THE EFFECT OF FLOWER-LIKE TITANIA TOWARDS CHARACTERISTICS AND PERFORMANCES OF POLYSULFONE MIXED MATRIX MEMBRANE

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For my precious parents,

En Azhar bin Abd Rahman & Pn. Roslindah binti Majid

For my beloved wife,

Nur Hamizah binti Hassan Basri

For my kind supervisor that give encouragement and support,

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Only Allah S.W.T can repay your kindness

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ABSTRACT

For ages, the polymeric membrane such as PSf is widely used in liquid separation for various application as the polymer itself offer versatile and attractive properties. However, due to strong hydrophobic nature of PSf property that create serious fouling problem to most of the separation process, thus modification of membrane by integrating strong hydrophilic particles is always practically used among industries and researchers. In this research, the effect of FLT as an additive in the PSf membrane was investigated. With consideration of the FLT that offer larger specific surface area as compared to ST that able to generate better performances and properties of polymer MMM. In this work, the polymer MMM of PSf/FLT and PSf/ST membranes were prepared via phase inversion method at five different concentrations of additive. Membrane characterization involved several observations such as cross-section area, particle distribution, surface roughness, hydrophilicity property, mean pore size, mechanical strength and porosity. Meanwhile, membrane performances were evaluated in terms of HA rejection, PWF, antifouling, antibacterial activity and photocatalytic properties based on self-cleaning antifouling efficiency. From the result, the addition of FLT was strongly influenced overall structure and characteristics of the membrane compared to ST. With a larger surface area of FLT and homogenous distribution inside membrane structure have resulted in better hydrophilicity effect thus improved the membrane performances. The PWF result was increased from 61.33 L/m^{2}h to 137.81 L/m^{2}h for PSf/ST and 155.46 L/m^{2}h for PSf/FLT as increased additive to 3 wt%. Same results were obtained by rejection analysis where the PSf/FLT membrane able to reject more than 96% of HA and improved antifouling and self-cleaning efficiency. It is clearly shown that the present of higher specific surface area of FLT has improved overall characteristics and performances of the membrane compared to ST especially at 3 wt% of concentration.

ABSTRAK

Selama bertahun-tahun, membran polimer seperti polisulfon (PSf) telah digunakan secara meluas dalam penapisan cecair untuk pelbagai aplikasi. Hal ini kerana PSf mempunyai sifat serba boleh dan menarik. Walaubagaimanapun, disebabkan sifat hidrofobik yang kuat telah menyebabkan masalah antikotor yang serius. Oleh itu, modifikasi membran dengan menggabungkan aditif hidrofilik yang kuat adalah lebih praktikal dan sering digunakan di industri dan dalam kalangan penyelidik. Dalam kajian ini, kesan titania berbentuk bunga (FLT) sebagai aditif dalam membran PSf telah dikajiselidik. Dengan mempertimbangkan FLT yang menawarkan luas kawasan permukaan spesifik yang lebih besar berbanding titania sintetik (ST), ianya dapat menghasilkan prestasi dan sifat membran polimer matriks campuran yang lebih baik. Dalam kajian ini, membran polimer matriks campuran PSf/FLT dan PSf/ST telah disediakan menggunakan kaedah penyonsangan fasa pada lima peratus kepekatan yang berbeza. Pencirian membran melibatkan beberapa pemerhatian seperti kawasan keratan rentas, pengagihan aditif di dalam membran, kekasaran permukaan, sifat hidrofilik, ukuran saiz liang, kekuatan mekanikal dan ujian keliangan. Sementara itu, prestasi membran telah dinilai dari segi pemisahan asid humik, kebolehtelapan air, sifat antikotor, antibakteria, dan kecekapan pembersihan diri. Hasil daripada kajian, penambahan FLT telah mempengaruhi keseluruhan struktur dan pencirian membran berbanding ST. Dengan kawasan permukaan FLT yang lebih luas dan pengagihan aditif yang lebih seragam di dalam struktur membran telah menghasilkan kesan hidrofilik yang lebih baik dan meningkatkan lagi prestasi membran. Keputusan kebolehtelapan air meningkat dari 61.33 L/m^2h kepada 137.81 L/m^2h untuk PSf/ST dan 155.46 L/m^2h untuk PSf/FLT pada 3% kepekatan. Hasil yang sama telah diperolehi dari pemisahan asid humik di mana membran PSf/FLT berjaya menapis lebih 96% asid humik dan meningkatkan prestasi antikotor dan kecekapan pembersihan diri. Hal ini jelas menunjukkan dengan kehadiran FLT yang mempunyai luas permukaan yang besar telah meningkatkan pencirian dan prestasi membran secara kesuluruhannya berbanding ST terutama pada 3% kepekatan.

