

**PES/TiO₂ MIXED MATRIX HOLLOW FIBER
MEMBRANE WITH ANTI-FOULING PROPERTIES
FOR HUMIC ACID REMOVAL**

PANG WEN YU

UNIVERSITI SAINS MALAYSIA

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**PES/TiO₂ MIXED MATRIX HOLLOW FIBER MEMBRANE WITH ANTI-
FOULING PROPERTIES FOR HUMIC ACID REMOVAL**

by

PANG WEN YU

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LIST OF ABBREVIATIONS

| | |
|-------|---|
| AAC | Acrylic acid |
| AFM | Atomic force microscopy |
| AG | Air gap |
| BSA | Bovine serum albumin |
| BFG | Bovine serum fibrinogen |
| CA | Contact angle |
| CAP | Cellulose acetate phthalate |
| CS | Crosshead speed |
| DG | Degree of sulfonation |
| DI | Deionized |
| DMAc | N-N-dimethylacetamide |
| EDX | Energy dispersive X-ray |
| EtOH | Ethanol |
| FA | Fulvic acid |
| FESEM | Field Emission Scanning Electron Microscopy |
| FRR | Flux recovery ratio |
| FS | Flat sheet |
| GO | Graphene oxide |
| HA | Humic acid |
| HCl | Hydrochloric acid |
| HF | Hollow fiber |
| HS | Humic substances |
| MBR | Membrane bioreactor |

| | |
|------------------|---|
| MM | Mixed matrix |
| MWCO | Molecular weight cut off |
| NaOH | Sodium hydroxide |
| NIPS | Non solvent induce phase separation |
| NOM | Natural organic matter |
| NPs | Nanoparticles |
| PAN | Polyacrylonitrile |
| PD | Polydopamine |
| PEG | Polyethylene glycol |
| PEO | Poly(ethylene oxide) |
| PES | Polyethersulfone |
| PP | Polypropylene |
| PSf | Polysulfone |
| PTFE | Polytetrafluoroethylene |
| PVA | Polyvinyl alcohol |
| PVDF | Polyvinylidene fluoride |
| PVP | Polyvinylpyrrolidone |
| PVP-b-PMMA-b-PVP | Poly(vinyl pyrrolidone)-b-poly(methyl methacrylate)-b-poly(vinyl pyrrolidone) |
| PWF | Pure water flux |
| RAFT | Reversible addition-fragmentation chain transfer |
| RFR | Recovery flux ratio |
| SEM | Scanning electron microscopy |
| SPES | Sulfonated polyethersulfone |
| TGA | Thermogravimetric analysis |

| | |
|------------------|--------------------------------|
| TiO ₂ | Titanium oxide |
| UF | Ultrafiltration |
| VIPS | Vapor induced phase separation |
| VP | Vinyl pyrrolidone |
| WHO | World Health Organization |
| ZnO | Zinc oxide |

LIST OF SYMBOLS

| | | |
|------------|--|-------------|
| A | Area | m^2 |
| AG | Air gap | cm |
| D | Outer diameter of hollow fiber | cm |
| d | Inner diameter of hollow fiber | cm |
| HAF | Humic acid flux | $kg/m^2.h$ |
| HAR | Humic acid rejection | % |
| J_{HA} | Humic acid permeate flux | $kg/m^2.h$ |
| J_{WF} | Initial permeate water flux | $kg/m^2.h$ |
| J_{WF} | Permeate water flux after washing with distilled water | $kg/m^2.h$ |
| ΔP | Operating pressure | $kg/m^2.h$ |
| Q | Pure water flux | bar |
| R_f | Fouling resistance | m^3/s |
| R_{ir} | Irreversible fouling resistance | m^{-1} |
| R_m | Membrane resistance | m^{-1} |
| r_m | Mean pore size | nm |
| R_r | Reversible fouling resistance | m^{-1} |
| R_t | Total filtration resistance | m^{-1} |
| t | Time | h |
| T_d | Decomposition temperature | $^{\circ}C$ |
| T_g | Glass transition temperature | $^{\circ}C$ |
| TMP | Transmembrane pressure | Pa |
| V | Permeate volume | L |

Greek letters

| | | |
|---------------|--------------------|------|
| ε | Membrane porosity | - |
| η | Water viscosity | Pa.s |
| μ | Permeate viscosity | Pa.s |

Subscript

| | |
|----|------------------|
| d | Dry |
| g | Glass transition |
| ir | Irreversible |
| m | Mean |
| r | Reversible |
| w | Wet |

PES-TiO₂ MEMBRANE MATRIK BERCAMPUR DENGAN SIFAT NYAHKOTORAN UNTUK PENYINGKIRAN ASID HUMIK

ABSTRAK

Kajian terkini memunjukkan pengotoran membran tidak dapat dipulih telah menghadkan aplikasi membran PES dalam proses rawatan air untuk menyahkan asid humik. Banyak kajian telah dijalankan sebelum ini dan rata-rata telah membuktikan bahawa pengotoran membran boleh ditangani dengan meningkatkan hidrofilik membran PES. Antara cara peningkatan hidrofilik membrane yang paling dikajikan oleh pengaji adalah pencampuran zarah nano titanium dioksida (TiO₂) yang murah dan mudah diperolehi. Walau bagaimanapun, kebanyakan kajian yang dibuat berfokus pada membran kepingan rata dan menggunakan membran jenis ini adalah terhad dalam industri. Oleh itu, kajian ini dibuat bertujuan untuk menyediakan membran PES jenis serat berongga dengan menggunakan bilangan TiO₂ yang berlainan. Pencampuran zarah nano TiO₂ dalam membran PES telah membuktikan bahawa hidrofilik membran dapat ditingkatkan selain meningkatkan stabiliti membran serat berongga terhadap haba atas sebab penyebaran zarah nano TiO₂ yang rata pada seluruh membran. Apabila prestasi membran diuji dengan larutan asid humik 50 mg/L pada pH 7.7, fluks yang tinggi diperolehi apabila bilangan TiO₂ dalam membran rendah manakala penolakan asid humik tinggi apabila bilangan TiO₂ tinggi. Selain itu, nisbah pemulihan fluks yang tinggi dan nisbah pengurangan fluks yang rendah diperolehi dalam membran yang banyak mengandungi TiO₂. Di samping itu, tujuan kajian ini adalah untuk mengkajikan sifat nyahkotoran membran. Berdasarkan rintangan tidak dapat dipulih dan rintangan kotoran membrane, rintangan dalam S3 adalah paling rendah dan ini menunjukkan S3 dapat nyahkotoran dengan baik. Fluks asid humik S3 adalah

