CHAPTER III

RESEARCH METHODOLOGY

3.1 General Preview

In a last decade, Pinnau and Koros (1992) produced an ultrathin defect-free skin layer by using a dry/wet phase inversion process. The thickness of the skin layer achieved was of the order of 200Å. One of the empirical rules for the formation of optimized membrane using this technique is that the dope solution must consist of at least three components: a polymer, a solvent and a non-solvent. Moreover, composition of dope solution, evaporation time and quench step are the important factors in the production of high performance nanofiltration membrane.

This chapter describes on the development of a new nanofiltration-surfactant membranes for removal of dye wastewater. The materials selection, dope preparation, membranes fabrication, performance evaluation and characterization are well discussed in this section. In addition, characterization of the developed NF membranes using Scanning Electron Microscope (SEM) allowed determination of the effects of rheological and preparation factors on the performances and morphological structures. Besides SEM, Fourier-Transform Infrared (FTIR) was used to confirm the functional group of the polymer used. In this study, Differential Scanning Calorimetry (DSC) was used to determine the thermograms of the polymer-solvent systems. Thermogravimetry Analysis (TGA) was also used in order to determine the thermal stabilities of the polymer material since polyethersulfone (PES) can withstand high temperatures. In order to produce high performance of nanofiltration-surfactant (NFS) membranes, membrane was fabricated using a simple semi-technical or technical membrane fabricator at different conditions based on an established dry/wet phase inversion technique.

3.2 Research Design

Fabrication of high performance nanofiltration-surfactant (NFS) membranes can be influenced by many factors. The parameters that determine the performance of NFS membrane include polymer selection, solvent and non-solvent selection, solution preparation method, casting parameters, flux and rejection test and microsolute transport test. Then, separation performance of NFS membranes is evaluated based on salt rejection, microsolute transportation and color removal of dyes. The research design of this study is as illustrated below:

FIGURE 15: Factors Affecting the Newly Developed Nanofiltration-Surfactant (NFS) Membrane

