The modification of polyethersulfone polymer membranes by incorporating functional ZnO nanomaterials

T.D Dipheko

Student number: 22603395

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Faculty of Agricultural, Science and Technology

Supervisor: Dr. M. Klink

Co-supervisor: Dr. R. Moutloali

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Declaration

I hereby declare that the dissertation entitled "The modification of polyehtersulfone membranes by incorporating functional ZnO nanomaterials" submitted to the Department of Chemistry, North West University, Mafikeng Campus in the fulfilment of the requirements for the degree *Magister Scientiae* in Chemistry is the original Research work conducted by myself under the supervision of Dr. M. Klink and Dr. R. Moutloali. None of this Research work has been submitted by any student, at the North West University or any other University.

Signature of candidate 

University number 22603395

Signed at NWU-MFK this 30 day of September 2016

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Abstract

The study addressed the modification of polymeric membranes (polyehersulfone, PES membranes) by incorporating functional nanomaterials to form nanocomposite membranes. The aim of the study was to improve the performance of polymeric UF membranes. The membranes were prepared using phase inversion via immersion precipitation method. ZnO (0.0, 0.5, 1.0, 1.5 and 2.0 wt%) nanomaterials were used as functional nanoparticles, PES (18 wt%) as polymeric material, PVP (2 wt%) as pore forming agent and N, N-Dimethylacetamide (DMAc) as solvent for this study. The membrane performance was studied by dead-end filtration cell and the hydrophilicity of the membranes by contact angle (CA) studies. The XRD analysis was employed to ascertain if ZnO nanoparticle remained in the ZnO/PES nanocomposite membranes.

The flux and flux recovery results revealed that the incorporation of ZnO nanoparticles (0.5 to 1.5 wt%) on the polymeric membranes improved membranes performance and yield more flux than unmodified PES membranes. AFM studies showed that addition of ZnO nanoparticle on polymeric membrane preparation solution improved the roughness of the membranes, and SEM studies revealed that as more ZnO nanoparticles was loaded on the membranes casting solution, more nanoparticles were found on the membrane surface and membranes morphology is improved. CA measurements indicated that the hydrophilicity of the membranes if improved, CA values decreased from 87.24° to 35.68°, therefore hydrophilicity and membranes performance are improved. Thermal stability of prepared membranes was studied by simultaneous thermal analyser (STA) and results revealed that as more nanoparticles are added, the decomposition is delayed and ZnO nanoparticles absorbed more heat, hence the delay in membranes decomposition. The modification of the polymeric membranes by incorporation of functional nanomaterial improves membranes performance and hydrophilicity.

Keywords: *Incorporation, PES, DMAc, PVP, hydrophilicity, nanocomposites, ZnO nanoparticles, phase inversion via immersion precipitation, ZnO, Absorbed.*

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List of abbreviations and symbols

A	Membrane area
AFM	Atomic Force Microscopy
BSA	Bovine Serum Albumin
CA	Contact Angle
c_f	BSA concentration of the feed solution
c_p	BSA concentration of the permeation solution
cm^2	Centimetre square
°C	Degree Celsius
CNTs	Carbon nanotubes
DMAc	N, N-Dimethylacetamide
DMF	Dimethyl formamide
DMSO	Dimethylsulfoxide
F	Flux
FR	Flux recovery
g	Grams
GS	Gas Separation
h	Hours
J_{ww}	Pure water flux of fouled membrane
J_{wi}	Pure water flux of virgin membrane
kV	Kilovolts
kPa	Kilopascals
L	Litres
NaOH	Sodium Hydroxide
NF	Nanofiltration
NOM	Natural Organic Matters
NMP	N-methyl-pyrrolidinone
mA	Milliampere
mL	Millilitre
mm	Millimeter
M_w	Molecular weight
nm	Nanometer

MF	Microfiltration
PEI	Poly(ether imide)
PES	Polyethersulfone
PSf	Polysulphone
PVDF	Polyvinylidene Fluoride
PVP	Poly(vinylpyrrolidinone)
R	Rejection
RO	Reverse osmosis
SEM	Scanning Electron Microscopy
STA	Simultaneous Thermal Analyser
t	Time
T_d	Decomposition Temperature
TFC	Thin Film Nanocomposite
TiO_2	Titanium Oxide
UF	Ultrafiltratiom
XRD	X-ray Diffraction
λ	Wavelength
V	Permeate volume
ZnO	Zinc Oxide

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Chapter 1

1.1 Introduction

Over 70% of the Earth's surface is covered by water; most of it is unusable for human consumption. Freshwater lakes, rivers and underground aquifers represent only 2.5% of the world's total freshwater supply. Unfortunately, in addition to being scarce, clean water is also very unevenly distributed.[1]

Clean water is essential to human life and is a critical feedstock in a variety of key industries including electronics, pharmaceuticals and food. The world is facing formidable challenges in meeting rising demands for clean water as the available supplies of freshwater are decreasing due to; [2]

- population growth,
- more stringent health-based regulations,
- competing demands from a variety of users, and
- extended droughts.

It has been estimated that around 700 million people in 43 countries suffer today from water scarcity. It is also estimated (Figure 1) that, by 2025, 1.8 billion people will be living in countries or regions with absolute water scarcity and two-thirds of the world's population could be living under water stressed conditions.[3] With the existing climate change scenario, almost half the world's population will be living in areas of high water stress by 2030, including between 75 million and 250 million people in Africa. In addition, water scarcity in some arid and semi-arid places will displace between 24 million and 700 million people. Sub-Saharan Africa, which includes South Africa, has the largest number of water-stressed countries of any region.[4]

With only 3% of all available water on the planet being fresh water, seawater is the most abundant available source of drinking water and water for industrial use in many regions.[3] The innovations in the development of novel technologies to desalinate water are among the

most exciting and promising. In previous years nanotechnology has been investigated as one of techniques of water purification.[5]

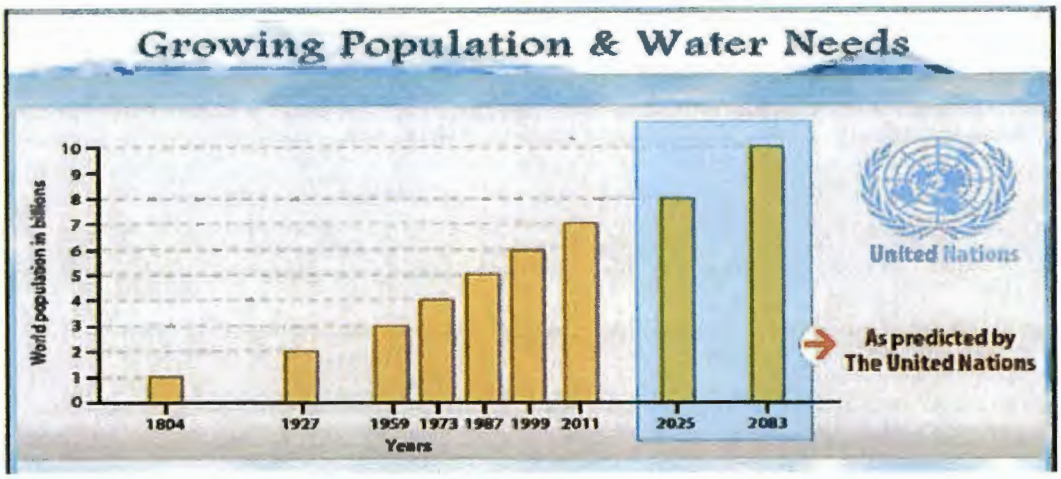

Figure 1.1: Growing population and water needs.[6]

The investigation and the development of nanomaterial technology in terms of their application for matrices are very important, and have recently raised a significant interest in various branches of industry for the fabrication of new types of microelectronic devices.[7] Nanostructured semiconductors have recently experienced exponential attention because of their interesting and widespread applications which are due to their unique size and shape dependent properties.[8,9]

The properties of materials can be different at the nanoscale for two main reasons, namely: [10]

- Quantum effects that dominate the behaviour of matter at the nanoscale, affecting the optical, electrical and magnetic behaviour of materials; and
- The nanomaterials have a relatively larger surface area when compared to the same mass of the same material produced in larger form. This results in the materials being more chemically reactive, in some cases materials that are inert in their larger form are reactive when produced on the nanoscale.

Recent advances suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration or other products resulting from the development of nanotechnology. Innovations in the development of novel technologies to desalinate water are among the most exciting and promising.[11] The utilization of specific

nanoparticles either embedded in membranes or on other structural media that can effectively, inexpensively and rapidly render unusable water potable is being explored at a variety of institutions.[12]

A membrane is a thin barrier that permits selective mass transport.[13] Membranes can be fabricated from a wide variety of organic (e.g. polymers, liquids) or inorganic (e.g. carbons, zeolites) materials. In modern days, the majority of commercial membranes are synthesised from polymers.[14] Membrane material and membrane structure are some of the factors that control the properties of a membrane.[15] Membrane performance depends on the properties of the surface. As such, much attention has been given to membrane surface modification. For membranes to be useful in an industrial separation process, they should obey the following characteristics; [16]

- ability to be packaged into high surface area modules,
- tolerance to all feed stream components (fouling resistance),
- manufacturing reproducibility,
- high selectivity (rejection),
- high flux,
- tolerance to temperature variations,
- mechanical stability, and
- low manufacturing cost.

The use of nanotechnology in the textile industry has increased rapidly. This is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects; they will lose their functions after laundering or wearing.[17] Nanomaterials can provide high durability for treated fabrics, with respect to conventional materials, because they possess large surface areas and high surface energy that ensures better affinity for fabrics and leads to an increase in durability of the textile.[18] Nanotechnology is the collection of procedures for manipulating matter on the length scale between 1 nm to about 100 nm, it also studies the material with morphological features on the nanoscale and the formation of nanostructures.[19]

1.2 Problem statement

Over decades of application in daily life and industries, water pollution has increasingly a more serious problem. Therefore, membrane separation techniques play an important role in water treatment. It follows that, because of the increasing population around the world, water demand is increasing as not all groundwater can be used for daily life and for some activities because of its quality. This has led to the employment of methods employed to improve water quality, such as membrane modifications.[20]

Nanotechnology holds the promise of both incremental improvements of existing products and the potential for revolutionary changes that could transform industries and create entirely new ones. The government and the private sector have invested much money on nanotechnology research. Early applications of nanotechnology are already yielding dividends on those investments. Recently, it has been noticed that membrane fouling plays a role on the separation methods. Therefore, membrane modification has been employed to overcome such fouling on separation methods with the incorporation of nanomaterials being one of the promising solutions to fouling.[21]

Progress has been made in the recent years regarding the development of tailor made polymers having higher selectivity and permeability than current available commercial membrane materials.

Developments in the modification of polymer membranes are mainly for the treatment of membrane surfaces, that is, to reduce membrane fouling. This membrane fouling can be caused by some of the following: [22]

- The attachment of bacteria and subsequently colonization on the membrane surface (biofouling); and
- Plugging of the pore openings at the porous membrane surface by the suspended solid particles or large solutes in the feed.

1.3 Aim and objectives

1.3.1 Aim

The purpose of the study was to develop polymeric membranes (PES membranes) with improved antifouling properties than the current commercial membranes for selective removal of specific toxic metals from wastewater.

1.3.2 Objectives

The objectives of the study were to:

- Develop a synthetic route for the production of zinc oxide with the substrate nanomaterial with enhanced conductivity, compatibility and increased surface area with excellent catalytic efficiency.
- Fabricate polymer membranes into which ZnO nanomaterials were incorporated in PES membranes to form PES/ZnO nanocomposite membranes. The ZnO nanoparticles were synthesised to produce composites with antimicrobial action in order to reduce biofouling properties).
- Test the performance, antifouling properties and rejection capabilities of modified PES membranes by performing pure water permeation studies before and after protein filtrations.

1.4 Outline of the thesis

Chapter 1 introduces the reader to a general overview of the basic significance of the background to the study, the problem that the research seeks to solve aim and the research objectives.

Chapter 2 Presents the literature review for the study. The literature review communicates current and previous studies that have been conducted relating to zinc oxide nanoparticles and membranes across the world.

Chapter 3 outlines the research methodology followed in the study. The rationale, research design and analysis followed in the current study are covered. The aspects to be covered are research design, sampling, measuring instruments and data analysis.

Chapter 4 deals with the results of the study and their interpretation to the objectives of the research as indicated in Chapter 1

Chapter 5 presents the conclusions drawn from this study.

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Chapter 2

Literature review

2.1 Introduction

Chapter 1 provided an introduction to the study its significance and background. The problem statement and research objectives were also presented. In chapter 2 membrane technology is discussed in detail, with reference to factors that influence membrane fouling as well as how to improve membrane fouling resistance by membrane modification.

