of polyethersulfone for aqueous solutions is restricted due to hydrophobicity of PES. This important characteristic may be improved by modification of polyethersulfone through blending. (Rahimpour & Madaeni, 2007).

Polyethersulfone (PES) can be considered as a standard material in membrane manufacturing. It has been widely used in preparation of ultrafiltration membranes due to its extra features such as high glass transition temperature, high chemical stability against aggressive materials, high values of tensile strength, and high amount of elongation at break (Hwang et al., 2012). Nevertheless, the PES membranes are restricted with relatively high hydrophobicity.

When solutions containing proteins or other hydrophobic substances are filtered, fouling phenomenon occurs and the flux permeation of membrane decreases (Peyravi et al., 2012). A useful technique to overcome this limitation of the PES membranes is enhancement of membrane hydrophilicity by blending hydrophilic polymers. The blending of a hydrophilic polymer as an additive in the PES matrix as a membrane forming polymer offers combination of their properties (Jalali et al., 2016).

2.7.2 MODIFIED PES MEMBRANE

The blending modification is the common method used to modify PES membranes both for flat-sheet and hollow fiber membranes. The PES membrane is modified by blending together with the hydrophilic polymers (modified agent) which also known as polymeric additives. The blending of PES membrane will increase the hydrophilicity of the membranes which would increase in the anti-fouling property and blood compatibility (Zhao et al., 2013). Even though blending technique can involve significant changes in composition of the casting solution which can lead to different membrane structure formed during the phase separation and consequently, membrane properties can be quite different from the unmodified reference material. It is simple and no additional step is needed during membrane manufacturing.

Although stability of the modifying agent in the membrane matrix can be a problem, the effect of hydrophilization of the polymer membrane can be clearly observed. Therefore, this technique seems to be of highest relevance from practical point of view. Polymeric additives in a casting solution are also used in order to increase both pore size and porosity (pore forming agent) and to suppress macrovoid formation (Susanto & Ulbricht, 2009).

2.7.3 ADDITIVES

Additive is a modifying agent that is used in fabricating the polymer membrane. It function is to improve the permeability of the membrane and also the antifouling property (Zhao et al., 2011). Additives play a crucial role in modifying and adjusting the membrane properties as they change the kinetic and thermodynamic properties of the casting solution and contribute to the pore formation, improving pore interconnectivity, and can influence the creation of morphology structure such as spongy, finger like or macrovoids containing cross-section morphology.

Aside from that, additives can also yield a hydrophilic character of the resulting membrane. The technique of addition is usually by blending these modifying agents (additives) with the principle polymer during membrane manufacturing process with no further steps. This technique is simple and practically feasible and there are many polymeric additives have been studied to enhance the performance of PES based membranes (Abdel-Karim et al, 2016). There are several additives that have been used in fabricating the polymer membrane such as Polyvinylpyrrolidone (PVP), Plunoric F127 and also Polyethylene glycol (PEG) which are the soluble polymers (Chakrabarty et al., 2008).

2.7.3.1 Polyethylene glycol

PEG polymer has been known to be utilized as additives in the membrane to control its structure (Wang et al., 2006). PEG additive is also known as Polyethelyene oxide (PEO). It is used as hydrophilic modification for improvement of antifouling property of ultrafiltration membranes (Wagner et al, 2004). The protein-resistant character of PEO may attribute to the lack of ionic charge, high hydrophilicity, flexibility, and mobility in the aqueous environment (Zhao et al, 2008).

The characterization of the membrane has shown that resultant membrane properties and morphology depends on certain molecular weight of PEG (Zuo et al, 2008). The addition of PEG lead to properties altered and change in pore structure in casting solution that eventually affects membrane formation and permeability properties. The study by Zhao et al. (2008) states that, PEG with various molar mass shows that the resulting membrane is influenced by both molar mass and concentration of PEG. The membrane with higher molar mass of PEG has higher pure water permeation and larger pores. Aside from that, the increase in PEG molar mass will also increase the membrane porosity leading to increase in water permeability for both systems.

2.7.3.2 Pluronic F127

The role of Pluronic F127 was previously considered as only a surface modifier. Then it was found that the Pluronic F127 could improve the permeation performance of the membrane which functions as pore forming agent (Zhao et al, 2008). Aside from that, the study also shows that when the Pluronic F127 is blended with PES membrane, the membrane exhibited improved fouling resistant ability. The hydrophobic poly(propylene oxide) (PPO) segments in Pluronic F127 ensured the firm anchorage in the polymer matrix, while the hydrophilic PEO segments stretching out of the polymer matrix ensured the efficient improvement membranes surface hydrophilicty (Wang et al, 2006).

2.8 MEMBRANE FABRICATION

The membranes play a key role in membrane-based water treatment processes and determine the technological and economic efficiency of the aforementioned technologies. Membrane improvement can greatly affect the performance of current technology. The material selection and pore size of the membranes depend on the application for which it would be used. Membrane fabrication is the selection of a technique for preparation of polymeric membrane that depends on a choice of polymer and desired structure of the membrane. There are few commonly used techniques to prepare the polymeric membranes which are phase inversion, interfacial polymerization, stretching, track-etching and electro spinning.

2.8.1 PHASE INVERSION

Phase inversion is a demixing process whereby the initially homogeneous polymer solution is transformed from a liquid to a solid state in a controlled manner (Drioli and Giorno, 2009). This transformation can be accomplished in several techniques which are:

- Immersion precipitation. The demixing process is when the polymer solution is immersed into the non-solvent coagulant bath which is usually water and the precipitation occurs due to the exchange of the polymer solution and non-solvent that is, the solvent and non-solvent should be miscible.

- Thermally induced phase separation. This method is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying.
- Evaporation-induced phase separation. The polymer solution is made in a solvent or in a mixture of a volatile non-solvent, and the solvent is allowed to evaporate, leading to precipitation or demixing or precipitation. This technique is also known as a solution casting method.
- Vapor-induced phase separation. The polymer solution is exposed to an atmosphere containing a non-solvent (typically water), absorption of non-solvent causes demixing or precipitation.

However, between all these techniques, immersion precipitation is the most commonly used method in the fabrication of polymeric membranes with various morphologies.

2.8.2 IMMERSION PRECIPITATION

Phase inversion process induced by immersion precipitation is a well-known technique to prepare asymmetric membranes. By immersion the substrate in the coagulation bath, the solvent in the casting solution film is exchanged with non-solvent in precipitation media and phase separation occurs. This process results in an asymmetric membrane with a dense top layer and a porous sub-layer containing macrovoids, pores and micropores (Rahimpour & Madaeni, 2007).

Immersion precipitation is a process where a polymer solution is cast and then immersed in a coagulation bath that contains a non-solvent. The exchange of solvent and non-solvent takes place and the membrane is formed (Boussu et al., 2006). Immersion precipitate technique can be categorized into three more sub techniques, which are wet phase inversion technique, dry phase inversion technique and dry/wet phase inversion technique (Amin, 2006). Schematic diagram of processes after polymer solution immersion in a non-solvent bath is shown in Figure 2.10.

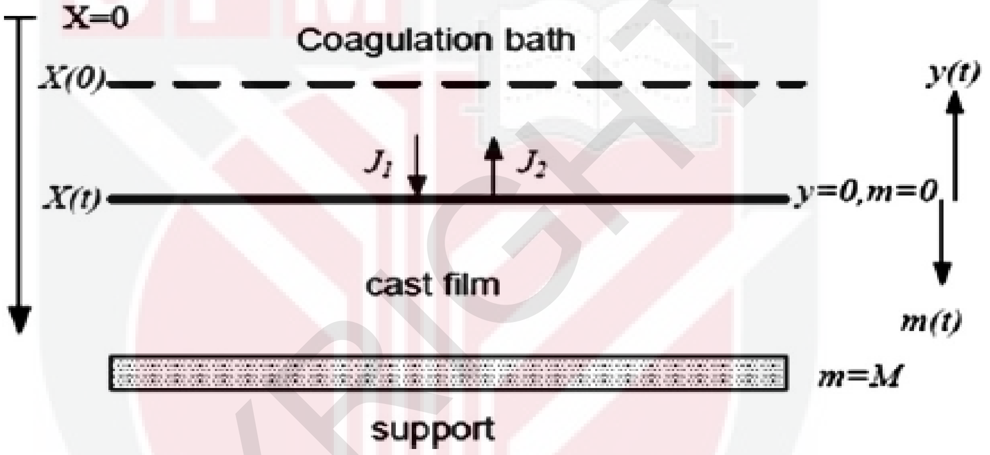


Figure 2.10 A Film or Bath Interface Schematic Representation

At flux equal to J2, the solvent diffuses into the coagulation bath whereas the non-solvent will diffuse into the cast film, at a flux equal to J1. After a certain time the exchange of solvent and non-solvent proceeds until the solution becomes thermodynamically unstable and demixing takes place. A solid polymeric film finally is obtained with an asymmetric structure.

