MORPHOLOGY AND PERFORMANCE EVALUATION OF POLYETHERSULFONE/ZINC OXIDE (PES/ZnO) MIXED MATRIX MEMBRANE FABRICATED USING NON SOLVENT ADDITIVE

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AA	Acetic acid
CA	Contact angle
DGDE	Diethylene glycol dimethyl ether
DMAc	Dimethyl acetamide
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
EtOH	Ethanol
HA	Humic acid
HAR	Humic acid rejection
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
NOM	Natural organic matter
NSA	Non-solvent additives
PEG	Polyvinyly
PEG	Poly(ethyleneglycol
PES	Polyethersulfone
PVP	Poly(vinyl pyrrolidone)
PWF	Pure water fluw
RO	Reverse osmosis
TiO_2	Titanium oxide
UF	Ultrafiltration
ZnO	Zinc oxide

LIST OF SYMBOLS

FRR	Flux recovery ratio	%
HAR	Humic acid rejection	%
J_{HA}	Humic acid permeate flux	$g/m^2.s$
J_{WF}	Initial water flux	$g/m^2.s$
J_{WF2}	Water flux after HA filtration	$g/m^2.s$
R_a	Average roughness	nm
R_f	Total fouling resistance	m^3/s
R_t	Total filtration resistance	m^{-1}
RFR	Relative flux reduction	%
R_{ir}	Irreversible fouling resistance	%
R_m	Membrane resistance	m^{-1}
rm	mean pore size	nm
R_q	Root-Mean-Square (RMS) roughness	nm
R_r	Reversible fouling resistance	m^{-1}

MORPOLOGI DAN PENILAIAN PRESTASI POLIETHERSULFON/ZINK OKSIDA (PES/ZNO) MEMBRAN CAMPURAN MATRIKS DIPERBUAT MENGGUNAKAN TAMBAHAN BUKAN PELARUT

ABSTRAK

Dalam kajian ini, kesan zarah nano dalam membran yang diubahsuai digunakan tambahan 'bukan pelarut' dikaji. Nisbah aseton/NMP akan dimanipulasikan dan kesan daripada manipulasi kepada morpologi dan prestasi membran akan diperhati, nisbah aceton/NMP yang menunjukkan prestasi baik akan digunakan untuk memfabrikasikan membran matriks campuran dengan zarah nano Zink Oksida (ZnO). Tambahan aseton dalam membran menghasilkan membran yang berkulit tebal dan juga yang mempunyai lompang macro berupa jejari. Tambahan aseton juga meningkatkan penolakan tetapi mengurankan fluks air tulen. Membran yang diperbadankan dengan aseton mengurangkan hidrofilik dan kekasaran permukaaan jua sedikit menurun. Membran yang diubahsuai oleh aseton mempunyai permukaan kulit yang ketat dengan keliangan dan saiz liang yang kecil boleh mengurangkan kesan kotoran. Nilai nisbah pemulihan fluks untuk nisbah aseton/NMP 0.05 adalah 97.93% tetapi nilai ini berkurang sebanyak 24.92% apabila nisbah aseton/NMP adalah 0.20. Membran difabrikasi dengan zarah nano ZnO dan aseton boleh meningkatkan kesan hidrofilik dan keliangan, oleh itu , fluks air tulen meningkat. Tetapi kekotoran yang tidak dapat dipulih meningkat apabila 0.5 peratus berat ZnO digunakan dibandingkan dengan membrane dengan aseton sahaja kerana adanya liang yang buka (Saiz liang dan keliangan tinggi). Walau bagaimanapun, nilai nisbah pemulihan fluks akan terus bertambah dengan peningkatan ZnO kerana kesan hidrofilik mengurangkan penyerapan Humik asid. Mekanisma penyekatan liang PES/NMP/Aseton dan PES/NMP/Aseton/ZnO dikaji berdasarkan model penyekatan liang. Penapisan kek merupakan mekanisma penyekatan liang yang paling dominan dalam kedua-dua

membran pada fasa yang awal (20 min) dan fasa akhir (21min hingga 60 min). Tetapi, nilai pekali untuk penentuan, R^2 untuk model penyekatan liang yang lain jua hampir sama denga penapisan kek, oleh itu, kotoran boleh berlaku hasil daripada gabungan semua model ini.

MORPHOLOGY AND PERFORMANCE EVALUATION OF POLYETHERSULFONE/ZINC OXIDE (PES/ZnO) MIXED MATRIX MEMBRANE FABRICATED USING NON SOLVENT ADDITIVE

ABSTRACT

The effect of nanoparticles (NPs) in the non solvent additive modified membrane is studied in this paper. The ratio of acetone/NMP is manipulated and its effect to morphology and performance of membrane is observed and the best performing ratio of acetone/NMP is used to fabricate a mixed matrix membrane with ZnO-NPs. Addition of acetone results in thick skin layer followed by reduced finger like macrovoids which improved the rejection but decreased pure water flux. Acetone incorporation into membrane reduces hydrophilicity while, the surface roughness decrease slightly. The tight skin layer with reduced porosity and pore size of acetone modified membrane can minimize the fouling effect. The FRR value of acetone/NMP ratio of 0.05 is as high as 97.93 % but the value decreased by 24.92% when the ratio of solvent is 0.20. High concentration of acetone reduce the hydrophilicity cause several fouling. The incorporation ZnO-NPs into the NSA modified membrane can improve the hydrophilicity and porosity, hence the pure water flux improves. But, the irreversible fouling of membrane with 0.5 wt.% of ZnO increase significantly compared to the membrane with acetone alone which is again due the open pore in ZnO modified membrane. But, the Flux Reduction Ratio (FRR) values improves with the increase of ZnO, as the membrane become hydrophilic reduce the humic acid adsorption.The pore blocking behaviour PES/NMP/Acetone and PES/NMP/Acetone/ZnO are evaluated based on 4 pore blocking models. The cake filtration is the dominant pore blocking cause for both membrane at initial (20 min) and final stage (21 min to 60 min). But, the coefficient of determination, R^2 value for other pore blocking models is nearly same as the cake filtration so, fouling may be due the combination of all the models.

