ANTI FOULING AND WATER FLUX pH REGULATED SWITCHABLE POLYMERIC MEMBRANES

BY

Shumail Irfan

Mudassir Ali

Ali Mushtaq

School of Chemical and Materials Engineering
National University of Sciences and Technology
July, 2020

ANTI FOULING AND WATER FLUX pH REGULATED SWITCHABLE POLYMERIC MEMBRANES

By

Leader-00000191445 Shumail Irfan

Member 1-00000125355 Mudassir Ali

Member 2-00000177055 Ali Mushtaq

A THESIS

Submitted to

National University of Sciences and Technology

In partial fulfillment of the requirements for the degree of

B.E. MATERIALS AND METALLURGICAL ENGINEERING

School of Chemical and Materials

Engineering (SCME)

National University of Sciences and

Technology (NUST)

July, 2020

CERTIFICATE

This is to certify that work in this thesis has been completed by Ms. Shumail Irfan, Mr. Mudassir Ali and Mr. Ali Mushtaq under the supervision of Dr. Nasir Mehmood Ahmad and Dr. Mohsin Saleem at the school of Chemical and Materials Engineering (SCME), National University of Science and Technology, H-12, Islamabad, Pakistan.

---------------------------------------   ----------------------------------

Advisor: Co-Advisor:

Dr. Nasir Mehmood Ahmad   Dr. Mohsin Saleem
Department of Materials   Department of Materials
Engineering   Engineering
School of Chemical and Materials
Engineering

Submitted Through:

HOD-------------------------------------

Dr. Zakir Hussain
Department of Materials Engineering
School of Chemical and Materials
Engineering
National University of Sciences and
Technology

Principal/Dean -----------------------
Dr. Zakir Hussain
School of Chemical and Materials
Engineering
National University of Sciences and
Technology

DEDICATION

This thesis is dedicated to our parents, who have raised us to be a person we are today. It was a result of their untiring efforts; love and support which give us the strength to achieve this milestone. Thank you for your prayers, unconditional love, support and guidance throughout this journey.

ACKNOWLEDGEMENT

ABSTRACT

In Pakistan, water quality is deteriorating day by day and there is a need for efficient membrane filtration system but due to excessive fouling the life of membrane is highly reduced and to replace a membrane is very costly. So, a cost effective solution to this problem is to design a membrane that foul less and have greater efficiency. This antifouling nature of membrane can be achieved by polymeric 'grafting to' of ter-Butyl acrylate to TFC-PA membrane surface. As a result of grafting body of bacteria that are usually made up of protein are repelled by membrane due to the hydrophilic nature of grafted brushes. The localized charge on the surface of membrane helps to repel the fouling agents from the membrane surface. Moreover, Young's equation was used to find surface energy and work of adhesion, and theoretical water flux is calculated through Poiseuille Equation. An increase in water flux with increasing pressure indicates that, water flux is regulated. Moreover, with a change in pH the water flux varied due to protonation and deprotonation and maximum flux is at pH 3 having a value of 85.5 L/ $(m^2.h)$

Table of Content

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

ATRP   Atomic Transfer Radical Polymerization

PES   Polyether Sulfone

APTMS   3-Aminopropyl)triethoxysilane

NMP   N-Methyl-2-pyrrolidone

PVP   Polyvinylpyrrolidone

PMDETA   N,N, N′,N′′,N′′-Pentamethyldiethylenetriamine

TBA   Tert Butyl Acrylate

α-BIBB   Alpha- Bromo Isobutyrl Bromide

TFC-PA   Thin Film Composite Polyamide

RO   Reverse Osmosis

DCM   Dichloromethane

PAA   Poly Acrylic Acid

INTRODUCTION

1.1 Background

During the last decade, membrane technology has evolved significantly as there is immense need of water due to increase in population day by day. As the water demands increases the fresh water sources are depleting so water treatment is effective way to resolve water scarcity. But membranes are fouled by external agents which decreases the efficiency and life of membrane. So antifouling membrane is thus prepared by altering the surface of the membrane by different kinds of surface modification techniques, so that challenge of the membrane water treatment can be met.

1.2 Water Pollution in Pakistan

In Pakistan, one of the major threats to public health is water pollution. Water sources are contaminated by industrial waste and different types of metals that get dissolved into the underground water bodies due to the release of untreated industrial waste into the water bodies. Pakistan is standing on the verge of depletion of fresh water by 2025 and many diseases have spread among the people, due to drinking unhealthy water. So to provide fresh water to people, different filtration methods have been designed. One method for filtration is through membranes. Although different types of membranes are present in the market, but cheaper among those membranes are polymeric membranes [[1]].

1.3 Emergence of Polymeric Membrane

The membrane acts as a barrier that allows some things to pass through them and block the rest. Although, there are different types of membranes available in market but the most common among them is Polymeric membranes which are highly used for water filtration nowadays due to low cost and high efficiency. But there is one problem with these

membranes that they are prone to fouling and due to excessive fouling the water quality and water flux are deteriorated over time. So, there is a need to design such membranes that foul less and have increased efficiency [[6]].

1.4 Research Framework

Our research work revolves around the idea of making membrane technology more efficient and effective for filtration of sea water and underground water. It is comprised of three phases.

Phase 1:

Synthesis of high density Poly Ether Sulfone membrane by Phase Inversion Method

Phase 2:

Grafting of commercialized Polyamide membrane by Atomic Transfer Radical Polymerization by using Ter Butyl Acrylate as a monomer

Phase 3:

Identification of antifouling properties of grafted membranes by conducting water flux, water retention and different tests

1.5 Aims and Objectives

The main objectives of our work are listed below:

- Synthesis of densified PES membrane
- Achieve grafting on a Reverse Osmosis commercialized membrane
- Enhance the efficiency of RO membrane
- Prevent fouling by using pH responsive membranes

LITERATURE REVIEW

2.1 Membrane Technology

Almost 53% of world fresh water is purified by membrane technology (Anon., n.d.). Polymeric membranes are effective for water treatment because of poor solubility, porosity, high chemical stability and high strength. A membrane is a porous medium that acts as a barrier for selective absorption of the media. The wanted media is passed through the pores by application of the high pressure [2]. The types of membranes include polymeric, inorganic and ceramic membranes. Polymeric membranes include poly-amide, polyethylene, polyether sulfone, poly-acrylonitrile, polyvinyl chloride, poly vinyl alcohol, cellulose acetate [3]. Inorganic is the ceramic membrane that includes carbon, and other oxides that have high strength and thermal stability.

The membrane works on a principle that allows the wanted material to pass through the pores and unwanted materials is blocked. The purification and water treatment depend on the nature of the membrane, porosity, and life of membrane. As membrane gets older, the efficiency of the membrane decreases.

2.2 RO Membrane Fouling

Membrane fouling refers to the accumulation of the bacteria or particle on the porous, membrane surface. Fouling agents either block the membrane pores or make film on the surface of membranes hence decreasing the flux density and efficiency of the membrane [[3]]. Membrane fouling is caused by the four fouling agents, these are organic, inorganic, colloidal and biological agents like bacteria, fungi and other small microorganisms. The adsorption of fouling layer on membrane is considered as major factor of membrane fouling. The factors that affect the fouling are surface roughness, hydrophobicity, hydrophilicity, charge, polarity and contact angle [[6]].

2.3 Types of Fouling

2.3.1 Microbial Fouling

Microbial fouling is caused by biological agents like bacteria that form a bio film on membrane surface thereby decreasing the efficiency and flux rate [[6]].

2.3.2 Inorganic Fouling

Inorganic fouling is caused by the inorganic salts that become accumulated in the pores of the membrane with increase in the salt concentration. Major inorganic fouling agents are metal hydroxides, salts and sand particles [[4]].

2.3.3 Organic Fouling

 Organic fouling is caused by the dissolved organic carbon in the pores of the membrane, mainly occur when the membrane is exposed to water that contains high organic matter.

2.3.4 Colloidal Fouling

Colloidal fouling is caused by the suspension of the particles of salts like metallic hydroxides, and other salt ranging in size from micrometer to millimeter.

2.4 Mechanism of Fouling

The fouling of membrane occurs by either pore narrowing, pores blocking or by formation of bio film. Pore narrowing occurs when the particles clogged along sideways of the pore decreasing the pathway. Pore blocking occurs when particles and bacteria completely clog the pore opening. Film formation on membrane occur when bacteria and other particles resides on the surface, normally occur when the size of the fouling agent is greater than pores. [[4]]

a. Pore narrowing   b. pore blocking   c. film formation
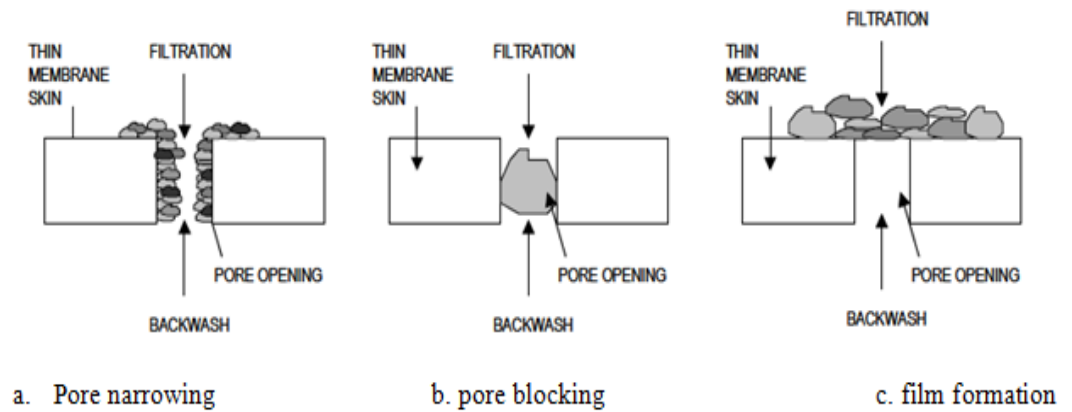
Figure 1: Fouling of membrane

2.5 Surface Modification Methods on membranes for Antifouling

Recent research shows that following are methods that make the membrane antifouling or aid the antifouling property of membranes. Increasing the hydrophobicity of the membrane increases the antifouling properties of membrane because the fouling agent being hydrophobic, are not adsorbed on the surface. For the hydrophilic fouling agent the fouling increases.

If a surface is smooth then there are lesser chances of fouling as compared to rough surface because surface with more groves allows more adsorption of fouling agents. The surface charge has greater influence on the fouling of the membrane, if the membrane surface has repulsive charge as compared to fouling agents there is enhanced antifouling property of the membrane, so membrane that has antifouling property are prepared according to charge of fouling agent [7].

Some of the research results showed that anti-fouling decreases if the surface of the membrane is bonded to long-chain molecules like polyethylene glycol. By this modification the steric repulsion of the surface increases that prevent the adsorption of the protein [[8]]. The hydrophilic chains when grafted on the membrane surface due to steric repulsion the fouling agent become unable to adsorb on the surface of the

membrane [[9]]. The application of grafting of the polymer brushes increases the antifouling property of membrane by increases the configurational entropy due to volume repulsion. Antifouling depends upon the length of chains, degree of uniformness and nature of functional group.

2.5.1 Physical Adsorption

This is the simplest method of surface modification. Researchers used this method to increase the hydrophilicity of the membrane. Use of polyethylene oxide surfactant on the cellulose acetate blend and polyamide membrane [[10]].The charged surfactants are also used to modify the polymeric membranes. Researchers show that the charge reversal of the membrane occurs by electrostatic self-assembly of polyethylenamine (PEI) on the membrane surface [[11]]. The charge reversal on the membrane surface increases the fouling resistance of membrane to cationic fouling agents because of the electrostatic repulsion and hydrophilicity increases.