2.2 Membrane technology

Membrane technology has become the most popular method for separation processes (**Figure 2.1**). It is known as a key step in food packaging, bio-separations, water treatment, and gas separation, among others.[1] The advantage of membrane technology over other filtration techniques are that it can be used with or without the addition of chemicals. The process uses relatively little energy mostly the low pressure driven membranes, and can be operated with ease and under well-arranged process conditions.[2, 3]

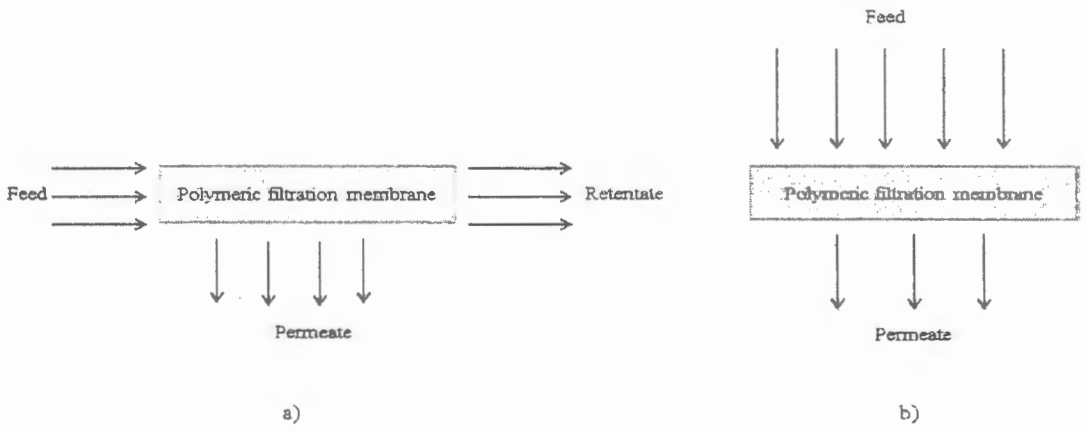


Figure 2.1: The schematic of polymeric membrane designs; a) cross-flow filtration, b) dead-end filtration.[3]

Researchers are making materials such as nanofibers, polymer nanocomposites and carbon nanotubes (CNTs) with controlled shape, pore size, and suitable dimensions for filtration

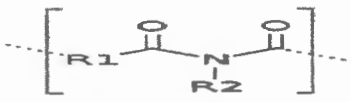
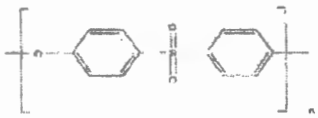
applications.[4] Studies have shown that modified polymeric membrane have higher water fluxes and rejections of pollutants than unmodified polymeric membranes.[5]

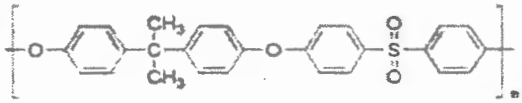
2.3 Factors that influence membrane morphology

2.3.1 Selection of polymer for membrane synthesis

A polymer used for membrane synthesis has a greater influence on membrane performance and membrane morphology. It has been reported that, polymers used as membrane materials are tough amorphous thermoplastics. They have a glass transition of near 50 °C above the end-use temperature but are not brittle because the membrane might break during handling.[6] **Table 2.1** illustrates some of polymer materials commonly used for synthesizing filtration membrane synthesis. Among the list of polymeric material, PES, which is largely employed for ultrafiltration (UF) was used in this study. Researchers reported that, PES dissolves in most solvents and is often blended with other polymers.[7] This makes the membrane hydrophilicity.

Table 2.1: Common polymers used for production of membranes.[7, 8]

Polymer type	Structure	Membrane type
Polyvinylidene fluoride (PVDF)		Microfiltration (MF) Ultrafiltration (UF)
Aromatic polyimide		Reverse Osmosis (RO)
Polyethersulfone (PES)		Ultrafiltration (UF) Microfiltration (MF)
Poly(ether		Gas separation (GS) Ultrafiltration (UF)

imide) (PEI)		
Polysulphone (PSf)		UF RO

2.3.2 Selection of organic solvent

The choice of solvent used for depends on the type of polymer selected for filtration membranes. Some polymers dissolve in certain organic solvents at given temperature.[7] The chemicals structures of common and widely used solvents are shown in **Figure 2.2.**[9] The use of combination of solvents has been adopted in order to alter the anisotropic structure of the membrane. Researchers have found that a rapid and slow precipitation is induced. This method was successfully employed when using dimethyl formamide (DMF) and N-methyl-pyrrolidinone (NMP) solvents. DMF is responsible for the formation of sponge-like voids while NMP is responsible for the formation of finger-like voids in the internal structure of the membrane.[10] The variation of surface pores formed on the PES membranes skin layer using these organic solvents was due to a different response to thermodynamic properties of the system and formation of the polymeric membranes. In this study water was used as a solvent and N, N-Dimethylacetamide (DMAc) as organic solvent, during the phase inversion by immersion process.[11]

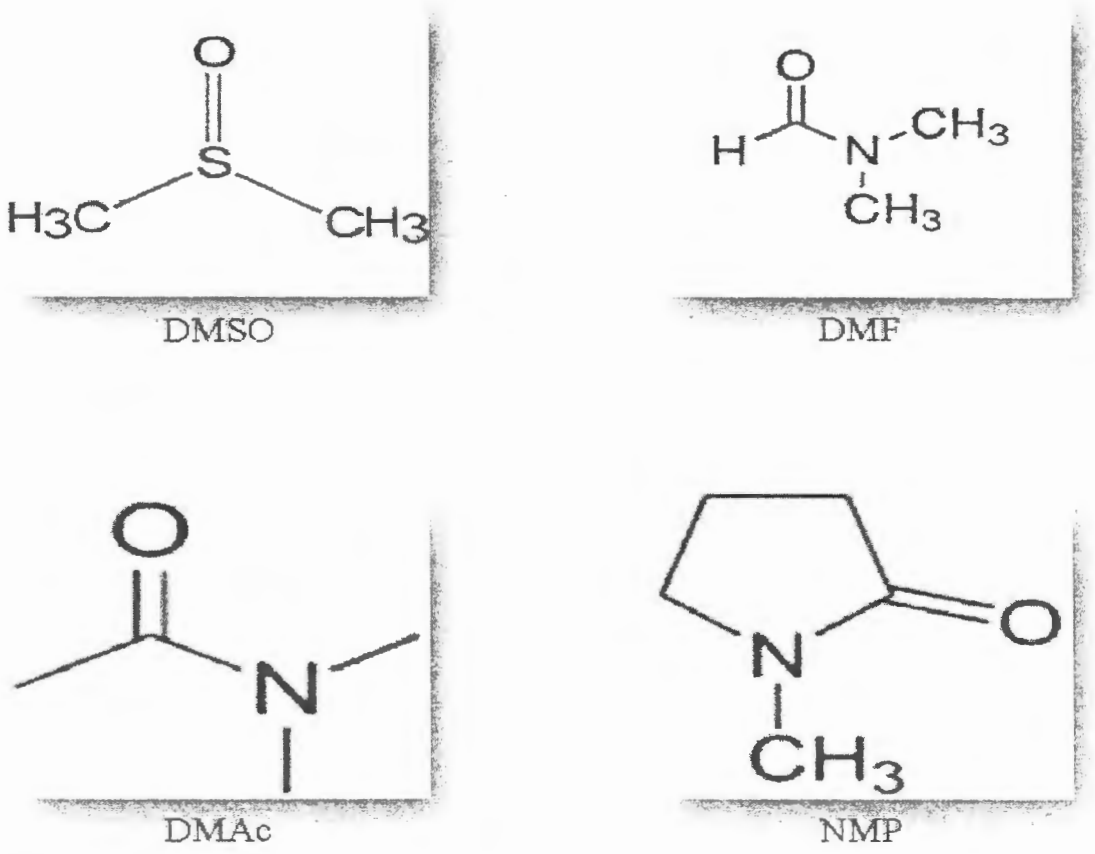


Figure 2.2: Chemical structures of widely used organic solvents.[12]

2.4 Polyethersulfone (PES) properties

PES is a common polymer for preparing ultrafiltration membranes due to its high glass transition temperature (T_g~220 °C), chemical stability against caustics, acids and other aggressive substances as well as high values of tensile strength and elongation at break.[13] In comparison to other polymers with similar or even superior properties, PES (**Figure 2.3**) is a standard material for many membrane manufacturers due to its availability in well-defined qualities. The main disadvantage of PES is the high hydrophobicity of the prepared membrane. Its membrane surface properties often cause intense fouling when solutions containing substances like proteins are filtered. Accordingly, the modification of PES membrane is required for reducing the membrane fouling.[14]

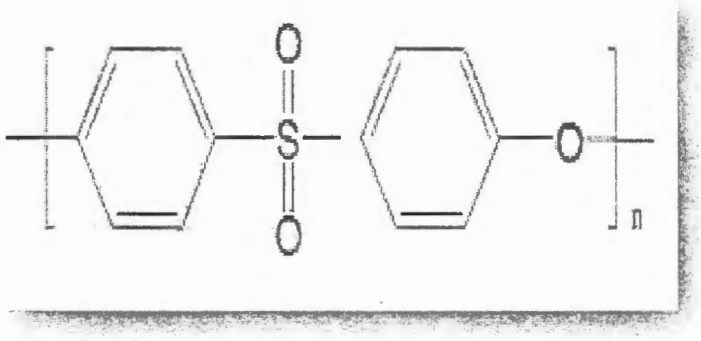


Figure 2.3: Chemical structure of PES.[15]

2.5 Properties of zinc oxide

Zinc oxide, (ZnO) has been synthesised as a nanostructured semiconductor which possesses a wide band gap (3.37 eV) with a large excitation binding energy of about 60 meV at room temperature.[16] The oxide has therefore become one of the most important electronic and photonic materials studied. It has attracted increasing interest due to its specific electrical, optoelectronic properties and wide potential application in luminescence, surface acoustic wave filters, piezoelectric transducers, actuators, gas sensors and solar cells.[13, 16] It has also attracted attention due to its wide application in environmental protection procedures such as air purification, hazardous waste remediation, water purification, and water disinfection.[14, 17]

The size and morphology of ZnO nanoparticles have a great impact on their performance and application aspects. Therefore, efforts have been made to synthesise ZnO with different nanostructures which include nanocubes, nanorods, nanowires, nanobelts, nanotubes, nanoflowers and nanosheets.[18] These morphologies were fabricated by synthetic, high temperature or long reaction time methods such as chemical vapour deposition, thermal decomposition, and thermal evaporation, sol-gel, and precipitation techniques.[19]

Nanoparticles having unique physico-chemical properties that differ from bulk materials are of interest in the manufacturing of membranes to achieve a high degree of control over membrane fouling and the ability to produce desired structures as well as functionalities.[20] Membrane fouling is the main problem that limits the use of membranes in a wide range of

applications from both an economic and a technical point of view. Nanoparticles may offer a key to resolve this problem.[21]

2.6 Zinc oxide polymer nanocomposites

The development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of industries.[22] Polymer nanocomposites have shown many advantages due to the smaller size of nanofillers which provide a large surface area. The reinforcement of fillers in polymers has played a major role in the polymer industry.[23, 24] Different types of nanofillers have been introduced to provide a synergetic enhancement in electrical and optical properties. A simple method for obtaining an organic–inorganic composite is the mixing of an organic polymer with metal oxide nanofiller followed by solution grown technique.[25, 26, 27] From the last few decades, ZnO has been known as a transparent electro-conductive and piezoelectric material. ZnO has many other promising properties which provide different applications.[47] ZnO nanoparticles were chosen as a filler and PES as a polymer matrix in the present study.[26, 28]

PES membranes have been widely used as membrane materials in many industrial fields due to their low cost, superior film forming ability, good mechanical properties, high thermal stabilities and outstanding acidic and alkaline resistance.[29] However, the major disadvantage of PES is its hydrophobic characteristic which makes it easy for pollutants to adsorb on the membrane surface and cause serious fouling behaviour.[30] Thus the current investigation to improve PES surface uses various methods such as low molecular weight hydrophilic polymer, inorganic additives and chemical modification such as grafting and crosslinking.[31] Blending inorganic additives such as titanium dioxide, silica, zinc oxide and silver oxide in the PES membrane was found to improve hydrophilicity and reduce the fouling properties of the membrane.[32, 33]

2.7 Classification of membranes

Membranes are classified by their rejection mechanism, composition, chemical structure, the geometry of construction and the force applied. The maximum permeate particles size is used as the most important measure and characterization parameter for classifying membranes.

Based on the permeate particles size measurement, there are four major classes of filtration membranes processes known;[34] These are discussed in the following sections.

2.7.1 Nanofiltration (NF)

NF is a crosss-flow filtration technology with nominal pore size of about 1 nanometre. NF membranes do not work according to the principle of pores as separation takes places by diffusion through the membrane. The pressure that is required for UF membrane is much higher than the pressure needed in UF and MF, while that for water flux is much lower.[1, 2, 34] It differs from RO in that the separation line is slightly lower. The dissolved materials in water are kept back by NF, and this happens in a lower process in RO. NF is used for the removal of pesticides from ground water, heavy metals from polluted water and in the softening of water.[35]

2.7.2 Microfiltration (MF)

MF is a membrane separation process with pore size of about 0.03 – 10 microns. The MF systems are designed to remove suspended solid down to 0.1 micrometres. It is very suitable for use in place of traditional clarifiers or as a pre-filter to water recycling or recovery RO system. It is also used as pre-treatment to surface water, seawater and biologically treated municipal effluent before RO and other membrane system. Its application includes the promotion of drinking water, irrigation and industrial water for re-use.[36]

2.7.3 Reverse osmosis (RO)

RO is a membrane process in which pressure is required to force water across a membranes, leaving the impurities behind. RO is a capable of removing 95 – 99% of total dissolved solids and 99% of all bacteria, thus providing safe and pure water. It uses a semipermeable membrane to separate and remove viruses and organics from water. The application of RO include processes involved in pure water production and in the concentration of molecular solvents for food and dairy industries.[35]

RO membranes are effectively nonporous and leave out particles that are of low molecular weight such as organics and ions. NF membranes which are also called Loose RO

membranes are porous and exhibit performance between that of UF and RO. The separation of solutes from water using selectively permeable membranes has proved to be effective and economical methods of water purification. The techniques of NF and RO involve the use of these membranes that are able to prevent migration of most dissolved salts, allowing passage of water through their pores.[37]

2.7.4 Ultrafiltration (UF)

UF is a separation technique using membranes with pore sizes ranging between 0.1- 0.001 microns. UF membranes remove substance of high molecular weight such as organic and inorganic polymeric molecules. Low molecular weight organics and ions such as sulphate, sodium and calcium are not removed by UF membranes. Its use includes electrode position point recovery, post-treatment of pure water production for microelectronics and bottled water fabrication. **Figure 2.4** summarises the maximum permeate particles size for each membrane process and the particles size of pollutants.[35, 38]