CHAPTER 1 : INTRODUCTION

1.1.   Research Background

Phase inversion induced by immersion precipitation is a common technique used for the preparation of polymer membranes with asymmetric structure. Traditionally, membrane casting system at least composed of 3 different components such as polymer, solvent and non-solvent. Polymer solution is cast on a suitable support and immerse in a coagulation bath containing non solvent. The exchange of solvent and non-solvent in coagulation bath lead to the formation of precipitation. There are few key factors in membrane preparation that significantly affect the chemical and physical property of membrane such as the solvent type, polymer type and concentration, non solvent type and composition, additives to the polymer solution, and film casting conditions (Guillen et al., 2011).

Adding a additive to polymer solvent to enhance its performance is widely practised in membrane industry, specifically many literature highlighted the capability of non-solvent to act as additives was reported in numbers of papers (Aroon et al., 2010; Xu and Alsalhy, 2004). The addition of NSA into the membrane induce morphological variation in the membrane as it can bring the initial composition of the casting solution nearer to the precipitation point. In another word, the NSA can alter the phase separation behavior during the phase inversion process and can speed up the coagulation process from solution to gel state when the casting solution is immersed in a coagulant (Wang et al.,1995).

Lan and Wang (2012) mentioned that by using weak non-solvent such as glycerol, the structure of PES membrane changed from finger-like pore to sponge-like pore, the porosity also found decrease significantly. The similar scenario also

witnessed by Amirilargani and Mohammadi (2011) by using methanol, ethanol and 1-propanol as NSA. They also mentioned that the rejection of BSA increase while the flux decrease as the concentration of NSA increases. Appropriate amount of NSAs enhances the formation of macrovoids, while too much non solvent suppresses their formation (Smolders et al., 1992). Hence, the NSA/solvent ratio does play an important role in determining the performance of membrane.

1.2.   Problem Statement

As mentioned in section 1.1., the NSA presence in membrane suppress the macrovoid formation and it is well known that for filtration of liquid, macrovoid or finger-like structure of membrane are more preferable to get reasonable flux. Based on Aroon et al. (2010), NSAs such as alcohols (methanol, ethanol, propanol, butanol, pentanol) and ethylene glycol, diethylene glycol are most widely used as additives for gas separation applications due to their tendency to form very porous structure with little or no macrvoids. On the other hand, Ahmed et al. (2013), Kim et al. (2002) and also Amirilargani and Mohammadi (2011) mentioned that the rejection can be tremendously improved by addition of NSA. So, the NSA has the potential to contribute positively to the performance of membrane. However it cannot be denied that the fact that NSA alone cannot create membrane with all the superior quality such as durability and resistant to harsh environment.

While, the Mixed Matrix membrane (MMM) which can be defined as being incorporation of nano materials dispersed/embedded in a continuous phase (Qadir et al.,2017), possess some attractive advantage compared to the polymeric membrane. The comparison of organic membrane and MMM is listed in Table 1.1 which shows that MMM has some advantage such as higher flux and stability compared organic

membrane. Ahmad et al. (2013) stated that the 2 important benefits of the NPs in membrane are these materials can assist in the production of membranes with a required structure and these materials can control membrane fouling caused by the functional groups. It is popularly believed that PES membrane are prone to fouling especially in aqueous filtration system due to hydrophobic nature (Ahmad et al., 2013). NPs such as ZnO in PES membranes improve the surface hydrophilicity to a great extent as well as reduce the fouling effect (Dipheko et al., 2017).

To improve the performance of NSA modified membrane, the ZnO is considered to be used as NPs additive in the membrane due its great potential, Balta et al. (2012) mentioned that the lower cost of ZnO and the increase of the surface to volume ratio obtained when ZnO is used as NPs make this alternative, a potential system that can meet the demand of an efficient and lower-cost device. Furthermore, they also specified that use of ZnO-NPs does not produce an increase in toxicity since the size distribution and surface area are not related to toxicity. These are the added advantage for ZnO-NPs to be used in water treatment application.

So to evaluate the effect of NSA toward membrane, acetone used as NSA and the ratio of acetone/NMP is varied in PES membrane to observe performance of membrane. The best performing ratio of acetone/NMP is used to fabricate membrane with different loading of ZnO to know the improvement on the NSA modified membrane after NPs addition.

Table 1.1 : Comparison between MMM and organic membrane

Parameters	Organic membranes	MMM
Water flux	Low-High	High
Improved stability	No	Yes
Tunable selectivity	No	Yes
Issues/Challenges	Fouling	Scale-up
	Low Membrane life	Compatibility of
	Low mechanical strength	inorganic phase
	Low chemical resistance	Membrane defects
	High energy consumption	Fouling

1.3. Research Objective

The objectives of this research are: -

i. To synthesize, characterize and evaluate fouling resistance of PES membrane fabricated using different ratio of acetone/NMP

ii. To synthesize, characterize and evaluate fouling resistance of PES/NMP/Acetone membrane fabricated using different loading of ZnO-NPs

iii. To evaluate the pore blocking behaviour of PES/NMP/Acetone and PES/NMP/Acetone/ZnO membranes during fouling by using pore blocking model simulation

1.4.   Scope of Study

In this work, first the flat sheet PES membrane was fabricated using different ratio of acetone/NMP solvent by immersion precipitation method. After the membrane was cast on the clean glass plate, the nascent membrane was left in the room condition for 1 minute followed by immersion of the membrane into distilled water and left for 24 h to allow precipitation. The produced membrane was characterized in term of surface morphology, surface roughness, hydrophilicity, pore size using SEM, AFM, CA. To test the flux performance, the membrane was first compressed at 10 bar. Then, PWF was run for an a hour followed by HA filtration for 1 h at 9 bar. Then, the membrane was flushed using DI water before the second cycle of water filtration started again at 9 bar for 1 h. The data of J_{WF}, J_{HA}, J_{WF2} and HAR was analyzed and used to calculate FRR, RFR, membrane resistance R_m, total fouling resistance R_f, reversible fouling resistance, R_r and irreversible fouling resistance R_{ir}. The ideal acetone/NMP ratio was obtained from the analysis.

