EFFECTS OF COPOLYMERS ON THE PROPERTIES OF POLYSULFONE MEMBRANES

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A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Honours) Chemical Engineering

Lee Kong Chian Faculty of Engineering and Science
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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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ABSTRACT

This study investigates the effects of copolymers such as acacia gum (AG) and polyvinylpyrrolidone (PVP) at different compositions (2, 4, 6, 8 wt%) on the properties of polysulfone (PSF) membranes. The morphology of membranes can be observed by scanning electron microscope (SEM) and the membranes permeation can be evaluated in terms of pure water flux (PWF) and solute rejection. Based on the experimental results, each copolymer contributed to different outcomes when the performance of the fabricated membranes was evaluated. When the loadings of PVP increased from 2 to 8 wt%, the PWF of PSF/PVP composite membranes increased from 33.50 LMH to 264.35 LMH whereas the solution rejection of PSF/PVP composite membranes decreased. When the loadings of AG increased from 2 to 4 wt%, the PWF of PSF/AG composite membranes increased from 3.03 LMH to 7.62 LMH whereas the solute rejection of PSF/AG composite membranes increased. When the loadings of AG increased from 4 to 8 wt%, the PWF of PSF/AG composite membranes decreased from 7.62 LMH to 6.73 LMH whereas the solute rejection of PSF/AG composite membranes increased as well. In terms of PWF and solute rejection capability, AG is believed to be a better candidate to be utilized in the fabrication of membranes for water treatment purpose. In this study, the most suitable composition of copolymer was determined to be 4 wt% of AG as it has considerable potential to enhance the performance of membranes with high PWF and excellent solute rejection capability. In short, AG can be used as a novel hydrophilizing agent as well as an enhancer to the rejection properties of the PSF membranes.

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LIST OF SYMBOLS / ABBREVIATIONS

$wt\%$	weight percent
J_W	pure water flux, L/m^{2}h
t	time, h
A	surface area, m^2
V	volume, L
P	pressure, bar
R	retention, %
C_p	solute concentration in the permeate, mg/L
C_f	solute concentration in the feed, mg/L
T	temperature, ℃
FRR	flux recovery ratio, %
$S_{1/2}$	selectivity of solute 1 over solute 2

PSF	polysulfone
PES	polyethersulfone
CA	cellulose acetate
NMP	*N*-methyl-2-pyrrolidone
PVP	polyvinylpyrrolidone
AG	acacia gum
PEG	polyethylene glycol
PVDF	polyvinylidene fluoride
PVA	polyvinyl alcohol
DI	deionized
SEM	scanning electron microscopy
FTIR	Fourier-transform infrared

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Membrane technology has been extensively utilized in water and wastewater treatment as it requires less space and low chemical consumption (Vatsha, Ngila and Moutloali, 2014). Due to the rapid growth in this field, membrane technology acts as a feasible means of water treatment (Sagle and Freeman, 2004).

Generally speaking, a membrane is a barrier that prevents mass transfer but selectively allows one or more species to pass through it (Manning, 2015). In other words, dissolved substances and fine particles can be separated from certain solutions via membrane filtration (Muro, Riera and Carmen Diaz, 2012). A membrane selectively separates dissolved substances according to the molecular or physical size of the dissolved substances (Muro, Riera and Carmen Diaz, 2012). During the membrane separation, a driving force is required to transport certain species through the membrane, which in the case of synthetic membrane used for industrial applications is a transmembrane pressure (TMP) difference (Manning, 2015). By passing through membranes, the feed solution is separated into two streams which are permeate and retentate streams (Peters, 2010). The components rejected by the membrane are concentrated in the retentate stream (Manning, 2015).

Polymer such as polysulfone (PSF), is an excellent material for membrane preparation because PSF shows good mechanical strength, good chemical stability, high thermal resistance and high degree of flexibility (Aryanty and Khoiruddin, 2013). PSF membranes are usually formed by phase inversion method. Through this method, a polymeric solution is casted onto a plate as a thin film which is then inserted into a coagulation bath containing non-solvent and the thin film will solidify to form a membrane (Chakrabarty, Ghoshal and Purkait, 2008). Asymmetric membrane produced by this method has a dense layer at the top and a sublayer with porous structure. The top layer is a layer that permits selective permeability whereas the porous sublayer has macrovoids and micropores that can provide exceptional mechanical resistance to the membrane.

The hydrophobicity of PSF membranes tends to lower the water flux and eventually causes membrane fouling (Aryanty and Khoiruddin, 2013). In water treatment, membranes are subjected to flux decline due to fouling phenomena (Ariono et al., 2017). Fouling creates additional membrane resistance, which is greater than the intrinsic membrane resistance and this leads to the deterioration of membrane performances and flux loss (Ariono et al., 2017). In addition, the operating pressure required for membrane separation will also increase due to the fouling impact, which further increases the energy consumption as well as the operating costs (Vatsha, Ngila and Moutloali, 2014). Therefore, most of the membrane modification methods are focused on enhancing membrane hydrophilicity. Addition of hydrophilic copolymers into the membrane casting solution is likely to achieve this goal as it is also one of the simplest methods (Ariono et al., 2017). Copolymer like polyvinylpyrrolidone (PVP), is suggested to improve the membrane performance due to its high hydrophilic properties (Aryanty and Khoiruddin, 2013). The addition of copolymers in the membrane will form well-defined pores. Hence, the membrane containing copolymers is less prone to fouling (Vatsha, Ngila and Moutloali, 2014). Copolymers tend to increase the membrane pore size and porosity as the copolymers exhibits exceptional pore-forming ability (Zhao et al., 2012).

1.2 Importance of the Study

Nowadays, the utilization of membrane processes in water and wastewater treatment has drastically increased (Aminudin et al., 2013). Membrane separation is more effective and economical than conventional separation approaches. Due to this reason, membrane technology has become an alternative for water and wastewater treatment (Sagle and Freeman, 2004). Polysulfone (PSF) membrane can be employed to separate metal ions and dyes from water when the contaminated water flows through the membrane (Chakrabarty, Ghoshal and Purkait, 2010). PSF membrane is subjected to fouling because of its natural hydrophobic characteristic (Ariono et al., 2017). As membrane fouls, permeate flux declines and leads to low throughput (Miller et al., 2014). Therefore, most of the membrane modification methods are focused on improving membrane hydrophilicity. Blending process by incorporating hydrophilic copolymers has been extensively used as it is the simplest method to improve the membrane performance (Ariono et al., 2017). Copolymers prevent fouling issue and simultaneously enhance the membrane properties by yielding more porous structure as well as increasing the hydrophilicity of the fabricated membranes (Aminudin et al., 2013). By adding copolymers into the membrane dope solution, the properties of PSF membrane such as water permeability, hydrophilicity, porosity, tendency of fouling as well as the removal efficiency of metal ions and dyes from water can be altered.

1.3 Problem Statement

Water pollution is a critical environmental issue that has drawn the attention from researchers worldwide. Water containing metal ions and dyes is toxic and is able to bring adverse effects to living organisms (Jaishankar et al., 2014). Since high concentration of metal ions and dyes in water is harmful to living organisms, effective removal of heavy metal ions and dyes from water is needed. Polysulfone (PSF) membrane can be used to achieve this goal (Yin, Fan and Zhou, 2016). Due to its hydrophobicity, PSF membrane is susceptible to membrane fouling due to the presence of foulants in the feed stream (Shukla et al., 2017). When fouling takes place, the flux, water permeability and retention capability of membrane are affected (Yuan et al., 2014). To cope with this issue, the addition of copolymers into the membrane casting solution is one of the approaches that can be considered. In this study, the copolymers to be used in membrane fabrication are acacia gum (AG) and polyvinylpyrrolidone (PVP). The use of copolymers may alter the membrane characteristics by forming more porous membrane structure, increasing the hydrophilicity of the fabricated membranes and eventually enhancing the membrane performance (Aminudin et al., 2013). However, performances of PSF membranes modified by AG and PVP are not compared and evaluated in any reported study.

1.4 Aims and Objectives

The following are the objectives of this experiment:

- To evaluate the effects of different loadings of copolymers such as acacia gum (AG) and polyvinylpyrrolidone (PVP) on the properties of polysulfone (PSF) membranes.
- To determine the most suitable composition of copolymers in order to enhance the performance of membranes in terms of solute retention and flux recovery.

1.5 Scope and Limitation of the Study

In this research, polysulfone (PSF) membranes are prepared by phase inversion. Due to the hydrophobic nature of PSF membranes leading to fouling, copolymers such as acacia gum (AG) and polyvinylpyrrolidone (PVP) are added into the membrane casting solution. The effects of different loadings of copolymers on the properties of polysulfone (PSF) membranes are to be studied. Properties of membranes such as pure water flux, hydrophilicity, porosity and fouling tendency are investigated as well. All these properties can be evaluated via the application of scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and contact angle measurements on the fabricated PSF membranes.

1.6 Contribution of the Study

Water which contains metal ions and dyes tends to bring adverse effects to human beings. One of the measures to separate heavy metal ions and dyes from water is through membrane separation. High separation efficiency of PSF membranes can be achieved due to their good mechanical strength and chemical resistance. However, the hydrophobicity of PSF membranes can cause membrane fouling and lower the water flux (Aryanty and Khoiruddin, 2013). Addition of hydrophilic copolymers such as acacia gum (AG) and polyvinylpyrrolidone (PVP), can possibly produce membranes with better performances. This study can provide data to analyse the effects of different copolymers on the membrane antifouling capability. In addition, this study can be used to determine the most suitable composition of copolymers in order to enhance the performance of PSF membranes.

1.7 Outline of the Report

Phase inversion method is used to fabricate polymeric membranes and this is a process by which a polymer is converted from liquid state into solid state. In this project, heavy metal ions and dyes are separated from water via PSF membranes. In order to improve the properties of PSF membranes, copolymers such as acacia gum (AG) and polyvinylpyrrolidone (PVP) are added into the membrane dope solution for membrane modification. As a result, metal ions and dyes remain as retentate whereas water with high purity is yielded as permeate.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Polysulfone (PSF)

Polysulfones are a family of thermoplastic polymers, which are commonly used as membrane material in liquid and gas separations (Popa et al., 2012). Polysulfone is formed by a group of polymers that consist of a sulfonyl and alkyl- or aryl- groups, as illustrated in Figure 2.1.

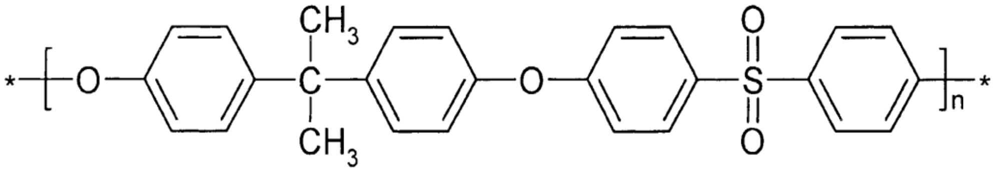


Figure 2.1: Structural Formula of Polysulfone (Kim et al., 2002)

Polysulfone (PSF) membranes have been extensively used in water and wastewater treatment (Phale and Chendake, 2016). PSF provides excellent heat resistance, good mechanical strength and high chemical stability (Zhao et al., 2012). Besides its abovementioned properties, polysulfone has high degree of flexibility and good film-forming properties (Dizman, Tasdelen and Yagci, 2013). It remains unchanged at temperature between 66 ℃ and 150 ℃ (Hamzah et al., 2014). Polysulfone-based membranes not only exhibit intrinsic biocompatibility and high permeability for low-molecular weight molecules, but also meet the solute and fluid removal requirements in various applications (Jenderal et al., 2016).

PSF has hydrophobic surface property, which leads to membrane fouling during its application because nonpolar and hydrophobic solutes easily accumulate on the membrane surface (Classi, 2011). When fouling occurs, the flux, permeability and rejection capability of membrane are greatly affected (Yuan et al., 2014). This is because membrane fouling creates additional resistance on the membrane, greater than the intrinsic membrane resistance, which induces the deterioration of membrane performance and flux loss (Ariono et al., 2017). The operating pressure will increase due to the fouling impact, which further increases the energy consumption as well as the operating costs (Vatsha, Ngila and Moutloali, 2014).

2.2 Copolymers

Generally speaking, a copolymer is a product that can be obtained when two or more distinct monomers combine to polymerize and this process is known as copolymerization. In order to reduce the hydrophobicity of membrane, it is believed that blending hydrophilic copolymers with membrane casting solution is one of the feasible approaches (Zhao et al., 2012). The incorporation of hydrophilic copolymers in the membrane increases the membrane porosity and inhibits the macrovoids formation in the membrane (Sun et al., 2009). The copolymers in membrane casting solution affect the thermodynamic and kinetic properties of membrane solution. With the help of copolymers, the interaction between polymer and solvent is reduced. Furthermore, the exchange between solvent and non-solvent can be performed at higher rate. Hence, the membrane precipitation rate is increased (Aryanty and Khoiruddin, 2013). The commonly used hydrophilic copolymers are polyethylene glycol (PEG), polyvinylpyrrolidone (PVP) and lithium chloride (Aminudin et al., 2013).