2.8.2.1 Wet Phase Separation

Wet phase separation is most typical method used in order to prepare and produce the polymeric membrane. A cast thin layer of polymer solution that is miscible in polymer solvent is immersed in a non-solvent liquid. The exchange of solvent with the non-solvent from the coagulant bath produce thermodynamic instability that resolved by the separation on polymer-rich and polymer-lean phases and the polymer-rich phase forms a solid membrane matrix while the polymer-lean phase leaves a porous structure by leaching out of the system. By varying conditions of the wet phase separation technique (polymer concentration, the thickness of the cast solution, the coagulation medium and temperature) polymeric asymmetrical porous membranes with a very large variety of properties can be made. (Vorgin et al., 2002)

2.8.2.2 Dry Phase Separation

Dry phase separation or which also known as dry cast process is actually one of the alteration processes of polymer solution in thermodynamic state to achieve the phase inversion. This technique is characterized by evaporation of non-solvent and solvent from initially homogeneous single phase solution (Young et al., 2002). The external effects of homogeneous polymer solution initially cause the unstable of thermodynamic but the two phase of solution then is formed due to the evaporation (Altinkaya and Ozbas, 2004). This is why the membrane formation is called dry phase separation where the non-solvents components are removed alone by the evaporation process (Amin, 2006).

2.8.2.3 Dry-Wet Phase Inversion

By combining two methods of immersion precipitation and the dry-casting process, a process called dry–wet phase inversion is initiated in which the dope solution is exposed to a nonsolvent vapor (usually water) for a time interval prior to immersion into a coagulation bath (Gao et al., 2008). The dry–wet phase inversion technique is also known as *Loeb-Sourirajan* technique, were it was used by Loeb and Sourirajan in their development of the first cellulose acetate membrane for seawater desalination (Khulbe et al., 2008).

The membrane is prepared by casting the dope solution on a plate using a pneumatically casting machine. Then the membrane is immersed immediately in aqueous bath at room temperature (Amin, 2006). Due to a sequence of two desolvation steps, the solidification of the polymer film takes place. During the first step of desolvation by solvent evaporation, a thin skin layer of solid polymer is formed instantly at the top of the cast film due to the loss of solvent. In the solvent and non-solvent exchange process that follows, the non-solvent diffuses into the polymer solution film through the thin solid layer while the solvent diffuses out (Khulbe et al., 2008). After that, the membrane is immersed in an alcohol non-solvent bath for 24 hours and then is left to dry at room temperature (Amin, 2006).

2.9 THE ADVANTAGES AND LIMITATIONS OF MEMBRANE

Membrane technology have been developed and considered as the best available technologies in many process and waste management applications (Muralidhara, 2010). The advantage of membranes separation has been found in certain processes such as producing, separation, recovering, and drying (Koros et al., 1998). In many applications such as water treatment, the membrane processes are more energy efficient, yield a high quality product and simpler to operate rather than using the conventional water treatment techniques (Strathmann, 2011).

Furthermore, there is no chemical, biological or thermal change of the component is involved for most membrane process compared to the conventional method. Thus, membrane separation is a technology attraction to the industry processing of food, beverage and bio products where these products can be sensitive to temperature and solvents (Chui et al., 2010). Aside from that, membrane process is highly selective so it is more effective in the separation process. It is also characterized by low energy consumption, possibility of different module design and easy to scale-up. Thus, these advantages make these processes superior to many other established separation processes (Amin, 2006).

However, there are also some limitations such as the membrane process is still expensive and less environmentally friendly (Muralidhara, 2010). Moreover, the membrane processes sometimes require excessive pre-treatment due to their sensitivity to concentration polarization and membrane fouling, (Strathmann, 2011). Thus, a significant progress has been made where performing research and development (R&D) has been made in order to overcome the limitations and also to make them suitable for wide variety of applications (Muralidhara, 2010).

CHAPTER 3

METHODOLOGY

3.1 GENERAL REVIEW

Polyethersulfone flat sheet ultrafiltration (UF) membranes have been prepared by phase inversion method where the polymer solution is immersed into the non-solvent coagulant bath which is water and the precipitation occurs due to the exchange of the polymer solution and non-solvent. The additives used are Pluronic F127 and also Polyethylene glycol (PEG) of molecular weight of 6000. These two additives were blended together during the dope preparation with different ratio. All these membranes were evaluated by evaluation of pure water permeation, apple juice and tap water filtration. Moreover, the effect of additives on the mechanical properties of membranes is tested with analysis of tensile strength while the morphological structures of the membranes are analyzed using SEM.

3.2 RESEARCH FLOW

Schematic diagram for membrane preparation is illustrated in Figure 3.1 below,

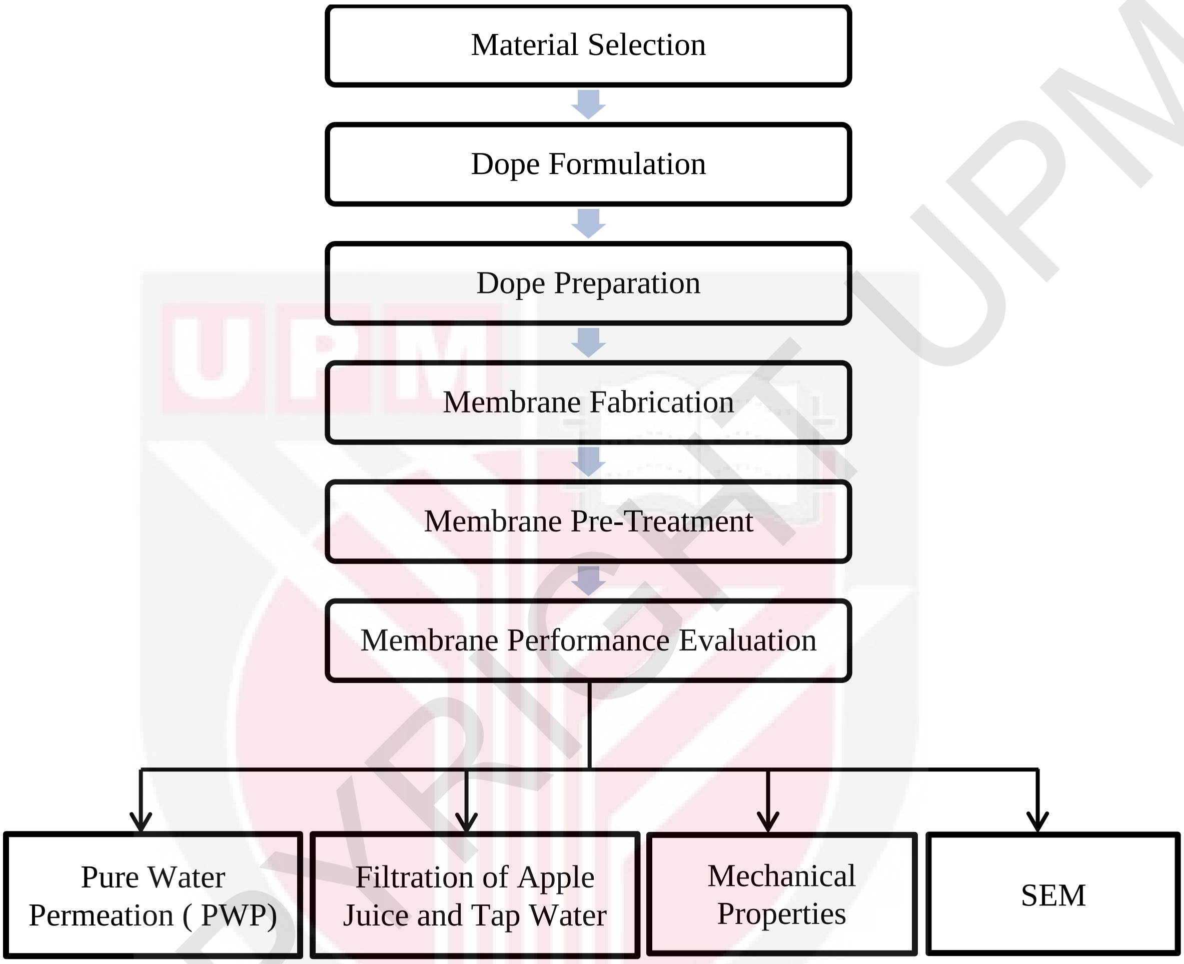


Figure 3.1 Schematic diagram for membrane preparation

3.3 MATERIALS

In order to prepare the dope formulation for the membrane, there are few materials required. According to the experiment, the doped solutions will be prepared from the mixing of polymer, solvents and also additives.

3.3.1 POLYMER

Polyethersulfone (PES) polymer is selected as the membrane based material for the ultrafiltration membrane in this experiment due to the favorable properties such as wide temperature limits, wide pH tolerances, fairly good chlorine resistance, easy to fabricate membranes in a wide variety of configurations and modules and has wide range of pore sizes available for the ultrafiltration process. The structure of PES polymer is shown as in Figure 3.2 below.