By using the selected acetone/NMP ratio, the different amount of ZnO-NPs (0 to 2 wt. %) are dispersed in the mixed solvent. The membrane was cast using the above mentioned process. Membrane characteristic analysis for MMM is not only included the surface morphology, surface roughness, hydrophilicity and pore size but additional tests such as EDX and TGA were performed on the membrane to know the dispersion of NPs on the membrane. Flux and rejection of HA was tested and the antifouling ability of this ZnO modified PES/NMP/Acetone was evaluated based on RFR, FRR, R_f, R_{ir} and R_r values. The different pore blocking behaviour of PES/NMP/acetone and PES/NMP/acetone/ZnO was evaluated based on 4 pore blocking models by evaluate the R^2 value for best fitted regression line.

CHAPTER 2: LITERATURE REVIEW

2.1.   Membrane Formation by Immersion Precipitation

Immersion precipitation is one of the membrane casting technique of phase inversion which is widely used for asymmetric membrane formation. In the immersion precipitation process, phase separation can be induced by solvent/non-solvent exchange during the coagulation step. Immersion precipitation membranes formation can be explained in a simple way by considering a ternary system consist of polymer/solvent/non solvent. A polymer solution consisting of a polymer and a solvent is cast as a thin film upon a support and then immersed in a non solvent bath. The solvent diffuses into the coagulation bath while the non solvent will diffuse into the cast film. After a given period of time the exchange of solvent and non solvent has proceeded so far that the solution becomes thermodynamically unstable and demixing takes place (Mulder, 2000). Finally a solid polymeric film is obtained with an asymmetric structure. Figure 2.1 explains about the simple phenomena of solvent and non solvent exchange in forming a membrane
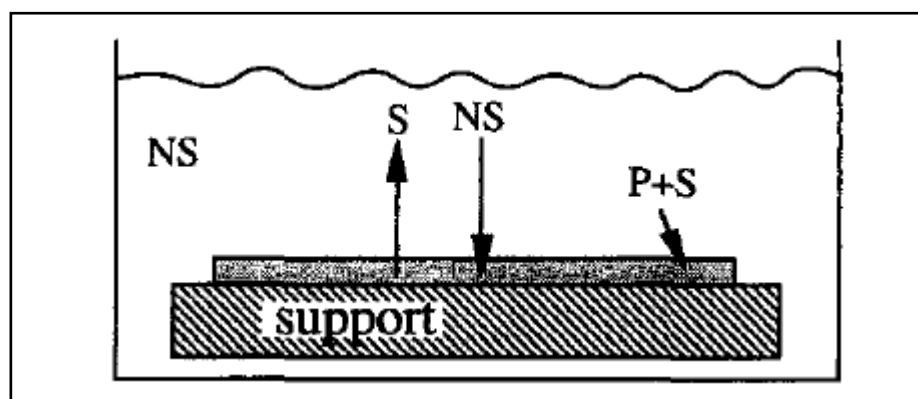
Figure 2.1 : Schematic depiction of the immersion precipitation process

Ternary phase diagram can be used to describe the thermodynamic behaviour of these three component to form membrane with different morphology. In the ternary phase diagram, the system is composed of a single phase region and two phase region. In the single phase region, there exists miscibility of three components, while with the two phase region, the solution is separated into two phase, polymer-poor and polymer-rich phase. The boundary delimiting the liquid-liquid demixing is known as binodal curve (Machado et al., 1999). The region between the spinodal and the binodal curves is called metastable region, where phase separation appears under certain initiation (nucleation). The region within the spinodal curve corresponds to unstable composition where immediate demixing occurs after entering this region.

Once demixing polymer solution arrives in the metastable region between the binodal and the spinodal, the region is referred to "binodal demixing" and therefore represents path A. In this region, the polymer solution is separate into a polymer-lean phase and a polymer-rich phase (Buonomenna at al., 2011). Another pathway towards miscibility gap (path B) is called "spinodal decomposition". In this pathway, the composition path passed through the thermodynamically unstable zone (critical point), in which the binodal and spinodal curve converge, and two co-continuous phases formed. This process yields asymmetric membranes with a dense top layer and porous sublayer containing macrovoids, pores, and micropores (Rahimpour and Madaeni, 2007).

