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**Preparation of thin-film-composite polyamide membranes for desalination using novel hydrophilic
surface modifying macromolecules**

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**Preparation of thin-film-composite polyamide membranes for
desalination using novel hydrophilic surface modifying
macromolecules**

By

Belal Abu Tarboush

**A thesis submitted in partial fulfillment of the requirements
for the degree of
Master of Applied Science**

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Abstract

Reverse osmosis (RO) by polymeric membranes is known to be the most successful technology for brackish and seawater desalination processes. For the development of these polymeric RO membranes, two different techniques have been used: The phase inversion method for asymmetric membranes, such as cellulose acetate (CA) membrane and the interfacial polymerization for thin film composite (TFC) membranes. Polyamide composite membranes which are characterized by a thin film supported on a chemically different asymmetric porous membrane have become commercially successful for certain applications, especially for seawater desalination.

Although TFC aromatic polyamide membrane has excellent characteristics and performance among other types of RO membranes, it suffers from some drawbacks such as biofouling and fouling caused by chemical foulant such as natural organic matter (NOM).

The objective of this work is to present a new concept for the preparation of thin-film-composite (TFC) reverse osmosis (RO) membrane by interfacial polymerization on porous polysulfone (PS) support using novel additives. Hydrophilic surface modifying macromolecules (LSMM) were synthesized both ex-situ by conventional method (cLSMM), and in-situ within the organic solvent of the TFC system (iLSMM). The effects of these LSMMs on the fouling of the TFC RO membranes used in the desalination processes were studied.

Fourier transform infrared (FTIR) results indicated that both cLSMM and iLSMM were present in the active layer of the TFC membranes. Scanning electron microscopy (SEM) micrographs depicted that heterogeneity of the surface increases for TFC membranes compared to the control PS membrane, and that higher concentrations of LSMM provided smoother surface. Atomic force microscope (AFM) characteristic data presented that the surface roughness of the skin surface increases for TFC membranes compared to the control. The RO performance results showed that the addition of the cLSMM significantly decreased the salt rejection of the membrane and slightly reduced the flux, while in the case of the iLSMM, salt rejection was improved but the flux declined at different rates for different iLSMM concentrations. The membrane prepared by the iLSMM exhibited less flux decay over an extended operational period.

Résumé

On connu que l'osmose contraire (RO) par les membranes polymères soit la technologie la plus réussie pour les processus de dessalaison salés et eau marine. Pour le développement de ces membranes RO polymères, deux différentes techniques ont été utilisées : la méthode d'inversion de phase pour les membranes asymétriques, comme l'acétate de cellulose (CA) la membrane et l'intersoin du visage polymerization pour le composite de film fin (TFC) les membranes. Les membranes de composite de Polyamide qui sont caractérisées par un film fin soutenu

Bien que la membrane polyamide aromatique TFC ait des caractéristiques excellentes et une performance parmi d'autres types de membranes RO, il souffre de quelques désavantages comme biofouling et l'encrassement provoqué par le produit chimique foulant comme la question organique naturelle (NOM).

L'objectif de ce travail est de présenter un nouveau concept pour la préparation de composite de film fin (TFC) l'osmose contraire (RO) la membrane par l'intersoin du visage polymerization sur polysulfone poreux (le PS) le soutien en utilisant des additifs originaux. La surface de Hydrophilic le fait de modifier des macromolécules (LSMM) a été synthétisée tant ex-situ par la méthode conventionnelle (cLSMM), que dans - situ dans le solvant organique du système TFC (iLSMM). Les effets de ces LSMMs sur l'encrassement du TFC RO les membranes utilisées dans les processus de dessalaison ont été étudiés.

Les résultats de FTIR ont indiqué que tant cLSMM qu'iLSMM ont été présent dans la couche active des membranes TFC. Les micrographiques de SEM ont représenté cette diversité des augmentations de surface pour les membranes TFC comparées à la membrane de PS de contrôle et que de plus hautes concentrations de LSMM ont fourni la surface plus lisse. Les données de caractéristique d'AFM l'ont présenté l'âpreté de surface des augmentations de surface de peau pour les membranes TFC comparées au contrôle. Les résultats de performance RO ont montré que l'adjonction du cLSMM a de façon significative diminué le refus de sel de la membrane et a légèrement réduit le flux, pendant qu'en cas de l'iLSMM, le refus de sel a été amélioré mais le flux a décliné à de différents taux pour de différentes concentrations iLSMM. La membrane préparée par l'iLSMM a exposé moins de décadence de flux au cours d'une période opérationnelle prolongée.

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List of Abbreviations

AFM	Atomic Force Microscope
Å	Angstrom
ATR	Attenuated Total Reflection
BSA	Bovine Serum Albumin
CA	Cellulose Acetate
CA°	Contact Angel
cLSMM	Solid LSMM prepared ex-situ by conventional method
CSA	Camphor Sulfonic Acid
DMAc	N,N-Dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential Scanning Calorimeter
ED	Electro Dialysis
EDTA	Ethylenediamine-tetra acetic Acid
ESCA	Electron Spectroscopy for Chemical Analysis
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HMWC	High Molecular Weight Components
HSQC	Heteronuclear Single Quantum Coherence
IDA	International Desalination Association
iLSMM	LSMM prepared in-situ within the organic solvent
IP	In-Situ Polymerization
kD	Kilo Dalton
LMWC	Low Molecular Weight Components
LSMM	Hydrophilic Surface Modifying Macromolecules
MDI	4,4'-Methylene bis(phenyl isocyanate)
MED	Multi-Effect Distillation
MF	Microfiltration
M_n	Number Average Molecular Weight

MPD	<i>1,3-Phenylenediamine</i>
MSF	Multistage Flash Distillation
MSF	Multistage Flash Distillation
MVC	Mechanical Vapor Compression
M_w	Weight Average Molecular Weight
MWCO	Molecular Weight Cut-Off
NF	Nanofiltration
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
PA	Aromatic Polyamide
PDI	Polydispersity Index
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PP	Polypropylene
PPD	p-Phenylenediamine
PPG	Poly(propylene glycol)
PS	Polysulfone
PS-mPA	Thin Film Composite membrane prepared from MPD
PS-pPA	Thin Film Composite membrane prepared from PPD
PVA	Polyvinyl alcohol
PVDF	Poly (vinylidene fluoride)
PWP	Pure Water Permeation
R_a	Average Surface Roughness
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
TEA	Triethylamine
TFC	Thin Film Composite Membrane
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
TMC	<i>1,3,5-Benzenetricarbonyl trichloride</i>
UF	Ultrafiltration

1. Introduction

1.1. Seawater Desalination

The demand for high quality drinking water has been increasing around the world over the last few decades as the result of an accelerated growth in population, in addition to rising health concerns. Due to the fact that available fresh water accounts for less than 0.5% of the earth's total water supply and 97% of the water on the earth is saline water in the oceans, oceans represent the earth's major water reservoir. Despite this fact, many regions in the world suffer severely from a shortage in drinking water. Thus, securing an alternative source of drinking water has become vital [1-5].

Since seawater is inappropriate for human consumption and for industrial and agricultural uses, desalination has become a valuable process to achieve fresh water [2, 5]. Desalination, which is defined as the removal of dissolved solids – primarily salts – from water, is one of the most familiar methods, used around the world for a long time, to reduce water salinity to acceptable quality for human use [2, 5-7]. The major sources of feed water for desalination processes are seawater which accounts for 59 % and the remaining 41% are brackish water sources of various quality [1, 4-9]. Seawater desalination is a crucial and reliable fresh water resource for some countries, in particular, in the Middle East [3, 8, 9]. Those countries depend mainly on desalination technologies for the purpose of meeting their fresh water needs. More than 60% of the worldwide desalination plants are located in the Middle East [6, 8].

Seawater desalination process separates seawater (saline feed) into two streams: a fresh water stream with a very a low concentration of dissolved salts and a concentrated brine stream [2, 6]. Figure 1.1 explains the basic of seawater desalination process. This separation process requires some form of energy to desalinate, and make use of several different separation technologies. Based on thermal distillation, freezing, membrane separation, and electrodialysis, many desalination technologies have been developed [2, 3, 10]. The most widely applied and commercially proven technologies for seawater desalination fall into two categories [2-8]:

1- Thermal methods (Distillation) which include:

- Multistage Flash Distillation (MSF)
- Multi-Effect Distillation (MED)
- Mechanical Vapor Compression (MVC)

2- Membrane based methods which involve:

- Reverse Osmosis (RO)
- Electro Dialysis (ED)

Commercially, RO, the leading membrane process, and MSF, the leading thermal process, represent the predominant technologies currently being used around the world [4, 7]. In 1999, about 78% of the world's seawater desalination capacity was made up of MSF plants while RO produced only 10% [2, 11]. Though, there has been a successive increase in RO seawater desalination mainly due to its lower cost and simplicity. In 2002, the International Desalination Association (IDA) estimated that the most widely installed process is RO, followed closely by MSF [5, 12]. Figure 1.2 illustrates the percent installed capacity of the major desalination processes, as estimated by the (IDA) in 2002.

Figure 1.1: Seawater desalination process.

Figure 1.2: World's installed desalination capacity by process [5, 12].

1.2. Membrane Separation Processes

Membrane can be defined as a selective barrier between two phases. There are several types of membrane filtration technologies available in the market that produce different levels of product water quality [6]. Figure 1.3 illustrates the concept of membrane separation processes. Pressure driven liquid filtration processes can be categorized based on the size of the particle or molecule the membrane is able to reject or pass [6, 13]. A comparison between the main four membrane liquid separation processes is summarized in Table 1.1.

Common types of membrane technologies include [6, 13, 14]:

- Microfiltration (MF) is a process where suspended solids are rejected. It screens particles in the range from 0.1 to 1.0 microns in diameter which include turbidity, algae, giardia, and bacteria. Proteins pass the membrane freely.
- Ultrafiltration (UF) is a process where the high molecular weight components (HMWC), such as protein, and suspended solids are rejected, though, all low molecular weight components (LMWC), such as salts, amino acids, organics, inorganic acids or sodium hydroxide, pass through the membrane freely. Generally, it screens particles from 20-1000 Angstrom in diameter. Most of UF membranes have molecular weight cut-off in the range between 1,000 and 100,000.
- Nanofiltration (NF) rejects only ions with more than one negative charge, such as sulfate or phosphate, while allowing single charged ions to pass freely through the membrane. Also, NF rejects uncharged, dissolved materials and positively charged ions based on the size and shape of the molecule. Typically, it screens

particles in the approximate size range of 1 nanometer, such as, organic chemicals.

- Reverse Osmosis (RO) which is considered as the tightest membrane process in liquid-liquid separation. The only material passing through the membrane is water. RO membrane serves as a barrier to all dissolved salts, inorganic molecules, and organic molecules with a molecular weight greater than 100. The above classification, however, is very arbitrary.

Figure 1.3: Membrane separation process.

Table 1.1: Comparison between the main four liquid- liquid membrane separation processes [13, 14].

