SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF POLYSULFONE/CELLULOSE ACETATE PHTHALATE/ POLYVINYLPYRROLIDONE (PSf/CAP/PVP) BLEND ULTRAFILTRATION MEMBRANES

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SUPERVISOR’S DECLARATION

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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DEDICATION

To my mother, late farther, wife, and kids..

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ABSTRACT

Polysulfone (PSf) is an important class polymer that has been most widely used in the manufacture of synthetic asymmetric ultrafiltration membranes. However, the main disadvantage of PSf membrane is due to its hydrophobic characteristic which in turn fouled the membranes. In practical application of UF systems, membrane fouling is a serious problem that causes high cost energy, operation, and maintenance. Polymer blend is a simple and an efficient method for designing new materials to improve performance of the hydrophobic membranes. The polymer blend is a proven tool to obtain new types of UF membrane, which has better hydrophilicity compared to the original membranes. Cellulose acetate phthalate (CAP) is one of the potential hydrophilic organic polymers that can be used and explored in PSf polymer blend technique to improve hydrophilicity and performance of PSf membranes. PSf/CAP blend membranes with blend composition of 95/5, 90/10, 85/15 and 80/20 wt% of total polymer concentration in the membrane casting solutions were developed via wet phase inversion process. The effect of CAP composition on characteristics, morphology and performance of PSf/CAP blend membranes were investigated. The hydrophilicity of the PSf/CAP blend membranes were improved evidently by blending with CAP. Based on BSA protein separation performance study, the PSf/CAP blend ultrafiltration membrane which contains 10 wt% of CAP shows the best performance membrane due to its high productivity and separation performance as well as it has good membrane characteristics in terms of high hydrophilicity properties, pore properties and membrane morphological structure. The effect of polyvinylpyrrolidone (PVP) additives in the range of 1 to 5 wt% on the best PSf/CAP blend membranes was studied. The results revealed that an addition of 1 to 3 wt% of PVP additive formed membrane with small average pore size and low MWCO due to the strong interpenetrating network between PSf-CAP-PVP and consequently increased protein rejections. Further increment of PVP additive promoted PVP leached out during wet phase inversion process and formed membranes with big pore size and high MWCO. These membranes had high permeate flux but low rejection of proteins. The PSf/CAP/PVP blend membrane that contains 3 wt% of PVP was selected as the best high performance membrane. Further, there were five different shear rates (42.0, 52.5, 70.0, 105.0 and 210.0 s^{-1}) applied during fabrication process of PSf/CAP/PVP blend membranes by using the best PSf/CAP/PVP dope formulation. The experimental results showed that an increase in shear rate from 42.0 to 105.0 s^{-1} decreased the water content, porosity and permeability of the membranes. Further increment of shear rate to 210.0 s^{-1} increased the water content, porosity and permeability of the membranes due increased in porous structure of PSf/CAP/PVP membrane and a decrease in membrane thickness. In terms of BSA separation performance, the PSf/CAP/PVP blend membranes fabricated at the shear rate of 105.0 s^{-1} showed the best performance due to high rejection of BSA at favorable permeation flux of BSA protein solution. In an evaporation time study, the PSf/CAP/PVP blend membranes fabricated at shear rate of 105.0 s^{-1} were introduced to evaporation time of 5, 10, 15 and 20 s before immersed in a coagulation bath. The results showed that the effects of evaporation time significantly changed the properties and morphological structures of the PSf/CAP/PVP blend membranes. In this experiment study, PSf/CAP/PVP blend membrane which was fabricated at evaporation time of 10 s exhibited the best performance membrane due to high membrane productivity and separation ability.

ABSTRAK

Polisulfon (PSf) adalah polimer yang penting digunakan dalam pengeluaran membran ultraturasan (UF) asimetrik sintetik. Walaubagaimanapun, kelemahan utama membran PSf adalah ciri hidrofobiknya yang menyebabkan kotoran membran. Secara praktiknya, kotoran membran adalah satu masalah yang sangat serius kerana ia menyebabkan kos tenaga, operasi dan penyelenggaraan yang tinggi. Adunan polimer adalah kaedah paling mudah dan cekap untuk mendapatkan bahan baharu bagi mempertingkatkan prestasi membran hidrofobik. Adunan polimer terbukti sebagai satu cara untuk menghasilkan membran UF baharu yang mempunyai sifat hidrofilik lebih baik berbanding membran asal. Selulosa asetat phthalate (CAP) adalah salah satu polimer organik hidrofilik berpontensi yang boleh digunakan dalam teknik adunan dengan PSf bagi meningkatkan sifat hidrofilik dan prestasi membran PSf. Membran adun PSf/CAP dengan komposisi adunan 95/5, 90/10, 85/15 dan 80/20 wt% dari kepekatan keseluruhan polimer dalam larutan tuang membran dibangunkan melalui proses penyongsangan fasa basah. Kesan komposisi CAP ke atas ciri-ciri, morfologi dan prestasi membran adun PSf/CAP dikaji. Sifat hidrofilik membran adun ini terbukti meningkat dengan mengadunkan CAP. Berdasarkan kajian prestasi pemisahan protein BSA, membran adun PSf/CAP yang mengandungi 10 wt% kandungan CAP dipilih sebagai membran yang terbaik kerana menunjukan produktiviti dan pemisahan yang tinggi di samping ciri yang baik bagi sifat hidrofilik, sifat liang dan struktur morfologi. Kesan bahan tambah polivinilpirolidon (PVP) dalam julat 1 hingga 5 bt% ke atas membran adun PSf/CAP terbaik dikaji. Keputusan menunjukkan penambahan 1 hingga 3 wt% bahan tambah PVP membentuk membran bersaiz purata liang dan MWCO yang kecil kerana rangkaian saling jalinan yang kuat antara PSf-CAP-PVP dan seterusnya meningkatkan pemisahan protein. Penambahan seterusnya bahan tambah PVP akan menyebabkan PVP melarut resap semasa proses penyongsangan fasa basah dan membentuk membran bersaiz purata liang dan MWCO yang besar. Membran ini mempunyai aliran telapan yang tinggi tetapi pemisahan protein yang rendah. Membran adun PSf/CAP/PVP yang mengandungi 3 wt% PVP dipilih sebagai membran prestasi terbaik. Selanjutnya, lima kadar ricih yang berbeza (42.0, 52.5, 70.0, 105.0 and 210.0 s^{-1}) digunakan dalam proses pembikinan membran adun PSf/CAP/PVP menggunakan formulasi dop PSf/CAP/PVP yang terbaik. Keputusan ujikaji menunjukkan peningkatan kadar ricih dari 42.0 ke 105.0 s^{-1} menurunkan kandungan air, keporosan dan ketelapan membran. Peningkatan kadar ricih ke 210.0 s^{-1} meningkatkan kandungan air, keporosan dan ketelapan membran kerana peningkatan keporosan struktur membran dan penurunan ketebalan membran. Membran adun PSf/CAP/PVP yang dibikin pada kadar ricih 105.0 s^{-1} menunjukkan prestasi terbaik dengan pemisahan BSA yang tinggi pada aliran yang sesuai. Dalam kajian masa penyejatan, membrane adun PSf/CAP/PVP yang dibikin pada kadar ricih 105.0 s^{-1} didedahkan dengan masa penyejatan selama 5, 10, 15 dan 20 s sebelum direndamkan ke dalam sebuah rendaman penggumpalan. Keputusan menunjukkan kesan masa penyejatan secara signifikan merubah sifat-sifat dan struktur morfologi membran adun PSf/CAP/PVP. Dalam ujikaji ini, membran adun PSf/CAP/PVP yang dibikin pada masa penyejatan selama 10 s menunjukkan membran prestasi terbaik dengan produktiviti dan pemisahan yang tinggi.

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A	the permeability constant or membrane area or water content
A_k	Membrane surface porosity
b.p.	Boiling point
C_p	Solute concentration in the feed solution
C_f	Solute concentrations in the permeate
d	mean pore diameter
d_{water}	Density of water at room temperature
J	Volume flow or flux
k	Consistency index
K	Kozeny-Carman constant
L_p	Hydraulic permeability
N	Flow behavior index
P_m	Membrane permeability
R_a	Adsorption resistance
R_{cp},	Concentration polarization resistance
R_g,	Resistance of gel layer formation
R_m,	Membrane hydraulic resistance
R_p	Pore blocking resistance
R_{tot}	Total resistance
S	Internal surface area
V	Volume of permeate solution collected
$W_{wet/1}$	Wet weight of membrane
$W_{dry/2}$	Dry weight of membrane

ΔC	Concentration difference
ΔP	Pressure difference or driving force difference
$\mathit{\Delta} t$	Difference of sampling time
Δx	Difference of membrane thickness
ε	Surface porosity
r	*P*ore radius
η	*S*olvent viscosity
τ	Pore tortuosity.
τ	Shear stress
γ	Shear rate
$\bar{a}$	Solute radius
$\overline{R}$	Average pore size
θ	Contact angle

LIST OF ABBREVIATIONS

AFM	Atomic force microscope
Al_2O_3	Alumina
ATR-FTIR	Fourier transform attenuated total reflection
BSA	Bovine serum albumin
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate phthalate/cellulose acetate propionate
CH_4	Methane
CMCA	Carboxymethyl cellulose acetate
CN	Cellulose nitrate
CO_2	Carbon dioxide
CP	Cellulose propionate
CPSU	Carboxylated polysulfone
DER	Dope extrusion rate
DMFC	Direct methanol fuel cell
EA	Egg albumin
EC	Ethyl cellulose
ED	Electrodialisis
EPES	Epoxy functionalized poly(ether-sulfone)
GS	Gas separation
KH_2PO_4	Pottasium dihydrogen phosphate
K_2HPO_4	di-Pottasium hydrogen phosphate
MF	Microfiltration

MPC	2-methacryloyloxyethyl phosphorylcholine polymer
MWCO	Molecular weight cut-off
N_2	Nitrogen
NF	Nanofiltration
NMP	N-methyl pyrrolidone
O_2	Oxygen
PA	Polyamide
PAA	Polyarcrylic acid
PAI	Poly(amide-imide)
PAN	Polyacrylonitrilic/polyacronitrile
PC	Polycarbonate
PE	Polyethylene
PEEK	Poly(ether ether ketone)
PEG	Polyethylene glycol
PEMFC	Electrolyte membrane fuel cell
PES	Polyethersulfone
PESA	Poly(ether sulfonamide)
PFSA	Perfluorosulfonic acid
PI	Polyimide
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PS	Polyphenylene sulfide
PS/PSf/ PSF/PSU	Polysulfone
PSO	Polyphenylene oxide

PSR	Polystyrene
PSSNa	Poly(sodium styrene sulfonate)
PTFE	Poly tetrafluoro ethylene
PU	Polyuethane
PV	Pervaporation
PVA	Poly(vinyl alcohol)
PVAC	Poly(vinyl acetate)
PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
P(VP-AN)	Poly(1-vinylpyrrolidone-co-acrylonitrile) copolymers
P(VP-S)	Poly(1-vinylpyrrolidone-co-styrene) copolymers
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
SHP	Steric-hindrance pore
Span-80	Sorbitan monooleate (surfactant)
SPEEK	Sulfonated poly(ether ether ketone)
SPEI	Sulfonated poly(ether imide)
SPS	Sulfonated polysulfone
SPSEBS	Sufonated polystyrene ethylene butylene polystyrene
S&S	Schleicher and Schuell
TGA	Thermogravimetric analysis
TMS	Teorell-Meyers

UCLA	University of California, Los Angeles
UF	Ultrafiltration
ZrO_2	Zircornia

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Filter medium is the most important component of any filtration process. Filter medium is permeable to one or more components of a mixture, solution, or suspension, and is impermeable to the retaining component. The permeable component (permeate or filtrate) is normally consists of suspending fluid or solvents or the mixture solvent and other components. While, solid, or colloidal material, or molecular, or ionic species in solution is the retaining component (retentate) at the surface side of the filter medium in filtration process (Cheryan, 1998: Mulder, 1996 and Sutherland, 2005).

Filters media are manufactured using several methods and variety materials such as natural fibers, synthetic fibers, synthetic sheet materials, and/or inorganic materials. The common materials used in the fabrication of this filter media include cotton, polymers, fiberglass, asbestos, sintered metals, carbon, ceramic, and natural minerals (Sutherland, 2005). The filters can be classified into two categories: depth filter or screen filter. In depth filtration, the component to be separated can be filtered on its upstream surface or be penetrated through the surface pore and moves along the pore, and then trapped within the thickness of the filter medium due to size exclusion or adhered on the filter medium wall.

The screen filter operates in the same manner with a sieve where the separated component retains on the upstream of a surface medium. Thus, membrane is generally categorized as a screen filter since its separation technique is similar to the screen filter (Cheryan, 1998). Filtration is the physical-mechanical process to separate two or more components from a fluid (gas or liquid) based primarily on size differences (Geankoplis, 2003). In view of conventional application, filtration process generally refers to the separation of solid immiscible particles from liquid or gaseous stream. The suspended solids in a fluid are separated in part or totally from fluid, by passage of the fluid through a permeable barrier (a filter medium) (Sutherland, 2005 and Cheryan, 1998). The particles larger than 5 to 10 µm and/or above are separated by conventional filtration method.

Membrane separation processes are employed to separate particles or solutes with size diameters lower than 5 to 10 µm in a fluid (Cheryan, 1998). Compare to the conventional separation process, this membrane separation process is also refers to the separation of a solute from fluid by diffusion of this solute from a liquid or gas through a semi-permeable membrane barrier to another fluid. This is because the membrane separation process is not only accomplished by using mechanical-physical forces but also involved molecular or chemical forces and diffusion (Geankoplis, 2003).

The term of membranes is primarily used for separation, and membrane processes are generally refers to separation processes. Hence, the core in the membrane separation process is the membrane itself (M’Bareck et al., 2006). The primary role of a membrane is to act as a selective barrier which it permits passage of certain components and retain certain other components of a mixture in fluid. The membrane can be considered as a permselective barrier or interphase between two phases and the ability of the membrane to transport one component from feed mixture more readily than other components is known as membrane separation process (Mulder, 1996).

The structure of a membrane is vital for the performance of the membrane. There are two types of membrane structures, i.e. symmetric structure and asymmetric structure. Membranes with symmetrical structure do not change throughout the cross section of the membrane while asymmetric membrane consist of a thin selective layer and a strong support layer giving mechanical strength. In term of membrane productivity, asymmetric membranes are in general superior compared to symmetric membranes (Rijn, 2004).

1.2 ASYMMETRIC MEMBRANE

In early 1960’s, Loeb and Sourirarajan made a novel discovery of reverse osmosis process by developing an asymmetric cellulose acetate membrane via phase inversion method with high permeation rate and high selectivity for desalination of saline water. This is due to the unique structure of these types of membranes comprising of a very thin, relatively dense skin layer supported by an open porous sub-layer. The permeability and high selectivity of the membrane is imparted by the skin layer while the mechanical strength is provided by the porous sub-layer. The fabricated asymmetric membranes via phase inversion process can be tailored to the specific application in order to produce the desired purity of permeate by manipulating some membrane parameters condition during the membrane fabrication process applications (Baker, 2004 and Mulder, 1996).

The characteristics and morphological structure of a dense top layer and porous sub-layer can be optimized by adjusting the membrane preparation conditions. The optimization usually requires time consuming and extensive trial and error experimentation. Nowadays, most asymmetric membranes are fabricated by phase inversion, which can be achieved through five principal methods: vapor induced phase separation, thermally induced phase separation, dry phase separation, wet phase separation and dry wet phase separation (Hamzah et al., 2012; Nguyen et al., 2010; Peng et al., 2012; Rajabzadeh et al., 2012, and Riyasudheen and Sujith, 2012)

In all these techniques, an initially homogeneous polymer solution thermodynamically becomes unstable due to different external effects and phase separates into polymer rich and polymer lean phases. The former forms the matrix of the membrane and the latter fills the pores. The formation of a thin dense skin layer and a porous sub-layer of a membrane is a typical structure of an asymmetric membrane (Ismail et al., 2011)

1.3 MEMBRANE TECHNOLOGY

The invention of the asymmetric membranes by Loeb and Sourirajan has made a great impact on the growth of membrane science and technology. Their breakthrough has put a milestone in the history of membrane technology progress. This remarkable finding has opened the door to commercialize the membrane technology from lab-scale membrane application turn to large-scale commercial. Since that, membrane technology has been found to be an alternative and attractive approach for separation. This technology has been widely adopted by different industries over 50 years.

Large-scale commercial industries have been employed membrane separations processes to displace conventional separation processes such as in the water treatment, water purification, waste water treatment, pharmaceutical, biotechnology, chemicals and paper industries as well as petrochemical-related industries. This is due to the membrane separation processes are compact, faster, and more capital and energy efficient compare to conventional separation methods (Anadao et al., 2010). Most of the membrane technology applied in commercial industries employed pressure-driven membrane separation processes. The membrane separation process based on pressure-driven can be classified into four categories, i. e. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).

MF membrane is designed to retain particles in the ‘micron’ range of about 0.10 to 5 µm while UF used to separate macromolecules or particles larger than about 0.001 to 0.02 µm (10 to 200 Å) (Cheryan, 1998). Both membranes can be considered as porous membrane where rejection is determined mainly by the size and shape of solutes relative to the membrane pore size. The transport of solvent is directly proportional to the applied pressure (Mulder, 1996). Nanofiltration (NF) membrane is a membrane filtration process using membrane with a pore size ranging from 1 to 10 nm (5 to 10 Å). It lied between ultrafiltration and reverse osmosis. In general, NF membrane employed to separate organic compounds and (multivalent) ions from a solvent (Baker, 2004 and Schafer et al., 2005).

RO is mainly employed in the desalination of brackish and seawater to produce portable water. It also applied to produce ultrapure water in an electronic industry. The RO membrane shows different transport rates of molecules as small as 2 to 5 Å. The separation principle of NF and RO are based on solution-diffusion mechanisms. Among these membrane processes, ultrafiltration (UF) has the largest potential membrane process employed in various industries application fields (Baker, 2004; Kubota et al., 2008; Mulder, 1996 and M’Bareck et al., 2006). Ultrafiltration (UF) process uses a finely porous membrane to filter and separate water and microsolutes from macromolecules and colloids. The UF membrane has the average pore diameter in the 10 - 1000 Å range (Baker, 2004).