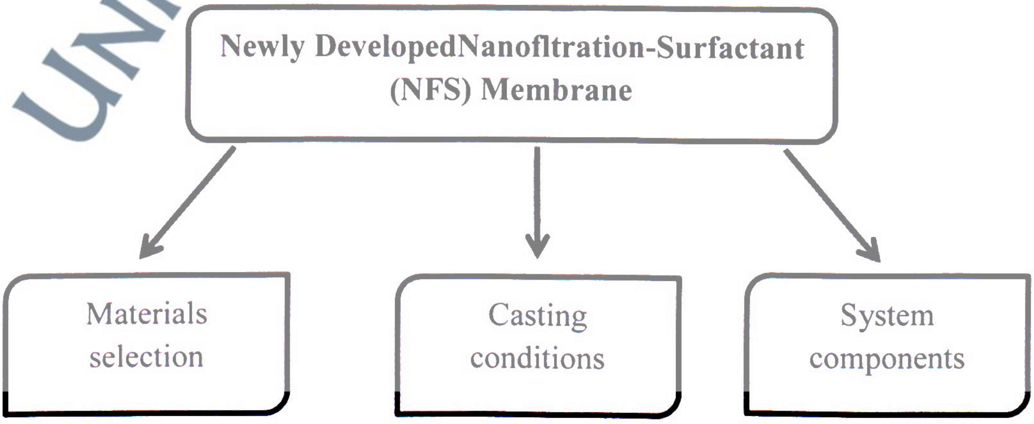
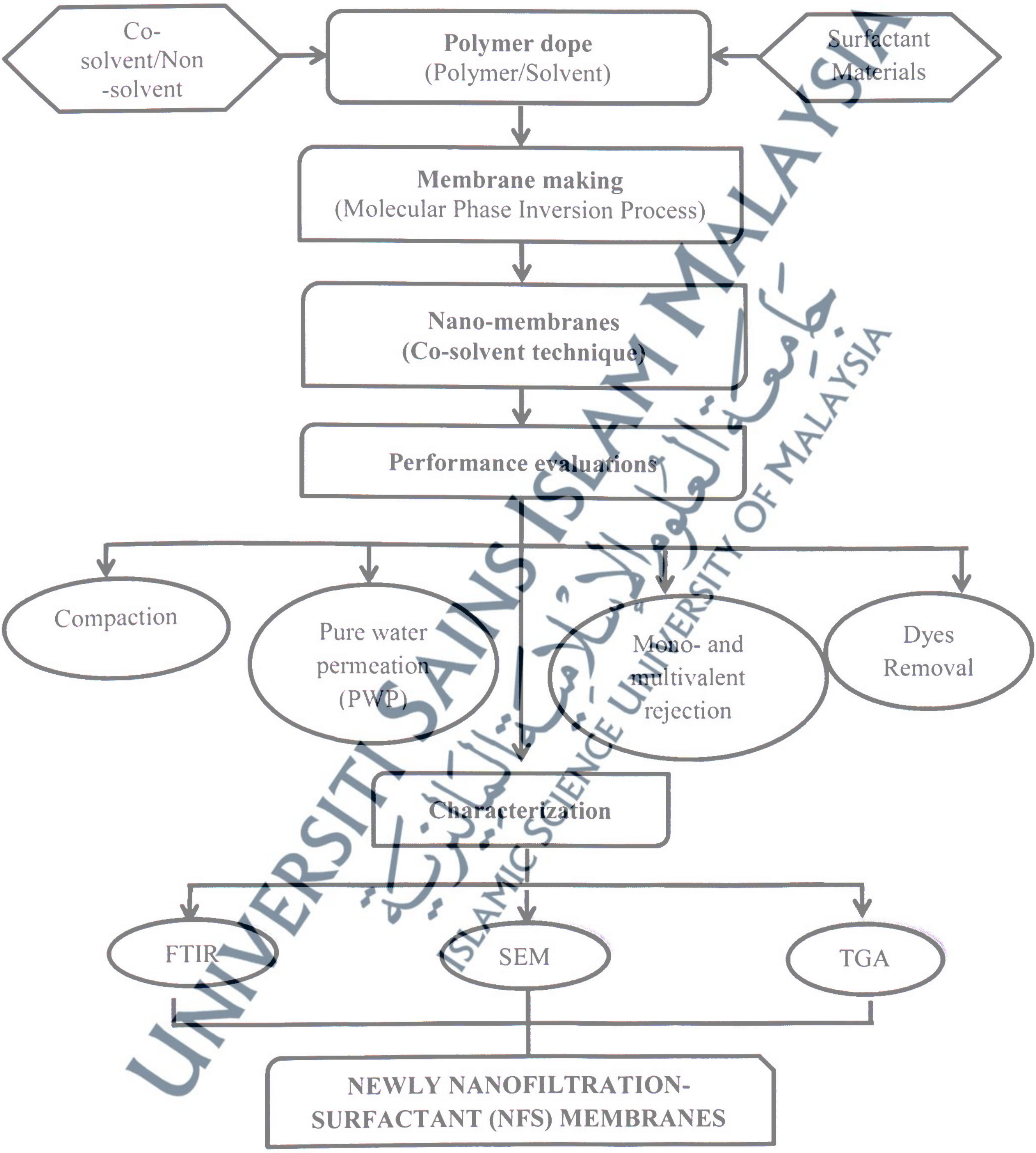


FIGURE 16: Research Framework



3.3 Materials Selection

3.3.1 Polymer

Because of its toughness, good thermal resistance and chemical inertness, polyethersulfone (PES) is commercially available, thermally stable polymer used in high-performance applications. For important separation processes, PES has been conformed as the membrane material including for biological process, pharmaceutical process and sterilization filtration. In many cases, using PES needs use of wetting agent prior to filtration due to its high hydrophobicity which severely restricts its long-term applicability. For the membrane industry, achieving the desired surface properties without modification of the advantageous properties of PES membrane is the important goal (Rahimpour et. al., 2010).

In order to develop nanofiltration-surfactant (NFS) membranes, dope solutions for this study are prepared in the range of 17-21%. The less concentration of polymer solutions tends to produce a more hydrophilic and porous membrane. Therefore, this aspects will help on the determination of better membranes performances with a highly permeation rate.