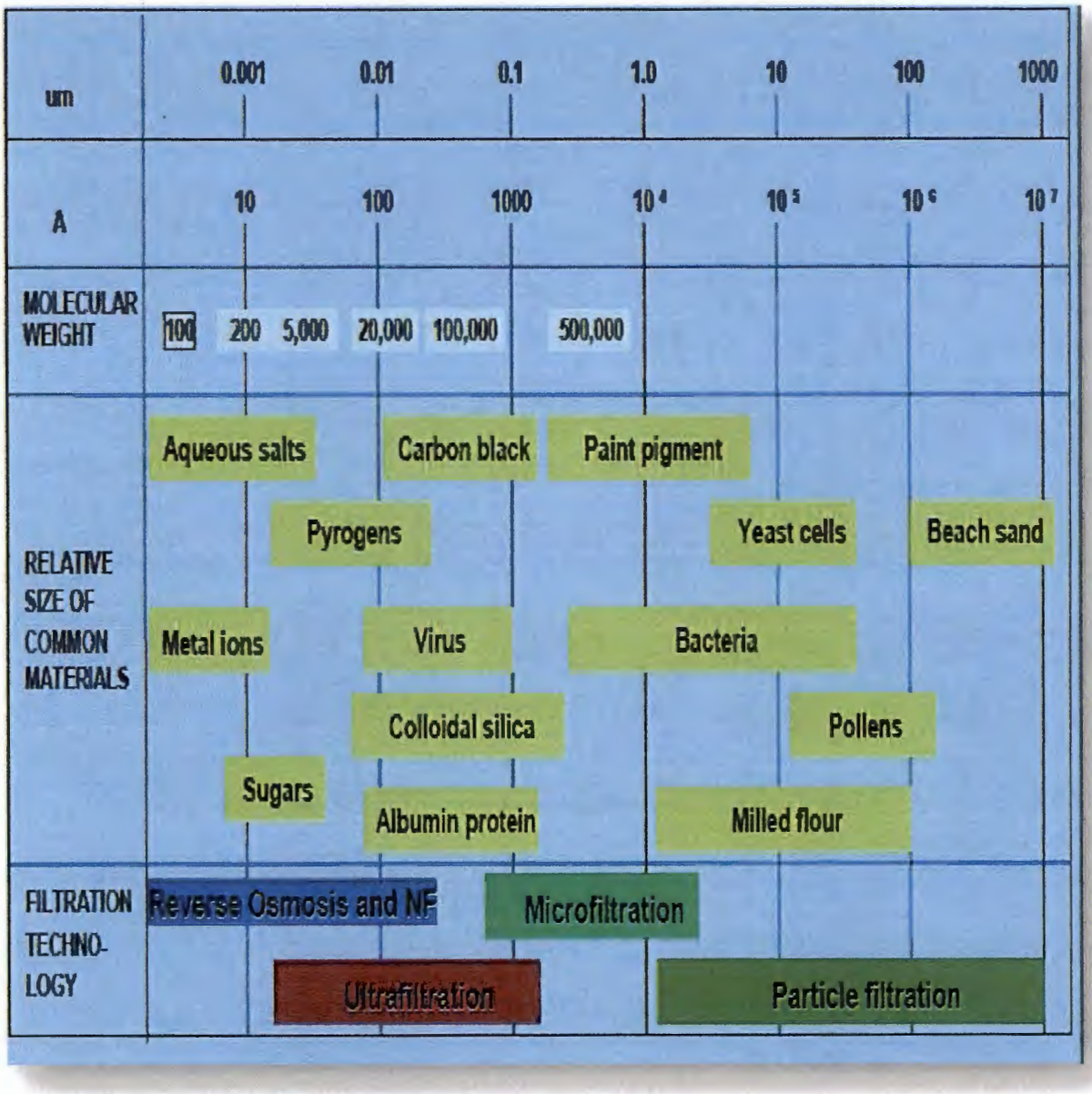


Figure 2.4: Filtration spectrum of the membrane separation processes.[39]

2.8 Preparation of NF membranes

There are different methods that are used to synthesis and fabricate NF membranes. NF membranes based on PVP and PES have been synthesised since the early 1980's[40, 41] The phase inversion method appears to be a method of choice in the fabrication of NF membranes due to its simplicity and flexibility.[42, 43] The phase inversion and other methods are discussed below.

2.8.1 Immersion precipitation

Immersion precipitation method is when a polymer solution is cast on a suitable support such as glass, then quickly immersed on a coagulation bath comprising a non-solvent. The phase separation occurs when the solvent and the non-solvent in the coagulation bath undergo an exchange. The process can be seen as a useful technique in the fabrication of NF membranes due to its simplicity.[44, 45]

2.8.2 Phase inversion process

Phase inversion process is a process where a viscous liquid polymer solution (casting solution) is transformed in a systematic manner from liquid into solid (i.e membrane). This process can be achieved in various ways being; [46]

- precipitation from vapour phase,
- thermally induced phase, and
- immersion precipitation.

It is reported that among the methods mentioned, thermally induced phase separation and immersion precipitation methods (**Figure 2.5**) find a greater use because of the simplicity of these processes.[47] The choice of a suitable solvent is one of the difficulties being experienced on casting a successful membrane through phase inversion.[48] Therefore, to ascertain which solvent works best, optimisation step must be investigated.

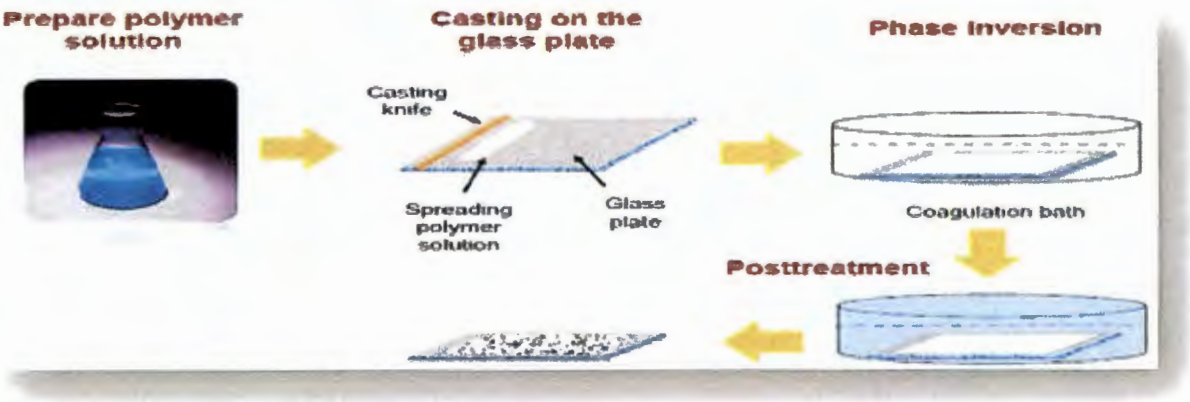


Figure 2.5: Schematic diagram of phase inversion via immersion precipitation method.[45]

2.8.3 Interfacial polymerisation

In the interfacial polymerization method, the process is executed by polymerization of two monomers that react in a dual phase system. The interface between the aqueous phase as well as the organic phase is called polymerization. The technique has enjoyed a widespread application in the preparation of thin film composite flat sheet membranes and is widely used as a reverse osmosis membrane.[49]

2.9 Membrane shapes

There are two known standard different membrane shapes, namely flat-sheet and hollow fiber membranes. Because of the different shapes, the procedure for their preparation is different. For the flat-sheet PES membrane, a phase inversion technique **(Figure 2.5)** is usually used.[50] The preparation is done by casting the polymer solution on the support material (i.e polymer, glass, metal), and after immersing into non-solvent (usually water), the flat-sheet PES membrane will be obtained.[51] The flat-sheet **(Figure 2.6)** membranes are more widely used because of their preparation is simpler.[50, 53]

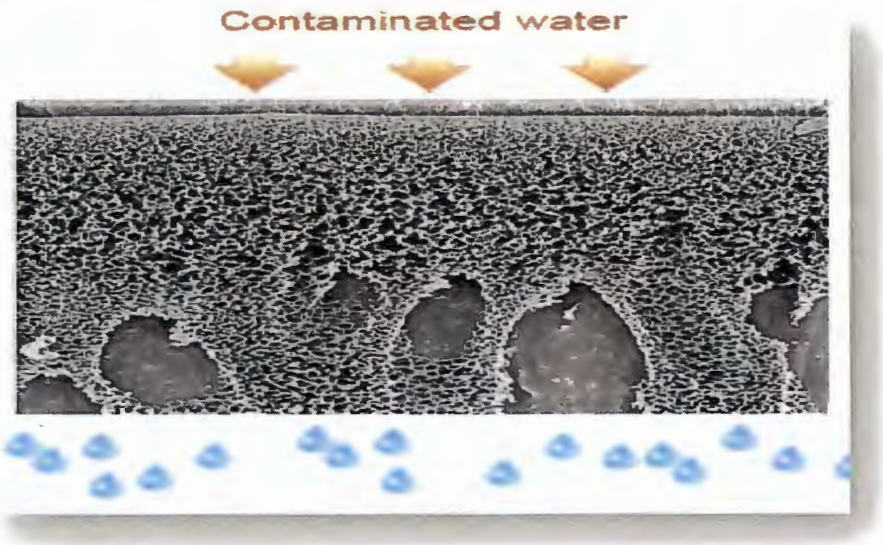


Figure 2.6: Schematic diagram of flat sheet filtration membrane.[53]

A hollow fiber PES membrane contains at least a spinneret and a take-up unit are needed. A dry-wet spinning technique is used to prepare the PES hollow fiber based on the phase inversion method.[52] There are two different shapes, flat-sheet and hollow fiber.

For industrial processes, hollow fiber membranes (**Figure 2.7**) are believed to be more effective and cheaper than flat-sheet membranes because their surface area or volume ratio is larger. However, for research purpose, flat sheet PES membrane are usually used due to simple preparation method.[54] Hollow fibers possess the minimum dead space, which can be cleaned with frequent backwashing, thus they yield longer life to the membranes and are designed to have dimensions specifically suitable for minimizing the membrane fouling.[50, 55]

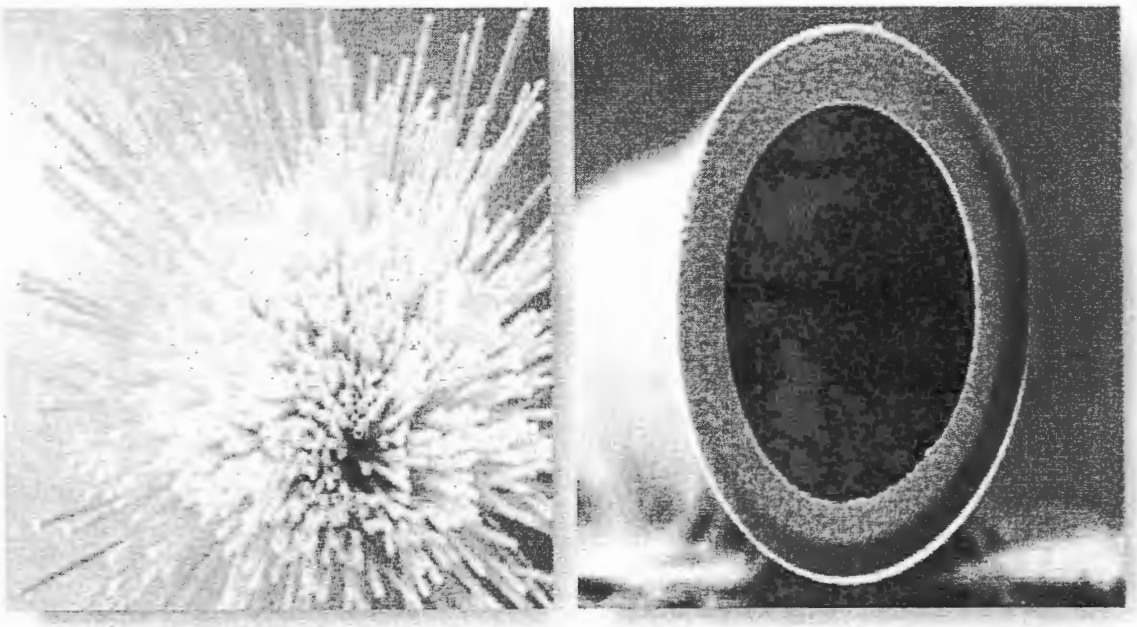


Figure 2.7: Schematic diagram of hollow fiber filtration membranes.[55]

2.10 Membrane challenges

2.10.1 Low flux

Flux reduction caused by organic macromolecules may result from the concentration of polarization, from pore blockage by solute adsorbed on the membrane surface (**Figure 2.8**) or within the pores, and from the formation of a cake layer on the membrane surface.[56] It is

reported that materials such as proteins, humic acid, polysaccharides and other non-humic substances, have been shown to be some of the most dominating fouling matters. It is known that during the water filtration, unwanted pollutants in water should be rejected.[57] Therefore, this is only effective when the membrane has the capacity to generate high flux.

