CHAPTER III

MATERIALS AND METHODS

3.1 General Preview

This chapter describes on the development of low pressure reverse osmosis surfactant (LPROS) membrane for water desalination. The materials selection, dope preparation, membranes fabrication, performance evaluation and characterization are well discussed in this section.

In addition, characterization of developed LPROS membranes based on Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and Thermal Gravimetry Analysis (TGA) allowed determination of the effects surfactant concentration on morphological structures, physico-chemical properties and thermal study of the membranes.

3.2 Materials Selection

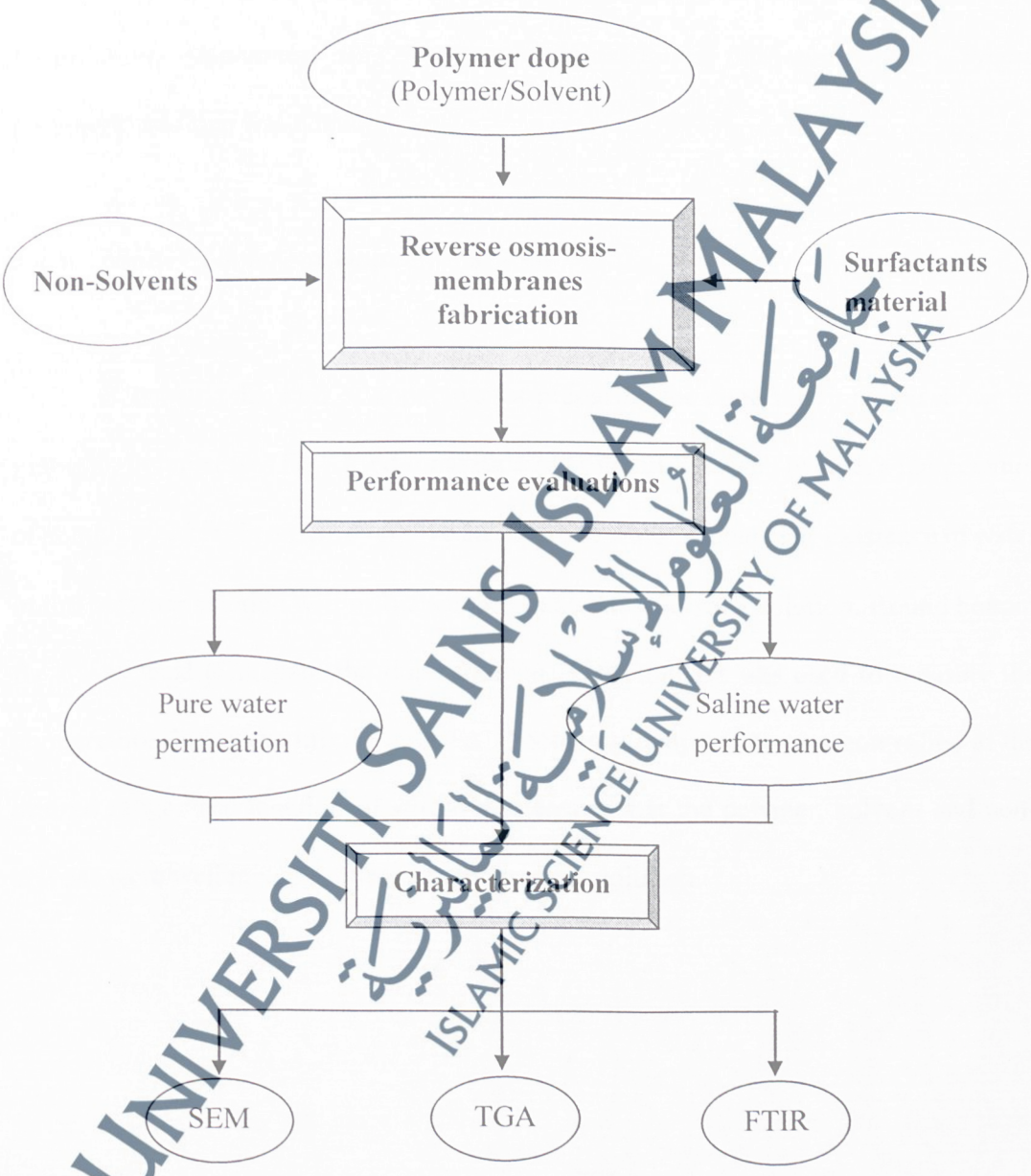
Polysulfone (PSF (Udel-P1700)) supplied by Solvay was used as polymer, while N-methyl-2-pyrrolidone (NMP, > 99%) supplied by Merck was used as non-solvent for membrane preparation. The additive, Polyvinylpyrrolidone, (PVP, K29-32) was