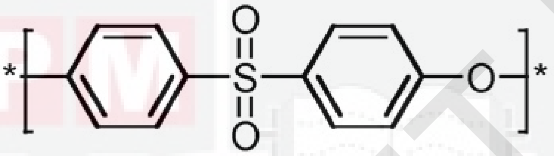


Figure 3.2 Polyethersulfone (PES) Polymer Structure

3.3.2 SOLVENTS

Solvent selection is important as the solvent chosen must be the one which can dissolve in the polymer and rapidly diffused into the precipitating solution when it contacts the non-solvent. Aside from that, the solvents also will affect the membrane preparation as it will leave some effects on the final morphology of the fabricated membrane. The miscibility in the solvent will cause different formed of the membrane porosity. High miscibility will give cause membrane to have high porosity and vice versa.

In this experiment, the solvent used is N-methyl-2-pyrolidone (NMP). It is proved that NMP enhances its utility as a solvent many synthetic reaction systems. Moreover, the NMP solvent has a strong interaction with the polymer which it will completely miscible with the polyethersulfone (PES) polymer. NMP also known to has high solvency, low volatility as well as high chemical and thermal stability. The solvent will tend to release fewer organic emissions to the atmosphere compared to other solvents when it had low volatility (Ali, 2013).

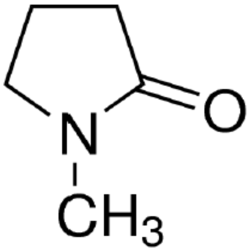


Figure 3.3 The Chemical Structure of NMP Solvent

3.3.3 ADDITIVES

As mention in the previous chapter, additives play a crucial role in modifying and adjusting the membrane properties as they contribute to the pore formation and can influence creation of either spongy, finger like and/or macrovoids containing cross-section morphology which they can also yield a hydrophilic character of the resulting membrane. The technique of addition is usually by blending these modifying agents (additives) with the PES polymer. The additives used in this experiment are PEG and Pluronic F127.

3.3.3.1 Polyethylene glycol

Polyethylene glycol (PEG) is a polyether compound with various applications from industrial manufacturing to medicine. PEG is also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight. Polyethylene glycol, referred to as PEG, is used as an inactive ingredient in the pharmaceutical industry as a solvent, plasticizer, surfactant, ointments and suppository base, and tablet and capsule lubricant. The molecular weight of PEG will affect the characterization of membrane (Zuo et al., 2008). The addition of PEG was leading to alter properties and change in pore structure in casting solution that eventually affects membrane formation and permeability properties. The PEG additive used in this study is from Acros Organic which is distributed by Fisher Scientific (M) Sdn Bhd, Malaysia with the molecular weight of 6000. The structure of PEG 6000 is shown as Figure 3.4 below.

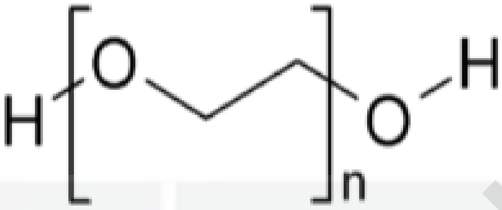


Figure 3.4 The Chemical Structure of Polyethylene glycol

3.3.3.2 Pluronic F127

The role of Pluronic F127 was previously considered as only the surface modifier. Pluronic F127 is a nonionic, surfactant polyol that has been found to facilitate the solubilization of water-insoluble dyes and other materials in physiological media. Pluronic F127 may also be useful for dispersing other lipophilic probes. Appropriate controls should be performed to make certain that Pluronic F127 is not altering the membrane properties of the cell. The hydrophobic polypropylene oxide (PPO) segments in Pluronic F127 ensured the firm anchorage in the polymer matrix, while the hydrophilic PEO segments stretching out of the polymer matrix ensured the efficient improvement membranes surface hydrophilicity (Wang et al., 2006). The Pluronic F127 used as the additive in this study is purchased from Sigma Aldrich.

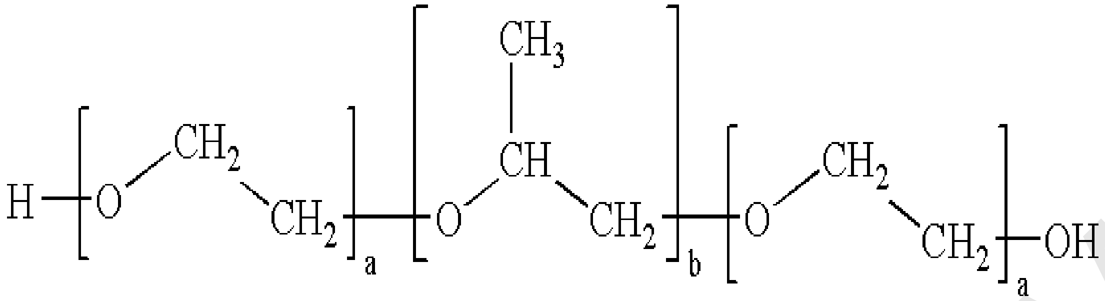


Figure 3.5 The Chemical Structure of Pluronic F127

3.4 METHODS

For this experiment, all membranes are prepared with different dope formulation which will be explained later. The membranes performance then is evaluated by pure water permeation test, apple juice and tap water filtration test, tensile strength and also SEM analysis.

3.4.1 MEMBRANE DOPE FORMULATION

PES membranes were prepared by phase inversion of immersion precipitation. The dope solution must be prepared first before membrane is fabricated. The dope solution is prepared by dissolve Polyethersulfone (PES) polymer which is dried overnight with the NMP solvent at temperature below 60 ℃ under a constant stirring rate for 8 hours in order to form homogenous solution. The dope formulation is prepared with different ratio of the additives(Zainal et al., 2014). Table 3.1 shows the dope formulation used in this study.

Table 3.1 Dope Formulations

Dope Name	PES (wt %)	Additives		NMP (wt %)
		Pluronic F127 (wt %)	PEG (wt %)	
M1	17	-	-	83
M2	17	2	3	78
M3	17	3	2	78
M4	17	4	1	78
M5	17	5	-	78

Figure 3.6 Preparation of Dope Solution

3.4.2 MEMBRANE CASTING

Membrane casting is done after the dope solution is obtained. However the dope solution need to be kept at constant temperature first after the preparation is finished in order to remove the air bubbles due to the heating and stirring process. For the casting process, the dope will be uniformly spread onto glass plate and will form a layer of dope with thickness of 100-150 μm by using the casting knife. Then the glass plate with the layer of dope will be immersed into the coagulation bath composed of pure water immediately. The layer will solidify and formed the new membrane which then peeled off from the glass plate.

After that, the new membrane formed will be immersed in pure water for 24 hours in order to eliminate the residual solvents (Xu et al., 2004). Then, the membrane will be immersed in ethanol for another 24 hours and followed by hexane for another 2 hours. Lastly, the membrane was dried at room temperature (Susanto & Ulbricht, 2009). Few steps of membrane casting are shown in Figure 3.7.

For this process, the multi-stage solvent exchange and evaporation method is applied. In this method, a water-miscible solvent such as ethanol first replaces the water in the membrane. Then, a second volatile solvent such as hexane replaces the first solvent. The second solvent is subsequently air-evaporated to obtain a dry membrane. Another reason for replacing water with hexane is to reduce the capillary force inside the pore so that it will not collapse during the drying process.

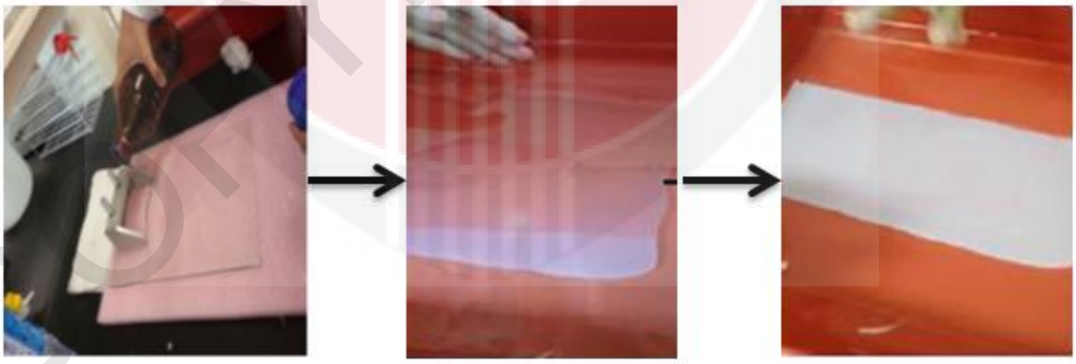


Figure 3.7 Membrane Casting Process

3.4.3 EVALUATION TEST AND PERFORMANCE

3.4.3.1 Membrane Compaction

Membrane compaction is performed by filtration of pure water. This permeation test is carried out by using permation cell which connected to a resevoir and presurized by nitrogent from tank gas. This test is to measure the pure water flux and also the solute rejection (Susanto & Ulbricht, 2009). The membrane compaction is performed at pressure 1.5 bar within 30 minutes. Then, the membrane permeability is measured at different pressure within the range of 0.5-3.0 bar.