2.5.2 Surface Coating

The surface coating also modifies the membrane surface. The surface is coated with both water soluble polymer layer and insoluble layer this layer act as a barrier, which prevents the fouling agent to adsorb on the surface of membrane. It is the most simple and cost effective method of surface modification. Researchers coated the hydrophilic and electrical neutral PVA on PA membrane. This increases the hydrophilicity of the membranes and also zeta potential [[12]]. Therefore these membranes give better antifouling property. In some research results, it has been shown that membrane surface coated with glutaraldehyde and hydrochloric acid has increased the stability of the layer coated [[13]].

Louie-tal studied a coating of which is a copolymer of nylon 6 and polyethylene glycol. This surface modification increases surface smoothness by changing the contact angle of the surface. With this surface coating decline in the flux rate, is lower in modified membrane [14]. Some

researchers modified the surface of the polyamide membrane by a copolymer, poly N-isopropylacrylamide-co-acrylic acid [[15]]. The modification increases the hydrophilicity of the membrane and repulsive charge of the surface at normal pH. This surface modification of the membrane increases the antifouling property.

2.6 Chemical Methods of Surface Modification

2.6.1 Surface Hydrophilization

Surface hydrophilization increases the antifouling of the membrane if the membrane is exposed to the hydrophobic fouling agents. In some researches, hydrophilizing agents like hydrofluoric acid, hydrochloric acid, sulfuric acid, phosphoric and nitric acids that cross-link with the membrane surfaces thus modify the surface [[16]]. This surface modification increases the hydrophilicity of the membrane surface after treatment, the concentration of the acid should be kept so that to prevent the breakdown of the polymer back that results in decrease salt rejection.

2.6.2 Chemical Coupling

The polyamide membrane that is used commercially has a carboxylic and amine group. These groups react with the reagent that forms compound on the surface. Van-wanger modified the polyamide membrane by reacting to the membrane surface with epoxy and polyethylene glycol [[17]]. As a result of chemical reaction, the surface properties are changed after modification. This modification results in improving the hydrophilicity and smoothness of the membrane. The modified membrane show balanced flux and fouling resistance.
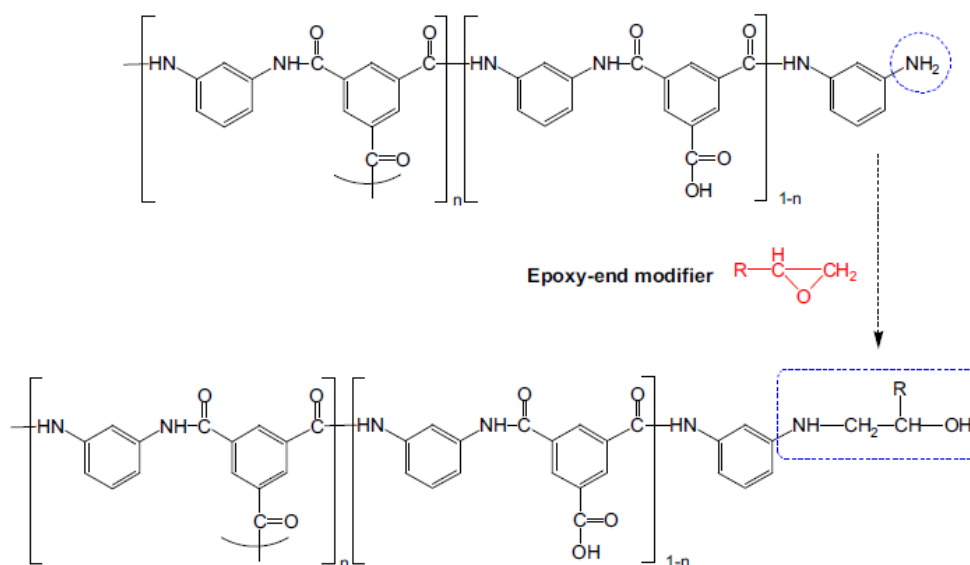
Figure 2: Chemical Coupling

2.6.3 Radical Grafting

In this type of surface modification, free radical produced from the initiators molecules, are attached to the surface of the membrane where polymer reacts with the free radical to generate the monomer. Researchers grafted a vinyl monomer on to the membrane surface. Redox system of potassium per-sulphate and potassium meta-bi-sulphite is used to generate the radicals. These react with the backbone of the polymer and leave the hydrogen atom free in polymer chain that initiates the grafting of the monomers on the membrane surface and polymerization proceeds through propagation [[18]].

Monomers like acrylic acid, methyl-meth-acrylic acid, poly-ethylene-glycol-methacrylate, 3-sulfopropyl methacrylate, 2-acrylamido-2-methylpropane-sulfonic acid, vinyl-sulfonic acid. In radical grafting of methyl-meth-acrylic acid modified membrane there is an increase in the zeta potential because of the higher dissociation of the of the carboxyl group[[19]] . The surface modification of the membranes with 3-sulfopropyl methacrylate and poly-ethylene-glycol-methacrylate showed low contact angle and advancing contact angle. This make modification makes the membrane more hydrophilic. Also, the modified membranes show reduction in roughness of the membrane surface which increases

the antifouling property of the membrane. The polymeric membrane surface modified with the hydrophilic monomer shows lesser adsorption of the fouling agents on the surface of the membrane and surface of the membrane is smooth as compared to the unmodified membrane.

Some researchers grafted 3-allyl-5,5-dimethylhydantoin on polymeric membrane showed lower contact angle as compared to unmodified membranes significant increase in the hydrophilicity of the membrane [[20]].
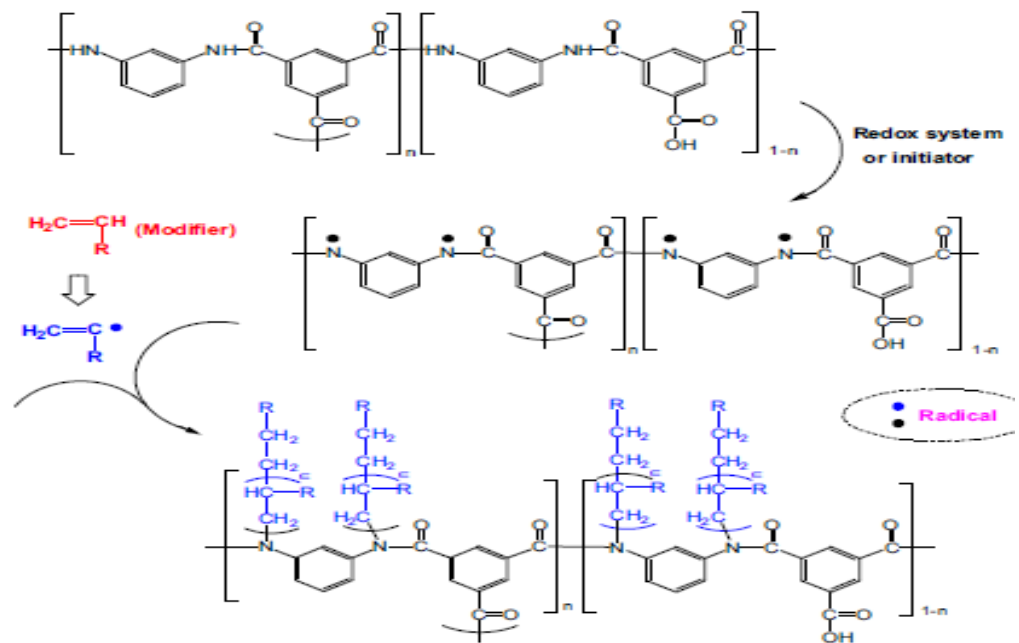
Fig. 4 — Surface modification of polyamide RO membrane via radical grafting.

Figure 3: Radical Grafting

2.7 Atomic Transfer Radical Polymerization

This process involves the production of free radicals by initiator on a functionalized membrane. An initiator attacks on the backbone of the polymer that generates the free radical [[14]]. After the generation of the free radical the surface is grafted as a result of reaction between membrane surface and poly-acrylic acid.

The overall reaction is

$$P_n\text{-}X + Mt^n/L \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^* + X\text{-}Mt^{n+1}/L$$

Monomer k_p k_t
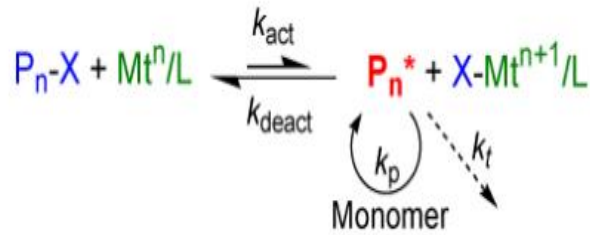
Figure 4: Atomic Transfer Radical Polymerization

2.7.1 Atomic Transfer Radical Polymerization Process

In ATRP reaction on the membrane surface the alkyl Halides R-X is used as the initiators while the catalyst is Cu, Ni, Os, Fe solutions, the function of the catalyst is to activate the chemical reaction and to reduce the energy barrier. In this process the electron transfer is carried out via a transition metal to generate the free radical. As a result of this the oxidation state of the metal increases. [[11]] The equilibrium establishes rapidly in this process and is shifted toward low concentration side. In this chain reaction, the polymer chains grow with the monomers with uniform size and weight.

2.7.2 Components of ATRP:

There are four components of ATRP Process, monomer initiator, catalyst and solvent

2.7.2.1 Monomer

The function of the monomer is to stabilize the propagating radicals and have functional groups like styrene, (meth)acrylates, (meth)acrylamides and acrylonitrile.[[15]]

2.7.2.2 Initiator

The initiator controls the growth of the polymer chains. Rapid initiation results in the narrow weight and length distribution among the polymeric chains. The most commonly used initiators are alkyl halides (R-X)[[18]] The advantage of using alkyl halides as initiators because their structure resembles the organic frame work in propagating radical. More reactive

the alkyl halide more spontaneous initiation occurs and has good control of the polymeric chains.

2.7.2.3 Catalyst

In ATRP reaction the rate of polymerization is important to control reaction and the distribution of length among the polymeric chains. Equilibrium constant between the dormant and active specie is dependent upon the catalyst. If it is low the polymerization rate is low, to initiate the reaction and if high there is non-uniform distribution among the polymeric chains [[12]].

There are some requirements for the metal catalyst to be used in ATRP.

a) There need to be two accessible oxidation states that are separated by one electron
b) The metal center should have high affinity for halogen
c) The coordination sphere of the metal will able to accommodate halogen when it is subjected to oxidation.
d) Transition metal catalyst should by inert so it cannot give side reactions such as reversible coupling with the propagating radicals and catalyst radical termination, etc.

2.7.2.4 Solvent

The solvents which are most likely to be used are toluene, 1.4-dioxane, xylene, anisole, DMF, DMSO, water, methanol, acetonitrile and DMC,[[20]]

2.8 Polymer brushes

Polymeric brushes are the long chains of acid that are attached to the membrane surface. The purpose to attach the polymeric brushes on the surface is to modify the properties of the surface like surface charge, polarity, topography, hydrophilicity, hydrophobicity, surface roughness and surface energy.

There are two methods to graft the polymer brushes called physical and chemical processes.

The physical process refers to the coating of the surface without any chemical bond and it is called physisorption. The major limitation is chance of desorption. Only the electrostatic and Vander Waal's attraction exists. The chemical process involves the formation of a chemical bond between the substrate and coating. There are two types of chemisorption processes namely grafting to and grafting from.

The grafting to approach involves already prepared end functionalized polymer with suitable molecule exposed onto the surface. The main drawback of this method is the inherent diffusion limitation affecting the grafting reaction [[6]].