FIGURE 17: Monomer Unit of Polyethersulfone (PES)

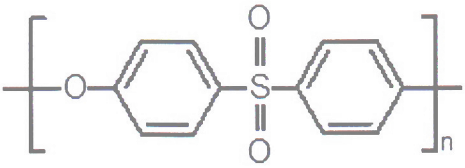


TABLE 6: Physical, mechanical and thermal properties of Polyethersulfone (PES)

Property	Average
Molecular weight of repeat unit (g/mol)	232.26
Weight average molecular weight (Dalton)	15 000
Density (g/cm^3)	1.40
Glass transition Temperature (°C)	220.0
Tensile strength (yield) (psi)	12 000
Shear strength (MPa)	50.0
Tensile modulus (psi)	385 000
Elongation at break (%)	50.0-100.0
Compressive strength (yield) (psi)	14 500
Thermal conductivity (W/m.K)	0.22
Dieletric strength (V/mil)	380
Transparency (%)	76

3.3.2 Solvent

The selection of proper solvents for casting of polyethersulfone membranes involves the following conditions; the solvent must be miscible with the coagulating agent and the solvent must provide good mechanical properties. In such a casting procedure, it is recommended that good solvents be used which have the power to open and solvate the polymeric chains. Lau et. al. (1991) reported that NMP shows high solvent miscibility and high ranking in solvent dissolution power compared to the other solvent (Tetramethylurea, Dimethylacetamide, Dimethylsulfoxide and Dimethylformamide). The solvent mixture of NMP and water is easily miscible with water as the coagulant; fast coagulation took place from both sides of the nascent membrane and the fast solidification across the overall membrane wall restricted the growth of macrovoids in the polymer-lean phase (Wang et. al., 2000). In this study, the organic chemical used in dope solution isN-methyl-2-pyrrolidone (NMP, >99%). Three steps of solvent exchange fluids included water, ethanol and n-hexane are used in order to produce the membrane with the best permeation properties. Tap water used as the coagulation medium and temperature is controlled at 25°C.

FIGURE 18: Formula structure of N-methyl-2-pyrrolidone

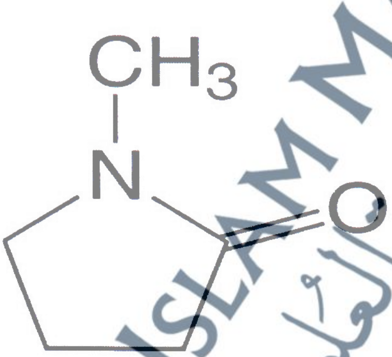


TABLE 7: Properties of N-methyl-2-pyrrolidone (NMP)

Physical and Chemical Properties	
Solubility in water: very good	
Formula molecule	C_5H_9NO
Molecular weight (g/mol)	99.1
Boiling point (°C)	202
Relative vapour density (air = 1)	3.4
Relative density of the vapour/air-mixture at 20°C (air = 1)	1.00
Vapour pressure, Pa at 25°C	66
Liquid viscosity (Pa.s)	1.66×10^{-3}

3.3.3 Non-Solvent

Distilled water is used as non-solvent in this study. With a molecule weight of 18.02 g/mol, it is strong non-solvent because of its deviates strongly from ideal behavior where most organics mixtures do not behave ideally caused by the resistance of polar interactions or hydrogen bonding (Mulder, 1996). Water normally used as non-solvent in phase inversion technique by precipitating a cast polymer solution for PES membranes (Lau et. al., 1991).

When water is added into the polymer solution, the polymer coil in the solution is shrunk because water is a strong non-solvent for PES. As a result, super molecular polymer aggregates with big size may be easily formed in this solvent system (Wang et. al., 2000). It is an evident that the internal coagulant plays an important role in fabricating good membranes. Water is a good internal coagulant for making membrane because water is non-solvent strength for polymer and miscibility with the solvent (Wang et. al., 2000). Water molecule will enter the surface of membrane during the evaporation of the solvent. Thus, this will lead to the formation of the finger-like structure in the membrane.

3.3.4 Poly (ethylene glycol) (PEG)

Instead of chemical modification of polymer, addition of additives such as poly (ethylene glycol) (PEG) is proposed to increase the hydrophilic property of the membrane and also the diffusive transport properties of solute through the nanofiltration membrane. Researcher has been discovered that addition of PEG additives in cellulose acetate ultrafiltration membrane influenced the membrane characteristic in terms of pore size, permeate flux and the rejection rates. The combination of polymer, solvent and additives used in membrane making technology is vast (Idris and Yet, 2006).