23.851 kg/m².j di bawah tekanan transmembran setinggi 1 bar dengan penolakan asid humik setinggi 97.89%. S3 adalah membran optimum berdasarkan fluks dan penolakan asid humik yang dapat diterima dan sifat penyahkotorannya yang sangat baik.

PES-TiO₂ MIXED MATRIX HOLLOW FIBER MEMBRANE WITH ANTI-FOULING PROPERTIES FOR HUMIC ACID REMOVAL

ABSTRACT

Recently, studies showed that the irreversible fouling of membrane limited the application of PES membrane in the application of water treatment for removal of humic acid. Large amount of study being performed previously and it been well proven that the fouling of membrane can be mitigated by improving the hydrophilicity of the PES membrane. One of the most studied method to improve PES membrane hydrophilicity is through blending of TiO₂ nanoparticle which is a low cost and widely available nanoparticles. However, most of the research regarding PES/TiO₂ mixed matrix membrane is being done in flat sheet configuration. Compared to hollow fiber, flat sheet has much limited real application. Looking at this situation, this study has fabricated PES hollow fiber membrane using different TiO₂ loading. The blending of TiO₂ nanoparticle into the PES membrane is proven to improve the hydrophilicity of the membrane as well as improve the thermal stability of the hollow fiber (HF) membrane due to the well dispersion of TiO₂ through the membrane. When the membrane performance is being tested using 50 mg/L of humic acid (HA) solution at pH 7.7, high flux is obtained at lower TiO₂ loading but higher HA rejection is obtained at high TiO₂ loading. Moreover, at highest TiO₂ loading the flux recovery ratio (FRR) can increase up to 99.027 % and the recovery flux ratio (RFR) can reduce to as low as 4.175 %. This indicate that membrane with high TiO₂ loading has greater performance. Nevertheless, the intention of this study is to evaluate the anti-fouling properties of the membrane. Based on irreversible resistance and fouling resistance found on the membrane, the resistance on S3 is the lowest showing that it's most anti-fouling. The S3 membrane has HA permeate flux of 23.851 kg/m².h under transmembrane pressure

of 1 bar with HA rejection up to 97.89 %. S3 is optimum justified based on its acceptable trade-off between permeate flux and HA rejection despite its excellent fouling resistance properties.

CHAPTER ONE : INTRODUCTION

1.1. Research Background

The presence of humic acid (HA) in soil is essential for the growth of plants. However, HA can be a threat to life if it is found in water streams. HA will form dangerous metal complexes as well as carcinogenic substances in wastewater treatment processes especially during the chlorination process. Urged by the reduction in water source, recovery of water through wastewater treatment will be an important alternative. In this process, removal of HA from wastewater has become a big challenge. According to World Health Organisation (WHO), the permissible HA concentration in potable water will be about 100 ppb.

Since the removal of HA from wastewater is important, various methods have been investigated which included coagulation (Sudoh, et al., 2015), electrocoagulation (Feng, et al., 2007), electromagnetic treatment (Ghernaot, et al., 2009), flotation (Brum & Oliveira, 2007; Zouboulis, et al., 2003) and oxidation process (Wu, et al., 2011). However, these methods are prone to electrode fouling, high operating cost, maintaining cost and energy requirement (Teow, et al., 2016). Looking at this situation, a relatively simple, advanced and cost-effective membrane method has appeared as a better approach for HA removal. However, the major concern regarding membrane separation methods will be the fouling sensitivity of the membrane. Therefore, extensive researches have been done to improve the fouling resistance of membranes toward HA to make the separation of HA from water feasible in the future.

1.2. Problem Statement

To improve the fouling resistance properties of the membrane, researchers has used different modification method to improve the properties of membrane. Membrane modification method can be classified into three categories, those are, bulk modification, surface modification and blending. Depending on the original properties of the polymeric material used to cast the membrane, one or two of the method can be used to maximize the fouling resistance of the membrane without compromising its own polymer benefit.

PES remain as one of the most important polymeric material in fabrication of membrane. This may due to their excellent thermal and mechanical stability and less likely to swell in water unlike some hydrophilic polymer. However, such stability come with a price in that is PES membrane will prone to fouling due to adsorption of HA. The hydrophobicity has been identified as major cause of fouling in HA separation. HA adsorption can cause irreversible fouling on the PES membrane. Irreversible fouling not only will plug the membrane pore and reduce the overall filtration efficiency of the membrane besides extra energy will be needed for the same filtration process if the membrane is being reused. Irreversible fouling is, hence, said to reduce the membrane lifespan and reusability. Looking at high price of flesh membrane, the reusability of the membrane become an important factor for real membrane application to reduce the plant operation cost by reduce the frequency of membrane replacement. To mitigate the problem, extensive research been done to reduce the fouling tendency of the polymeric membrane and one of the alternative is blending of polymeric membrane with various nanoparticles to produce mixed matrix (MM) membrane.