2.2.1 Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is a polymer obtained from the condensation of ethylene oxide and water. As shown in Figure 2.2, the chemical formula of PEG is $H(OCH_2CH_2)_nOH$, where n denotes the number of repeating oxyethylene groups (Wongchitphimon et al., 2011).

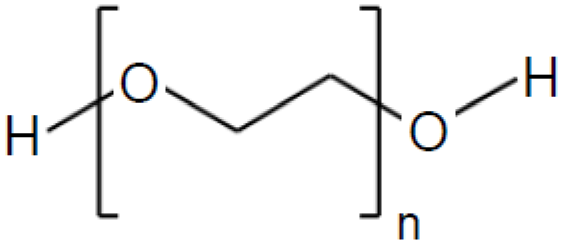


Figure 2.2: Structural Formula of PEG (Shinzawa et al., 2017)

PEG is sometimes added into membrane dope solution in order to increase the permeability of membranes (Chen et al., 2010). PEG shows hydrophilicity and modifies the wettability and biocompatibility of the membranes (Amirilargani and Mohammadi, 2009). As a result, the membranes containing PEG are expected to have higher permeability and greater fouling resistance (Li et al., 2014). Figure 2.3 shows the cross section images of PSF/PEG composite membranes containing different loadings of PEG.

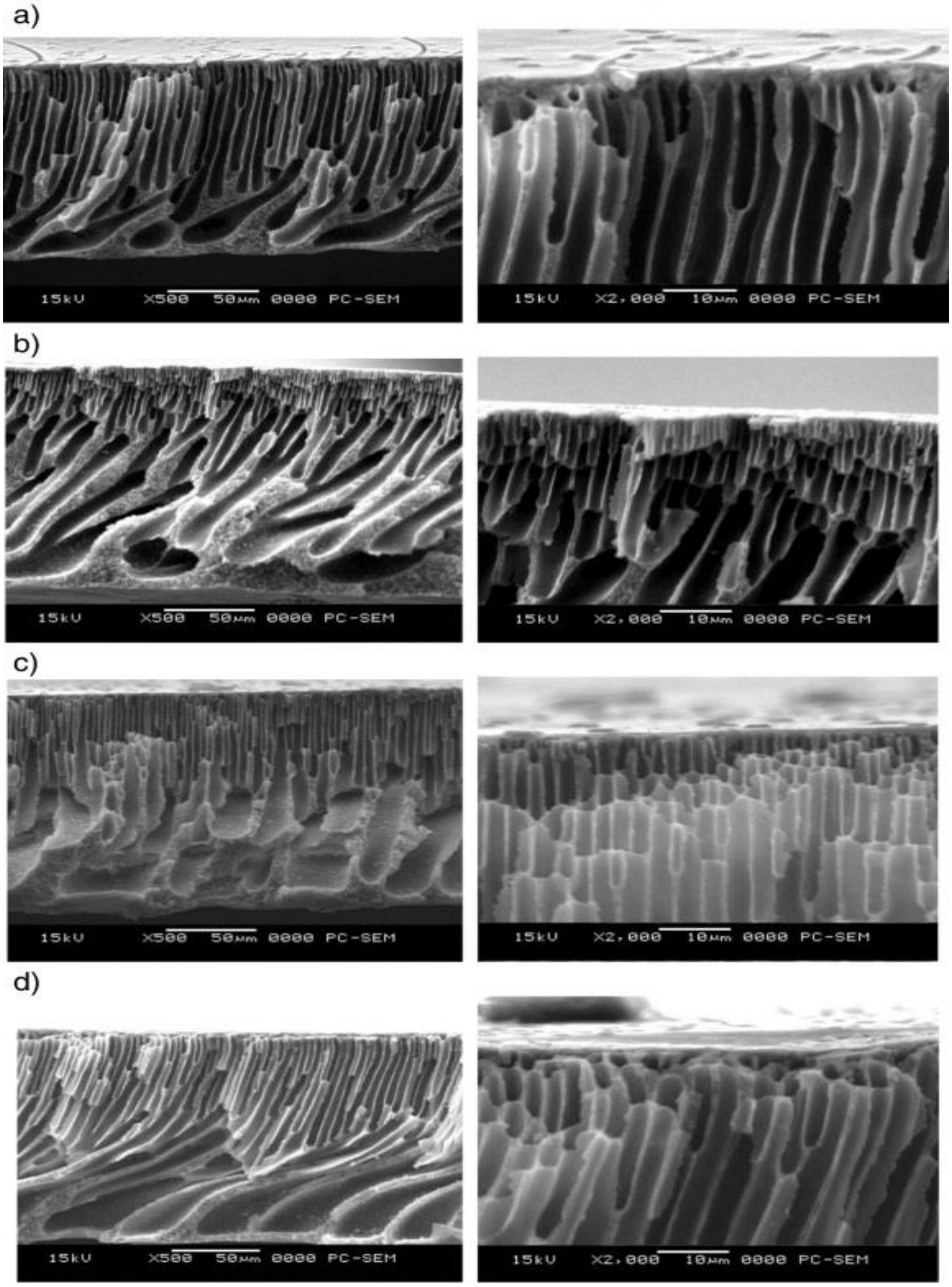


Figure 2.3: Cross Section Images of PSF/PEG Membranes with Different PEG Loadings: a) 4 wt% PEG, b) 8 wt% PEG, c) 10 wt% PEG, d) 16 wt% PEG (Yunos et al., 2014)

The interplay of PEG relies on the molecular weight and concentration of PEG, which may influence the kinetics and thermodynamics of membrane fabrication, leading to different structural and functional properties of membranes (Wongchitphimon et al., 2011). Low concentration of PEG leads to instant demixing and enlarges the membrane pores. However, high concentration of PEG up to 20 wt% can result in delayed demixing of membrane solution. This is because the viscosity of polymer solution has been increased and inhibiting the macrovoids formation (Aryanty and Khoiruddin, 2013). This reversibility indicates a balance between thermodynamic improvement and kinetic resistance. At high concentration, the copolymer is unlikely to induce thermodynamics enhancement when kinetic hindrance is caused by high viscosity of membrane casting solution (Lee et al., 2003).

2.2.2 Acacia Gum (AG)

Acacia gum (AG), also known as arabic gum, is dried exudates obtained from Acacia senegal trees (Lelon et al., 2010). It is composed of high molecular weight polysaccharides and a proteinous fraction. The main monosaccharides in AG are arobinopyranose (Ara), glucuronic acid (Glca), galactose (Gal) and rhamnose (Rha) while the main amino acids in AG are alanine, arginine, glutamic acid, glycine and histidine. AG is a heterogeneous material that exhibits amphiphilic nature. It is chosen as a suitable material to enhance the hydrophilic and antifouling properties of polymeric membranes (Manawi et al., 2017).

Addition of amphiphilic AG into casting solution is believed to be able to contribute to the formation of porous membrane structures which is a result of instantaneous demixing during the phase inversion. By enhancing the thermodynamic instability in the casting solution, AG serves as a non-solvent agent in the demixing process owing to its high solubility in water. Hence, the exchange rate between non-solvent and solvent increases during the demixing process. At the same time, this phenomenon increases the porosity of the fabricated composite membranes (Manawi et al., 2017).

Besides increasing the membrane porosity, the presence of AG in membrane casting solution is also believed to be capable of enhancing the hydrophilicity of the fabricated composite membranes. This can be explained by the interaction of AG macromolecules with the membranes surfaces and pores. During the casting of polymeric membranes, the hydrophobic macromolecules in AG interact with the hydrophobic groups in the polymer. At the same time, polysaccharide fragments found in AG hydrophilize the membrane surfaces and pores of the fabricated composite membranes. Hence, the hydrophilicity of polymeric membranes can be increased due to the presence of AG in the membrane casting solution (Manawi et al., 2017).

2.2.3 Polyvinylpyrrolidone (PVP)

Polyvinylpyrrolidone (PVP) is a water-soluble and chemically inert amorphous polymer made from its monomer, *N*-vinylpyrrolidone. Its chemical formula can be expressed as $(C_6H_9NO)_n$, as shown in Figure 2.4. PVP possesses excellent adhesion, high solubility in polar and non-polar solvent and promising capability to interact with hydrophilic substances (Khan, Hamadneh and Khan, 2017).

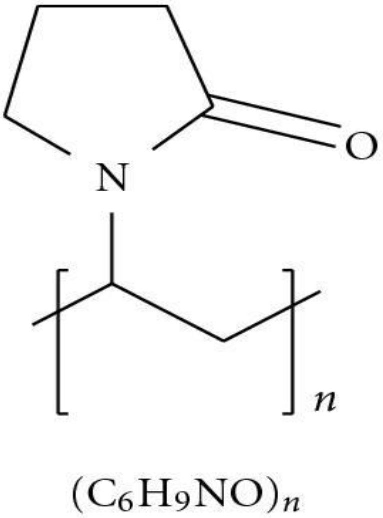


Figure 2.4: Structural Formula of PVP (Negahdary et al., 2012)

The addition of hydrophilic polymers into membrane casting solution to form porous membranes has been a feasible approach to enhance the performances of membrane, such as permeability and selectivity (Yuan and Dan-Li, 2008). PVP enhances the hydrophilic nature of polymeric membranes due to their high water solubility, which has been well-related to increase the membrane porosity (Guo et al., 2014). Hence, the antifouling property of membranes can be improved when PVP is used as a hydrophilic modifier in the fabrication of membranes (Sun et al., 2009).

The morphology of membranes can be affected by the concentration of PVP in membrane casting solution. Higher concentration of PVP can form modified composite membranes with larger pores that result in lower retention capability (Yuan and Dan-Li, 2008). PVP increases the water permeability since the fouling tendency of the membranes has been lowered. The presence of PVP reduces the tendency of delayed demixing of membrane casting solution and inhibits the formation of macrovoids (Sengupta et al., 2007). Furthermore, PVP can be used to produce membranes with large amount of interconnected pores. As a result, the fabricated composite membranes have excellent mechanical properties as well as high thermal stability (Ahmad et al., 2015). Figure 2.5 shows the SEM micrographs of cellulose acetate (CA) membranes with different loadings of PVP.

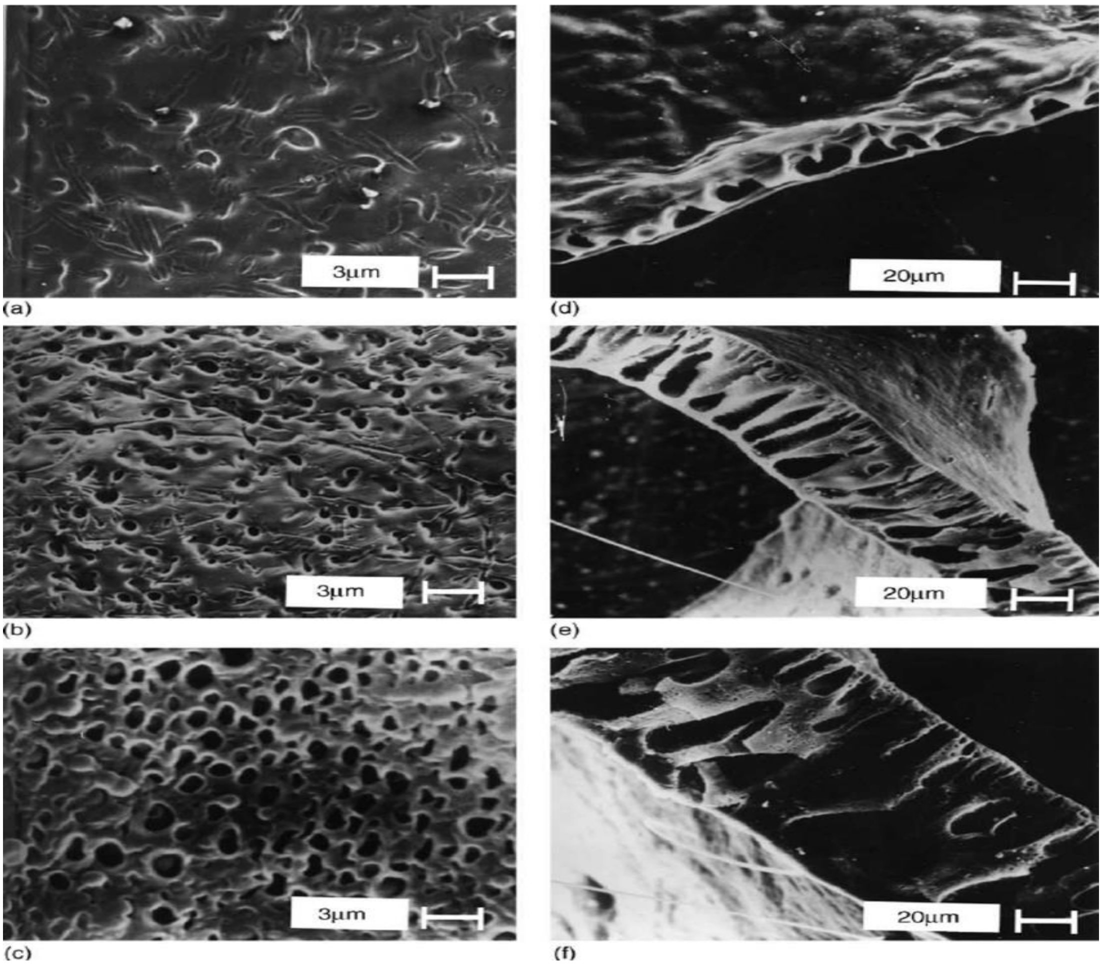


Figure 2.5: SEM Micrographs of CA Membranes with Different Loadings of PVP. Membrane Surface: (a) 2.5 wt% PVP; (b) 5 wt% PVP; (c) 7.5 wt% PVP. Cross-Section: (d) 2.5 wt% PVP; (e) 5 wt% PVP; (f) 7.5 wt% PVP (Sivakumar, Mohan and Rangarajan, 2006)

2.2.4 Polyvinylidene Difluoride (PVDF)

Polyvinylidene fluoride (PVDF) is a highly non-reactive thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. Its chemical formula can be expressed as -($C_2H_2F_2$)$_n$-, as shown in Figure 2.6.