According to Kim and Lee (1998), the used of PEG in polymer solution is to control the thermodynamics and kinetics in casting system. Through SEM pictures, it resulted the changes on morphological structure of the membrane when different molecular weight of PEG is used.

FIGURE 19: Structure of Poly (ethylene glycol) (PEG)

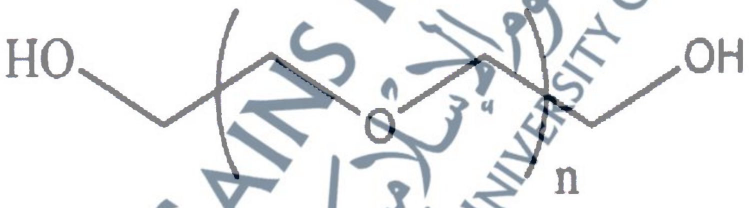


TABLE 8: Physical properties of Poly (ethylene glycol) (PEG)

Physical properties	
Formula	H $(OCH_2CH_2)_n$ OH
Physical State	Clear to white semi-solid
Solubility in water	Soluble
Stability	Stable under ordinary condition. Hygroscopic

3.4 Formulation of Polymer Solution

In general, a polymer solution formulation for asymmetric fabrication consists of polymer, solvent and non-solvent. This can be called as multi component casting formulation. Sometime, this formulation consists of four components, where polymeric additive is added. According to Chakrabarty et. al. (2008), addition of additive into the casting solution is one of the major factors. In order to have an optimal membrane structure, additive is used in casting solution. Besides, additive can be single component or a mixture. Generally, additive being a weak non-solvent for the polymer reduces the solvent power in the solution.

3.4.1 Turbidimetric Titration Method

Equilibrium thermodynamic data on ternary system (polymer/solvent/non-solvent) can be determined by turbidimetric titration method. Cloud point represents an approximate transition boundary beyond which demixing (phase separation) takes place, indicating that a polymer solution has become thermodynamically unstable (Zeman and Fraser, 1993). At the cloud point, the polymer solution changes from clear to turbid condition. Therefore, equilibrium composition of dope solution consisting polymer, solvents and non-solvents additive can be determined by using turbidimetric titration method.

FIGURE 20: Cloud Point of Polymer Solution

In turbidimetric titration, as shown in Figure 25, a homogenous polymer solution with specific composition was initially prepared by dissolving a polymer in a solvent (a non-volatile solvent) and polymer additive at room temperature (35°C). Then, surfactant was added when all the additives were dissolved in the polymer solution. Subsequently, 100g of polymer solution was titrated with a pure non-solvent (water). The titrated solution was stirred and held at constant temperature (30°C), while caution had to be exercised to minimized solvent loss. Cloud point (turbidity end point) could be easily recognized by visual observation. The amount of added non-solvent was then determined gravimetrically.

As customary, coagulation value of a ternary system can be determined by cloud point measurements. Coagulation value (CV) is defined as quantity of non-solvent required to make 100g-polymer solution containing 2g polymer turbid (Wang et. al., 2000). Each set of data was obtained as an average of at least three measurements.

FIGURE 21: Apparatus for Turbidimetric Titration Step

3.4.2 Multi Component Dope Preparation

In making polymer solution, polymer was first dried for at least 24 hours in a vacuum oven at a temperature of about 100±2°C in order to remove all absorbed water vapor. The existence of water in the polymer solution will influence the quality of a polymer solution. Thermometer was used to measure the temperature during the demixing process. Processing temperature is controlled at the desired range. The function of stirrer was to ensure that the polymer, solvent and non-solvent were well mixed to form a homogenous solution.

Figure 22 showed on how we prepared our membrane. Firstly, the solvent and water was poured into the round bottom flask until the temperature increase to 50-60°C. Thermometer measured the temperature while heater controlled the required temperature range. The mixing temperature must be controlled and maintained not exceed the boiling point of the solvents and non-solvent (100°C) because they tend to vaporize. However, the low temperature will not encourage the mixing process. When temperature has reached 50°C, polymer was added gradually until the entire polymer had dissolved. When the polymer had dissolved, an additive was added. The solution was being stirred for 1 hour before surfactant was added into the polymer solution. The best time to add surfactant is 3 hours before the polymer solution is completely done.