3.4.3.2 Pure Water Permeation Test (PWP)

The pure water permeability, also know as the pure water flux is defined as the volume of water that passes through a membrane per unit time, per unit area and per unit of transmembrane pressure (Malek et al., 2012). Permeation cell was used for measurement of pure water flux of the Polyethersulfone (PES) membranes. Pure water permeation (PWP) was determined with distilled water at room temperature with different pressure. The pure water flux was define as,

$$\text{Pure Water Permeation } (\mathrm{L} / \mathrm{m}^2\mathrm{h}) = \frac{Q}{(A.\Delta t)} \qquad \text{Eq (3.1)}$$

Where, Q = the permeate volume (L),

A = the membrane area (m^2),

Δt = the time of permeation (h).

3.4.4 APPLE JUICE AND TAP WATER FILTRATION

Filtration test was done to evaluated the influence of additives on the brown pigments absorption in the apple juice and also the organic materials absorption in the tap water. It can be determined by pure water flux measurement where the membranes first need to be evaluated with pure water permeation test to obtain initial water flux with the operating pressure of 1.0 bar. Then the membranes were tested with filtration of both solution with pressure 1.0 bar for 1 hours. Afterwards, the membranes were regenerated in 0.1 NaOH solution for 30 minutes and rinsed with water. The water flux of regenerated membranes is measured by using same operating pressure (Borneman et al., 2001).

3.4.4.1 Permeation Flux

The flux of pure water for this analysis is determined by using same equation as pure water permeation test before. For the apple juice and tap water filtration, the permeate is collected at an interval of 5 minutes within the range of 1 hour. The flux of both solution filtration is also calculated by using same formula as Equation 3.1.

3.4.4.2 Flux Recovery Ratio

The flux recovery is used to evaluate the membrane performance after recovering from fouling during filtration (Zhao et al., 2008). The flux recovery factor can be determined by;

$$\text{FRR}(\%) = \frac{J_f}{J_i} \times 100 \qquad \text{Eq (3.2)}$$

Where J_i = Pure water flux before performing the filtration (L / m^2h)

J_f = Pure water flux of regenerated membrane after perfo

filtration (L / m^2h)

3.4.4.3 Relative Flux Reduction Ratio

The relative flux reduction is used to determine the extent of absorptive fouling on the membrane performance. It can be calculated by using equation below,

$$\text{RFR}(\%) = \frac{J_i - J_f}{J_i} \times 100 \qquad \text{Eq (3.3)}$$

Where, J_i = Pure water flux before performing the filtration (L / m^2h)

J_f = Pure water flux of regenerated membrane after performing filtration (L / m^2h)

3.4.4.4 Membrane Rejection

The absorbance of permeate apple juice was determined by using the UV-Vis with the wavelength of 420 nm and 254 nm for the tap water. The absorbance of permeate determine the solute concentration rejection of the solution. There is a direct relationship between absorbance and concentration where is the higher the absorbance of a substance, the more concentrated the solution will be in water or another medium. This principle is known as the Beer-Lambert Law. Thus, by knowing the absorbance of permeate solution of apple juice and tap water, the solute rejection can be determine by using equation below (Wang et al., 2006);

$$\text{Rejection, R } (\%) = (1 - \frac{C_p}{C_f}) \times 100 \qquad \text{Eq (3.4)}$$

Where, C_f = Original apple juice or tap water absorbance value

C_p = Permeate apple juice or tap water absorbance value

3.4.5 TENSILE STRENGTH

Tensile test is mechanical test that was performed on the membranes. Tensile tests are simple, relatively inexpensive, and fully standardized. It provides information about the tensile strength, yield strength and ductility of a material. Material strength testing, using the tensile test, involves applying an ever-increasing load to a test sample up to the point of failure. The process creates a stress-strain curve showing how the material reacts throughout the tensile test. The tensile test for the membranes is done by using the texture analyzer. All membrane were cut to standard shape and three samples of each type of membranes were tested and the mean values were calculated (Malek et al., 2012).

3.4.6 MEMBRANE CHARACTERIZATION

3.4.6.1 Scanning Electron Microscopy (SEM) Analysis

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The top surface and cross-section of membrane is observed using scanning electron microscope at standard high-vacuum conditions. For cross-section analysis, the membrane is being broken naturally by using nitrogen for 1.5 min, while for analysis of outer mem- brane surface, sputteringwas done for 0.5 min (Ding et al., 2016).

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

In this experiment, the performance of five PES membranes with different type of formulations is investigated. PES membranes are added with the total 5 wt% of Pluronic F127 and PEG additives that were blended together with different concentrations. The details of formulations PES membranes are shown in Table 4.1. All the membranes will be tested with few analyses in order to determine their performances.

Table 4.1 Different Formulations of PES Membranes

Membranes	Formulations (%)			
	PES	NMP	Pluronic F127	PEG
M1	17	83	-	-
M2	17	78	2	3
M3	17	78	3	2
M4	17	78	4	1
M5	17	78	5	-

These membranes firstly will undergo compaction with pressure of 1.5 bar for about 30 minutes in order to stabilize the membranes porosity. Then the membranes are tested for analysis of pure water permeation (PWP) with the pressure range of 0.5 bar to 3.0 bar. The analysis is continued with the filtration of apple juice in order to determine the absorption capacity of these membranes for the selective removal of brown-pigment in the apple juice. Then the two membranes that shows the best performance is selected to be tested with tap water filtration which is to investigate the effect of additives on the removal of natural organic materials in tap water.

Furthermore, the flux recovery and reduction will be calculated to determine whether the membrane performance can be restored from fouling during the filtration. Moreover, the effect of additives on the mechanical properties of membranes is tested with analysis of tensile strength while the morphological structures were observed using scanning electron microscope (SEM).

4.2 MEMBRANE PERMEATION PERFORMANCES

As stated before, the effect of additives on the membrane performances will be evaluated by the permeability tests which are pure water permeability (PWP) and also the filtration of apple juice and tap water. The membrane selectivity is expressed by the percentage of solute rejection whereas productivity expressed as permeate flux through the membrane for a range of operating pressures. The details of the evaluations and results will be discussed throughout this chapter. PES ultrafiltration membrane without additive was used as a control sample to compare the performance of PES ultrafiltration membranes with additives of different concentrations.

4.2.1 MEMBRANE COMPACTION

Membrane compaction is a compression of the membrane structure under a transmembrane pressure which will reduce the membrane porosity volume and gives the membrane a significant permeability loss or increases membrane resistance (Persson et al., 1995). The membrane compaction helps to stabilize the membranes pores to achieve a steady flux in order to perform pure water permeation later. By adding different concentrations of additives will give different structure of the membranes thus it will affect the membrane flux.

Figure 4.1 shows a gradual decrease in flux over the duration of compaction time. All of the membranes that were prepared with additives which are M2, M3, M4 and M5 had initially high flux with flux of 878.05 $Lm^{-2}h^{-1}$, 890.59 $Lm^{-2}h^{-1}$, 848.78 $Lm^{-2}h^{-1}$, and 790.24 $Lm^{-2}h^{-1}$ respectively compared to membrane without additives which is M1 with value of flux 593.73 $Lm^{-2}h^{-1}$. This proved that the additives influence the porosity of the membranes. The compaction would cause the porous supports to become denser which will then leading to the thickening of the membrane selective layer (Susanto, 2008). As a result, the increased in membrane thickness will lower the flux.

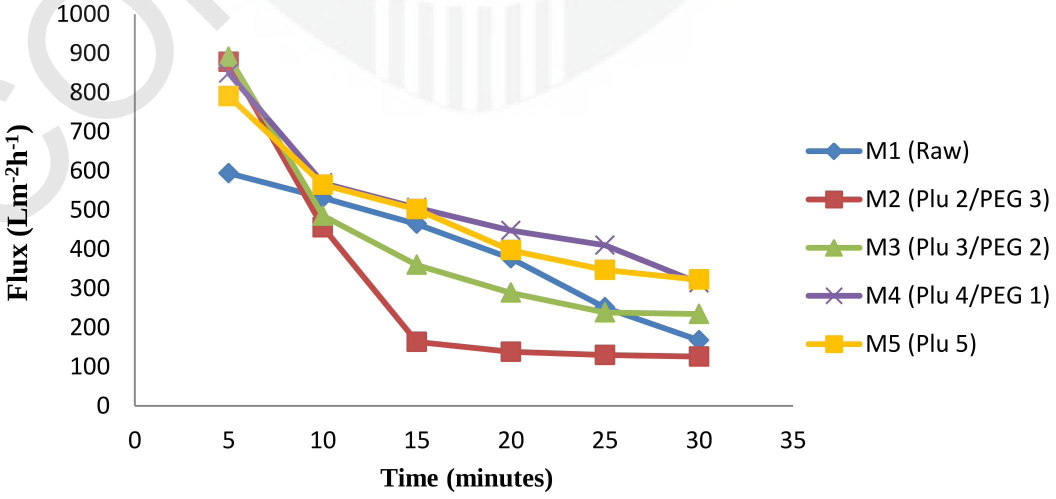


Figure 4.1 Compaction of the Membranes

4.2.2 EFFECT OF ADDITIVES ON PURE WATER PERMEABILITY (PWP)

Based on Figure 4.2, it shows that the membrane M4 reached the highest value of PWP at operating pressure of 3 bar compared to the other membranes. The value of M4 is 1045.29 $Lm^{-2}h^{-1}$ and followed by M5, M3, M2 and M1 with the value of 783.97 $Lm^{-2}h^{-1}$, 627.18 $Lm^{-2}h^{-1}$, 348.43 $Lm^{-2}h^{-1}$, and 158.78 $Lm^{-2}h^{-1}$ respectively. It can be seen that the permeability of pure water increases gradually as the concentration of Pluronic F127 increased. Pagidi et al. (2014) have also concluded that addition of small amount of polymer additive, Pluronic to PES UF membrane will increase both permeation flux and anti-fouling properties of the membrane.