Usually when the polymer concentration is low, the precipitation path crosses the equilibrium line below the critical point and nucleation of a polymer-rich phase initiates the phase separation process. But when the polymer concentration is high, the

mentioned path passes through the binodal curve above the critical point. In this case, nucleation of the polymer-lean phase may occur (Aroon et al. 2010).
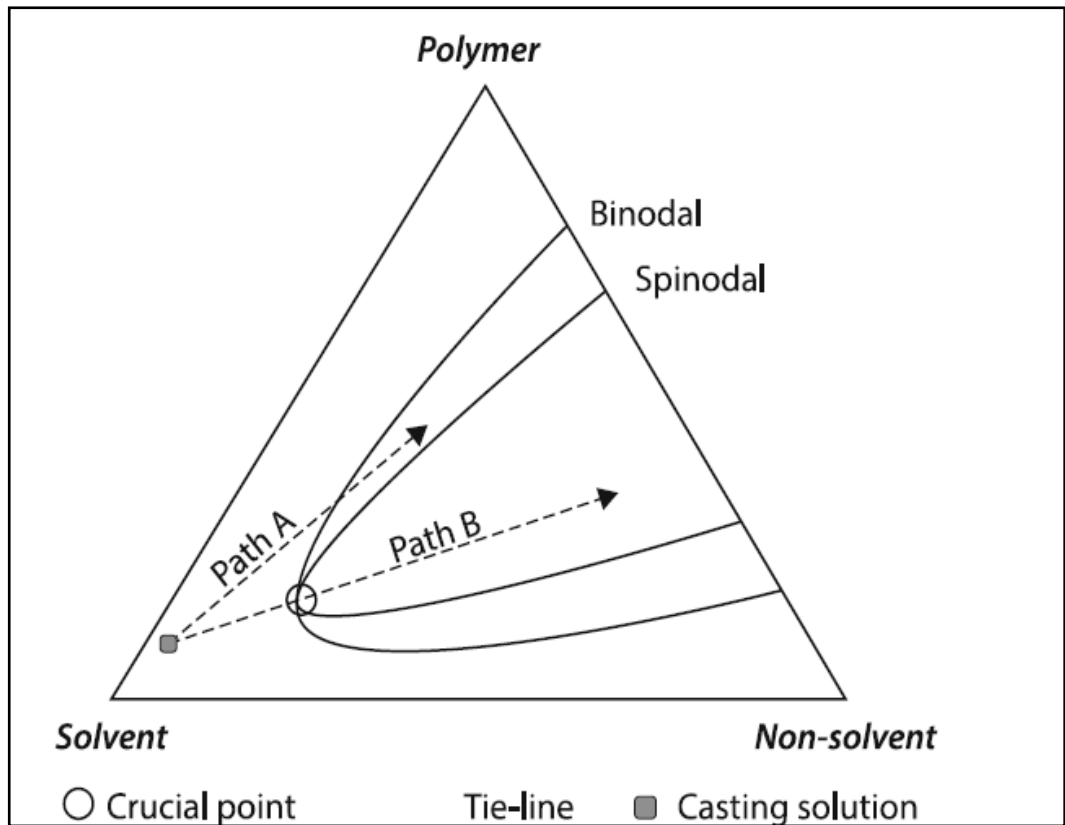
Figure 2.2 : Ternary diagram of polymer/solvent/ non solvent (Machado et al., 1999)

2.2.   Humic Acid

Humic acids (HA) are widely existed in the environment, such as in groundwater, surface water, drinking water, and soil (Han et al., 2014). HA is a heterogeneous mixture of many compounds, a mixture of weak aliphatic and aromatic organic acids, which are not soluble in water under acidic conditions but are soluble in water under alkaline conditions (Cacco and Dell'Agnola, 1984), that formed due to bio-chemical degradation of plants and animal residues (Feng et al., 2007). HA is produced commercially and intended for organic fertilization. Its components improve soil fertility and increase nutrients availability, enhance plant growth, yield, and decrease the harmful effect of stresses through various mechanisms inside plants and soil (Unlu et al., 2011; Moraditochaee 2012).

Although HA has been proven to be useful in agricultural sector, but these molecules could also cause some adverse environmental consequences due its characteristics. For example, HA molecules could bring undesirable color, odor and taste to drinking water (Bond et al., 2010). Due to amorphous, hydrophilic, acidic nature and dispersive molecular weights of HA, some complicated chemical and physical processes can be generated. For instance, various functions on the surface of HA become easily complex with metal ions in the water. Moreover, HA can be adsorbed on the surface of colloid granules to form a protective organic film, which greatly enhances the stability of colloid granules. These factors provide grounds to give the removal of HA from water high priority (Feng et al., 2007)

Blackfoot disease which prevails in south western Taiwan is associated with the daily intake of high concentration HA in artesian well water (approximately 200 mg/L) to be the root cause of the disease (Lu et al., 1988). It is believed that HA

initiates growth arrest and apoptosis in fibroblasts. As a result of these potential threats to human health, the removal of HA from drinking water is crucial to maintain human health. (Sudoh et al., 2015).

There are several methodologies which have proven to be very useful to remove HA from water such as oxidation, electrocoagulation, photocatalysis, membrane technology, activated carbon adsorption, coagulation, and biosorption have been widely used for the removal of HA. However, one of the disadvantages of HA removal process is the high operational cost, especially in the application of membrane technology. This is because of HA tendency to severely foul the membrane (Katsoufidou et al., 2010).

2.3.   Polymer Blending

The polymer blends can be classified as either miscible (homogenous) or immiscible (heterogeneous). Polymeric blends have been used to make high performance materials due to their high degree of simplicity and efficiency. Enhancement of characteristics of the final product can be achieved by blending these polymers with other materials which will combine the advantages of these individual materials. The additives can be classified as organic and inorganic. Organic additives are normally pore forming additives and non solvent additives. The most popular inorganic additives are NPs.

2.3.1.   Organic Additives

PEG and PVP which are known as pore-enhancing agents, Xu and Qusay (2004) tested different molecular weight of PEG and different ratio of PEG to PVP. As PEG molecular weight increases, pure water permeation fluxes increased but, rejections of proteins for PES/PEG hollow-fiber membranes were not significantly change. They also reported that in PES/(PEG + PVP) system, a decrease of PEG concentrations in the dope solution cause the permeation flux to decrease, whereas the addition of PVP in the dope solution resulted in more smooth surfaces (internal or external) of PES/(PEG + PVP) hollow-fiber membranes than those of PES/PEG hollow-fiber membranes.