Nowadays, UF is a well-developed membrane separation technology and recently, its application is growing up rapidly in a wide range of applications, including water/wastewater treatment, reverse osmosis pretreatment, and separations in the food, dairy, paper, textile, pharmaceuticals, chemical and biochemical industries (Celik et al., 2011 and Guo et al., 2010). It is also one of the promising separation tools in drinking water and wastewater reuse because of its effectiveness to remove waterborne pathogens (such as bacteria, viruses, and protozoa cysts). In this respect, particulate matter and small pore size provide an absolute barrier to particles, bacteria, high molecular weight organic molecules, emulsified oils and colloids (Adout et al., 2010; Shen et al., 2011 and Shong et al., 2011).

Some of the major profits of the application of the UF membrane process include low energy cost; the ability to operate near ambient conditions; ease of use and the quality of permeate produced. As a consequence of this, increasing demand efforts to improve UF process performance are gaining more and more attention. In general, those efforts are focusing mainly on feed pretreatment, advanced membrane module design and process condition optimization. However, in many cases, the membrane itself is the main key material for the performance of the UF process and most of the commercial polymeric UF membranes are prepared by phase inversion technique (Teli et al., 2012).

Phase inversion technique is a common technique and a well-known method in producing asymmetric UF membranes in nowadays. The main important component in membrane preparation via phase inversion process is the polymeric materials, which determine the characteristics and properties of the produced membranes. Some of these polymeric materials such as cellulosic's (e.g. cellulose acetate, cellulose nitrate), polyacrylonitrile (and related block-copolymers), polysulfone/polyetehersulfone/ sulfonated polysulfone/sulfonated poly(ether-ethersulfone), polyvinylidene flouride, polyimide/poly ether imide, aliphatic polyamides, polyetherketone and ulfonated poly(ether–ether-ketone) are used as a back-bone of ultrafiltration membrane (Mulder, 1996 and Nady et al., 2011). The selection of polymer material as a polymer back-bone to prepare an UF membrane via phase inversion process is very crucial due to the physical, chemical and mechanical properties of this membrane is strongly related to the selected polymer and this in turn affects the separation performance of the respective UF membrane.

1.4 PROBLEM STATEMENT

Cellulose acetate (CA) and polysulfone (PSf) are the most common polymers employed as polymer back-bone in the fabrication of commercial UF membranes. These polymers are selected due to their fairly important characteristics for UF applications (Cho, et al., 2011). CA is the classic membrane materials and still being successfully used especially in water treatment. The membrane fabricated from this polymer is relatively easy to manufacture and low manufacturing cost. Another several advantages, CA membrane posses a good fouling resistance, a more stable performance, high flux, and has moderate chlorine resistance. However, the disadvantages of CA membranes are poor mechanical strength, less stable in organic solvents, narrow pH range (pH 3-7), a narrow temperature range (lower than 50 ^{o}C) and less resistance to biological attack (Cheryan, 1998; Nunes and Peinemann, 2006, and Zavastin, et al, 2010)

PSf is an attractive and important class polymer which is more stable and high performance in harsh operating conditions compare to CA membrane. It has been most widely used in the manufacture of synthetic asymmetric UF membranes. Besides it used as a basic material for synthetic UF membranes, this polymer also used as support material for composite membrane (Mulder, 1996). PSf membrane has been employed in various application in UF processes due to it poses an excellent mechanical property, a very good chemical and thermal stability as well as its high rigidity and creep resistance (Arthanareeswaran et al., 2007a; Bowen et al., 2001; Mulder, 1996, and Rahimpour and Madaeni, 2007)

However, the main disadvantages of PSf membrane are due to its hydrophobic characteristic. The hydrophobicity of polysulfone membrane has restricted the application of the commercial PSf membranes in various aqueous applications. This is due to the nature of the membrane surface leads to an easy deposition of hydrophobic macromolecular solutes or particles (such as in protein filtration) on/at the membrane surface. This phenomenon is known as membrane fouling. In this circumstance, the larger pressure is required to induce the solvent transport through the membrane to increase water flux through membrane pore due to increase in the membrane surface resistance (Blanco et al., 2006).

In practical application of UF systems, membrane fouling is a serious problem. In the drinking water production, even though UF is a very promising process due to its compactness, easy automation and high performance but the main obstacle for wider application of UF in this industry is the membrane fouling. Pore blocking, pore stricting and cake formation are the major factors that contributed to the membrane fouling and these factors usually cause high cost energy, operation, and maintenance (Gao et al., 2011).

Therefore nowadays, many research groups have focused on enhancing property and anti-fouling capability of PSf membrane in order to prolong the lifetime and therefore widen the application of PSf membranes (Zhang et al., 2011). It is well-known and generally accepted among membranologist that increasing the hydrophilicity of membrane will improve antifouling of the membrane. It is also recognized that modification of hydrophobicity of polysulfones membrane is helpful to reduce membrane fouling and prevent the flux-decreasing (Yi et al., 2010). Recently, many membranologist has attempted to improve the hydrophilicity of hydrophobic UF membrane via several methods such as surface modification, plasma treatment, grafting and blending (Rahimpour et al., 2008)

Polymer blend is a simple and efficient method for designing new materials to improve performance of the hydrophobic membranes. Polymer blend is a process, in which two organic polymers are blend in a homogeneous membrane casting solution, which generally contains a solvent or/and an additive. The polymer blend is a proven tool to obtain new types of UF membrane, which has better hydrophilicity compared to the original membranes (Sivakumar et al., 2006 and Bowen et al., 2001). The hydrophilization of hydrophobic UF membrane materials will improve permeability and permselectivity of membrane towards producing of a high performance of UF blend membranes. Recently, many researchers had reported their study on blending of hydrophobic membranes with hydrophilic polymers.

Cellulose acetate phthalate (CAP) is one of the potential hydrophilic organic polymers that can be used and explored in PSf polymer blend technique. CAP has a superior characteristics compared to cellulose due to the presence of numerous acidic and carbonyl functional groups on its structure and was added to PSf casting solutions to improve hydrophilicity and performance of PSf membranes. Rahimpour and Madaeni (2007) claimed that CAP plays a role as a remarkable antifouling agent due to addition of small amount of CAP in polyethersulfone (PES) membrane casting solution significantly improved the performance and antifouling property of PES membrane. Even though, PES has similar chemical and thermal limits to PSf, however, its performance when in contact with the process fluids can be markedly different (Scott and Hughes, 1996). In view of this, an attempt has been made to investigate the effect of using different composition of CAP in casting solution in terms of hydrophilicity properties, morphology and performance of PSf based membranes.

The production of asymmetric UF membrane is not only influenced by polymers used but three other components, which are solvent, non-solvent and additive, and these factors have significant effects on membrane characteristics. The presence of additive in membrane casting solutions plays a crucial role in adjusting the membrane properties. Generally, additives create spongy membrane structure by preventing the macrovoids formation, enhance pore formation, improve pore interconnectivity and introduce hydrophilicity (Rahimpour et al., 2007 and Liu et al., 2003). Usually, a hydrophilic additive such as polyvinylpyrrolidone (PVP) or polyethylene glycol (PEG) is mixed in casting solution to obtain hydrophilic membrane (Rahimpour et al., 2008). These additives were employed in polymer blend membranes in order to improve hydrophilicity and performance of the blend membranes. Investigation on the rheological factors (such as shear rate) and the effect of convective evaporation time (dry phase) during membranes fabrication process provides a potential platform for developing high performance membrane. It is believed that these two factors play an important role in the membrane fabrication process by altering molecular orientation during formation of the high performance membranes.

In this study PSf is considered as the main polymer for PSf/CAP blend UF membranes. The effects of different polymers composition of PSf/CAP blend were studied in terms of membrane morphology, pore properties, hydrophilicities properties and performance of PSf/CAP blend membranes. The results of the PSf/CAP blend membranes were compared to the original membrane, PSf membrane. Then, the best PSf/CAP blend membrane was selected to study the role of an organic additive, PVP in the blend membrane. PSf/CAP/PVP blend membranes were prepared by varying the concentrations of PVP in the best PSf/CAP blend membrane. The effects of PVP were studied to find the best PSf/CAP/PVP blend membrane performance.

Next, two membrane fabrication condition parameters (shear rate and evaporation time) were used to produce PSf/CAP/PVP blend membrane with high rejection performance. First, the best PSf/CAP/PVP blend membranes were cast at different shear rate and then, the best blend membrane was determined based on protein separation performance test. Finally, the PSf/CAP/PVP blend membranes were fabricated at different evaporation time at the best shear rate condition. It were tested to find the best high performance of PSf/CAP/PVP blend membrane in terms of high permeate flux and high rejection of protein solution at the best membrane fabrication condition parameters (shear rate and evaporation time).

1.5 OBJECTIVES

The objectives of this study are as follows:

i. To study the effects of CAP in PSf/CAP blend membranes on hydrophilicity properties, pore properties, morphological structures and performance of PSf/CAP blend membranes.
ii. To investigate the role of organic additive, PVP in improving the membrane properties and performance of PSf/CAP/PVP blend membranes.
iii. To study the effects of fabrication condition, i.e. shear rate during membrane fabrication on the characteristics, performance and morphology of PSf/CAP/PVP blend UF membranes.
iv. To investigate the influence of convective evaporation time (dry phase) on PSf/CAP/PVP blend membranes in order to find the best preparation condition for high performance membrane.
v. To determine the best dope formulation and the best fabrication condition of dry/wet phase inversion process for producing high performance asymmetric PSf/CAP/PVP blend ultrafiltration membranes.

1.6 SCOPES

In order to achieve the above mentioned objectives, the following scopes of works have been drawn:

i. Preparing PSf dope solution and PSf/CAP blend dope solutions which containing different polymer composition of PSf/CAP.
ii. Fabricating PSf and PSf/CAP blend UF membranes via wet-phase inversion technique by using an electrically-automatic casting machine.
iii. Characterizing PSf and PSf/CAP blend UF membranes in terms of water content, contact angle, pore characteristics and morphology.

iv. Determining the best PSf/CAP blend UF membrane in terms of pure water permeation and performance test of proteins.
v. Preparing and fabricating PSf/CAP/PVP blend UF membranes containing different concentrations of PVP additive.
vi. Characterizing PSf/CAP/PVP blend UF membranes and determining the best PSf/CAP/PVP blend UF membrane.
vii. Preparing the blend UF membrane by varying fabrication process parameters such shear rate and evaporation time.
viii. Determining the best fabrication process parameters in order to produce the best PSf/CAP/PVP blend UF membrane performance.

1.7 OVERVIEW OF THE THESIS

This thesis is organized in five chapters including introductory chapter in Chapter 1, literature review in Chapter 2, materials and methodology in Chapter 3, Chapter 4 about results and discussion and finally, conclusion and recommendations in Chapter 5. Firstly in Chapter1, the information about filter media and types of filtration is briefly discussed. Then, the difference between a conventional separation and membrane separation process is explained. The information about asymmetric membranes and membrane technology processes are also described. The problem statement, objectives and scope of study in preparing PSf/CAP and PSf/CAP/PVP blend membranes are included in this chapter.

Chapter 2 covers detail explanations about membrane and membrane separation processes. A historical literature about chronological development of ultrafiltration (UF) membranes and UF membrane materials are covered. Background on formation of asymmetric UF membranes via dry phase, wet phase and dry/wet phase method well explained. The fundamental knowledge and theories about transport mechanisms in UF membranes are also explained. The role of materials, additive, shear rate and evaporation time effects on membrane structures properties and separation performance is discussed. This chapter also described about characterization of UF membranes in terms of water content, contact angle, MWCO and pore properties as well as SEM. Explanations about membrane fouling was also included.

Materials and methodology of this study were described in Chapter 3. In this chapter, all the materials employed in this study such as PSf, CAP, NMP, PVP and proteins are discussed. The details about the preparation of PSf/CAP and PSf/CAP/PVP membrane casting solutions and membrane fabrication system are well explained. Chapter 3 also describes the details of membrane characterizations and membrane performance tests. There are two types of membrane separation performance tests, i.e. pure water permeation test and protein separation test.

All the characterization and performance test results of PSf/CAP and PSf/CAP/PVP blend membranes are discussed in detail in Chapter 4. In this chapter, the effects of CAP and PVP on PSf/CAP/PVP blend membranes are explained in terms of water content, contact angle, membrane permeability and porosity. The membrane surface properties are also described in term of MWCO, average pore size and pore density. Pure water flux, proteins rejection and proteins permeate flux are used to study the membrane performance. SEM photographs are used to support the explanation about membrane performance. The best membrane performance is determined based on the membrane characteristics and membrane separation performance. The effects of shear rate and evaporation time on PSf/CAP/PVP blend membranes are also well discussed in this chapter.

Finally, Chapter 5 deals with the conclusion and recommendations. This chapter presents the conclusion derived from this research study. Recommendations for future study in order to improve fundamental knowledge about PSf/CAP/PVP membrane blends and to enhance separation performance are discussed. The raw experimental data and sample calculations are presented in the Appendices.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE

Over the last 50 years, membrane separation technology is in a state of rapid growth and innovation. Membrane science and technology is an expanding field and has become a prominent part of many activities within the process industries. Industrial membrane separation with synthetic membranes has been strongly developed since the introduction of asymmetric polymeric membranes in the early sixties.

Membrane science and technology is interdisciplinary fields which involved chemist, physical chemist, mathematicians and chemical engineers. The role of chemists is to develop new membrane structures, while physical chemists and mathematicians take part to describe the transport properties of different membranes using mathematical models in order to predict membranes separation characteristics. Meanwhile, chemical engineers contribute in designing separation processes for large scale industrial utilization (Strathmann, 1990).

However, the most important element in membrane science and technology is the membrane itself. The membrane is the heart of every membrane processes (Scott and Hughes, 1996). There are a number of definitions of the word “membrane” and it is difficult to covers all of its aspects and roles. A membrane can often be better described in terms of what it does rather than what it is. Prof. George Solt, a former Director of the School of Water Sciences, Cranfield has defined a membrane as “a material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process" (Judd and Jefferson, 2003). For the purpose of this research, Solt's definition can be considered adequate to describe what the membrane itself is.

Membranes can be classified according to different viewpoints but generally it can be divided into four categories as below (Cheryan, 1998 and Mulder, 1996):

a) Nature of the membrane – natural (biological) or synthetic membranes
b) Structure or morphology of the membrane – porous versus nonporous membranes, its morphological characteristics, or as liquid membranes
c) Applications of the membrane – gaseous phase separation, gas-liquid, liquid-liquid, etc.
d) Mechanisms of membrane action – adsorptive versus diffusive, ion-exchange, osmotic, or nonselective (inert) membranes

2.2 MEMBRANE SEPARATION PROCESSES

Membrane technology is now well accepted as a cost-effective technology and conferring unique advantages over conventional separation processes. The driving expansion in environmental applications due to the improvements of the underlying technology, a more competitive market, a more stringent regulatory environment, broader range of membrane processes offered and the availability of new fabrication materials make membrane processes as the best available alternative separation technologies. Membrane technology plays an increasingly important role as unit operations for resource recovery, pollution prevention, energy production, environmental monitoring and quality control, fuel cells and bio-separation applications.

Most of the membrane separation processes are pressure-driven. In pressure-driven membrane separation process, separation is achieved due to a driving force, i.e. pressure, acting on the components in the feed and this driving force has induced one component to transport through the membrane readily than any other components in the feed. The major pressure-driven membrane separation processes which cover a wide range of particles or molecular sizes, and applications are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) (Cheryan, 1998). Table

2.1 shows a classification of various membrane separation process based on particle or molecular size, driving force and transport mode. Characteristics of retentate and permeate in different membrane processes is presented in Table 2.2.

Table 2.1: Characteristics of membranes used in different membrane separation processes

Process	**Structure**	**Pore size (μm)**	**Driving force, bar**	**Transport mode**
MF	Symmetric, asymmetric	0.05 to 10.0	Pressure, (Δ*P*) 0 to 1	Sieving
UF	Asymmetric	0.001 to 0.1	Pressure, (Δ*P*) 1 to 10	Sieving
NF	Thin film asymmetric	< 0.002	Pressure, (Δ*P*) 10 to 25	Solution diffusion
RO	Thin film asymmetric	< 0.002	Pressure, (Δ*P*) 10 to 100	Solution diffusion
Dialysis	Symmetric, asymmetric	0.001 to 0.1	Concentration (ΔC)	Sieving + diffusivity
PV	Asymmteric, homogeneous	nonporous	Partial pressure	Solution diffusion
ED	Cations and anions exchange	nonporous	Electrical potential (current/voltage)	Ion migration
Gas Separation (GS)	Asymmetric, composite, homogeneous	nonporous (or porous < 1.0 μm)	Pressure, (Δ*P*) 10 to 100	Solution diffusion

Source: Baker (2004), Porter (1990), Scott (1995) and Mulder (1996)

Table 2.2: Characteristics of retentate and permeate in different membrane processes

Process	Retentate	Permeate
MF	Suspended particles, water	Dissolved solutes, water
UF	Large molecules, water	Small molecules, water
NF	Small molecules, divalent salts, dissociated acids, water	Monovalent ions, undissociated acids, water
RO	Solute, water	Water
Dialysis	Large molecules, water	Small molecules, water
PVP	Non-volatile molecules, water	Volatile small molecules, water
ED	Non-ionic solutes, water	Ionized solutes, water

Source: Cheryan (1998)

MF is widely used for the separation, purification and clarification of protein-containing solutions including the recovery of extracellular proteins produced via fermentation and for the removal of bacteria and viruses in the final formulation of therapeutic proteins. In all these processes the macromolecules and proteins involved are much smaller in size than the pores of the MF membrane and should not normally be retained by the membranes (Kelly and Zydney, 1995). The basic operational concept of MF leads to a solute concentration that is higher and close to the membrane surface than it is in the bulk feed stream (Wakeman and Williams, 2002). Module configuration of MF include hollow-fiber, tubular, flat plate, spiral-wound and rotating devices. The two standard modes of operation are dead-end and cross-flow configurations.

UF membranes process is between MF and NF membranes. The UF membranes were discussed in the next sub-chapter. NF membrane has two extraordinary characters. First, they have intermediate molecular weight cutoff between pure RO with a salt rejection higher than 90 %, and pure UF with a salt rejection of less than 5%. The MWCO of NF membranes ranged from 0.2 to 10 kDa; the pore diameters estimated from the Stokes-Einstein relationship range from 1 nm to a few nm (Wang, et al., 1995). NF membranes pore sizes are in the ionic and molecular range, multivalent ions and larger organic molecules are well rejected, while monovalent ions are unsuccessfully rejected. In NF membrane, solutes having sizes larger than the pore size of membranes cannot pass through the membrane and retained on the membrane surface (Mohammad, 1998).