The grafting from approach the surface to be modified is activated by attaching a suitable initiating species, and then the growth of polymer chain takes place. The initiating species comprise the molecules which could carry out polymerization by ATRP [[20]].
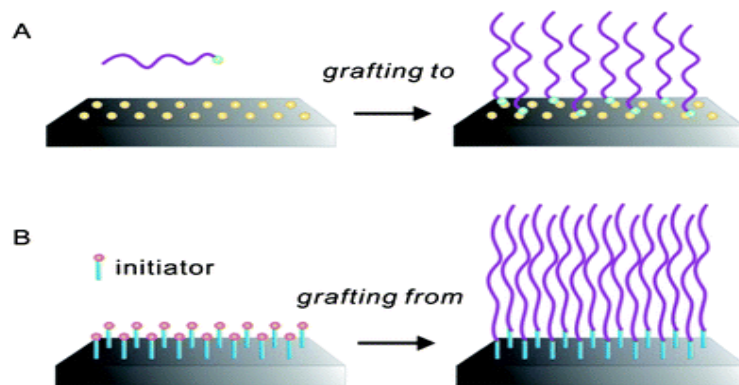
Figure 5: Grafting to and grafting from techniques

This study is about the growth of polymer brushes by ATRP in which grafting from approach is used.

2.8.1 Working of Polymeric Brushes

The polymer brushes have a localized charge on themselves. When a charged body of bacteria and fouling agent came in the vicinity of brushes, the brushes due to the opposite charge become elongated and repel the bacteria.[[6]]

2.8.2 Switchability of Polymeric Brushes

The Poly acrylic acid brushes are switchable because there localized charge changes upon change in the pH. The change in pH cause brushes to coil down or elongated up depending upon the charge of the bacteria and fouling agents.[[20]] The switchability helps selectively filter the fouling agents

2.8.3 Applications of polymer brushes:

Polymer brushes have several applications in the field of membrane separation such as

- Protein adsorption and separation [[20]]
- Solution diffusion separations such as water purification
- Pervaporation of organic compounds
- Gas separation

Polymer brushes can also be used for the stimuli response material.

2.9 Young's Equation

Young's model provides the basis of concept of wettabilty and relation of wettability with surface roughness. It relates to the intrinsic contact angle and surface tension. It is a useful tool which is extended to determine effect of roughness on wettability of different surfaces by incorporating Wenzel and Cassie-Baxter model. According to these two models the intrinsic wettability of surface is changed by introducing roughness. So according to the concept given by Wenzel, that a surface that tends to be hydrophilic will become more hydrophilic by the introduction of roughness. Whereas Cassie- Baxter model states that reverse of Wenzel state takes place with increase in surface roughness. Young's equation plays an important role in calculating surface energy and work of adhesion as given by following relations.

$$\gamma_s = \frac{\gamma l}{2}(1 + \cos\theta) \quad (1)$$

Work of adhesion

$$W_A = (1 + \cos\theta)\gamma_l \quad (2)$$

2.10 Poiseuille Equation

This equation is based on a mathematical model that relates differential pressure with water flux. It serves as an important tool for calculating the changes in theoretical water flux with an increase in differential pressure. This equation serves as a major tool for calculating water flux of different types of membranes. This equation is given as:

$$J = [\pi n r^4 \Delta P]/[8\mu\tau l] \qquad (3)$$

Where J is the water flux, n is the number of pores per m^2, r is the average pore radius, τ is tortuosity which is generally assumed 1 and l is membrane thickness.

EXPERIMENTAL PROCEDURES

3.1 Materials

The main material for the fabrication of the membrane is polyether sulfone, Poly-vinyl-pyrrolidone (PVP) and N-methylpyrrolidinone (NMP) were used as pore-forming agent and solvent, respectively

3.2 Fabrication of the PES Membrane

The base membrane is fabricated by different polymers like poly ether sulfone in NMP solution, pore-forming agents like poly-vinyl-pyrrolidone (PVP) is used to form pores. For the fabrication of the dense membrane amount of the PES is doubled. The ordinary membrane that is less dense is fabricated by making the solution of 1.9g of Poly-ether-sulfone in 8g of NMP and 0.1 g of pore-forming agent PVP is added at the end. The overall solution is stirred for 24h for homogenization and then allowed to rest for 30 minutes. Then this solution is sonicated for 20 minutes and allows us to rest for 30 minutes before casting. The supersaturated solution is casted in cold water to get membranes. For the dense membrane the amount of PES is doubled which gives high strength and long life to the membrane.

Table 1: amount of chemicals used for dense PES membrane

Chemicals	Amount (grams)
Poly-ether-sulfone PES	6
N-methyl-pyrrolidinone NMP	3.8
poly-vinyl-pyrrolidone PVP	0.2

3.2.1 Phase Inversion Method

This method is used to fabricate asymmetric membrane by casting homogenous saturated solution of polymer in cold water bath on a glass slab at lab scale.
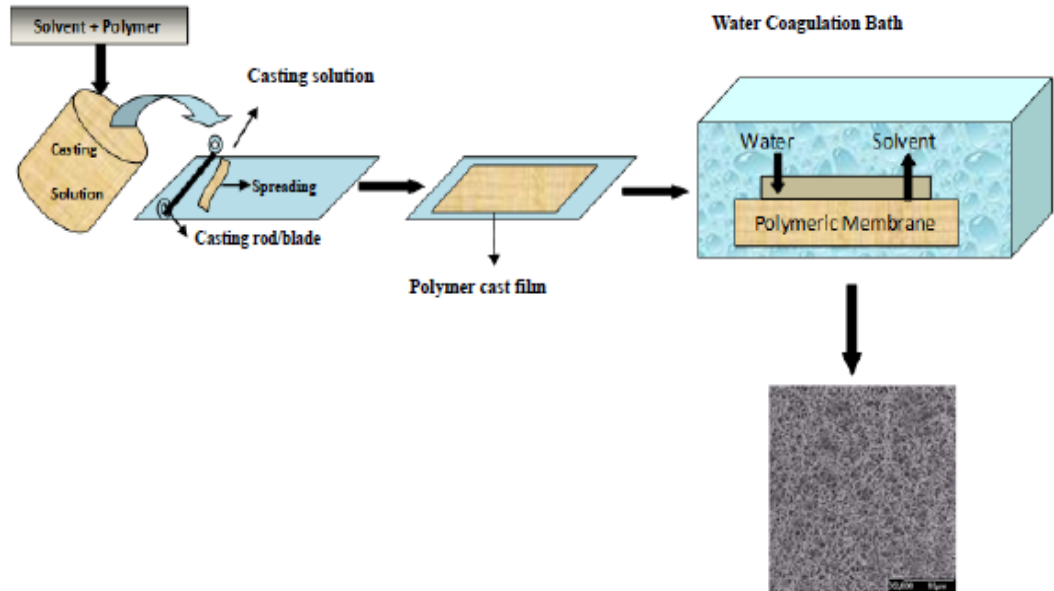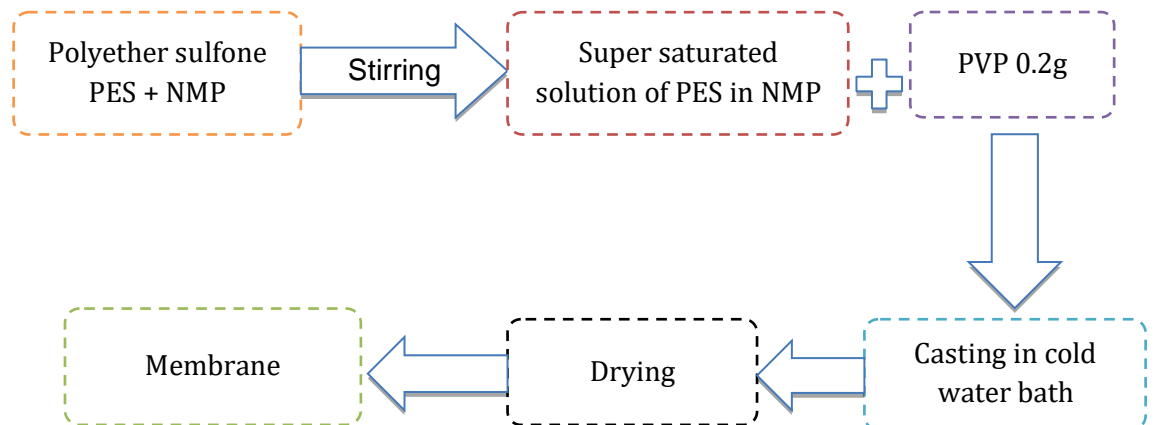

Figure 6: Phase Inversion Method

3.3 Grafting on Commercial Membrane

The conventional polyamide membrane is grafted by poly-acrylic acid via Atomic transfer radical Polymerization

3.3.1 Chemical Used

The chemical used for grafting are as follow:

For Functionalization:

16

Table 2: Chemicals for functionalization

Chemicals used	Amount
(3-Aminopropyl)-trimethoxysilane (APTMS)	5 Drops
Distilled water	250ml

For Initiation:

Table 3: Chemical for initiation

Chemicals used	Amount
Dichloromethane (Solvent)	50ml
α – Bromoisobutyryl bromide (initiator)	4 to 5 drops
Diethylenetriamine (ligand)	4 to 5 drops
Absolute ethanol	Few ml

For grafting:

Table 4: Chemicals for grafting

Chemicals used	Amount
Ter Butyl Acrylate (monomer)	5ml
Cu(I) Bromide (catalyst)	90mg
PMDTA (ligand)	4 drops
Tetra hydrofuran (washing)	Few ml

3.3.2 Procedure

Grafting of Poly Acrylic Acid on a Polyamide commercial membrane by using Ter butyl acrylate involves three steps:

Step 1: Functionalization of the membrane

The commercial polyamide membrane is first functionalized with the dilute solution of 3-Aminopropyl triethoxysilane APTMS in distilled water. The membrane is placed in APTMS solution for 15 minutes to

17

attach the silane group. And then it is placed in a vacuum oven for 40 minutes, for drying purposes. As a result, the membrane becomes negatively charged. The advantage of functionalization is the better attachment of the initiator molecule on the membrane due to presence of a silane group.
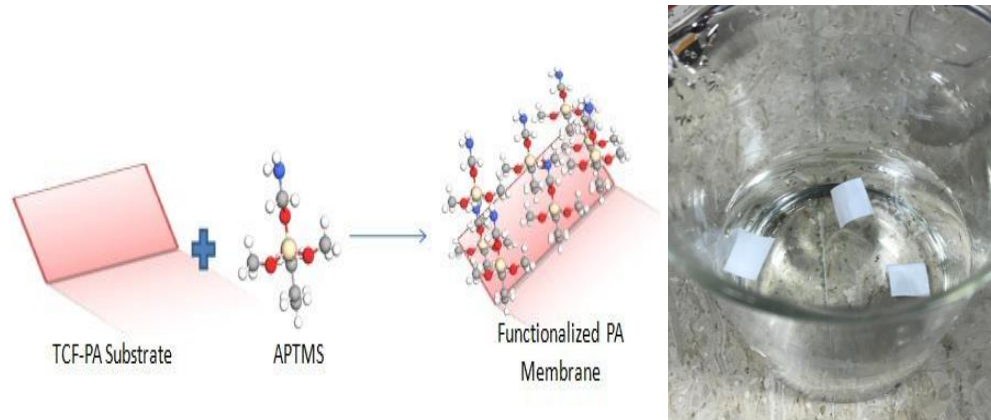