The addition of NSA in the polymer solution has been shown to play an important role in the development of membranes with improved separation characteristics. In formulating these polymer solutions, it was recognized that the solution composition could be controlled to close to the point of phase separation by adjusting the addition of a NSA. Combination of non-solvent proved to be useful in the

formation of integrally skinned membrane. Kim et al. (2001) shows that combination of the ratio of diethylene glycol dimethyl ether (DGDE) to acetic acid (AA) can form the integrally skinned membranes exhibiting moderate pure water flux and high rejection rate of PEG 600.

While Feng et al. (2008) shows that different technique such as vapor induced phase separation (VIPS) process also can be utilized in fabricating the NSA modified membrane. Using diethylene glycol (DegOH) as NSA, when the mass ratio of NSA/S changes from 0.3 to 1, the precipitation rate decreased due to the increased viscosity of casting solution, the cross section morphology of the product membranes changed from macrovoid (finger like) to sponge like.

In this research acetone used as the NSA, few researchers have mentioned about acetone usage as NSA in their works. For example, Barth et al. (2000) studied the effect of small amount of acetone in PES/DMF membrane. Although the presence of 3 wt.% acetone in the 16 wt.% polymer solutions has no obvious effect on the cross-section structure of the membranes, but, they assumed based on their experience and taking into account the high volatility of acetone that more acetone will be lost by evaporation from the film's surface and this situation results in higher polymer concentrations in the upper layer of the membrane forming films and hence form a denser coating layer with smaller pores in the final membranes.

While Ahmed et al. (2013) who actually tested 20% PES in DMF solution with acetone content until 25 wt. % mentioned that PES/DMF/Acetone membrane exhibit thinner skin layer with slash-type macrovoids. They also mentioned that the presence of acetone, which is a co-solvent and a weak non-solvent for PES/DMF membrane, has brought it close to the cloud point axis and thus helps instantaneous

demixing, resulting in the formation of a thin skin layer. This proves that addition of non-solvent will alter the thermodynamic property of the solution that lead to different morphology of membrane. The paper also highlighted that this type of morphology influence the performance of membrane which lead to excellent rejection of solute with lower permeation.

NMP and acetone mixed solvent in PVDF membrane also proved to be useful in acetone and ethanol binary mixture separation via pervaporation. The membrane was fabricated using dry/wet method, before the membrane immersed in water coagulation bath, the nascent membrane together with the glass plate is undergo controlled evaporation of volatile latent solvent for 20 min at elevated temperature. Ong et al. (2011) came to conclusion that NMP/Acetone mixed solvent system, coupled with the evaporation of volatile latent solvents at elevated temperatures in this study resulted in asymmetric PVDF membrane consisting of (1) a dense skin layer, (2) no macrovoids, (3) open-cell structure, and (4) good mechanical strengths, for acetone and ethanol separation via pervaporation. They also formed a ternary phase diagram of the PVDF/solvents/water system at 25 °C, which shows that the polymer dope from a mixed solvent has drifted the phase separation line towards the solvent and polymer axis which means lesser amount of water is required to induce phase separation for PVDF/NMP/Acetone systems compared to that of PVDF/NMP.

Kim and Lee (2003) investigated about the effect of various additives such as 4-dioxane, Diethylene glycol dimethyl ether (DGDE), Acetone and γ-Butyrolactone (GBL) on pore size of polysulfone membrane by phase-inversion process. Solubility parameter , viscosity and coagulation value (CV) of the solvents are listed in this paper. As the solvent ratio of acetone increase in 15 wt. % PSf in NMP solution system, the

viscosity increase as the CV decrease. This results indicates that for acetone, the interaction between polymers decreased; instead, the interaction between polymer and solvent became greater. They also observe the top layer became denser and thicker with the presence of acetone and this increase the rejection rate. Kim and Lee implies that when a casting solution containing 1,4-dioxane, DGDE, and acetone is immersed in water, the inflow rate of coagulant will become slower compared with that of NMP alone cause dense and packed top layer which leads to higher rejection. Among all the stated additive, acetone result in highest rejection with ratio of acetone to NMP of 0.5:1 and 1:1.

Sometimes acetone is tested in the presence of another additives to enhance the permeation, rejection and as well as the antifouling property of membrane. Aryanti et al. (2013) added PEG and acetone as additives in polysulfone membrane with DMAc as solvent. Both pure water flux (PWF) and peat water flux were increased by increasing of PEG concentration in membrane solution. The water flux believed to be increased because of the addition of hydrophilic material which improves hydrophilicity of membrane. Antifouling performance of polysulfone membrane was characterized by measuring water flux recovery ratio (FRR) which is increase as the PEG concentration increases., however, too much of PEG increases irreversible fouling in membrane structure due to more open pore formed in the skin layer. At the same time, increase the acetone concentration in membrane leads to increase in HA rejection and also reduce in irreversible fouling due to formation of tight skin layer.

Table 2.1 : Summary of effect of acetone on membrane morphology and performance

Parameters	(Ahmed et al., 2013)	(Idris and Ahmed 2007)	(Aryanti et al., 2013)	(Kim and Lee 2003)
Polymer	PES	PES	PSf	PSf
Polymer (wt. %)	20	20	20	15
Solvent Type	DMF	DMF	DMAc	NMP
Acetone dosage (wt. %)	0, 20, 21,22,23, 24 and 25	17	0,2,4,6,8 and 10	28, 43 and 57
Additives	-	$LiClH_2O$ (4wt%)	PEG (0-25wt%)	-
Membrane type	Not specified	Not specified	UF	Not specified
PWF	Increase until 23 wt.% of acetone	Membrane with $LiClH_2O$ shows highest PWF	Increasing PEG concentration with acetone, increases water flux.	Not tested
Rejection	Excellent rejection of PEG at 22 wt. % of acetone and decrease afterward	Membrane with $LiClH_2O$ shows highest rejection rate.	Highest rejection of HA at 8 wt.% f acetone	Rejection of PEG 3500 is higher when NMP/acetone ratio 1:1
Membrane morphology	Thinner skin layer with slash-type macrovoid	Acetone produce thinner skin layer compared to acetone+$LiClH_2O$	Tight skin layer	Denser and thicker top layer