Moreover, most of the PES membrane modification research being done only focussed on flat sheet (FS). FS has much limited usage in large scale industry and mostly practicable under lab scale. Under real application, hollow fiber (HF) membrane is said to be more effective and economic compared to FS. This is because HF has high surface area to volume ratio, hence, the size of the equipment needed will be much smaller. Besides, HF is configured with cross flow unlike some FS which involve dead end filtration. Compared to dead end filtration, cross flow has mechanism to reduce reversible fouling of the membrane. As far as author aware, there is no published work dedicated to study the performance and anti-fouling ability of PES/TiO₂ mixed matrix membrane hollow fiber membrane. Therefore, in this work, TiO₂ been chosen to reduce the hydrophobicity of the PES membrane and, hence, enhance the anti-fouling behaviour of PES membrane. To enable the finding to be applicable in industry scale, the membrane will be fabricated as HF.

1.3. Research Objectives

The objectives of this research are: -

- i. To synthesize and characterize the mixed matrix hollow fiber (MM HF) membrane at different concentration of TiO₂.
- ii. To investigate the efficiency of HA removal using MMHF membrane with different concentration of TiO₂ nanoparticle through membrane flux and HA rejection.
- iii. To examine the fouling resistance behaviour of PES/TiO₂ MM HF membrane.

1.4. Scope of Study

In this present work, the MM HF membrane was produced by using dry-jet wet phase inversion method. Polyvinylpyrrolidone (PVP) was added in all formulation to minimize agglomerations in the membrane structure and enhance the dispersion of TiO₂-NP. Different dope solution was prepared by blending 18 wt% PES, 4 wt% PVP and various amount of TiO₂ (ranging from 0 to 4 wt%). The rest of the weight percent is made up of DMAc solvent.

The casted HF membrane was characterized in term of surface morphology, surface roughness, hydrophilicity, surface charge, pore size and surface functional group using SEM, AFM, CA, BET, zeta potential machine and FTIR spectroscopy. The characterized MM HF membrane was first test using compression at 1.5 bar. Then, pure water flux (PWF) and humic acid rejection (HAR) of the MM HF membranes were performed at 1 bar. Then, the membrane was flushed before the PWF been tested again at 1 bar. The data been analysed and used to calculate the FRR for fouling resistance evaluation.

CHAPTER TWO : LITERATURE REVIEW

2.1. Humic Substances

Traditionally humic substances (HS) is part of humus which can be divided into three fraction based on their solubility in water as a function of pH and these group included humins, fluvic acid (FA) and humic acid (HA). Humins are alkali insoluble fraction of humus while HA is dark coloured organic matter extracted from soil using various reagents. Meanwhile, FA is coloured organic matter which remain in the solution after the removal of HA via acidification (Stevenson, 1994). The formation HS can be related to the geochemical carbon cycle. One of the major processes of that cycle will be oxidative weathering of sedimentary organic matter in Earth's surficial environment. In this oxidative process where oxidation of coal occurs, HS can be produced as besides carbon dioxide (CO₂) (Chang & Berner, 1998).

Over the century, various HS application in agriculture, industry, environment and biomedicine field been summarized by Pena-Mendez et. al. (2005). For instance, in last decant the attention of utilizing humus extract as cosmetic and pharmaceutical product been increased due to the antiviral and anti-inflammatory properties of HA (Yamada, et al., 1998). In term of plant growth, HS play an important stimulatory effect that enhance the root growth of the plant (Mayhew, 2004). HS is non-toxic in their original form. However, their present in drinking water purification process possesses a major problem (Joo & Foldenyi, 2009). This is because HS found in water are normally in aromatic form. It been proven that the formation of harmful carcinogenic disinfection by products such as trihalomethanes and haloacetic acids during chlorination of drinking water is related to aromatic compound in water (Singer,

1999). Hence, it can be said that the present of HS in portable water can be harmful to human health.

2.1.1. Humic Acid (HA)

HA is one of the major components of HS which composed of soil (humus), peat, upland streams, dystrophic lakes and ocean water (Stevenson, 1994). It been produced by the biodegradation of organic matter in the nature carbon cycle. Instead of simple single acid, HA comprise of mixture of weak aliphatic and aromatic organic acid which is insoluble in water under acidic condition but soluble in alkaline conditions (Pettit, 2004). Hence, the major component of HA will be oxygen (O) and carbon (C) which range between 33-38% and 54-59% respectively. This C and O was mostly comprised of the acidic functional group which included the carboxylic group (COOH), phenolic or alcoholic group (OH) and carbonyl group (C=O) (Reddy & DeLune, 2008). It's been proven that the solubility of HA in water is affected by both pH and ionic strength of the water. HA solubility increase as the pH of water increase (e.g. alkaline condition). However, increasing ionic strength will in turn reduce the solubility of HA (Kipton, et al., 1992). The structure of HA is rather complex and some said to be unknown. However, Stevenson (1994) suggested the most widely accepted HA structure which shown in Figure 2.1. The HA structure suggested consists of variety of functional group such as carbonyl or quinone group, phenol, catechol and sugar moieties with a motif of aromatic nuclei.