	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical, Asymmetrical
Thickness	150 μm	150 μm	150 - 250 μm	10-150 μm
Thin film	1 μm	1 μm	1 μm	
Rejection of	HMWC, LMWC, sodium chloride, glucose, amino acids	HMWC, color Divalent anions	Macro molecules, proteins, polysaccharides	Particles, clay, Bacteria
Membrane materials	CA Thin film	CA Thin film	Ceramic, PS, PVDF, CA, Thin film	Ceramic, PP, PS, PVDF
Membrane Module	Tubular, spiral wound, plate-and- frame, hollow fiber	Tubular, spiral wound, plate-and-frame	Tubular, spiral wound, plate-and- frame, hollow fiber,	Tubular, hollow fiber,
Operating Pressure	15-150 bar	5-35 bar	1-10 bar	<2 bar

1.3. Seawater Desalination Using RO Technology

The common desalination method, distillation by MSF and MED, consumes a lot of energy and those technologies were limited to countries where cheap energy was achievable [10]. The concepts of "osmosis" and "reverse osmosis" have been known for many years. Nevertheless, the use of reverse osmosis (RO) as a profitable separation process is a relatively young technology. The development of RO membranes during the 1960s by Loeb and Sourirajan and its final technological improvements in the 1980s cut down the energy demand to a lower level, made the possibility for cheap and reliable desalination methods more approachable and made the membrane desalination process industrially practical [10, 14]. Subsequently, the desalination market was approximately equally divided between MED, MSF on one side, and reverse osmosis on the other side with a decreasing market share for MSF in favor of reverse osmosis [10]. Currently, reverse osmosis is the major contributor in the brackish and seawater desalination market with 85% market share [14].

Reverse osmosis desalination has many advantages over thermal desalination, such as: effective separation at room temperature, continuous improvements in membrane materials leading to lower production cost, consumption of less energy, no need to be linked to the power plant [2,4-8], possibility to be linked to ultrafiltration, pervaporation, distillation, and other separation techniques to produce hybrid processes that result in very high separation and requirement of less surface area than distillation plant for the same production rate [7].

RO is a pressure-driven process where the osmotic pressure is overcome by exerting external pressure higher than the osmotic pressure on the seawater (Feed) causing the water to flow in the reverse direction of the normal flow across the membrane, leaving behind the dissolved salts which represent the brine stream with very high salt concentration [14-17]. All the energy required is for pressurizing the seawater feed. No heating or phase separation change is required [2-6, 14].

Osmosis is a natural phenomenon where a solvent (usually water) flows through a semipermeable barrier from the side with lower solute concentration (pure water) to the higher solute concentration side (sodium chloride solution) [14-17]. Water flow continues and the water level in the sodium chloride side rises until the flow stops at the steady state (chemical potential equilibrium of the solvent is established) [2, 6, 14]. The difference between the water level in the pure water side and the aqueous side at steady state represents the osmotic pressure. When a pressure higher than this osmotic pressure is exerted on the sodium chloride side solution, the flow of the pure water is reversed; the flow will be from the sodium chloride side to the pure water side [14]. Since there is no flow for the sodium chloride through the membrane, pure water can be obtained from the sodium chloride solution. This process is known as reverse osmosis [2, 14]. Figure 1.4 illustrates the principal of reverse osmosis.

Reverse osmosis membrane works as the semipermeable barrier to control the flow in the RO process, allowing a particular species (solvent, usually water) to pass freely across the membrane while retaining partially or completely other species (solutes) [14-

19]. Chemical potential gradients across the membrane produce the driving forces for solute and solvent transport across the membrane. The water chemical potential gradient is generally expressed in terms of pressure difference across the membrane, while the solute chemical potential gradient is usually expressed in terms of concentration [14-16, 19].

Figure 1.4: Principle of Reverse Osmosis [14].

1.4. Available Commercial Membranes for Reverse Osmosis

Generally, RO membrane performance is governed by the properties of the membrane used in the process. These properties depend mainly on the chemical nature of the membrane material (polymer) as well as its physical structure [17-20].

Properties for the perfect RO membrane materials include:

- Excellent salt rejection
- High water flux rates
- Resistant to biological, colloidal and suspended materials fouling
- Tolerant to chlorine attack
- Excellent mechanical strength (can withstand very high pressure)
- High chemical stability
- Tolerate high temperature
- Inexpensive and available in the market
- Easy to form into thin films, hollow fibers

Currently, most of available RO membranes can be classified into two categories: asymmetric membranes containing one polymer, and thin-film composite membranes consisting of two or more polymer layers. Asymmetric RO membranes consist of a very thin (0.1 to 1 μm) permselective skin layer on the top surface, supported on a more porous sublayer of the same polymer [19-21]. Figure 1.5 shows a schematic cross-section of the integrally skinned asymmetric membrane and of the RO composite asymmetric membranes. The performance of these membranes is controlled by the dense skin layer while the porous sublayer acts only as a mechanical support for the skin top layer and has

negligible effect on the membrane performance. Phase inversion (polymer precipitation), using nonsolvent immersion, is the most important asymmetric membrane preparation technique [14, 19-24]. In this process, a polymer solution is precipitated into a polymer-rich solid phase which forms the porous sublayer and a polymer-poor liquid phase that forms the membrane pores or void spaces (thin, top layer) [14,19-24]. In-situ polymerization technique is usually applied to fabricate composite membranes. The details of this technique will be described later.

The most common membrane materials for reverse osmosis membranes are cellulose acetate, polyamide and the “thin film composites”, prepared by interfacial polymerization on the surface of a porous support [17, 18, 24].

Figure 1.5: Schematic structures of integrally skinned asymmetric and composite membranes.

1.4.1. Cellulose Acetate

In the late 1950's, Reid showed that cellulose acetate RO membranes were able to separate salt from water, although the water fluxes acquired were too small. Later, in 1960's, Loeb and Sourirajan used phase inversion (polymer precipitation), using nonsolvent immersion, to prepare asymmetric cellulose acetate membranes with relatively high water fluxes and separations [15, 23, 24]. Using this technique, a polymer solution is cast into a film and then the polymer is allowed to precipitate by immersion into a nonsolvent. The nonsolvent could be water that quickly precipitates the polymer on the surface of the cast film, producing the very thin, dense skin layer of the membrane [14, 15]. The polymer underneath the skin layer precipitates more slowly, forming a more porous polymer sublayer. After that, the membrane is annealed in order to improve solute rejection [19, 21, 23].

One of the first RO membrane materials was Cellulose Acetate (CA). CA membranes are prepared from cellulose diacetate and cellulose triacetate and blends of the two [14, 17, 18]. CA membranes still have a lot of successful uses especially in water treatment. They usually give high water flows with low salt solubility [17, 23]. When compared to polyamide based membranes, CA membranes have higher chlorine resistance. Also CA membranes usually show more stable performance than polyamide membranes, in particular, for application where the feed water has high fouling potential and this is believed to be due to the CA membrane characteristics such as; neutral, and low roughness surface [17]. Still, CA membranes are less stable in organic solvents than polyamide and they are less resistant to biological attack. CA membranes exhibit poor

chemical stability and tend to hydrolyze over time at a rate that depends mainly on the temperature and pH. Therefore, the recommended pH range is between 3 and 7, and the recommended temperature is lower than 50°C [17,18].

1.4.2. Aromatic Polyamide (Aramid)

Integrally skinned asymmetric aromatic polyamides membranes were invented by Du Pont in the hollow fine fiber form produced by solution spinning. A thin layer, approximately 0.1-1.0 μm thick, is placed on their external surface from controlled evaporation of the spinning solvent [18, 22]. This thin layer controls the performance of the membrane. Aramid membranes have an excellent chemical stability compared to CA membranes but they are susceptible to chlorine attack. Recommended temperature and pH for Aramid membranes are 0°C-30°C, and 4-11 respectively [18].

1.4.3. Thin Film Composite Membranes

In the middle of 1960s, the work conducted at the North Star Research and Development Institute, resulted in developing thin film composite (TFC) membranes. In the early 1980s, FilmTech Inc. brought in its FT-30 composite membranes. The structure of those TFC membranes composed of an ultrathin barrier layer to be formed on the top surface of a microporous polysulfone that has been cast on a porous fabric supporting layer [25]. More details about TFC synthesis and characters will be presented in the next chapter.

2. Thin Film Composite Membranes

2.1. Background

The most common reverse osmosis (RO) membranes used in water treatment and seawater desalination are the Thin Film Composite (TFC) membrane based on aromatic polyamide (PA) [26-29]. TFC membrane is an asymmetric membrane which is comprised of a fabric, a porous support layer made of polysulfone, and a dense ultra thin salt rejection barrier layer [27]. The porous support layer, which is in most cases polysulfone, is made by the phase inversion technique, while the thin layer is made by interfacial polymerization (polycondensation) [16]. Many routes were described to form the ultrathin barrier layer in the composite membranes. These techniques include [27]: 1) Casting an ultrathin dense layer separately and then cover the microporous support layer with the thin dense layer (lamination), 2) Interfacial polymerization, 3) To dip-coat a polymer solution onto a microporous layer and then dry the coated layer, 4) To use a gaseous phase monomer plasma to deposit the barrier film directly on the microporous support layer (plasma polymerization). Among those methods, interfacial polymerization is the most widely used technique and polyamide TFC membranes are industrially produced by this method [27, 28].

TFC membranes were successfully developed to replace integrally skinned asymmetric reverse osmosis made of cellulose acetate by the phase inversion method [30]. A TFC membrane is composed of two (without including polyester support layer) or three layers; a polyester support web, a microporous polysulfone layer and an ultra thin polyamide barrier layer [26-31]. Each of these three layers can be optimized and

synthesized for its special function [26-33]. The thin layer can be optimized to achieve the maximum water flux and solute rejection characteristics. The microporous sublayer can be optimized for high porosity, and strength. Both layers can be fabricated to have the best chemical resistance [25]. The surface thin layer controls the flux and separation characteristics of the membrane while the porous backing layer underneath serves only as a support for the barrier layer and has almost no effect on membrane transport properties. The barrier layer is very thin, on the order of 0.1 μm or less, therefore allowing high water fluxes [21, 25].

A Large number of reverse osmosis TFC membranes have been successfully prepared from various polymers such as; polyurea, polyamides, polyurea-amides, polyether-amides, polybenzhydrazides, polybenzimidazole, and other polymers. Those TFC membranes have shown excellent salt rejection with low water permeability [31, 32, 34]. This low water permeability of membranes formed from different polyamides comes from the rigid cross linked structure [27, 32]. FT-30 membranes are considered as the most successful reverse osmosis TFC membrane. In the FT-30 membrane the thin active layer is aromatic polyamide that is prepared via interfacial polymerization of m-phenylenediamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase [27, 34, 35].

2.1.1. Advantages of TFC Membrane

Compared to CA membranes, TFC membranes have greater chemical stability. They can operate continuously at temperatures between 0°C and 40°C and pH range 2 to 12

and they are able to give higher flux and higher salt rejection at moderate pressures. Also, different kinds of chemical compositions can be used to form the thin barrier layer of TFC, including linear and non-linear polymers, and each layer in the composite membrane can be synthesized and optimized for a special function. For example; the thin layer can be optimized for the required combination of water flux and salt rejection [25, 27]. Moreover, TFC membranes are claimed to be less susceptible to microbiological fouling than other reverse osmosis membranes [16].

2.1.2. Disadvantages of TFC Membrane

Despite the high quality of the water produced by TFC-RO process, TFC membranes are susceptible to chlorine and other disinfectants, which are commonly used in the feedwater to reduce the potential of biological fouling. Although this practice is generally effective, it can result in degradation of TFC membranes, which are sensitive to chemical attack by strong oxidizing agents such as chlorine on the nitrogen sites on the TFC surface [36, 37]. Wu et al. increased the chlorine resistance of the PA composite membrane using argon plasma modification technique, which caused cross-linking to take place at the nitrogen site on the surface of the TFC [37]. Lang et al. produced an excellent chlorine-resistant polyvinyl alcohol (PVA) RO-TFC membrane using malic acid as a cross-linking agent and acetic acid as a catalyst [38]. Kim and Kim found that plasma treatment of support material enhanced the chlorine resistance of the TFC [29]. Another important obstacle that greatly limits the successful utilization of the RO processes is fouling [39, 40] and it is also true for the TFC membranes. Thus, the development of TFC membranes with reduced fouling is called for.

2.2. Interfacial Polymerization

The TFC membrane preparation technique is based on interfacial polymerization (polycondensation) reaction between two monomers (a polyfunctional amine and an acid chloride), dissolved in water and hydrocarbon solvent, respectively [27, 41-46]. The interfacial polymerization reaction takes place under ambient temperature and in a non stirring system [46].