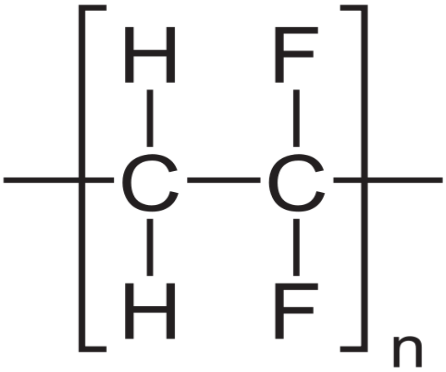


Figure 2.6: Structural Formula of PVDF (Wahab, 2017)

PVDF exhibits excellent engineering properties and has been employed an established polymer in industrial applications. Its properties include ferroelectric behaviour of piezo- and pyro-electricity, excellent biocompatibility and chemical resistance (Ruan et al., 2018). It is a semi-crystalline polymer, for which the crystalline phase provides mechanical strength and impact resistance while the amorphous phase offers flexibility (Ji et al., 2014). It is already being used as medical sutures and hernia meshes where it shows improved elasticity and strength over polyester and polypropylene.

PVDF is one of the most commonly used copolymers in membrane fabrication owing to its outstanding properties such as high chemical resistance, good thermal stability and low surface energy (Mokhtar et al., 2015). PVDF exhibits excellent chemical resistance and compatibility among thermoplastic materials. It is believed to be inert to strong acids, weak acids, aromatic solvents, oxidants, hydrocarbons as well as salt solutions. Besides its chemical compatibility, PVDF is also subjected to high-heat applications due to its high thermal resistance. It can remain unchanged at 150 ℃ without the occurrence of thermal or oxidative breakdown (Mokhtar et al., 2015). The cross sectional morphology of pure PSF membrane as well as modified PSF membranes prepared using different loadings of PVDF is shown in Figure 2.7.

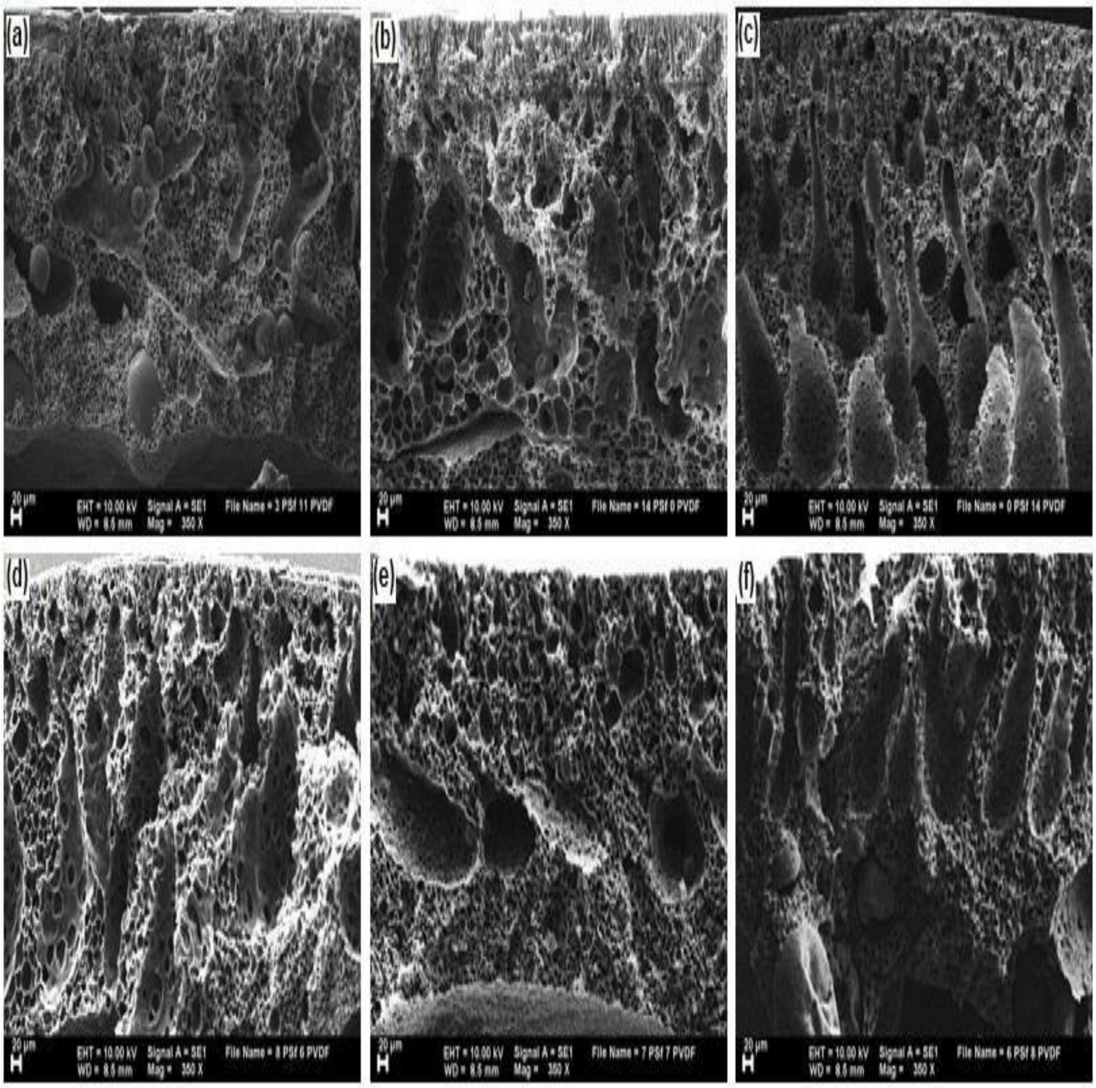
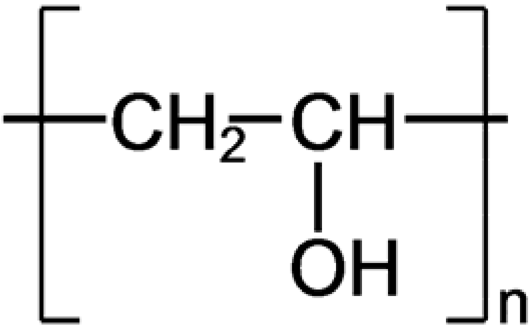


Figure 2.7: Cross-Section Images for: (a) PSF/PVDF (6 wt%); (b) PSF/PVDF (7 wt%); (c) PSF/PVDF (8 wt%); (d) PSF/PVDF (11 wt%); (e) Pure PSF; (f) PSF/PVDF (14 wt%) Membranes (Kusumawati et al., 2018)

2.2.5 Polyvinyl Alcohol (PVA)

Polyvinyl Alcohol (PVA) is a water-soluble synthetic polymer which is synthesized through the saponification process of polyvinyl acetate. Its chemical formula can be expressed as $[CH_2CH(OH)]n$, as shown in Figure 2.8.



$[-CH_2-CH(OH)-]_n$

Figure 2.8: Structural Formula of PVA (Majewski, 2015)

PVA is an artificial polymer that is easily degradable by biological organisms and in water is a solubilized crystalline structure polymer. It has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food. It is also utilized in various industrial applications to enhance the mechanical properties of films because of its compatible structure and hydrophilic properties.

Moreover, PVA is a thermoplastic polymer that is benign to living tissues, harmless and nontoxic. This polymer is widely investigated because of its uses in cross-linked products and nanofillers. It is a biodegradable polymer and its degradability is enhanced through hydrolysis because of the presence of hydroxyl groups on the carbon atoms. All PVA grades are hydrophilic and depend on certain factors such as molecular weight, element dimensions of distribution and particle crystal structure (Gaaz et al., 2015).

PVA is an excellent hydrophilic modifier in the fabrication of membranes. PVA exhibits good film-forming and outstanding chemical-resistant properties. It is a desirable material to be added in the membrane dope solution so that a novel type of ultrafiltration membrane with good antifouling properties can be fabricated. Besides its high hydrophilicity, this polymer provides high level of mechanical strength, long term thermal resistance and pH stability. The inherent hydrophilicity of PVA makes it an attractive polymer for water treatment applications based on membranes. High chemical resistance and outstanding anti-fouling properties of the fabricated composite membranes are accompanied by high water permeability (Hou et al., 2013). The cross sectional morphology of modified PVDF membranes prepared using different loadings of PVA is shown in Figure 2.9.

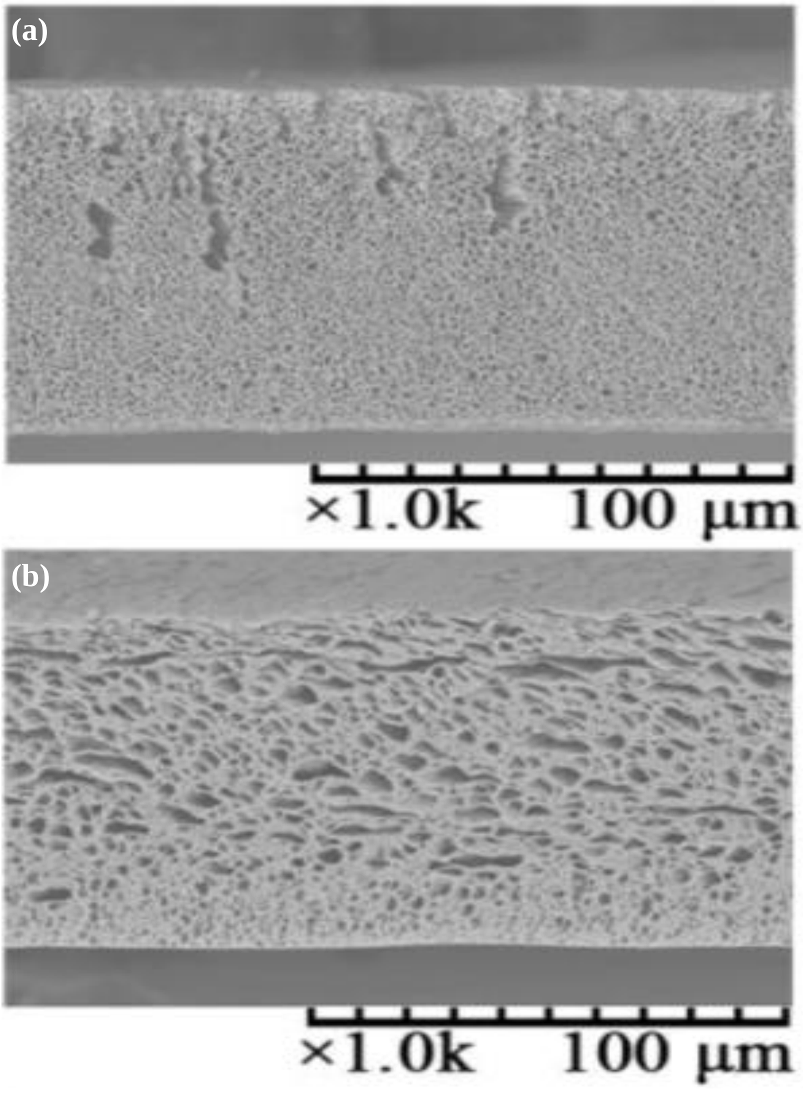


Figure 2.9: Cross-Section Images for: (a) PVDF/PVA (20 wt%); (b) PVDF/PVA (22 wt%) Membranes (Hu et al., 2016)

2.3 Phase Inversion Method

Phase inversion method is a conventional way to produce asymmetric membranes. Through phase inversion method, a polymeric solution is first casted onto a glass plate as a thin film which is then immediately immersed into a coagulation bath containing non-solvent (Chakrabarty, Ghoshal and Purkait, 2008). The thin film eventually solidifies to form a membrane via the exchange and diffusion of solvent and non-solvent (Guillen et al., 2011).