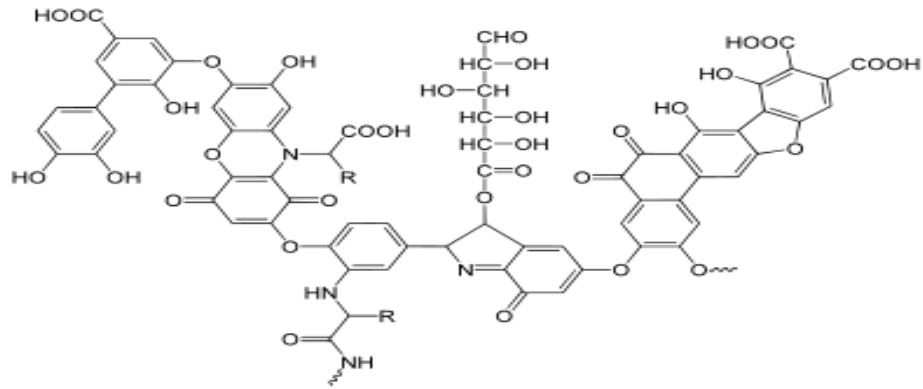


Figure 2.1: Typical humic acid (HA) structure (*Stevenson, 1994*)

2.2. PES Membrane Properties

With increasing population and rapid development of industry, water pollution has become the main concern of current society. Looking at this situation, membrane technology was found to be useful in handling and treating this polluted water which provides many advantages compared to conventional method (Zularisam, et al., 2006). Membrane can be considered as versatile water treatment method that can be used for various water sources such as brackish water, well water, surface water and seawater. Development of membrane also make it possible to recover drinking water from unexpected sources (Nicolaisen, 2002). In United State, membrane technology played various role in drinking water treatment process which include desalting, disinfection by-product control, disinfection, clarification and removal of synthetic and inorganic chemical (Jacangelo, et al., 1997).

Depending on the pore size of the membrane, the process involved can be considered as microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Nicolaisen, 2002). Different material can be used to produce membrane with different pore size and application. The polymeric material used to produce membrane include

cellulose acetate (CA), polysulfone (PSf), polyethersulfone (PES), sulfonated PSf or PES, polyacrylonitrile (PAN), polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) (Pendergast & Hoek, 2011).

Out of the listed polymeric material, PES is one of the most important membrane fabrication. This may due to their outstanding oxidative, thermal, hydrolytic stability and good mechanical property (Zhao, et al., 2013a). These properties are granted due to the present of aromatic compound which able to reduce the chain mobility (Bowen, et al., 2001; Mockel, et al., 1999). The structure of PES is shown in Figure 2.2. Due to this high stability, PES has a relatively high glass transition temperature (230°C). Despite all this advantages, the major disadvantage of the PES membrane may due to its high hydrophobicity (Burggen, 2009). Its high hydrophobicity make it prone to fouling due to adsorption of organic solute on the membrane material especially (Bruggen, et al., 2002; Zularisam, et al., 2006).

Looking at this situation, lot of researches been carried out to increase the hydrophilicity of PES membrane in order to improve the fouling resistance of PES membrane (Wang, et al., 2009; Gohari, et al., 2014; Zinadini, et al., 2017; Gzara, et al., 2016; Mahlangu, et al., 2017). When the membrane surface become more hydrophilic, it will adsorb water molecule and form a layer between the membrane surface and the organic molecules (i.e. HA). Moreover, foulants such as HA is hydrophobic in nature. Hence, a more hydrophilic surface will repel these hydrophobic foulant and will not has tendency to adsorb them (Mehrparvar, et al., 2014).

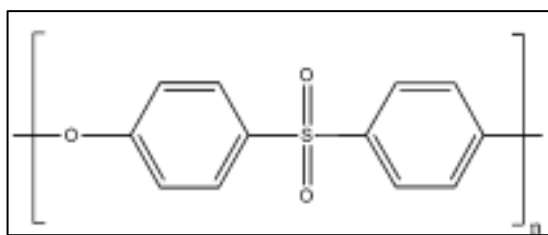


Figure 2.2: Structure of PES monomer (*Burggen, 2009*)

2.3. Limitations of Ultrafiltration Membranes in Humic Acid Removal

Ultrafiltration (UF) is a pressure driven process in which certain component is selectively forced through the membrane. The membrane can be configured to operate as dead end filtration or cross flow filtration. Dead end filtration normally applied in lab scale for membrane testing and cross flow filtration is widely used in real application. Moreover, more supplier is available for membrane fabricated in HF configuration compared to FS (Zhao, et al., 2013a). In dead end filtration, the feed will flow perpendicular to the membrane whereas for cross flow filtration, the feed will flow parallelly with the membrane. Due to the parallel flow in cross flow filtration, it has a swept mechanism which help to reduce the deposition of foulant on the membrane. Hence, cross flow filtration is said to less sensitive to concentration polarization. Membrane module can be configured as FS, tubular, spiral wound and HF (HF) which able to operate in cross flow mode. Due to higher surface area to volume ratio, HF been an attractive module for industry due to its ability to produce a compact and space saving membrane module.

With the increasing demand on quality life, ultrafiltration has drawn large attention in drinking water industry for its better ability to remove particles, turbidity, microorganisms and natural organic matter (NOM) compared to conventional

filtration and clarification (Katsaufidou, et al., 2005). Since the presence of HA in drinking water is life threatening, lot effort been done to remove HA via membrane filtration. However, HA is hydrophobic in nature and this will cause membrane fouling to occur more often on hydrophobic membrane. The fouling occurs due to the adsorption of HA onto the hydrophobic membrane surface as recorded by several researchers (Jones & O'Melia, 2000; Yuan & Zydney, 1999; Hong & Elimelech, 1997). This kind of HA hydrophobic adsorption been investigated by Mozia et. al. (2005) using 3 different polymeric membrane material (i.e. PSf, PAN and CA). Out of the 3 investigated materials, PSf and CA are very susceptible to fouling when tested using water containing phenol and HA. The fouling is reported due to the adsorption of HA. Meanwhile, HA is less susceptible to HA fouling due to its hydrophilic surface properties. However, there will be drawback on directly using hydrophilic membrane material for HA separation. This is because hydrophilic membrane has high tendency to swell in water and loss its mechanical strength. Hence, modification on hydrophobic membrane material to find a compromise between the material hydrophobicity and hydrophilicity is considered as the best method to increase the membrane flux and reduce the fouling occurrence (Zhao, et al., 2013a).