Since water and the hydrocarbon solvent are immiscible, polymerization reaction takes place at the water/hydrocarbon interface, which results in the formation of a thin skin layer on the surface of the porous substrate membrane. Interfacial polymerization takes place in the organic phase side of the interface and not the aqueous phase side because of the highly non favorable partition coefficient for the acid chloride which limits the availability of the acid chloride in the aqueous phase. In other words, the acid chloride has negligible solubility in water while the amine has a fairly good solubility in organic solvents [27, 33]. So the polyfunctional amine must diffuse across the water-hexane interface to make reactive connection with the acid chloride. The polyfunctional amine must continuously cross the water – hexane interface, diffuse through the polyamide film which is already formed, and then meet to react with the acid chloride on the organic phase side of the polyamide to ensure the build up of the film thickness which causes a new polymer film on the organic phase side of the polyamide film to be formed [27,30,44-46].

Since the acid chloride is insoluble in water, the polymer formation is dependent mainly on the rate of mixing of reactant, especially the mass transfer rate of the amine to the organic phase. This means that polymerization reaction is strongly affected by the factors that influence the diffusion rate of the amine toward the organic phase, such as the nature of solvent, the reactant concentration, the phase miscibility etc. [47-50]. Then, it is better to use a large excess of amine over acid chloride (typically about 20:1), in order to drive partitioning and diffusion of the amine into the organic phase. Any factors that disturb the diffusivity and solubility of the amine monomer in the organic phase affects not only the reaction rate but also the morphology and structure of the resulting polyamide film, which ultimately determines separation performance and interfacial properties [48, 49].

The thin film active layer from 10nm to several micrometers is quickly formed at the interface and strongly attached to the substrate [41]. One of the most important characteristic of polyamide film is the presence of unreacted charged groups (carboxylic and amine groups) which are believed to play a major role in the rejection and fouling resistance [33, 51]. The thin film active layer is the main factor that determines the performance of the TFC membrane, which means that selecting the monomers used in the reaction is crucial and even small changes in the monomer structure can largely affect the performance of the formed TFC [17, 50, 52]. For example; piperazine is a well known monomer for interfacial polymerization and using piperazine as a diamine will produce nanofiltration TFC membranes [52] while using m-phenylenediamine and p-phenylenediamine will produce RO TFC membranes [53].

Sundet [53] suggested that the reaction between amines and acid chlorides is a second order reaction and it takes place rapidly and the absolute reaction rate constant is very high and of the order of $10^2 - 10^6$ L/mol s and the functionality of the reactants should be enough to produce a very highly branched structure. Since the fast polycondensation reaction takes place within the organic phase, so the nature of solvent and the distribution coefficient of diamine become dominant factors. He also claims that the quick development of the barrier layer prevents further reactant diffusion and stops the reaction within seconds.

Recently, Kwak [47] used dimethylsulfoxide (DMSO) as an additive in the interfacial polymerization and the produced TFC membranes showed large increases in water flux up to 5 folds compared to the normal TFC membrane with no considerable loss in rejection. He also found that addition of DMSO increased surface area and surface roughness by reducing the solubility difference between the water and organic phase. Furthermore, addition of DMSO increases the number and size of network pores which can explain the large increase of flux. On the other hand, his experimental work showed that the thin films of cross-linked aromatic polyamide RO membranes were composed of two different types of pores having radius of 2.1-2.4 Å of network pores, and 3.5-4.5 Å of aggregate pores. Figure 2.1 represents network pores and aggregate pores according to Kwak.

Figure 2.1: Schematic representation of possible molecular structure of network and aggregate pores in aromatic TFC membranes [47].

Many factors affect the composition and morphology of the interracially formed polymer film, including [25-27, 53];

- 1- Concentration of reactants.
- 2- Partition coefficients of reactants.
- 3- Reactivity ratio of reactants.
- 4- Solubility of the formed polymer in the solvent phase as it is formed.
- 5- Diffusion rates of the reactants.
- 6- Hydrolysis or any other competitive by-reaction.
- 7- Post reactions or treatment of the resulting film.
- 8- Cross linking reactions.

One problem that often occurs in the in situ polymerization is the formation of ultra thin layer with a large number of defects, which results in poor membrane performance (very high flux with very low separation). To overcome this difficulty diacyl halides like isophthaloyl chloride, terephthaloyl chloride, 2, 6-pyridinedicarboxylic acid chloride, and phenylphosphoric dichloride should not be used alone without the addition of acyl halides with functionality greater than 2, like trimesoyl chloride (TMC) [54].

Polyamine may be primary or secondary, aliphatic or aromatic. The aliphatic polyamide could be linear or cyclic, which includes ethylenediamine, polyethylenediamine, n-cyclohexanediamine, cyclohexanetriamine, and piperazine. Valuable aromatic polyamines include phenylenediamine such as m-phenylenediamine (MPD), p-phenylenediamine (PPD), and triaminobenzene. Aromatic polyamide is more preferable than aliphatic ones [46].

The concentration of the polyamine in water is not critical. A concentration range from 0.1 to 10 wt% of the polyamine is preferred, more preferably 0.5 to 3 wt%. The optimum concentration of phenylenediamine seems to be about 2% by weight. For the acyl halides which are soluble in the organic phase the optimum concentration is around 0.1-0.2 wt%. High solubility or even total solubility of acyl halides in the organic solvent is not required [25, 43, 54, 55]. Best results could be obtained using 0.1% wt/v TMC in hexanes and 2wt% MPD in distilled water [25, 27].

Roh et al. [55] studied the effect of changing concentration of TMC and MPD on the TFC performance. Their results indicate that the TMC concentration has a more remarkable effect on the in-situ polymerization (IP) film properties than the MPD concentration. Their experiments show that higher TMC concentration gives a clear increase in the IP film thickness and surface hydrophilicity while in the case of increasing MPD the increase in thickness is smaller and surface hydrophilicity decreases. On the other hand, water flux is strongly depending on the IP film thickness and surface hydrophilicity.

2.3. Thin Film Composite (TFC) Membrane

Polyamide composite membranes which are characterized by a thin film supported on a chemically different asymmetric porous material have become commercially successful for certain applications, especially for seawater desalination [23-30]. TFC membrane is an asymmetric membrane composed of three layers; a polyester support web, a microporous polysulfone layer and an ultra thin polyamide barrier layer [25-31]. TFC aromatic polyamide membranes with excellent performance (water flux and salt rejection) are prepared by interfacial polymerization with the addition of alcohols, ethers, sulphur-containing compounds, dimethyl sulfoxide and monohydric aromatic compounds as additives into the aqueous phase [47].

2.3.1. Support Material

A large number of support materials have been tested with certain degree of success. The most suitable support membranes for the aromatic RO TFC membranes are

those prepared from organic polymeric materials such as polysulfone, polyethersulfone [44], chlorinated polyvinyl chloride, polyvinyl butyral, polystyrene, cellulose esters, and other organic polymeric materials with millions of pores per square centimeter. The average pore sizes are allowed to range from 1 to around 1000 millimicrons (1 nanometre to about 1 micrometer). Pores larger than 1000 millimicrons are difficult to bridge over with the active thin barrier, which means that the polyamide film is not easy to be built while pores of one millimicron are not necessary for salt rejection [44, 54]. The most effective support material for the condensed ultrathin polyamide layer is the porous polysulfone substrate of pore sizes around 15 - 20 millimicrons [43, 53, 54]. Polysulfone is preferred for the preparation of TFC membranes because of the fact that polysulfone is relatively hydrophilic and can be easily soaked in the aqueous amine solution in the interfacial polymerization [29].

Kim and Kim [29] studied the effect of substrate materials on the TFC membrane performance. They used hydrophilic monomers such as acrylic acid, acrylonitrile, allylamine, ethylenediamine to hydrophilize support material made of polypropylene (PP) which is hydrophobic. Their results showed that there was a remarkable enhancement in the membrane performance after hydrolyzing the polypropylene substrate. Their experiments also enabled the PP substrate to be used in the preparation of TFC.

The porous support layer, when polysulphone (PS) is used, is made by the liquid-solid phase inversion technique as follows; a 15wt% solution of polysulfone Udel P-3500 in N, N-dimethylformamide is prepared and kept under vigorous stirring until

homogenous solution obtained [25, 27]. The solution is cast onto a very smooth glass plate with a polyester non-woven fabric using a special knife with specific size and dimension. After that the plate is immersed immediately and smoothly into a water bath (gelation bath) at room temperature. After 30 seconds the PS substrate is gelled into a white microporous polysulfone sheet and the top face (which is exposed to air) is used as a support surface for the TFC membrane [27, 56, 57].

2.3.2. Additives

Sometimes some additives can be added to the interfacial system to improve the interfacial polymerization reaction and the formation of the film in order to enhance the performance of TFC membranes. It is common practice to use combinations of additives to improve monomer solubility, diffusivity, or hydrolysis [50]. These additives can be added to the organic phase or the aqueous phase but most likely to the aqueous phase. Below are some of the remarkable additives which have been used in the TFC research a long time ago for many different purposes;

- 1- Hydrophilic water- soluble polymers or a polyhydric alcohol: can be added as small amounts to the amine solution to produce high flux RO membranes with good rejection [58].
- 2- Aprotic solvents: such as N,N-dimethylformamide (DMF) is added to the aqueous aromatic amine solution. It initially reacts with an acyl chloride to produce an amidinium chloride, which is not reactive toward aromatic amines. Following, the amidinium chloride hydrolyzes to produce a carboxylate group,

which restrains crosslinking and produces membrane with more negative charge and higher water flux [59].

- 3- Dodecylbenzenesulfonic acid: It is used as a surfactant to reduce solubility difference between the organic and aqueous phase in the polymerization system. It is always dissolved in the aqueous phase [57].
- 4- Sodium hydroxide, sodium tertiary phosphate, dimethyl piperazine, triethylamine (TEA), and other acylation catalysts to speedup the MPD–TMC reaction by removing hydrogen halides formed during amide bond formation. They are soluble in the aqueous phase [27, 50].
- 5- Dimethylsulfoxide: It is used as an additive in the aqueous phase to reduce the solubility difference between the organic and aqueous phase, increase the miscibility between the two phases, decrease the interfacial tension and facilitate the mass transfer of diamine molecules to the organic phase, which means that the diamine molecules can penetrate rapidly and deeply into the acid chloride layer, resulting in an increase in the rate of diffusion, in the polymerization area and in the surface roughness [47]. As a result, addition of the DMSO can improve membrane water flux by producing a thinner polyamide film. In fact, increasing water-organic miscibility can cause hydrolysis of the acid chloride, then reducing acid chloride reactivity and the degree of crosslinking [35,47].
- 6- Surfactant or organic acids: camphor sulfonic acid (CSA) can be added to the aqueous phase to enhance absorption of the amine solution in the support [60, 61].

Many attempts have been made to improve the TFC membrane performance through membrane modification or addition of different additives. Kuehne et al. increased TFC-RO flux up to 30-70% by soaking the freshly prepared TFC membranes with solutions containing various organic species, including glycerol, sodium lauryl sulfate, and the salt of triethylamine with camphorsulfonic acid [60]. More recently, Jeong et al. doubled the water flux of RO-TFC membranes without affecting the salt rejection using zeolite nanoparticles in preparing mixed matrix RO-TFC membranes [62]. Additionally, an aqueous solution composed of poly(vinyl alcohol), PVA, and a buffer solution was applied as a post treatment step during the preparation of the TFC membranes to improve TFC physical properties (improved abrasion resistance) and enhance flux stability [63, 64]. On the other hand, high flux TFC membrane at low pressure can be produced by using PVA-based amine compound having a side chain amino group as the aqueous phase monomer instead of the MPD [65].