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LIST OF SYMBOL AND ABBREVIATIONS

Ag	-	Silver
AgNPs	-	Silver nanoparticles
ASTM	-	American Society and Testing Method
BSA	-	Bovine serum albumin
BET	-	Brunauer-Emmett-Teller
CA	-	Cellulose acetate
Cu	-	Copper
DMF	-	Dimethylformamide
DMAc	-	Dimethylacetamide
E.coli	-	Escherichia coli
EDX	-	Energy Dispersive X-ray Spectroscope
EIPS	-	Evaporation Induced Phase Separation
FLT	-	Flower-like titania
FESEM	-	Field Emission Scanning Electron Microscopy
g	-	gram
HA	-	Humic acid
HCl	-	Hydrochloric acid
IPA	-	Iso-propanol
MMM	-	Mixed matrix membrane
MF	-	Microfiltration
NIPS	-	Non-solvent induced phase separation
NOM	-	Natural organic matter
NF	-	Nanofiltration
PSf	-	Polysulfone

PES	-	Polyethersulfone
PVDF	-	Polyvinylidene fluoride
PAN	-	Polyacrylonitrile
PC	-	Polycarbonate
RO	-	Reverse osmosis
ST	-	Synthetic titania
TiO^2	-	Titania
$Ti(OBu)_4$	-	Titanium butoxide
TFC	-	Thin film composite
TIPS	-	Thermally Induced Phase Separation
UV	-	Ultraviolet
UF	-	Ultrafiltration
UN	-	United Nations’
VIPS	-	Vapor Induced Phase Separation
Wt%	-	Weight percentage
XRD	-	X-ray Diffraction
ZnO	-	Zinc oxide

CHAPTER 1

INTRODUCTION

1.1 Research background

In recent years, membrane separation technology such as gas separation, pharmaceutical industries, and water treatment has become the most competitive method among others since it offers better performances like high productivity, selectivity, and permeability [1–4]. Besides that, this technology also can be easily integrated with another processes or mechanism. Basically, membrane separation is a technology which is able to selectively separates particles and dangerous contaminant such as humic, heavy metals, bacteria and viruses through pores and gaps in membrane structure [5]. This membrane structure with a controlled pore size and good asymmetric structure is strongly depended on the type of polymers, solvent, and non-solvent which can be described through thermodynamic of ternary diagram [6, 7]. The most frequent technique of phase inversion is non-solvent induced phase separation (NIPS) and it was fabricated by controlling the interaction between polymers and solvents [8]. By controlling the interaction and ratio in casting solution between polymers, solvent and non-solvent, the formation of membrane structure will be different due to the influence of thermodynamic instability and kinetic polymer solution [6, 9].