2.4. Flux/ Hydrophobicity Enhancement Methods of PES Membrane

To enhance PES membrane hydrophobicity, several methods can be used to modify the membrane. These methods included bulk modification, surface modification and blending (Zhao, et al., 2013a). In the following section, several PES membrane modification methods via bulk modification and surface modification will

be discussed followed by a subsection that will further discuss on blending modification method.

One of the PES membrane bulk modification method will be sulfonation reaction. Sulfonation is an electrophilic reaction in which part of the aromatic ring, normally the hydrogen ion, being replaced with hydroxysulfonyl radical or sulfonic acid group (-SO₃H). However, this process is difficult due to electron withdrawing effect of the sulfone linkage which eventually deactivate the adjacent aromatic rings for electrophilic substitution (Bikson, et al., 1985). Hence, the reaction condition is said to play an important role in the sulfonation process.

Lu et. al. (2005) has investigated the sulfonation of PES using chlorosulfonic acid as sulfonating agent with sulfuric acid as the solvent. Various reaction condition that may affect the sulfonation process has been studied. High degree of sulfonation is obtained when the reaction temperature remained at 10°C with 10 h of reaction time. The hydrophilicity of highly sulfonated PES (SPES) membrane is said to be more hydrophilic that its even can dissolve in water. Similar method of sulfonation is also being carried out by Guan et. al. (2005) to prepare SPES membrane. It been reported that membrane with high degree of sulfonation has reduced tensile strength. Nevertheless, similar observation as Lu et. al. (2005) is being reported that is SPES membrane has reduced contact angle with water compared to unsulfonated PES membrane. This mean that SPES is more hydrophilic compared to unsulfonated PES.

Another facile modification method is being investigated by Zhao et. al. (2013b) in which sulfonation of PES occur via post-functional method. This method is claim to be more controllable beside able to avoid unnecessary side reaction and polymer degradation. In this method, amino substituted PES will be produced via

condensation polymerization method. Then, the amino substituted PES will be sulfonated using SO₃-pyridine at 40°C and 2 h. When the prepared SPES is blended with PES membrane, the hydrophilicity of PES membrane is reported to be increased.

Apart from sulfonation, bulk modification also can be done via grafting the PES membrane with carboxylic group. However, as reported by Zhao et. al. (2013a), grafting carboxylic group into PES membrane is more difficult compared to PSf membrane. Deng et. al. (2008) have investigate the preparation of PES membrane grafted with acrylic acid (AAC) via simultaneous irradiation. In their research, the grafted PES powder, named PES-g-PAAc powder is being used to produce microfiltration (MF) membrane. When characterized under contact angle using water, it been found out that MF membrane casted from PES-g-PAAC powder is more hydrophilic compared to pristine PES membrane. The contact angle is reported to be decrease with increasing degree of grafting (DG) due to the present of hydrophilic carboxylic group in PAAc grafts. Nevertheless, when the DG is investigated against pH value, maximum DG can only be obtained at low pH of 1.2.

Besides bulk modification, recently, surface modification of PES membrane has attracted lot attention from biomedical field too. One of the method of surface modification will be protein grafting onto PES membrane. Liu et. al. (2009) have modified PES by blending it with co-polymer of AAc and *N*-vinyl pyrrolidone (VP) followed by the immobilization of bovine serum albumin (BSA) onto the surface. When PES is blended with the co-polymer, the contact angle reduced due to increased hydrophilicity. After the immobilization of BSA, the hydrophilicity is reported to be increased significantly. Thus, it been proven that immobilization of BSA protein will further enhance the blended PES membrane.

Wang et. al. (2012), meanwhile, combine both grafting and surface modification to maximize the hydrophilicity of PES membrane. In their research, they prepare carboxylic PES membrane by a controlled acetylating and surface-oxidating reaction. Then, the carboxylic PES membrane is grafted with both BSA and bovine serum fibrinogen (BSF) onto the surface. The process is clearly summarized in Figure 2.3. The hydrophilicity of the modified membrane been characterized with the water flux of PES membrane. Compared to unmodified PES membrane, carboxylic PES membrane has increased water flux due to higher hydrophilicity while the grafted BSA and BSF can further increase the water flux significantly due to further enhancement of the membrane hydrophilicity.

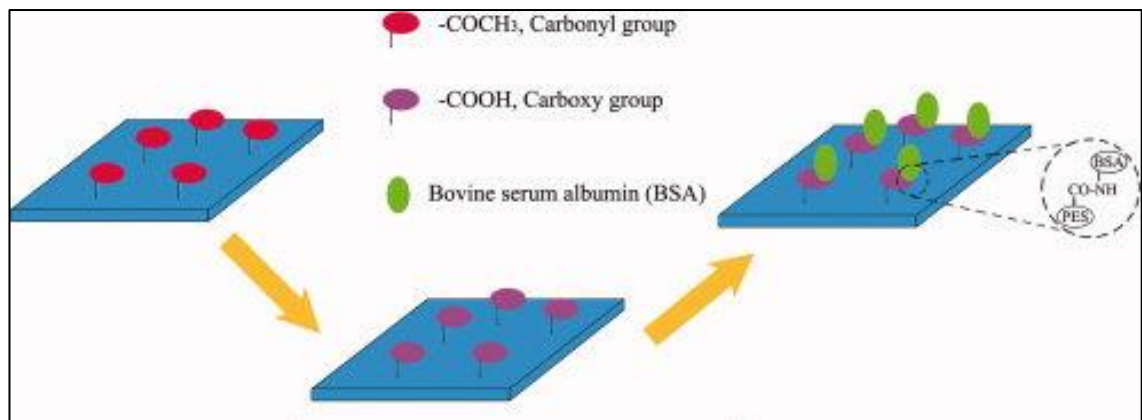


Figure 2.3: Grafting of BSA onto carboxylic PES membrane (Wang, et al., 2012)

Surface modification of PES can also be done through coating of hydrophilic material onto the surface of the PES membrane. Li et. al. (2014a) modified the PES membrane surface by polydopamine (PD) coating and PD-graft-poly(ethylene glycol) (PD-g-PEG). The modified membrane is tested on its antifouling ability toward BSA. When the membrane is being tested using adsorption isotherm for BSA, the modified membrane has less BSA adsorbed due to the increased hydrophilicity.