2.3.3. Organic Solvent

Selecting the organic solvent is crucial because it controls, at least, the amine monomer solubility and diffusivity in the reaction region. In a recent study, both hexane and isopar solvent were used to prepare TFC membranes. The two solvents produced significantly different TFC membranes [66]. Reaction conditions, in particular temperature, affect the solvent properties such as, density, viscosity, and surface tension. Solvent surface tension governs the amine solubility and, as a result, the amine to acid chloride concentration ratio in the reaction area and the degree of polymerization [25, 26]. Also solvent surface tension controls the miscibility of the two liquid phases which might affect hydrolysis state of the acid chloride and amine moieties and the degree of

crosslinking. Many organic solvents were used for the preparation of TFC membranes including, hexane, heptane, cyclohexane, and a proprietary isoparaffin, known as Isopar G. Until now, the most common organic solvent is the hexane. Recently, Ghosh et al. found that the best TFC performance can be achieved by using high surface tension, and low viscosity solvents [50].

2.3.4. Post Treatment – Heat Curing

One of the most important steps to stabilize the polyamide thin film is the heat curing. Heat curing step is applied after the film formation in order to remove residual organic solvent from the film and to increase the degree of crosslinking by dehydration of amine and carboxylic acid residues [26, 31]. Heat curing tends to enhance salt rejection but with increasing the curing time or temperature, the porosity of the polyamide film is reduced by the high degree of crosslinking and this results in a huge decrease in water flux. Also high curing temperature or long curing times can damage the microporous skin layer of the polysulfone support membrane which can lead to reduce both water flux and salt rejection [50]. In general, curing temperatures ranging from 40 to 120°C are used [67].

2.4. FT-30 Membrane

Using interfacial polymerization technique, Cadotte found that aromatic diamines could react with triacyl halides to give membranes with exciting different reverse osmosis performance characteristics than membranes based on aliphatic diamines. Until Cadotte's invention, little attention was given to the area of aromatic amines in

membrane formation by interfacial polymerization. This was due to two factors. The first factor was the need to develop a chlorine resistant composition for TFC membrane preparation which preferred the use of secondary aliphatic amines such as piperazine. The second factor was the poor performance obtained on interfacially formed aromatic polyamides. A common formula for an interfacially formed aromatic polyamide composite membrane composed of a 2.0% aqueous solution of the aromatic diamine and a 0.1% nonaqueous solution of trimesoyl chloride [25, 27]. The chemistry of the reaction is illustrated in Figure 2.2.

FT-30 membranes, developed by Filmtec Corporation, were of commercial success for RO. In the FT-30, the thin film active layer is aromatic polyamide (PA) that is prepared via interfacial polymerization of m-phenylenediamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase [35, 55, 68]. The average thickness of the barrier layer in the FT-30 membrane was estimated to be 2000 Å and the membrane can withstand high pressure because of the polysulfone microporous support. The average thickness varies from 400 Å (valley) to 2600 Å (ridge top) [25, 27, 43]. FT-30 membranes commercially produced in spiral-wound gives 99.3 % salt rejection at 24 gfd flux in seawater desalination at 800 psi [25, 27]. Figure 2.3 shows a schematic cross-section of the FT-30 membrane. Table 2.1 summarizes separation data for FT-30 using different solutes in the feed.

Figure 2.2: Chemical structure of the FT-30 membrane.

Figure 2.3: Schematic structures of FT-30 membrane [47].

Table 2.1: Rejection of different solutes by FT-30 (operation conditions, 2000 ppm solute, 1.6 MPa, 25 °C, pH7) [17].

Solute	Molecular weight (g/mol)	Rejection (%)
Sodium chloride	58	99
Calcium chloride	111	99
Magnesium sulfate	120	>99
Copper sulfate	160	>99
Formaldehyde	30	35
Methanol	32	25
Ethanol	46	70
Isopropanol	60	90
Urea	60	70
Lactic acid (pH2)	90	94
Lactic acid (pH 5)	90	99
Sucrose	342	99

3. Membrane Fouling and Surface Modification

3.1. Membrane Fouling

Despite the high quality of the water produced by TFC-RO process, TFC membranes are susceptible to fouling [39, 40, 69]. Fouling, which is defined as the accumulation of substances on the membrane surface or within the membrane pore structure [39, 40, 70], always worsens the membrane performance, shortens its life [39], and reduces the flux and salt rejection [71]. In RO membrane desalination, fouling is caused by the interaction between the membrane surface and solute particles and depends strongly on membrane surface morphology [69, 71] and chemical properties [72]. RO fouling includes; salt precipitation (i.e., scaling), colloidal fouling, organic fouling, and biofouling [71-78].

Biofouling is considered as the most serious problem since biofouling can not be prevented using pretreatment [79, 80]. For microbial fouling the adhesion of bacteria to the reverse osmosis membrane is affected by the ionic strength of the feed solution and the nature of membrane surface, but not by pH of the solution [8, 21]. Subramani and Hoek [81] found that the higher the permeate flux, salt rejection, concentration polarization, membrane hydrophobicity, and membrane surface roughness the higher the microbial cell deposition rates will result. A new type of anti-fouling membranes was developed by introduction of TiO_2 nanoparticles on the TFC membranes. It was demonstrated that this method had the ability to prevent the microbial fouling by reducing the loss of RO permeability [74, 82, 83].

The rate of colloidal fouling can be controlled by a special and unique interplay between permeation drag and electric double layer repulsion [84], which means that colloidal fouling of RO membranes (including TFC aromatic polyamide membrane) involve strong and critical relation between physical and chemical interaction [71]. The three main scale forming components of seawater are calcium bicarbonate, magnesium salts and calcium sulphates [85]. For natural organic matter (NOM), there are many factors affecting the NOM fouling such as; NOM characteristics, membrane characteristics, hydrodynamic conditions and chemical compositions of the feed [84]. It was found that there is a strong relation between permeation drag and electrostatic repulsion since fast fouling occurs at high initial permeation rate even if the chemical conditions are not favorable for fouling (low ionic strength, high pH, and low concentration of calcium ion etc.) [84]. Thus, in order to solve the fouling problem it is important to understand the morphology of the membrane surface and the characteristics of the feed composition. To prepare a membrane with optimum performance, the membrane should possess physical and chemical properties which give the appropriate and best interactions between the membrane surface and the solute particles. The most important properties seem to be pore size distribution, surface morphology, appropriate electrostatic interactions and minimum interaction between solutes and membrane surface [73].

3.2. Methods to Reduce Fouling

Many routes were examined to mitigate fouling problem. The successful and most reliable operation of the RO system needs the application of best available methods to prevent fouling. Fouling can be controlled and reduced but not eliminated by:

- 1- Selection of the suitable membrane [16, 86], the change in membrane materials can reduce membrane fouling. Fouling with porous membrane (microfiltration (MF) and ultrafiltration (UF)) is generally more severe than the case in dense membranes (reverse osmosis (RO)). Also the use of hydrophilic membrane materials and negatively charged membranes can help in reducing fouling.
- 2- Pre-treatment of the feed solution: pretreatment is required to eliminate the unwanted contaminants in the seawater feed, which could cause membrane fouling. Common pretreatment includes chlorination, dechlorination, acid addition, coagulation, multi-media filtration, micron cartridge filtration, pH adjustment, and addition of complexing agent such as ethylenediamine-tetra acetic acid (EDTA) [2, 16]. Many factors determine the type of pretreatment needed such as, feed water characteristics, membrane type and configuration, and the quality of the produced water [2]. Different chemicals can be added to the seawater feed such as; sodium hypochlorite to prevent the microorganism growth, ferric chloride as a flocculant, sulfuric acid for the adjustment of pH and the control of scale formation, and sodium bisulfite for dechlorination [2, 85]. Addition of a strong chelating agent like EDTA to the feed solution is an effective way in reducing fouling by removing and reducing free and NOM complex calcium ions [86].

- 3- Cleaning [16], this technique can be achieved by different methods with certain limitations for each method. Those methods involve: Hydraulic cleaning which includes the back-flushing and it is only applicable to UF and MF membranes. Mechanical cleaning, electrical cleaning and chemical cleaning which are considered as the most important methods for fouling reduction. Chemical cleaning utilizes certain chemicals such as alkali (NaOH) and acids (citric acids).
- 4- Modification of membrane surface properties (changing surface – foulant affinity) (hydrophilicity and hydrophobicity, and charges) [47, 87, 88], membrane surface modification can be achieved through grafting, coating, and blending. Many hydrophilic monomers have been used for surface modification by grafting such as; poly(ethylene oxide), (PEO), and poly(ethylene glycol), (PEG). PEG, which is a hydrophilic, uncharged, highly water-soluble, and flexible long chain polymer, is well known for its exceptional ability to resist protein adsorption [89, 90]. This property is believed to be due to PEG hydrophilicity, large excluded volume, and unique coordination with surrounding water molecules in an aqueous medium [87, 91]. Because of its excellent ability to reduce hydrophobic interactions and to repel solutes like proteins, PEG was widely used in preparing fouling-resistant membranes [91, 92]. Thom et al. [88] used PEG derivative to produce hydrophilic PS-UF membranes with high resistance to bovine serum albumin (BSA) fouling. Kang et al. grafted PEG chains onto the surface of TFC-RO membranes to improve membranes resistance to fouling [87]. More details about membrane surface modification will be presented in the next section in the discussion of the major reasons for membrane fouling.

3.3. Effects of Membrane Surface Properties on Fouling

After a long period of academic and industrial research it is generally accepted that hydrophilicity, surface charge, and surface roughness are the major factors which affect the membrane fouling. In this literature review, the contribution of each factor to the membrane fouling will be thoroughly discussed.

3.3.1. Surface Charges

Membranes prepared by interfacial polymerization may possess fixed charges, either positive or negative, from the unreacted amine and acid groups [27]. It was documented in many papers that these charges play a primary role in the adhesion of foulants on the membrane surface [93-95]. If the acid chloride is hydrolyzed, the membrane will be negatively charged, which may be favorable since most of the naturally occurring materials are negatively charged [71] and precipitation of these materials on the surface of the membrane is prevented or reduced by electrostatic repulsion forces. When the solution is brought into contact with membrane surface, some charged components of the solution will be deposited on the membrane surface. These charges will also influence and disturb the distribution of ions at the membrane-solution interface. Co-ions that are repelled from the membrane surface and counter-ions that are attracted to the surface will result in the formation of electrical double layer at the membrane surface [94, 95]. The electrical potential between these two layers (the fixed charge layer on the membrane surface and the mobile charge layer of the solution) is called the zeta potential which gives the indication about the charges on the membrane surface [94]. The membrane

surface charges are characterized by zeta potential which is measured by streaming potential [84, 94, 95]. Zeta potential of the membrane surface is an important measurement factor for membrane fouling [71, 94]. There are, however, some drawbacks of using streaming potential to characterize surface charges. It was documented that the zeta potential measured by streaming potential was not always correct and did not always give the correct indication about the surface charges especially when the cross-flow device system is used [96]. Other techniques may be used instead of streaming potential like, sedimentation potential, electro-osmosis, and electrophoresis [94].

The surface charge is also affected by many factors. These factors include; pH, ionic strength, isoelectric point, the presence of divalent cations and anions, and the presence of cationic or anionic surfactants in the solution [71, 84, 94]. It is also suggested that the increase in salt concentration at the membrane surface has a great effect on reducing the membrane charge repulsion (Donnan repulsion) through the formation of the cake fouling layer [93]. Changing the pH of the aqueous diamine phase can also be used to control the surface charge during the in-situ polymerization. On the other hand, addition of multifunctional (often mixture of di-functional and tri-functional) amine or acid chloride is a common practice to introduce fixed charges to the thin polyamide layer [95]. To reduce fouling, several trials were made by introducing ionisable functional groups.