2.3.2. Inorganic Nanoparticle Additives

Recently, scientists have come up with the research of modifying conventional polymeric membranes with NPs, where in NPs are incorporated into/onto membranes. Various nanomaterials like carbon based nanomaterials, metal and metal oxide NPs, organic NPs, water channel proteins and metal organic framework are can be incorporated in membrane to enhance membrane's solvent permeability, solute selectivity, structure stability and antifouling property

Carbon based nanoparticle such as carbon nanotubes (CNTs) is tested by Celik et al. (2011). According to their research, functionalized multi-wall carbon nanotubes (MWCNTs) in PES membrane increased the membrane roughness, hydrophilicity, porosity, and PWF. Moreover, it was found that amount of MWCNTs in blending the determines the morphology and the separation properties of membranes. The membrane with MWCNTs also proved to have superior fouling resistance.

Combination of carbon based and metal based NPs is also possible as Vatanpour et al. (2012) showed in their research. They combine TiO_2 and CNTs in PES membrane to investigate about their antibiofouling property. The fouling resistance and flux recovery ratio of TiO_2 coated MWCNTs membranes revealed that coating of MWCNTs with TiO_2 had a synergistic effect and improved the induced effect of photocatalytic activity. The synergistic effect of coupling NPs leads to superior antibiofouling property of TiO_2–MWCNTs compared to the bare TiO_2.

Other metal based NPs like silver also proven to be an effective antibiofouling agent (Salomoni et al., 2017). This is very interesting result that the presence of 10 wt. % silver NPs in PES membrane does not improve the membrane

rejection and flux, but upon antibiofouling test of the membranes, the colonies of Pseudomonas were almost killed after cultivation in the PA/Ag membranes. The authors also stated that Ag NPs played a crucial role as a bactericidal effect for bacteria cells and thus preventing the biofouling of the membranes, but the toxicity of silver particle and suitability of that particle in water treatment are not mentioned in the paper.

TiO_2 has attracted considerable attention of researchers because of its stability, commercial availability, and ease of preparation. Sotto et al. (2011) tested effect of TiO_2 in the presence of ethanol (EtOH). The presence of TiO_2 and TiO_2+EtOH hardly affect the rejection of membrane, but addition of ethanol helped to improve the fouling resistance of membrane. Comparing both effects of TiO_2 and EtOH, it is evident that the addition of nanoparticles has a larger impact than the EtOH effect, especially for gel formation resistance that does not change by the EtOH effect. However, the foulant adsorption (R_f) is less pronounced for membranes synthesized with ethanol as co-solvent.

TiO_2 is known as excellent fouling resistance agent which is confirmed by many researchers (Li et al., 2009; Hamid, Ismail et al., 2011). But, Balta et al. (2012) considered ZnO as an excellent competitor to TiO_2 as an antifouling material. They experimented by blending wide range of ZnO nanoparticles concentrations (0.035–4 wt. %) in PES membranes manufactured by diffusion induced phase inversion in NMP. As the ZnO concentration increase, the hydrophlicity did not change significantly but even the ultra-low concentration of 0.035 wt. % of ZnO can drop the contact angle significantly compared to membrane without ZnO. Water permeability is directly related to hydrophilic condition of membrane and this is

reflected in the result of the experiment that they observe higher permeability for the higher ZnO concentration. Fouling resistance in these membranes are tested using 5 mg/L of humic acid. The relative flux of humic acid tested for 25 h and there was a 23 % increment in permeate flux at just 0.5 wt. % ZnO compared to the neat membrane. The same scenario also observed with PES/TiO$_2$ membrane in another paper written by Wu et al. (2008) but, the concentration of TiO$_2$ used there was five times higher than proposed in Balta et al. to achieve the same amount of increment in flux. Thus, ZnO also possess some advantage over TiO$_2$ and ZnO potential should be explored more in the future.

Leo et al. (2012) also studied the effect of zinc oxide concentration in PSf membrane with PVA as pore forming agent. The addition of ZnO into PSf membranes causes the mean pore size of the composite membranes to be larger than the mean pore size of neat membrane. In term of fouling of oleic acid, membrane which incorporated with ZnO exhibit less decline in permeate flux. In this experiment, PSf membrane with 2 wt.% of ZnO NPs show the smallest pore enlargement, the greatest hydrophilicity enhancement, the highest water permeability and most importantly the least flux decline in the filtration of aqueous solution containing oleic acid.

Shape of nanofiller also influence characterization and fouling resistance of membrane as shown by Rajab et al. (2015). The difference between the performance of nanorod and normal NPs ZnO in PES membrane with 2 wt. % PVP is investigated. The nanorod shape ZnO is observed to induce a more serious increment in the PWF and antifouling capability of the MMM due to the particular surface characteristics of

the nanorod shape even with a very low content of the embedded nanofiller (around 0.01 wt. %).

The ZnO-NPs also used with NSA as Liang et al. (2012) modified PVDF membrane with 0 wt. % to 4 wt. % of ZnO in presence of glycerol and PVP. The tensile strength of 2 wt. % ZnO and 3 wt. % ZnO almost doubled compared to the neat membrane. Water permeability ratio and FRR is significantly improved with the addition of ZnO and another interesting finding is that all the nano-ZnO modified membrane possessed 100% recovery after the physical cleaning, whilst neat membrane only recovered by about 78%. It demonstrated that the nano-ZnO modified membranes were successfully endowed with vital properties of anti-irreversible fouling.