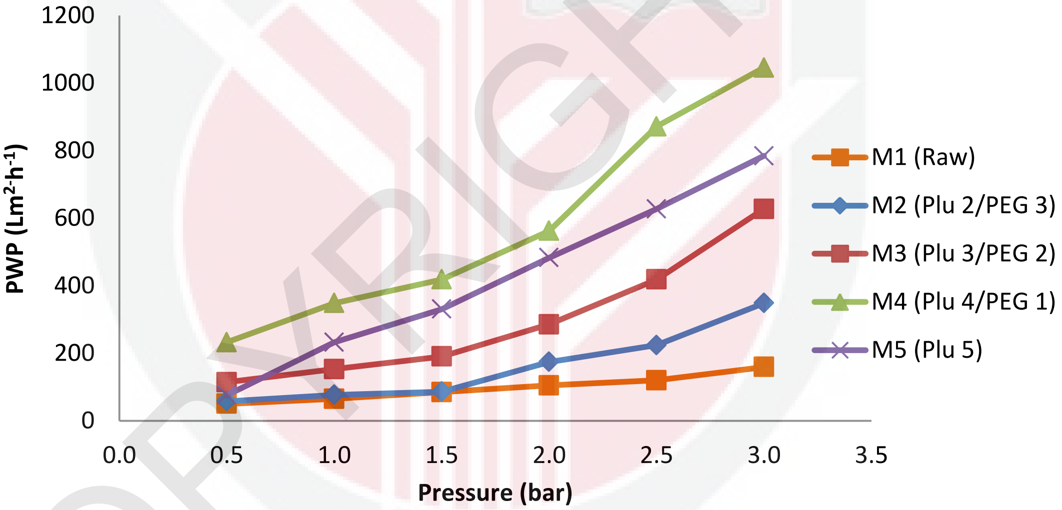


Figure 4.2 Pure Water Permeations of the Membranes

Despite of that, flux of membrane M4 which consists of 4% of Pluronic F127 and 1% of PEG concentration is shown to be higher compared to the membrane M5 which consist of solely 5% of Pluronic F127 concentration. This shows that the PEG also has an influence toward the flux and 1% of PEG concentration in this experiment is the best optimum concentration to achieve the high flux when blend together with Pluronic F127.

The flux of membrane M2 and M3 that has higher PEG concentration is a bit lower compared to M4. This can be explained that further increasing the PEG polymer concentration until a specific point will increase the viscosity of the casting solution which then will slow down the exchange rate of solvent and non-solvent during phase inversion. In such case, demixing is delayed and caused the top layer of membrane become denser and decreasing the permeate flow.

However, flux of these membranes is still higher compared to PES membrane without any additives, M1 which proved that additives helped to enhance the membrane performances. This result is apparent that the introduction of hydrophilic additives to the membrane casting solution makes the membrane porous and more hydrophilic. It also evidently shows that the introduction of additives had an impact the development of porous structure in the membrane, where the permeability properties of the ultrafiltration membranes were significantly affected.

4.3 EFFECT OF ADDITIVES ON APPLE JUICE FILTRATION

The effect of additives on membrane performance was investigated with respect to adsorptive fouling and ultrafiltration. Adsorptive fouling was determined by filtration of flat sheet membrane to polyphenol concentration inside the apple juice.

4.3.1 PERMEATION FLUX AND REJECTION

Flux and rejections not only depends on the transmembrane pressure but also influenced by the membrane structure and the feed solutions properties. Therefore, formulated ultrafiltration PES membranes were characterized by estimating flux and rejection during permeation experiment with the apple juice solutions as the feed.

The permeate flux-time curves were divided into two sections which is a rapid initial permeate flux decline region for the first 30 minutes and a relative slow decline section for another 30 minutes. It was observed the flux rate of all membranes is slowly decreased as the time increase. This indicates that the adsorption of brown pigments from the apple juice caused the membranes to foul, leading to decrease in permeate flux. After 30 minutes, flux of all membranes shows quite similar trends where the flux decline was still continuing but there is no drastic decrease observed after this point. This is well known as a problem of dead-end filtration systems.

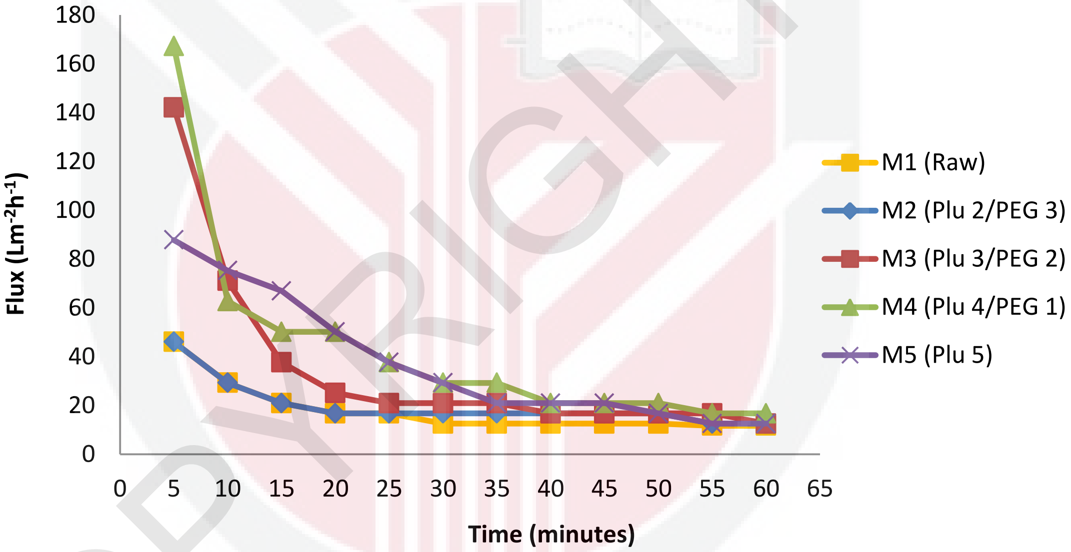


Figure 4.3 Permeate Flux of Apple Juice Filtration

Based on Figure 4.3, it shows that there is immediate flux drop for membrane M3 and M4 which show high flux value which is 142.16 $Lm^{-2}h^{-1}$ and 167.25 $Lm^{-2}h^{-1}$ at the beginning process. According to the research by Bruijn (2002), he stated that the sharp decrease observed at the beginning is probably attributed to the adsorption of colloidal species and the build-up of a concentration polarization layer. However, it could also cause by internal fouling due to pore plugging at the early stage of ultrafiltration process.

Therefore, the immediate decline of membrane M4 and M3 at the beginning 5 minutes can possibly be related to the concentration polarization where the solute is being retained by the membrane when the solvent which is apple juice, is passing through the membrane. The solute then will accumulate to form a layer at the membrane interface with a relatively high concentration. The concentrated layer near the membrane will become less permeable for the solvent to pass through the membranes. For membrane M5, the flux is slowly decline without showing any sharp decrease within the 30 minutes while membrane M1 and M2 shows quite similar trend at first 25 minutes where the initial flux is lower compared to other membranes with value of 45.99 $Lm^{-2}h^{-1}$.

However after 25 minutes, the flux of membrane M1 is decreasing from 16.72 $Lm^{-2}h^{-1}$ to 12.54 $Lm^{-2}h^{-1}$ which is possibly caused by slow consolidation of the secondary layer formed by concentration polarization and also by the adsorption of the brown pigments from the apple juice on the membrane surface. The results also help to determine the effect of additives on the membrane resistance towards fouling. Although the flux of membranes decline as the time increase, but it clearly shows that the membrane are still able to filter the solution for a long time before the flux reach the dead end of the filtration system.

Rejection data presented on Figure 4.4 show that the PES membrane prepared without additives had a lower rejection while all membranes that prepared with additives showed high value of rejection which is 70% and above. The different concentration of additives could give effect toward surface and cross-section of membrane. The increasing concentration of additives could also increase the number of pores. Membrane M5 shows the highest value of rejection and this could be due to the high content Pluronic F127 that functions as a hydrophilic modifier and pore forming agent which possibly leading to high surface porosity among the membranes. Furthermore, it can also be conclude that the membranes which were fabricated with additives shows high rejection value above 70 % which indicate the presence of additives influenced the high selectivity of membranes. Therefore, the hydrophilic macromolecular additive with membrane polymer could indeed significantly increase the hydrophilicity of the resulting membranes which then lead to higher membrane rejection.