FIGURE 22: Apparatus for Dope Solution Preparation

TABLE 9: Dopes formulations for NFS membrane fabrication

Membranes		PES (%)	NMP (%)	PEG (%)	SDS (%)	CTAB (%)
MO	**1**	17	83	-	-	-
	2	19	81	-	-	-
	3	21	79	-	-	-
MP	**1**	17	78	5	-	-
	2	19	76	5	-	-
	3	21	74	5	-	-
MPS	**1**	17	76	5	2	-
	2	19	74	5	2	-
	3	21	72	5	2	-
MPC	**1**	17	76	5	-	2
	2	19	74	5	-	2
	3	21	72	5	-	2

3.5 Membrane Casting

Asymmetric nanofiltration membranes were fabricated according to the dry/wet phase separation process using manual casting blade. The casting speed was kept constant at 10 seconds with the casting knife gap at 150μm.

FIGURE 23: Casting Knife

The casting process was conducted at room temperature (30±2°C) and approximately 84% relative humidity. A small amount of casting solution was poured onto a glass plate with a casting knife gap setting of 150μm and at casting rate of 10 seconds.

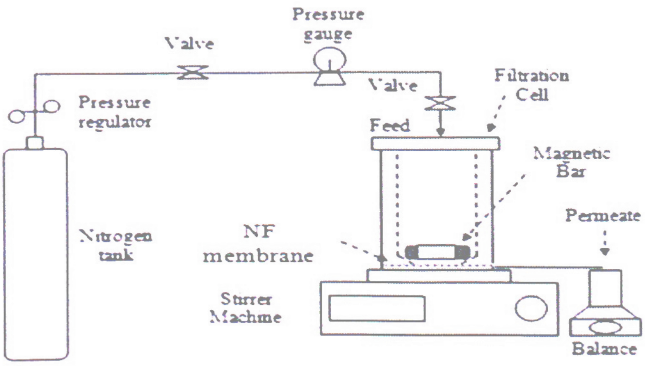
After the membrane was cast, the glass plate support together with the membrane was then immersed into the coagulation bath (composed of water as the coagulant medium). After the of process coagulation complete, the membranes were transferred into a water bath for 24 hours (1 day). After that, the membrane will soak into ethanol for another 24 hours (1 day). Finally, membrane was soaked in n-hexane for 2-3 hours before air dried for at least 24 hours at room temperature to remove residual organic compounds. The use of the liquid exchange treatment was to prevent changes in the structure and properties of membranes caused by large capillary forces during drying. This is especially important when non-volatile solvents were being dried afterwards, water will be removed first and the solvent left behind may damage the membrane structure.

3.6 Performance Evaluation

3.6.1 Nanofiltration Permeation Rig

Using the designated filtration cell as in Figure 28, a circular disk membrane were being cut and mounted in a stainless steel, cylindrical membrane test cell by a porous support and being tightened by a rubber *O*-ring. Effective area of the membrane being mounted under the cell was 1.39 x 10^{-3} m^2. The operating pressure for filtration process is being supplied by pressurized nitrogen gas. The nitrogen gas outlet pressure was regulated using a pressure regulator where the equilibrium pressure was shown in the pressure gauge. A pressure relief valve was being installed between the nitrogen gas and cell.

FIGURE 24: Schematic Diagram of NF Filtration Set-up



3.6.2 NF Permeation Test

Nanofiltration permeation was done using dead end filtration unit at different pressure. For each operating pressure, distilled water was used to determine the pure water permeability (PWP) parameter/constant. PWP was obtained from the slope of volume flux versus pressure. Prior to the each nanofiltration test, membrane was subjected for the passage of the first 10 ml permeate whilst the following 10 ml permeate was collected for concentration analysis. All the results presented were averaged data obtained through 12 membranes samples with a variation of about ±10%. The permeate was collected and weight was measured by an electronic balance for every minute. The volume flux was calculated based on the weight and time as follow,

$$Jv = \frac{V}{A \times \Delta t}$$

Where;