2.10.2 Mechanical strength and flexibility

The application of filtration membranes owes their success to the inherent mechanical strength of the fabricated membranes. For a sustainable membrane, membrane mechanical strength of the membrane must be sufficient to avoid premature rapture when pressure is applied. The PES membrane mechanical strength was studied by electrospinning.[58] The membranes were modified using solvents such as dimethyl formamide (DMF), N-methyl-pyrrolidinone (NMP) and also modified by inorganic materials. It was found that the modification of PES membranes improves the mechanicals strength and the flexibility of the membranes.[59]

2.10.3 Membrane fouling

Membrane fouling is one of the key obstructions to the success of membrane technologies. This can be described as an irreversible or reversible adsorption (**Figure 2.8**) of particles such as salts, viruses, bacteria, etc. on the membrane surface. It is reported that as a result of the build-up, these materials impede the flow of water across the membrane and consequently, the lifespan of the membrane is shortened.[56, 60, 61] A fouled membrane results to more pressure needed to pump water across the membrane. It is stated that this subsequently leads to higher operational costs for filtration plants.[62]

2.10.3.1 Membrane bio-fouling

Membranes bio-fouling is one of the critical challenges in the water treatment process using membranes. It occurs due to all biologically active organisms. During filtration the process involves the growth and the formation of biofilm attached on a membrane surface. It has been reported that, the biofilm may reduce water and water flux.[63, 64] Increase in filtration pressure due to the drop in membrane productivity results high energy and this is caused by excessive

bio-fouling.[65] In literature, it is stated that bio-fouling can be reduced by incorporation of bactericide agents on a membrane. [66]

2.10.3.2 Membrane organic fouling

Organic fouling is when substances that are dissolved in the feed solution are susceptible to stick on a membrane surface as a results of natural organic matters (NOM). Organic compounds such as protein, oil and macromolecules, where the repulsion or electrostatic attraction between the solute species and the membranes are responsible for the degree of fouling.[67] The hydrophobic force overcomes the electrostatic forces, resulting in more fouling of the membrane. This contributes to the formation of additional layers and subsequently deterioration of membrane productivity.[68, 69]

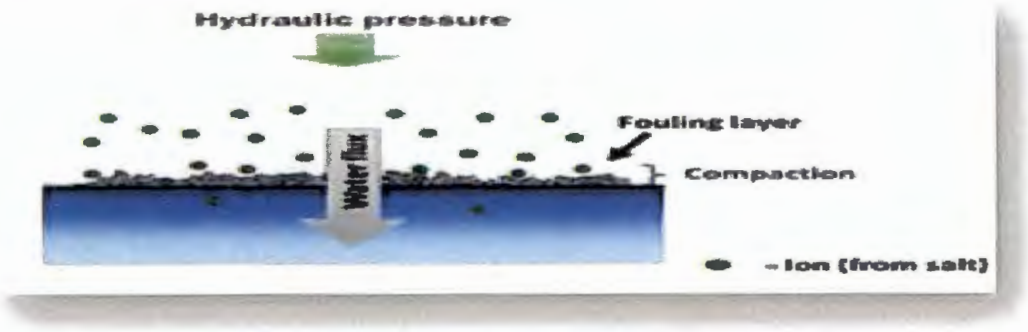


Figure 2.8: Schematic diagram of an irreversible or reversible adsorption of particles such as salts, viruses, and bacteria on the membrane surface.[67]

2.11 Membrane modification

Membrane modification is one of the factors that a great influence on improving the membranes roughness, surface charge and hydrophilicity. There are several methods that have been studied to improve membrane performance and some of these methods are discussed below. The objective was to synthesis composite polymeric membranes that will exhibit high water permeability, greater fouling resistance and maintain high rejection capacities.[68]

2.11.1 Chemical modification method

Chemical modification methods are post-treatment procedures such as radical grafting, plasma-induced polymerisation, chemical coupling and hydrophilisation treatment. These methods entail the use of chemicals to modify membranes in order to increase membrane performance.[69] Literature states that hydrophilisation treatment was performed to commercial TFC RO membranes by using nitric acid, phosphoric acid, sulphuric acid and hydrochloric acid. The reaction between amine and carboxylic functional group on the surface of the membranes with the acids caused partial hydrolysis to more hydrophilic amine and carboxylic group.[70]

2.11.2 Physical modification method

Physical modification is a post-treatment method that was modifiers connected to the surface of a membrane by Van der Waal forces attraction, electrostatic interaction or H-bonding. Surface coating and surface adsorption are known as two types of physical membrane modifications.[71]

2.11.2.1 Surface coating

Surface coating is a convenient and efficient process of post-treatment of membrane surface. The membranes are directly coated with water-insoluble polymers. The TFC membranes coated with water-insoluble molecules are then crosslinked to make them water-insoluble. The membrane coated layer becomes a protective layer that reduces the adsorption and deposition of foulants on the membrane surfaces.[72]

2.11.2.2 Surface adsorption

Surface adsorption involves the utilisation of a homologous series of polyethyleneaxide surfactants in modifying cellulose acetate and polyamide filtration membranes. The hydrophobic portion of the surfactant has a favourable free energy of attraction to the polymeric membrane surface. The modification with these surfactants reduced the roughness of the modified membranes, which ultimately improved their antifouling properties.[73] Researchers used charged polyelectrolytes to modify the polyamide TFC RO membranes by

employing the electrostatic self-assembly of polyethyleneimine on the surface of the membrane.[70, 71] It is reported that the charge reversal on the membrane surface increased the antifouling capacity of the membranes because of the enhanced electrostatic repulsion and increased hydrophilicity.[74]

2.11.3 Incorporation of nanoparticles

This process involves embedding nanoparticles into the polymeric membranes surface **(Figure 2.9)** in order to increase fouling resistance, water permeability, hydrophilicity, mechanical strength, thermal stability and antimicrobial properties of filtration membranes.[75] Synthesis of polymeric membranes with various additives is attractive because of new specific functionalities adding to the parent membrane material or bare membrane properties. Improving membrane hydrophilicity is assumed to yield better performance in terms of permeability, antifouling properties and material rejection.[76, 77]

Studies have shown that when TiO_2 nanoparticles are incorporated into polyamide TFC membranes and led to increase in membrane performance. Moreover, TiO_2 nanoparticles leach away from the membrane interface during operation due to bidendate coordination of the carboxylate to Ti^{4+} and H bonding interaction between –COOH functional group and TiO_2 nanoparticles.[78] In this study, incorporation of functional nanoparticles modification method was adopted to produce multifunctional polymeric membrane with desired membrane performance and improved antifouling properties.

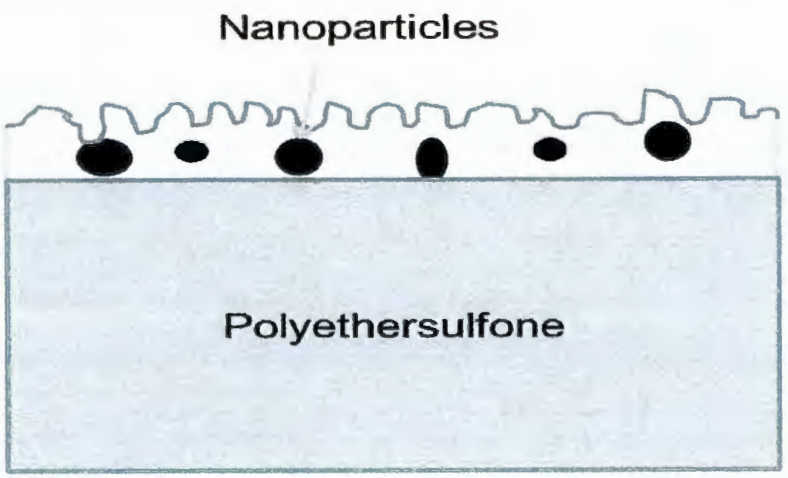


Figure 2.9: Schematic diagram of thin film nanocomposite membrane structure.[78]

2.12 Conclusion

Chapter 2 presented literature review on membrane filtration technology. The chapter gave a detailed overview of the challenges of membranes facing (e.g fouling) and factors to overcome membrane fouling and improve membrane performance. It also stated some of approaches on membrane modification.

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Chapter 3

Experimental

3.1 Introduction

In Chapter 2, applications and different properties of ZnO nanoparticles and membranes were discussed in detail. In Chapter 3 the method for synthesis of zinc oxide nanoparticles and ZnO/polyethersulfone membranes is outlined in detail. Characterisation was performed using various techniques including scanning electron microscopy (SEM), atomic force microscopy (AFM), and thermal gravimetric analysis (TGA).

3.2 Materials

All reagents used for syntheses and characterisation were of analytical grade. Polyethersulfone (PES M_w = 10 000 g/mol) was supplied by Solvay plastics. Dimethylacetamide (DMAc), Poly(vinylpyrrolidinone) (PVP M_w = 10 000 g/mol), zinc acetate di-hydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], sodium hydroxide (NaOH) obtained from Sigma-Aldrich. All reagents were used without any further purification. Distilled water was used throughout this study.

3.3 Synthesis of zinc oxide nanoparticles

$Zn(CH_3COO)_2 \cdot 2H_2O$ (0.2 M) and NaOH (0.4 M) solutions were prepared using distilled water from a millipore water purification system. Precipitation was induced by drop-wise addition of NaOH into the [$Zn(CH_3COO)_2 \cdot 2H_2O$] solution under continuous stirring for 1 hour at reaction 60 °C at pH 12. The reaction mixture was cooled down to room temperature, centrifuged and washed with copious amount of high purity water and ethanol for effective removal of impurities. The final product was dried at 60 °C for 24 hours and calcined at 500 °C.[1]

3.4 Membrane preparation

Polyethersulfone (PES) ultrafiltration membranes were prepared via phase inversion induced by immersion precipitation.[2-4] A using casting solutions (**Table 3.1**) containing PES (18 wt%), polyvinylpyrrolidone (PVP 2 wt%) as a pore former and different concentrations of ZnO nanoparticles (0, 0.5, 1, 1.5, and 2 wt%). For preparing the homogonous solution, all components were simultaneously blended with DMAc and mixed by mechanical stirrer for 12 hours.[5] The solution was sprinkled and cast using self-made casting knife with 75 mm thickness on polyester non-woven fabric. This was immediately moved to the non-solvent bath for immersion at room temperature without any evaporation. After primarily phase separation and membrane formation, the membranes were stored in water for 24 hours to guarantee complete phase separation.[6] At the final stage, membranes were taken for the fouling test and membranes characterization.

Table 3.1: The composition of casting solutions

Membranes	PES wt%	PVP wt%	ZnO wt%	DMAc wt%
Pure PES	18	2	0	80
PES/ZnO0.5	18	2	0.5	79.5
PES/ZnO1	18	2	1	79
PES/ZnO1.5	18	2	1.5	78.5
PES/ZnO2	18	2	2	78

3.5 Membrane characterization

3.5.1 Dead end filtration cell

The performance of the prepared membranes was tested using a dead end cell system. Figure 3.1 represents the scheme of the experimental system.[7]

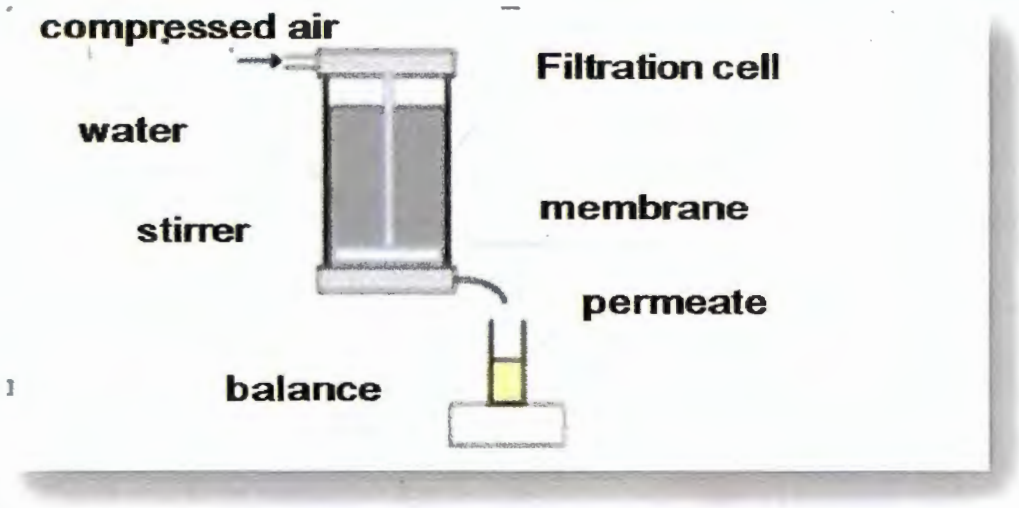

Figure 3.1: Schematic diagram of dead end cell unit.[8]

The dead end filtration is the one where the flow of water is perpendicular to the membrane surface. The water is pushed through the membrane by pressure. All the water that is introduced in the dead-end-cell passes through as the permeate, in other words there is no rejected water.[9] In dead end filtration the retained particles build up with time on the membrane surface or within the membrane pores. In either case, the particle builds results in an increased resistance to filtration and causes the permeate flux to decline, as a result dead end filtration requires the stopping of filtration in order to clean or replace the membrane. This type of filtration is also called batch filtration.[10]

3.5.2 Membrane performance

The water fluxe across of the membranes was tested with a SCM-300 ultrafiltration cup having 12.56 cm^2 of membrane surface area. The membrane was first compacted for 30 min at 150 kPa to minimize compaction effects, and then the pressure was lowered to 100 kPa and the pure water flux (i) was measured after the flux reached steady state and calculated with the following equation.[11]

$$F = \frac{V}{A.t} \qquad \text{(i)}$$

where F is the pure water flux ($L/m^2.h$), V, the permeate volume (L), A, the membrane area (m^2) and t is the time (h). For each membrane, 5 samples were tested and the water flux was the average value of 5 tests.[12]

The rejection (ii) was measured by filtrating Bovine Serum Albumin (BSA) solution (0.5 g/L, pH = 7.4, PBS as buffer solution). After 15 min of filtration, the BSA concentrations in the feed solution and permeation solution were measured, respectively.[13] The rejection was calculated according to

$$R = \frac{Cf - Cp}{Cf} \times 100\% \qquad \text{(ii)}$$

where C_p is the BSA concentration (g/L) of the permeation solution and C_f is the BSA concentration (g/L) of the feed solution. The BSA concentration was determined by a UV-3010 spectrophotometer at λ_{max} = 595 nm.[14]