Another type of PES membrane surface modification is being investigated by Ma et. al. (2007a) in which poly(vinyl alcohol) (PVA) is being introduced to the surface of PES membrane via adsorption-crosslinking process. Different PVA modified PES membrane is being prepared using different PVA solution concentration. Based on contact angle characterization, it again being proven that PES membrane hydrophilicity increase as the concentration of PVA solution increase. However, when higher PVA concentration is used to adsorption-crosslinking PES membrane, the water flux is being reduced as more PVA is being adsorbed on the membrane surface and the crosslinked PVA eventually block the membrane pore.

2.4.1. Enhancement of PES by Blending/Composite

Despite bulk modification and surface modification, PES membrane can be modified and enhanced via blending method. Out of the three PES enhancement methods, blending is the most widely used and simplest method to produce high efficiency FS and HF membrane. Moreover, blending also relatively convenient in term of operation and only mild preparation condition is needed (Richard, et al., 2012). Over the decade, lot researches been carry out to blend PES membrane with other non-solvent additive to modify the properties of membrane to improve the hydrophilicity, antifouling properties and blood compatibility. These additives can be classified into hydrophilic polymers, amphiphilic polymers and nanoparticle or other composite material. In the following section, these three additives will be described individually.

2.4.1.(a) Hydrophilic Polymer

Hydrophilic polymer is one of the most widely used blending additive and it been proven by various researchers that the present of hydrophilic polymer with PES can successfully improve the filtration efficiency of PES membrane. Some of the widely investigated hydrophilic polymers are polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and cellulose phthalate (CAP).

To improve the fouling resistance of PES membrane when used in BSA filtration, Marchese et. al. (2003) have blended PES with 2 wt% PVP of two different molecular weight (40,000 Da and 360,000 Da). When the casted FS is test with BSA at is isoelectric point, it been shown that the fouling due to BSA pore blockage and cake formation occur more seriously in PES membrane compared to PES/PVP blended membrane. This is being explained due to the hydrophilic properties of PVP which can prevent the pore blockage by BSA and become site of nucleation for cake formation. Moreover, the present of PVP to some extent prevent the formed caked from excessive compaction. Thus, proving PVP improved the fouling resistance of PES membrane. Nevertheless, permanent fouling problem cannot be eliminated.

On the other hand, to enable application of PES membrane in biomedical field especially in haemodialysis field, Wang et. al. (2009) also attempted to modify PES membrane by blending it with PVP (2-10 wt%). In their study, PES membrane is blended with PEG400 as pore forming agent along with small amount of PVP as additive. Since UF membrane is not evaluated by molecular weight cut off (MWCO), it been reported that MWCO of PVP blended membrane is unaffected. Additionally, PVP blended membrane have improved performance with higher water flux and lower BSA adsorption. This may due to the increased PES membrane hydrophilicity.

However, the hydrophilicity of only increase with increasing PVP content up to 6 wt%. Besides reduce membrane fouling due to BSA adsorption, the addition of hydrophilic PVP also retard the blood clotting time of the membrane. Thus, PVP is said to be able to modify PES membrane to made it blood compatible.

Due to PES chemical inertness and stability, PES can be used in beverage industry too. In this perspective, PES membrane been blended with PVP and casted via FS phase inversion method to remove polyphenols from apple juice. Polyphenol is the component that responsible to the browning of apple during storage. With the present of PVP, it again been proven that the UF flux increase. Since the aim of the fabricated membrane is to remove colour, when compared to commercial colour removing membrane, PES/PVP membrane showed a better colour reduction with polyphenol removal up 40% in a single UF process when PES/PVP ratio is 3.5. Despite all those advantage, it also being reported that the fouled membrane can be well regenerated using 0.1 M NaOH solution (Borneman, et al., 2001).

Apart from playing a role as hydrophilic polymer, PVP can also be a pore forming agent and its role in that field been studied by (Vatsa, et al., 2014). They fabricated PES membrane via phase inversion method with 40K PVP as pore forming agent. In their study with 18 wt% of PES and various PVP weight percent ranging from (0-10 wt%), they found that the pore size is quite similar when the PVP content is between 2-4 percent. Further increase in PVP will cause the pore to be smaller and eventually disappear. At the same time, the hydrophilicity of the membrane also increase as the PVP content increase up to 4 %. Beyond that, the contact angle with water increased. This may due to the formation of dense structure at high PES concentration which eventually increase its hydrophobicity.

Besides PVP, PES membrane also being modified with PEG also being widely studied. One of the important factor in blending will be the miscibility of the additive with the polymer and solvent in the casting or dope solution. Hence, Li et. al. (2008a) studied the thermodynamic of PES casting solution blended with PEG of different molecular weight (PEG200, PEG400, PEG400) at different concentration. In their study the concentration of PEG used is quite high which ranged from 30 wt% to 70 wt%. Based on the study, when PEG with lowest molecular weight (PEG200) is being used, the stability of the casting solution is lowest at high PEG concentration and, hence, cause it to easily experience phase separation in exposure. High PEG200 concentration also cause the macrovoid like structure in the membrane to change to sponge like form which reduce it water permeation. Since PEG also hydrophilic polymer, blending it into PES membrane also increase its hydrophilicity. However, similarly as PVP, this only true up to 60 wt% of PEG200. Beyond that the dense sponge structure caused the membrane to be hydrophobic. Therefore, PEG can also be said as one of the pore forming agent.