Various polymers such as polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) cellulose acetate (CA) and polysulfone (PSf) has been used for membrane fabrication [10, 11]. These polymeric membranes have been created and developed for a variety of industrial applications. Among these polymers, PSf is the most attractive material in membrane fabrication due to its excellent mechanical properties, favorable selectivity-permeability, resistance to chlorine, and stability of thermal and chemical properties [11–14]. In addition, the solubility of PSf itself that enables it to co-dissolution with other polymers has attracted many researchers to fabricate polymeric blended membranes using PSf. Although PSf has been intensively used, hydrophobic property in nature has reduced its surface wettability and easily causes deposition and adsorption of fouling problem on top of the membrane surface and inside the membrane pores [11, 15]. In other words, membrane fouling is strongly related to contaminant accumulation of the outer separation layer of the membrane and this accumulation also causes the buildup of organic contaminant that is capable of generating microorganism growth [16]. To overcome this fouling problem, recently the addition of the additive such as organic and inorganic particles into the membrane has become one of the most practical technique to be implemented. R. Jamshidi Gohari *et al.* in the studied of PSf membranes modified with hydrous aluminum oxide (HAO) nanoparticles showed the modified membrane exhibit complete elimination of oil molecules with flux recovery ratio around 67% after washing process [17]. While Sirus Zinadini *et al*. produced improvement results in fouling resistant ratio using graphene oxide as filler in PES [18].

Many intensively studies have been conducted regarding the modification of membrane in enhancing the structure, characteristics, and performances of the membrane. In fact, the use of the additive in membrane modification is widely used and it offers a simple method to improve the membrane's characteristic without any additional processes or complexity steps [3]. Additives addition have been widely implemented in most phase inversion membrane to develop a newly MMM that able to offer better hydrophilicity, wettability, pore structure and surface roughness. In addition, the additive also has played a major role in reducing the fouling problem of polymer membrane due to a stronger effect of additive [16]. Based from previous research, various inorganic particles have been used to solve the fouling and hydrophobicity problem such as Zinc Oxide (ZnO), Copper (Cu), Silver (Ag), and Titania (TiO^2) [16, 19, 20]. These inorganic particles offer unique properties such as unique magnetic, electrical, optical, mechanical and structural properties and also some particles show high toxicity to a broad spectrum of microorganism including bacteria, fungi, viruses and yeast and shows a better performance as anti-bacterial agents in different areas [21, 22]. This antibacterial property also able to avoid the fouling problem that caused by the growth of the microorganism. Due to the hydrophobic nature of the polymeric membrane, PSf also suffers a major fouling problem that able to reduce membrane performances. To improve the polymeric membrane properties, the addition of inorganic material to modify the membrane morphology is required. Mahesh Padaki *et al*. studied the improvement in antifouling properties of titanium nanotube into PSf and recorded the improvement of hydrophilicity in contact angle, porosity value. The filtrations from the study also produce a 100% flux recovery as a result [23].

Titania is believed to support polymer and has been widely used for decomposition of the microbial organism [23]. Min Cho *et al.* in the studied of different inactivation behaviors of *MS-2 Phage* and *Escherichia coli (E.Coli)* in titania photocatalytic disinfection proved that photo-activity of titania can effectively control *E.Coli* bacteria adhesion although the main purpose is to reduce bio-fouling in polyamide thin film composite membrane [24]. Titania has three different phases which are rutile, anatase, and brookite and among these three phases, anatase phase said to a have high photo-catalyst reaction while rutile has the most stable phase [9, 25–27]. Photocatalyst is connected in different utilizing of the environment and self-cleaning purposes. The self-cleaning is also one of the properties needed to overcome bacteria growth and fouling problem [28, 29]. Rahul A. Damodar *et al*. studied the self-cleaning, antibacterial and photocatalytic properties of titania entrapped PVDF membranes, the results showed the modified membrane remove *E.Coli* at a faster rate than the neat membrane. The results also stated that the performance of foul membrane flux can be recovered to its initial value by simple ultraviolet (UV) treatment thus proved the self-cleaning property [30]. From all the previous research, it is proved that titania produced very good results with their properties. In a different dimension, FLT also could produce the same results or maybe even better since the properties and characteristics of particles itself have been changed. The flower-like structure has more surface area than common ST thus give a meaning that the material can achieve a higher level of results than common structure particles. There are no reports or journals related to FLT used in modification with polymer membrane especially PSf membrane. So the novelty of this study can be achieved.