2.4.   Pore Blocking Model

Pore blocking is one of the major factors that influence the overall performance of membrane filtration systems. Pore blockage leads to a large resistance to filtration, give significant decline in the filtrate flux rate under constant pressure conditions and a severe increase in the pressure for operation under constant flux conditions during membrane filtration (Iritani, 2013). In membrane filtration work, blocking filtration laws are widely used to interpret the membrane fouling. Over past decades a lot of researchers have been developed a number of mathematical expressions to describe the fouling of filter media due to pore plugging and cake formation during liquid filtration. Among the pioneers to develop the blocking laws of membrane filtration are Hermans and Brede´e (1936). Subsequently, Grace (1956) elucidated filter performance using these blocking laws followed by Hermia (1982) re-derived the four blocking laws for filtration using Newtonian and

non-Newtonian fluids. The 4 classical blocking filtration laws describe these 4 distinctive fouling mechanism of membrane : complete blocking, standard blocking, intermediate blocking and cake filtration (Zheng et al., 2018) .
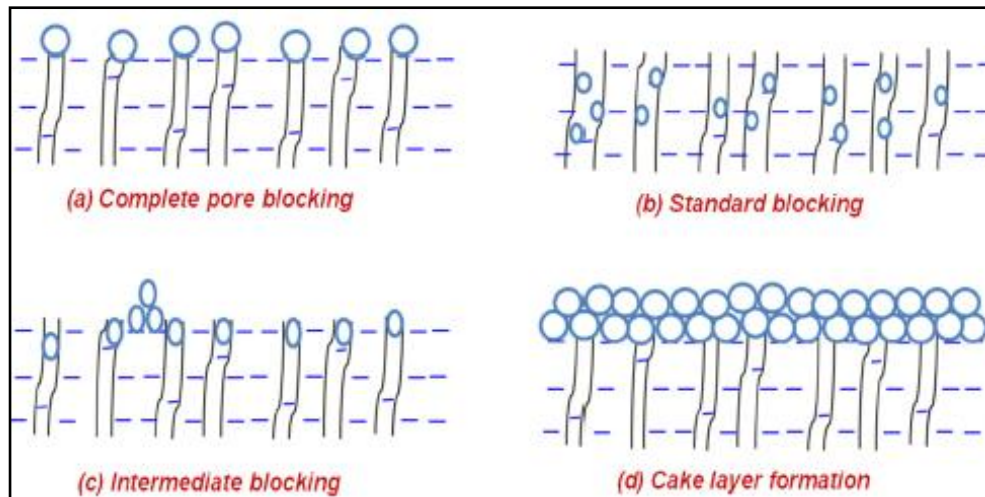

(a) Complete pore blocking

(b) Standard blocking

(c) Intermediate blocking

(d) Cake layer formation

Figure 2.3 : The schematic drawing of 4 pore blocking models

In complete pore blocking, all particles depositing on membrane surface only involve in ''sealing'' of membrane pores. Normally with the complete blocking law based on pore sealing, it is assumed that each particle reaching an open pore in a membrane with parallel pores of constant diameter and length seals the pore opening completely without superimposing over other particles. While, standard blocking are normally known as inner pore adsorption, internal pore blocking is due to constriction of membrane pores caused by small particles attached into pore walls. For intermediate pore blocking, each particle depositing on membrane not only cause pore blocking, but also attach on other particles on membrane surface. The irregularity of pore passages causes the particle to become tightly fixed blinding the pore (de Barros et. al. 2003) . In the case of cake formation, particles do not participate in any changes of membrane pores. A cake layer forms outside the external membrane and increases hydraulic resistance.

CHAPTER 3 : MATERIALS AND METHODS

3.1.   Introduction

This chapter briefly discussed about the materials, chemicals and equipment used in this experiment. The overall experimental flowchart, experimental procedure and methods used in this research also explained in this section. The beginning of this chapter highlighted about the properties of required materials and chemicals, followed by the experimental flowchart of the overall experiment. Then, the detailed procedures to fabricate PES/NMP/Acetone and PES/NMP/Acetone/ZnO flat sheet membranes are presented. The characterization as well as the performance evaluation methods of the membranes are outlined. The detail calculation of membrane performance and pore blocking modelling are explained at the end of this chapter

3.2.   Chemicals and Materials

Listed below are chemical and raw material used in the experiment.

Table 3.1 : List of chemical and raw material used in experiment

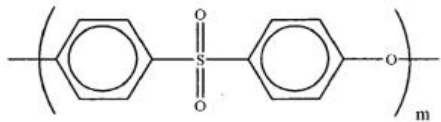| Chemical	Purity/Grade	Supplier	Purpose
Humic Acid (HA)	-	Sigma-Aldrich	Model solution.
Liquid Nitrogen	-	Wellgas, Malaysia	Membrane fracturing.
Polyethersulfone (PES)	Ultrason E6020P	BASF	Membrane polymer.
N-methyl-2-pyrrolidone (NMP)	99.50%	Sigma-Aldrich	Primary solvent for membrane polymer.
Acetone	99%	Merck, Malaysia	NSA for membrane polymer and also for cleaning.
Zinc oxide nanoparticle	99.50%	Sigma-Aldrich	Inorganic filler

Table 3.2 : The properties of PES

Properties	
Chemical Name	Polyethersulfone
Chemical Structure	
Molecular Weight	232.23 g/mol
Density	1.37 g/cm^3

Table 3.3 : The properties of NMP
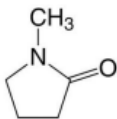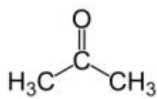
Properties	
Chemical Name	N-Methyl-2-Pyrrolidone
Chemical Structure	
Molecular Formula	C_5H_9NO
Molecular Weight	99.13 g/mol
Boiling Point	202 ^{o}C
Density	1.37 g/cm^3