All filtration experiments were conducted at a constant trans-membrane pressure of 100 kPa and a system temperature of 25 ^{0}C. Each membrane was first compacted for 30 min at 150 kPa.[15] The pressure was lowered to 100 kPa and the deionized water flux was measured. The BSA solution was added to the pressure tank and the BSA solution flux was measured after a total of 40 mL of permeate were collected.[16] Then the water flux was measured again. The membrane was cleaned with deionized water by filling and shaking the cell for 1 min thrice, and then the deionized water flux was measured.[17]

The retention of protein was obtained for the prepared membrane by measuring the amount of protein in the permeate using the standard Bradford method.[18] After 30 min of milk filtration, the membranes were washed with distilled water at room temperature for 15 min and the water flux of washed membranes was measured (J_{ww}). In order to evaluate the fouling resistant ability of membranes, flux recovery (iii) was introduced and calculated as follows:

$$FR\% = \frac{J_{ww}}{J_{wi}} \times 100 \qquad \text{(iii)}$$

where J_{ww} and J_{wi} are the pure water flux of fouled and virgin membrane, respectively. Fouling can be quantified by the resistance appearing during the filtration.[19]

3.6 Analytical techniques

3.6.1 Scanning electron microscopy (SEM)

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer.[20]

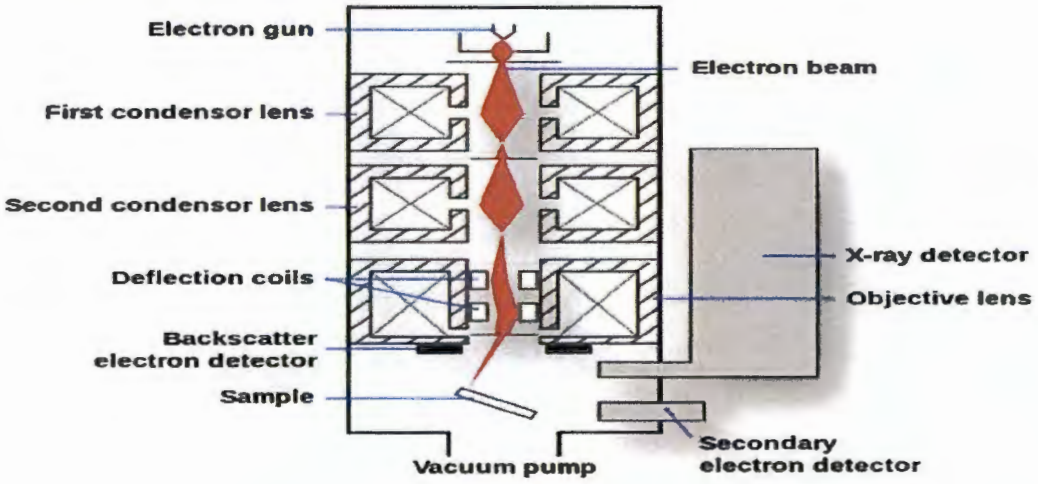

Figure 3.2: Schematic representation of a typical SEM spectroscopy.[21]

The morphologies of membranes were measured using a scanning electron microscope, SEM (FEI, NOVA-nano SEM 200). Samples were attached by carbon tape to the sample stage and sputtered with gold. The voltage was set at 30 kV and the current was set at 10 mA.[11]

3.6.2 Atomic force microscopy (AFM)

With the wide application of nanotechnology in scientific research as well as in industrial product development, it is urgent to develop appropriate tools for investigating and manipulating molecules, especially macromolecules at the nanoscale level. Different microscopes are typical equipment.[22] Due to the high resolution, being maximally close to

samples' original status and the low requirement of sample preparation, AFM has been applied as a nanotechnology tool since it was invented in 1986. As this equipment utilizes the force between the sample and scanning tip rather than the light signal as used by many other microscopes, samples with different optical properties can be investigated with AFM without limitations. AFM analysis is a critical step for revealing the fundamentals of macromolecules and the corresponding functions and applications.[23]

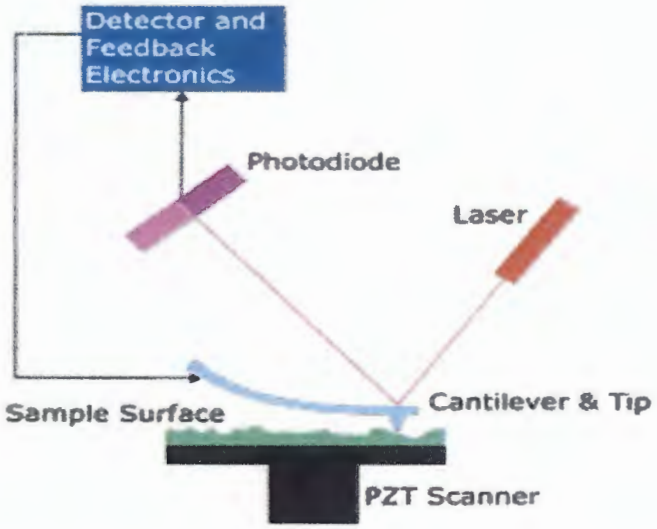

Figure 3.3: Schematic representation of a typical AFM spectroscopy.[24]

Atomic force microscopy was used to analyse the surface morphology and roughness of the prepared membranes. The AFM device was a DualScopeTM scanning probe-optical microscope. Small squares of the prepared membranes (approximately 1 cm^2) were cut and glued on glass substrate. The membrane surfaces were imaged in a scan size of 1 mm × 1 mm.[25]

3.6.3 Contact-angle (CA) measurements

By inflating a droplet in contact with a solid surface and increasing and decreasing the size of the droplet, the contact angle is measured when advanced and receded (advancing contact angle and receding contact angle).[26]

The CA is the angle conventionally measured through the liquid, where a liquid interface meets a solid surface. A given system of solid, liquid, and vapour at a given temperature and

pressure has a unique equilibrium contact angle. However, in practice contact angle hysteresis is observed, ranging from the so-called advancing (maximal) contact angle to the receding (minimal) contact angle. The equilibrium contact is within those values, and can be calculated from them. The equilibrium contact angle reflects the relative strength of the liquid, solid, and vapour molecular interaction.[27]

For the evaluation of the membranes surface hydrophilicity, the contact angle between water and the membrane surface were measured. The contact angles of membranes were measured following procedure.[28] A water drop was lowered onto the membrane's surface from a needle tip. A magnified image of the droplet was recorded by a digital camera. Static contact angles were determined from these images with calculation software. To minimize the experimental error, the contact-angle measurements were taken as the mean value of 5 different points on each membrane.[29]

3.6.4 X-ray diffraction (XRD)

XRD is a laboratory-based technique commonly used for identification of crystalline materials and analysis of unit cell dimensions. The technique was pioneered by Max von Laue in 1912, who discovered that crystalline substances act as a diffraction grating for X-ray wavelengths similar to the atomic-scale plane spacing in a crystal lattice. One of two primary types of XRD analysis (X-ray powder diffraction and single-crystal XRD) is commonly applied to samples to obtain specific information about the crystalline material under investigation.[30]

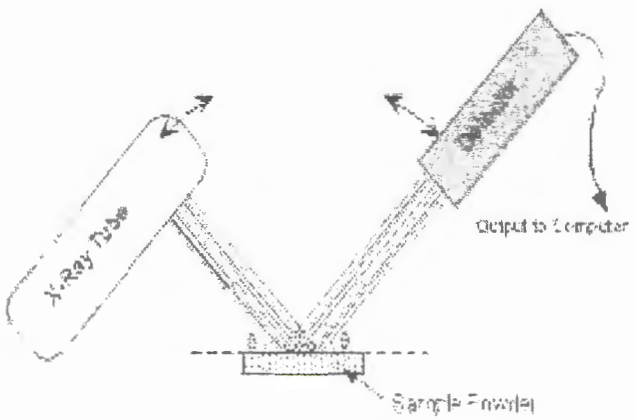

Figure 3.4: Schematic representation of a typical XRD spectroscopy.[31]

XRD analysis X-ray diffraction patterns of the membranes were collected on an X-ray diffractometer (Bruker D8 ADVANCE, axs) equipped with a monochromatic Cu Kα radiation (λ = 0.154 nm) source operated at 40 mA and 40 kV from 20° to 70°. The XRD results shows that ZnO nanoparticles remains in the ZnO/PES nanocomposites membranes.[32]

3.6.5 Thermal gravimetric analysis (TGA)

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles . Common applications of TGA are materials characterization through analysis of characteristic decomposition patterns, studies of degradation mechanisms and reaction kinetics, determination of organic content in a sample, and determination of inorganic content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis. It is an especially useful technique for the study of polymericmaterials, including thermoplastics, thermosets, elastomers, composites, plastics, films, fibers, coatings and paints.[33, 34]

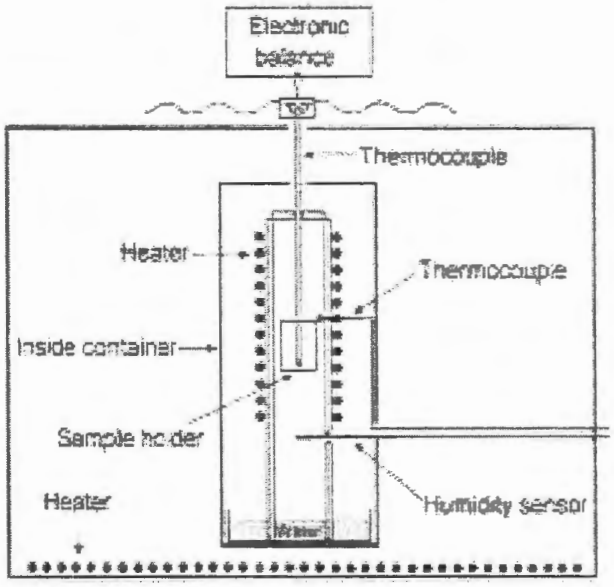

Figure 3.5: Schematic representation of a typical TGA.[35]

The thermal stability of membranes was evaluated by simultaneous thermal analyser, STA (Netzsch, STA 429 CD). The TG measurements were performed under nitrogen atmosphere at a heating rate of 10 °C/min from 20 ^{0}C to 800 ^{0}C. The decomposition temperature (T_d) was defined as the temperature at 3% weight loss.[36]

3.6.6 Transmission electron microscope (TEM)

TEM is a microscopy technique where by a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. An image is formed from the interaction of the electrons transmitted through the specimen; the observed image is magnified and focused onto an imaging device, such as fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.[22, 37] The morphology of prepared nonaparticles will be studied using transmission electron microscope.

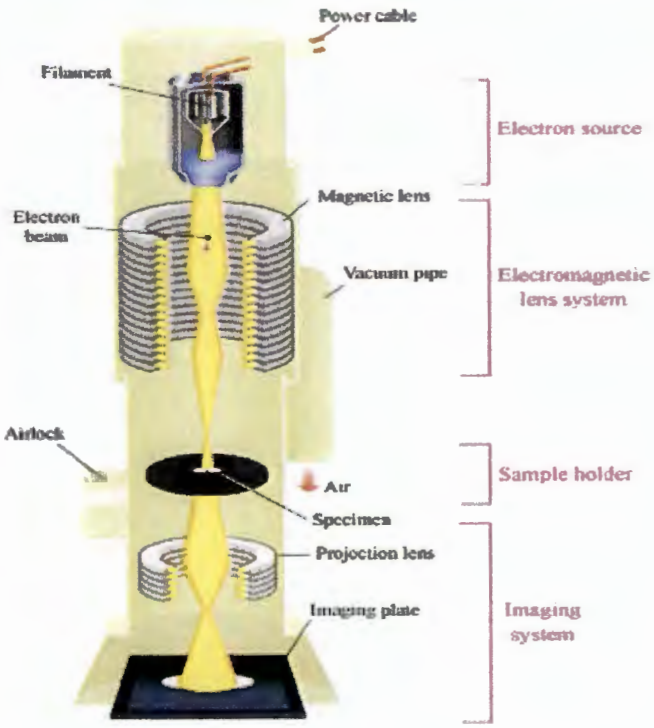

Figure 3.6: Schematic representation of TEM.[37]

3.7 Conclusion

Chapter 3 outlined the synthesis of zinc oxide nanoparticles, ZnO/polyethersulfone particles, preparation of ZnO/polyethersulfone membranes and the membrane performance. Characterisations were performed using SEM, AFM, TGA, TEM, XRD, and CA measurements.

3.8 References

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Chapter 4

Results and discussion

4.1 Introduction

In chapter 3, the different methods that were used for synthesis of zinc oxide nanoparticles were discussed in detail using different materials. Chapter 4 shows the results of zinc nanoparticles obtained using different analytical methods. The results are discussed further according to the general observation.

4.2 ZnO nanoparticles morphology

The morphology of zinc oxide was studied using the TEM. The micrograph was taken at 100 nm as depicted in **Figure 4.1**.

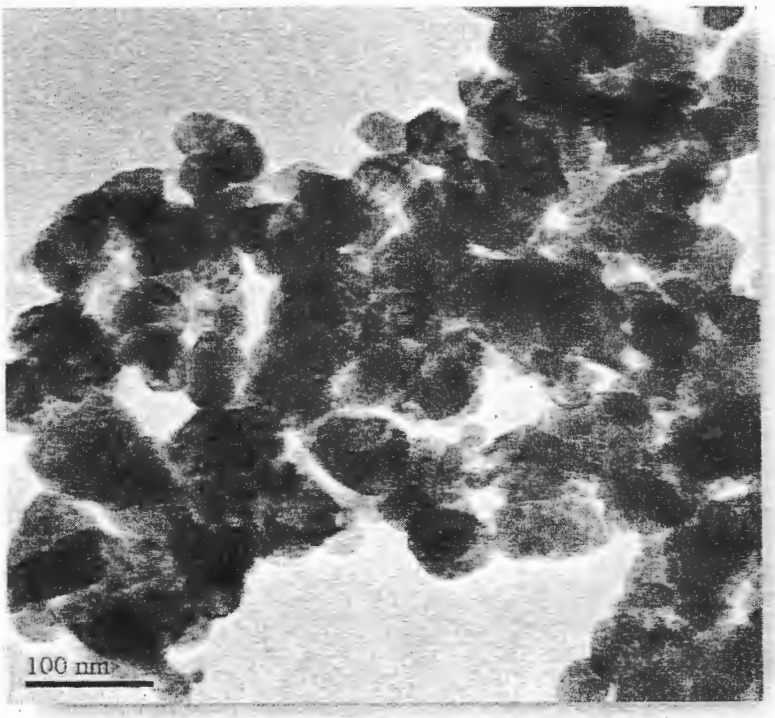

Figure 4.1: TEM images of ZnO nanoparticles.