More intensive research on PES/PEG blended membrane also being done by Khorsand-Ghayeni et. al. (2016) in which they have fabricated symmetry PES membrane by blending it with PEG of different molecular weight and concentration. They also demonstrated the effect of humidity on the membrane. Similar as Li. et. al. (2008a), they observed that as the concentration of PEG increase the pore of membrane will be smaller even though the number of pore increased. Thus, the cross-section structure also turn out to be finger-like rather than channel-like. Moreover, the sponge layer and membrane hydrophilicity also increase with the increase in PEG amount.

Meanwhile, study also being conducted to blend PES with some rare used hydrophilic polymer such as CAP. Similar with other hydrophilic polymer blending,

the blending of this CAP has a limit which is about 80/20 wt% of PES/CAP. Blending of PES with greater amount of CAP will form defect in which large visible pore will form on the surface. In term of ultrafiltration for milk water, fouling resistance is reported to be higher in CAP blended membrane and this may due to surface roughness and the membrane hydrophilicity. Maximum flux is recovery is recorded for 80/20 wt% PES/CAP membrane.

2.4.1.(b) Amphiphilic Polymer

Despite of hydrophilic polymer, PES membrane hydrophilicity can also be enhanced by blending with amphiphilic polymer. Amphiphilic mean the material is both water hydrophilic and lipophilic or hydrophobic. Since amphiphilic has both hydrophobic and hydrophilic segment, when blended with PES in the dope solution and subsequently undergo the phase inversion process, the hydrophilic segment will be segregated to the surface while the hydrophobic segment trapped firmly inside the membrane matrix. Thus, the amphiphilic properties will be able to remain in the membrane with long term stability (Walton, et al., 1997; Hancock, et al., 2000).

Ma et. al. (2007b) blended an amphiphilic copolymer comb of PEG and polystyrene (PS-b-PEG) with PES for BSA fouling resistance study. In their work, the amphiphilic polymer provided is produced by methoxy-polyethylene glycol 2000 and styrene as monomer via anionic living polymerization. The blending of PES with PS-b-PEG result in the reduction in BSA adsorption which able to increase the fouling resistance of the membrane toward BSA. Moreover, the blended copolymer has some pore-forming effect beside able to increase the hydrophilicity of the membrane surface. Hence, all the blended membrane show increased pure water flux compared to pristine PES membrane. Another remarkable finding in their study is that with the improved

fouling resistance, the membrane has greater reusability as flux recovery ratio of 80.4% can be maintained after three cycle of BSA filtration.

Apart from this, Wang et. al. (2006) modified PES membrane by blending it with some novel branched amphiphilic polymer, P-123-b-PEG with a lot of hydrophilic tunable poly(ethylene oxide) (PEO) arm. The utilisation of this branched amphiphilic polymer was claim to has higher PEO density. This was proven by the enriched PEO segment found on the membrane surface. The high amount of hydrophilic PEO deposited on the PES membrane surface not only aid to increase the hydrophilicity of the membrane but also effectively prevent the tested protein molecule from penetrate through the hydrated PEO layer. Instead of being adsorbed onto PES, the protein will only deposit on the PEO layer, thus, improve the fouling resistance ability of PES membrane.

On the other hand, Loh et. al. (2011) studied another type of amphiphilic polymer which gain its attention due to its role as both surface modifier and pore former. HF membrane been fabricated by blending PES with Pluronic triblock polymer of PEO and poly(propylene oxide) (PPO). Based on their study, the present of two type of the Pluronic triblock, Pluronic F127 and F108, at 5wt% successfully narrow down the pore size distribution of the fabricated membrane. Hence enable it to improve the solute rejection despite having high water flux. Both Pluronic F127 and F108 is copolymer that has long chain of hydrophobic block and the present of this long chain of hydrophobic block can aid in the anchorage of the polymer on PES and helps the formation of uniform hydrophilic layer on the surface.

Blending of amphiphilic polymer into PES membrane also applicable in biomedical field. The blending of amphiphilic triblock copolymer, poly(vinyl pyrrolidone)-b-poly(methyl methacrylate)-b-poly(vinyl pyrrolidone) (PVP-b-PMMA-

b-PVP) been successfully blended with PES to produce HF membrane via reversible addition-fragmentation chain transfer (RAFT) polymerization. Based on the research, utilization of RAFT enable the control of vinyl pyrrolidone during the polymerization process to make sure its functionality is remained. The blended HF membrane showed a good biocompatibility by having a longer blood clotting time beside able to suppress the adsorption of BSA and platelet adhesion onto it. Moreover, the flux recovery was nearly 100% due to the increased hydrophilicity of the membrane (Ran, et al., 2011).

2.4.1.(c) Inorganic and Nanomaterial Additives

Inorganic and nanomaterial additive is the most popular blending alternatives among three of the additives. Various researches been proven that blending inorganic and nanomaterial additives with PES able to modify the surface morphology and performance of the membrane. The major factor still concern on the ability of them to improve the hydrophilicity of PES membrane. Moreover, blending of nanomaterial much better in term of PES performance improvement since their relative smaller size particle compared to microparticle enable them to modify the entire pore and pore mouth as they able to reach deep down the pore.

Zinc oxide (ZnO) nanoparticle (NP) MM membrane is one of widely studied nanoparticle which able blending with PES membrane to improve the membrane hydrophilicity. As reported by Ahmad et. al. (2015), within the study concentration range ZnO-NP, maximum pure water and HA fluxes is recorded when the ZnO in the casting solution is about 1.25 wt%. In their study, it been found out that the at high ZnO concentration may eventually block the pore and the present of ZnO also reduce the membrane pore size. Nevertheless, ZnO did improve PES hydrophilicity and surface roughness which reflected at it contact angle measurement with water. Due to

the improved hydrophilicity too, the fabricated ZnO MM membrane is said to be more antifouling.