2.4 Removal of Dyes and Metal Ions from Water by Membrane Technology at Current Stage

Water has been scarce and getting vital with the rapid growth of the global population. Nowadays fresh water reservoirs have become unsuitable for daily usage due to untreated disposal of wastewater. Wastewater discharged from industries, contains harmful pollutants that might threaten the aquatic lives and human health (Alshabanat, Alsenani and Almufarij, 2013).

Industrial wastewater usually contains heavy metals as well as dyes. Industrial dyes can have negative impacts to living organisms (Zia Mohammadi et al., 2014). Metallic pollutants, for instance, platinum, copper and chromium, are of major concern as these heavy metals bring adverse health effects, such as diarrhoea, gastrointestinal disorders, tumours and paralysis (Logam and Kumbahan, 2018).

There are many conventional ways such as coagulation-flocculation and adsorption methods in order to separate metallic pollutants and industrial dyes from industrial effluent (Prabhu and Prabhu, 2018). However, the abovementioned techniques have their respective limitations and are subject to other problems. For example, chemical precipitation and coagulation-flocculation are widely used to treat industrial wastewater but these methods consume a great amount of chemicals and require extra handling costs (Wei et al., 2013). Due to the disadvantages of these conventional methods, effective and efficient treatments of chemically contaminated water has become one of the major issues of public interest (Ho et al., 2014). So far, membrane separation technologies have been reported as a promising way to separate heavy metal pollutants and dyes from water because of their high efficiency with minimum chemical consumption (Wei et al., 2013).

Several membrane-related experimental works have been conducted by researchers to evaluate the removal efficiency of heavy metal pollutants and dyes from industrial wastewater. First and foremost, membrane adsorption technology is a membrane technology integrated with the principles of adsorption. Generally, adsorption process takes place when a substance is transferred from liquid phase to solid surface via physical and/or chemical interactions with the medium. Chemical adsorption is feasible for metal ions and dyes removal as it creates stronger interactions and greater adsorption capability. In forming a membrane adsorbent, specific functional groups are linked to the membrane surface and membrane pores. The active sites found on the functional groups will bind to the contaminants with high adsorption rate before separating them from water stream (Khulbe and Matsuura, 2018).

The use of nanostructured affinity membrane has been introduced to remove heavy metal pollutants and dyes from water based on either physical, chemical or biological functions (Ma et al., 2016). Nanostructured affinity membrane is a kind of adsorption membrane which separates the contaminants by connecting specific functional groups to the membrane surface (Karim et al., 2016). For example, a micro-nano structure polymeric nanofibrous membrane fabricated with nanocrystals as functional additives can be used to adsorb dyes and heavy metal ions found in industrial effluent (Karim et al., 2016). However, the major challenge of this approach is to find a suitable and sustainable fabrication method using nanocellulose to yield desirable adsorption, high mechanical strength and high permeability.

2.5 Summary

Polysulfone (PSF)-based membranes are popular in water and wastewater treatment (Phale and Chendake, 2016). PSF is selected for membrane fabrication owing to its high thermal resistance, mechanical strength as well as chemical stability (Zhao et al., 2012). However, the main limitation of PSF is its hydrophobic nature which is the origin of membrane fouling (Classi, 2011). When membrane fouling occurs, flux permeation, water permeability and rejection capability are drastically reduced (Yuan et al., 2014).

To lower the hydrophobicity of the membrane, it is believed that blending hydrophilic copolymers with membrane casting solution is one of the feasible methods (Zhao et al., 2012). The commonly used hydrophilic copolymers are polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) (Aminudin et al., 2013). In this study, heavy metal ions and dyes in water will be removed via membrane filtration.

CHAPTER 3

METHODOLOGY

3.1 Membrane Preparation

PSF membranes were prepared using different loadings of copolymers such as acacia gum (AG) and polyvinylpyrrolidone (PVP) whereas *N*-methyl-2-pyrrolidone (NMP) was used as solvent (Aminudin et al., 2013). The composition of membrane casting solution is displayed in Table 3.1.

Table 3.1: Composition of the Membrane Casting Solution

Membrane	PSF (wt%)	AG (wt%)	PVP (wt%)	NMP (wt%)
Pure PSF	16	-	-	84
PSF/AG (a)	16	2	-	82
PSF/AG (b)	16	4	-	80
PSF/AG (c)	16	6	-	78
PSF/AG (d)	16	8	-	76
PSF/PVP (a)	16	-	2	82
PSF/PVP (b)	16	-	4	80
PSF/PVP (c)	16	-	6	78
PSF/PVP (d)	16	-	8	76

PSF was dissolved in NMP/additives mixture and being stirred for more than 4 hours at 60 ℃. The casting solution was further stirred for about 18 hours for homogeneous mixing of casting solution and was left for 3 hours to remove air bubbles from the casting solution (Vatsha, Catherine and Moutloali, 2013). The membrane casting solution was then casted on a glass plate with a casting knife by maintaining a thickness at 0.2 ± 0.02 mm at room temperature. The glass plate was then immediately immersed into the coagulation bath containing water, which was kept at room temperature (Aminudin et al., 2013). The membranes formed were washed for three times with DI water for half an hour and were kept at room temperature before the autopsy of membrane samples was carried out (Vilakati, Hoek and Mamba, 2014).

3.2 Functional Group Analysis

Fourier-transform infrared spectroscopy (FTIR) was employed for analysing the functional groups found in the membrane samples (Shaari, Rahman and Tajuddin, 2012). In this study, the presence of functional groups were investigated based on the peaks of the graph obtained through FTIR scanning (Şahİn, 2014). The analysis was conducted on pure PSF membrane and PSF membranes modified with 2, 4, 6 and 8% of different copolymers such as acacia gum (AG) and polyvinylpyrrolidone (PVP). All the membrane samples were dried in an oven at 40 ℃ prior to the autopsy (Zhao et al., 2012).

FTIR spectra can be obtained using a Thermo Scientific Nicolet iS10 FT-IR spectrometer. The spectra were recorded at 45 ° incident angle using a Ge crystal. 32 scans were taken with 4 cm^{-1} resolution between a wavenumber range of 4000 and 500 cm^{-1} (Yin, Fan and Zhou, 2016).

3.3 Membrane Surface Hydrophilicity Analysis

Hydrophilicity of membrane samples can be determined through contact angle measurement, which can be conducted at ambient temperature via sessile drop method using a goniometer with contact angle analyser (SEO Phoenix 300 Touch, Korea) connected to a computer with Surfaceware software.

Prior to the measurement, membrane samples were first dried at room temperature for 24 hours (Sahebi et al., 2016). A dangling droplet of 3 to 6 μL of deionized (DI) water at the end of 'I' shape needle was deposited on the membrane surface (Baek et al., 2012).

To investigate the surface hydrophilicity of membranes, the contact angle between a water droplet and membrane surface was observed (Ding et al., 2016). To minimize the experimental error, the measurements were performed at three different spots (Manawi et al., 2017). The values of contact angle calculated by Surface software were the average results within a period of 10 to 16 seconds. Higher value of water contact angle shows greater hydrophobicity of the membrane (Shaari, Rahman and Tajuddin, 2012).

3.4 Membrane Morphology

Morphologies of membrane samples can be observed by scanning electron microscopy (SEM) using a Hitachi S-3400N scanning electron microscope. The air-dried membrane samples were first immersed into liquid nitrogen, fractured and coated with gold sputtered on sample holders before being tested. The SEM studies were performed at room temperature and 10 kV with a magnification of 1000 so that high resolution SEM images of the membrane can be obtained (Chuang et al., 2000).

3.5 Pure Water Flux

The membrane permeation performance was tested at room temperature in a lab-scale dead-end stirred cell (Sterlitech HP4750, Sterlitech Corporation, USA) with a maximum capacity of 300 mL and an active membrane surface area of 14.6 cm^2. A pressure regulator was linked to the top part of the stirred cell to provide the pressure needed for membrane filtration. First, fresh membrane samples were pressurized with distilled water at 5 bar for an hour. Generally, this process is called compaction process, which is to obtain constant flux data of every membrane sample in pure water flux test and to remove residual solvent in the fabricated membrane. After achieving a constant state, the pure water flux (PWF) can be calculated using Equation (1):

$$J_{W1} = \frac{V}{A\Delta t} \tag{1}$$

where J_{W1} denotes the pure water flux (PWF), V denotes the volume of permeate (L), A represents the membrane surface area (m^2) and Δt is the permeation time (h) (Chakrabarty, Ghoshal and Purkait, 2008).

3.6 Retention Capability

In this study, the solute retention capability of membranes was evaluated using 10 ppm of methylene blue solution and 100 ppm of salt solutions (magnesium sulphate, sodium chloride and sodium sulphate) as membrane feed solutions. As solution stirring rate will affect the membrane retention test, a constant stirring rate of 500 rpm at 5 bar was employed. In order to measure the retention of metal ions, the conductivity values of feed and permeate were measured using a conductivity meter.

The concentrations of methylene blue solution in feed and permeate stream were indicated using spectrophotometer (Cary 100, UV-Vis Spectrophotometer, Agilent) at 668 nm wavelength in measuring the absorbance of methylene blue solution. The retention, R, was calculated according to Equation (2). C_p and C_f denote the concentration of permeate and feed solution, respectively (Manawi et al., 2017). The selectivities for all membranes were calculated using Equation (3), in which $S_{1/2}$ is selectivity of solute 1 over solute 2, $C_{p,1}$ is permeate concentration of component 1, $C_{f,2}$ is feed concentration of component 2, $C_{p,2}$ is permeate concentration of component 2, R_1 is retention of component 1 and R_2 is retention of component 2 (Yong et al., 2014).

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

$$S_{1/2} = \left(\frac{C_{p,1}}{C_{f,1}}\right)\left(\frac{C_{f,2}}{C_{p,2}}\right) = (100\% - R_1)(100\% - R_2) \tag{3}$$

3.7 Flux Recovery Ability

After the filtration of dye and salt solutions, the fouled membranes were backflushed with DI water for an hour at room temperature. The pure water flux of each membrane sample after backflushing was remeasured (Yuan et al., 2014). To evaluate the antifouling properties of membrane samples, the flux recovery ratio (FRR) can be measured based on Equation (4):

$$FRR(\%) = \left(\frac{J_{W2}}{J_{W1}}\right) \times 100 \tag{4}$$

where J_{W2} denotes the pure water flux (PWF) after flushing and J_{W1} represents the pure water flux (PWF) before flushing.

3.8 Summary

In this study, PSF membranes were fabricated by phase inversion technique using different loadings of AG and PVP whereas *N*-methyl-2-pyrrolidone (NMP) acted as solvent (Aminudin et al., 2013).

Fourier-transform infrared spectroscopy (FTIR) was employed for analysing the functional groups found in the membrane samples (Shaari, Rahman and Tajuddin, 2012). To determine the hydrophilicity of the membrane, contact angle measurement was conducted via sessile drop method at room temperature using a goniometer. The morphologies of the membrane samples were observed by scanning electron microscopy (SEM).

The membrane permeation performance was tested at ambient temperature in a lab-scale dead-end stirred cell. The solute retention capability of each membrane sample was evaluated using 10 ppm of methylene blue solution and 100 ppm of salt solutions (magnesium sulphate, sodium chloride and sodium sulphate) as membrane feed solutions.

After filtration of both dye and salt solutions, the fouled membrane was flushed with DI water for an hour at room temperature. The pure water flux (PWF) of the membrane after flushing was then remeasured (Yuan et al., 2014).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Functional Group Analysis

Fourier-transform infrared spectroscopy (FTIR) was employed for analysing the functional groups that present in the membrane samples. Figure 4.1 shows the infrared spectra of the fabricated membrane samples when copolymers, such as acacia gum (AG) and polyvinylpyrrolidone (PVP), were added into the membrane casting solution. Based on the infrared spectrum of PSF/PVP membrane, new absorption peak at 1659.92 cm^{-1} was more prominent while the rest of the spectrum remained similar to one another (Asmatulu, 2016). This new band was attributed to the stretching vibration of C=O groups found in PVP. This indicates that PVP was captured in PSF network and was forming an integral part of the polymeric structure, which can produce PSF/PVP composite membranes with hydrophilic surfaces (Vatsha, Ngila and Moutloali, 2014). The broad peak of O-H stretching was observed at 3417.78 cm^{-1}. This can be explained by the formation of hydrogen bonds between hydroxyl end groups of PVP and oxygen atoms in sulfonyl groups of PSF (Qu, Zhang and Wang, 2010).