supplied by Acros Organics. Cetyl trimethylammonium bromide (CTAB) supplied by EMD Chemicals, meanwhile Triton X-100 and Sodium Dodecyl Sulphate (SDS) supplied by Fisher Scientific were used as cationic, non-ionic and anionic surfactant for addition in the casting solution. Ethanol and n-hexane that used as the coagulation bath were supplied by Merck. Sodium chloride, NaCl supplied by Merck was used for the salt rejection test.

3.3 Research Design

This research emphasized on the preparation factors which found to affect the performance of LPROS membrane. The research framework of this study was illustrated in Figure 5.

FIGURE 5: Research framework



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. Sometimes, this formulation consists of four components, where polymeric additive was added.

3.4.1 Multi Component Dope Preparation

Schematic diagram of apparatus for preparing the dope solution was shown in Figure 6. 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 vapour. The existence of water in the polymer solution will influence the quality of a polymer solution. Round bottom flask was used to prepare the dope solution. Thermometer was used to measure the temperature during the mixing process. Processing temperature was controlled at the desired range. The function of stirrer is to ensure that the polymer, solvent and non-solvent were well mixed to form a homogeneous solution.

FIGURE 6: Schematic diagram for dope solution preparation

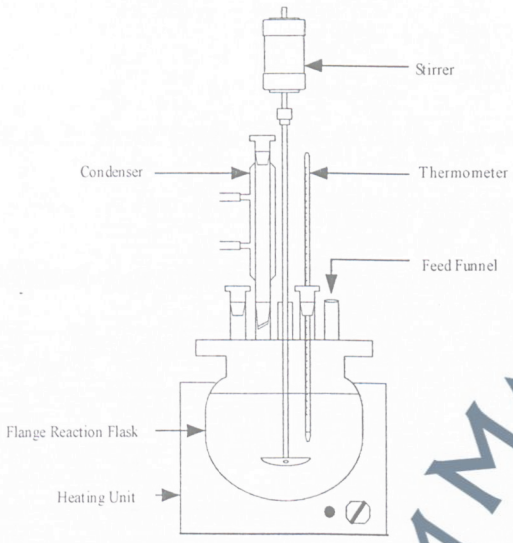


Table 8 described the dope formulation that had been prepared for this study. Firstly, the solvent which was NMP and water were poured into the round bottom flask until the temperature increase to 50-60 °C. Thermometer measured the temperature while heater controlled and maintained not exceeds the boiling 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 the temperature reached 50 °C, the polymer, PSF was gradually added until the entire polymer was dissolved. Then, the additive, PVP was gradually added to the dope after the polymer had been dissolved completely. The dope solution was stirred for about 1 hour before the surfactants (CTAB, Triton X-100 and SDS) being added into the solution. The best time to add surfactant is about 3 hours before the dope solution is completely done. The dope solution was left to stir until homogeneous, which typically takes of about 6-8 hours. After that, the solution was fully dissolved. It was poured into a clean bottle, and degassed using Branson

ultrasonics bath to remove trapped micro-bubbles of gases and particles prior to a casting process.

TABLE 2: Dope formulations of LPROS membranes

1) Membrane with different concentration of PSF polymer and without surfactant

Membrane	PSF (%)	NMP (%)	PVP (%)
PSP1	21	76	3
PSP3	23	74	3

2) Membrane with different concentration of PSF polymer and 2 wt. % surfactant

Membrane	PSF (%)	NMP (%)	PVP (%)	CTAB	Triton X	SDS
PSP1-C2	21	74	3	2.0	-	-
PSP3-C2	23	72	3	2.0	-	-
PSP1-T2	21	74	3	-	2.0	-
PSP3-T2	23	72	3	-	2.0	-
PSP1-S2	21	74	3	-	-	2.0
PSP3-S2	23	72	3	-	-	2.0

3) Membrane with 21 wt. % PSF with different concentration of CTAB

Membrane	PSF (%)	NMP (%)	PVP (%)	CTAB
PSP1-C1	21	75	3	1.0
PSP1-C1.5	21	74.5	3	1.5
PSP1-C2	21	74	3	2.0
PSP1-C2.5	21	73.5	3	2.5
PSP1-C3	21	73	3	3.0