Reverse osmosis membrane acts as a barrier to flow, allowing selective passage of a particular species (solvent) while other species (solutes) are retained partially or completely. Solute separation and permeate solvent (water in most cases) flux depend on the material selection, the preparation procedures, and the structure of the membrane barrier layer (Lloyd, 1985, and Sourirajan and Matsuura, 1985). Cellulose acetate (CA) is the material for the first generation reverse osmosis membrane. Utilization of this kind of membrane for sea water desalination triggered the applications of membrane separation processes in many industrial sectors. The great interest of reverse osmosis is a high-quality of permeate, and often even too good. The limitation of this membrane is operated at high operating pressure resulted in a considerable high energy cost.

2.3 CHRONOLOGICAL OF ULTRAFILTRATION DEVELOPMENT

The beginnings of ultrafiltration (UF) are coincident with reverse osmosis (RO) around 1960s. In 1906, Benchhold produced collodion (nitro cellulose) membranes with pore sizes below 0.01 micron. This is the first synthetic ultrafiltration membrane that has been fabricated and developed. He also introduced the term ‘ultrafilter’ to these collodion membranes. The collodion membranes produced by Benchhold were low in the hydraulic permeability and its pores were easily plugged (Baker, 2004 and Porter, 1990).

Other important early workers were Zsigmondy and Bachmann, and Ferry and Elford. Zsigmondy and Bachmann patented their collodian filter in 1918 (Baker, 2004). After a few stages of evolution and innovation in producing collodion membranes, collodion ultrafiltration and microfiltration membranes were widely used in laboratory studies by the mid-1920s. Before 1960s, although RO and UF membranes showing promising results in their retention properties but there were no application of RO or UF processes in any industry. It is due to the both membranes had impractical filtration rates (flux) (Cheryan, 1998 and Porter, 1990).

At the end of World War II, the United States (U.S.) Government became concerned about shortages in water before the end of the century and with the proactive action, the U.S. Government has funded substantial financial resources for the development of various separation processes in water desalination for over two decades (1950-1973). In the mid-1950s, Prof Charles E. Reid from the University of Florida and Sourirajan from University of California, Los Angeles (UCLA) has started the first work in RO by using cellulose acetate (CA) as a semi-permeable medium towards seawater electrolytes. They found that the salt rejection of 94% but the water fluxes were too low to be interesting (Porter, 1990).

In 1959, Sourirajan's partner, Sidney Loeb uncovered CA membrane recipe introduced by a French investigator, Dobry and he introduced acetone into Dobry's recipe as suggested by Llyod Graham, a UCLA graduate student. He found a remarkable results after annealed CA membrane at 80 ^{o}C to yield a salt rejection of 99% and the water flux was 200 times greater than Sorirajan's CA films and 5 times greater than the annealed Schleicher and Schuell (S&S) membrane (Schafer et al., 2005). This finding was a very promising result and consequently made a crucial breakthrough in producing RO and UF asymmetric or anisotropic membranes in a large fabrication scale especially for industrial applications.

The major reason for this significant breakthrough resided in the asymmetric structure of the membrane. Loeb has found there were two layers exists in the asymmetric membrane, a dense skin layer which less than 1 μm in thickness and a porous layer below the dense layer. The dense skin layer or thin layer is responsible to the rejection of solutes and at the same time it minimized the hydraulic permeability of water/solvent through the membrane. The porous layer provided mechanical strength of the asymmetric membrane at high operating pressure (Mulder, 1996 and Porter, 1990).

Prof. Alan S. Michaels from Massachusetts Institute of Technology and the founder of Amicon Corporation took initiative to make collaboration between Amicon and Dorr-Oliver in a joint development program to develop UF membranes. In 1966, they were succeeded in producing asymmetric UF membranes from many polymers such as polyacrylonitrile copolymers, aromatic polyamides, polysulfone and poly(vinylidene fluoride). The ten-year period between 1965 and 1975 was a period of intense development of chemically and thermally resistant UF membranes which were fabricated from the above mentioned polymers and today, these materials are still widely used in ultrafiltration membrane making (Baker, 2004 and Porter, 1990).

Hollow fibers were also developed during this decade and followed later by tubes, plate and frame unit, and spiral wound modules became available. First commercially significant ceramic membrane was introduced in 1988. Even though ceramic membranes much more expensive than polymeric membrane but ceramic membranes can be employed in high temperature operating condition or require regular cleaning with harsh solutions to control membrane fouling (Baker, 2004). Some of the milestones in the development of ultrafiltration membranes are summarized in Table 2.3.

2.4 ULTRAFILTRATION MEMBRANES

Currently, reverse osmosis (RO) and ultrafiltration (UF) are the two most important membrane separation processes in the wide range of industrial applications. The success of these membrane processes is due to a great extent in development of asymmetric membranes. Asymmetric membranes can be regarded as a dual-zone system, consisting of very thin active layer (skin) and a much thicker, porous support layer (Rautenbach and Albrecht, 1989). The schematic diagram of an asymmetric membrane consists of two layers is shown in Figure 2.1.

Table 2.3: Milestone in the development of ultrafiltration

Year	**Inventor**	**Milestone**
1906	Benchold	Prepared collodion membranes of graded pore size, measure bubble point points and use the term ultrafilter
1918	Zsigmondy and Banchman	Patent collodion filter
1926	Membrane Filter GmbH	Commercialized UF membranes
1963	Loeb-Sourirajan	Develop anisotropic RO membranes
1966	Amicon	Market laboratory-scale UF membranes, and developed PSf and PVDF membranes
1969	Abcor	Installed commercial tubular UF plant (electro paint)
1973	Romicon	Introduced hollow fiber capillary UF plants
1980	Abcor	Commercialized spiral wound UF modules
1988	Abcor	First commercially significant ceramic membrane introduced

Source: Baker (2004)

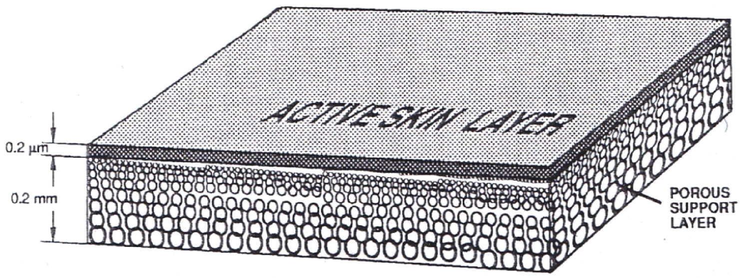

Figure 2.1: Asymmetric membrane structure

Source: Strathmann (1990)

The active layer on the top of the asymmetric membranes is the prominent feature of these membranes and generally, it thickness is around about 0.1 to 1.0 µm. This thin skin permits high hydraulic permeability of the permeate. The second layer or also known as a support layer is more open or porous substructure (typically 100 to 200 µm in thickness) provides good mechanical support to asymmetric membranes. High mass transfer rates and good mechanical stability are the unique properties offered by these two layers of asymmetric membranes that has been widely used in RO, UF or gas separation processes (Porter, 1990 and Scott and Hughes, 1996).

Asymmetric membrane separation performance can be determined by the nature of the skin polymer, membrane pore size and the mass transport rate, which mainly governed by the skin thickness. Furthermore, the thickness, porosity and pore size of the dense skin control permeability and selectivity of asymmetric membranes at a given operating pressure and temperature. The highly porous sub-layer reacts as a support layer for the fragile and thin skin as well as provides the mechanical strength or stability. This highly porous sub-layer allows the membrane to tolerate the pressure effects employed during membrane operations.

Ultrafiltration (UF) membranes typically refer to anisotropic (asymmetric) membranes with porous surface layer which have pore diameter from 10 to 1000 Å. UF membranes covers the region between MF and NF. The finely porous surface layer (also known as a skin layer or a top dense layer or a thin active layer or a very thin selective skin layer) performs separation of dissolved macromolecules by discriminating them by their sizes via sieve mechanism (Baker, 2004). In the sieve mechanism, the separation of the dissolved macromolecules is determined by the size and shape of the solutes relative to the pore size in the UF membranes (Mulder, 1996). In industrial applications, UF membranes are used to remove particles in the size range of 0.001 to 0.02 µm as retained materials, whilst solvents and salts of low molecular weight will pass through the UF membranes as depicted in Figure 2.2.

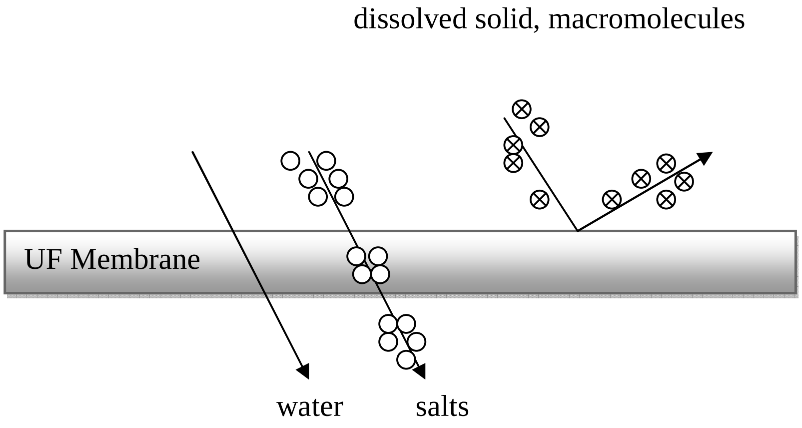

Figure 2.2: Separation by ultrafiltration membrane

Source: Scott and Hughes (1996)

UF membranes, based on variety of synthetic polymers, have high thermal stability, chemical resistivity, and restricted the use of fairly harsh cleaning chemicals (Reis and Zydney, 2007; Zydney and Kuriyel, 2000). UF are especially well suited for the separation of fine particles. The choice of membrane was usually guided by its molecular weight cut-off (MWCO), which is defined as the equivalent molecular weight of the smallest protein that would exhibit above 80% rejection. Although this choice is arbitrary, but it has been adopted by most of the UF membrane user community (Saxena et al, 2009). Hollow fiber, flat-sheet cassettes, spiral wound cartridges, tubular modules, and enhanced mass transfer devices have been developed for UF. These modules provide physical separation of the retentate and filtrate streams, mechanical support for the membrane (if needed), high membrane packing densities (membrane area per device volume), easy access for cleaning and replacement, and good mass-transfer characteristics (Reis and Zydney, 2007; Zydney and Kuriyel, 2000).

2.4.1 Materials of Ultrafiltration Membranes

Ultrafiltration (UF) membranes can be categorized according to the material composition which is either organic (polymeric) or inorganic (ceramic or metallic). Polymeric UF membranes such as polysulfone/polyetehersulfone/sulfonated polysulfone, polyvinylidene flouride, polyacrylonitrile (and related block-copolymers), cellulosics (e.g. cellulose acetate), poly(phenylene sulfide) and polyimide/ poly(ether imide) are prepared by phase inversion process and commercially used in these days in various applications (Mulder, 1996 and Nunes and Peinemann, 2006). Synthetic polymeric membranes can also be divided into hydrophobic and hydrophilic classifications. Table 2.4 shows the various hydrophilic and hydrophobic polymers used for membrane production.

Table 2.4: Commercial available hydrophilic and hydrophobic polymers for membrane production

Hydrophilic polymers	**Hydrophobic polymers**
Cellulose acetate (CA)	Polysulfone (PSf)
Cellulose acetate butyrate (CAB)	Polyethersulfone (PES)
Cellulose acetate propionate (CAP)	Poly(vinyidenel flouride) (PVDF)
Cellulose nitrate (CN)	Polycarbonate (PC)
Cellulose propionate (CP)	Polypropylene (PP)
Ethyl cellulose (EC)	Poly(methyl methacrylate) (PMMA)
Polyamide (PA)	Poly tetrafluoro ethylene (PTFE)
Poly(acryl acid) (PAA)	Polyethylene (PE)
Poly(vinyl alcohol) (PVA)	Polystyrene (PS)
Poly(vinyl acetate) (PVAC)	Polyphenylene oxide (PSO)
Poly(vinyl butyral) (PVB)	Polyphenylene sulfide (PS)

Source: Kesting (1985), Lloyd (1985) and Mulder (1996)

Alumina (Al_2O_3) and zircornia (ZrO_2) have been used as inorganic materials for developing ceramic UF membranes. These ceramic UF membranes were employed to replace polymeric UF membranes especially for harsh operating condition such as high operating temperature and various pH range (Mulder, 1996). Although membrane materials vary vastly according to chemical compositions, the principal objectives in manufacturing of commercial membranes are to produce membrane with high selectivity, high flux and less fouling as well as highly resistant to chemical and heat. The common commercial available polymeric membranes for MF, UF, NF and RO membranes in water industries with their advantages and disadvantages are demonstrated in Table 2.5.

Table 2.5: Advantages and disadvantages of phase inversion polymeric membranes in water industries

Polymer[a]	**Advantages**	**Disadvantages**	**Process**[b]
CA	Chlorine resistant Inexpensive More fouling resistance than PA	Susceptible to alkaline hydrolisis at pH > 6 Susceptible to biodegradation Limited thermal and chemical stability	UF, NF, **RO**
PA	More all-around stability than CA	Very limited chlorine tolerance (<0.1 ppm)	NF, **RO**
PAN	High resistance to hydrolisis High resistance to oxidation	Hydrophobic Requires copolymers to make less brittle	UF, RO
PSf, PES	Very good all-round stability Mechanically strong	Hydrophobic	UF, RO
PVDF, PTFE	Extremely high chemical stability High thermal stability	Highly hydrophobic Limited intrinsic permeability Expensive	**MF**, UF
PEI	High chemical stability Very high thermal stability Mechanically strong	Hydrophobic Less solvent resistant than PVDF Poorer alkaline stability than PSf or PAN	**UF**, RO
PP	Inexpensive	Hydrophobic	**MF**, UF

[a] CA, cellulose acetate; PA, polyamide; PAN, polyacrylonitrile; PSf, polysulfone; PES, polyether sulfone; PVDF, polyvinylidene fluoride; PTFE, polytetrafluoroethane; PEI, polyetherimide; PP, polypropylene. [b] Most usual application in **bold type**

Source: Judd and Jefferson (2003)

2.4.2 Formation of Ultrafiltration (UF) Membranes: Phase Inversion Process

Membranes can be formed by using one of several methods. The integrally skinned asymmetric membrane via the phase inversion process can be fabricated through three different precipitation processes. These precipitation processes are wet phase inversion, dry phase inversion, and dry/wet phase inversion. Pinnau and Koros (1991a) has explained and discussed the differences between wet, dry and dry/wet in the phase inversion processes as shown in Figure 2.3.

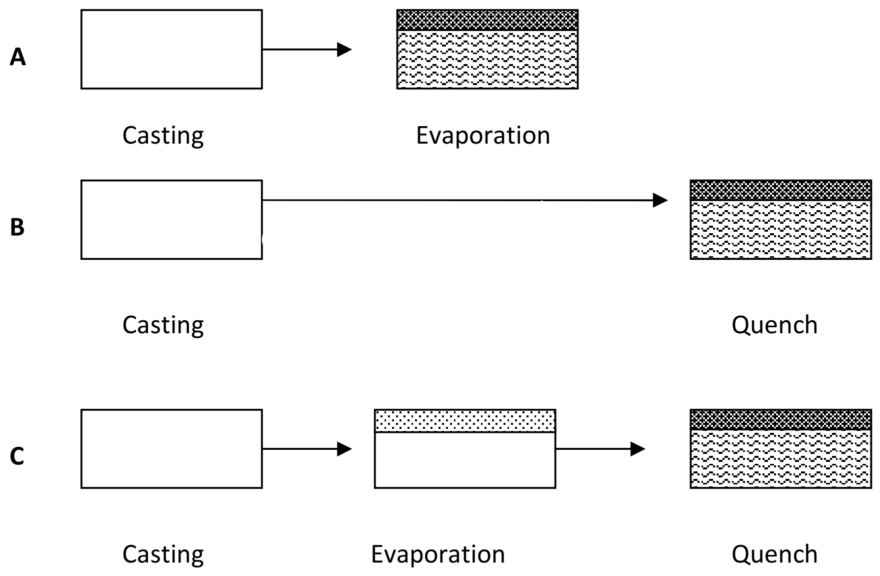

Figure 2.3: Schematic representation of phase inversion processes:
(a) dry-phase inversion, (b) wet-phase inversion,
and (c) dry/wet-phase inversion

Source: Pinnau and Koros (1991a)

Barth et al., (2000) has described that these three types of phase inversion can be distinguished during the formation processes of a membrane. The evaporation of volatile solvent in the casting solution film and/or by absorption of a non-solvent (water) from the air moisture in the atmosphere will ultimately produce a critical non-solvent concentration that causes the cast membrane to be transformed from a single-phase to a two-phase structure. This technique is known as a dry phase inversion process. The phase instability and structure formation can be also be achieved by the exchange of solvent and non-solvent by immersing the polymer solution film into a coagulation bath or a quench medium which contains a non-solvent. This phase inversion process is often referred as a wet phase inversion process.

The dry/wet phase inversion process is the process of making a membrane by combination of the dry phase inversion process and the wet phase inversion process. This process takes two stages of processes. The first stage is the polymer casting solution is exposed to the atmosphere for a certain period of time. The outermost region of the polymer film undergoes phase separation induced by solvent evaporation. This micro-phase separation process formed the membrane structure of the polymer solution film. Then for the second stage, the polymer solution film immersed in a coagulation bath. The bulk of the membrane structure is formed by solvent/non-solvent exchange process during this stage (Pinnau and Koros, 1991a and Barth et al., 2000).

In the phase inversion process, precipitation of polymer solution is generally well explained by using of a ternary mixing figure. During immersion of polymer casting solution into a coagulation bath or a quench medium, the exchange process takes place between non-solvent and solvent at the surface film of polymer casting solution. In this process, solvent in the polymer solution comes out into the bulk of coagulation bath and replaced by non-solvent from the coagulation bath. A non-solvent plays a role as a precipitation agent in precipitation process and a gel is formed which is known as membrane (Nunes and Peinemann, 2006).

Figure 2.4 shows a precipitation process of the ternary system of polymer casting solution which contains polymer, solvent and non-solvent. Point A represents polymer casting solution before immerse in a coagulation bath. Then, this cast solution is immersed in the bath and a solvent-non-solvent exchange occurs. The triple component mixture (polymer-solvent-non-solvent) reaches a solubility gap at point B. Further exchange between these two components leads to phase separation which results in a rigid polymer phase. Finally, all the solvent is replaced by non-solvent and precipitation process is finished at point C. The final precipitation process has resulted a polymer-rich phase (solid phase) which forms the membrane matrix at point D and a polymer-poor phase at point L which represents the pore volume filled with non-solvent (Rautenbach and Albrecht, 1989).