J_v = permeate flux (L/m^2 h)

V = volume of permeate solution collected (L)

A = the effective area of membrane (m^2)

Δt = the time (h)

The rejection characteristics of a membrane were described by determining observed rejection, R_{obs} and real rejection, R_{real}. In the membrane separation processes, the concentration on the membrane surface is always higher than in the bulk due to concentration polarization. A concentration on the membrane surface is not directly obtained from experiment thus the following equation is applied:

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

Where;
R = rejection
C_p = Permeate concentration
C_f = Feed Concentration

3.6.3 Pure Water Permeation

As PWP parameter and flux were obtained, the membrane permeation test was carried out according to the procedure stated in Section 3.6.2. At five different operating pressures that are 3bar, 3.5bar, 4bar, 4.5bar, and 5bar the permeation test was carried out using 0.01M NaCl. The flux and observed rejection were determined for each operating condition. In order to reduce the polarization effects, the stirring speed is fixed at 400rpm or 41.881 rad/sec. After each permeation test, NF membranes surface was rinsed with distilled water. The pure water permeability was measured to ensure the original flux (pure water) was recovered before next permeation test. The feed concentration of each salt solution is also fixed at about 0.01M.

3.6.4 Multivalent Salts (Na_2SO_4, $MgSO_4$, NaCl, $MgCl_2$)

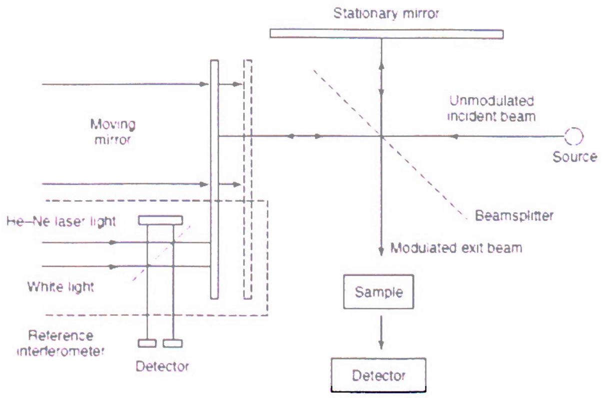
The permeation test was conducted similar to procedure as in Section 3.6.3. In order to study the effect of rejection under different volume flux, operating pressure has been constant at 4 bar to obtain its respective flux. The salt permeation test was carried out using 0.01M of Na_2SO_4 solutions. After each permeation test, NF membranes surface is rinsed with distilled water. The pure water permeability was measured to ensure the original flux (pure water) was recovered before next permeation test was running. The same procedure was repeated for the other type of salts ($MgSO_4$ and $MgCl_2$). The feed and permeate concentration for each salts were measured by using conductivity meter. The flux and rejection were determined for each operating condition.

3.7 Physico-chemical Characteristics of NFS Membranes

3.7.1 Fourier-Transform Infrared (FTIR)

FTIR exploits the well-established mathematical process and employs and interferometer. Based on the vibrations of the atoms of a molecule is how infrared spectroscopy works. By determining what fraction of the incident radiation, an infrared spectrum is commonly obtained by passing infrared radiation through a sample which is absorbed at a particular energy. Corresponding to the frequency of vibrations of a part of a sample molecule, the energy at which peak in absorption spectrums will appear (Stuart, 2004). In this study, the wavelength used was 400-4000 cm^{-1} in confirmation of material used in developing membrane polymer solution.

FIGURE 25: Operating Principle of Fourier-Transform Infrared (FTIR)

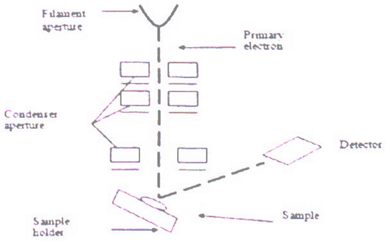


3.7.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) was a very useful technique for membrane morphological characterization. This method was used for the determination of membrane structure, membrane thickness and membrane surface. The principle of the Scanning Electron Microscope was illustrated in Figure 30. A narrow beam of electrons with kinetic energies in the order 1-25kV hits the membrane sample. The incident electrons are called primary (high-energy) electrons, and those reflected are called secondary electrons.