Attempts made by academic and industrial researchers to study the relation between the surface charges of the membrane and membrane fouling are summarized below.

Hong and Elimelech [84] studied the role of chemical and physical interactions in natural organic matter (NOM) in the presence of three samples of humic acids of different sources using streaming potential technique. Their results showed that fouling increased with increasing electrolyte (NaCl) concentration, decreasing solution pH, and the addition of divalent cations (Ca^{+2}). They explained the effect of divalent cations on fouling by the interaction between the carboxylic functional groups of the humic acid and divalent cations, which reduced the humic acid charges and the electrostatic repulsion between humic acid macromolecules.

Childress and Elimelech [94] studied the effect of solution chemistry on the surface charge of polymeric reverse osmosis membrane by streaming potential analyzer using various chemical compositions in a pH range of 2 to 9. They concluded that, in the presence of electrolytes (NaCl, CaCl_2 , Na_2SO_4 , and MgSO_4), all membranes were positively charged in the lower pH range, and were negatively charged in the higher pH range. Additionally, they found that the adsorption of humic acid and surfactant (anionic and cationic) had a strong effect on surface charges and this adsorption was enhanced by an increase in molecular weight of humic acid and addition of divalent cations to the solution. On the other hand, their results showed that divalent cations adsorbed more rapidly to the membrane surface than divalent anions.

3.3.2. Surface Hydrophilicity

It is generally accepted that fouling of polymeric membranes decreases with the increase in hydrophilicity of the polymeric materials. Many attempts have been made to increase membrane surface hydrophilicity by surface modification techniques, each one

having its own advantages and disadvantages. Membrane surface modification can be achieved through grafting, coating [97-100], and blending hydrophilic/hydrophobic surface modifying macromolecules, SMMs [101]. Addition of hydrophobic surface modifying macromolecules can reduce the fouling [102,103]. This clearly shows that as surface hydrophilicity or hydrophobicity is changed by adding SMMs, some other membrane properties, probably the surface charge also changes at the same time. It was also documented that acidic hydrolysis disrupted the chemical bonds, which resulted in producing more hydrophilic polymer and weakened the cross-linking (rigidity) of the polymer matrix [104].

Hydrophilization by wetting the membrane in water soluble solvent is one of the surface modification techniques; this method does not change the chemical structure but one of its disadvantages is that the water flux decreases with time because of the leaching of the hydrophilizing agent by water permeation [105].

Hydrophilization can also be achieved by treating the membrane surface with different materials including; acids, alcohols, and mixtures of acid, alcohol and water. Using a mixture of acid and alcohol in water for the surface treatment can improve the surface properties since acid and alcohol in water cause partial hydrolysis and skin modification, which produces a membrane with a higher flux and a higher rejection. It was suggested that the presence of hydrogen bonding on the membrane surface encourages the acid and water to react on these sites producing more charges [105,106].

Fluorination of membrane surface using hydrofluoric acid was used to modify the properties of thin film composite reverse osmosis membranes. This treatment increases the flux without any loss in ion rejection and this can be explained by partial fluorination along with surface etching. It was also claimed that this treatment method could be applied to other commercially available thin film composite membranes to achieve the same results [105,106]. It was documented that this treatment method did not affect the membrane life [106]. On the other hand, it was reported that decreasing the concentration of acids caused limited hydrolysis of the amide network leading to reduction of polymer chain length. The acid hydrolysis of the aromatic polyamide skin can, on the other hand, increase the number of the carboxylic and amidic groups on the membrane surface, which increases the hydrophilicity and also increases the salt rejection. Optimization of the acid concentration and the exposure time period is important to prevent the damage of the membrane polymer and to obtain the highest membrane flux and rejection [86].

Kulkarni et al. [105] hydrophilized a thin film composite (TFC) reverse osmosis membrane by using hydrophilizing agents of protic acid type (hydrofluoric acid, hydrochloric acid, sulphuric acid, phosphoric acid) for modifying the surface. They also characterized the surface by contact angle measurement. Their results show an increase in hydrophilicity by the smaller value of contact angle. When they exposed HR98PP and HR95PP membrane to various concentrations of some of the above mentioned acids, their results showed that there was a noticeable and large increase in water flux with no loss in ion rejection when the membrane was treated by ethanol, 2-propanol, hydrofluoric acid and hydrochloric acid. They also concluded that exposure of the membrane to mild

solvents (ethanol, 2-propanol) or to a mixture of acid and ethanol caused an increase in flux with no loss in ion rejection. They explained these results based on the Brown Theory of latex formation, which suggests that the defects in the membranes are removed resulting in an increase of rejection. Elimination of the defects in addition to removal of smaller molecular portions because of dissolution by alcohols makes the membrane smoother and thinner.

Mukherjee et al. [106] chemically modified SW30HR thin film composite reverse osmosis membrane by hydrofluoric and fluosilicic acid. Their results showed a large increase in flux. Also they studied the surface of the chemically treated membrane by X-ray photoelectron spectroscopy. They found that there were great morphological and chemical changes in the active skin layer compared to that of the untreated (fresh) membrane.

Mukherjee et al. [86] studied the effect of chemical treatment of the CPA2 and SWC1 aromatic polyamide thin film composite reverse osmosis membranes using hydrofluoric and fluosilicic acids and alcohol (isopropanol). Their results showed the water flux and rejection increased significantly.

Sforca et al. [107] prepared a composite nanofiltration membrane by polycondensation reaction between trimesoylchloride and different amines inside a dense layer of poly (ethylene oxide-b-amide). They found that using amines containing ethylene glycol blocks enhanced the performance of membrane and highly improved membrane water permeability by giving more hydrophilic membrane. They also found that, as the

amine concentration increased, the molecular weight cut-off and water permeability were improved.

Belfer et al. [40] used another surface modification technique by radical grafting of two monomers, methacrylic acid and polyethylene glycolmethacrylate onto a commercial composite polyamide reverse osmosis membrane. For the initiation they used a redox system while the grafting was done in an aqueous medium. They characterized the modified surface by ATR-FTIR, ESCA, and streaming potential. Their results showed that the modified membranes had no negative effects on their transport properties. On the other hand, they found that the grafted polymers possessed charged and hydrophilic groups and the modification reaction should be optimized by adjusting the reaction condition and reaction time.

Wu et al. [37] modified the surface of an aromatic polyamide reverse osmosis composite membrane using oxygen and argon plasma treatment. They found that the water permeability of the oxygen plasma treated membrane was enhanced; they explained that by the introducing of carboxylic group hydrophilicity of the treated membrane was increased. This was confirmed by the contact angle measurement. On the other hand, they found that for the argon plasma treated membranes, cross-linking took place at the nitrogen sites on the membrane surface, which enhanced the chlorine resistance of the membrane. The hydrophilicity increased only slightly.

3.3.3. Surface Roughness

Surface roughness, is another important factor that affects membrane fouling. In fact, there is a strong relationship between membrane performance (flux, rejection, permeability), and surface structure and morphology [108, 109]. The effect of surface roughness has not been fully understood. Hirose et al. [108] and Kwak et al. [109, 110] found that the rougher the surface of the PA-TFC membranes the larger the skin area, and the higher the water flux of the membrane. Preparation of the aromatic PA in the presence of alcohols, ethers, sulfur-containing compounds, and monohydric aromatic compounds and more specifically dimethyl sulfoxide (DMSO) in the aqueous phase can produce membranes with excellent water flux and reasonable salt rejection. These additives, whose polarity is intermediate between hydrocarbon and water, works as a surfactant to reduce the interfacial energy between the two phases, which result in an increase in the surface roughness and the surface area and consequently the permeation rate [35, 47, 58, 111]. On the other hand, addition of electrolytes will increase the interfacial energy, which will result in a decrease in the surface area and roughness. This would contribute to the reduction of fouling. Elimelech et al. found that commercial TFC membrane was fouled faster than cellulose acetate membrane because of the greater surface roughness of the TFC membrane [112]. The surface roughness and the surface area are mainly affected by the presence or absence of cross-linking and the free amide groups not shared in the formation of the hydrogen bonding, which affects water permeability.

Vrijenhoek et al. [90] investigated four aromatic polyamide thin-film composite membranes which were characterized for physical surface morphology, surface chemical properties and surface zeta potential. They also characterized the surface using atomic force microscope (AFM). Their results showed that the colloidal fouling of the reverse osmosis and nanofiltration membrane was strongly correlated to the membrane surface roughness, neglectful of the physical and chemical operating conditions. Their AFM images showed that initially more particles were deposited on the rough membranes than the smoother one and these particles accumulated in the valleys of the rough surface. They found also that the smoothest membrane had the lowest salt rejection, which means that the surface roughness is important for enhancing the membrane performance. This also means that surface roughness should be optimized by using the suitable membrane and the appropriate additives to give the lowest fouling and the highest membrane performance.

Kwak et al. [109] concluded that the surface roughness and the surface area of the aromatic polyamide TFC membrane are affected by the presence or absence of the cross-linking and the free amide groups which are not shared in the formation of hydrogen bonding. They found also that the surface roughness and the surface area were strongly correlated to the water flux of the membrane, which means that the rougher the surface and the larger the skin area, the higher the water flux membrane will result. The absence of cross-links and hydrogen bonding gives rougher surface with a larger area and as a result higher flux.

Hirose et al. [108] studied the relationship between the skin layers of cross-linked aromatic polyamide composite reverse osmosis membranes and their reverse osmosis performance using SEM and AFM techniques. They found that there was a strong relationship (approximately linear relationship) between surface roughness and membrane performance (flux); i.e. reverse osmosis membranes whose surface roughness values are high produce high fluxes. This was explained by the idea that the unevenness of the skin layers acts to enlarge the surface area.

Kwak et al. [110] prepared five novel TFC membranes by interfacial polymerization of an aqueous solution of homologous series of bisphenols, which have methyl or halogen substitutions in the phenyl rings of bisphenol, with an organic solution of trimesoyl chloride (TMC) on the polysulphone support. Their results showed that the methyl substitutions in bisphenol phenyl rings enhanced the water flux of the reverse osmosis membranes and decreased membrane rejection. The membrane surface morphology, a product of methyl substitution, has irregular nodular structure with small size and smooth surface. On the other hand, the halogen substitutions were found to enhance rejection of the resulting reverse osmosis membranes of characteristically rough, larger surface morphology, with uniformly distributed and well-defined nodule agglomerates.

A lot of efforts to reduce fouling in RO system have focused on the feed water pretreatment, such as addition of acid and antiscalants to the feed. Even with the success of these methods, membrane fouling remains as a great obstacle. It seems that

pretreatment procedures alone are not helpful; therefore, regular cleaning is required. Meanwhile, surface modification was considered as the most interesting way to prepare fouling-resistant membranes by changing surface-foulant affinity (hydrophilicity or hydrophobicity) or surface morphology [101].

4. Project Objective

Although there are a large variety of polymers that can be used in membrane preparation, it is still impossible to gather all the desired characteristics needed for the optimum performance using single polymer [16, 17, 22]. Since both the surface chemistry and morphology of the membrane play a crucial role in determining the performance of the membrane, there seems a scientific and technological approach behind the control of membrane surface properties. This approach is based on the idea that membrane performance can be enhanced through modification of the membrane surface [16, 17].

Introduction of an active additive is considered as the most interesting way and the least common approach for surface modification. This method is based on the fundamental concept that those additives can move toward the top film surface during membrane formation and alter membrane surface chemistry while keeping bulk properties unchanged [50, 51]. Blending is a conventional technique used for membrane surface modification, and recently much attention has been given to utilize this technique with hydrophilic/hydrophobic SMMs blended with the base polymer for membrane surface modification [45, 52-55]. For example, Rana et al. used hydrophilic SMM in producing hydrophilic poly(ether sulfone)-ultrafiltration (UF) membranes with high fouling resistance [52].