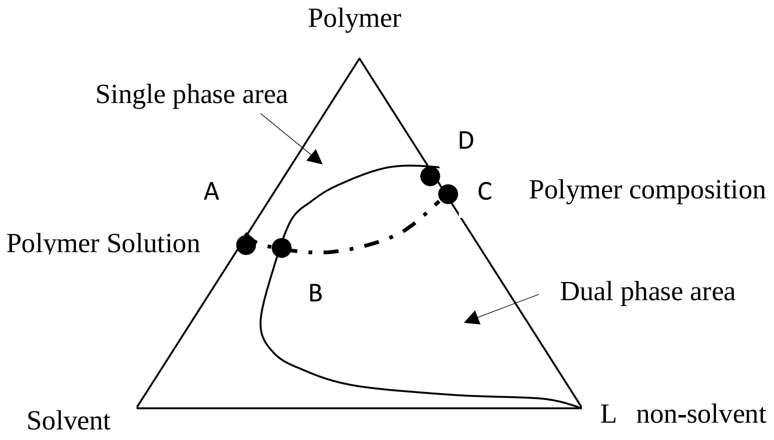

Figure 2.4: Triple component-dual phase separation for membrane production

Source: Rautenbach and Albrecht (1989)

2.5 TRANSPORT MECHANISMS OF ULTRAFILTRATION MEMBRANE

The transport of MF and UF membranes has been well explained by Mulder (1996). MF and UF membranes separate or remove particles or macromolecules from colloid or dissolved macromolecules by sieve mechanism. Pressure is employed as a driving force to make these membrane separations occurs. Solvent is forced to transport through pores distributed across these membranes structure and this transport mechanism is known as convective flow.

UF and MF membranes are porous membranes consist of a polymeric matrix in which a large variety of pore geometries may possible as shown in Figure 2.5. Different transports models have been developed to describe transport of permeate due to different pore geometries exist in these two membrane processes. Generally, the transport of permeate or the volume flow or the flux, *J*, through MF and UF membranes can be described by Darcy’s law:

$$J = A.\Delta P \tag{2.1}$$

where A is the permeability constant and ΔP is the pressure difference across the thickness of the membranes. In this equation, the volume flow (flux) through the membrane is directly proportional to the applied pressure.

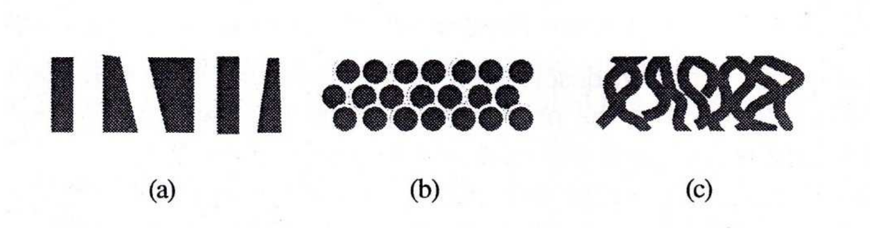

Figure 2.5: Some characteristic pore geometries found in membranes:
(a) Parallel cylindrical pores (b) close packed spheres
(c) a sponge-like structures

Source: Mulder (1996)

Figure 2.5(a) represents a number of parallel cylindrical pores perpendicular or oblique to the membrane surface. The Hagen-Poiseuille equation (Eq. (2.2)) is used to explain the volume flux (*J*) through these pores by assuming that all the pores have the same radius.

$$J = \frac{\varepsilon r^2}{8\eta\tau}\frac{\Delta P}{\Delta x} \tag{2.2}$$

where ΔP is the pressure difference across, Δx is the membrane thickness, ε is the surface porosity, r is the pore radius, η is the solvent viscosity and τ is the pore tortuosity.

The ratio between the pressure differences (ΔP) across thickness of a membrane (Δx) is known as the driving force. This equation describes that the solvent flux is proportional to the driving force and inversely proportional to the solvent viscosity. The hydraulic permeability, L_p in terms of the porosity (ε), pore radius (r), pore tortuosity (τ) and viscosity (η) has been introduced to the this equation.

$$L_p = \frac{\varepsilon r^2}{8\eta\tau} \tag{2.3}$$

So Eq. (2.3) substitute into Eq. (2.2)

$$J = L_p \frac{\Delta P}{\Delta x} \tag{2.4}$$

Which means

$$Flux, J = Hydraulic\ Permeability, L_p \times Driving\ Force, {}^{\Delta P}/_{\Delta x} \tag{2.5}$$

In organic and inorganic sintered membranes or in phase inversion membranes with a nodular top layer structure which consisting pore geometry of close packed spheres system (Figure 2.5(b)), the performance of the membrane is represented by the Kozeny-Carman relationship as shown in Eq. (2.6).

$$J = \frac{\varepsilon^3}{K\eta S^2(1-\varepsilon)^2}\frac{\Delta P}{\Delta x} \tag{2.6}$$

where ε is the volume fraction of the pores, S is the internal surface area and K is the Kozeny-Carman constant, which depends on the shape of the pores and the tortuosity.

A sponge-like structure as depicted in Figure 2.5(c) presented the characteristic pore geometry found in phase inversion membranes. The Hagen-Poiseulle or the Kozeny-Carman relation can be used to explain and describe the volume flux permeates through these asymmetric phase inversion membranes. It should be realized that the convective flow as described by these equations only involves membrane-related parameters and none which apply to the solutes.

2.5.1 Measurement of Pore Size by the Hagen-Poiseuille Equation

The principle of the water permeability method is the capillary pore diffusion model and the Hagen-Poiseuille equation, and the mean pore size can be calculated by the Hagen-Poiseuille equation (Hayama et al., 2000 and Zhao et al., 2000):

$$J = \frac{A_k d^2 \Delta P}{32\tau\eta\Delta x} \tag{2.7}$$

Where J is the water flux, ΔP is the transmembrane pressure, A_k is the membrane surface porosity, Δx is the thickness of membrane skin layer, η is the viscosity of water, τ is the tortuosity of pore, and d is the mean pore diameter.

Rearrange the Eq. (2.7), the mean pore diameter can be obtained as below:

$$d = \sqrt{\frac{32J\tau\eta\Delta x}{\Delta P A_k}} \tag{2.8}$$

2.6 FOULING OF ULTRAFILTRATION MEMBRANES

It is well known that membrane materials which have hydrophobic property are easy to foul during process operation. When all operating parameters are kept constant such as pressure, temperature, flow rate and feed concentration, a decline in flux with time in membrane process operation is known as membrane fouling. The flux decline is very severe especially in porous membranes such as microfiltration and ultrafiltration due to a concentration polarization, adsorption, gel layer formation (cake layer) and the pores plugging. Roughly there are three types of foulants can be distinguished (Mulder, 1996):

a. Organic precipitates (macromolecules, biological substance, etc.)
b. Inorganic precipitates (metal hydroxide, calcium salts, etc.)
c. Particulates

Fouling will depend on physical and chemical parameters such as concentration, temperature, pH, ionic strength and specific interactions (hydrogen bonding, dipole-dipole interactions). Hence, fouling phenomenon is very complex and difficult to describe theoretically. Generally, the membrane or system performance which involves fouling phenomenon can be written in terms of the convective flux as below:

$$flux = \frac{driving\ force}{viscosity.total\ resistence} \tag{2.9}$$

$$J = \frac{\Delta P}{\eta R_{tot}} \tag{2.10}$$

$$R_{tot} = R_m + R_{cp} + R_g + R_a + R_p \tag{2.11}$$

Where R_{tot} is total resistance comprises of R_m, membrane resistance, R_{cp}, concentration polarization resistance, R_g, resistance of gel layer formation, R_a, adsorption resistance and R_p, pore blocking resistance. Figure 2.6 depicted an overview of various types of resistance towards mass transport across a membrane in pressure driven process.

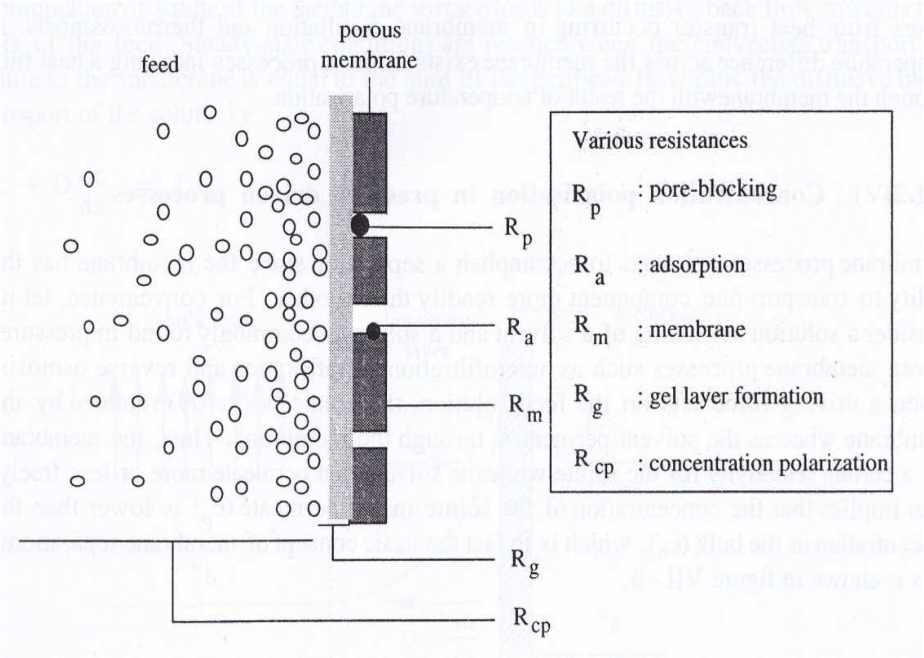

Figure 2.6: Overview of various types of resistance towards mass transport across a membrane in pressure driven processes

Source: Mulder (1996)

Membrane fouling is the major limiting step in membrane technology. This limiting factor reduces productivity as a result of low performance of membrane (Fersi et al., 2009). Fouling has a negative influence on the economics of a membrane operation process. It increases the operational cost due to usage of high energy, high maintenance and cleaning cost. This problem has made slow acceptance in early introduction of ultrafiltration membrane technology in industrial area applications.

There are several methods are employed to overcome or reduce fouling problems include (Sutherland, 2005);

a. The choice of a membrane material as little susceptible to fouling as possible
b. Pretreatment of the feed solution such as addition of complexing agents, pH adjustment and adsorption process (activated carbon).
c. The dosing of the surface of the membrane with substances than inhibit fouling
d. The increase of shear close to the membrane surface, either by increasing suspension flow rates, or by moving the membrane in relation to this flow (by

rotation or vibration), or by mounting moving surfaces near to the membrane (stirrer).

2.7 ULTRAFILTRATION BLEND MEMBRANES

In order to achieve a particular separation via a membrane process, the first step is to select a suitable membrane material. An ideal material have reasonable mechanical strength, maintain a high output and be selective for the desired permeate constituent (Judds and Jefferson, 2003). Generally, polymer materials used in membrane fabrication such as cellulose acetate has good fouling resistance, high flux and stable performance but the drawbacks of this membrane material are poor mechanical strength, less stable in organic solvents and less resistance to biological attack. Due to that, the alternative polymers such as PSf, PVDF and PEI are offered better properties with high mechanical strength, thermostable and chemical-resistant. The major disadvantages employed these polymers in membrane fabrication that they are quite hydrophobic and it is not always possible to prepare these membranes for specific applications.

The polymer such as CA has good surface properties but not good in mechanical property and the other hand, the materials those posses' good mechanical and chemical resistant properties are hydrophobic materials. Due to this dilemma, the UF manufacturers are still looking for the production of inexpensive membranes which have good mechanical, thermal and chemical properties as well as high performance that can be successfully used in specific UF applications. Almost 50% of the commercial marketed MF and UF membranes are surface-modified membranes in order to change their membrane chemistry properties to improve performance in targeted applications. There are four common surface modification used by membrane manufacturer which involve: (1) addition of a compatible modifier (such as a hydrophilic or charged polymer) into the casting solution; (2) adsorption of a modifier onto the membrane surface; (3) chemical or physicochemical post-treatments of the surface (e.g., hydrolysis or gas plasma treatment); and/or (4) grafting or cross-linking a modifier on the surface (Zeman and Zydney, 1996).

In surface modification, addition of hydrophilic polymer into casting solution which contains hydrophobic polymer (main polymer) to produce better membrane chemistry properties of the resultant membrane compared to the original membrane is known as polymer blend. Polymer blend has been recognized as the cheapest, easiest and versatile method in improving and modified polymer surface properties (Nady, et al., 2011, and Yan and Wang, 2011). Polymer blend was also employed to develop a new polymer membrane material which has high performance and low fouling as well as has adequate mechanical, thermal and chemical properties which can be tailored for many applications

Polymer blend is a physical process of blending the original polymer with one or more polymers to produce a blend polymer that having more suitable properties for membranes development (Nady et al., 2011, and Peng and Sui, 2006). While, a material that is produced from two or more materials with different physical and chemical properties which remain separate and distinct on a macroscopic level within the finished structured is known as a composite membrane material (Nady et al., 2011) such as polymer with chitosan (Mathew et al, 2008), polymer with ceramic materials (Maximous et al., 2009, and Zhang et al., 2011) and polymer with metals oxide (Wang et al., 2009). Table 2.6 shows a summary of investigated asymmetric blend membranes that have been developed and studied by many researchers. Generally, membranes prepared by blending hydrophobic polymers mixed with hydrophilic polymers show higher membrane fluxes and better fouling tolerance in comparing to the original membrane (Cho et al., 2011).

Table 2.6: Polymer blend membranes

Year	Polymer blend	Types of membrane	Researchers
1981	CN/PVP	UF	Tamura et al.
1981	PMMA/CAB	Oxygen permeability	Yang et al.
1985	PAN/PVP	PV	Nguyen et al.
1992	PVDF/PMMA	UF	Nunes and Peinemann
1993	PESA/PEI	UF	Blicke et al.
1993	PS/PU	UF	Nguyen and Solomon
1995	PAN/PS	UF	Ai-lian and Qing
1996	PSf/PI	Gas Separation	Kapantaidakis et al.
1997	PSU/PEEK	Pentene and pentane separation	van Zyl et al.
1999	CA/PU	UF	Sivakumar, et al.
1999a, b	PSf/MPC	Hemodialyis	Ishihara et al.
2000	PSf/Span-80	Pervaporation	Tsai et al.
2000	CA/PU	UF	Sivakumar et al.
2001	PSf/MPC	Hemodialyis	Hasegawa et al.
2002	CA/CPSU	UF	Sajitha et al.
2002	PU/SPS	UF	Malaisamy et al.
2004	CA/ERs and CA/SPS	UF	Mahendran et al.
2004	CA/SPEEK	UF	Arthanareeswaran et al.
2005	PSf/PV(P-AN)	UF	Kim et al.
2005	PES/P(VP-S)	UF	Kim and Kim.
2006	PSf/PAA	Ion-exchange UF	M'Bareck et al.
2006	CA/PSf	UF	Sivakumar et al.
2006	PVDF/PES	UF	Wu et al.
2006	PVC/PVB	UF	Peng and Sui
2007a	PSf/SPEEK	UF	Arthanareeswaran et al.
2007b	CA/SPEEK	UF	Arthanareeswaran et al.
2007	PVDF/PFSA	UF	Lang et al.

Table 2.6: Continued

Year	Polymer blend	Types of membrane	Researchers
2007	PES/CAP	UF	Rahimpour and Madaeni
2008	CA/SPEI	UF	Nagendran et al.
2008	CA/PC	UF	Vijayalakshmi et al.
2008	PES/PAN	UF	Reddy and Patel.
2008	PES/PAI	UF	Rahimpour et al.
2009	PSf/PAA	UF	M'bareck et al.
2009	PMMA/SPEEK	UF	Arthanareeswaran et al.
2009	CA/PSF	MF	Sikder et al.
2009	CA/PVP	UF	Saljoughi and Mohammadi
2009	PVDF/PFSA	UF	Yuan et al.
2010	PES/PI	NF and Gas Separation	Mansourpanah et al., and Han et al.
2010	PES/P(AN-AA-VP)	UF	Li et al.
2010	PSf/PI	Macro and meso porous materials	Ding and Bikson
2010	PVDF/PVA	UF	Li et al.
2010	CA/PU	UF	Zavastin et al.
2011	CA/PAI	UF	Rajesh et al.
2011	PVB/PVDF	UF	Yan and Wang
2011	SPSEBS/PSU	Fuel Cell	Bhavani and Sangeetha
2012	CAP/PVDF	UF	Tseng et al.
2012	CA/EPES	UF	Jayalakshmi et al.
2012	PVC/PSR	UF	Alsalhy
2013	CMCA/CA	UF	Han et al.

CA based membranes have been blended with other polymers to increase chemical resistance, fouling resistance, thermal stability and mechanical strength. Many studies have been conducted by blended CA with some hydrophilic polymers such as epoxy functionalized poly(ether-sulfone) (EPES) (Jayalakshmi et al., 2012), polycarbonate (PC) (Vijayalakshmi et al., 2008), sulfonated poly(ether imide) (SPEI) (Nagendran et al., 2008), sulfonated poly(ether ether ketone) (SPEEK) (Arthanareeswaran et al., 2007b), polysulfone (PSf) (Sikder et al., 2009, and Sivakumar et al, 2006), sulfonated polysulfone (SPS) (Mahendran et al., 2004), carboxylated polysulfone (Sajitha et al., 2002) and polyurethane (PU) (Zavastin et al, 2010, and Sivakumar et al., 2000).

Poly(vinylidene fluoride), PVDF is a popular choice material for fabrication of commercial UF and MF membranes. PVDF membranes are extensively employed in the clarification of fruit juices especially in the clarification of lime juice due to PVDF can resist exposure to limonene, which is present in citrus fruits and which will attack the membranes such as CA, PSf and PES (Scott and Hughes, 1996). Even though this polymer offered better performance in harsh operating condition compare to CA and PSf membranes, but this polymer is classified as highly hydrophobic material (Nunes and Peinemann, 2006).