Based on the infrared spectrum of pure PSF membrane, stretching vibration of C-C aromatic groups can be observed at 1583.86 cm^{-1} and 1486.70 cm^{-1}. From the infrared spectra of all membrane samples, the band at between 2900cm^{-1} and 3000 cm^{-1} was due to the stretching vibration of C-H groups found in PSF (Asmatulu, 2016). Besides the stretching vibration of C-H groups, it was believed that the band at 2967.94 cm^{-1} in the spectrum of PSF/AG membrane also signified the possible presence of sugar, galactose, arabinose and rhamnose owing to the presence of C-H groups and methylene groups in AG macromolecules (Daoub et al., 2016).

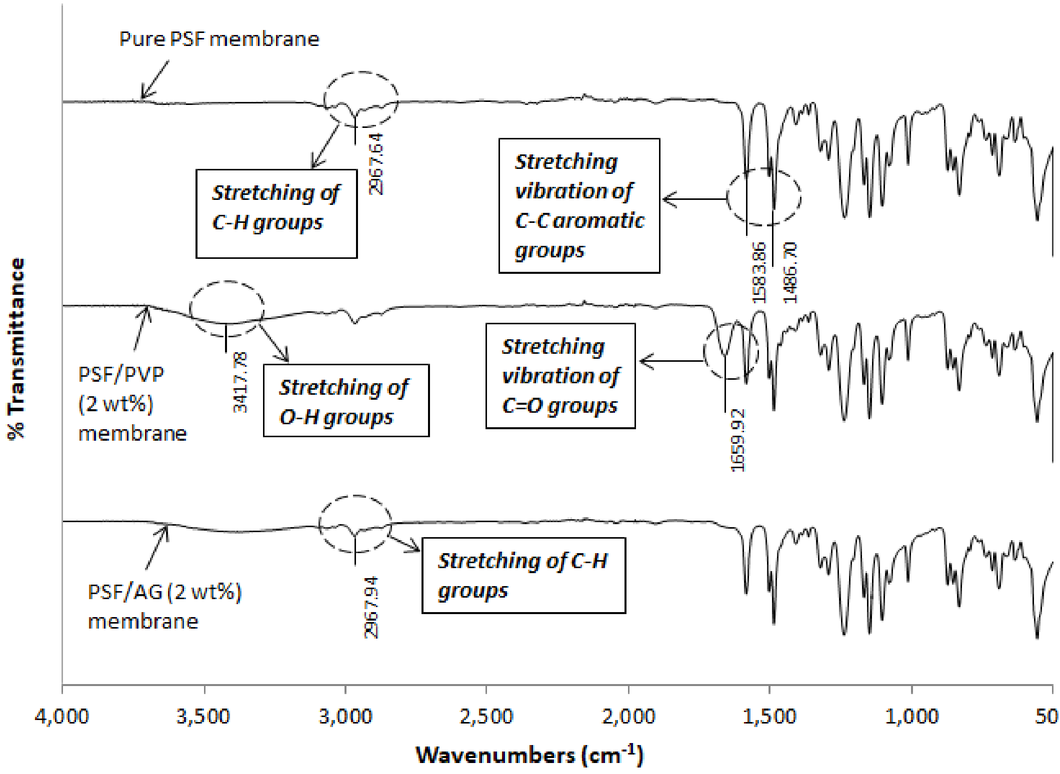


Figure 4.1: FTIR Spectra of Pure PSF, PSF/AG (2 wt%) and PSF/PVP (2 wt%) Membranes

4.2 Membrane Morphology

The cross sectional morphology of pure PSF membrane as well as modified PSF membranes prepared using AG and PVP as additives at 2 wt% loadings is shown in Figure 4.2. Pure PSF and modified PSF membranes have asymmetric structures consisting of dense top layers, porous sublayers and small portion of sponge-like bottom layers (Hamzah et al., 2014). The skin layer serves as a separation layer while the support layer provides mechanical strength to the membrane. The sublayer has finger-like structures beneath the top surface layer as well as macrovoids structure (Yin, Fan and Zhou, 2016). The formation of finger-like sublayer can be explained by the instantaneous demixing caused by high mutual affinity of solvent and non-solvent.

By introducing copolymers into the membrane casting solution, the resulted finger-like structures at top layer of the membrane and pores become larger in size and extend longer to the bottom of the membrane (Aminudin et al., 2013). From Figure 4.2, the top layer of modified PSF membranes is denser than pure PSF membrane. This is because the presence of copolymers in the membrane dope solution increases the viscosity of the membrane dope solution, which hinders the solvent-nonsolvent exchange. In highly viscous casting solution, outdiffusion of solvent from the casting solution is preferred over indiffusion of nonsolvent into the solution. The formation of dense top layer is due to the delayed polymer coagulation on the surface region of the casting solution.

In the presence of copolymers in the membrane casting solution, the macrovoids will become larger in size and the pore walls among the macrovoids will become looser with channel-like pores. It is believed that the addition of copolymers into the membrane casting solution could accelerate the phase separation process and thus enlarge the macrovoids and form more interconnected pores. There is an increase in membrane pore size and porosity as a portion of copolymers is possibly leached out of the casting film in the exchange of solvent and nonsolvent (Zhao et al., 2012).

The surface morphologies of pure PSF membrane and modified PSF membranes prepared using AG and PVP as additives at 2 wt% loadings are shown in Figure 4.2. Since the loadings of copolymers were relatively low, well-defined pores with narrow size distribution can be observed (Vatsha, Ngila and Moutloali, 2014). The formation of the membrane top surface was a result of spinodal demixing as the diffusion process during the formation of the top surface layer was fast enough for the polymer solution to become unstable and cross the spinodal curve, resulting in a membrane top surface with much interconnected pores (Chakrabarty, Ghoshal and Purkait, 2008).

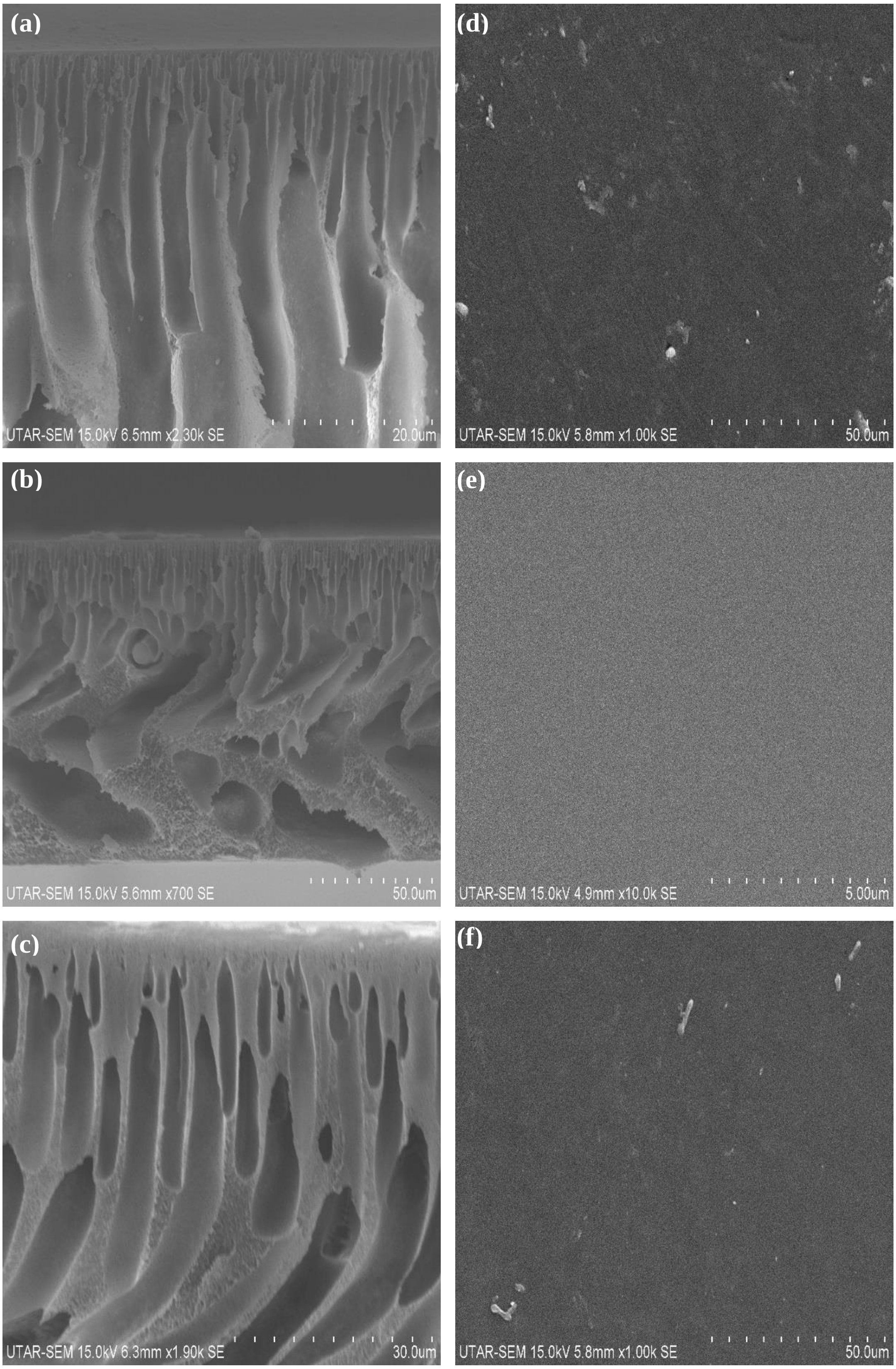


Figure 4.2: Cross-Section Images for: (a) Pure PSF; (b) PSF/AG (2 wt%); (c) PSF/PVP (2 wt%) Membranes, Membrane Surface Images for: (d) Pure PSF; (e) PSF/AG (2 wt%); (f) PSF/PVP (2 wt%) Membranes

4.3 Pure Water Flux (PWF) Analysis

The effect of different compositions of AG and PVP on the PWF performance is illustrated in Figure 4.3 and Figure 4.4. The PWF of pure PSF membrane, which served as a control membrane, was 2.35 LMH. The introduction of AG into the casting solutions of PSF was found to be able to increase the PWF of the modified PSF membranes. The flux increase can be attributed to the increase in the porosity and hydrophilicity of the modified PSF membranes when AG was added into the membrane casting solution. When the loadings of AG increased from 2 to 4 wt%, the PWF of PSF/AG membranes increased from 3.03 LMH to 7.62 LMH. When the loadings of AG increased from 4 wt% to 8 wt%, the PWF of PSF/AG membranes decreased from 7.62 LMH to 6.73 LMH.

Acacia gum (AG) is a kind of amphiphilic non-solvent modifier. The increase in PWF when AG was added into the casting solution can be explained by the distribution of AG macromolecules that hydrophilize the membrane surfaces and pores (Manawi et al., 2017). While casting PSF/AG composite membranes, the hydrophobic AG macromolecules interacted with the hydrophobic alkyl groups in PSF, whereas polysaccharide fragments in AG hydrophilized the membrane pores and surfaces (Manawi et al., 2017). After the hydrophilization of membrane surfaces and pores, water can permeate through the membrane easily. Hence, the PWF of PSF/AG composite membranes increased.

Based on Figure 4.3, from 4 wt% onwards, an increment in concentration of AG decreased the size of macrovoids in the membrane. High viscosity caused by high concentration of AG in the membrane dope solution led to low porosity of the resulted PSF/AG composite membranes. Increased loadings of AG led to the decline in the PWF because AG added to the casting solution could be leached out of the casting film when the casted film was immersed into a non-solvent bath. The thermodynamic instability in casting film could be increased, which caused the occurrence of instantaneous demixing (Mulyati et al., 2018). The addition of AG at loadings more than 4 wt% caused the casting solution to be more viscous, thus, the rate of solvent and non-solvent exchange in the coagulation bath decreased and led to delayed demixing (Mulyati et al., 2018). This phenomenon can cause the membrane top layer to become denser by suppressing its pore formation. The PWF tends to decrease due to the decrease in porosity and pore size of the membranes.

As shown in Figure 4.4, the PWF of PSF/PVP composite membranes increased with an increment in PVP loadings. The PWF of PSF/PVP composite membranes increased from 33.50 LMH at 2 wt% PVP to 264.35 LMH at 8 wt% PVP. The PWF can be affected by the concentration of PVP in the casting solution. PVP serves as a pore forming agent and its presence in the casting solution assists the formation of more pores on the surface of PSF/PVP composite membranes after the casted film is immersed into the coagulation bath (Mulyati et al., 2018). This allows more water to permeate through the membrane surface easily and results in the increase in PWF of PSF/PVP composite membranes. In this study, both additives can result in modified PSF membranes with better pure water fluxes when compared to pure PSF membranes.