Figure 7: Functionalization of Membrane

Step 2: Attachment of initiator

After that, the initiator molecule is attached to the membrane with the help of ligand, and solvent at temperature 60-70 ℃ in an inert atmosphere to prevent oxidization for 4 hours. Once initiator molecule is attached the membrane is dried in a vacuum oven for 30 minutes and then washed with ethanol and again dried for 20 minutes
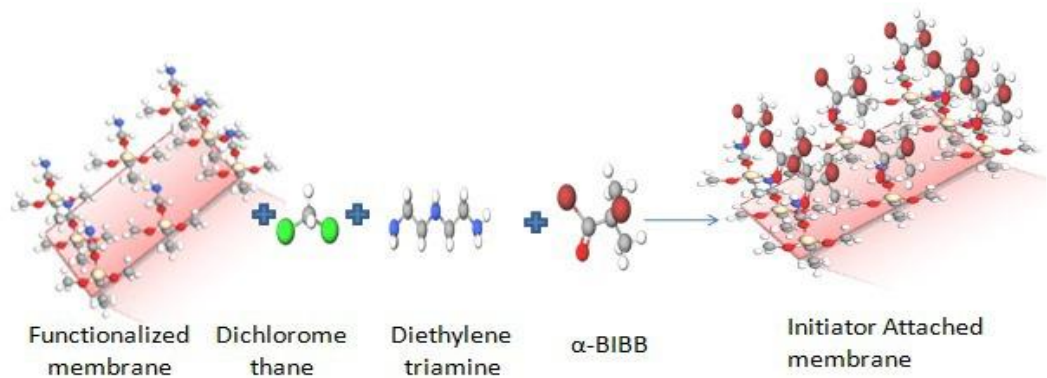

Figure 8: Schematic of the intialization step

The number of the chain or brushes growth on the membrane surface depends upon the amount of initiator attached. Commonly used initiators are alkyl halides
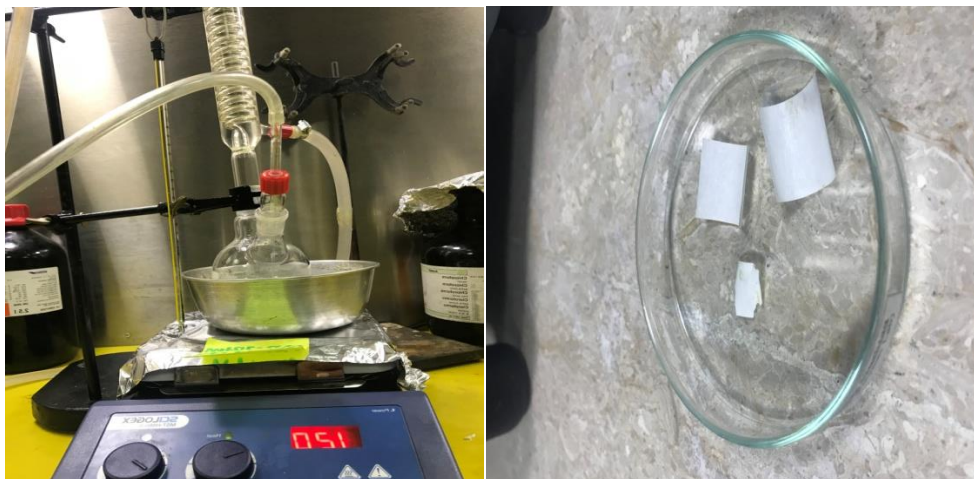

Figure 9: Grafting of membrane

As the grafting is completed the membrane is washed by tetra-hydro-furan and dried in a vacuum oven.

.

Step 3: Grafting on the membrane surface

For grafting, 90mg of copper 1-bromide is mixed with 5ml of Tertiary Butyl Acrylate monomer and 4-5 drops of PMDTA Penta-methyl-di-ethyl-ene-tri-amine is mixed in a glass viol and sealed with parafilm and then heated in an oil bath at 40-60 °C for 4 hours.
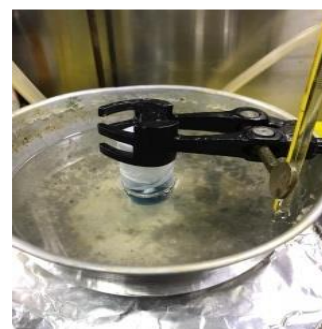

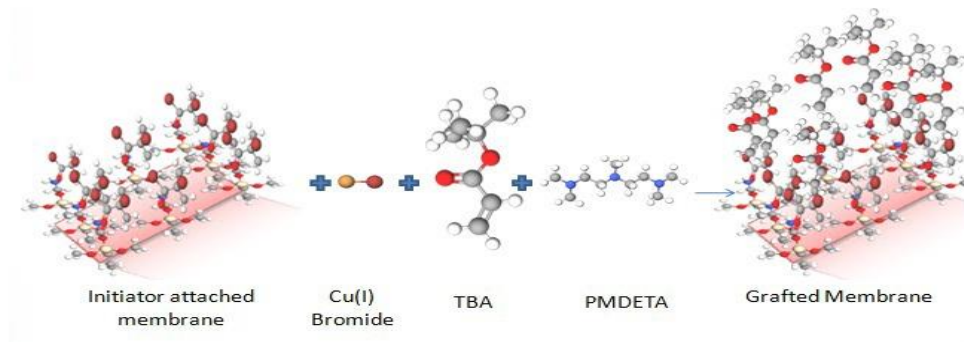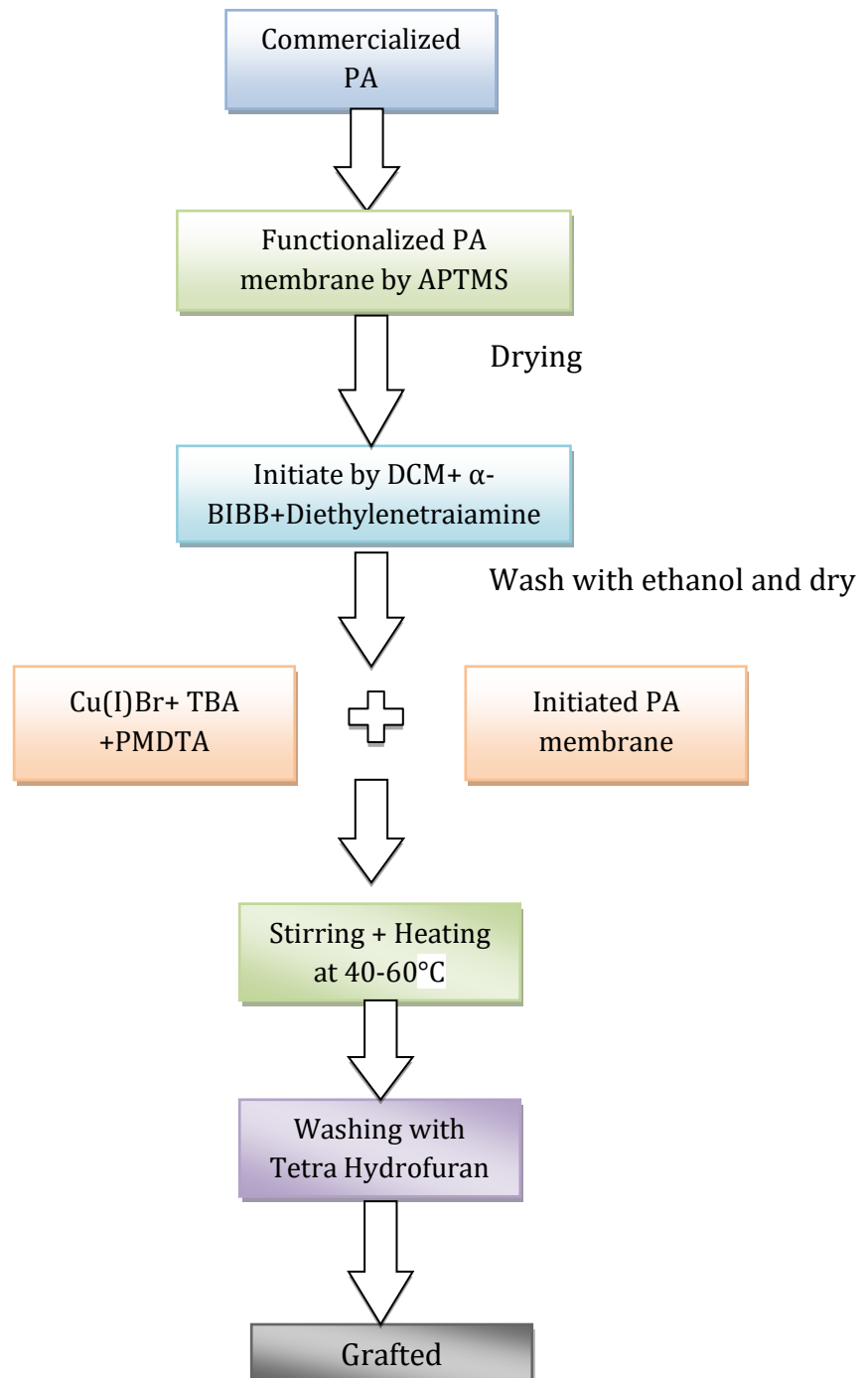**Figure 10: Grafting of the membrane in oil bath**

Flow Diagram of Atomic Transfer Radical Polymerization Process

Commercialized
PA

Functionalized PA
membrane by APTMS

Drying

Initiate by DCM+ α-
BIBB+Diethylenetraiamine

Wash with ethanol and dry

Cu(I)Br+ TBA
+PMDTA

Initiated PA
membrane

Stirring + Heating
at 40-60°C

Washing with
Tetra Hydrofuran

Grafted

CHARACTERIZATION TECHNIQUES

The characterization techniques that were used to get results are:

Table 5: Characterization Techniques

CHARACTERIZATION TECHNIQUE	APPLICATION
1.Optical Microscopy	To study surface morphology and preceding of chemical reaction on membrane
2. Scanning Electron Microscopy	To Study surface morphology of membrane in detail and to confirm attachment of polymer brushes
3. Water Contact Angle	To study hydrophobicity and hydrophilicity of membrane
4. Optical Profilometry	To study Surface roughness of membrane
5. Fourier Transform Infrared Spectroscopy	To study composition and functional group attachment on membrane surface

4.1 Optical Microscopy

The purpose of optical microscopy is to study the overall surface morphology. It is an index to study the proceeding of chemical reactions used to attach initiators, and brushes on membrane surface. It is a qualitative analysis to study the chemical reaction on membrane surface, change in membrane texture via functionalization, attachment of initiator molecule, attachment of brushes molecule on the membrane surface to the original membrane.

Figure 11: OPTIKA microscope

4.1.1 Principle of Optical Microscopy

The optical Microscopy technique uses photon to refract from the opaque surface of the polymeric sample by convex lens and mirrors. The contrast in the surface of sample enables optical path difference. These microscopes magnify images to about 1500 times to original sample. Optical microscopes are divided into two categories based on lightning method that are transmission and refraction type microscopes. In transmission optical microscope, light source is at bottom and light passes through the opaque sample. Mostly the Optical microscopes are refraction type with light source at top, the light source illuminates the opaque sample and due to refraction image is formed on the eyepiece. The image on the eyepiece is the result of constructive interference of two waveforms out of phase from sample. Different lens are used to enhance the resolution of the microscope, which is ability of microscope to distinguish between two smaller points. The microscope used bright field in contrast with the dense surface of the sample enable optical path difference. A digital optical microscope is equipped with the electronic detectors CCD. The function of the CCD is to create an image in the form of pixels. The pixel pitch should be smaller than the minimum resolution distance to avoid loss of resolution by detectors.

4.2 Scanning Electron Microscopy

Scanning Electron Microscopy uses beam of high energy electron to study, morphology, texture, topography, grain size of materials like polymers, composites, metals ceramics and biological samples. This technique is qualitative analysis to study the surface texture, change in surface morphology upon chemical reaction like functionalization, attachment of initiator molecule and growth of polymer brushes on membrane surface. Also this technique reveals surface roughness of membrane to some extent.

Figure 12: Jeol 4960LV Scanning Electron Microscope.

4.2.1 Principle of Scanning Electron Microscopy

This technique uses a beam of electron to be focused on the sample. For polymeric or biological samples the sample is made conductive by sputtering of gold on it. Due to surface texture the electrons are refracted from the surface called secondary electrons and are then passed through detector and amplified before image is obtained on screen. The characterization in SEM is due to secondary, backscattered and X- ray emitted from the sample. If the electron having sufficient energy is focused on sample the electron loss energy due to inelastic collision and knocks electrons from sample called secondary electrons, these secondary electron moves to the detectors and image is mapped on the screen. If the electrons have more energy than after collision elastic scattering of secondary electrons occurs known as backscattered

electrons. These electrons move to the detector and image is formed on the screen. If the incoming electrons have enough energy then after knocking electron X-rays are emitted from the sample and detected.