Several attempts to make PVDF polar, more hydrophilic and less hydrophobic have been described and investigated in the literatures via blending technique. Li et al., (2010) prepared poly(vinylidene fluoride)/poly(vinyl alcohol) (PVDF/PVA) hollow fiber membranes while Yuan et al., (2009) and Lang et al., (2007) fabricated and characterized poly(vinylidene fluoride)/perfuorosulfonic acid (PVDF/PFSA) hollow fiber UF blend membranes with low-molecular weight cut off around 10,000 to 20, 000 Da. Wu et al., (2006) investigated the effects of solvent sorts, polyethersulfone (PES) and polyvinylpyrrolidone (PVP) concentration on properties and morphology PVDF/PES blend membranes. Poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMMA) blend UF membranes were prepared by Nunes and Peinemann (1992) in attempts to turn hydrophobic PVDF to more hydrophilic characteristic. In these studies revealed that the addition hydrophilic organic polymers in PVDF membranes improve the hydrophilicity and the anti-fouling property of the original membrane.

PSf or PES is the most widely used polymers for preparation of UF membranes (Nunes and Peinemann, 2006). PES is a quite interesting material for UF and MF membrane manufacture but unfortunately, PES is also categorized as a hydrophobic material (Nady et al., 2011). Recently, few researchers have been investigated the blend of PES with hydrophilic polymers in order to develop anti-fouling PES blend membranes such as polyethersulfone/polyimide (PES/PI) (Mansourpanah et al., 2010), polyethersulfone/polysulfone-graft-poly(ethylene glycol) methyl ether methacrylate (PES/PSf-g-POEM) (Yi et al., 2010), polyethersulfone/sulfonated polyethersulfone (PES/SPES) (Rahimpour et al., 2010), polyethersulfone/poly (ether ether ketone) (PES/SPEEK) (Lau and Ismail, 2009), polyethersulfone/poly (amide-imide) (PES/PAI) (Rahimpour et al., 2008), polyethersulfone/cellulose acetate phthalate (PES/CAP) (Rahimpour and Madaeni, 2007) and polyethersulfone/pluronic polymers (Wang et al., 2006). These studies shown a promising performance and anti-fouling of PES blend ultrafiltration membranes compare to the virgin PES membrane via blending method.

2.8 POLYSULFONE BLEND MEMBRANES

Polysulfone is an excellent polymer for membrane fabrication with high mechanical, electrical and chemical resistant properties. This polymer remained relatively constant over a broad temperature range from -150°F to 300°F. Polysulfone is exceptional in steam up to 300°F. The chemical stability of PSf is much higher than cellulose polymer. The preparation of ultrafiltration membranes from PSf solutions leads to a large variety of porous asymmetric structures, which can be controlled by changing the composition of the solvent mixture (Peinemann and Nunes, 2001).

In membrane manufacturing, PSf allows reproducible formation of high quality membranes and forms membranes with different pore sizes. Moreover, it is generally ease to prepare asymmetric membranes by the immersion phase inversion method using water as a coagulant. Porous PSf membranes with a dense and thin top layer were initially prepared from a solution in a proper mixture. The addition of volatile non-solvents to the casting solution leads to the formation of even thinner top layers. A non-solvent slightly increases the solution viscosity and favors a sponge-like structure with finger-like cavities (Peinemann and Nunes, 2001).

More open asymmetric PSf supports have been used for ultrafiltration or as support for composite membranes. PSf is selected as the membrane material because of its commercial availability, ease of processing and favorable selectivity-permeability characteristics. It possesses good mechanical, thermal and chemical properties. PSf is stable to wide pH levels (from 2 to 13) and therefore can withstand many types of cleaning methods. It has fairly good chemical resistance and shows a hydrolytic and oxidative stability.

In spite of its good characteristics as membrane material for polymeric membrane, the hydrophobic surface of polysulfone also brings obstacles with severe fouling during ultrafiltration process, in particular during protein or enzyme separation. This fouling phenomenon contributes mainly from protein deposited onto membrane surface and the permeate flux of fouled membrane decreases up to less than 5% of initial flux with the increase of permeation time (Mulder, 1996). Another factors contributing to fouling are surface properties (chemistry, morphology, etc.), hydrodynamic conditions, physical-chemical environment of feed solution, and solute concentration (Kim et al., 1992).

The extent of protein deposition onto membrane surface depends on the interactions between foulants and membranes, among the foulants and between foulants and cleaning chemicals. Hydrophobic interactions between the membrane surface and protein molecules however become one of the dominant factors for this complicated mechanism (Marshall et al., 1993). Therefore, deposition of protein molecules on the membrane surface can be reduced by modifying hydrophobic membrane surface to hydrophilic membrane surface. And it is also easy to clean the hydrophilic surface of membranes because adsorbed protein molecules are more easily removed from the surface of membranes (Kim et al., 2002).

Although the modification of PSf has been widely explored using a few techniques such as use of additive and oxygen plasma treatment (Kim et al., 2002), such problem still remain to be unsolved which consequently reduce the membrane performance and increases the process complexity and manufacturing costs. Thus, research efforts have been continued to find out an excellent technique such as polymer blend technique to counter this problem during protein ultrafiltration.

It is well known that polysulfones (PSf) are the preferred polymer materials for many types of membrane processes from microfiltration to gas permeation but this hydrophobic polymer needs to be modified to obtain high fluxes, less fouling, low maintenance cost and widen application in various range of industries. Some researchers such as Nguyen and Solomon (1993), Ai-Lian and Cheng Qing (1995), Tsai et al., (2000), Kim et al., (2005), M'bareck et al., (2006), M'bareck et al, (2009), Sikder et al., (2009), Ding and Bikson (2010), and Bhavani and Sangeetha (2011) had fabricated PSf membranes via blending PSf with hydrophilic polymers in order to improve hydrophilicity properties and performance of the virgin PSf membranes in various membrane applications.

Nguyen and Solomon (1993) developed microporous composite polysulfone/polyurethane (PSf/PU) hollow fiber membranes via new one-step process. They used low reactivity polyurethane prepolymer which was blended with polysulfone in casting solutions. A polymerization catalyst was used in coagulation bath in order to promote the polymerization of prepolymer at the membrane/precipitation solution interface. This catalyst has polymerized polyurethane prepolymer by cross-linking reaction at polysulfone/polyurethane membranes surface. The more polyurethane cross-linked on the blend membrane surface will produced the microporous blend membranes which possessed excellent flux and very low protein adsorption due to increase in their hydrophilicity properties.

Ai-Lian and Qing prepared a partly miscible casting solution containing polyacrylonitrillic/polysulfone (PAN/PS) blend and the PAN/PS blend membranes were prepared according to the Loeb-Sourirajan method. In their investigation, they were found that PAN/PS blend UF membrane has good performance with an especially high flux compared to PAN membrane (Ai-Lian and Qing, 1995). In pervaporation performance studies, asymmetric PSf membranes were blended with a surfactant (Span-80) in the casting solutions and the blend membranes were prepared via the wet-phase inversion method (Tsai et al., 2000). The effect of surfactant content on the surface morphology and pervaporation performance of the PSf membranes were observed. Addition of surfactant suppressed macrovoids size in the asymmetric PSf membranes and consequently increases the separation factor while decrease the permeation rate. PSf membranes blended with 15 wt.% Span-80 content produces the optimum pervaporation results.

Kim et al., (2005) synthesized poly(1-vinylpyrrolidone-co-acrylontrile) copolymers, P(VP-AN) via radical copolymerization and this copolymers was used as a blended polymer with the hydrophobic polymer, polysulfone. The casting solutions containing 2 wt% to 16 wt% of P(VP-AN) were formed miscible blend with PSf to obtain hydrophilic blend ultrafiltration membranes that developed by phase inversion process. The resultant membranes, PSf/P(VP-AN) exhibited better performance in solute rejection and flux than membrane prepared from PSf or PSf/PVP.

Generally, a soluble polymer, polyacrylic acid (PAA) is used as a complexing agent in assisting ultrafiltration process to remove heavy metals from waste water via complexation-ultafiltration or also known as polymer enhanced ultrafiltration. Unfortunately, this technique decreased the hydrophilicity of membrane and fouling problem become severe. Mbareck et al., (2006) and Mbareck et al., (2009) introduced an efficient and economical method for fabricating ion-exchange ultrafiltration membranes for heavy metals removal.

In this new technique, PSf anf PAA were separately dissolved in DMF solvent and then these two solution were blended to form membrane casting solutions. PSf/PAA membranes were fabricated according to the wet phase inversion method. They had made PSf/PAA blend membranes with semi-interpenetrating PSf and PAA network. The high efficiency in rejection of lead, chromium and cadmium from water was attributed to the complexation metal ions and carboxylate groups (-COO-) on the inner surface of pores and membrane matrix. These high performance membranes make this new method attractive for metals separation in water and waste water treatment.

Sikder et al., (2009) focused on synthesized and characterized of cellulose acetate-polysufone blend microfiltration membrane for microbial cells separation from lactic acid fermentation broth in a continuous process. The PSf/CA blend membrane was successful 100% retention of microbial cells from the broth at reasonably high permeation broth flux in a continuous cross-flow membrane module integrated with the fermenter. The promising results in this integrated system pave the way for scale up for other similar systems as well. Ding and Bikson (2010) has prepared a novel macro and meso porous polymeric membrane materials from miscible blend of polysulfone/polyimide (PSF/PI) by chemical decomposition of polyimides. Macro and meso porous films with uniform pore sizes were developed via this novel approach. This blend films is potential to apply as membranes in nanoseparations, bioseparations, scaffoldings and substrates.

The potential polymer blend of SPSEBS/PSU in the proton exchange membrane for fuel cell application has been fabricated by Bhavani and Sangeetha (2011). In their investigation, they revealed that SPSEBS very well blended with PSU. The blended polymer has improved mechanical property and thermal stability of SPSEBS membrane. The introduction PSU into SPSEBS polymer solution has produced a promising SPSEBS/PSU blend membranes for the usage in direct methanol fuel cell (DMFC) and electrolyte membrane fuel cell (PEMFC).

2.9 ADDITIVES IN BLEND MEMBRANES

Many researchers have been investigated the effect of different types of organic and inorganic additives on membrane performance and morphology of polymer blend membranes. The role of organic and inorganic additives is to create a spongy like membrane structure by interruption of macrovoid formation, enhance pore formation, improve pore interconnectivity and/or introduce hydrophilicity. Polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) are two popular organic additives used in membrane fabrication due to these additives strongly influenced on the membrane characteristics in terms of pore size, permeate flux and the solute rejection rates (Ani and Lee, 2006). Others additive such as glycerol, alcohols, dialcohols, water, formamide, mineral fillers or the mixture of them are employed in membrane research studies which affect the properties of the final membranes (Ani et al., 2010).

In fabrication of polymeric ultrafiltration (UF) membranes, various organic and inorganic additives were tested for polyacrylonitrilic/polysulfone (PAN/PS) blend UF membranes (Ai-lian and Qing, 1995). The results showed that some effective additive for PAN and PSf did not suit for PAN/PSf blend membranes and the addition 95% acetic acid as additive gave the best performance of Bovine Serum Albumin (BSA) rejection. Sivakumar et al., (1999) studied the effect of different concentration of non-soluble swelling additive, PVP on the performance of ultrafiltration application of cellulose acetate-polyurethane (CA/PU) blend membranes. An increase in addition of PVP concentration from 0 to 2.5 wt% reduced the rejection of proteins while water flux and solute flux increased respectively due to increase of membrane pore size and hydrophilicity of blend membranes.

Sivakumar et al., (2000) further employed PVP additive with concentration from 0 to 7.5 wt% in CA/PU blend membranes to study membrane compaction, pure water flux, water content, membrane hydraulic resistance and morphology of the membranes. In their study showed that PVP plays a key role in controlling the pore size and miscibility of the blends, and these blends membranes were effectively better performance for separation of proteins and metal ions than pure membrane.

Sivakumar et al., (2006) prepared CA/PSf blend membranes by using PVP K30 as an additive at various concentration of 0 wt% to 7.5 wt%. The results showed that an increase in flux and Molecular Weight Cut-Off (MWCO) of blend membranes with increasing PVP concentration may be due to fast rate of leachability of PVP during precipitation process, which in turn produce a large pore on membrane surface. Wu et al., (2006) reported the same observation that PVP concentration in PVDF/PES blend has much influence on properties and morphology of these blend membranes. Small amount of PVP concentration (2 wt.%) in PES/CAP blend membrane improved the morphology, mechanical strength, permeability and protein rejection of the PES/CAP blend membrane (Rahimpour and Madaeni, 2007).

Malaisamy et al., (2002) investigated the effect additive concentration, PEG 600 on polyurethane and sulfonated polysulfone (PU/SPSf) blend ultrafiltration membrane. The morphology of the resultant membrane extensively changed which in turn altering the structural properties and then improving the flux performance. PEG 600 additive was claimed play major influence on characteristics of cellulose acetate/epoxy resin (CA/ER) blend ultrafiltration membranes such as pure water flux, membrane resistance and water content (Mahendran et al., 2004).

The effect of different molecular weights of PEG namely as PEG 200, PEG 400 and PEG 600 which represent their molecular weight respectively, in PES membranes has been studied by Ani et al. (2007). The presence of higher molecular weight of PEG has increased pure water permeation, pore size and MWCO of PES membranes due to increase the number and the size of macrovoids as well as the surface roughness of the membranes. Vijayalakshmi et al., (2008) reported that the presence of PEG 600 in cellulose acetate/polycarbonate (CA/PC) blend casting solutions had a considerable impact on the rejections and permeate flux of the proteins and metal ion complexes. An increase in additive concentration had increased permeate flux but solutes rejection were decreased due to increase in pore size of the blend membranes.

Vijayalakshmi et al., (2008) and Nagendran, et al., (2008) explained that increasing PEG 600 concentration in cellulose acetate/polycarbonate (CA/PC) and cellulose acetate/sulfonated poly(ether imide) (CA/SPEI) blend membranes respectively, tends to increase formation of pores and hence subsequently, the rejection of metal ions was decreased while the permeate flux increased. Arthanareeswaran et al., (2010) investigated the effects of PEG 600 on PSf/SPEEK blend membranes and the results revealed that increased in the concentration of PEG 600 in casting solutions resulted in improving performance and hydrophilicity of these membranes. PEG 600 also plays important role in organic-inorganic composite membranes by enhancing flux recovery ratio and decreased the total fouling resistance (Arthanareeswaran et al., 2009).

2.10 SHEAR RATE

In the last 30 years of membrane technology development, many efforts has been done in aspects of membrane materials, dope preparation, fabrication technology, and fundamental mechanisms for developing high performance membranes (Kusworo et al., 2008 and Ismail et al., 2006). In that period, the effect of rheological factors such as shear rate on membrane development has just little attention on the membrane research study. However recently, this fundamental research is recognized as one of the important parameters in membrane fabrication process in order to improve fundamental knowledge of membrane manufacture and performance in ultrafiltration, nanofiltration and gas separation processes (Idris et al., 2003, and Ismail et al., 2006).

The effect of low and high shear rate on selectivity of CO_2/CH_4 of asymmetric polysulfone and polyacrylonitile flat sheet membrane has been tested by Shilton et al., (1997). Polarized reflection i.r. dichroism was successfully used to determine molecular orientation occurred in the membranes at low and high shear rate. The experimental results showed that the degree of molecular orientation was enhanced with high shear rate which in turn exhibited more selectivity. The effect of shear rate on molecular orientation was more pronounced in the polyacrylonitrile compare to polysulfone membrane.

Sharpe et al., (1999) conducted a study of extrusion shear and forced convection residence time in the spinning of polysulfone hollow fiber membranes for gas separation. They found that membranes should be spun at high shear rate and at optimized residence time to minimize surface defects and hence subsequently enhanced selectivity and high flux. Chung et al., (2000a) investigated the effect of shear rate within spinneret on polyethersulfone hollow fiber membranes and for the first time, it was found the existing of a certain critical value of shear rate. When the shear rate was increased, the separation performance increased while the flux decreased dramatically but further increment of shear rate resulted in decreased in separation performance while the flux did not change. Chung et al., (2002) also have demonstrated there was a certain critical value of shear rate by characterized the outer surface morphology of polethersulfone hollow fiber ultrafiltration membranes via an atomic force microscope (AFM).

Idris et al., (2003) has studied the pure influence of shear rate that induced molecular orientation in reverse osmosis hollow fiber cellulose acetate membranes by using Fourier transform attenuated total reflection (ATR-FTIR). Their experiments revealed that ATR-FTIR can be used to determine the degree of molecular orientation in the sheared membranes. As Chung's finding, they also suggested an optimum shear rate induced a certain degree of molecular orientation to yield membrane morphology with optimum separation performance. Then, Ng et al., (2004) examined molecular orientation induced by rheological parameter on the surface of Polysulfone flat sheet membranes by using ATR-FTIR. The gas selectivities of O_2/N_2 and CO_2/CH significantly increased with increased in shear rate due to greater molecular orientation in the skin layer of the PSf membranes.

The effect of dope extrusion rate (DER) on morphology of hollow fibers membrane for ultrafiltration process was investigated by Ismail et al., (2006). The DER was varied from 2.0 to 4.0 cm^3/min with 0.5 cm^3/min increments in order to study the fibers performance and morphology. In their investigation, they found that an increase in DER decreased flux but increased solute rejection. The rejection increased with increasing DER until it reached maximum separation performance and then, further increment of DER decreased the solute rejection. In this study, they suggested that the increasing in rejection was due to the outer skin layer becomes apparently thicker and denser, and further increased DER after critical performance possibly made the outer skin structure are less tighten.

All these phenomena are related to molecular orientation occurs at membrane surface at different DER during fabrication process. The higher molecular orientation was responsible for higher separation performance of ultrafiltration membrane. Ismail and Hassan (2006) employed the combination of irreversible thermodynamic model, solution-diffusion model (Spiegler-Kedem equation), steric-hindrance pore (SHP) and Teorell-Meyers (TMS) model to study transport mechanisms and to determine the membrane structural properties of PSf nanofiltration membranes fabricated at different polymer concentrations and at different shear rates.

Based on the electrolytes transport performance test and modeling data, the results showed that increased in shear rate and polymer concentration has increased salt rejection until it achieved the optimum or the critical shear rate. An orientation of molecular polymer chains at the membrane skin layer to a certain extent during different shear rate affected the performance and membrane structural properties. Polyimide/polyethersulfone (PI/PES)-zeolite 4A mixed matrix membranes were prepared and cast at different shear rates by Kusworo et al., (2008). These flat sheet membranes were tested via O_2/N_2 gas separation performance and their molecular orientation has viewed through the Infrared (IR) absorption spectra study.