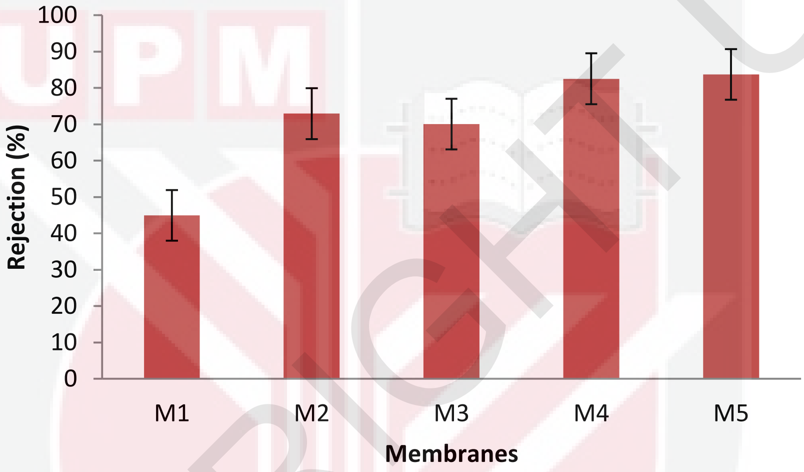


Figure 4.4 Rejection of Apple Juice Filtration

4.3.2 FLUX RECOVER AND RELATIVE FLUX REDUCTION

The effects of additives on the membrane performance were investigated with respect to the adsorptive fouling and ultrafiltration. The relative flux reduction (RFR) was used to determine the adsorption fouling of brown pigments that was filtered from the apple juice solution. From Figure 4.5, membranes that were prepared with additives showed higher resistance towards adsorptive fouling compared to membrane M1 which is prepared without the additive which shows the highest value of the RFR. This could be related to the characteristic of raw PES membrane where the hydrophobicity of PES seemed to have additional impact of the RFR. This shows that PES membrane without additives has a high fouling tendency. It is also observed that membrane M5 consisted of 5% of Pluronic F127 has the highest resistance towards the fouling. This can be related with the characteristic of Pluronic F127 where it can create hydrophilic membranes with superior fouling-resistant ability.

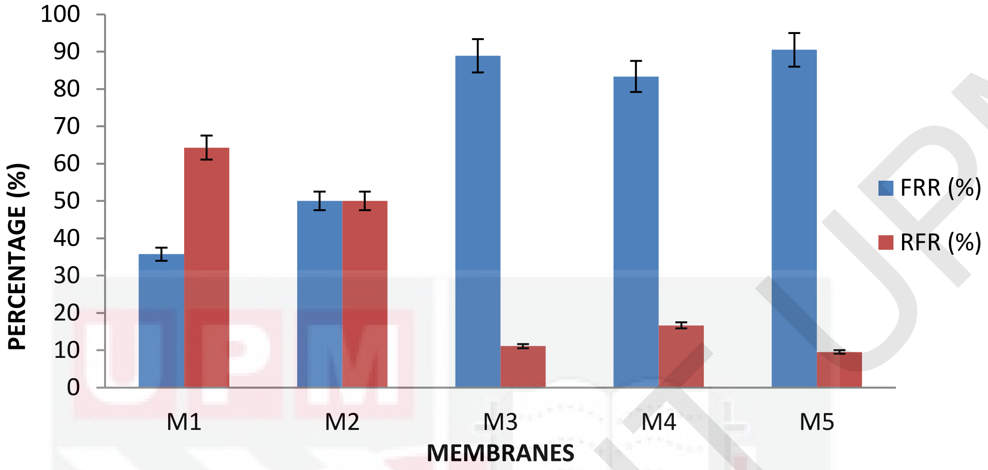


Figure 4.5 Flux Recovery and Reduction of Apple Juice Filtration

In order to test the recovery potential of PES blended membranes, the membranes that were fouled with yellowish-brown colour components of apple juice were regenerated with 0.1 NaOH solutions where this solution helps the membrane to remove the adsorbed brown pigments and deposits. The membranes will recover their original white colour and the flux was restored to the original value.

Based on the Figure 4.5, membrane M5 shows the highest value of flux recovery ratio (FRR) which is about 90% recovery followed by membrane M3, M4, M2 and M1 with 89%, 83%, 50% and 36% of recovery respectively. FRR values for all the fabricated ultrafiltration were calculated and compared to PES control membrane M1 and it was seen clearly that PES membranes with additives had higher FRR values which indicate high ability to recover from fouling. Excellent flux recovery ratio (FRR) of PES blend membranes also imply that the blend membranes could be reused for several runs. Moreover, the higher FRR value for the membrane, the better anti-fouling and hydrophilicity properties it possess.

4.4 EFFECT OF ADDITIVES ON TAP WATER FILTRATION

For tap water filtration, two membranes that showed the best performance are selected for further investigation with respect to adsorptive fouling and ultrafiltration. The two membranes, M4 and M5 were selected based on the high values of rejection and flux recovery from the apple juice filtration before. Adsorptive fouling was determined by filtration of flat sheet membrane to organic material concentration dissolved within the tap water.

4.4.1 PERMEATION FLUX OF TAP WATER

The study was aimed to evaluate of the ultrafiltration membranes for separation of natural organic matter (NOM) particles from the tap water. The efficiency of NOM separation with use of the UF membranes is influenced by many factors such as NOM character, molecular weight distribution, pH and ionic strength of water (Kabsch-Korbutowicz, 2008). From Figure 4.6, it shows that both of membranes have high initial flux with value of 91.99 Lm^{-2}h^{-1} and 87.80 Lm^{-2}h^{-1} respectively. The maximal permeate flux always occurs at the beginning of filtration because membrane pores are clean and open at that moment. Then, as the time increased the flux rate of both membranes decreased.

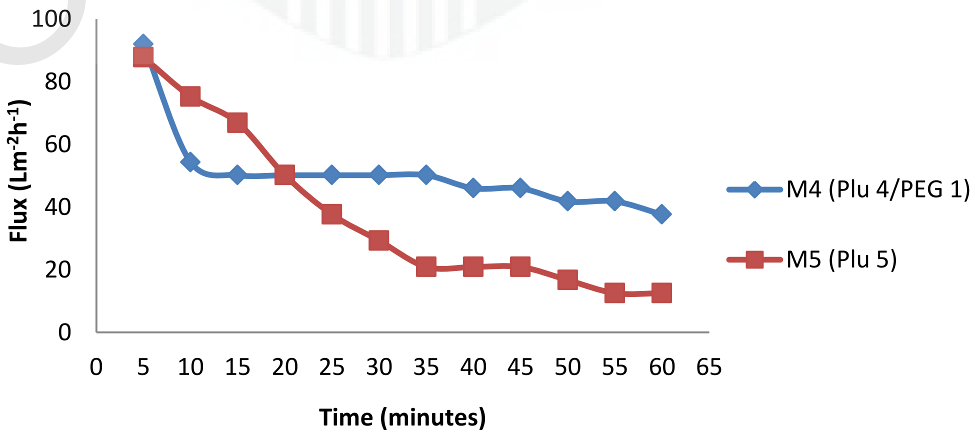


Figure 4.6 Permeate Flux of Tap Water

Membrane M5 has rapid flux decline compared to M4 which indicate that the membrane M5 has high adsorption towards the organic materials. Moreover, the rapid decline of membrane M5 also can possibly be related to the attributed to the pores size of the membranes. Dal-Cin et al. (1995) stated that when the pore size is considerably smaller than the foulant size, the decrease of flux might be only due to surface adsorption of macromolecules. Whereas, if the pore size is much larger than the foulant size, the macromolecules will enter the pores and adsorbed within the pore walls which then cause internal pore blocking. It will reduce the effective pore size which leads to the flux decreased as the flow area is reduced.

Rejection data presented on Figure 4.7 show that the PES membrane prepared with additives had quite lower rejection compared to apple juice filtration. Based on the study by M. Kabsch (2008), the efficiency of separation of natural organic matter was found to be strongly influenced by membrane properties. The increase of membrane pore size will resulted in decrease of NOM removal efficiency as the NOM size is much smaller compared to the pore size.