Based on the extensive analysis above, a novel method is proposed to modify TFC-RO membrane surface. The idea is to incorporate the hydrophilic SMMs (LSMMs) with

PEG end groups to the active polyamide layer in order to render the TFC membrane surface more hydrophilic. In this way, TFC membranes of high fouling resistance can be prepared. The objectives of this research are to:

1. Establish the method to incorporate LSMM to the TFC membrane.
2. Test the performance of the prepared membranes.
3. Characterize the surface of these membranes.

Figure 4.1 illustrates the concept of the membrane surface modification.

Figure 4.1: Schematic representation of TFC surface modification using hydrophilic SMM (LSMM).

5. Experimental Work

5.1. Materials

All chemicals used in this work are listed in the Table 5.1. The chemicals, 4,4'-methylene bis(phenyl isocyanate) (4,4'-diphenylmethane diisocyanate, MDI), 1,3,5-benzenetricarbonyl trichloride (trimesoyl chloride, TMC), 1,4-phenylenediamine (p-phenylenediamine, PPD), 1,3-phenylenediamine (m-phenylenediamine, MPD), were used without further purification. Commercial UF polysulfone (PS) membranes of molecular weight cut-off (MWCO) 500 kD used as the support membrane were obtained from the TriSep Corporation, Goleta, CA, USA.

5.2. Synthesis of cLSMM, iLSMM and TFC Membrane

Preparation

The conventional hydrophilic surface modifying macromolecule (cLSMM), end-capped with poly(ethylene glycol), PEG, was synthesized using a two-step solution polymerization method. The initial step involved the reaction of MDI with poly(propylene glycol), PPG, in a common solvent of DMAc. This mixture formed a urethane prepolymer solution. The prepolymer is a segment-blocked urethane oligomer, poly(4,4'-diphenylenemethylene propylene-urethane) having both ends capped with isocyanate. The reaction was then terminated by the addition of PEG resulting in a solution of hydrophilic surface modifying macromolecule (cLSMM). The chemical structure of the cLSMM is presented in Figure 5. 1.

Table 5.1: The materials used in this work.

Material description	CAS number	Source
Deuterated N,N-dimethylformamide (DMF-d ₇ 99.5 atom % D)	4472-41-7	CDN Isotopes, Point-Claire, PQ, Canada
1,3,5-Benzenetricarbonyl trichloride (TMC)	4422-95-1	Sigma-Aldrich, Inc., St. Louis, MO, USA
p-Phenylenediamine (PPD)	106-50-3	Sigma-Aldrich, Inc., St. Louis, MO, USA
1,3-Phenylenediamine (MPD, Flakes, 99+%)	108-45-2	Sigma-Aldrich, Inc., St. Louis, MO, USA
Octyl acetate, 99+%	112-14-1	Sigma-Aldrich, Inc., St. Louis, MO, USA
n-Propyl acetate	109-60-4	BDH Limited, Poole, England
Hexyl acetate, 99+%	142-92-7	Sigma-Aldrich, Inc., St. Louis, MO, USA
Nonyl acetate, 97+%, FCC	143-13-5	SAFC Supply Solutions, St. Louis, MO, USA
Heptyl acetate, 98+%	112-06-1	SAFC Supply Solutions, St. Louis, MO, USA
Cyclohexane, 99.9+%	110-82-7	Aldrich Chemicals Co, Inc., Milwaukee, WI, USA
n-Hexane, > +99%	110-54-3	Sigma-Aldrich, Inc., St. Louis, MO, USA
N,N-Dimethylacetamide (DMAc, anhydrous 99.8%)	127-19-5	Aldrich Chemical Company, Inc., Milwaukee, WI, USA
4,4'-Methylene bis(phenyl isocyanate) (MDI, 98%)	101-68-8	Sigma-Aldrich, Inc., St. Louis, MO, USA
Poly(ethylene glycol) (PEG, average mol. wt. 200, and 1000 Dalton)	25322-68-3	Sigma Chemical Company, St. Louis, MO, USA
Poly(propylene glycol) (PPG, typical M _n 3500 Dalton)	25322-69-4	Aldrich Chemical Company Inc., Milwaukee, WI, USA

Figure 5.1: Chemical structures of the polymer materials.

To eliminate the effects of moisture, the glass apparatus used was dried at 100°C, and the prepolymerization reaction and end capping steps were performed in a controlled atmosphere of purified nitrogen inside the reaction vessel. The initial reaction step was: 0.02 moles (70 gm) of degassed PPG of average molecular weight 3500 Dalton in 100 mL of degassed DMAc was added drop-wise to 0.03 moles (7.5 gm) of MDI in 50 mL of degassed DMAc in a 1L Pyrex round bottom flask with a stirrer. The temperature was controlled at 48-50°C. PPG and MDI were allowed to react for 3 hrs. Then 0.02 moles (20 gm of PEG of average molecular weight 1000 Dalton) dissolved in 50 mL of degassed DMAc was added drop-wise. The molar mixing ratio of the chemicals MDI:PPG: PEG is 3:2:2. The solution was left under stirring for 24 hrs at 48-50°C, resulting in a solution of cLSMM. The cLSMM solution was added drop-wise into a 4L beaker filled with distilled water under vigorous stirring to precipitate the polymer. When separated from the solvent and water the cLSMM was elastic. The material was kept immersed in distilled water for 24 hrs under stirring in order to leach out residual solvent. They were then placed in a glass beaker and dried in an air circulation oven at 50°C for 5 days until a constant weight of approximately 64.8 gm was obtained.

The thin-film-composite (TFC) membrane preparation technique is based on interfacial polymerization between two monomers, di-amine (2 wt %, MPD or PPD) and tri-acid chloride (0.2 wt% TMC), dissolved in water and in hydrocarbon or ester solvent, respectively. The schematic diagram of TFC membrane formation is presented in Figure 5.2. Three sets of experiments were made for membrane preparation: the first set using

MPD, the second set using PPD, and the third set using MPD. Table 5.2 summarizes the three sets.

Figure 5.2: Schematic illustration of TFC membrane formation.

In the first set, TFC membranes were formed by dipping the PS support in an aqueous MPD solution for approximately 2 hrs. The saturated membrane was drained and all the excess di-amine solution was removed by holding the membrane in a vertical position for around 3 minutes. The saturated membrane was then immersed in the organic solution of TMC, with or without cLSMM, for around 2 minutes, which resulted in the formation of a thin film of polyamide (PA), hereafter called mPA, since it is based on MPD, on top of the PS support. Then, the resulting composite membranes were heat-cured at 90°C for around 3 minutes. The membranes were kept under ambient temperature and after 24 hrs they were washed with distilled water and finally stored in fresh distilled water at ambient temperature.

Table 5.2: Summary of the three membrane preparation sets.

Set #	Monomers in aqueous phase ^a	Monomers in the organic phase ^b	Organic Solvent	Adding cLSMM to organic phase	Synthesis of iLSMM in organic phase
1	MPD	TMC	n-Propyl Acetate	NO	NO
			Octyl Acetate	NO	NO
			n- Hexane	NO	NO
			Cyclohexane	Yes	NO
2	PPD	TMC	n-Propyl Acetate	NO	NO
			Hexyl Acetate	NO	NO
			Octyl Acetate	NO	NO
			Nonyl Acetate	NO	NO
			n- Hexane	NO	NO
			Cyclohexane	NO	NO
3	MPD	TMC, PEG, MDI	Cyclohexane	NO	Yes

^a monomers for in-situ polymerization

^b TMC is monomer for in-situ polymerization. PEG and MDI are monomers for the synthesis of iLSMM.

In the second set, TFC membranes were formed by the same procedure as the first set except that PPD was used instead of MPD, and that the saturated membrane was then immersed in the organic solution of TMC, without cLSMM, for 2 minutes. The thin PA film formed on top of the PS support is hereafter called pPA since it is based on PPD. The post treatment and the storage of the resulting membranes were the same as the first set. In both the first and second sets, n-propyl acetate, n-hexyl acetate, n-octyl acetate, n-nonyl acetate, hexane and cyclohexane were tested as solvents for the TMC.

In the third set of TFC membrane formation, MDI and PEG (di-isocyanate, MDI, and di-ol, PEG) were added to the organic hydrocarbon solvent, cyclohexane, as monomers to let the condensation polymerization (LSMM formation) reaction take place in the organic phase parallel to the in-situ polymerization (for thin film formation) that was taking place also in the organic phase. The molar ratio of reagents MDI: PEG (average molecular weight 200 Dalton) was 1:2. The chemical name of the iLSMM is poly(4, 4'-diphenylenemethylene ethylene-urethane) with both ends capped by PEG (Figure 5.1). The value of the n (4.14) was calculated from the average molecular weight of PEG.

The membranes so fabricated are coded as PS-a-b-w, where PS indicates that the support membrane is polysulfone membrane, "a" indicates whether the in-situ polymerized thin layer is made of mPA or pPA, "b" indicates whether the LSMM is cLSMM or iLSMM, and "w" indicates the concentration of c(i)LSMM in the organic phase. The concentration of cLSMM is defined as the wt/vol percent of cLSMM polymer in the organic solvent, while the concentration of iLSMM is defined as wt/vol % of (MDI + PEG) in the solvent. Thus, membrane code PS means polysulfone support membrane, PS-pPA means polysulfone support membrane coated with a thin film of pPA without any LSMM, and PS-mPA-cLSMM-0.25 means that 0.25 wt% of cLSMM was added to the organic phase.

5.3. Characterization of cLSMM

A sample for NMR analysis was prepared by dissolving as much polymer as possible in DMF-d₇. All NMR data were collected on a Bruker AVANCE 300 NMR

spectrometer. The ^1H NMR spectra were acquired under quantitative conditions with 16 scans using a 30° pulse, and a 3.6 sec interpulse sequence. The proton decoupled ^{13}C NMR spectra were collected using 10240 scans, a 30° pulse, a 1 sec recycle delay and a 1 sec acquisition time. The ^{13}C DEPT 135 spectrum was collected using 5120 scans, a 2 sec recycle delay and a 1 sec acquisition time. A ^1H - ^{13}C heteronuclear single quantum coherence (HSQC) spectrum was collected with 16 scans for each of 256 increments with a 170 ppm ^{13}C spectral window. The recycle delay was 1 sec. The acquisition time was 0.175 sec. The data were treated with a shifted sine squared weighting function prior to Fourier transform.

Average molecular weights (weight average molecular weight, M_w , and number average molecular weight, M_n) and polydispersity index (PDI, M_w/M_n) were measured by gel permeation chromatography (GPC) of Waters Associates, Milford, MA. The system equipped with three Waters styragel-HR packed columns. Waters 600 Fluid Unit, Waters 600 Controller, and Waters 410 refractive index (RI) detector. Tetrahydrofuran (THF) was used as the mobile phase. The polymer molecular weights were calculated using the universal calibration curve.

The glass transition temperature (T_g) was examined by differential scanning calorimeter (DSC) equipped with universal analysis 2000 program (DSC Q1000, TA Instruments, New Castle, DE). About 10 mg of polymer was crimped into aluminum pan. The polymers were annealed at about 75°C for 10 min and then quenched to -50°C , and

scanned at a heating rate of 10 °C/min. The T_g value was recorded of the corresponding heat capacity transition.

5.4. Membrane Characterization

The contact angle (CA°) of the membrane surface was measured using a VCA Optima Surface Analysis System (AST Products, Inc., Billerica, MA). Sample coupons with an area of about 5 cm×1.5 cm were prepared by cutting pieces at random locations within the membrane sheet. The skin layer surface of membrane was placed on a glass plate, and fixed with a tape. Then, a drop of distilled water (2 μ L) was placed on the sample surface using a micro syringe (Hamilton Company, Reno, NV). The CA° was measured within a 30 sec period after the water drop was placed. The CA° s were measured both right and left sides of the drop at five different spots on each membrane sample coupon and the values averaged.