In the gas separation study, Kusworo et al., (2008) found that molecular chains become more aligned at 581 s^{-1} of shear rate as shown via normalized of different FTIR spectrum. An optimum shear rate for PI/PES-zeolite 4A mixed matrix membranes existed at this shear rate and it was proved by optimum selectivity of O_2/N_2 and permeability of O_2. Nora'aini et al., (2010) studied the effect of shear rate on the flat sheet of Polyethersulfone nanofiltration membranes for ammonia-nitrogen removal. They used casting speed at 5 s, 10 s, 15 s, 20 s, 25 s and 30 s, which in turn the shear rate of membrane casting process decreased by increasing the casting speed of a casting knife. Their experimental works revealed that the pore size was reduced while the membrane thickness increased by increasing the shear rate and hence subsequently increased the membrane selectivity. A casting of 10 s or shear rate at 200 s^{-1} was found the most recommended parameter condition due to its favorable separation performance.

2.11 EVAPORATION TIME

Nowadays, most commercial available membrane obtained by phase inversion. It is a process whereby a polymer is transformed in a controlled manner from a liquid to a solid state. The simplest technique for preparing phase inversion membrane is precipitation by solvent evaporation. In this method a polymer is dissolved in a solvent and the polymeric solution is cast on a suitable support. The solvent is allowed to evaporate in an inert atmosphere in order to exclude solvent from the polymeric solution to form a dense homogeneous membrane (Mulder, 1996). This inversion method is known as dry phase inversion. The time required to evaporate solvent from the polymeric solution during membrane fabrication process is known as evaporation time.

There are many researchers studied on the effects of evaporation time during dry phase inversion process on membranes characteristics and performance. It is due to different membrane morphology and properties can be obtained for tailor-made membranes by varies the evaporation time. The integrally skinned asymmetric membrane can be developed by introducing dry phase inversion for polymer casting solution before wet phase inversion take place during fabrication of asymmetric membranes. The combination of these two techniques was reported successful in producing membrane with high productivity and selectivity.

The combination of ultrathin and defect-free skin layers are generally not achieved for membranes made by the wet phase inversion process. The membranes were fabricated by wet phase inversion processes always contains defects due to incomplete coalescence of the skin layer. Integrally skinned asymmetric membranes can be formed by dry/wet phase inversion process. It is due to phase separation is induced in the outermost region of the cast membrane during an evaporation step, while liquid-liquid phase separation in the bulk films occurs subsequently during a quench step (Ahmed, 2009).

Pinniau et al., (1990) demonstrated that essentially defect-free membranes with skin layer thickness as thin as 500 Å can be formed from a variety of polymers by dry/wet phase inversion process using forced-convective evaporation. Pinnaiu (1991) presented a physically meaningful mechanism for the formation of ultrathin and defect-free skin layers of membranes made by dry/wet phase inversion. Pinnau and Koros (1991a) have summarized the empirically developed rules for the formation optimized asymmetric membranes by dry/wet phase inversion process. Pinnau and Koros (1991b) demonstrated clearly that the physical processes which occurred during the evaporation step were of utmost importance for the skin layer formation of asymmetric membranes made by dry/wet phase inversion.

Pesek and Koros (1993) investigated the effects of aqueous quenched asymmetric polysulfone membranes prepared by dry/wet phase separation and they found that this technique produced the polysulfone membranes with ultrathin selective layer, which can be made as thin as 200 to 800 Å. Pesek and Koros (1994) also reported that a dry/wet spinning process produced very thin, defect free and small diameter of hollow fiber membranes for gas separations. Furthermore, the defect-free selective skins of these hollow fibers were performed prior coagulation in less 0.5 s compared to 10 to 15 s that allowed for flat sheet membranes prepared by this same dry/wet process.

Ohya et al., (1997) studied on molecular weight cut-off performance of aromatic polyimide membrane and they revealed that shortened the evaporation time decrease the thickness of the active layer and consequently increased the molecular weight cut-off of the membrane surface which in turn decreased membrane resistance. In other words, an increase in evaporation time formed membrane with thick active layer and small molecular weight cut-off and hence, reduced the permeate flux. Chung and Hu (1997) and Tsai, et al., (2002) investigated on the effects of the air gap during hollow fiber fabrication process and they found that the increasing air gap length enhanced a greater extent of molecular orientation. Ren et al., (2008) observed that the hollow fiber membranes fabricated with air gap not less than 1 cm strongly influenced the performance and a relatively low permeation flux and small MWCO were obtained due to the accumulated stress was released greatly in the air gap and some big pores were suppressed.

Hasbullah et al., (2011) also studied the effects of air gap on the preparation and performance of polyaniline (PAni) asymmetric hollow fiber membranes towards gas separation. They discovered a substantial improvement in the gas performance of the PAni hollow fiber membranes as the air gap was varied. It was observed that the gas flux was significantly decreased while the selectivity was increased with an increase in air gap from 2.5 to 50 cm. SEM and the mechanical properties results proved that molecular orientation and skin layer thickness increased with an increase in air gap which in turn enhanced the gas separation performance.

Recently, Ismail et al., (2011) successful developed hyperthin-skinned and high performance asymmetric polyethersulfone membranes for gas separation. Evaporation time and casting shear have been identified as the dominant fabrication parameters in controlling skin layer thickness and skin integrity. These combination effects improved membrane performance in terms of O_2 and N_2 separation. The optimum range was found to be in the range of 149 to 447 s^{-1} and 10 to 14 s for the shear rate and the evaporation time respectively. The thinnest skin layer thickness was 538±95.6 Å.

2.12 CHARACTERIZATION OF ULTRAFILTRATION MEMBRANE

Generally, membrane processes cover a wide range of separation problems with a specific membrane structures. Thus, membrane may differ significantly in their structures and consequently in their functions. Hence, membrane characterization is important in order to determine the structural and morphological properties of a given membrane. Many attempts have been made to relate membrane structures to transport phenomenon in a membrane process in order to enhance fundamental knowledge of separation performance.

2.12.1 Water Content and Contact Angle

Water content and contact angle are two physical measurements of membranes property in order to know quantitatively hydrophilicity of the membranes. In water content measurement, membranes are soaked in water for overnight and then the difference of weight between dry and wet membranes is used to determine the percentage of water content. This measurement is indirectly describes the hydrophilic nature of the corresponding membranes and the pure water flux can be predicted based on this information.

The importance of contact angle information is used to study hydrophilicity property of polymeric membranes. The terms of water contact angle, θ, presented hydrophilicity of solid surfaces (Zeman and Zydney, 1996). The contact angle of polymeric membranes can be measured based on the principle of the degree of wettability of water droplets on the membrane surface. The interaction between water and polymeric materials is known as wettability. A droplet of water is placed upon a surface of polymeric membrane and then, the contact angle (θ) of liquid droplet is measured (Mulder, 1996).

Figure 2.7 is schematically shown the effect of the equilibrium contact angle, θ, on the pore intrusion phenomenon. Hydrophilic surfaces have the contact angle, θ, close to 0^o (i.e., $\cos(\theta) = 1$), while for low affinity of membrane surface, the contact angle, θ, will have a value greater than 90^o, (i.e., $\cos(\theta) \leq 0$). For hydrophilic materials, the liquid will penetrate spontaneously into the pores of the membrane while no liquid intrusion occurs on hydrophobic membrane surface (Mulder, 1996 and Zeman and Zydney, 1996).

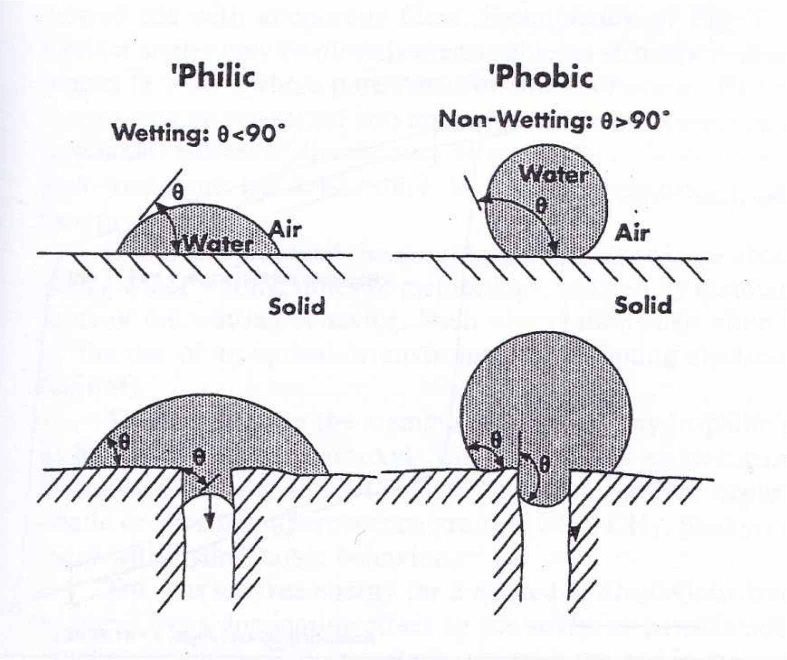

Figure 2.7: The effect of the equilibrium contact angle, θ, on the pore intrusion phenomenon

Source: Zeman and Zydney (1996)

2.12.2 Molecular Weight Cut-Off and Pore Properties

Many manufacturers used the concept of `cut-off' to characterize their ultrafiltration membranes. Generally, the molecular weight cut-off (MWCO) is determined by identifying the solute of the lowest molecular weight that has a solute rejection up to 90% in steady state condition (Comerton et al., 2009). Sarbolouki (1982) stated that MWCO of RO or UF membrane in a steady-state experiment can be determined as more than 80% but definitely less than 100% rejection of the lowest molecular weight of an inert solute from feed solution. Based on this MWCO, cut-off is defined as the molecular weight of solute which is 80% rejected by the membrane. The solute rejection or solute retention (%) of RO or UF membrane is represented by Eq. (2.12):

$$Rejection\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2.12}$$

Where C_p and C_f are the solute concentrations in the permeate and the feed solutions, respectively.

Sarbolouki developed figures and mathematical model which correlates between the molecular weight cut-off and the membrane pore size. In this correlation, the sieving effects at the entrance are only to be considered since the molecular weight of the inert solute retained depends only on the structure of the upstream of the membrane. Eq. (2.13) represents the entrance sieve models for Rejection (%) values greater than 80%.

$$Rejection\ (\%) = 100\left({}^{\bar{a}}/_{\bar{R}}\right) \tag{2.13}$$

Where $\bar{R}$ and $\bar{a}$ are the average pore size and the solute radius, respectively.

Figure 2.8 shows a general correlation between the average membrane pore size and the solute molecular weight at Rejection (%) = 80, 85, and 95%. By using this figure, the average pore size of the corresponding membrane can be directly read off once the solute molecular weight of Rejection (%) = 80, 85, and 95% has been determined. The pore properties of the RO or UF membranes can be determined by calculation of surface porosity and pore density of the membrane, respectively. The surface porosity of the membrane, ε, is calculated based on the following equation.

$$\varepsilon = \frac{3\pi\eta J}{\bar{R}\Delta P} \tag{2.14}$$

Where $\bar{R}$ is the average membrane pore size (cm), η is viscosity of the permeate (g/cm.s), J is pure solvent flux (cm/s), and ΔP is the applied pressure (dyn/cm^2).

Since knowing ε and $\bar{R}$, the pore density of the corresponding membrane, n (pore/cm^2), can be calculated by Eq. (2.14)

$$n = \frac{\varepsilon}{\pi\bar{R}^2} \tag{2.15}$$

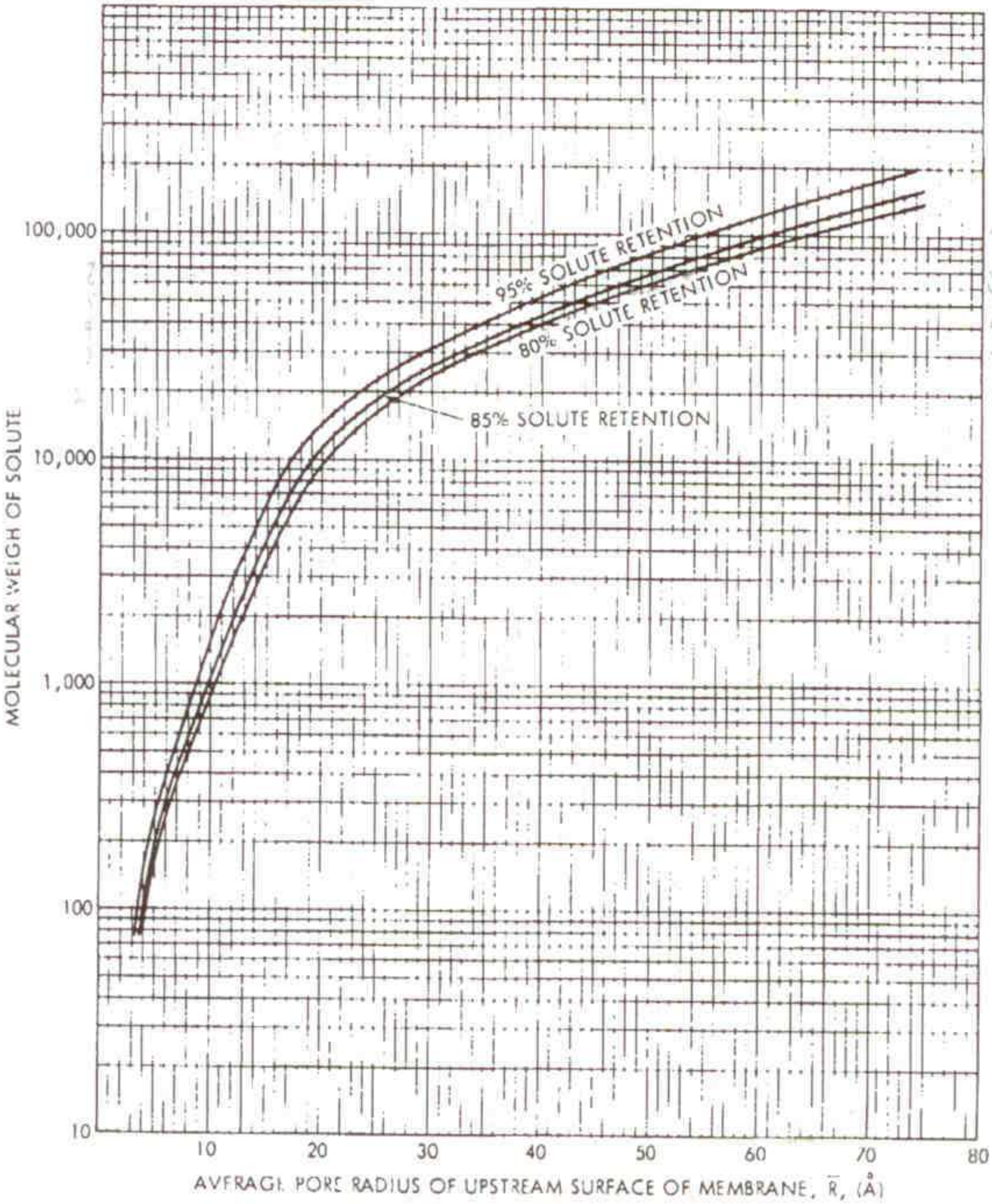

Figure 2.8: Relation between solute molecular weight and the average pore radius of the upstream surface of the membrane at 80, 85, and 95% solute retention levels

Source: Sarbolouki (1982)

2.12.3 Surface Characterization

The membrane structures are characterized using the Scanning Electron Microscopic (SEM). The morphological structures of the surface skin layer, pores and cross section of membranes can be viewed at different magnificent through SEM. SEM is a very useful characterization tool in research and development of membrane due to it provides direct and practical structural membrane information, couple with fast response and impressive analytical output. In SEM, a narrow beam of high-energy electrons hits the membrane and the secondary electron with low energy are liberated from atoms in the membrane surface produced image of membrane on the screen or the micrograph. The pore size, the pore size distribution and the surface porosity also can be obtained from the micrograph. Moreover, the geometry of the pores can be clearly visualized via this technique (Zeman and Zydney, 1996 and Mulder, 1996).

2.13 RHEOLOGICAL PROPERTIES

In fabrication of a flat sheet asymmetric membrane, polymer casting solution is cast and flows with a certain thickness between a support plate and a knife blade, and then immersed into a coagulation bath for precipitation process. The properties study of the flow-fluid is important in order to relate its properties with membrane performance and morphological structural analysis. The study of the deformation and flow of the polymer casting solution is known as rheological study (Brookfield, 2004). Sharpe (1999) and Chung et al., (2000b) explained that the polymer casting solutions were cast at certain shear rate will decreased its viscosity due to molecular orientation occurred in the polymer films. The decrease in viscosity tends to create slight imperfections in the membrane skin layer due to deterioration of molecular orientation takes place at the skin membrane surface layer

Viscosity is the measure of the internal friction of a fluid. If the greater internal friction is existed, so the greater amount of force is required to flow the fluid. This phenomenon is called shear. Hence, viscosity of a fluid is defined as a measure of its resistance to shear or angular deformation (Finnemore and Franzini, 2002).

$$viscosity(\eta) = \frac{shear\ stress\ (\tau)}{shear\ rate\ (\gamma)} \tag{2.16}$$

Typically, polymer solutions may display as Newtonian and non-Newtonian flow characteristics. Figure 2.9 depicted the typical gradient curves for these fluids behavior. The regions where the apparent viscosity is approximately constant are known as Newtonian regions. The behavior between these regions can usually be approximated by a straight line on the axes. It is known as the power-law region and the behavior is represented by the following equation (Brydson, 1981):

$$\tau = \eta\gamma \tag{2.17}$$

where τ (mPa) is shear stress, η (mPa.s) is apparent viscosity and γ (s^{-1}) is shear rate.