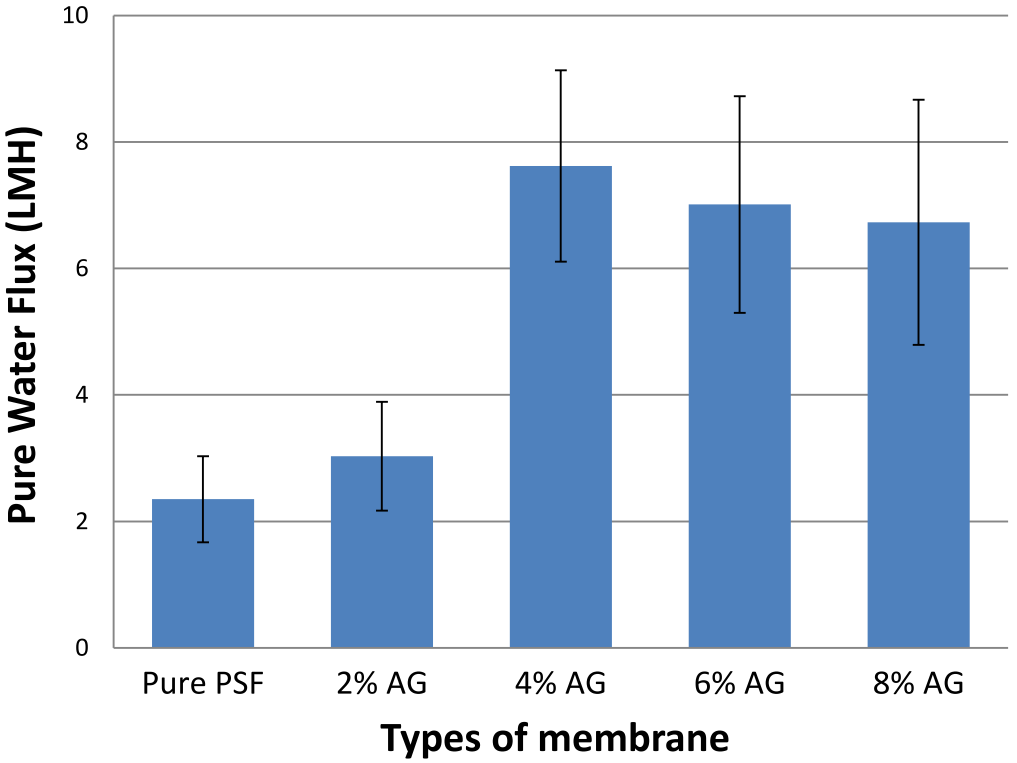


Figure 4.3: Pure Water Flux (PWF) of PSF and PSF/AG Membranes at 5 Bar

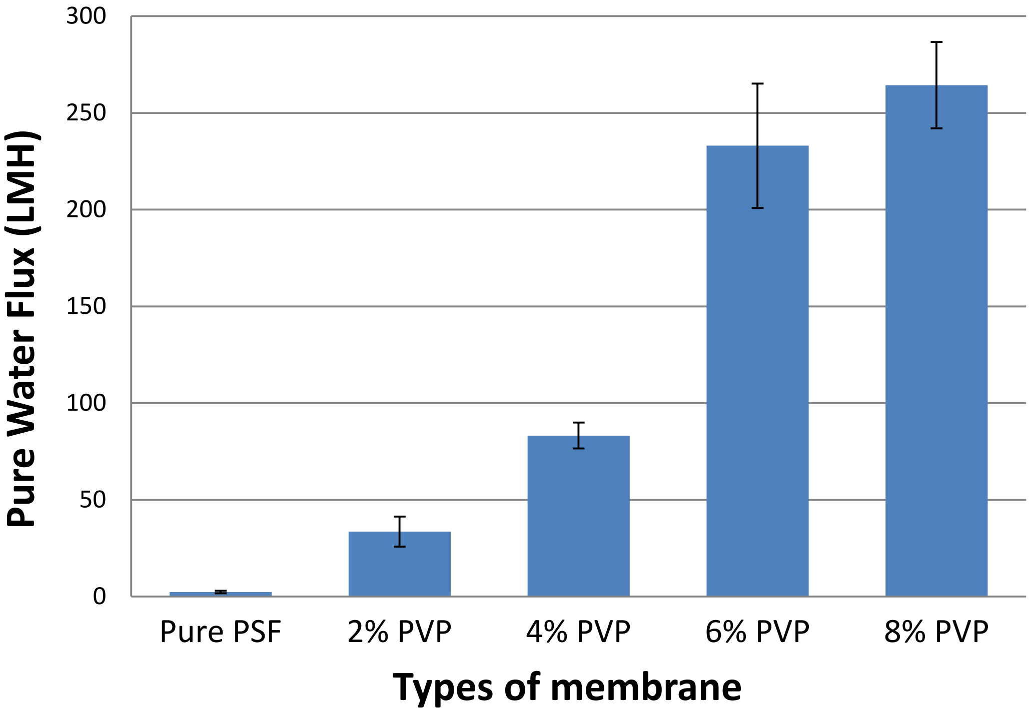


Figure 4.4: Pure Water Flux (PWF) of PSF and PSF/PVP Membranes at 5 Bar

4.4 Contact Angle Measurement

Hydrophilicity of the fabricated membrane samples can be indicated by measuring the contact angle between the membrane surface and water droplet (Ding et al., 2016). Figure 4.5 shows the water contact angle values of pure PSF membrane as well as PSF composite membranes with different AG and PVP loadings. The contact angle of pure PSF membrane was measured to be 70°. The addition of AG into the casting solution increased the hydrophilicity of the fabricated membranes by lowering the contact angle by 15% when compared to pure PSF membrane. Based on the experimental results, the contact angle of PSF/AG composite membranes dropped from 66° at 2 wt% AG to 60° at 8 wt% AG. The decrease in the contact angle of PSF/AG composite membranes can be explained by the distribution of AG macromolecules that hydrophilize the membrane surfaces and pores (Manawi et al., 2017). While casting PSF/AG composite membranes, hydrophobic AG macromolecules could interact with the hydrophobic alkyl groups in PSF whereas polysaccharide fragments in AG could hydrophilize the membrane pores and surfaces. After the hydrophilization of membrane surfaces and pores, water can permeate through the membrane easily. Hence, the contact angle of PSF/AG composite membranes decreased.

The contact angle of PSF/PVP composite membranes dropped from 68 ° at 2 wt% PVP to 44 ° at 8 wt% PVP. The contact angle of PSF/PVP composite membranes decreased with increasing PVP concentrations, indicating increasing hydrophilicity of the fabricated PSF/PVP composite membranes (Yuan et al., 2014). The contact angle can be significantly affected by the concentration of PVP added into the casting solution. PVP can act as a pore forming agent and its presence in the casting solution can assist the formation of more pores on the membrane surfaces after the casted films are immersed into the coagulation bath (Mulyati et al., 2018).

Based on Figure 4.5, modified PSF/AG and PSF/PVP membranes have lower contact angle values than pure PSF membrane as both AG and PVP are capable of enhancing the hydrophilicity of the modified membranes. AG can increase the hydrophilicity of the membranes via the hydrophilization of membrane surfaces and pores. Meanwhile, PVP can serve as a pore forming agent which forms membranes with more pores and higher porosity, which in turn allow more water to pass through the membranes.

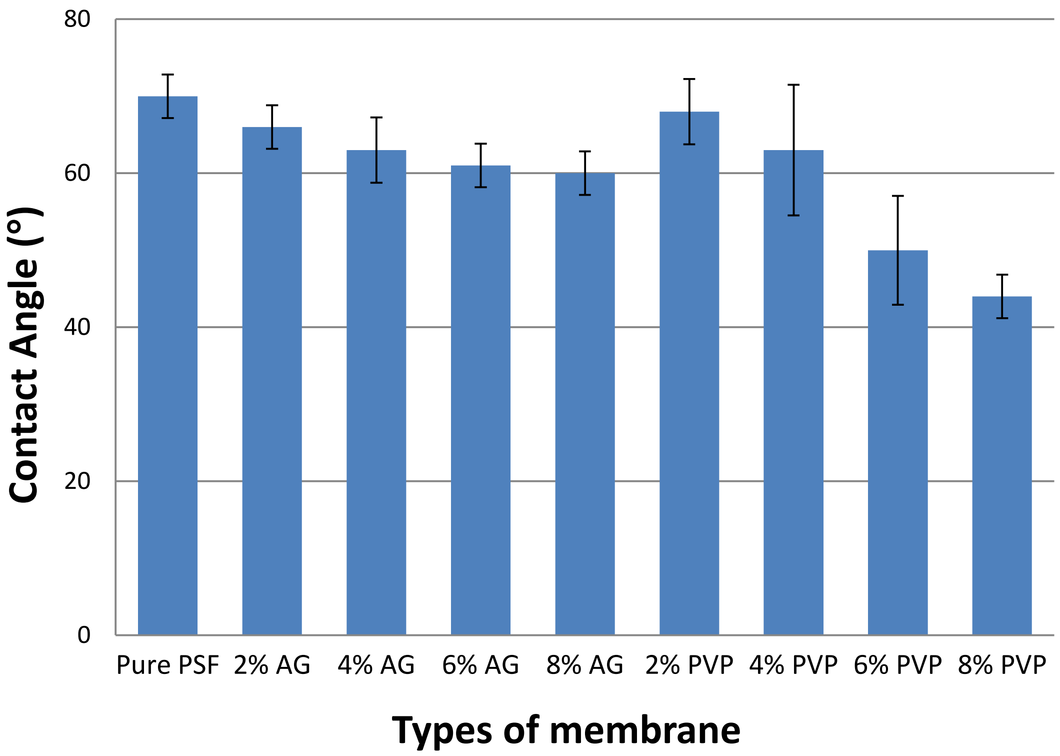


Figure 4.5: Contact Angle of Different Membranes

4.5 Membrane Retention Capability and Selectivity Study

Solute retention capability of the fabricated membranes can be evaluated using 10 ppm of methylene blue solution and 100 ppm of salt solutions (magnesium sulphate, sodium chloride and sodium sulphate) as membrane feed solutions. Figure 4.6 shows the percentages of solute rejection of pure PSF and modified PSF membranes at different AG and PVP loadings.

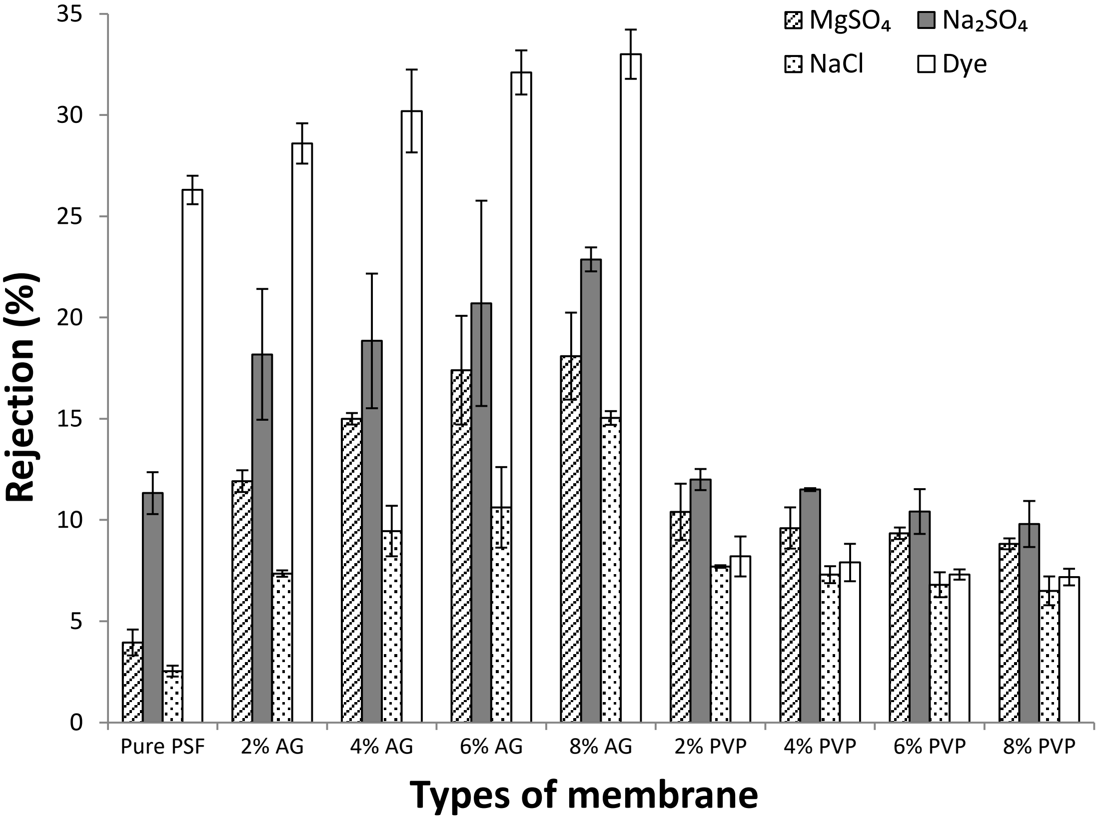


Figure 4.6: Salt and Dye Rejection Capabilities of Pure PSF, PSF/AG and PSF/PVP Composite Membranes

From Figure 4.6, solute rejection capability of PSF/AG membranes was higher than that of pure PSF membrane. The retention capability of PSF/AG composite membranes can be explained by the sieving (steric) retention and the ability of different metal ions to form complexes with amino groups of proteinous fraction of AG (Manawi et al., 2017). PSF/AG composite membranes have a large number of chelating sites for the binding of salt ions. Moreover, proteinous fraction of AG contains different amino acids that have strong affinity and distinctive kinetics towards chelating of metal ions. Amino acids serve as natural ligands and have the ability to form metal/amino acid complexes that reduce the permeation of salt ions through the membrane.