4) Membrane with 21 wt. % PSF with different concentration of Triton X-100

Membrane	PSF (%)	NMP (%)	PVP (%)	Triton X-100
PSP1-T1	21	75	3	1.0
PSP1-T1.5	21	74.5	3	1.5
PSP1-T2	21	74	3	2.0
PSP1-T2.5	21	73.5	3	2.5
PSP1-T3	21	73	3	3.0

5) Membrane with 21 wt. % PSF with different concentration of SDS

Membrane	PSF (%)	NMP (%)	PVP (%)	SDS
PSP1-S1	21	75	3	1.0
PSP1-S1.5	21	74.5	3	1.5
PSP1-S2	21	74	3	2.0
PSP1-S2.5	21	73.5	3	2.5
PSP1-S3	21	73	3	3.0

3.4.2 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 which demixing (phase separation) takes place, indicating that a polymer solution has become thermodynamically unstable. At the cloud point, the polymer solution changes from clear to turbid condition. Therefore, equilibrium composition of dope solution consisting of polymer, solvents and non-solvent additive can be determined by using turbidimetric titration method. Turbidimetric titration was carried out using an apparatus shown in Figure 7.

In turbidimetric titration, a homogeneous polymer solution with specific composition was initially prepared by dissolving a polymer in a solvent (a nonvolatile solvent) and polymer additive at room temperature (35 °C). Subsequently, 100 g of polymer solution was titrated with a pure nonsolvent (water). The titrated solution was stirred and held at constant temperature (30 °C), while caution had to be exercised to minimize solvent loss. Cloud point (turbidity end point) was easily recognized by visual observation. Figure 8 shows the cloud point of the dope solution after being titrated. The amount of added nonsolvent (in grams) was determined gravimetrically.

FIGURE 7: Apparatus for turbidimetric titration step

FIGURE 8: Cloud point of dope solution

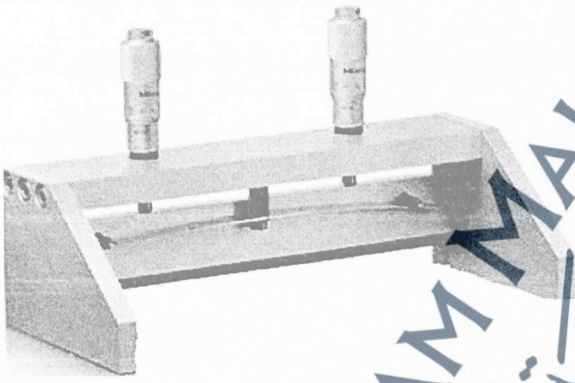
3.5 Membrane Fabrication

LPROS membrane was fabricated according to the dry/wet phase separation process. Casting process was done by using casting knife as shown in Figure 9 below. A small amount of casting solution was poured onto a glass plate with a casting knife gap setting of 150 μm and at an appropriate casting shear. Then, the glass plate together with the membrane was immersed into the coagulation bath (composed of water as the coagulant medium).

After the process of coagulation complete, the membranes were transferred into water bath for 1 day, then transferred into ethanol for 1 day and finally immersed into n-hexane for 2-3 hours before air dried for at least 48 hours at room temperature to remove any residual organic compounds. The use of the liquid exchange treatment is 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 are used with

water as the non-solvent. When such membranes are being dried afterwards, water will be removed first and the solvent left behind may damage the membrane structure.