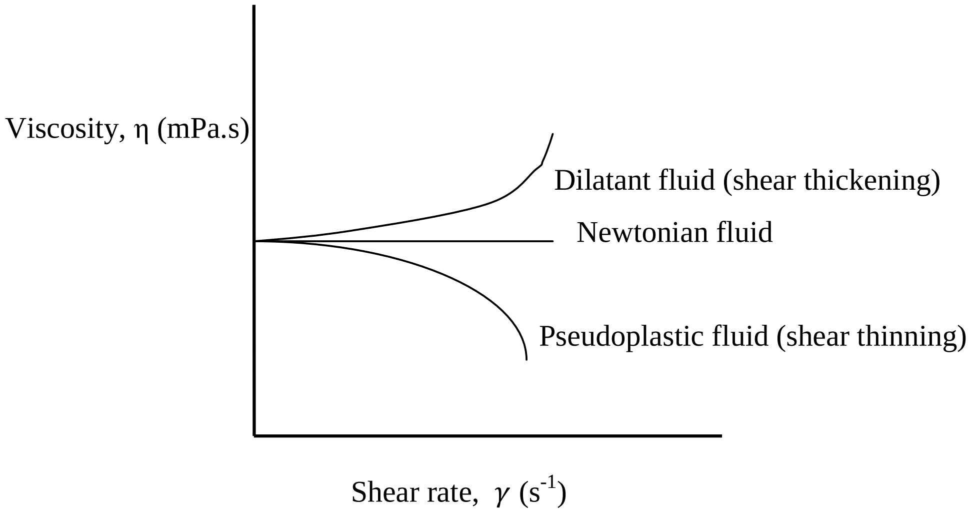

Figure 2.9: Apparent viscosity – shear rate curves for three fluids which the same apparent viscosity at zero shear rate

Source: Brydson (1981)

A non-Newtonian fluid is broadly defined as the non linear relationship between shear stress and shear rate. There are two types of non-Newtonian fluids: dilatant fluid (shear thickening) and pseudoplastic fluid (shear thinning) (Eposito, 1998). It is described by the given equation (Brydson, 1981)

$$\eta = k\gamma^n \tag{2.18}$$

Where n is the flow behavior index (dimensionless) and k is the consistency index (Pa.s).

Upon using the relationship between the shear stress, apparent viscosity, and the shear rate, the power-law model is obtained and n is called the power-law index. Note that n =1 corresponds to Newtonian behavior. Typically, if $n < 1$, a shear thinning fluid is obtained, which characterized by a progressively decreasing apparent viscosity with increasing shear rate. If $n > 1$, a shear-thickening fluid in which the apparent viscosity increases progressively with increasing shear rate is observed. Generally, polymer casting solutions used in membrane fabrication process are shear thinning fluid due to its viscosity decrease with increasing shear rate which in turn affects the characteristics and performance of the respective membranes.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 INTRODUCTION

The preparation of PSf/CAP/PVP blend membranes can be influenced by many factors. Those factors include selection of materials (such as polymer, solvent and additive), fabrication conditions and coagulation bath composition. In this study, polysulfone was employed as the main back-bone polymer to produce blend membranes which consist of different composition blend of PSf and CAP in the PSf/CAP blend UF membranes before this blend membrane was added with PVP to produce PSf/CAP/PVP blend membrane. In order to produce high performance asymmetric PSf/CAP/PVP blend membranes, the factors of polymer composition, additives concentration, shear rates and evaporation time which affects the resultant membranes characteristics and performance were investigated throughout this study.

The fabricated membranes were characterized in terms of water content, contact angle, membrane permeability coefficient and porosity of membranes. Molecular weight cut-off (MWCO) and pore properties of the upstream surface membranes (average pores size and pores density) were determined to relate the permeation and rejection of solutes. The membranes performance was investigated through pure water flux and proteins separation tests by using a dead-end cell ultrafiltration unit. SEM was employed to study morphological structures of membranes that affected the membrane separation performance.

3.2 WORK FLOW OF RESEARCH

Figure 3.1 shows the work flow of the research from the beginning until the end of this study. Detail methodology has been described in the sub-sections of this chapter.

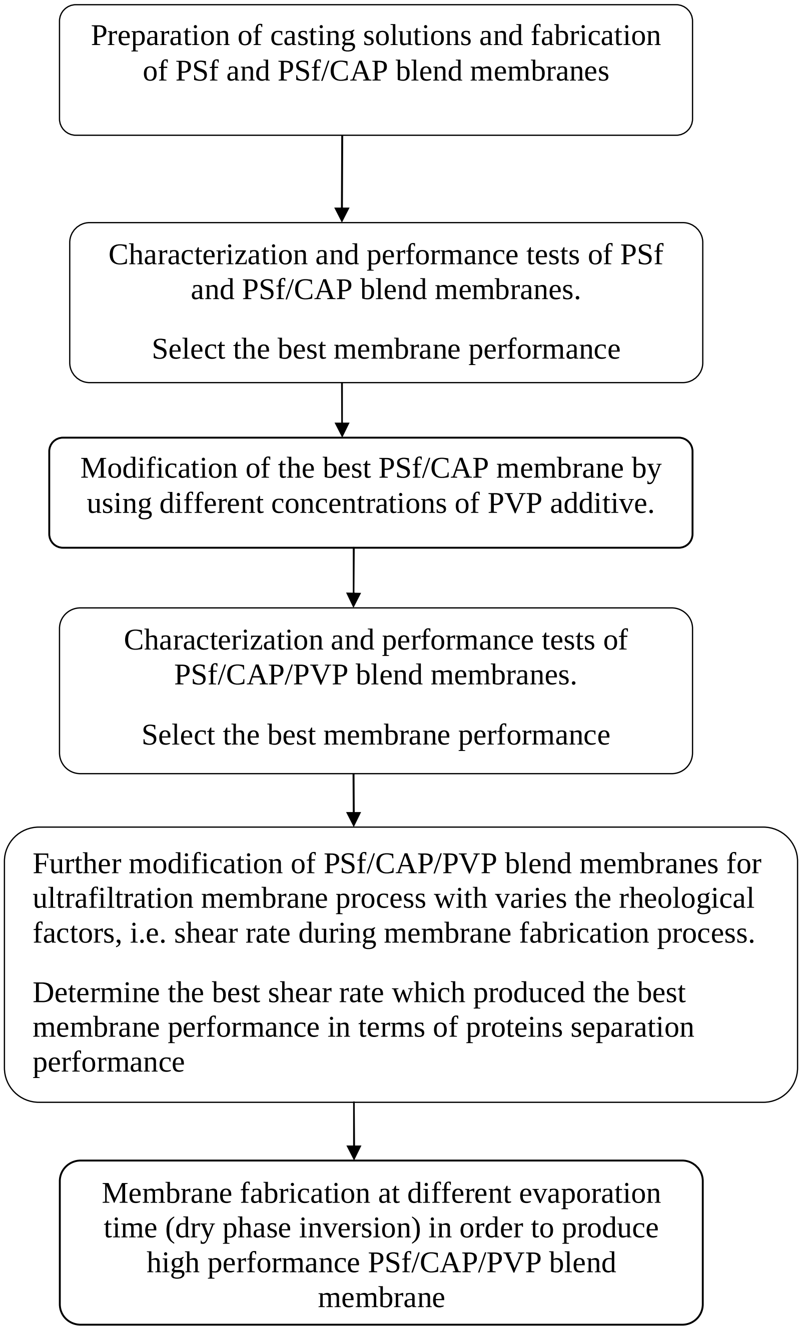

Figure 3.1: Work flow of research

3.3 MATERIALS

The basic formula to prepare and fabricate membrane consists of polymer and solvent. This membrane casting solution is known as binary solution. If additive is added into the binary solution, the membrane casting solution is known as ternary solution. This ternary solution consists of three main components, namely polymer, solvent and additive.

As mentioned in the scope of study in this thesis, polysulfone (PSf) was used as the polymer backbone for ultrafiltration (UF) membrane and cellulose acetate phthalate (CAP) was used as polymer blend material in order to improve hydrophilicity of the native membrane property. N-methyl-2-pyrrolidone (NMP) was chosen as solvent in binary solution and ternary solution of polymer casting solutions. An organic additive, polyvinylpyrrolidone (PVP) was selected as an additive in order to improve performance of blend UF membranes.

Distilled water was used as coagulation medium in a coagulation bath. It plays a key role as non-solvent in precipitation process where the exchange between solvent and non-solvent in polymer films formed asymmetric blend UF membranes via wet phase inversion method. In pure water permeation test, distilled water was employed to compact PSf, PSf/CAP and PSf/CAP/PVP blend UF membranes and to study the flux of the pure water for each UF membranes at steady-state condition. Proteins with different molecular weights were used in order to study permeation rate and proteins rejection as well as molecular weight cut-off and pores properties of the blend UF membranes.

3.3.1 Polymers

In this study, an armophous polymer, Polysulfone (PSf) (Udel Polysulfone P-1700) with molecular weight of 34,500 g/mol was supplied by Amoco Chemical (USA) S. A. PSf is the preferred polymer material for many types of membranes because it has repeating phenylene rings which contribute to high degree of molecular immobility, and consequently made it high rigidity, strength, creep resistance and dimensional stability as well as excellent mechanical property (Blanco et al., 2006; Ng et al., 2004 and Sivakumar et al., 2006). PSf is also known as a high performance-engineering thermoplastic which resists degradation, low cost, good permeability and selectivity values (Ng et al., 2004).

PSf posses very good chemical and thermal stability as indicated by Tg value (PSf T_g = 190 ^oC). This polymer is widely used as basic materials for ultrafiltration membranes and as support materials for composite membranes (Mulder, 1996). The major drawback of using this traditional polymer is due to the fact that PSf is categorized as hydrophobic polymer materials and this limits its membrane application in many aqueous separation processes. The polymer structure of PSf is shown in Figure 3.2.

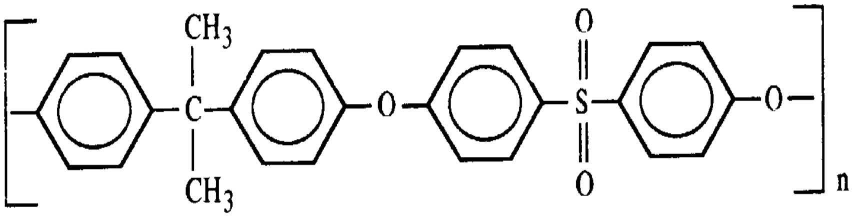

Figure 3.2: Polysulfone polymer structure

Source: Blanco et al. (2006)

Cellulose acetate phthalate (CAP) brand Fluka was procured from Sigma-Adrich Co. CAP is a white powder with molecular weight of 2,534.12 g/mol. This substance is not classified as dangerous material, tasteless, light odor of acetic acid and low water solubility (Bechard et al., 1995). It could be used as received without any purification. In pharmaceuticals, CAP is one of the cellulose derivatives that have been commonly used in controlled release drug delivery system as an enteric coating material (Reshmi et al., 2009).

In this system, a polymeric oral tablet coating, CAP plays a role as a protection material for drugs during its transit through the stomach and it will release the drugs when it reaches the small intestine (Mayhew et al., 2009 and Oliviera et al., 2010). The drugs are protected from dissolved in stomach due to the changes in pH environment. This cellulose polymer commonly contains 21.5-26.0% (w/w) acetyl content and 30.0-36.0% (w/w) phthalyl content according to USP specifications (Lai et al., 2008). Its empirical formula is $C_{116}H_{116}O_{64}$ and Figure 3.3 shows the polymer structure of CAP.

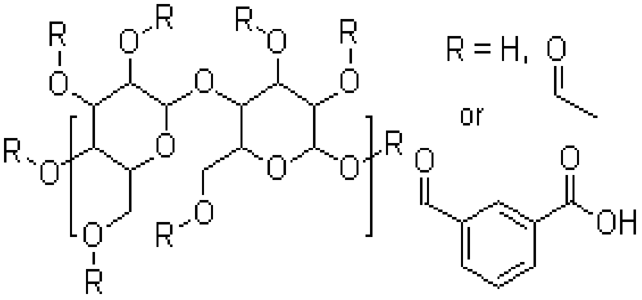

Figure 3.3: Polymer structure of cellulose acetate phthalate

Source: Rao et al. (1999)

3.3.2 Solvent and Non-Solvent

Solvent is one of the important materials in the polymer casting solution as it will influence the final morphology of the fabricated membrane. The solvent is also recognized as one of the main variables that affect the thermodynamic and kinetics of the phase inversion process. The aprotic solvents such as dimethylacetamide (DMAc, b.p. = 165 ^{o}C), dimethylformamide (DMF, b.p. = 153 ^{o}C), dimethyl sulfoxide (DMSO) and N-methylpyrrolidone (NMP, b.p. = 202 ^{o}C) are generally among the best choice of casting solution solvents (Mulder, 1996).

These aprotic solvents with high solubility parameters have been used as polymer solvents in preparation of blend UF membranes (Wu et al., 2006). These solvents also are widely used in fabrication of the MF and UF membranes since it can dissolve a wide variety of polymers. In addition, porous and anisotropic membranes will be produced by using these solvents due to rapid precipitation process in a coagulation bath system (Baker, 2004). In this study NMP was used as the solvent to dissolve polysulfone and cellulose acetate phthalate blend polymers in order to prepare polymer blend casting solutions.

N-Methyl-2-Pyrrolidone (NMP) from MERCK Schuchard OHG, Germany was used as solvent for PSf, PSf/CAP and PSf/CAP/PVP polymer blend membranes in this research. *N*-Methyl-2-Pyrrolidone (NMP) was selected due to its high solvency, low volatility and high chemical and thermal stability. The advantages of its lower volatility may release fewer organic emissions to the atmosphere than other solvents. NMP has a stronger interaction with polymer and has the highest ranking for dissolution power with polymer solution if compared to other solvents usually used (Lau et al., 1991). Figure 3.4 shows the molecular structure of *N*-Methyl-2-Pyrrolidone.

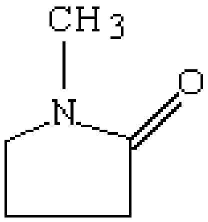

Figure 3.4: Molecular Structure of *N*-Methyl-2-Pyrrolidone

Source: Barth et al. (2000)

In addition, NMP is an organic solvent which is more soluble in water. Therefore, NMP is removed from membrane by diffusion in water (Lau et al., 1991). The solvent mixture of NMP and water is easily miscible with water as the coagulant; fast coagulation took place from both sides of the nascent fiber and the fast solidification across the overall membrane wall restricted the growth of macrovoids in the polymer-lean phase (Wang et al., 2000a). According to Chaturvedi et al. (2001), NMP also contributes towards tighter pore formation. The viscosity of casting solution with NMP as the solvent is low which indicates relatively small size polymer aggregates in solution because of the high solvating power of NMP. Thus, gelling process or gelation in coagulation bath is slower, signifies more gradual solidification of the polymer aggregated forming closer pores resulting in a narrow pore channel.

In preparation of PSf and PES membranes, water is used as a non-solvent in wet-phase phase inversion technique by precipitating PES and PSf casting solutions in a coagulation bath (Lau et al., 1991). Water is a strong non-solvent for the polymers solutions. It was used as non-solvent due to its ability in producing a homogeneous and thermodynamically stable polymer solutions (Bornemen et al., 2001). Water is the best non- solvent since it has a high boiling point and low melting point. Moreover, water can be employed to interact between polymer and coagulant to promote a faster diffusion in order to improve the performance and structures of asymmetric membranes (Xu and Qusay, 2004).

3.3.3 Additive

Generally, in order to improve membrane permeation rate, hydrophilic polymers such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) are used as an additive in polymer casting solutions. These polymers are recognized as the suitable polymer additive to produce high performance membranes (Bowen et al., 2001). The PVP additive is added to the mixture of base polymer and solvent in order to enhance the phase inversion process. Many research studies have been conducted to investigate the role of PVP additive on the membrane preparation process. The relationship between PVP additive concentration on membrane performance and structural properties has already been studied by Ismail and Hassan (2007).

Boom et al. (1992) investigated the effect of PVP on the formation of membranes and found that addition of PVP to the ternary system suppresses the formation of macrovoids in the sub-layer but Wang et al. (2009) reported that the addition of PVP to PES membrane promoted formation of macrovoids as a result these membranes had higher water flux, water absorption, and lower water contact angle (CA) than the pure PES membrane. In this study, polyvinylpyrrolidone (PVP) K15 was used in preparing PSf/CAP blend casting solutions. PVP K15 with molecular weight of 10 000 kDa was purchased from Fluka and directly used without any purification.

3.4 MEMBRANE PREPARATION

In this study, there are two types of polymer casting solutions were prepared, a casting solutions containing PSf/CAP blend solution and the PSf/CAP/PVP casting solutions containing an additive polymer, PVP. Table 3.1 shows the formulation of PSf/CAP casting solutions and Table 3.2 tabulates the composition of the PSf/CAP/PVP casting solutions that were prepared in this study. The materials used in preparing these casting solutions were PSf and CAP as polymers, PVP as additive and NMP employed as solvent. Firstly, polymers (PSf and CAP) were heated at about 60 ^{o}C for 24 hrs in order to remove moisture content in a convective oven. The presence of the moisture in polymers affected the quality and composition of polymer casting solutions which in turn changed the casting solution properties.

After that, PSf polymer was added into a round bottom flask which contains solvent, NMP that was heated by using a heating mantle. The mixture of polymer and solvent heated up about 90 °C and stirred using WiseStir^{TM} Digital Overhead Strirrer supplied from DAIHAN Scientific, Co., Ltd. The casting solutions were stirred at 200 rpm in order to ensure the polymer and solvent were well mixed. Then, CAP polymer was added when PSf polymer absolutely dissolved in the solvent. The casting solution was kept stirred for 7 to 8 hrs to form a homogeneous PSf/CAP polymer casting solution. Finally the prepared PSf/CAP blend casting solutions were placed in an ultrasonic bath for about 3 hours to remove the trapped air bubbles.

Table 3.1: Formulation of PSf and PSf/CAP blend casting solutions

Membrane Code	**Polymer composition (%)**[a]		**Solvent (wt%)**	**PSf/CAP in polymer composition (%)**
PC	PSf	CAP	NMP	PSf/CAP
PC-0	17.00	0.00	83.00	100/0
PC-5	16.15	0.85	83.00	95/5
PC-10	15.30	1.70	83.00	90/10
PC-15	14.45	2.55	83.00	85/15
PC-20	13.60	3.40	83.00	80/20

[a] Total polymer composition in casting solution is 17.00 wt%

Table 3.2: Formulation of PSf/CAP/PVP blend casting solutions

Membrane Code	**Polymer composition (%)[a]**		**Additive (wt%)**	**Solvent (wt%)**
PCV	PSf	CAP	PVP	NMP
PCV-1	15.3	1.7	1.0	82.0
PCV-2	15.3	1.7	2.0	81.0
PCV-3	15.3	1.7	3.0	80.0
PCV-4	15.3	1.7	4.0	79.0
PCV-5	15.3	1.7	5.0	78.0

[a] Total polymer composition in casting solution is 17.0 wt% with PSf/CAP polymer composition of 90/10

For the preparation of PSf/CAP/PVP casting solutions, after all polymers (PSf and CAP) were dissolved then the PVP additive was added into the solutions and left for about 8 hrs to ensure the dissolution process completed. After the casting solution was homogenously dissolved, it was poured into a bottle and degassed for about 3 hrs using an ultrasonic bath to remove any trapped micro-bubbles of gases prior to a casting process. Finally, the PSf/CAP/PVP blend casting solutions was kept at room temperature for membrane fabrication process. The apparatus for preparing the polymer casting solutions is shown in Figure 3.5.