TEM studies were carried out to find out exact particle size of synthesized ZnO. The structure of ZnO mainly adopt a hexagonal configuration as a number of alternating planes composed

of tetrahedral coordinated O^{-2} and Zn^{+2} ions, stacked alternatively along the c-axis according to Nejati et. al (2011). TEM images of ZnO nanoparticles observed in the image were well defined and small spherical shaped with agglomerated particles.[1] TEM images, **Figure 4.1**, show that ZnO nanoparticles have particle size in the range of 50 nm - 80 nm.

4.3 Effect of ZnO nanoparticles on the performance and the morphology of PES membrane.

4.3.1 Observation of membrane morphology

The surface morphology of the membranes synthesized were studied with SEM. The influence of the addition of ZnO nanoparticles to the membrane surface is shown in the figures below (**Figures 4.2 to 4.6**). The incorporation of nanoparticles into polymeric membranes is known to improve membrane hydrophilicity, stability and membrane mechanical properties.[2]

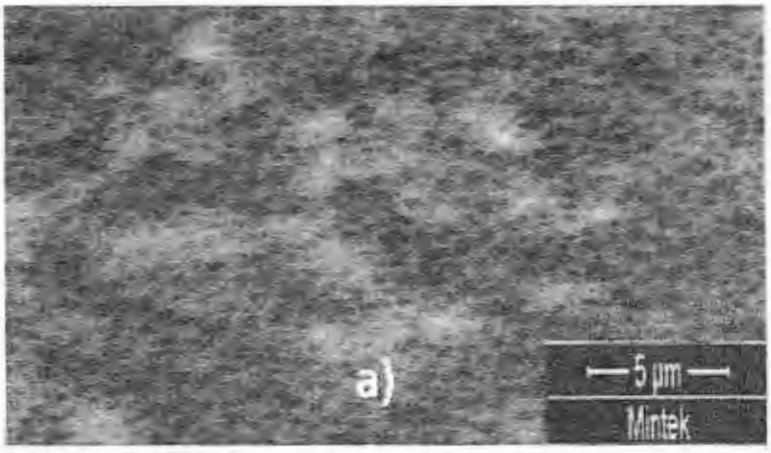

Figure 4.2: SEM image of pure PES membrane.

Figure 4.2 show an SEM image of pure PES membrane surface before addition of ZnO nanoparticles. The pure PES membrane shows numerous nodules on the surfaces that were similar to those of the same membranes after embedding ZnO.

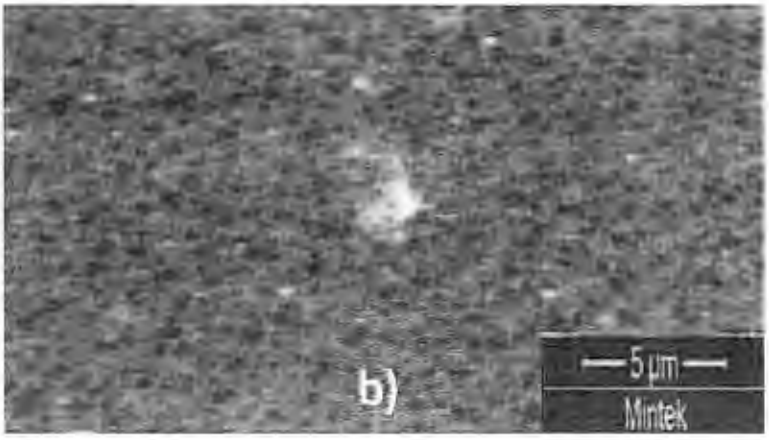

Figure 4.3: SEM image of PES/ZnO(0.5 wt%) nanocomposite membrane.

The addition of inorganic oxide nanoparticles (**Figure 4.3**) causes an increase in tensile strength to some extent. The reason reported was that the free motion of polymeric chains is partly restricted by the intermolecular forces between the polymeric chains and the inorganic oxide nanoparticles dispersed uniformly in PES and the tensile strength of membranes is sequentially enhanced. At the same time inorganic oxide nanoparticles are packed by polymeric chains twisting mutually, so the tensile strength of membranes is also improved.[2]

Figure 4.3 shows the PES/ZnO nanocomposites membrane after the addition of ZnO nanoparticles (0,5 wt%). It can be observed from the image that ZnO nanoparticles start to form clusters or aggregates on membrane surface significantly.

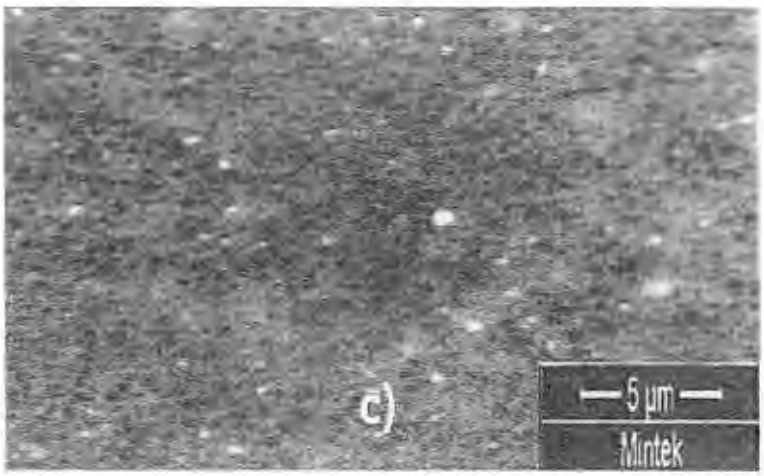

Figure 4.4: SEM image of PES/ZnO(1.0 wt%) nanocomposite membrane.

As it was also observed from **Figure 4.3** and **Figure 4.4** shows uniform distribution of ZnO nanoparticles on the membrane surface. However, some particles start to form a large aggregation on the surface. It was reported that the higher the concentration of nanoparticle on the membrane surfaces, the more the amount of pores on the membranes are formed and that improves membrane performance and hydrophilicity.[3]

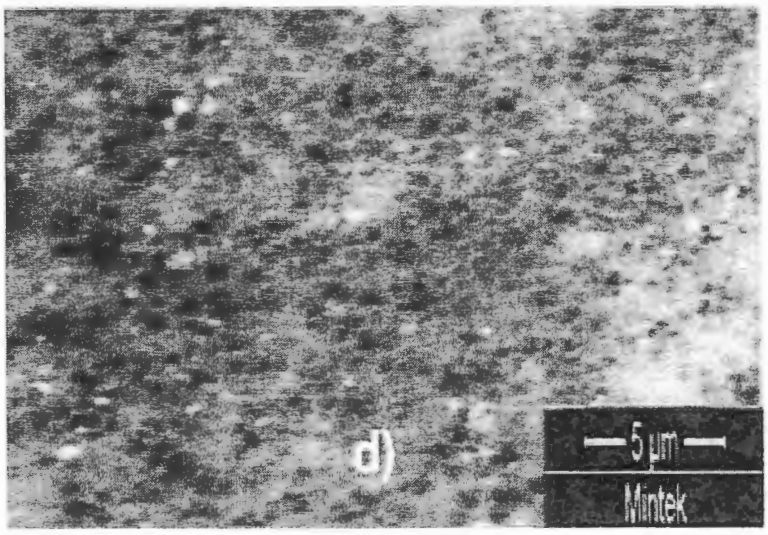

Figure 4.5: SEM image of PES/ZnO(1.5 wt%) nanocomposite membrane.

Figure 4.5 also shows the SEM of PES/ZnO nanocomposite membrane with the addition of ZnO nanoparticles (1.5 wt%) on the membranes surface. It can be observed that more nanoparticles (white spots) are incorporated on the membrane surface as compared to previous images (**Figure 4.2 to 4.4**) and nanoparticles forms more aggregation on the membrane surface because of the increased amount of nanoparticles added.

The amount of pores increased with the increasing amount of added ZnO nanoparticles. However, when the weight of added ZnO nanoparticles was at around 2.0 wt% (**Figure 4.6**), the amount of pores tends to stabilize. The size of the pores changes a little. The improved amount of pores is favorable to water flux.[4]

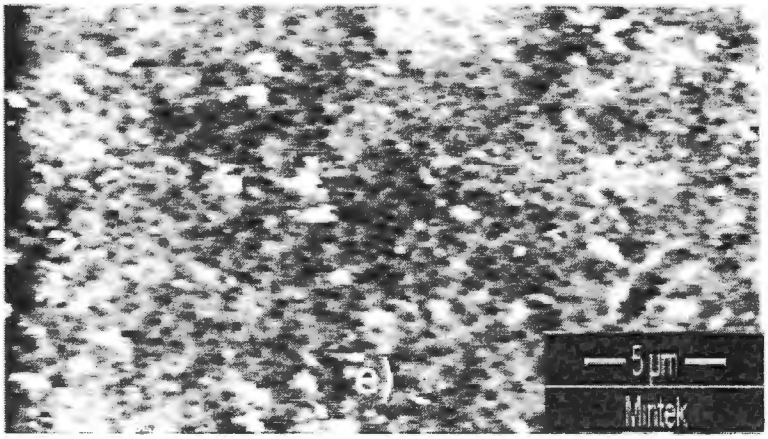

Figure 4.6: SEM image of PES/ZnO(2.0 wt%) nanocomposite membrane.

As ZnO nanoparticles concentration was increased to about 2.0 wt%, this resulted in a huge difference between viscosities of pristine and modified membranes. It can be observed that the ZnO nanoparticles aggregate on membrane surface and the degree of aggregation was increased with increasing of ZnO nanoparticles amount. The aggregation of the nanoparticles on the membrane surface increase the chance of pore plugging especially at higher concentration (2.0 wt%) of the nanoparticles. Hence decrease in flux as compared to PES/ZnO (0.5, 1.0, 1.5 wt%) nanocomposites membranes.[5]

In the **Figures 4.2 - 4.6**, from the surface images of membranes (0.5, 1.0, 1.5, 2.0 wt%), it can be seen that the ZnO nanoparticles aggregates on the surface of PES/ZnO nanocomposites membranes. The aggregated ZnO nanoparticles on the surface continuously increases with the increasing weight of added ZnO nanoparticles.[6] It was reported that, the aggregation of ZnO naoparticles on the surface may make some pores blocked. From the images of 0.0, 0.5, 1.0, 1.5 and 2.0 wt% (ZnO) respectively, it can be seen that the pores present on the surfaces of membranes.[7]

4.3.2 XRD analysis

In **Figure 4.7**, the dominant peaks of ZnO nanoparticles appear at 2θ angles around 36.908°, 39.978°, 42.166° and 55.774°. The corresponding indices of these diffraction peaks according to literature were (100), (002), (101), (102) and (110) respectively.[8] The ZnO/PES composite membrane also shows peaks corresponding crystalline characteristic peaks at 2θ angles

around 35.621°, 37.729°, 39.197°, and 53.250°, which are analogous to the main characteristic peaks of ZnO nanoparticles. The XRD results shows that ZnO nanoparticles remains in the ZnO/PES nanocomposites membranes.[9] However, all the characteristic peak locations in the ZnO/PES composite membranes were shifted to slightly lower angles compared with those of ZnO nanoparticles.

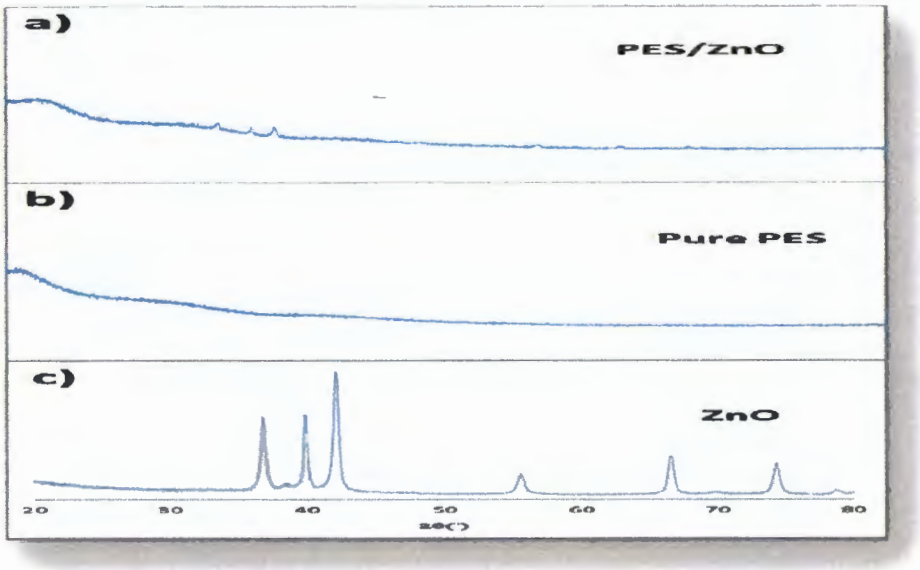

Figure 4.7: XRD patterns of PES membrane, a) ZnO/PES composite; b) pure PES and c) ZnO nanoparticles.