In this study, titanium butoxide ($Ti(OBu)_4$ and hydrochloric (HCl) mixture was synthesized using a facile hydrothermal method to make a FLT which was used as an additive to modify PSf polymer MMM with the purpose to investigate the characteristics and performances of the modified membrane. ST with an irregular structural form was used as an additive with the purpose to compare different structure results. The MMM was fabricated using a phase inversion method which is non-solvent induced phase separations (NIPS). Both FLT and ST powders were tested with several characteristics analyses such as Field Emission Scanning Electron Microscopy (FESEM), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), UV-vis spectrophotometer and Energy Dispersive X-ray Spectroscope (EDX). Meanwhile, for membrane characterization, cross-section area analysis, particle distribution, surface roughness, hydrophilicity property, mean pore size, mechanical strength and porosity test were conducted. As for the membrane performance test, the pure water flux (PWF), humic acid rejection, antibacterial activity, anti-fouling and self–cleaning study were performed. The finding of this research has proved that the MMM membrane with FLT structure which has higher specific surface area can play a major role in enhancing overall characteristics, properties and performances of the membrane.

1.2 Problem Statement

For ages, the polymeric membrane is widely used in water separation for various ranging applications. PSf is one of the most favored membranes as it can be adjusted in their application according to its capabilities and types. Basically, PSf polymer membrane has the hydrophobic nature property that able to create easily deposition and caused adsorption or fouling problem on the surface as well as inside the membrane pores [15]. Current trends in improving the membrane performances and enhancing the antifouling properties of the membrane are through additive modification. Basically, additive effect shows a very strong effect in changing pore formation, enhance pore interconnectivity, give better hydrophilicity properties and suppress the macrovoids formation.

For example, ST as an additive has proven that the particles can enhance the properties of the membrane but also has photocatalytic capabilities [19, 31–35]. The photocatalytic capability in term of self-cleaning property helps in reducing the maintenance cost that has become one of the major problem in membrane technology. This property shows that the titania has the advantage that was not possess by other additive. However, at higher concentration of ST, the particle tends to aggregate inside membrane structure and reduce the performance of the membrane. Therefore, the modification of titania particle structure could definitely improve better properties of the membrane and indirectly give better performances since the particle offers higher surface area with special property of anti-agglomeration that could homogenously distribute at higher concentration inside membrane structure. Thus in this research, FLT which has more surface area with numerous formation of nanorods as petals is predicted to give more interesting characteristic and properties as an additive of the membrane compared to ST.

1.3 Research Objectives

The objectives of this research are:

i. To synthesis and analyze the characteristics of hydrothermal synthesized FLT under the controlled processing parameter.
ii. To investigate the effect of FLT loadings as comparison to ST towards PSf polymer MMM base on characteristics, properties and performances.
iii. To determine the best loadings of FLT into the membrane structure with a comparison to the ST.

1.4 Research Scopes

In order to achieve the objectives stated above, the following research scopes were drawn:

i. Synthesizing of FLT via hydrothermal method under the volumetric ratio of 1:1 processing parameter using $Ti(OBu)_4$ and HCl as a mixture inside the teflon-lined autoclave.

ii. Characterizing the synthesized FLT and ST in term of the microstructure (FESEM), powder crystallization and the intensity pattern (XRD), element determination (EDX), and specific surface area (BET).
iii. Fabricating polymer MMM by preparing a dope solution from 18 wt% of PSf as a polymer material, 82 wt% N-methyl-2-pyrolidone (NMP) as a solvent, 10 wt% PEG as pore-forming agent, room temperature distilled water as non-solvent and FLT and ST as additives at different percentage concentration (0 - 5 wt%) via the phase inversion method.
iv. Characterizing the fabricated MMM membrane in term of cross-section morphologies, surface roughness, particles distribution inside the membrane, porosity, pore size formation, hydrophilicity, and membrane tensile strength.
v. Measuring membrane performances via PWF, HA rejection, antibacterial, anti-fouling and self-cleaning properties and evaluating the best loadings from the MMM membrane.
vi. Comparing overall characteristics and performances between PSf/ST and PSf/FLT composite membrane.