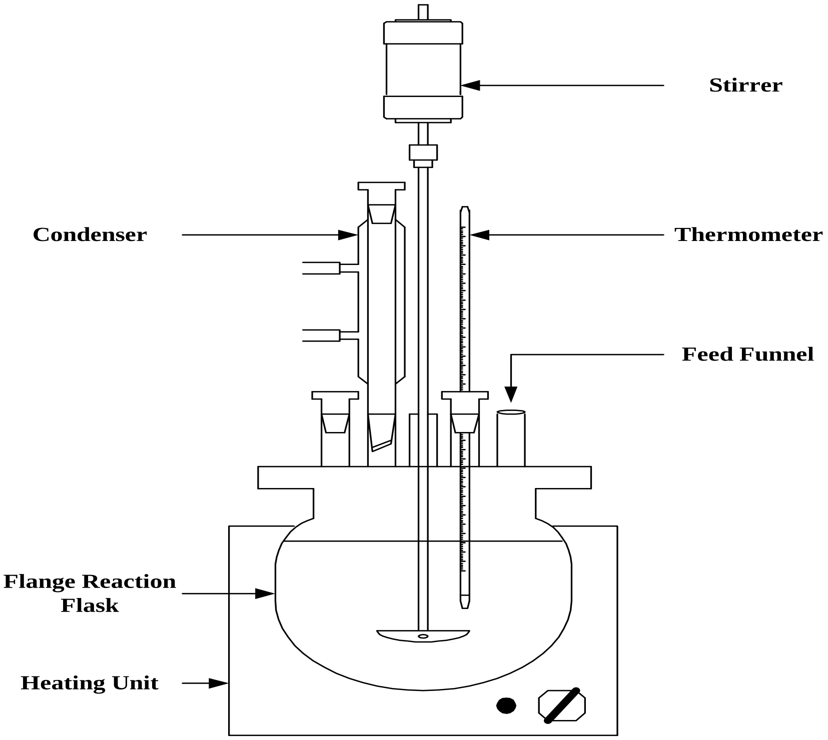

Figure 3.5: Schematic diagram of apparatus used for preparation of polymer casting solution

3.5 MEMBRANE SYNTHESIS

A flat sheet of PSf/CAP and PSf/CAP/PVP blend membrane was prepared via a simple wet phase inversion process. A high precision casting machine supplied by Kras Instrument & Services (Malaysia) was used to fabricate the membrane as shown in Figure 3.6. Firstly, a casting solution poured on a clean stainless steel plate at room temperature. The stainless steel plate moved at certain velocity (shear rate) towards a casting knife and then, the dope solution was cast by the casting knife with a thickness of about 200 µm.

Immediately after the casting process finished, the plate with the cast film was immersed into a coagulation bath which contains tap water as coagulation medium. After a few minutes, a thin polymeric film formed and separated out from the stainless steel plate due to the wet-phase inversion process. After the precipitation process was completed, the membrane was washed with distilled water and dipped in a container containing distilled water for 24 hrs to remove any excess solvent in the flat sheet membrane. Then finally, the flat sheet blend membrane is ready for performance test and characterization. All flat sheet membranes were visually inspected for defects and only good areas were chosen for membrane evaluation.

Figure 3.6: A high precision casting machine

3.6 SHEAR RATE

Shear rate during the membrane casting process can be varied by adjusting velocity of a casting plate. The different shear rates can be determined by changing the velocity of the casting plate as shown in the Eq. (3.1) and Eq. (3.2) respectively. Five different shear rates were employed, viz.: 42.0 s^{-1}, 52.5 s^{-1}, 70.0 s^{-1}, 105.0 s^{-1} and 210.0 s^{-1}, to fabricate membranes in order to study the effect of shear rate on the performance of PSf/CAP/PVP blend UF membranes. Table 3.3 shows membrane code for PSf/CAP/PVP blend membranes fabricated at different shear rates.

$$Velocity\ of\ casting\ plate\ (ms^{-1}) = \frac{Membrane\ lenght\ (m)}{Casting\ plate\ speed\ (s)} \tag{3.1}$$

$$Shear\ rate\ (s^{-1}) = \frac{Velocity\ of\ casting\ plate\ (ms^{-1})}{Membrane\ thickness\ (m)} \tag{3.2}$$

Table 3.3: Membrane code for PSf/CAP/PVP blend membranes fabricated at different shear rates

Shear rate (s^{-1})	**Membrane Code**
42.0	PCS-1
52.5	PCS-2
70.0	PCS-3
105.0	PCS-4
210.0	PCS-5

3.7 EVAPORATION TIME

In order to optimize the membrane separation performance, dry-phase inversion method was introduced before wet-phase inversion process took place during preparation of PSf/CAP/PVP blend membrane. In the dry phase inversion method, the cast polymer solution was introduced with a convective inert stream (nitrogen) for a certain period of time which is known as evaporation time. During this evaporation time, the convective stream removed the most volatile solvent from membrane surface, which results in a region with locally elevated polymer concentration at the nascent membrane surface. The complete phase inversion process was followed by wet-phase inversion method. In this study, the effect of evaporation time on membrane characteristics and separation performances in the range of 5, 10, 15 and 20 s were studied. Table 3.4 shows membrane code for PSf/CAP/PVP blend membranes fabricated at different evaporation time.

Table 3.4: Membrane code for PSf/CAP/PVP blend membranes fabricated at different evaporation time

Evaporation Time (s)	**Membrane Code**
5	PCE-5
10	PCE-10
15	PCE-15
20	PCE-20
25	PCE-25

3.8 MEMBRANE PERFORMANCE TESTS

The performance of PSf/CAP and PSf/CAP/PVP blend membranes were tested in terms of pure water flux, permeate flux and solute rejection. These testing were carried out using a Sterlitech HP4750 Stirred Cell supplied by Sterlitech as shown in Figure 3.7. Ultrafiltration membrane process was operated in the dead-end filtration cell with volume capacity of 300 ml and an active area of 14.6 cm^2. The Sterlitech HP4750 Stirred Cell is a chemical resistant cell with a maximum pressure rating of 69 bar (1000 psig). This cell is also suited to perform microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) separation.

Figure 3.7: Dead-end permeation cell

The flat sheet blend membranes were cut into circular disc and placed over center o-ring with the active skin layer installed facing the cell reservoir. The porous stainless steel support disc was placed on the disc membrane to hold the flat sheet membrane in place. For these performance tests, there are 3 samples of membranes were tested for each conditions so as to ensure the reproducibility of the data and the average value was tabulated.

A Teflon-coated magnetic stir bar was used to provide agitation to reduce concentration polarization or cake formation during dead-end filtration. A stirring plate with variable speed was used to operate the Teflon-coated magnetic stirrer. The operating pressure for filtration test was supplied by pressurized nitrogen gas and it was regulated by using a pressure regulator. A pressure relief valve was installed between the nitrogen gas and cell for safety purposes. The schematic diagram of dead end ultrafiltration permeation rig is shown in Figure 3.8.

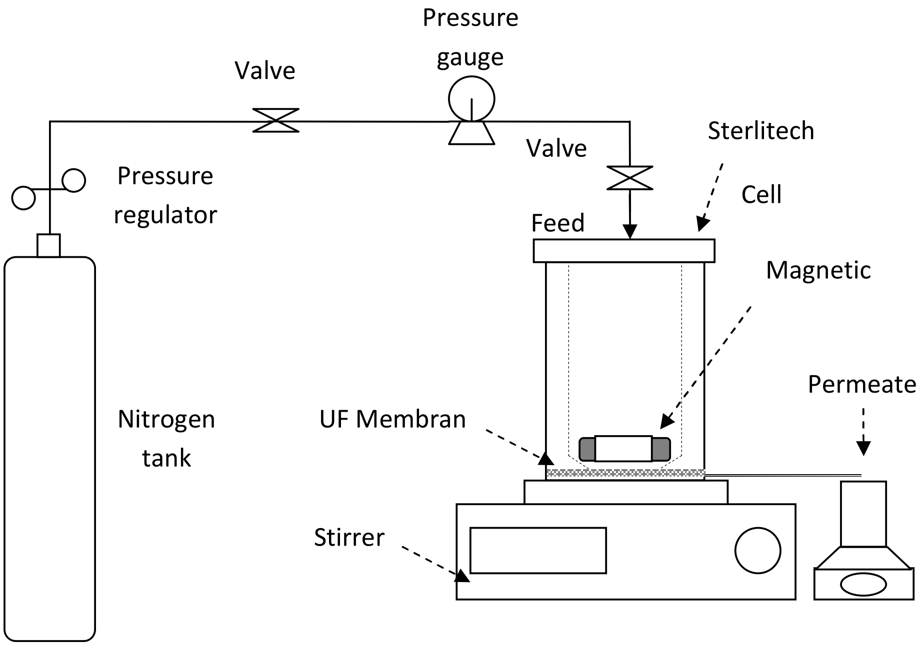

Figure 3.8: Schematic diagram of dead-end UF filtration set-up

3.8.1 Pure Water Permeation

Pure water flux is important in order to determine the membrane stability and its hydraulic properties. In this experiment, distilled water was used to determine pure water flux of each sample of blend membranes using a dead-end filtration cell. Firstly, the fresh membranes initially pressurized with distilled water at 5 bar for membrane compaction process between 30 minutes till 1 hour. This compaction process is important in order to get a stable and reliable data of each membrane in terms of pure water flux and proteins separation tests. The compaction process was finished when the pure water flux attained steady-state or constant flux.

Then, membranes were subjected to pure water flux test with varying operating pressure in the range 1 to 5 bar. The pure water flux was measured at steady-state conditions and it can be calculated by Eq. (3.3).

$$J_v = \frac{V}{A\, x \Delta t} \tag{3.3}$$

where;

J_v = the permeate flux or water flux (l/m^2 h)
A = the effective area of membrane (m^2),
Δt = sampling time (h)
V = Volume of permeate solution collected, (l)

In the pure water flux test, the permeability of each membrane was determined by the measurement of water permeability as a function of applied pressure. It was evaluated from the slope figure of pure water flux versus operating pressure.

$$P_m = \frac{J_v}{\Delta P} \tag{3.4}$$

where;

P_m = Membrane permeability (l/m^2 h.bar),
J_v = Flux (l/m^2 h)
ΔP = Pressure (bar)

Membrane hydraulic resistance, R_m (m^{2}h.bar/l) can be calculated from the inverse of the membrane permeability and the calculated equation as shown as below:

$$R_m = \frac{\Delta P}{J_v} \tag{3.5}$$

3.8.2 Protein Separation Performance

Different molecular weight of proteins was used to study membrane separation performance and to determine molecular weight cut-off (MWCO) of each membrane. Four different molecular weight of proteins were used in this separation such as trypsin (23 kDa), pepsin (35 kDa), egg albumin, EA (44.3 kDa) and bovine serum albumin, BSA (66 kDa). Trypsin, pepsin and EA were supplied by Sigma-Aldrich, and BSA was procured from Fluka, USA. All the proteins were used as received.

Pottasium dihydrogen phosphate (KH_2PO_4) with molecular weight of 136.08 g/mol and di-Pottasium hydrogen phosphate (K_2HPO_4) with molecular weight of 174.18 g/mol were obtained from Merck and used for preparation of phosphate buffer solution in protein analysis. Distilled water was used as a solvent agent in preparing phosphate buffer solution. For protein permeation, a single solution of protein was prepared at concentration of 500 ppm by dissolving a pre-weighed protein powder in phosphate buffer of 7.2 pH. Protein solution was prepared no longer than one hour before used and was stored at 4 ^{o}C to ensure protein molecules were active and had no bacterial contamination.

The protein separation for the low molecular weight was first done following the consequent increasing molecular weight of proteins. The separation was performed in the order of trypsin (23 kDa), pepsin (35 kDa), EA (44.3 kDa) and BSA (66 kDa) to avoid the hindrance effect of the bigger proteins on the active surface of the membrane if the protein separation performed first by the separation of a high molecular weight of proteins followed by the separation of low molecular weight of proteins (Arthanareeswaran et al., 2007c)

For the protein separation study, protein solution was filled in the dead-end cell with an effective permeation area of 14.6 cm^2. The protein solution was pressurized at a constant pressure of 3 bar and the volume of permeate solution of the corresponding membranes was measured and collected in a graduated glass cylinder. The protein solutions were stirred homogenously at 100 rpm to avoid concentration polarization and fouling of proteins. The absorbance of feed and permeate of proteins were analyzed by

UV-Vis spectrophotometer (Hitachi U-2000) at wavelength of 280nm. From the feed and permeate concentrations, the percentage rejection was calculated using Eq. 2.12. The average data of three replicates were reported.

Finally, after each protein separation process finished, the cell was emptied and filled with distilled water and then, stirred at 400 rpm for 30 minutes in order to remove any adhered protein on the membrane surface. The membrane was removed and washed gently many times with distilled water and then placed in the dead-end cell for the next protein separation.

3.9 MEMBRANE CHARACTERIZATION

3.9.1 Water Content

The water content of the PSf/CAP and PSf/CAP/PVP blend membranes were evaluated by their capacity for water absorption and calculated by Eq. (3.6) :

$$A = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100\% \qquad (3.6)$$

where

A = the water content (wt%),
W_{wet} = the wet weight of membrane (mg)
W_{dry} = the dry weight of membrane (mg)

The water content of the membranes was determined by soaking the membranes in water for 24 h at room temperature. The weights of the wet blend membranes were first measured after mopping the membranes with blotting paper, and then the membranes were dried in oven at 75 ^{o}C for 48 h (Sivakumar, et al., 2006). The weights of the dry blend membranes were measured again after it cooled. At least three measurements of water content were measured and the results were averaged to get a reliable value.

3.9.2 Porosity

The porosity of blend membranes were evaluated by their capacity of water absorption and calculated using the expression below (Machado, et al., 2006):

$$Porosity = \frac{(W_{1}-W_{2}/d_{water})}{V} \times 100\% \tag{3.7}$$

where

W_1 and W_2 = the mass of membrane in the wet and dry states (mg)

d_{water} = the density of water at room temperature (ml/mg)

V = the volume of the membrane in the wet state (ml)

3.9.3 Contact Angle

The measurement of hydrophlicity of blend membranes via contact angle measurement was done at Malaysian Nuclear Agency (MINT) in Bangi, Sedang, Selangor. Contact angles of the dry membranes were measured using a FACE Contact Angle Meter, model CA-A. (FACE Kyowa Kaimenkagaku Co. LTD). A droplet of ultrapure water was delivered onto the dry membrane surface and a static image of the droplet was taken immediately after contact with the membrane surface. The contact angles measurement were performed three times for each sample and the average measurement was reported.

3.9.4 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) (JSM P/N HP475 model) at Institute of Oceanography, Universiti Malaysia Terengganu (UMT) was used to analyze morphological structures of blend membranes as shown in Figure 3.9. The membrane morphology is one of the basic requirements to understand and explain relation between morphology of membranes and the performance of the membranes.

Membranes were cut into small specimens and immersed into liquid nitrogen in a small container. The membranes were fractured after immersion and the fractured membranes were then placed in an automatic coater (JFC 1600 model) to coat the membrane samples. The samples were coated with a thin gold layer for 30 minutes to prevent charging up of the membrane surface by electron beam which in turn damaged or burned the samples. Cross sections of the flat sheet blend UF membranes were obtained after coating process using SEM equipment.

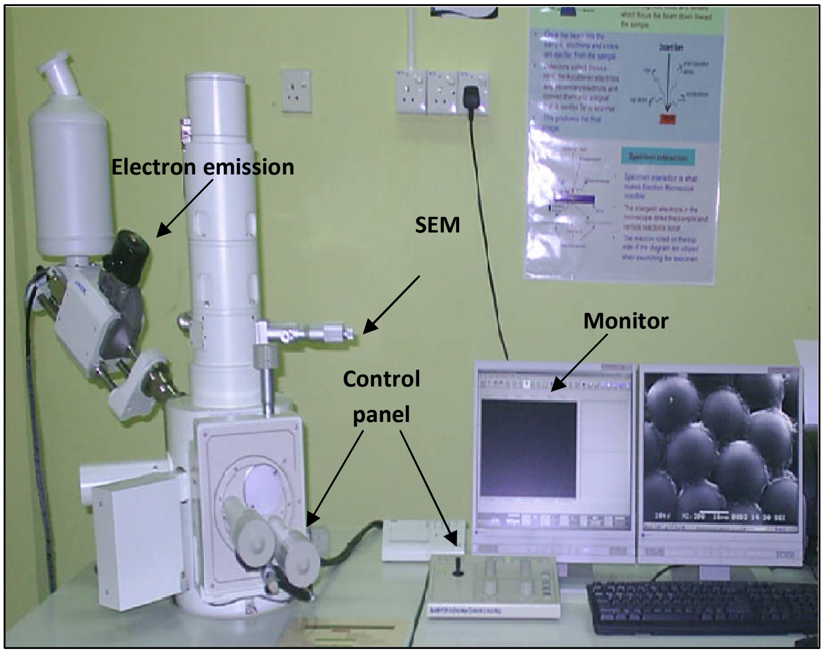

Figure 3.9: A full set of scanning electron microscope (SEM)

3.9.5 Molecular Weight Cut-off and Pore Properties

Molecular Weight Cut-off (MWCO)

Molecular Weight Cut-off (MWCO) of the PSf/CAP and PSf/CAP/PVP blend membranes were determined by the rejection studies of different molecular weights of proteins such as trypsin (23 kDa), pepsin (35 kDa), egg albumin, EA (44.3 kDa) and bovine serum albumin, BSA (66 kDa) in an ultrafiltration cell filter (Arthanareeswaran, et al., 2010 and Sivakumar, et al., 2006). In this study, MWCO of the blend membranes were obtained based on the lowest molecular weight of protein that was rejected at 80% in the figure of protein rejection versus molecular weights of protein. The calculation of the solute rejection is presented by Eq. (2.12).

Pore Properties

Pore properties of the surface of blend membranes was determined in terms of the average pore size and pore density. As MWCO of blend membranes were determined, the average pore size of blend membranes can be obtained by using Figure 2.9. The results of the ultrafiltration of different molecular weights protein solutions were used to calculate the pore density of the membranes from Eq. (2.14) to Eq. (2.15) as explained by Sarbolouki (1982).