Electrons are emitted from electron gun that is made of tungsten filament and accelerated by positively charge plate. SEM may have objective lens, its function is not to resolve image but act to focus an electron beam on the sample spot.

4.3 Fourier Transform Infrared Spectroscopy (FTIR)

This technique is used to determine the chemical composition and the functional groups in the polymeric sample. FTIR is used for the study of chemical composition of the membrane and changes in chemical composition upon different chemical reaction. FTIR confirms the attachment of initiator molecule functionalization and attachment of polymer brushes by a change in functional groups.

Figure 13: FTIR Instrument

4.3.1 Principle of FTIR

Use the Infrared radiation to absorb in the material that alters the vibrational energy of the molecule like bond stretching, bond elongation. The instrument consists of source to generate infrared rays and Inferometer whose function is to split the beam into two halves. The one beam falls on the flat mirror and other form refraction on the sample.

After that beams are recombined back to give interference and frequency decoded, the signal is sent to the detector and result is displayed on output device. Different functional groups have different frequencies and thus functional groups are identified. The change in frequency is detected and matched regarding revealing information about functional groups.
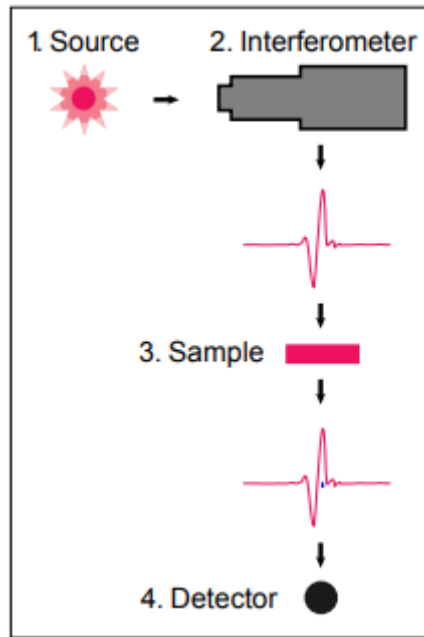

Figure 14: FTIR Layout

4.4 Optical Profilometry

The optical Profiler is used to study surface roughness and topography of the materials. It reveals the surface morphology of the materials whether the surface is smooth or rough. For membrane the surface morphology is important to control antifouling, chemical fouling and water-flux.

4.4.1 Principle of Optical Profilometry

The optical profiler measures the surface roughness by interference of light on the sample. The reflected light wavelength measures the surface height and roughness. It uses a light probe to scan the surface in the X, Y and Z direction of the sample. The inhomogeneity in the surface cause light to refract that is sent to detector and signal is interpreted and graph is obtained. In Optical Profiler, light beam is splitted in two halves one from the test sample is passed through the microscope objective and other is passed through the mirror for reference. Then both beams are

recombined to get the interference fringes or bands. The constructive interference band is bright while destructive interference gives darker bands. The reference mirror gives flatness while the other splitter halves measures height variation on the surface. The advantage of this technique is that it is nondestructive and both 2D and 3D images can be obtained by this technique.
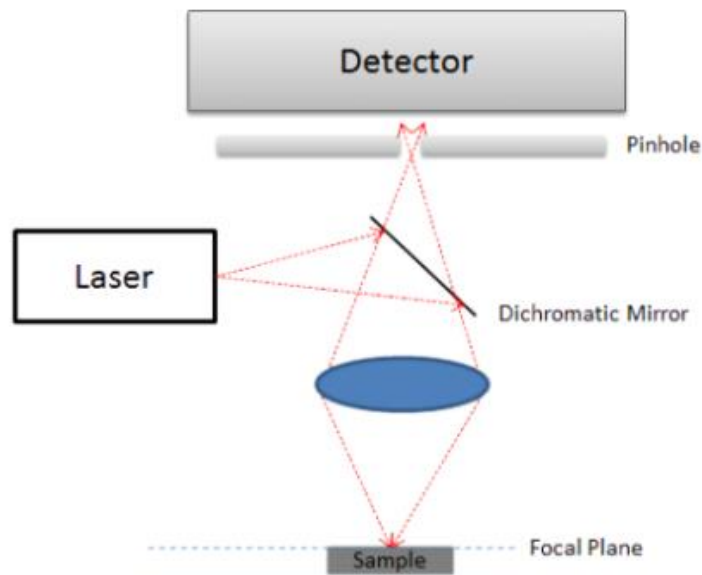

Figure 15: Working Principle of FTIR

4.5 Water Contact Angle Measurement

Contact Angle is measured by sessile drop method. It is the angle at which, liquid-vapor interface form with solid sample. It tells us about the hydrophobicity and hydrophilicity of the material.
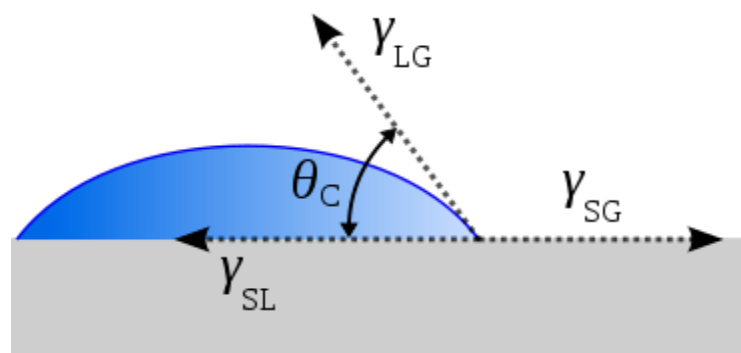

Figure 16: Water Contact Angle Measurement

4.5 Water Contact Angle Measurement Device Principle

The static contact angle is measured by placing a drop of water on the sample, and the image is recorded that is analyzed by the computer software. This static angle is measured by a young Laplace equation and process known as optical tensiometry.

Figure 17: Water Contact Angle Goniometer

Typically contact angle is measured by goniometer. The method employed for measurement is static sessile drop method. In this method, an optical sub method is used to capture a profile of pure liquid onto the solid substrate. The angle formed between the liquid-solid interface and the liquid-vapor phase is the contact angle. A high-resolution camera is used to capture the image and then software is employed to analyze the contact angle.

A 10μml of distilled water is dropped onto the membrane surface. Images are taken through the camera and three different measurements are taken to calculate the contact angle. For the removal of experimental errors, the average of the measured values is taken.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Optical Microscopy Results
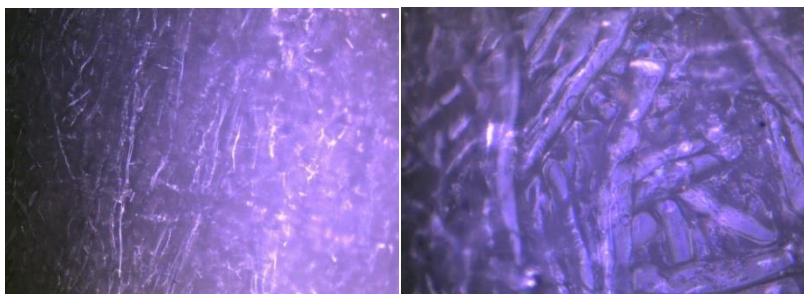
TFC-PA Membrane Functionalized:

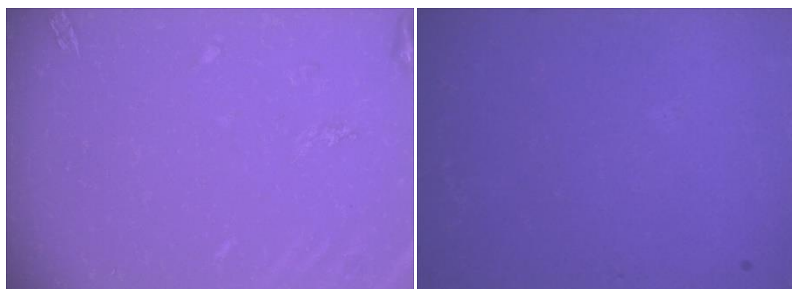**Figure 18: TFC-PA Membrane at 20x and 50x**

Figure 19: PA-APTMS 20x and 50x

As it can be seen in figure 18 that, there are some scratches and some type of tubular structure on TFC-PA membrane. But after functionalization by APTMS the surface of membrane becomes clear as shown by figure 19. Surface roughness is reduced which is further confirmed by optical profilometry.

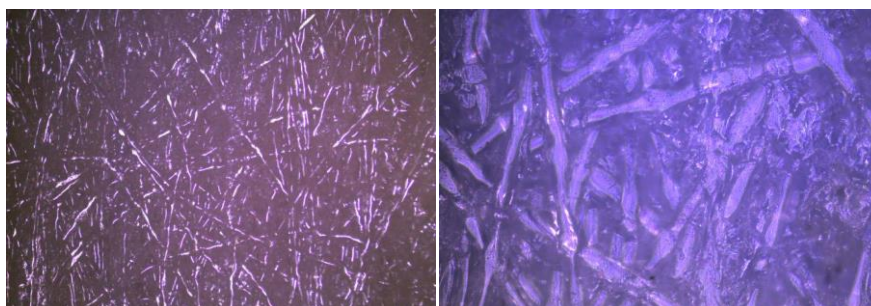**Initiator Attached Polyamide Membrane:**

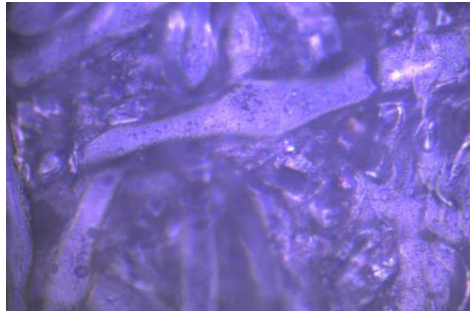**Figure 20: initiator Attached PA Membrane at 5x and 20x**

Figure 20a: Initiator Attached PA Membrane at 50x

As it can be seen from figure 20 and 20a that some type of tubular structure again appears on the surface of membrane, this shows that some sort of reaction occurs at surface which again increases surface roughness and surface is not clearer as it was in figure 19.
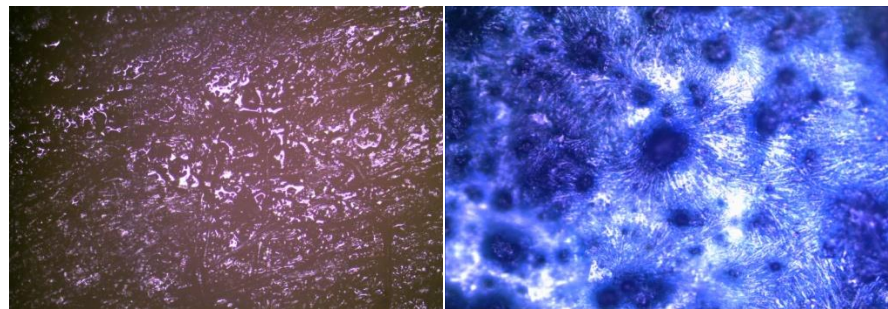
Grafted Polyamide Membrane

Figure 21: Grafted PA Membrane at 5x and 20x
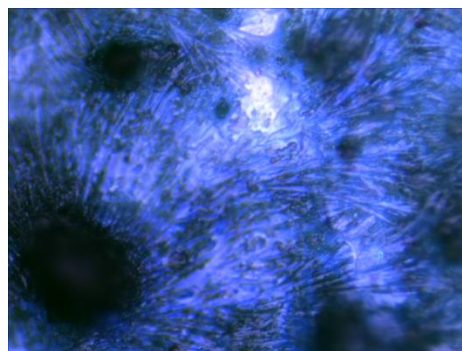

Fig.21a: Grafted Polyamide Membrane at 50x

These results of the optical microscopy show the change in membrane surface upon chemical reaction done on the membrane surface with grafting.