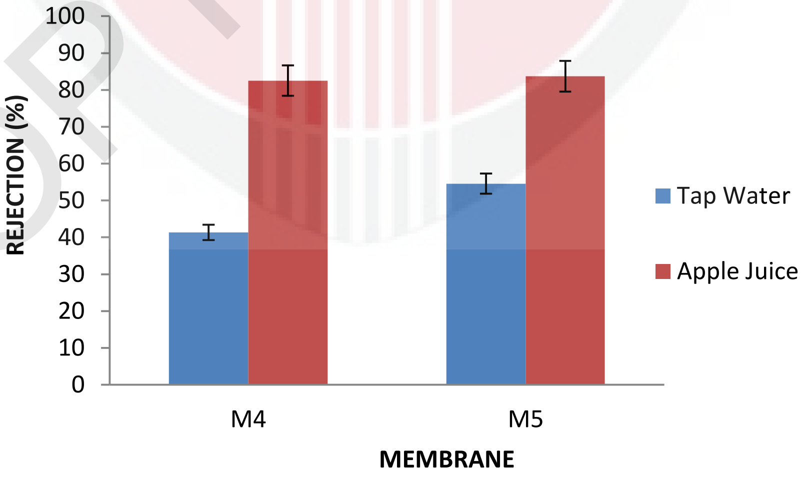


Figure 4.7 Rejection of Tap Water Filtration

4.4.2 FLUX RECOVERY AND RELATIVE FLUX REDUCTION

The effects of additives on the membrane performance were investigated with respect to the tap water adsorptive fouling and ultrafiltration. Same method as before is used for the analysis where the relative flux reduction is used to determine the adsorption of organic material that was filtered from the tap water.

As seen on Figure 4.8, membrane M5 has higher resistance towards adsorptive fouling compared to membrane M4 which shows the highest value of the FRR which is 55%. It also observed that membrane M5 that consist of 5% of Pluronic F127 has the highest resistance towards the fouling. As mentioned before, this can be related with the characteristic of Pluronic F127 where it can create hydrophilic membranes with superior fouling-resistant ability. FRR values were introduced to evaluate the surface modification, the higher the FRR value, the better the hydrophilicity and anti-fouling property of the membrane. Although membrane M4 has lower FRR value which is 41% compared to membrane M5 which is 55%, the membrane is still acceptable for recycled as it can be recovered up to 79%.

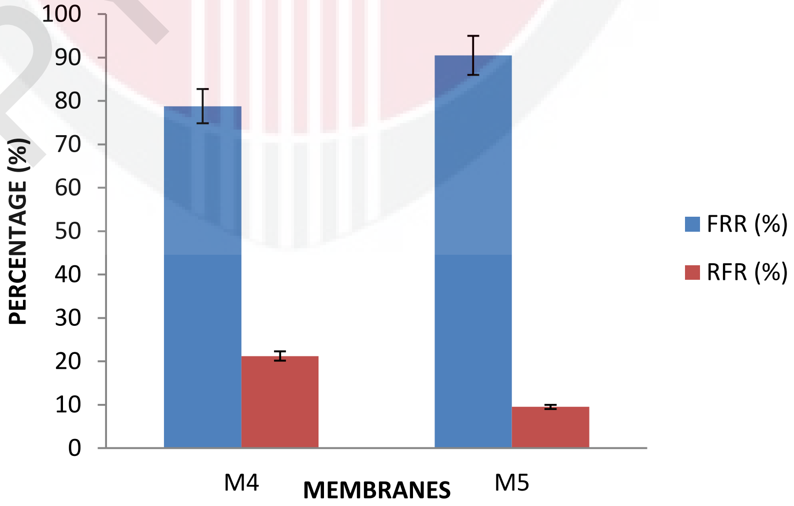


Figure 4.8 Flux Recovery and Reduction of Tap Water Filtration

4.4.3 TOTAL DISSOLVE SOLID

Total Dissolved Solids (TDS) are the total amount of mobile charged ions, including minerals, salts or metals dissolved in a given volume of water, which is expressed in units of parts per million (ppm). TDS is directly related to the purity of water and the quality of water purification systems. Membranes M4 and M5 are used to determine the efficiency of the TDS removal. Based on Figure 4.9, the value of TDS after membranes filtration only shows insignificant change in after the filtration process. Both of the membranes showed lower TDS removal efficiency which means these two membranes is not suitable to remove the dissolves solid content in the tap water even with the present of additives.

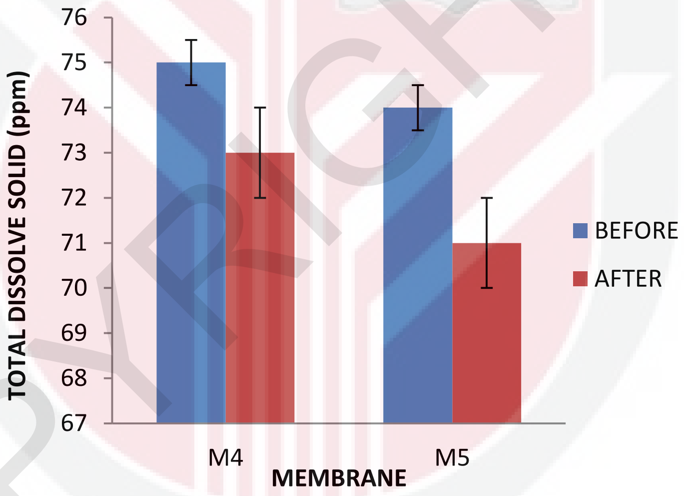


Figure 4.9 Total Dissolve Solid of Tap Water

4.5 EFFECT OF ADDITIVES ON MEMBRANES TENSILE STRENGTH

The tensile strength can be influenced by the polymer concentration where it has a strong effect on number and size of macrovoid of the membranes. When a polymeric additive is used in preparing the membranes, it may contribute to the higher formations of macrovoids where it will increase the fragility of the membranes which lead to lower tensile strength. According to the study of Susanto et al. (2008), the PEG additive normally could not suppress the formation of macrovoid This can be seen in Figure 4.11(b) where the SEM image shows the formation of macrovoid for membrane that consist PEG additives.

The best tensile strength can be attributed to high polymer concentration where the chance of macrovoids formation is lower. The mechanical testing results in Figure 4.10 indicate that maximum tensile strength is the membrane M5 with the elongation of 8.4% followed by membrane M1 which is without additive. The high tensile strength for membrane M5 is possibly due to high concentration of Pluronic F127. Moreover, study by Loh et al. (2012) states that the slight enhancement in dope viscosity with the addition of Pluronic F127 may cause a slower solvent-nonsolvent exchange in the nascent fibers and suppress macrovoid formation.

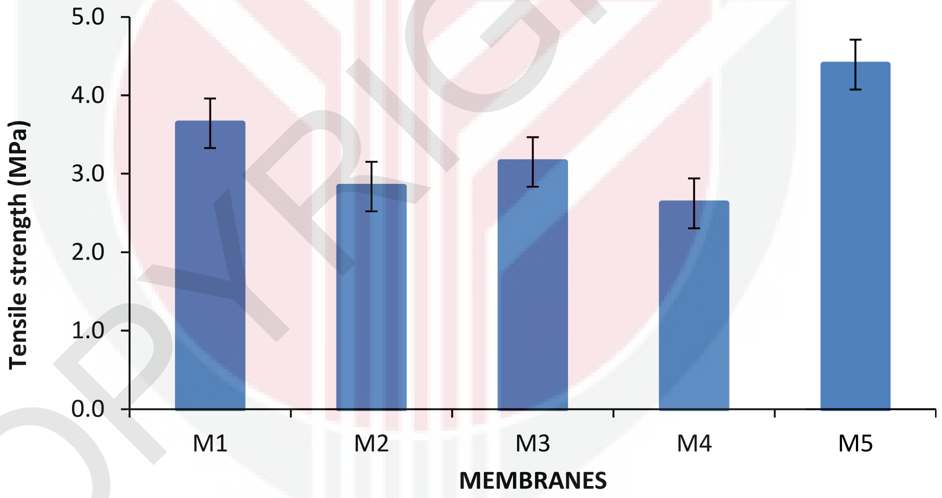
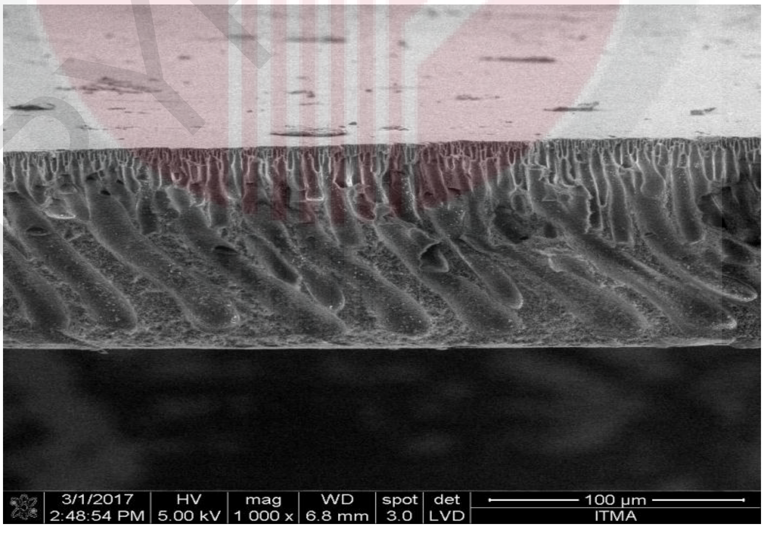