It was reported that the peak locations of TiO_2 in PES/TiO_2 hybrid membranes shifted somewhat. It was also believed that there may be slight interactions between TiO_2 and PES. In ZnO/PES nanocomposites membranes, there might be also slight interactions between ZnO and PES, which make the peak locations shift slightly.[10]

4.3.3 Atomic force microscopy (AFM)

The surfaces of the unmodified and modified PES membranes were characterized using AFM at a projection areas of 10 μm × 10 μm. **Figure 4.8** and **Figure 4.9** are the AFM images showing surfaces morphology of pure PES membrane and PES/ZnO nanocomposite prepared with different concentrations of ZnO nanoparticles in the casting solution. In these images,

the brightest area presents the highest point of the membrane surface and the dark regions indicate valleys or membrane pores.[2]

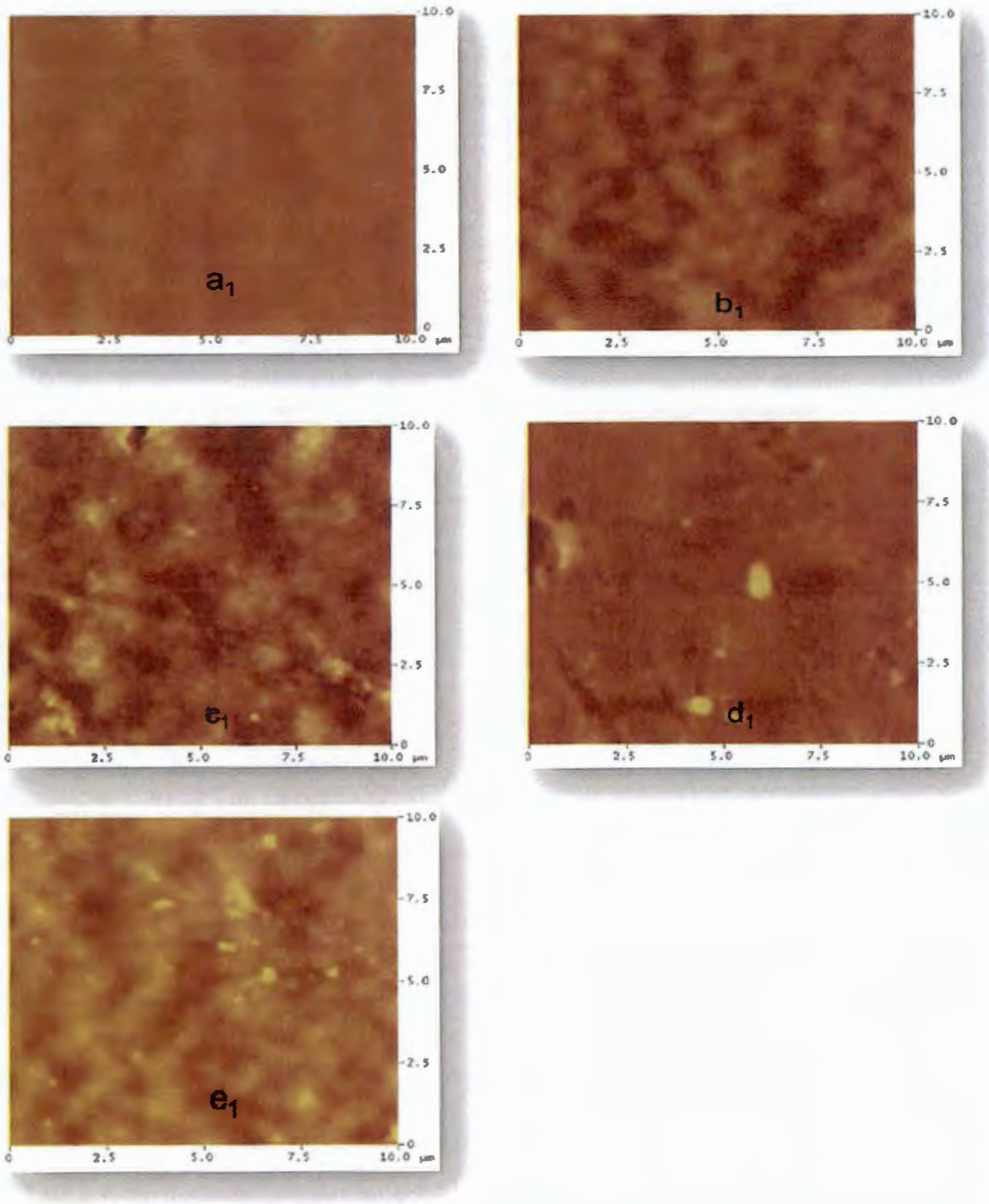

Figure 4.8: AFM image of a_1) pure PES, b_1) PES/ZnO(0.5 wt%), c_1) PES/ZnO(1.0 wt%), d_1) PES/ZnO(1.5 wt%), e_1) PES/ZnO(2.0 wt%)

AFM is an important compliment to SEM, as both study the surface morphology of the prepared polymeric membranes. **Figure 4.8** indicates that as the amount of ZnO nanoparticles was increased in the casting solution, the amount of ZnO nanoparticles increased (from 0.5 – 2.0 wt%) on the surface of the membranes. This was also observed during the studies of surface morphology by SEM (section 4.3). It was reported that the surface morphologies of membranes are strongly influenced by the addition of ZnO nanoparticles on the casting solution.[11] As the concentration of ZnO nanoparticles is at 2 wt% (image e_1), nanoparticles stabilise the membrane pores and causes pore blockage, hence decrease in flux as compared to PES/ZnO(0.5 – 1.5 wt%) nanocomposite membranes. To be observed late during pure water flux studies (section 4.4)

Figure 4.9 shows 3D AFM images of the pure PES membranes (a_2) and those modified with ZnO nanoparticles to form PES/ZnO nanocomposite membranes (b_2, c_2, d_2, e_2). The 3D AFM studies indicate the membranes surface roughness. Researchers reported that as more nanoparticles (ZnO, TiO_2, etc) are loaded to the membrane casting solution, the roughness of the polymeric membrane morphologies increases.[12] This can be observed in **Figure 4.9,** as the roughness of the membranes increases from ZnO nanoparticles 0 – 2.0 wt%.

Table 4.1: Outlines the membranes surface roughness parameters, where R_q is taken as the root mean square roughness and R_a is taken as the mean roughness of the membranes. The pure PES gave a smaller R_a value as compared to PES/ZnO nanocomposite membranes, and the R_a increases with the amount of ZnO nanoparticles present on the membrane surfaces.[11, 13] It was reported that, the different morphologies observed between the modified (i.e PES/ZnO) and unmodified (i.e pure PES) membranes maybe be due to the different polymerisation, interaction of nanoparticles with the polymer material and diffusion rates.[14]

Table 4.1: AFM surface roughness values of PES/ZnO nanocomposites membranes and pure PES membrane

Roughness parameters	Pure PES	PES/ZnO (0.5 wt%)	PES/ZnO (1.0 wt%)	PES/ZnO (1.5 wt%)	PES/ZnO (2.0 wt%)
R_q	9.365 nm	14.087 nm	15.473 nm	15.691 nm	22.268 nm
R_a	7.099 nm	11.184 nm	12.254 nm	11.927 nm	13.701 nm

R_a is the mean roughness; R_q is a root mean square roughness

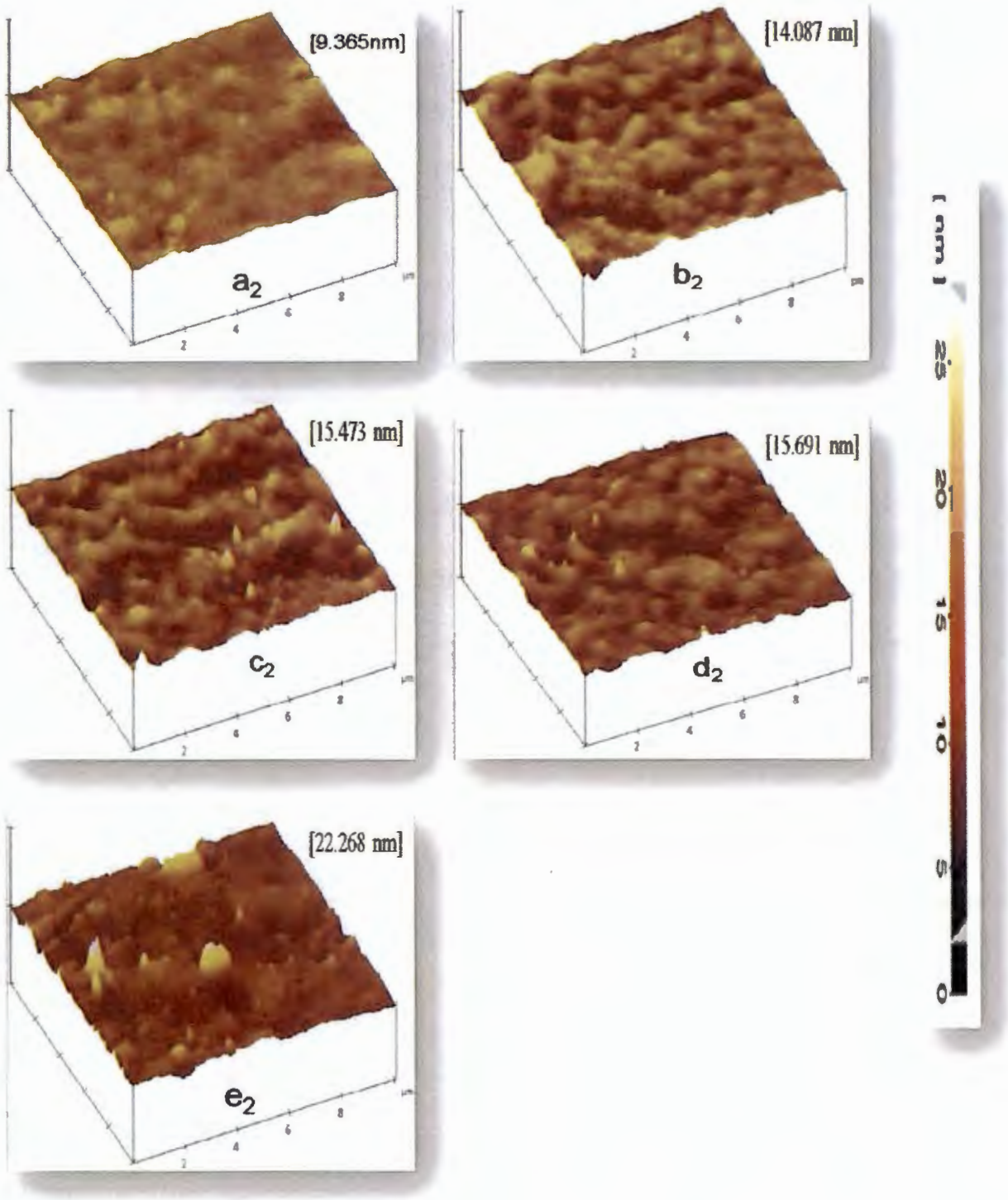

Figure 4.9: 3D AFM image of a_2) pure PES, b_2) PES/ZnO(0.5 wt%), c_2) PES/ZnO(1.0 wt%), d_2) PES/ZnO(2.0 wt%)

The surface morphologies of membranes were strongly influenced by addition of ZnO nanoparticles in the casting solution, especially at higher concentration. The surface of the pure PES membrane was not homogeneous but heterogeneous, whereas modified PES membranes have more or less lower roughness than the pure PES membrane.[9, 11]
The roughness was observed when loading 0.5 wt% of the ZnO nanoparticles. It was reported that low ZnO nanoparticles loading, the electrostatic interaction between the ZnO nanoparticles and the polymeric membrane is low. Hence the nanoparticles are well positioned in enhancing the surface smoothness of the membrane. The observed roughness increases due to the increasing of ZnO nanoparticles on our cast solution (0.5 to 2.0 wt%).[12, 13]

4.4 Effects of ZnO and ZnO/PES membrane membrane performance

4.4.1 Pure water flux and flux recovery

The presence of ZnO nanoparticles generates two effects: hydrophilicity effect and viscosity effect. Hydrophilic ZnO nanoparticle easily draws water into the casting suspension in the phase inversion process.[15] The viscosity effect severely hinders the exchange rate between water and solvent during the phase inversion. The higher addition weight of ZnO nanoparticle leads to a higher viscosity. When the weight of added ZnO nanoparticle is high, the viscosity of casting suspension is so high that the viscosity effect dominates the hydrophilicity effect.[16]

The dead end cell was used to measure the filtration properties of membranes at 25 °C. The water fluxes (**Figure 4.10**) of all the PES/ZnO membranes nanocomposites are higher than that of the PES membrane. As the weight of added ZnO nanoparticles is increased (0 to 2 wt%), the water flux of the membrane increases to a peak value and then begins to decrease.