The difference in the membrane surface due to chemical reaction increases the contrast and changes the surface morphology of the

membrane. The commercial membrane has a smooth surface as shown in figure 18, while the initiated membrane surface has different morphology as compared to the parent membrane. The membrane after grafting has increased surface roughness and texture as shown in Figures 21 and 21a. From the optical microscopy characterization technique, change in membrane surface indicates the preceding of chemical reaction of functionalization, initiator molecule attachment and grafting of polymeric brushes on membrane surface.

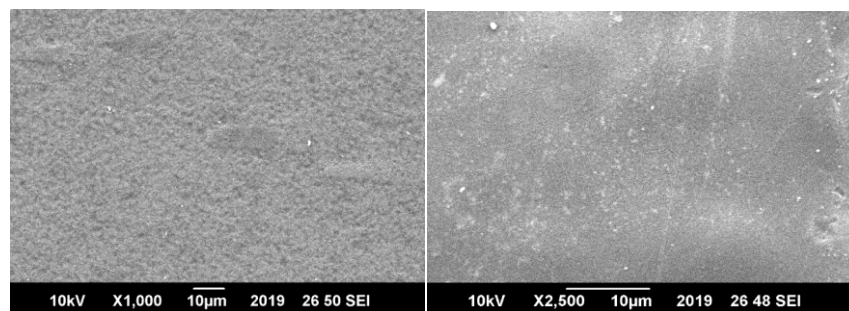## 5.2 Scanning Electron Microscopy Results

Figure 22: Polyamide Membrane at 1000x and 2500x

This image indicates the surface of TFC-PA membrane at 1000x and 2500x. These images show that the surface of the membrane is smooth before grafting.

5.2.1 SEM Images of Cross-sectional view of TFC-PA membrane
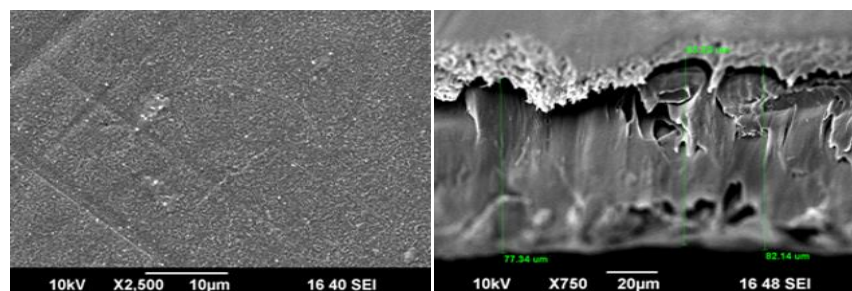

Figure 23: TFC-PA Cross sectional Membrane at 2500x and 750x

These images indicate the cross-sectional view of membrane at 2500x and 750x. The cross sectional view indicates that there is no type of structure present on the pristine membrane surface and this membrane is highly prone to fouling before grafting.

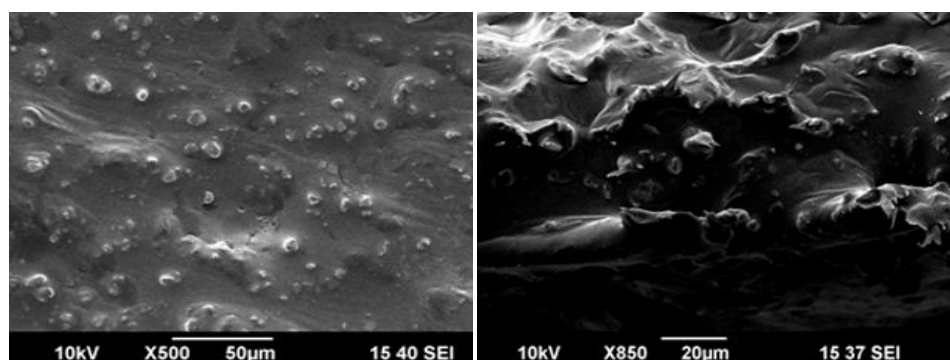## 5.2.2 SEM Images of Grafted Polyamide Membrane

Figure 24: Grafted Polyamide Membrane 500x and 850x

These images indicate the surface and cross-sectional view of the grafted membrane. As it can be seen in figure24 that the membrane surface has some sort of pits on its surface after grafting and the cross-sectional view at 850x indicates that brushes are grown on membrane surface, which shows that grafting has been done and after grafting the properties of membrane are improved.
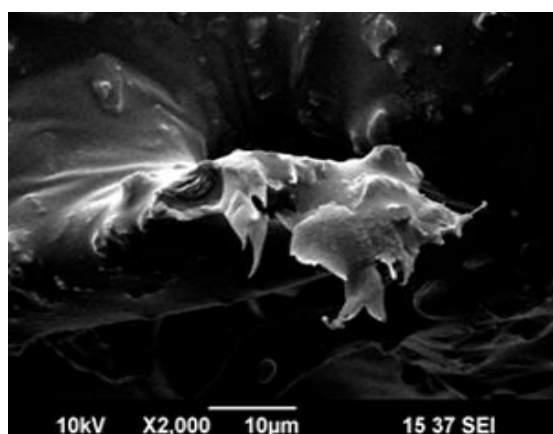

Fig. 24a: Grafted Polyamide Membrane 2000x

From the images above the surface of the sample commercial Polyamide membrane is smooth and has less surface texture. The SEM images of the grafted membranes show the relatively highly textured surface and special type of coil brushed structure on the surface at both surface and cross section of polyamide membrane at contact mode of Scanning electron microscope. The grown brushes on the surface increase the contrast as shown in image of magnification of 2000x. These specials structures enable special wettability of the polyamide membrane.
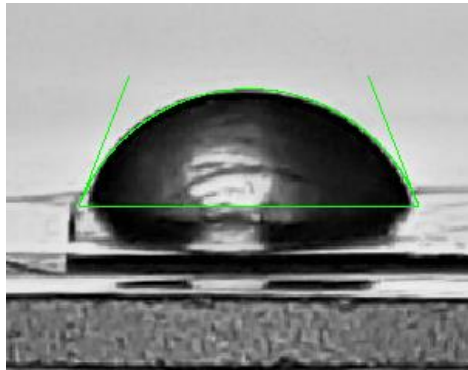
5.3 Contact Angle Measurement

Figure 25: TFC-PA
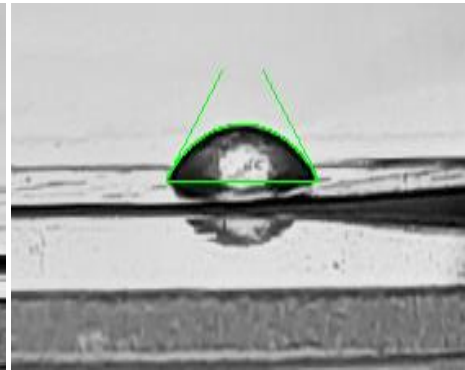
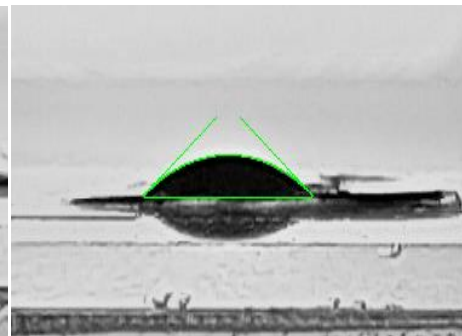**Figure 26: PA-APTMS**
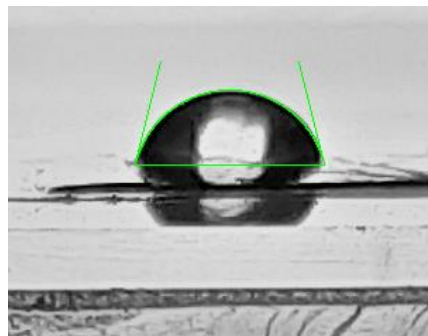
Figure 27: PA-Br

Figure 28: PA-PAA

Table 6: Contact angle of Membranes

Sample	Contact Angle(degree)
Commercial PA Membrane	68.676
Functionalized PA Membrane	51.66
Initiator Attached Membrane	75.73
Grafted PA Membrane	36.381
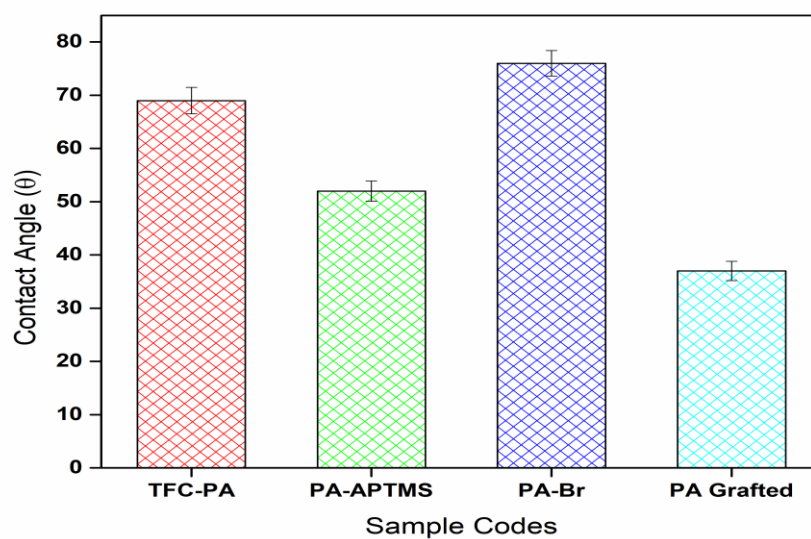
Figure 29: Figure showing contact angle of Membrane

As can be seen the contact angle in case of pristine TFC-PA is 68.676^0, after the functionalization of this membrane with APTMS the contact angle is reduced to 51.66^0. The contact angle is reduced because the surface becomes smooth and when the initiator molecule is attached the contact angle is increased due to an increase in roughness and contact angle for PA-Br is 75.73^0. And with grafting the contact angle is reduced to 36.38^0 with an increase in hydrophilicity which will increase wet ability.

5.4 Optical Profilometry

As it can be seen from graph, that surface roughness is increased with grafting. Before grafting, the intrinsic roughness of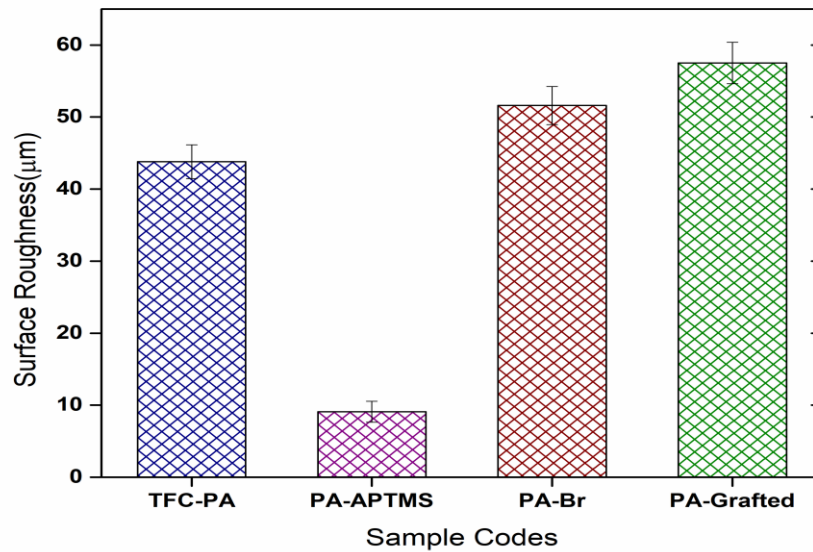 TFC-PA is 43.8μm. On functionalization with APTMS the intrinsic roughness is reduced to 9.1μm and membrane surface becomes smooth. When initiator is attached to this functionalized surface, surface roughness again increased to 51.23μm and on grafting the roughness increased to 58.23μm which is greater than intrinsic roughness. This increase in roughness indicates that the grafted membrane is in Wenzel State so with increase in roughness the intrinsic wettability will be increased and surface will become more hydrophilic. Surface roughness increases due to growth of polymer brushes. As a result of which membrane will foul less.