Table 3.4. : The properties of Acetone

Properties	
Chemical Name	Acetone
Chemical Structure	
Molecular Formula	C_3H_6O
Molecular Weight	58.08 g/mol
Boiling Point	56 °C
Density	0.7845 g/cm^3

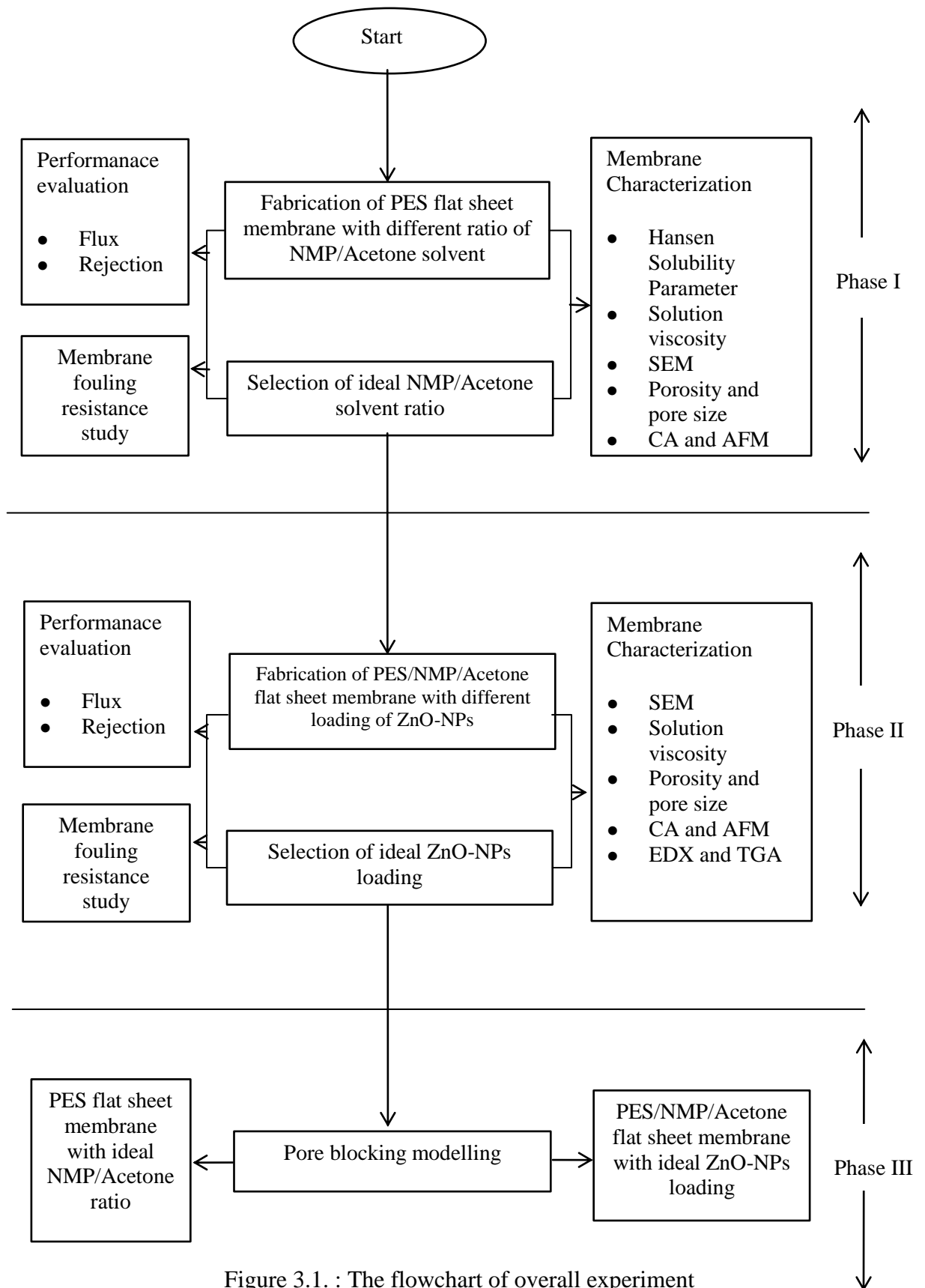## 3.3. Flowchart of the Experimental Activities

Figure 3.1. : The flowchart of overall experiment

3.4. Flat Sheet Membrane Production

In this section, the procedures for the preparation of casting solution and membrane casting process will be briefly discussed.

3.4.1. Casting Solution Preparation of PES/NMP/Acetone

The dope solution was prepared by blending the PES polymer in different ratio of NMP/Acetone solvent. The solution of NMP and acetone with different ratio was prepared . The solution was mechanically stirred at 600 rpm for 1 h and then dried PES polymer was added slowly in the solvent over a period of 2 h. The solution was kept under mechanical stirring of 500 rpm at temperature of 50°C for 24 h. To remove bubbles in the solution, the dope solution is degassed by placing the solution in an ultrasonic bath for 1 hour.

Table 3.5 : Composition of casting solution of PES/NMP/Acetone

Membrane	PES (wt. %)	NMP (wt. %)	Acetone (wt. %)
PA1	18.00	82.00	0
PA2	18.00	77.90	4.10
PA3	18.00	73.80	8.20
PA4	18.00	69.70	12.30
PA5	18.00	65.60	16.40

3.4.2. Casting Solution Preparation of PES/NMP/Acetone/ZnO

After the ideal Acetone/NMP ratio is obtained, the dope solution with different loading of ZnO-NPS was prepared using that ideal ratio of Acetone/NMP. The dope solution was prepared by disperse various amount of NPs (ranging from 0