FIGURE 9: Casting Knife



3.6 Preparation of saline water samples

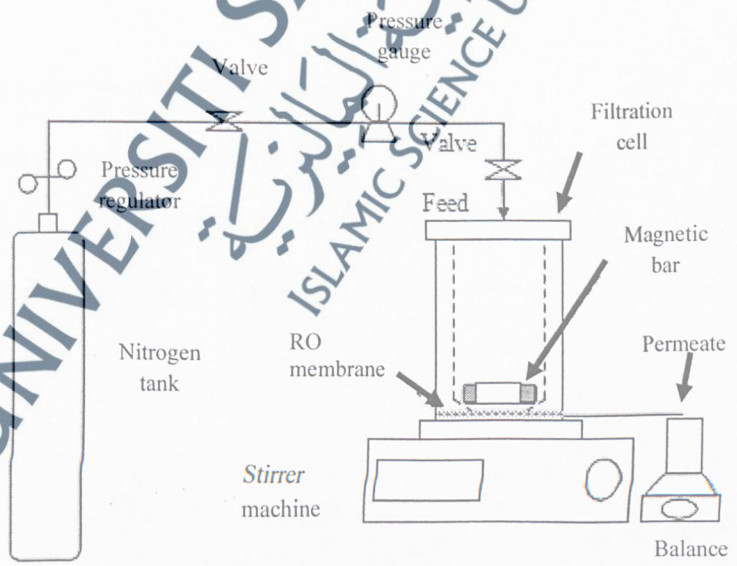
The preparation of saline samples were done using the formula, 1g/L is equivalent to 1000 ppm of solution concentration. This is the example of preparation of 2,000 ppm of saline water. Firstly, 2g of sodium chloride was weighed, and poured into a volumetric flask containing about 800ml of distilled water. Once the sodium chloride has dissolved completely, add water to bring the volume up to the final 1000 ml. These steps repeated to obtain six concentration of saline water which were 2 000, 5 000, 10 000 ppm, 30 000, 40 000 and 50 000 ppm.

3.7 Performances Evaluation

3.7.1 RO Permeation Rig

The schematic diagram of reverse osmosis permeation rig was being shown as in Figure 10. Using Millipore filtration cell, circular disk membranes were 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 is 1.38 x 10^{-3} m^2. The operating pressure of 5 bar for filtration test was 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 installed between the nitrogen gas and cell.

FIGURE 10: Schematic diagram of RO filtration set-up



3.7.2 RO Permeation Test

The RO performance in terms of pure water permeation (PWP), permeate flux and salt rejection for the membranes were tested using lab-scale dead end filtration apparatus with circular filtration cell having an effective area of 1.38×10^{-3} m^2. To begin with, the circular membrane coupons loaded in the filtration cells were pressured at 5 bar with deionized water for at least 30 minutes for compaction. Permeation tests were then carried out with aqueous solution containing 2 000, 5 000, 10 000, 30 000, 40 000, and 50 000 ppm NaCl to represent saline water samples at 5 bar of operating pressure. The PWP and permeate flux were determined by measuring the water and permeate volume collected over a certain period in terms of liter per square meter per hour (L/m^2h) and calculated through the Equation 3.1 and Equation 3.2:

$$Jw = \frac{Q}{A \times \Delta t} \tag{3.1}$$

Where,

J_w = the pure water permeation (L/m^2h)

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

Δt = the time (h)

Q = Volume of water collected, (L)

$$Jv = \frac{Q}{A \times \Delta t} \tag{3.2}$$

Where,

J_v = the permeate flux of salt solution (L/m^2h)

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

Δt = the time (h)

Q = Volume of permeate solution collected, (L)

Meanwhile, the salt rejection was evaluated using the Equation 3.3:

$$R\,(\%) = (1 - \frac{C_p}{C_f}) \times 100\% \tag{3.3}$$

In which C_p and C_f are the salt concentrations in permeate and feed, respectively. The salt concentration was determined by measuring the electrical conductivity of the salt solution using a conductivity meter (CON 700, Eutech Instruments).

3.8 Characterization of LPROS Membrane

3.8.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a very useful technique for determination the membrane surface morphology and membrane thickness. For the preparation of membrane samples that had to be analyzed, the samples were cut into small piece and fractured cryogenically in liquid nitrogen and mounted on the sample stubs with double-surface tape. After the samples were sputtered with gold by an

automatic gold coater (JFC 1600), they were scanned by employing a JEOL JSM 6360LA Scanning Electron Microscopy (Tokyo, Japan) under magnification of 500x to 5000x with potentials 15kV.

3.8.2 Thermal Gravimetric Analysis (TGA)

Thermal property of membranes were determined by Thermogravimetric Analysis (TGA). TGA study was carried out using a Mettler Toledo thermal analysis system under nitrogen atmosphere. The heating rate was 10 °C/min in the temperature range from 30 °C to 800 °C. The flow rate is about 20 ml/min. The thermal stability of the samples were evaluated in terms of decomposition temperature.

3.7.3 Functional Group Analysis via FTIR

FTIR analysis was done to study the functional group of the membrane. FTIR Variance 3100 was used for this analysis. The spectra were obtained from 32 scans at 4 cm^{-1} resolution from 4000 to 400 cm^{-1}.