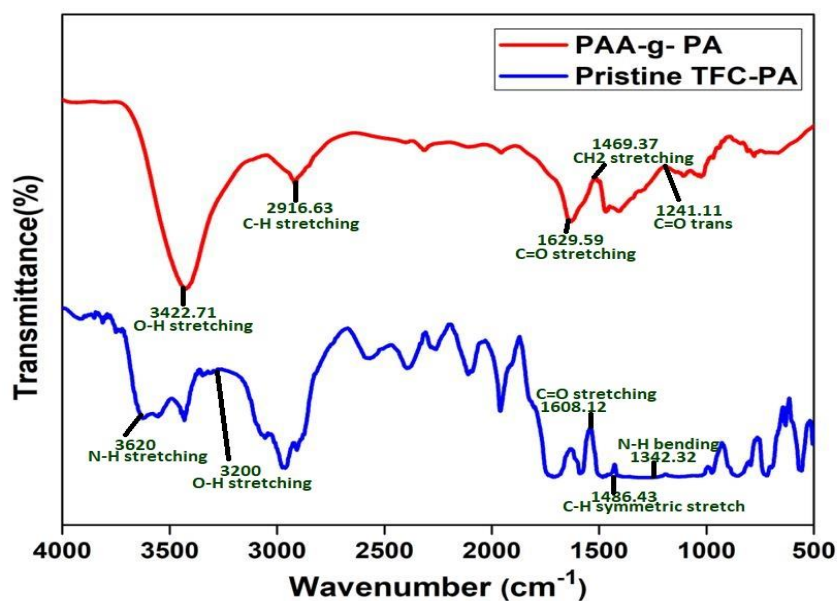## 5.5 Fourier Transform Infrared Spectroscopy:

Figure 31: FTIR of Membranes

In the Figure above it has been shown the FTIR results of the different samples of commercial and grafted membrane. In the FTIR Graph of TFC-PA at a wave number of 3620cm^{-1} there is N-H intermolecular bond stretching of primary amine group. The broad peak indicates weak bonding. At wave number of 3200cm^{-1}, there is stretching of intermolecular bond O-H and broad peak indicates that bond is weak. At wave number of 1486.4cm^{-1}, there is a C-H stretching of methylene group. At wave number of 1342.32cm^{-1} there is stretching of N-H. In the graph of PAA grafted membrane there is bond stretching of hydroxyl group at 3422.71cm^{-1} and C-H bond stretching occurs at 2916.3cm^{-1} which is weak. At wave number of 1629.59cm^{-1} the tertiary amide group is present. At 1469.37cm^{-1} methylene group is present. The presence of hydroxyl group and methylene group confirms grafting of PAA on TFC-PA membrane.
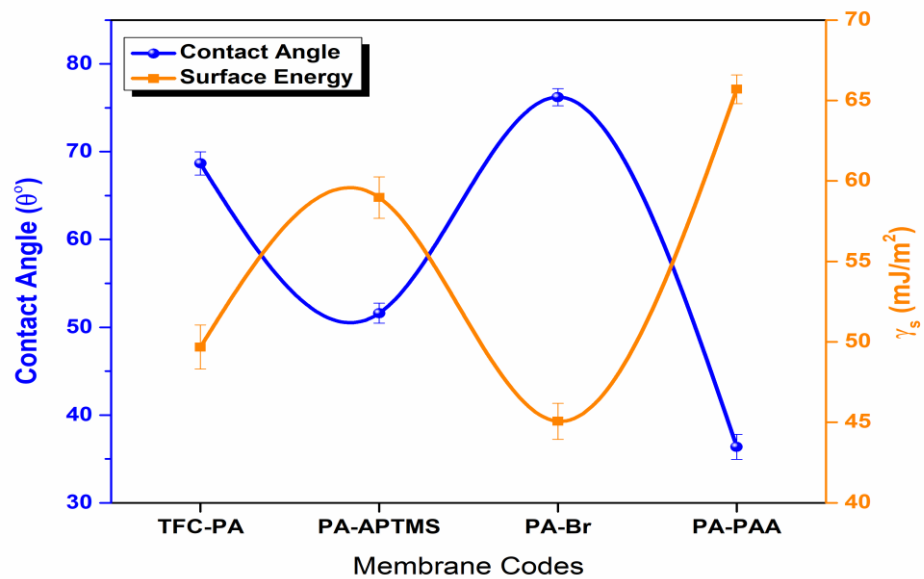
5.6 Surface Energy

Figure 32: Graph showing surface energy of Membranes

The wetting angle of the commercial TFC membrane is 68.67^0 and membrane is hydrophilic. The surface energy is calculated by young Dupree equation have a value of $50mJ/ m^2$. The functionalized membrane has angle of 51.66^0 and surface energy increases about $58.5mJ/m^2$. This shows that is membrane is ready to attach the initiator molecule because of increase in smoothness due to increase in energy. The initiator attached membrane PA-Br has angle of about 76^0 and surface energy decreases to $45mJ/m^2$. The grafted membrane PA-PAA has contact angle of 36.38^0 and surface energy is increased to 130 mJ/m^2 the decreased contact angle will prevent the attachment of antifouling agents and increase surface energy indicates the increase in surface charge and surface roughness. The polymer brushes will repel the charged bacteria and fouling agents by forming opposite localized charges.
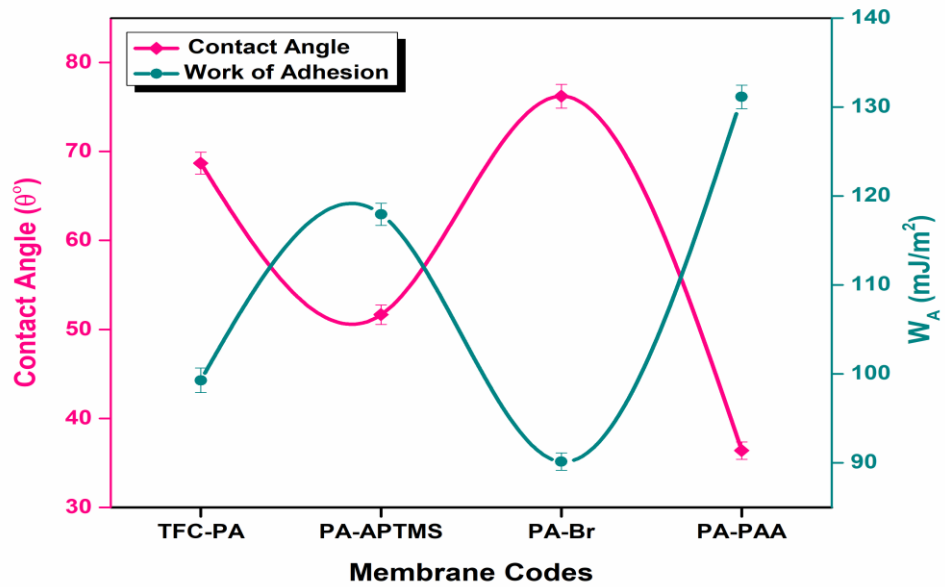
5.7 Work of adhesion

Figure 33: Work of Adhesion

The work of adhesion is the amount of energy required to separate two layers at infinite distance at equilibrium. The commercial membrane has a work of adhesion of 43 mJ/m^2 while the grafted membrane PA-PAA has an increase in the work of adhesion to 130 mJ/m^2 which shows that the energy required to separate apart the membrane surface increases thus upon an increase in pressure membrane will be more stable. Moreover, with increase in work of adhesion and surface energy the membrane will foul less due to an increase in surface tension and contaminants are not strong enough to break through this surface tension due to increase in hydrophilicity.

5.8 Water Flux

Water flux and different pressures are calculated by Poisseullie Equation. This equation relates to water flux with differential pressure. It is a theoretical way to determine water flux through average number of pores per m^2. In the case of grafted membrane, the average number of pores was found to be 16 per 0.5μm. And the average pore radius was found to be 90nm. Different values for pressure were taken and water flux was then calculated against these values as shown in the graph.
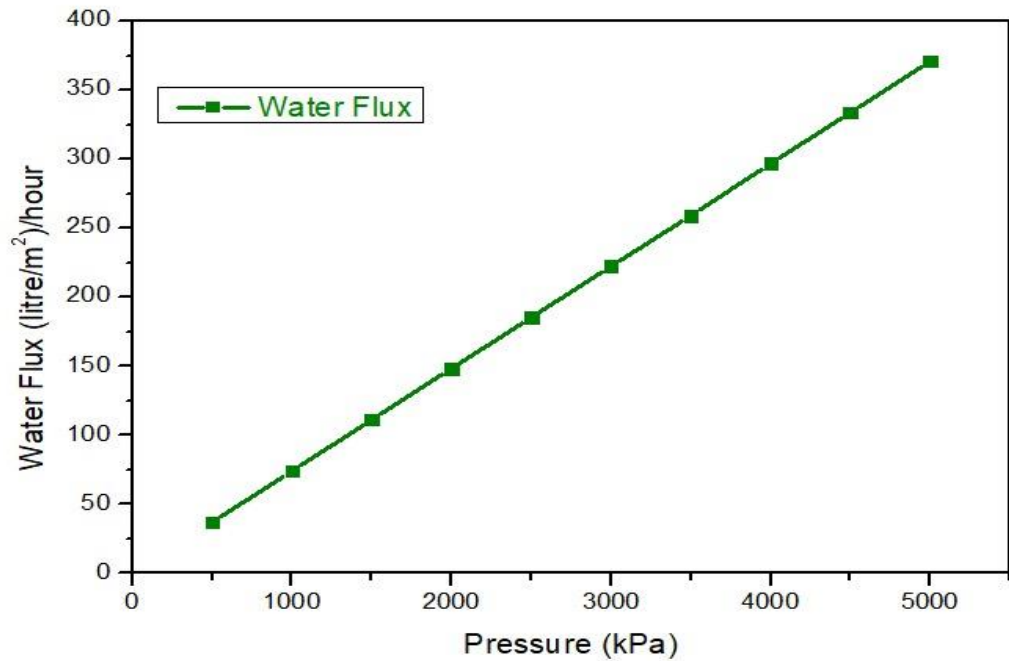
Figure 34: Graph showing water flux

This graph between water flux and Pressure confirms the water flux regulation. It is an important step to decide whether the membrane is water flux regulated or not. Reverse osmosis membranes are wrapped in the form of cylinder and place in the water feed in parallel direction. The transverse side contains pores and allows water flow to pass while longitudinal side is smooth. An increase in the pressure increases the water flux rate confirms the water flux regulation.