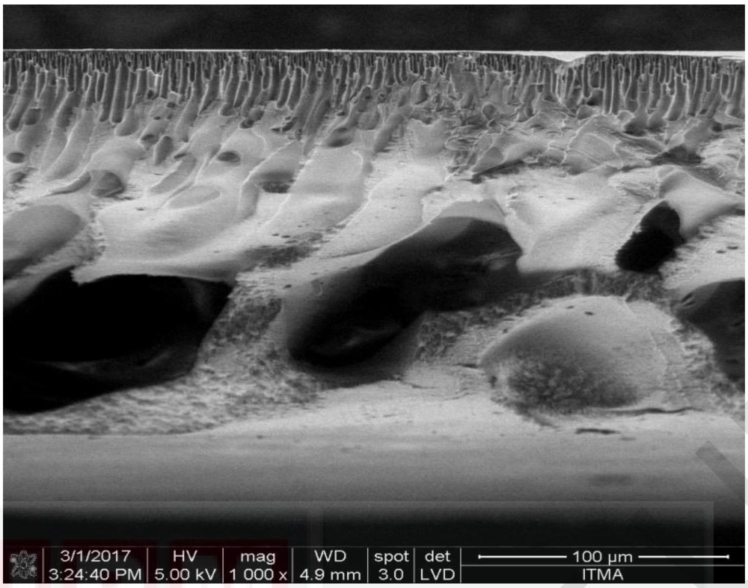
Figure 4.10 Tensile Strength of PES membranes

4.6 MEMBRANES MORPHOLOGY

Figure 4.11 (a) shows SEM images of cross-section PES membrane without any additives. This membrane has porous skin-layer and finger-like pores in the bottom. Whereas, the SEM image on Figure 4.11 (b) is the cross sections of PES membrane that was added with additives of Pluronic F127 and PEG. It can be observed that the membranes formed are having asymmetric structure consisting of a dense top layer and a porous sub layer. The sub layer showed sponge-like cavities and macrovoid structure at the bottom. The macrovoids formed in the bottom layer of the PES membrane may be caused by PEG concentration where large macrovoids in the substructure typically resulted in increased permeability. A study by Zuo et al. (2008), found that as PEG molecular weight increased from 200 to 20000, the macrovoids will developed initially and then suppressed. This proved that PEG could induce or suppress the macrovoids formation but depends on the concentrations. The macrovoids formations can also be suppressed by increasing the viscosity of casting solution. While for the sub layer sponge-like structure, it may be caused by the Pluronic F127 concentrations. Several researchers mention that Pluronic F127 usually will resulted a dense skin layer and a porous sublayer with sponge-like structures.



(a) PES



(b) PES/ 3% PLU F127/ 2% PEG

Figure 4.11(a)(b) SEM images of PES membranes

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Flat sheet Polyethersulfone (PES) membrane has been fabricated with different concentration of two additives which is Pluronic F127 and Polyethylene glycol (PEG). The effect of these additives on the performance and morphology of the PES membrane has been studied in term of pure water permeation (PWP) and solute rejection proficiency. Aside from that, the effect of additives to increase the ability of these membranes to recover from the fouling is also investigated.

From the analysis, it was clearly seen the highest PWP is obtained from membrane M4 (4% Pluronic and 2% PEG) with value 1045.29 $Lm^{-2}h^{-1}$ while the lowest PWP is obtained from raw PES membrane, M1 (no additives) with value 158.78 $Lm^{-2}h^{-1}$. These show that the presence of additives could improve the permeability of the membranes for about 84%. For the apple juice filtration, the permeate flux of all membranes decline as the time increase and the membrane M5 with total 5% wt of Pluronic F127 shows the best performance as it decline slowly without any immediate drop as the time increased. While for the rejection, the membranes with additives shows the rejection value up to 70 % compared to PES membrane without additives. This can be concluded that the additives influenced the selectivity of the membranes.

Moreover, the additives also increased the ability of the membranes to recover from the fouling as the flux recovery ratio (FRR) value of the membranes with additives shows quite high value compared to the without additives. For the total dissolve solid (TDS) removal, both of the membranes, M4 and M5 shows lower TDS removal efficiency which mean these membranes are not suitable to filter dissolved solid content in the tap water even with the presence of additives.

Furthermore, the additives also showed their influence on the mechanical properties of the membrane where it can be conclude the additives that attributed to macrovoids formation will decrease the tensile strength of the membrane. The morphology of the membrane prepared with and without additives is mention in discussion before. From the morphology study it can clearly be seen that the addition of additives can change the morphology structure of PES membrane which the will affect the membrane performances.

5.2 RECOMMENDATION

As recommendation for future research, there are few aspects which can be improved, which are:

a) Analyze the best or optimum concentration of Pluronic F127 and PEG combinations that could achieve the best membrane performances.

b) The analysis on the effect of additives can be improved by adding new parameters such as the analysis on pore size, contact angle and membrane thickness.

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APPENDICES

APPENDIX A

MEMBRANE PERFORMANCES

Table A.1 Result of Membrane Compaction

Time (minutes)	PWP ($Lm^{-2} h^{-1}$)				
	M1	M2	M3	M4	M5
5	593.73	878.05	890.59	848.78	790.24
10	531.01	455.75	485.02	568.64	564.46
15	464.11	163.07	359.58	505.92	501.74
20	376.31	137.98	288.50	447.39	397.21
25	250.87	129.62	238.33	409.76	347.04
30	167.25	125.44	234.15	313.59	321.95

Table A.2 Result of Pure Water Permeability

Pressure (bar)	PWP ($Lm^{-2} h^{-1}$)				
	M1	M2	M3	M4	M5
0.5	49.97	57.53	114.03	232.29	75.56
1.0	64.66	76.47	152.97	348.43	232.29
1.5	84.75	85.89	190.05	418.12	330.09
2.0	104.53	174.22	285.08	561.99	482.44
2.5	119.46	223.83	418.12	871.08	627.18
3.0	158.78	348.43	627.18	1045.29	783.97

Table A.3 Mechanical Properties of the Membranes

MEMBRANES	Tensile Strength (Mpa)	Elongation at Break (%)
M1	3.64	11.29
M2	2.84	27.70
M3	3.15	13.57
M4	2.62	27.44
M5	4.39	8.42

APPENDIX B

APPLE JUICE FILTRATION

Table B.1 Permeation Flux of Apple Juice Filtration

Time (minutes)	Permeate Flux ($Lm^{-2}h^{-1}$)				
	M1	M2	M3	M4	M5
5	45.99	45.99	142.16	167.25	87.80
10	29.27	29.27	71.08	62.72	75.26
15	20.91	20.91	37.63	50.17	66.90
20	16.72	16.72	25.09	50.17	50.17
25	16.72	16.72	20.91	37.63	37.63
30	12.54	16.72	20.91	29.27	29.27
35	12.54	16.72	20.91	29.27	20.91
40	12.54	16.72	16.72	20.91	20.91
45	12.54	16.72	16.72	20.91	20.91
50	12.54	16.72	16.72	20.91	16.72
55	11.71	12.54	16.72	16.72	12.54
60	11.71	12.54	12.54	16.72	12.54

Table B.2 Flux Recovery and Reduction Ratio

Membranes	Flux before ($Lm^{-2}h^{-1}$)	Flux After ($Lm^{-2}h^{-1}$)	FRR (%)	RFR (%)
M1	58.54	20.91	36	64
M2	58.54	29.27	50	50
M3	75.26	66.90	89	11
M4	75.26	62.72	83	17
M5	87.80	79.44	90	10

Table B.3 Membrane Rejection of Apple Juice Filtration

Membrane	Absorbance, at 420 nm		Rejection (%)
	C_f	C_p	
M1	0.230	0.095	59
M2	0.418	0.113	73
M3	0.418	0.125	70
M4	0.418	0.073	83
M5	0.418	0.068	84

APPENDIX C

TAP WATER FILTRATION

Table C.1 Permeation Flux of Tap Water FIltration

Time (minutes)	Permeate Flux ($\mathrm{Lm^{-2}h^{-1}}$)	
	M4	M5
5	91.99	87.80
10	54.36	75.26
15	50.17	66.90
20	50.17	50.17
25	50.17	37.63
30	50.17	29.27
35	50.17	20.91
40	45.99	20.91
45	45.99	20.91
50	41.81	16.72
55	41.81	12.54
60	37.63	12.54

Table C.2 Flux Recovery and Reduction Ratio

Membranes	Flux before ($\mathrm{Lm^{-2}h^{-1}}$)	Flux After ($\mathrm{Lm^{-2}h^{-1}}$)	FRR (%)	RFR (%)
M4	137.98	108.71	79	21
M5	87.80	79.44	90	10

Table C.3 Membrane Rejection of Tap Water Filtration

Membranes	Absorbance, at 420 nm		Rejection (%)
	C_f	C_p	
M4	0.295	0.173	41
M5	0.295	0.134	55

Table C.4 Membrane Rejection of Apple Juice Filtration

Membranes	Total Dissolve Solid (ppm)	
	Initial	After
M4	75	73
M5	74	71