1.5 Novelty of work and significant of study

The hydrophobic property in nature of PSf membrane has caused deposition and adsorption of fouling problem on top of the surface and inside the membrane pores, therefore the enhancement to overcome this fouling problem is needed. Based on previous study, the use of ST shows the drastically enhancement in term of characteristics and performances of the membrane but investigation on the effect using FLT is not yet being reported. The fact that FLT provides a higher specific surface area that able to give better interaction and bindings to the membrane structure significantly will affect membrane characteristics as well as membrane performances. The finding of this research will contribute to the membrane development where the shape and structure of additives can play a major role in enhancing overall characteristics, properties and performances of the membrane.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to membrane technology

Generally, a membrane can be defined as a thin layer whether a permeable or semi-permeable film with different structures that are able to separate fluids [5]. According to Mulder, a membrane is a selective barrier between two phases [36]. This barrier allows particles to pass through and able to remove contaminants. The system of membranes is very attractive since they can give an absolute barrier to pathogens and remove turbidity, thus increasing the palatability of the water [37]. The membrane technology plays a major part in many applications such as desalination, air pollution control, hazardous industrial, dairy purification, hemodialysis, microorganism separation and of course wastewater reclamation. In terms of wastewater reclamation, it is crucial in the process of removing bacteria, microorganism, particulates and natural organic material (NOM) [38].

Continuing development in advance of new membranes with better chemical, thermal and improved transport properties has led to various new applications of the membrane nowadays. For the records, the first membrane phenomena appear to have seen by the Frenchman Abbe Nollet in 1748 followed by the first synthetic membrane prepared by Fick in 1855 until the year of 1972. Cadotte and Rozelle developed the so-called thin-film composite (TFC) reverse osmosis membranes from a new class of membrane materials but the breakthrough was in 1959 when Sourijan and Loeb discovered a way to produce a very thin membrane using the phase inversion method. Table 2.1 shows the membrane milestones from the first creation of the membrane until the creation of thin-film composite membrane.

Table 2.1: Membrane milestone [39]

Event	Scientist	Year
Osmosis	Abbe Nollet	1748
Law of Diffusion	Fick	1855
Dialysis, Gas Permeation	Graham	1861,1866
Osmotic Pressure	Traube, Pfeffer, Van't Hoff	1960-1887
Microporous Membranes	Zigmondy	1907-1918
Distribution Law	Donnan	1911
Membrane Potential	Teorell, Meyer, Sievers	1930s
Hemodialysis	Kolff	1944
Skinned Membrane	Sourirajan and Loeb	1959
Membrane Transport Models	Kedem, Katachalsky, Lonsdale, Merten, Pusch, Sourirajan	1960-1970
Spiral-Wound Membrane Element	Westmoreland, Bray	1965-1970
Hollow-fiber RO Membranes	Mahon, Hoehn, and Milford	1965-1970
Thin-film Composite Membrane	Cadotte and Rozelle	1972

To be concluded, the remarkable in development of commercial membrane process for liquid separations such as reverse osmosis (RO), microfiltration (MF), nanofiltration (NF), ultrafiltration (UF) would not even possible without the discovery and subsequent development of high-flux and extremely thin membranes by Sourijan and Loeb, and climax in the development of thin-film composite membranes by John Cadotte and Rozelle [39]. The current technology of the membrane was much derived from their work.

Basically, there are two types of membranes which are biological membrane and synthetic membrane [40]. A biological membrane is a living organism membrane and it is a very complex membrane. While for the synthetic membrane, it is a man-made membrane and not as complicated as a biological membrane. The difference between both membranes is biological membrane using active transport while synthetic using passive transport which can be driven by pressure, concentration and temperature differences. Most membrane processes are pressure-driven and usually referred as membrane filtration process [37]. The filtration process of a membrane is based on the presence of semi-permeable membranes. The principle is simple as the membrane acts as a specific filter that will let water flow through while it catches suspended solids and other substances.

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