The blended ZnO into PES membrane can also be in form of nanorod. The utilization of ZnO nanorod as additive able to produce a more hydrophilic PES membrane compared to ZnO nanoparticle as most of the nanorod will migrate to membrane surface and the high surface area of nanorod enable it to adsorb more water. Due to the better improvement in hydrophilicity, water flux is much higher on MM membrane produced with ZnO nanorod. Based on this research, it giving us insight that the shape of the nanofiller may eventually affect the performance of the fabricated membrane too (Rajabi, et al., 2015).

Despite drinking water and biomedical field, membrane also found its application in oil and gas field to treat water that has been contaminated by oil. Ghandashtani et. al. (2015) fabricated MM membrane by embedding nano-SiO₂ into PES membrane via combination of vapor induced phase separation (VIPS) and non-solvent induced phase separation (NIPS) methods. The fabricated membrane is more hydrophilic than unmodified PES membrane. Besides due to the present of SiO₂, the improved hydrophilicity may also due to the VIPS step which enable the more water droplets onto the film surface whereas the NIPS step made the pore size of the larger. However, the membrane still suffers from pore blockage at higher SiO₂ concentration due to SiO₂ agglomeration.

Al₂O₃ is another example of nanoparticle which usually blended with PES too. Maximous et. al. (2010) been blended Al₂O₃ with PES for membrane bioreactor (MBR) application. The produced membrane is subjected to ultrafiltration of water with activated sludge. Through the finding, blending of Al₂O₃ made the membrane

more fouling resistive toward activated sludge due to increase hydrophilicity. The permeability of 5 wt% Al_2O_3 PES membrane is 12-fold of that in unmodified PES membrane. Highest permeability and lowest fouling is recorded at Al_2O_3 concentration of 5 wt% with PES.

Besides those nanoparticles mentioned before, titanium oxide (TiO_2) also being studied by lot researchers due to its stability, high hydrophilicity, antibacterial properties, availability and low toxicity and cost (Khataee & Kasiri, 2010; Khataee & Mansoori, 2012). The high antibacterial properties may attribute to the high photocatalytic activity of TiO_2 as proven by several studies (Jyothi, et al., 2014; Ngang, et al., 2012; Leong, et al., 2014). The photocatalytic activity of TiO_2 able to improve the reusability of the membrane. With UV irradiation, photocatalytic activity can be triggered to remove microorganisms found on the surface due to the present of TiO_2 . Hence, granted the membrane anti-biofouling ability and self-cleaning ability (Kim, et al., 2003).

The effect of blending TiO_2 ranging from 0-5 wt% into PES membrane been studied by Li et. al. (2009b). In their work, PES- TiO_2 nanoparticle membrane is casted with FS configuration via combined vapor induced phase separation/immersion precipitation. Since TiO_2 nanoparticle is a type of hydrophilic nanoparticle, blending only tiny amount of it into PES membrane dope solution is proven to improve the hydrophilicity of PES membrane. Moreover, a more complete character of the modified membrane been reported in this work too. With a tiny amount of TiO_2 nanoparticle, the membrane permeation been improved due to the formation porous surface and loose skin layer with the addition of TiO_2 .

Vatanpour et. al. (2012), on the other hand, studied the effect of TiO₂ nanoparticle size on the PES membrane performance. It been found that the smaller TiO₂ nanoparticles able to produce a membrane with greater performance. This is because large TiO₂ nanoparticle will tend to agglomerate and affect the ultrafiltration performance. In this paper, it also been showed that the blending of TiO₂ able to improve the hydrophilicity of the membrane, hence, has greater antifouling ability as the hydrophilicity prevent the gel formation on the membrane surface. This is proven with the greater water flux and whey flux in the ultrafiltration test.

The composition of casting solution used to form MM membrane also may affect the morphology and performance of the membrane. When ethanol (EtOH) is being added to the casting solution, the length of microvoid increase even though the number of microvoid unchanged. This may due to properties of EtOH which favour flocculation of nanoparticle and, hence, encouraged the formation of large membrane pore on the surface due to TiO₂ agglomeration. When larger pore available, hydrophilicity of the membrane will increase due to increased water adsorption on the pore. However, in this study, the membrane hydrophilicity and permeation only increase as TiO₂ concentration increase up to 0.2 wt%. Beyond that, both permeation and hydrophilicity will reduce (Sotto, et al., 2011).

Besides directly blended into PES membrane, Safarpour et. al. (2016) used TiO₂ and graphene to synthesis nanocomposite of reduced graphene oxide (GO) and TiO₂ (rGO/TiO₂). The produced composite is then blended with PES to produce FS membrane via phase inversion method. As expected the produced membrane has higher hydrophilicity with improved water permeation. The advantage of blending PES with such composite is that the distribution of TiO₂ in the membrane matrix will be better.

There are still a lot more researches that being conducted by researcher to blend TiO₂ with PES membrane via various method as summarized in Table 2.1. This researches shown their own innovation in mitigating the problem regarding blending of TiO₂ with PES membrane as well as further enhance the TiO₂ mixed matrix membrane for various purpose such as improve the uniform NP dispersion across the surface. Based on the table, it is worth notice that TiO₂ MM membrane really has lot advantage in separation of organic material such as BSA, organic dye and HA from water due to its better anti-fouling ability. Moreover, high flux recovery also possible with this kind of membrane which make membrane technology to be economically feasible in separation field. However, it worth notice that, despite all the benefit of TiO₂ MM membrane, up to now, all TiO₂ MM membrane researches that being carried out is only fabricated as FS. As mentioned before, HF has greater benefit and demand in industry compared to FS. Therefore, this study was presented to show the potential for developing TiO₂ MM HF membrane for application in separation field especially for removing HA from water. This may encourage the further development of TiO₂ MM HF membrane in future and eventually made it feasible to be applied in large scale industry.