Fourier transform infrared (FTIR) spectroscopy was used to observe the presence of functional groups of the membrane. The FTIR spectrometer (Varian 1000, Scimitar series, Varian Inc., Palo Alto, CA, USA) equipped with diamond w/ZnSe lens single reflection attenuated total reflection (ATR) plate. An IR source at 45° incident angle was employed, and the skin layer of the membrane surface samples were mounted with facing the crystal surface. The spectra were measured in transmittance mode over a wave number range of 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1} .

The morphology of the membrane was investigated using scanning electron microscopy (SEM) of a model JSM-6400 JEOL (Japan Electron Optics Limited, Japan).

Specimen for the SEM of cross-section measurement was prepared by freezing the membrane sample in liquid nitrogen, and cutting it using a sharp scissor. Fresh cross-sectional cryogenic cut pieces and skin-layer surface were mounted in chair-shaped sample holders for the SEM with double-sided tape; then, they were coated under vacuum with a thin layer (60% gold and 40% palladium) in a Hummer VII sputting system (Anatech, Springfield, VA).

An atomic force microscope, AFM, (Nanosurf AG, Grammetstrasse, Liestal, Switzerland) was used for characterization of membranes. A static force operating (contact mode) AFM in air was used. The average surface roughness (R_a) in an area of $1.008 \times 10^{-12} \text{ m}^2$ was obtained for the skin layer of the membrane surface from the software (Nanosurf® easyScan 2, version 1.3) calculation.

5.5. Reverse Osmosis Experiment

The reverse osmosis (RO) experiments were conducted at ambient temperature ($25 \pm 1^\circ\text{C}$) using a laboratory-scale system consisting of a reservoir, a pump, a pressure regulator, and six small RO cells connected in series. The cross-flow cells house membrane coupons with an effective area of about 13.2 cm^2 . The feed flow rate was $36 \text{ L}\cdot\text{hr}^{-1}$. Both the final retentate and all permeates are re-circulated to the reservoir to maintain a uniform feed concentration. The schematic diagram of the RO set-up is shown in Figure 5.3. The details of the design of the cell and description of the apparatus of RO experiments are given elsewhere [15]. All the experiments were conducted using an operating pressure of 800 psig. Each membrane was pre-compressed by filtering pure

water at 1000 psig for 8 hrs and then for 4 to 5 hrs at 800 psig. Pure water permeation (PWP) rates were measured at 800 psig after the pressurization. The sodium chloride concentration in the feed solution was 3.5 wt%. The concentrations of the feed and the permeate solution were determined via a conductivity meter (model CON 110, Oakton Instruments, Vernon Hills, IL, USA).

Figure 5.3: Schematic illustration of the RO setup.

6. Results and Discussion

6.1. Characterization of cLSMM

The ^1H , ^{13}C , and the HSQC spectrum of cLSMM are shown in Figure 6.1.a, b, and c, respectively. The characteristic peaks of the ^1H and ^{13}C -NMR based on ^1H , ^{13}C , and ^{13}C DEPT spectrum are listed in Table 6.1.a and b. The presence of the hydroxyl group of the cLSMM sample was confirmed by 2D heteronuclear single quantum coherence (HSQC) spectra in DMF- d_7 solvent as peaks were observed at about 4.7 and 5.1 ppm in the ^1H spectra (Fig. 6.1.a) but no signal appeared in the HSQC spectrum (Fig. 6.1.c).

Figure 6.1.a: ^1H -NMR spectrum of cLSMM.

Figure 6.1.b: ^{13}C -NMR spectrum of cLSMM.

Figure 6.1.c: HSQC -NMR spectrum of cLSMM.

The chemical name of the cLSMM is poly(4, 4'-diphenylenemethylene propylene-urethane)-co-poly(4,4'-diphenylenemethylene ethylene-urethane) with both ends capped by PEG. The values of the n (60.03) and q (22.32) were calculated from the average molecular weight of PPG and of PEG. The values of m and p were calculated using the ^1H NMR and M_w of the cLSMM. The ratio between the integrated peak area of the signals corresponding to all hydrogen (AH_T) and the peak area of the methyl signal (AH_M) is expressed as

$$\frac{\sum AH_T}{AH_M} = \frac{6nm + 12m + 12p + 8q + 4pq + 14}{3nm}$$

The right hand side of the equation is formulated from chemical structure of cLSMM (Figure 5.1.). The left hand side of the equation is equal to 2564.57 / 1000 from ¹H NMR spectra (Figure 6.1.a). Together with the weight average molecular weight (M_w) data given below, m and p values were calculated and the results were 3.61 and 17.77, respectively.

The molecular weights characterization data of the cLSMM is M_n = 1.97x10⁴, M_w = 3.84 x10⁴, PDI = 1.95. The T_g values at the onset and the midpoint of cLSMM are 22.85 °C and 29.59 °C, respectively. The molecular weight data indicates that the polymer is well homogeneous while T_g data indicates that the polymer is amorphous and rubbery in nature.

Table 6.1.a: The assignments of ^1H NMR characteristic peaks of cLSMM.

Assignment	Chemical shift (ppm)
CH_3 of PPG	1.1 - 1.6
CH_2 between the phenyl groups of MDI	3.7
CH_2 (PEG, PPG)	3.8
CH (PPG)	3.9
OH (PEG) end groups	4.7, 5.1
Aromatic hydrogen (MDI)	7.3 - 7.7
Urethane NH	8.8, 9.6, 9.8

2.9 - 3.1 ppm peaks due to CH_3 of DMF; 8.2 ppm peak due to CH of DMF

Table 6.1.b: The assignments of ^{13}C NMR characteristic peaks of cLSMM.

Assignment	Chemical shift (ppm)
CH_3 (PPG)	17.2 - 18.8
CH_2 between the phenyl groups of MDI	61.5
CH_2 (PEG)	70.8
CH_2 (PPG)	73.3 - 73.5
CH (PPG)	75.5 - 75.7
Aromatic C (MDI)	118.9, 129.4
Quaternary aromatic C	136.9 - 138.7
Urethane C	153.5, 153.9, 154.2

30.1, 35.2 ppm peaks due to CD_3 of DMF; 162 - 165 ppm peaks due to CD of DMF

6.2. Membrane Characterization

The CA° s of the membranes are shown in Table 6.2. TFC membranes with and without addition of LSMM are lower in CA° values, and thus are more hydrophilic, than the control PS membrane. According to the table, presence of the thin polyamide layer decreases the CA° (CA° for PS is 52.8° and for PS-mPA is 31.5°). Upon addition of LSMMS, CA° further decreases (CA° for PS-mPA-cLSMM-0.25 is 19.8° and for PS-mPA-iLSMM-0.25 is 25.8°). However, increasing the amount of LSMMS to 1wt%

increases the CA° value (CA° for PS-mPA-cLSMM-1.0 is 29.7° and for PS-mPA-iLSMM-1.0 is 43.9°), indicating a slight increase in hydrophobicity.

Table 6.2: The contact angle and surface roughness data of the skin layer surface membranes.

Membrane	CA (°)	R_a (nm)
PS	52.8 ± 1.9	2.44
PS-mPA	31.5 ± 3.0	9.99
PS-mPA-cLSMM-0.25	19.8 ± 7.3	62.88
PS-mPA-cLSMM-1.00	29.7 ± 4.1	27.97
PS-mPA-iLSMM-0.25	25.8 ± 1.2	55.28
PS-mPA-iLSMM-1.00	43.9 ± 7.3	8.75

The purpose of FTIR spectroscopy is to examine the presence of functional groups present in the skin layer surface of membrane samples. The FTIR spectra of PS, PS-mPA, PS-mPA-cLSMM-0.25, PS-mPA-cLSMM-1.00, PS-mPA-iLSMM-0.25, and PS-mPA-iLSMM-1.00 membranes are shown in Figure 6.2. The membranes chosen for the FTIR study are presented in Table 6.3. The spectra of the base PS membrane shows the peak at 1241.33, and 1150.63 cm⁻¹, assigned to C—O—C and O=S=O, respectively. On the other hand, no PS peaks appeared in the spectrum of the PS-mPA membrane. Instead, peaks appeared at ~3300, 1659.54 and 1609.86 cm⁻¹, which can be assigned to O—H (and N—H), C=O and N—H of mPA. These results confirm the full coverage of the surface by mPA. The presence of carboxylic acid was confirmed by the 1449.86 cm⁻¹ peak (see

Table 3 for PS-mPA). The presence of cLSMM in the PS-mPA-cLSMM-0.25 and PS-mPA-cLSMM-1.0 membranes was also confirmed by the peaks at 2971.1, and 1103.86 cm^{-1} , which were assigned to C—H of PPG, and C—C—O of PEG and PPG, respectively. Moreover, the intensity of the peak at 2971.10 cm^{-1} increased from 19.51 to 52.43 when the concentration of cSMM in the organic phase was increased from 0.25 wt% to 1.0 wt%. However, the less than 4-fold increase in the peak intensity indicates that not all the added cLSMM was incorporated into the mPA skin. It should also be noted that the peak intensity does not necessarily indicates the amount of the functional group. Similarly, the presence of iLSMM was confirmed by the peaks at 2874.13 and 1103.69 cm^{-1} , which are assigned to C—H of PEG, and C—C—O of PEG, respectively. FTIR data support the presence of the hydrophilic amide, hydroxy, and carboxylic acid groups at the membrane surface containing cLSMM and iLSMM which is confirmed by the previous CA data.

Figure 6.2: FTIR spectra of the chosen membranes.

Table 6.3: The significant peak assignment for FTIR spectra.

FTIR peaks (cm^{-1})	Peak assignments
PS membrane	
1585.55, 1487.72	C—C (s) [†] of aromatic
1324.15	C—H of >C(CH ₃)
1294.55	O=S=O (s) symmetric
1241.33	C—O—C (s)
1150.63, 1105.83	O=S=O (s) asymmetric
PS-mPA membrane	
~ 3300	O—H (s) and N—H (s)
1659.54	C=O (b) [‡] of amide
1609.86	N—H (s) of amide
1537.17	C—N (s) of amide
1449.86	C=O (s), O—H (b) of carboxylic acid
PS-mPA-cLSMM membrane (x = 0.25 and 1.00)	
3321.49	O—H (s) and N—H (s)
2971.10	C—H (s) of methyl (PPG)
2868.96	C—H (s) of methylene (PEG, PPG)
1665.10	C=O (b) of amide
1609.86	N—H (s) of amide
1536.65	C—N (s) of amide
1445.29	C=O (s), O—H (b) of carboxylic acid
1103.86	C—C—O of PEG, PPG
PS-mPA-iLSMM membrane (x = 0.25 and 1.00)	
3300.15	O—H (s) and N—H (s)
2874.13	C—H (s) of methylene (PEG)
1722.02	C—O of carboxylic acid
1664.17	C=O (b) of amide
1608.11	N—H (s) of amide
1536.27	C—N (s) of amide
1485.47	C=O (s), O—H (b) of carboxylic acid
1103.69	C—C—O of PEG

[†]s for stretching, [‡]b for bending

The SEM micrographs of the cross-section and the top skin layer of the membranes are presented in Figures 6.3 to 6.5. The cross-sectional images of the PS membrane and the PS-mPA membrane show that the top surface of the former is very smooth (Figs. 6.3.a and 6.4.a) whereas the top thin film of the composite PS-mPA membrane is rough (Figs. 6.3.b and 6.4.b). Upon addition of LSMM, both PS-mPA-cLSMM and PA-mPA-iLSMM membranes showed a rough surface when the concentration of LSMM in the solvent phase was 0.25 wt% (Figs. 6.4.c and 6.4.e), while the roughness decreased considerably when the concentration of LSMM was increased to 1 wt% (Figs. 6.4.d and 6.4.f). Similar images were obtained when the pictures were magnified 10 times at the TFC location of cross-sectional side (Fig. 6.5). These pictures indicate that the addition of lower concentration (0.25 wt %) of both LSMMs tends to increase the roughness of the thin mPA film. However, the addition of higher concentration (1 wt %) of both LSMMs decreases the surface roughness of the membrane surface. It can be postulated that two phases, one LSMM and the other polyamide, are formed when a small amount of LSMM is added, leading to an increase in surface roughness. However, when a larger amount of LSMM is added the surface is covered by LSMM with a single phase formation, which results in a smoother surface.