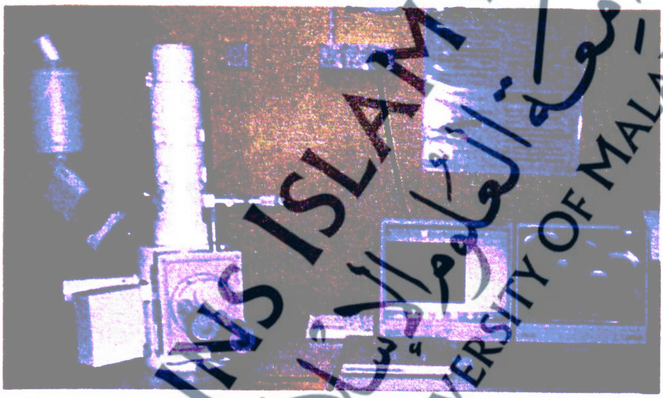
Secondary electron (low energy) are not reflected but liberated from atoms in the surface, determine the imaging (what is seen on the screen or on the micrograph). When a membrane was placed in the electron beam, the sample can be burned or damaged, depending on the type of polymer and accelerating voltage employed. This can be avoided by coating the membranes with a conducting layer (gold palladium) to prevent charging up the surface. Scanning electron microscopy allows a clear view of the overall structure of the membranes; the top surface, the cross section and the bottom surface can all be observed nicely. In addition, the porosity and the pore size distribution can be estimated from the micrographs obtained.

FIGURE 26: The Principle of Scanning Electron Microscopy



c For this purpose, samples of the membranes (surface and cross-section) were fractured cryogenically in liquid nitrogen and mounted on sample stubs with double-surface tape. After the samples were sputtered with gold by an automatic gold coater (JFC 1600), they are scanned by employing a JEOL JSM 6360LA Scanning Electron Microscope (Tokyo, Japan) as shown in Figure 31 under magnification of 500x to 5000x with potentials of 20kV.

FIGURE 27: JEOL JSM 6360LA Scanning Electron Microscopy (SEM)



3.7.3 Thermogravimetric Analysis (TGA)

To measure the amount and rate of change in the weight of a material, thermogravimetric Analysis (TGA) is an analytical method technique as a function of temperature or time in a controlled atmosphere.. In TGA, the measurements were used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. To determine the characteristics of materials such as polymers, TGA is commonly employed in research and testing to determine degradation temperatures, absorbed moisture content of materials, the composition of inorganic and organic components in materials, decomposition points of explosives and solvent residues (Patton, 2008)

FIGURE 28: TGA Instrumentation

3.7.4 UV-Vis Spectrophotometer

Ultraviolet and visible spectrophotometers have become the most important analytical instrument in the modern day laboratory where it has been used in general analysis for the last 35 years. UV-visible spectrometry have several advantages that make it used in many applications such as simplicity, versatility, speed, accuracy and cost effectiveness (www.molecularinfo.com, accessed on 17th July 2014).

TABLE 10: Various spectral regions

Region	Wavelength (nm)
Far ultraviolet	10-200
Near ultraviolet	200-380
Visible	380-780
Near infrared	780-3000
Middle infrared	3000-30,000
Far infrared	30,000-300,000
Microwave	300,000-1,000,000

In UV-vis analysis, substance will absorbed the amount of ultraviolet or visible radiation where the radiations will be calculated. To ascertain the quantity of molecular species absorbing the radiation, organic compounds can be identified by spectrophotometers with addition of any recorded data that available for the certain organic compounds (Behera et. al., 2012).

UV-vis spectrophotometers are commonly used by most analytical scientist to measure the concentration and wavelength scanning absorbed by analytes in liquids. A basic principle of UV-vis is where light is generated by a source lamp for the visible region of spectrum and deuterium for the ultra-violet range. Resulting in narrow band of the dispersed spectrum, the light is then dispersed into a certain wavelengths in a monochromator. In the spectrophotometer, sample will absorbs a certain amount of light and the remaining light is detected by detector. To determine the amount of absorbed light, Beer-Lambert law is usually applied to calculate the concentration of specific analyte in the sample at a specific wavelength (www.labint-online.com, accessed on 17th July 2014).