Based on Figure 4.6, the overall solute rejection of PSF/PVP composite membranes was lower than that of pure PSF membrane and PSF/AG composite membranes. The solute rejections of PVP-containing PSF membranes were reducing at higher PVP loadings. The change in morphological structure of the membrane (which includes top-layer and sub-layer) due to the addition of PVP at different loadings, is an important factor that determines the solute rejection. In this study, PVP is used as a pore-forming agent that causes the solutes to easily permeate through the membrane, leading to the reduction in rejection, and this can be explained by size exclusion principle (Mulyati et al., 2018). The presence of PVP in the casting solution has contributed to the enlargement of microvoids in the membrane structure (Aminudin et al., 2013). Larger pores and higher porosity of membranes enhance the solution flux at the expense of lower rejection.

Other than size exclusion, solute rejection can be explained by adsorption principle (K et al., 2015). The dye removal capability of the membranes is ascribed to the electrostatic interaction between the negatively charged membrane surface and positively charged cationic dye (methylene blue in this study) (Maroofi and Mahmoodi, 2019). This can be explained by the absence of electrostatic forces between pure PSF or PSF/PVP composite membranes and methylene blue molecules. The dye removal mechanism in the pure PSF and PSF/PVP composite membranes is based on the trapping of dye molecules in the membrane cavities (Maroofi and Mahmoodi, 2019). The amount of dye removal in pure PSF and PSF/PVP composite membranes decreased because dye molecules were captured in the membrane cavities and the ability of the membranes to remove dye contaminant diminished. In short, PSF/PVP composite membranes have lower solute rejection capability owing to its high porosity, large pore size and poor adsorption ability when compared to PSF/AG composite membranes.

All the fabricated membranes showed higher retention capability towards $MgSO_4$ than NaCl. This phenomenon can be explained by the negatively charged membrane surfaces that contributed to higher rejection towards sulfate ions compared to chloride ions (Yong et al., 2014). Higher retention of magnesium and sulfate ions in comparison to sodium and chloride ions can be due to their ionic radius. Greater transport resistance would be imposed on the ions when the pore size of the fabricated membranes is close to the ionic radius of ions. In addition, sodium and chloride ions have higher diffusion coefficient values than magnesium and sulfate ions, thus, the steric hindrance effect contributed to greater resistance towards bivalent salts (Yong et al., 2014). All the membranes showed higher retention capability towards Na_2SO_4 than NaCl and $MgSO_4$. This can be explained by the Donnan exclusion mechanism where divalent anions are preferred to be rejected over monovalent anions, by pure PSF membrane and modified PSF membranes with negatively charged surfaces (Taylor et al., 2012).

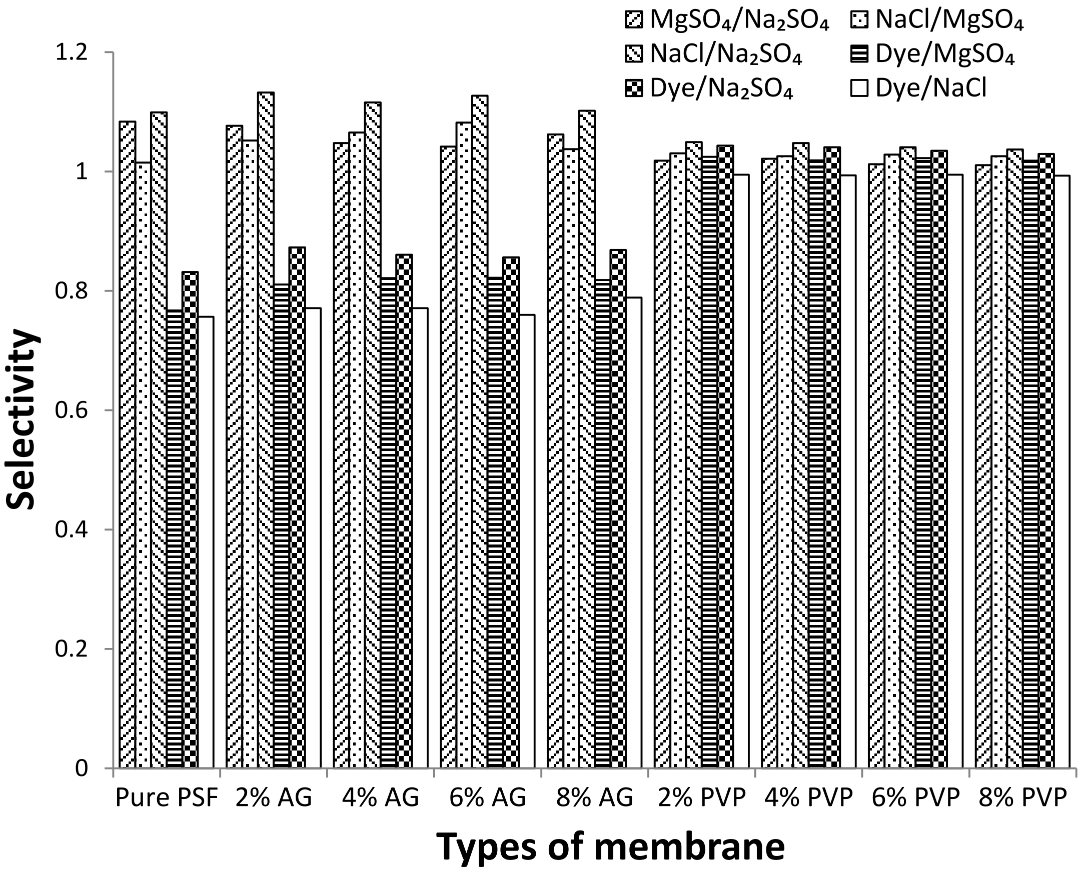


Figure 4.7: Selectivities of Pure PSF, PSF/AG and PSF/PVP Composite Membranes

Figure 4.7 shows the selectivities for pure PSF, PSF/AG and PSF/PVP composite membranes. By comparing all the fabricated membrane samples, the salt selectivity for PSF/AG composite membranes prepared using different loadings of AG, was increasing when two different salt solutions permeated through the membrane surfaces. This phenomenon can be explained by the steric rejection and the ability of different metal ions to form complexes with amino groups of proteinous fraction of AG. PSF/AG composite membranes have chelating sites for the binding of metal ions. Furthermore, proteinous fraction of AG contains different amino acids that have different affinity towards chelating of metal ions. Amino acids act as natural ligands and have the ability to form metal/amino acid complexes that selectively reject the salt ions in the membrane matrices. The selectivity for PSF/AG composite membranes increased with increasing AG loadings because the fabricated PSF/AG composite membranes could have more binding sites for the formation of metal/amino acid complexes.

Pure PSF membrane and PSF/AG composite membranes showed lower selectivities of dye over salts when compared with PSF/PVP composite membranes, owing to the combination of steric and Donnan effects. During the filtration of dye and salt solutions, Donnan effect could be less prominent whereas the electrostatic interactions between the negatively charged membrane surface and positively charged cationic dye could promote the dye rejection. Furthermore, PSF/PVP composite membranes showed higher selectivities of dye over salts when compared with pure PSF membrane and PSF/AG composite membranes. This can be explained by the absence of electrostatic forces between PSF/PVP composite membranes and methylene blue molecules. Instead, the dye removal mechanism in PSF/PVP composite membranes is based on the trapping of dye molecules in the membrane cavities (Maroofi and Mahmoodi, 2019). Since PSF/PVP composite membranes have larger membrane pores and higher porosity, salts can easily permeate through the membrane surfaces while dye molecules can be trapped in the membrane matrices, thus, the selectivities of dye over salts could be increased.

By comparing all the fabricated membrane samples, the selectivity for PSF/PVP composite membranes was decreasing with increasing PVP loadings. PVP is a pore-forming agent which causes the solutes to easily permeate through the membrane, leading to the reduction in rejection, and this can be explained by size exclusion principle (Mulyati et al., 2018). The presence of PVP in the membrane casting solution has contributed to the enlargement of microvoids in the membrane structure (Aminudin et al., 2013). Larger pores and higher porosity of membranes enhance the solution flux at the expense of lower rejection. PSF/PVP composite membranes could possibly perform poorly in water treatment applications.

4.6 Membrane Flux Recovery Study

Concentration polarization and membrane fouling are the most common and major issue that can be correlated with the flux decline. Concentration polarization reduces the driving force of water flow across the membrane due to the increase in foulant concentration on the membrane surface. The fouling of membranes can be classified into reversible fouling and irreversible fouling. Reversible fouling corresponds to the build-up of solutes on the membrane surface, which can be reduced or minimized with the increased stirring rate near the membrane surface. Irreversible fouling, however, corresponds to the deposition or aggregation of solute molecules within the membrane matrices that result in flux decline (Hamzah et al., 2014).

Figure 4.8 shows the flux recovery results based on different membranes. Each membrane sample is found to have relatively consistent flux recovery ratio after the backflushing process. Among the fabricated membrane samples, pure PSF membrane has the lowest flux recovery ratio, which could be explained by its membrane hydrophobicity and porosity. PSF/AG and PSF/PVP composite membranes have displayed better flux recovery ability due to the addition of additives into the membrane casting solution that enhances the performance of membranes. For instance, AG increases the hydrophilicity of PSF membranes while PVP increases the porosity and pore size of PSF membranes.

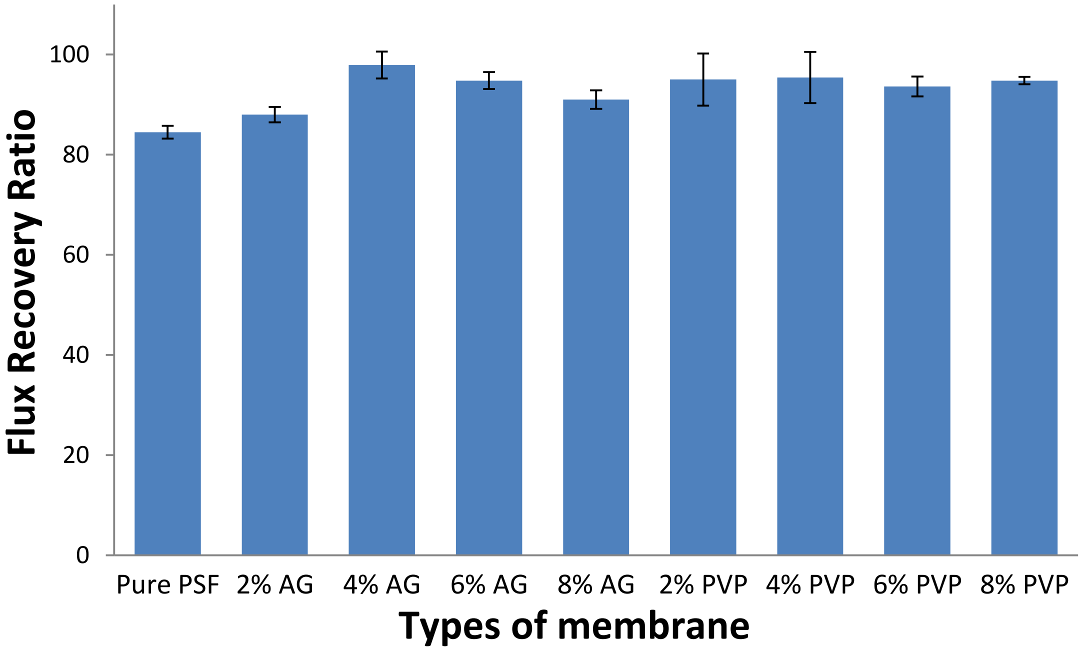


Figure 4.8: Flux Recovery Results Based on Different Membranes

Slight reductions of flux occurred after the membranes were backflushed because reversible fouling blocked membrane pores starting from the initial stage of filtration. After the retention test using salts and dye solution, the membrane pores were likely to be blocked by the particles retained on the membrane surface. The formation and growth of cake layers on the membrane surfaces reduced the pure water fluxes after the permeation of salts and dye solution. The flux recovery ratio was decreased because the membrane fouling increased the hydraulic resistance and reduced the filtration efficiency.