The R_a value of the membranes is also cited in the Table 6.2. The R_a value increases from the control PS membrane to the composite PS-mPA membrane due to the thin-film-layer formation over the PS membrane. With addition of lower concentration (0.25 wt%) of LSMM, the R_a increases significantly for both PS-mPA-cLSMM and PS-mPA-iLSMM membranes. With further addition (1.0 wt %) of LSMM, the R_a value tends to decrease. The AFM observation is closely related to the SEM pictures.

Figure 6.3: SEM photographs (100 μm length scale) of the cross section at surface of the membranes: (A) PS; (B) PS-mPA.

Figure 6.4: SEM photographs (1 μm length scale and 25,000 magnifications) of the skin layer surface of the membranes: (A) PS; (B) PS-mPA; (C) PS-mPA-cLSMM-0.25; (D) PS-mPA-cLSMM-1.00; (E) PS-mPA-iLSMM-0.25; (F) PS-mPA-iLSMM-1.00.

Figure 6.5: SEM photographs (100 nm length scale and 40,000 magnifications) of the cross section surface of the membranes: (A) PS; (B) PS-mPA; (C) PS-mPA-cLSMM-0.25; (D) PS-mPA-cLSMM-1.00; (E) PS-mPA-iLSMM-0.25; (F) PS-mPA-iLSMM-1.00.

6.3. RO Membrane Performance

The effect of organic solvent used for the in-situ polymerization on the RO performance was studied for the LSMM-free membranes PS-mPA and PS-pPA as shown in Table 6.4. From the table, it is quite obvious that PS-mPA (based on MPD) is superior to PS-pPA (based on PPD) in terms of salt rejection for all solvents used. This agrees with the common practice of using MPD, rather than PPD, in the making of RO membranes by most researchers in this field [2, 17]. It should be noted that it was extremely difficult to fabricate PS-mPA membranes when esters were used as solvents for the organic phase. Often, white particles were visually noticeable on the membrane surface upon dipping the membrane into the organic phase, indicating a non-uniform PA layer. Nevertheless, TFC membranes could be obtained for n-propyl acetate and octyl-acetate and RO data are given for those membranes in Table 6.4. Membranes could be readily fabricated, on the other hand, with hexane and cyclohexane and the separation data are in the tight nano-filtration (NF) range. In the case of PS-pPA, on the other hand, the separation was poor for most membranes when they were fabricated using esters for the organic phase. In some cases, the top thin film seemed visually detached from the substrate PS membrane. Again, membranes of relatively good performance were obtainable when hexane or cyclohexane was used for the organic phase, although the separation was not as high as PS-mPA membranes.

Table 6.4: RO performance of various solvents of two different types of TFC coating.

PS-mPA membrane			
Solvent	PWP (L/m²h)	Flux (L/m²h)	NaCl rejection (%)
n- Propyl acetate	106.88 ± 6.42	100.3 ± 1.07	36.4 ± 1.62
Octyl acetate	108.34 ± 3.62	93.1 ± 8.63	50.05 ± 4.45
Hexane	73.87 ± 5.83	30.2 ± 3.25	89.35 ± 2.19
Cyclohexane	75.86 ± 3.465	32.4 ± 3.9	90.2 ± 0.57
PS-pPA membrane			
Solvent	PWP (L/m²h)	Flux (L/m²h)	NaCl rejection (%)
n- Propyl acetate	215.45 ± 7.70	206.1 ± 8.06	21 ± 1.4
Hexyl acetate	289.6 ± 24.89	181 ± 15.55	16 ± 2.88
Octyl acetate	160.4 ± 54.9	120.2 ± 55.2	38.9 ± 5.09
Nonyl acetate	257.4 ± 7.63	147 ± 7.55	17.9 ± 2.08
Hexane	54.6 ± 2.77	36.4 ± 4.72	77.9 ± 0.90
Cyclohexane	56.7 ± 5.73	37.9 ± 4.93	78.9 ± 2.10

It is interesting to note that for both PS-mPA and PS-pPA membranes (except for a notable exception of PS-pPA membrane made with octyl acetate), the separation increased while the flux decreased as the hydrophobicity of the solvent increased as we moved from n-propyl acetate to n-nonyl acetate and further to hydrocarbons (hexane and cyclohexane). This is probably because the boundary between aqueous and organic phases becomes sharper as the hydrophobicity of organic solvent increases. It is known that hydrophobicity increases as the hydrocarbon chain length of the ester compounds

increases and that esters are less hydrophobic than hydrocarbons, including cyclohexane and hexane.

In the next phase of the study, and based on the better performance of PS-mPA compared to PS-pPA, demonstrated so far, PS-mPA membranes with LSMM were studied. In view of the better solubility of cLSMM in cyclohexane than in hexane, the former was chosen for the organic phase to be used thereafter. The effect of LSMM concentration in the organic phase is summarized in Table 6.5. The table shows that salt rejection decreased significantly upon addition of cLSMM for all cLSMM concentrations. On the other hand, a 50% flux increase, over the control PS-mPA, was observed for the PS-mPA-cSMM-0.05. On the contrary, salt rejection values were considerably higher for membranes with iLSMM than for the PS-mPA, except at the highest iLSMM tested (1 wt %). The best performance with the highest salt separation (96.1 %) and a reasonably high flux value (24.3 L/m²h) was obtained for PS-mPA-iLSMM-0.25 membrane. It is interesting to note that the above membrane exhibited one of the lowest CA values (25.8°) and its surface seemed rougher than other membranes. It should also be noted that addition of a larger amount of iLSMM increased the CA value (43.9° for PS-mPA-iLSMM-1.0 membrane) and the surface became smoother. The membrane performance became poorer, in terms of both salt rejection and flux, correspondingly.

Being the best-performing iLSMM membrane so far, the PS-mPA-iLSMM-0.25 membrane was compared with the LSMM-free PS-mPA for their long term performance. The results are shown in Figure 6.6.a for flux and Figure 6.6.b for salt rejection. The

difference in flux data between Table 6.5 and Fig. 6.6.a reflects the variation of flux data among different membrane coupons, while hardly any difference is noticed between the salt rejection data of Table 6.5 and those of Figure 6.6.b. The flux data shown in Figure 6.6.a clearly indicates the much improved stability of PS-mPA-iLSMM-0.25 membrane as compared to the PS-mPA membrane. It is important to remember that the membranes used here have already been compacted at 1000 psi prior to testing at 800 psi (refer to the experimental procedure section), so the observed decline in flux cannot be attributed to membrane compaction. The decline in the flux was only $< 10\%$ for the PS-mPA-iLSMM-0.25 membrane while it was almost 40% for the PS-mPA membrane during the operational period of 50 hrs. The improved stability is probably due to the dispersed iLSMM macromolecules in the mPA layer that increases the mechanical strength of the thin mPA layer. The increase in flux stability from PS-mPA membrane to PS-mPA-iLSMM-0.25 membrane is probably due to the presence of PEG groups which has large excluded volume as well as very large coordination number of water molecules at the top surface. The presence of bulky, hydrophilic functional groups at the surface is supported by the low CA value and the rough surface image of this membrane. Figure 6.6.b indicates that the salt rejection of the PS-mPA-iLSMM-0.25 membrane is much higher than the control PS-mPA membranes. Both membranes remained almost constant in rejection performance throughout the test period.

Table 6.5: RO performance of various concentrations of two different types of LSMM of TFC coating.

PS-mPA membrane			
Conc. of LSMM	PWP (L/m²h)	Flux (L/m²h)	NaCl rejection (%)
0	75.86 ± 3.46	32.40 ± 3.9	90.4 ± 0.76
PS-mPA-cLSMM-x membrane (x = 0.005 to 1.00)			
Conc. of cLSMM	PWP (L/m²h)	Flux (L/m²h)	NaCl rejection (%)
0.005	28.17 ± 0.56	21.77 ± 1.2	66.55 ± 3.32
0.05	50.21 ± 7.0	46.79 ± 14.3	51.5 ± 1.3
0.10	18.56 ± 2.37	15.92 ± 2.68	57.5 ± 2.8
0.30	17.85 ± 7.5	14.95 ± 5.98	65.55 ± 11.6
1.00	12.04 ± 3.27	9.5 ± 3.2	45.7 ± 2.3
PS-mPA-iLSMM-x membrane (x= 0.10 to 1.00)			
Conc. of iLSMM	PWP (L/m²h)	Flux (L/m²h)	NaCl rejection (%)
0.10	52.94 ± 1.94	18.55 ± 1.06	94.3 ± 1.46
0.25	63.93 ± 0.67	24.3 ± 5.20	96.1 ± 2.03
0.50	34.75 ± 7.55	17.9 ± 2.26	91.25 ± 1.48
0.75	11.938 ± 2.42	5.20 ± 0.37	94.2 ± 4.53
1.00	19.93 ± 1.68	9.88 ± 1.93	72.3 ± 7.76

Figure 6.6.a: RO performance (flux).

Figure 6.6.b: RO performance (separation versus time).

7. Conclusions

A new concept for the preparation of TFC RO membrane by interfacial polymerization on porous PS support using hydrophilic surface modifying macromolecules (LSMMs) is presented. Those LSMMs are called either cLSMM or iLSMM depending on whether the LSMM is synthesized before (cLSMM) or during (iLSMM) the in-situ polymerization. From the experimental results we conclude that both cLSMM and iLSMM could be incorporated in the aromatic polyamide layer of the TFC membrane effectively. The NaCl separation increases while the flux decreases as the hydrophobicity of the solvent is increased in a series of solvents, including either esters or hydrocarbons.

The performance of the membrane was better for iLSMM incorporated membrane than cLSMM incorporated membrane. In more details, the addition of the cLSMM considerably decreased the salt rejection of the membrane and slightly reduced the flux, while in the case of the iLSMM, salt rejection was enhanced but the flux declined at different rates for different iLSMM concentrations. TFC membranes with and without addition of LSMM are lower in CA° values, and so are more hydrophilic, than the control PS membrane. Based on the CA° measurements, the presence of the thin polyamide layer increases the hydrophilicity of the membrane. Addition of the LSMMs causes further decrease in the contact angle. Even though, at high LSMMs concentration a slight increase in the hydrophobicity can be seen.

The heterogeneity of the surface, as revealed by the SEM micrographs and AFM, increases for TFC membranes compared to the control PS membrane. Addition of both cLSMM and i-LSMM increased the surface roughness but their higher concentration produced smoother surface. The AFM observation is closely related to the SEM pictures. Finally we found that the incorporation of iLSMM increased the stability of membrane desalination performance considerably.

8. Future Work

1. The prepared membranes should be tested for their performance in the presence of scaling foulants such as, calcium bicarbonate, magnesium salts and calcium sulphates.
2. The membranes should also be tested for their biological fouling.
3. Different LSMMs should be prepared using different monomers such as polypropylene glycol (PPG) or polyethylene glycols (PEG) of different molecular weights for the synthesis of prepolymers.
4. TFC membranes should be prepared with hydrophobic SMMs and charged SMMs and tested for their desalination performance and fouling.
5. The solvent effect should be studied more in detail.

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