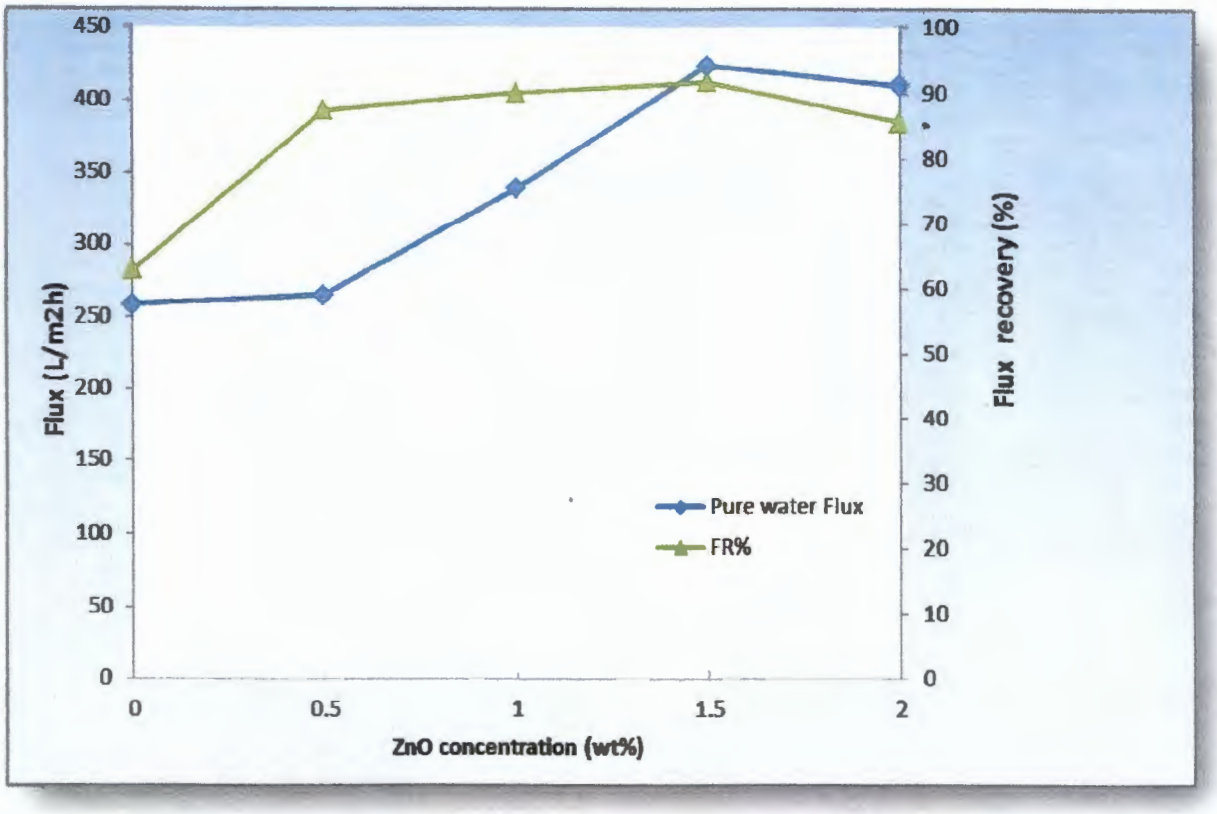

Figure 4.10: Pure water flux and flux recovery, FR% (after filtration of BSA) changes with the addition of ZnO nanoparticles.

It has been reported that hydrophilicity and membrane structures are the two main factors that govern the filtration properties of membranes. First, the presence of hydrophilic ZnO nanoparticles improves the hydrophilicity of membranes, which is much favourable to the water flux.[17]

Furthermore, the membrane structure of the improve membrane pores and the better connectivity between up-layer and the sub-layer are also favourable to improve the water flux. Consequently, improved hydrophilicity and advantageous membrane structure contribute to higher water flux of ZnO/PES membrane than that of PES membrane.[18] When the weight of added ZnO nanoparticles exceeds 1.5 wt%, the water flux begins to decrease **(Figure 4.5)**.

This phenomenon is the synergetic result of decreased pore size and aggregation of ZnO nanoparticles on the membrane surface at about 2 wt% ZnO nanoparticles. These aggregations of nanoparticles on membrane surface increase the chance of pore plugging especially when ZnO nanoparticles concentration increases to more than 1.5 wt%.[19]

4.5 Analysis of membrane contact angle

The contact angle (**Figure 4.11**) of each membrane was measured at 25 ^{0}C. The contact angle of the membranes decreases continuously with increasing weight of added ZnO nanoparticles and suddenly increases after the addition of ZnO (2 wt%) nanoparticles.[1, 20] For the added weights of ZnO nanoparticles of 0.0, 0.5, 1.0, 1.5, and 2.0 wt%, the membrane contact angles were observed at 87.24°, 71.28°, 63.92°, 52.74° and 35,04° respectively.

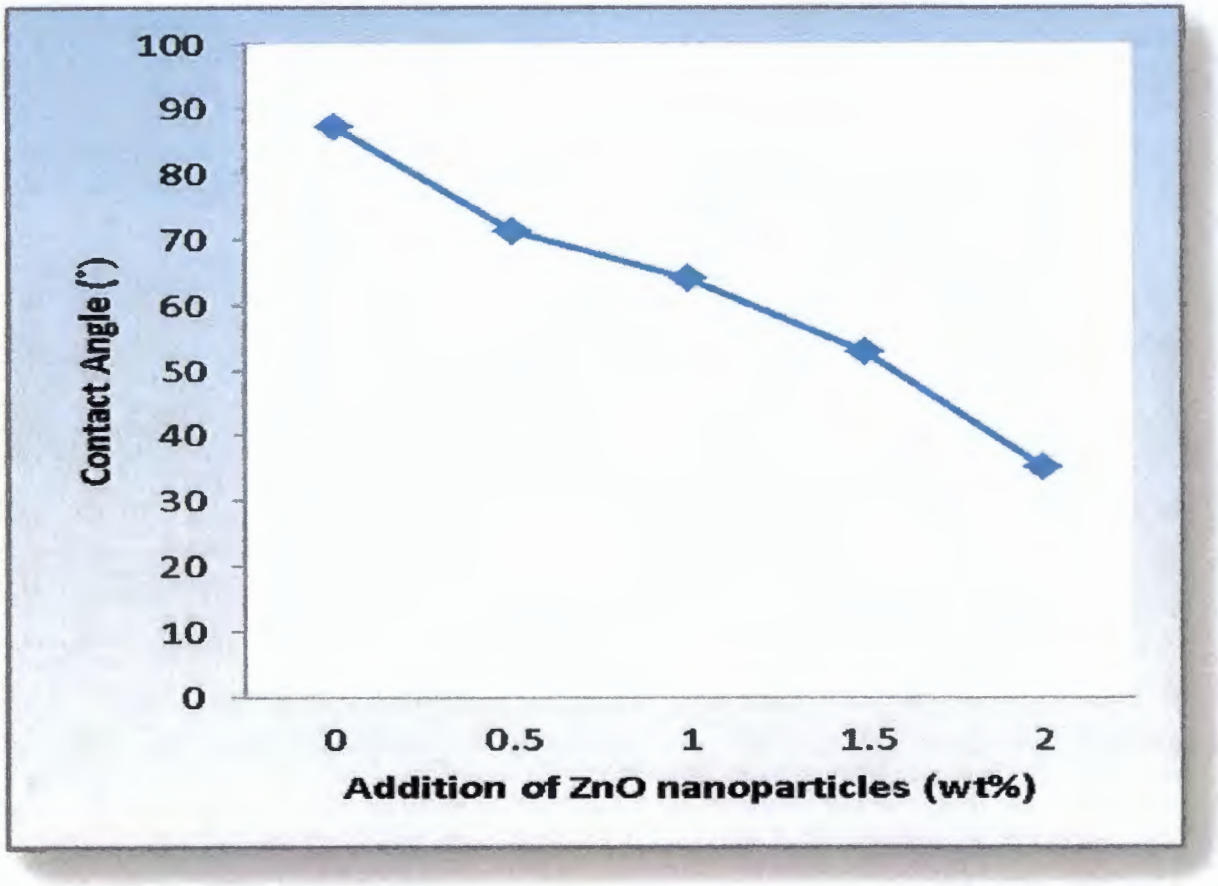

Figure 4.12: Contact angle changes as the increasing weight of added ZnO nanoparticles.

From the figure above (**Figure 4.12**), it is observed that all of the PES/ZnO membrane samples poses lower contact angle than the pristine PES membrane. This disparity in the contact angle values between the pristine and the modified membranes could be attributed to the effect of the added ZnO nanoparticles to the casting solutions. It is reported that, this phenomenon is manifested in the modified membranes due the hydrophilicity of the added ZnO nanoparticles, which was interrupted within the membrane structure and possibly resulted in a membrane material with higher attraction toward the water molecules. The hydrophilic ZnO nanoparticles significantly improve the hydrophilicity of the PES membranes. It is also known that hydrophilicity is favourable for improving the water flux and antifouling ability.[21]

4.6 Analysis of thermal property of the membranes

Thermal property of each membrane was characterized by investigation of their weight losses with increasing temperature. The thermal analysis results of all the prepared membranes are illustrated in **Figure 4.13**. It was found that the decomposition temperature (Td, defined as the temperature at 3% weight loss) increased with increasing amount of ZnO nanoparticles.[15]

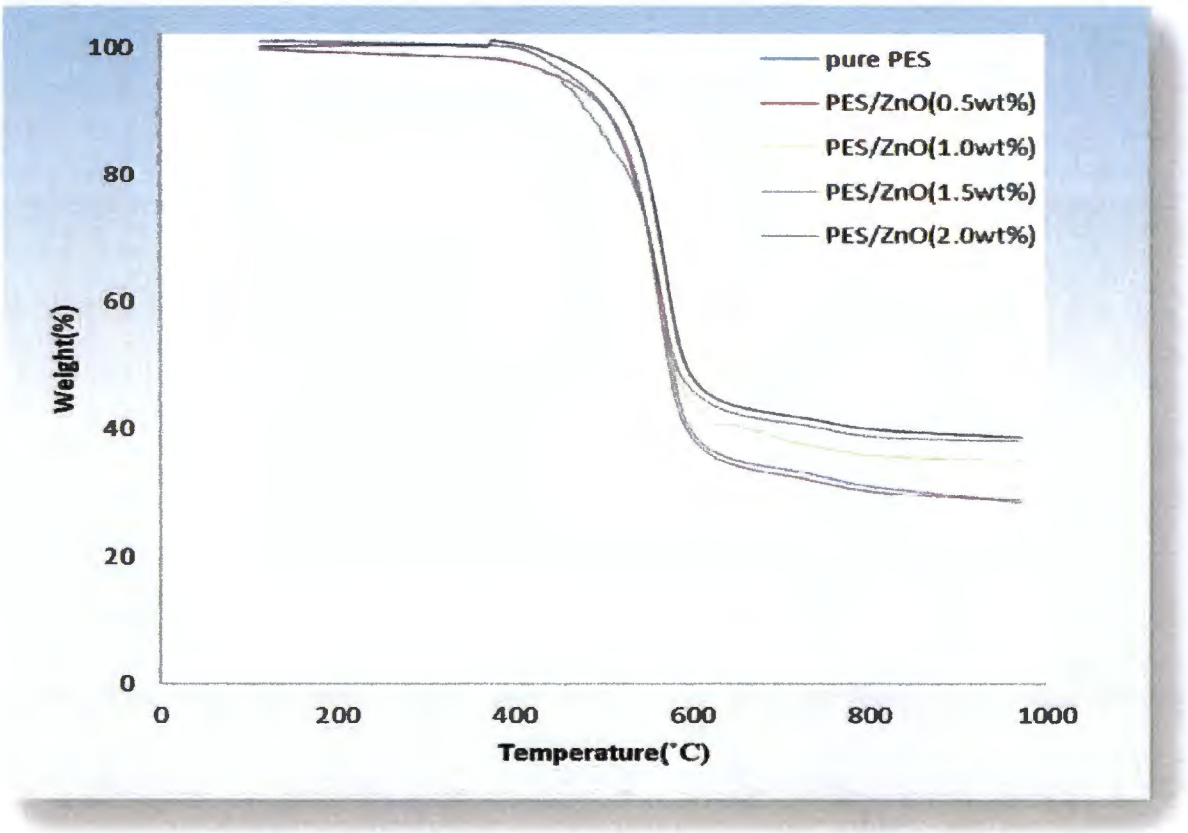

Figure 4.13: Weight loss of each prepared membrane with increasing temperature (0, 0.5, 1.0, 1.5 and 2.0 wt%).

The figure indicates that the PES membrane and the PES/ZnO nanocomposte membranes show analogous thermal decomposition tendencies. The decomposition temperature (T_d) increases continuously with increased weights of added ZnO nanoparticles. When the weight of added ZnO nanoparticles reaches 2.0 wt%, the Td of the ZnO/PES nanocomposites membrane is improved relative to that of the pure-PES membrane. Kim et al.[22] and Xiaochun et al.[23] have also observed that the addition of inorganic particles improved the thermal stability of polymer membranes decomposition.

The results further show that the ZnO nanoparticles were dispersed uniformly in the membrane and show the good compatibility between ZnO nanoparticles and PES. With increasing ZnO nanoparticles content, more heat was absorbed by the ZnO nanoparticles in the membranes during heating-up, the decomposition of PES was thus delayed, and the decomposition temperature of PES/ZnO nanocomposite membrane was enhanced.[17, 24]

4.7 References

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Chapter 5

Conclusion

PES/ZnO membranes were prepared by phase inversion induced by immersion precipitation technique. The addition of ZnO to the polymer casting solution changed the properties of the polymeric UF membranes. The main conclusions are listed as follows;

i. Transmission electron microscope analysis was employed to characterize ZnO nanoparticles. The structure of ZnO mainly adopt a hexagonal configuration as a number of alternating planes composed of tetrahedral coordinated O^{-2} and Zn^{+2} ions. TEM images, **Figure 4.1**, show that ZnO nanoparticles are having particle size in the range of 50 nm - 80 nm.

ii. XRD indicated that ZnO nanoparticles remained in PES/ZnO membranes, after the incorporation of ZnO nanoparticles on PES membranes.

iii. Hydrophilic ZnO nanoparticles significantly improve the hydrophilicity of the PES membranes (decrease in contact angle). It is known that hydrophilicity is favourable for improving the water flux and antifouling ability.

iv. The appropriate addition of ZnO nanoparticles improved the antifouling ability of the membrane; water flux and PES/ZnO decomposition were enhanced.

v. The ZnO/PES membrane exhibits the highest water flux (**Figure 5**) when the weight of added ZnO nanomaterial is 1.5 wt%.