During the permeation of salts and dye solution, solvent passes through the membrane surface while the retained solutes can cause the solute concentration at the membrane surface to increase. This leads to concentration polarization phenomenon that accounts for the gel and solute rich layer formation at the membrane surface. The pure water flux of fouled membranes becomes lower owing to the increase in hydraulic resistance, thus, the flux recovery ratio decreases.

4.7 Summary

In this study, polysulfone (PSF) membranes containing different loadings of acacia gum (AG) and polyvinylpyrrolidone (PVP) were successfully fabricated. Properties of the fabricated membranes such as pure water flux, hydrophilicity, porosity and fouling tendency were evaluated. All these properties were evaluated via the application of scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and contact angle measurements on unmodified and modified PSF membranes.

FTIR was employed for analysing the functional groups found in the membrane samples. Based on the infrared spectra of PVP-containing PSF membrane, new absorption peak at 1659.92 cm^{-1} was more prominent while the rest of the spectrum remained similar (Asmatulu, 2016). Pure PSF and modified PSF membranes have asymmetric structures consisting of dense top layers, porous sublayers and small portion of sponge-like bottom layers (Hamzah et al., 2014). The skin layer serves as a separation layer while the support layer provides mechanical strength. The sub layer has finger-like structures beneath the top surface layer as well as macrovoids structure (Yin, Fan and Zhou, 2016). The formation of finger-like sublayer can be explained by the instantaneous demixing caused by high mutual affinity of solvent and non-solvent. The formation of the membrane top surface was a result of spinodal demixing as the diffusion processes during the formation of the top layers were fast enough for the polymer solutions to become highly unstable and cross the spinodal curve, resulting in top surfaces with much interconnected pores (Chakrabarty, Ghoshal and Purkait, 2008).

The introduction of AG into the casting solutions of PSF was found to be able to increase the PWF of PSF/AG composites membranes. The flux increase can be attributed to the increase in the porosity and hydrophilicity of the modified PSF membranes when AG was added into the casting solution. The PWF of PSF/PVP membranes was increasing with the increment in PVP loadings. PVP serves as a pore forming agent and its presence in the casting solution can assist the formation of more pores on the membrane surface after the casted film is immersed into the coagulation bath (Mulyati et al., 2018).

The addition of AG in the casting solution increased the hydrophilicity of the modified membranes by lowering the contact angle by 15% when compared to pure PSF membrane. The decrease in the contact angle of PSF/AG composite membranes can be explained by the hydrophilization of membrane surfaces and pores by AG macromolecules (Manawi et al., 2017). The contact angle of PSF/PVP membranes dropped from 68 ° at 2 wt% PVP to 44 ° at 8 wt% PVP. The contact angle of PSF/PVP membranes decreased with increasing PVP concentrations, indicating increasing hydrophilicity of the fabricated PSF/PVP membranes (Yuan et al., 2014).

The solute rejection of PSF/AG composite membranes was higher than that of pure PSF membrane. The retention capability of PSF/AG membranes can be explained by the sieving (steric) rejection and the ability of different metal ions to form complexes with amino groups of proteinous fraction of AG (Manawi et al., 2017). The overall solute rejection of PSF/PVP membranes was lower than that of pure PSF and PSF/AG membranes. The salt selectivity for PSF/AG composite membranes prepared using different loadings of AG was increasing when two different salt solutions permeated through the membrane surfaces. This phenomenon can be caused by the proteinous fraction of AG containing different amino acids that have different affinity towards chelating of metal ions. The selectivity for PSF/PVP composite membranes was decreasing with increasing PVP loadings. All the fabricated membranes showed higher retention capability towards $MgSO_4$ than NaCl. This phenomenon can be explained by the negatively charged membrane surfaces that contributed to higher rejection towards sulfate ions compared to chloride ions

(Yong et al., 2014). All the membranes showed higher retention capability towards $NaSO_4$ than NaCl and $MgSO_4$. This can be explained by the Donnan exclusion mechanism where divalent anions are preferred to be rejected over monovalent anions, by pure PSF membrane and modified PSF membranes with negatively charged surfaces (Taylor et al., 2012). Pure PSF membrane and PSF/AG composite membranes showed lower selectivities of dye over salts when compared with PSF/PVP composite membranes, owing to the combination of steric and Donnan effects. Meanwhile, PSF/PVP composite membranes showed higher selectivities of dye over salts when compared with pure PSF membrane and PSF/AG composite membranes. This can be explained by the absence of electrostatic forces between PSF/PVP composite membranes and methylene blue molecules. Instead, the dye removal mechanism in PSF/PVP composite membranes is based on the trapping of dye molecules in the membrane cavities (Maroofi and Mahmoodi, 2019).

All fabricated membranes were found to have relatively consistent flux recovery ratio after the backflushing process. PSF/AG and PSF/PVP composite membranes had better flux recovery ability due to the presence of additives in the membrane casting solution, which enhanced the performance of membranes.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, polysulfone (PSF) membranes containing different loadings (2, 4, 6 and 8 wt%) of acacia gum (AG) and polyvinylpyrrolidone (PVP) have been successfully fabricated. The effects of the abovementioned copolymers have been studied and evaluated. Since different compositions of copolymers added into the membrane casting solution can contribute to different outcomes on the properties of fabricated PSF membranes, the most suitable composition of copolymers has been identified in order to enhance the performance of membrane filtration.

To date, application of AG in the preparation of PSF membranes has not been reported in literature whereas the application of PVP in the preparation of PSF membrane is relatively common. PVP mainly serves as a pore-forming agent that increases both the porosity and pore size of membranes. Based on the experimental results, the presence of PVP in the membrane casting solution increased the pure water flux (PWF) at the expense of lower solute retention of the PSF/PVP composite membranes. Hence, PVP is found to be less suitable to be used as an additive in the preparation of membranes for water treatment purpose if high solute retention is greatly desired in the application. For this reason, AG emerges as an alternative choice of additives to be added into the membrane casting solution.

Lately, AG has received significant attention due to its amphiphilic nature. As widely reported, one of the main issues that limit the application of membranes in water treatment, is the high hydrophobicity of membrane surface. In order for membrane to achieve excellent performance in water treatment application, its hydrophobic nature has to be altered. For the first time AG is used as an additive to prepare the casting solution of PSF membranes and this has brought unexpected outcomes in this research. PVP is hydrophilic whereas AG is amphiphilic in nature, meaning that AG can be either hydrophilic or hydrophobic. When 2 and 4 wt% of AG were used, the PWF of PSF/AG composite membranes were increased. However, when 6 and 8 wt% of AG were used, the PWF of PSF/AG composite membranes were decreased. When PVP was added into the membrane casting solution, the PWF of PSF/PVP composite membranes increased. Increase in the PWF of PSF/AG composite membranes can be explained by the distribution of AG macromolecules that hydrophilize the membrane surfaces and pores. In opposite, the decrease in the PWF of PSF/AG composite membranes can be explained by high viscosity of the membrane casting solution which can be caused by the addition of AG at higher loadings (6 wt% and 8 wt%). High viscosity caused by high concentration of AG in the membrane casting solution leads to low porosity of the resulted membranes that reduces the PWF of PSF/AG membranes.

The effect of AG is prominent in terms of solute rejection. The solute rejection of PSF/PVP composite membranes was lower than pure PSF and PSF/AG composite membranes. This is because PVP is a pore-forming agent that increases the porosity and pore size of the fabricated membranes, thus, leading to low solute rejection. However, the overall solute rejection of PSF/AG composite membranes was higher than pure PSF and PSF/PVP composite membranes. The retention capability of PSF/AG composite membranes can be explained by the sieving (steric) rejection and complexation of metal ions with amino groups of proteinous fraction of AG. PSF/AG composite membranes have a large number of chelating sites for the binding of metal ions. Moreover, proteinous fraction of AG contains different amino acids, which have strong affinity towards chelating of metallic ions.

In terms of PWF and solute rejection capability, AG is a better candidate to be used in the modification of PSF membranes for water treatment purpose. In this study, the most suitable composition of copolymer was determined to be 4 wt% of AG as it has considerable potential to enhance the performance of membranes with high PWF and excellent solute rejection capability. In short, AG can be considered as a novel hydrophilizing agent as well as an enhancer to the rejection properties of membranes. This research contributes greatly to membrane material study and water treatment industry.

5.2 Recommendation for Future Work

In this study, copolymers such as AG and PVP at different loadings have been added into the membrane dope solution in order to evaluate the resulted effects on the properties of PSF membranes. The most suitable composition of copolymers that can produce membranes with better performance has been determined as well.

Generally speaking, both copolymers can bring positive effects on the properties of the resulted membranes. It is recommended that the abovementioned copolymers can be applied in the fabrication of other polymeric membranes such as cellulose acetate (CA) and polypropylene (PP) membranes. It is believed that copolymers have the potential to contribute to unexpected outcomes when being employed in the fabrication of other kinds of polymeric membranes, since this research serves as a reference for future approach regarding the fabrication as well as the application of membranes in water treatment industry.

Membranes containing copolymers are found to be capable of removing heavy metals as well as dyes from wastewater. In fact, it is a good practice to scale up the fabricated membranes in the form of either flat sheet or hollow fibre membranes, on a view to treating contaminated water and yield substantial amount of clean water for potable use.

As a matter of fact, the efficiency of using membranes in water and wastewater treatment is higher than traditional water treatment system. Traditional water treatment plants require lots of spaces for primary, secondary and tertiary treatment of water, whereas water treatment via membrane technology saves spaces. One of the drawbacks of application of membranes in water treatment is the cost, since this approach is not common in our country. It is believed that the cost of membrane fabrication and setup can be relatively lower once this initiative has been commercialized.

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APPENDICES

APPENDIX A: Raw Data

Table A-1: Pure Water Flux (PWF) of Different Membranes at 5 Bar

Membrane	**Pure Water Flux (PWF), LMH**		
	1	**2**	**Average**
Pure PSF	1.87	2.83	2.35
PSF/AG (2 wt%)	3.64	2.42	3.03
PSF/AG (4 wt%)	6.55	8.69	7.62
PSF/AG (6 wt%)	5.80	8.22	7.01
PSF/AG (8 wt%)	5.36	8.10	6.73
PSF/PVP (2 wt%)	28.00	39.00	33.50
PSF/PVP (4 wt%)	78.50	87.92	83.21
PSF/PVP (6 wt%)	210.30	255.76	233.03
PSF/PVP (8 wt%)	248.60	280.10	264.35

Table A-2: Salt and Dye Rejection Capabilities of Different Membranes

Membrane	**Rejection, %**											
	$MgSO_4$ (1)	**$MgSO_4$ (2)**	**$MgSO_4$ (Avg)**	**Na_2SO_4 (1)**	**Na_2SO_4 (2)**	**Na_2SO_4 (Avg)**	**NaCl (1)**	**NaCl (2)**	**NaCl (Avg)**	**Dye (1)**	**Dye (2)**	**Dye (Avg)**
Pure PSF	3.5	4.4	3.95	10.6	12.06	11.33	2.35	2.73	2.54	25.8	26.8	26.3
PSF/AG (2 wt%)	12.3	11.54	11.92	15.9	20.46	18.18	7.46	7.24	7.35	27.9	29.3	28.6
PSF/AG (4 wt%)	14.8	15.2	15	16.5	21.2	18.85	8.57	10.33	9.45	28.75	31.65	30.2
PSF/AG (6 wt%)	15.5	19.3	17.4	17.11	24.29	20.7	12.03	9.21	10.62	31.33	32.87	32.1
PSF/AG (8 wt%)	16.58	19.62	18.1	22.45	23.29	22.87	14.8	15.28	15.04	32.14	33.86	33
PSF/PVP (2 wt%)	9.42	11.38	10.4	11.63	12.37	12	7.74	7.66	7.7	7.5	8.9	8.2
PSF/PVP (4 wt%)	8.88	10.32	9.6	11.45	11.55	11.5	7	7.6	7.3	7.25	8.55	7.9
PSF/PVP (6 wt%)	9.14	9.54	9.34	11.2	9.64	10.42	6.36	7.24	6.8	7.13	7.49	7.31
PSF/PVP (8 wt%)	9.02	8.64	8.83	9	10.6	9.8	6	7	6.5	6.89	7.47	7.18