5.9 pH-Responsive Water Flux Study

The water flux varied due to change in pH because of the phenomena of Protonation and deprotonation of carboxylic acid group. At low pH, the chains are protonated with helical conformation and at high pH, the chain is in extended conformation due to deprotonation .
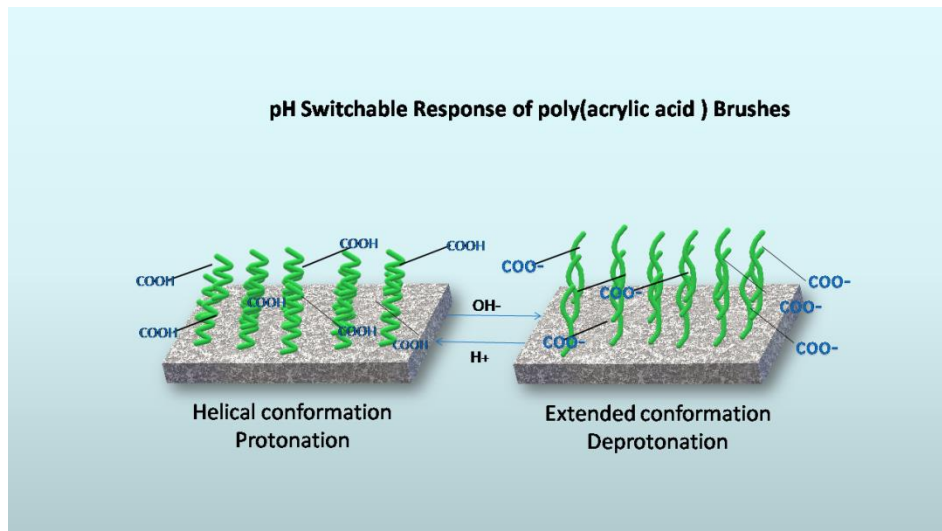
Figure 35: pH switchable response of PAA
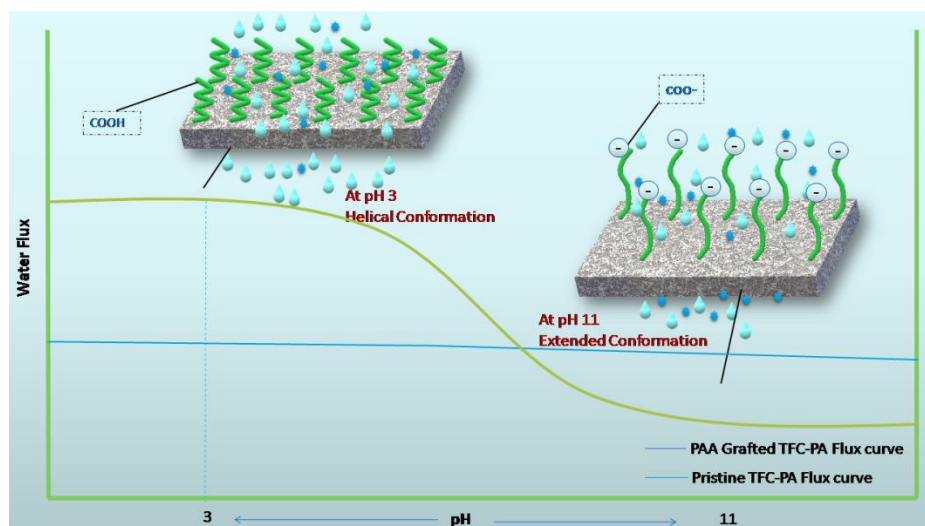
Figure 36: Schematic relation of water flux with change in pH

As it can be seen in figure.36 at pH of 3 water flux is maximum and brushes have a helical conformation and at pH 11 the brushes are deprotonated and have an extended conformation, but the water flux is low at pH 11 and it is maximum at pH 3 and it decreases afterward. Change in water flux is due to protonation and deprotonation. At low pH, there is no charge on membrane surface and pores are wide open due to helical conformation so flux is greater and with increase in pH negative charge appears on membrane surface due to deprotonation and pores become narrow due to which water flux decreases.
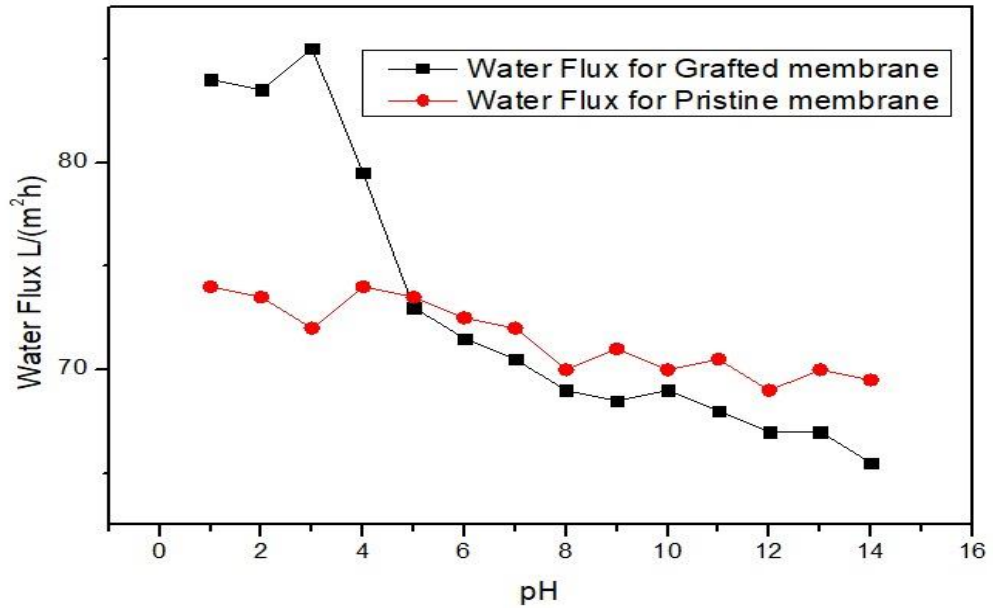
Figure 37: Graph presenting relation of change in water flux with pH

As it can be seen from figure 37, for pristine membrane there is no frequent change in water flux at 3200 KPa Pressure with change in pH this is because pristine membrane is neutral. Whereas there is a significant change in water flux of PAA grafted membrane due to protonation at low pH and deprotonation at high pH as can be seen through figures 35 and 36. For grafted membrane maximum flux is observed at pH 3 having a value of 85.5 $L/(m^2.h)$ whereas at pH 11 the flux is reduced to 68 $L/(m^2.h)$.

CONCLUSION

The polymeric brushes were successfully grafted on the TFC- PA commercial membrane by ATRP on lab scale. This was a controlled reaction and took place in inert atmosphere to avoid reaction of oxygen with initiator attached surface. The results are satisfactory and are as per the literature. There is increase in the hydrophillicity and surface energy of the membrane. The behaviour of the contact angle and Surface energy is studied and the following conclusion is drawn based on this research project and these results are found in accordance with literature.

1. First phase of project represents successful synthesis of densified membrane of PES at lab scale, whose major purpose is to learn membrane fabrication at lab scale.

2. Grafting of the polymeric brushes of polyacrylic acid on to the membrane surface and proceeding of reaction is monitored by the optical microscopy, contact angle, FTIR, SEM.

3. Membrane characterization results revealed that grafting of PAA brushes has remarkable effect on the membrane properties such as Surface energy, hydrophilicity contact angle and permeation flux was observed. Due to the growth of PAA brushes the membrane morphology has also been changed.

4. Rate of Flux regulation

5. SEM and Optical Microscopy results show that some type of brush like structure is present on surface.

6. The effect of change in pH on water flux indicates that, the membrane is switchable and maximum flux is obtained at pH 3.

7. The increase in hydrophilicity contributes to antifouling properties.

8. The increase in surface roughness with grafting confirms the presence of brushes on membrane surface after grafting.

FUTURE RECOMMENDATIONS

- By adjusting the flux rate, salt rejection rate can be enhanced.
- Effect of temperature, pressure and mechanical parameters on the modified membrane
- Study of antifouling properties
- Study for investigating the performance of membrane for seawater and brackish water

REFERENCES

[1].   Water U (**2007**) Coping with water scarcity: Challenge of the twenty-first century. Prepared for World Water Day.

[2].   Shi W, He B, Ding J, Li J, Yan F, et al. (**2010**) Preparation and characterization of the organic-inorganic hybrid membrane for biodiesel production. Bioresour Technology 101: 1501-1505.

[3].   Jhaveri JH, Murthy Z (**2016**) A comprehensive review on anti-fouling nano-composite membranes for pressure driven membrane separation processes. J Desal 379: 137-154.

[4].   Van de Lisdonk C, Van Paassen J, Schippers J (**2000**) Monitoring scaling in nanofiltration and reverse osmosis membrane systems. J Desal 132: 101-108

[5].   Rezakazemi M, Dashti A, Harami HR, Hajilari N (**2018**) Fouling-resistant membranes for water reuse. Environ Chem Letters: 1-49.

[6].   Kochkodan V, Hilal N (**2015**) A comprehensive review on surface modified polymer membranes for biofouling mitigation. J Desal 356: 187-207.

[7].   Jeshi, S.A., Neville, A., (**2006**). An investigation into the relationship between flux and roughness on RO membranes using scanning probe microscopy. Desalination 189, 221e228.

[8].   Louie, J.S., Pinnau, I., Ciobanu, I., Ishida, K.P., Ng, A., Reinhard, M., **2006.** Effects of polyether-polyamide block copolymer coating on performance and fouling of reverse osmosis membranes. Journal of Membrane Science 280, 762e770.

[9]. Wang, J., Pan, C.J.,Huang, N., Sun, H., Yang, P., Leng, Y.X., Chen, J.Y., Wan, G.J., Chu, P.K., **2005**. Surface characterization and blood compatibility poly(ethylene terephthalate) modified by plasma surface grafting. Surface & Coatings Technology 196, 307e311.

[10]. Wu, S.Y., Xing, J., Zheng, C., Xu, G.F., Zheng, G.D., Xu, J.P., **1997**. Plasma modification of aromatic polyamide reverse osmosis composite membrane surface. Journal of Applied Polymer Science 64, 1923e1926.

[11]. Zou, H., Jin, Y., Yang, J., Dai, H.J., Yu, X.L., Xu, J., **2010**. Synthesis and characterization of thin film composite reverse osmosis membranes via novel interfacial polymerization approach. Separation and Purification Technology 72, 256e262.

[12]. Hachisuka, H., Ikeda, K., **2001**. Composite reverse osmosis membrane having a separation layer with polyvinyl alcohol coating and method of reverse osmosis treatment of water using the same. US Patent 6,177,011 B1.

[13]. Kim, I.C., Lee, K.H., **2006**. Dyeing process wastewater treatment using fouling resistant nanofiltration and reverse osmosis membranes. Desalination 192, 246e251.

[14]. Louie, J.S., Pinnau, I., Ciobanu, I., Ishida, K.P., Ng, A., Reinhard, M., **2006**. Effects of polyether-polyamide block copolymer coating on performance and fouling of reverse osmosis membranes. Journal of Membrane Science 280, 762e770.

[15]. Zou, H., Jin, Y., Yang, J., Dai, H.J., Yu, X.L., Xu, J., **2010**. Synthesis and characterization of thin film composite reverse osmosis membranes via novel interfacial polymerization approach. Separation and Purification Technology 72, 256e262.

[16].   Kulkarni, A., Mukherjee, D., Gill, W.N., **1996**. Flux enhancement by hydrophilization of thin film composite reverse osmosis membranes. Journal of Membrane Science 114, 39e50.

[17].   Van Wagner, E.M., Sagle, A.C., Sharma, M.M., La, Y.H., Freeman, B.D., **2010**. Surface modification of commercial polyamide desalination membranes using poly(ethylene glycol) diglycidyl ether to enhance membrane fouling resistance. Journal of Membrane Science 367, 273e287.

[18].   Belfer, S., Purinson, Y., Kedem, O., 1998a. Surface modification of commercial polyamide reverse osmosis membranes by radical grafting: an ATR-FT-IR study. ActaPolymerica 49, 574e582.

[19].   Cadotte, J.E., Petersen, R.J., Larson, R.E., Erickson, E.E., **1980**. A new thin-film composite seawater reverse osmosis membrane. Desalination 32, 25e31.

[20].   X.Y.,Wang, Z., Zhang, Z.,Wang, J.X.,Wang, S.C., 2010b. Surface modification of commercial aromatic polyamide reverse osmosis membranes by graft polymerization of 3-allyl-5,5- dimethylhydantoin. Journal of Membrane Science 351, 222e233.