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Effect of Jet Stretch in the Fabrication of Polyethersulfone Hollow Fiber Spinning for Water Separation

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ABSTRACT

The effect of jet stretch on the morphology, pure water permeation and sodium chloride rejection of hollow fiber membranes is analyzed by varying the spinning take up speed. Polyethersulfone hollow fibers were spun using dry-wet spinning technique. The membrane formulation of PES/NMP/Water/PVPk10 is spun at constant extrusion rate of 3.0 cm^3/ min. The fiber take up speed during spinning varied from 19.7 to 29.5 cms^{-1}, revealed that the flux of hollow fiber membranes is minimal when the fiber take up speed is equivalent to the velocity of dope extrusion. At low jet stretch, the permeability of membranes is high with elevated ionic solutes rejection produced. The influence of elongation stress towards hollow fiber membranes morphology and its performance for water separation is also highlighted.

Keywords: Polyethersulfone membranes, Hollow fiber spinning process, jet stretch

1.0 INTRODUCTION

Polyethersulfone (PES) were favored for the preparation of membranes due to the characteristics of wide temperature limit, wide pH tolerance, fairly good chlorine resistance, easy to fabricate membranes in a wide variety of configurations and modules, wide range of pore sizes ranging from 10Å to 0.2(m and good chemical resistance to aliphatic hydrocarbons, alcohols and acids [1, 2].

In spite of the advantages of membrane applications and processes, most commercial polymer membranes are asymmetric membranes prepared by the so-called phase-inversion process developed by Loeb and Sourirajan [3]. In this process, a solution consisting of a polymer and a suitable solvent or a solvent-additive mixture is immersed into a nonsolvent to bring about phase separation, which forms the membrane. The homogenous polymer solution is converted into two phases namely solid polymer rich phase (forming the rigid membrane structure) and polymer lean phase representing the liquid filled pores. The controlled transformation of polymeric solution that cast from liquid into solid state relies on the phase separation of polymer solutions in producing polymer films. That is why parameters that govern the phase inversion and the resulting membrane morphology and performance are vital and becomes major studies in membrane making.

It is widely known that the preparation of hollow fibers cannot be approached by the same method that led to successful casting of the flat sheet porous support. This is because in the case

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hollow fiber preparation, the spinning process involves the extrusion of dope solution through an annular spinneret to form a hollow fibre. The expression of spinning means forcing a material through a small die to form a free liquid jet at the exit. Compared to flat sheet casting, hollow fibre spinning is slightly more complicated because demixing occurs not only from one side as in flat sheet casting but from both sides, ie. The bore side (internal surface) and shell side (external surface). Other major differences during hollow fibre membrane spinning were the annular spinneret to form a hollow fibre (spinneret geometry), bore fluid composition and temperature, take up speed, dope extrusion rate, internal and external coagulant temperature, coagulant flow rate, polymer solution flow rate, air gap and etc. The controlling parameters studied such as dope extrusion rate [4-6], spinneret dimensions [6,8], bore fluid properties [2,9], dope viscosity [10], air gap length [11-13]]etc. provides useful information towards the improvement of hollow fiber fabrication process.

During phase inversion, the two dominant mechanisms that induce molecular orientation of fiber formation are the elongation stress (outside spinneret) and spinline stresses (within spinneret) [7]. It is also believed that higher air gap would give an impact to the formation of hollow fiber [12], as elongation stress due to gravity were become more pronounced with higher air gap. Study of elongation and shear rate for PES membranes by Cao *et al.* [8] for gas separation shows that elongation rate has affect selectivity than permeance whereas shear rate influence more to permeance than selectivity.

Take up fiber has been correlated with elongation rate, as velocity of take up drum is connected with the velocity of extruding dope from tip nozzle. When take-up fiber higher than dope extrusion velocity, the fiber was pulled and as consequences, hollow fiber attenuation and draw ratio increased. Likewise, the take-up roller would induce tensile stress on the nascent fiber and oriented the molecules in the spinning jet to precipitate into a more compact structure [8]. In relation to take up speed fiber, small diameter fibers that associated with high tensile stress would be advantage to increase membrane surface area in a module volume and hence build up module productivity. However, to suits the separation requirement, the fiber take up influences may need to further studied.

Thus the focus of the present work was to study the influence of membrane stretch during spinning process to the nature of polyethersulfone polymer as base polymer and the effect in its filtration performance. We studied the influence of membrane stretch by increasing the take up speed of the fibers on both the physical properties and permeation properties of Polyethersulfone (PES) hollow fibers using scanning electron microscope (SEM) and Sodium chloride separation. As to focus the membrane stretch effect, here the extrusion rate of polymer dope in the spinneret were kept constant to reduce extrusion effect at spinneret such as fiber dragging or varied mixing of bore fluid flow rate on fiber formation.

2.0 EXPERIMENTAL

2.1 Materials

Polyethersulfone (PES) RADEL A-300 with a molecular weight of about 15,000 Da was purchased from Amoco Chemicals, was used as a membrane binder material. N-methyl-2-pyrrolidone (NMP, >99%) was supplied by MERCK, Darmstadt, Germany, had been used as a solvent whereas water was used as a coagulation medium. Second polymer of poly (vinylpyrrolidone) PVP with a molecular weight of 10K was also used for membrane formulation, whereas Sodium chloride (NaCl) of analytical purity grade used for separation testing. Both were supplied by Merck, Darmstadt, Germany and was used as received.

2.2 Hollow Fibers Preparation

Hollow fibers were made by dry-wet spinning process. The spinning system was the same as that described by Ismail *et al.* [4], except there were no force convection applied in this work. Here, the casting formulation or 'dope' was consisting of homogenous solution of PES/NMP/water/PVPk10 at weight ratio of 22/72/5/1. The dope was extruded through an annular spinneret into air at the initial stage with a bore fluid composed of water.

Table 1 Spinning process parameter

Parameter	Process condition/value
Bore coagulant fluid composition	Distilled water at 20-25°C
Bore coagulant fluid flow rate	1.0 ml/min
External coagulant	Tap Water at 18°C
Spinneret dimension	ID/OD 0.3/0.6 (mm/mm)
Dope extrusion rate	3 ml/min
Air gap	5 cm
Hollow fiber post treatment step	(i) 24 h: rinsed with water for NMP removal (ii) 24 h: immersed in aqueous glycerol solution (50%) (iii) 7 days: fibers vertically air-dried at room temperature

In order to study the effect of membrane stretching during spinning, the spin line (drawing) or elongation stress on fiber formation as the jet stretch ratio (ratio of drum take-up speed to dope extrusion speed) was varied at 0.83, 1.0 and 1.25, while the dope extrusion rate was kept constant at 3.0 cm^3/min. The details of hollow fiber spinning process conditions were summarized in Table 1.

2.3 Morphology Studies

In order to study the stretching effect on the morphology of the hollow fiber, samples were prepared for SEM investigation. Cross-section of hollow fiber membranes were prepared by quick immersing it in liquid nitrogen and fractured to obtain a clean break. The sample was then attached on a stainless steel stub using conductive tape and then followed with gold sputtering to avoid electrostatic charging of the membrane surface due to the electron beam.

2.4 Permeation Performance

To quantitatively test the hollow fiber separation performance in terms of permeation flux and sodium chloride rejection, permeation modules were prepared. Each module consisted of thirty fibers with a length of 20±2 cm. The shell sides of the two ends of the bundles were glued into two stainless steel tees using a normal-setting epoxy resin. These modules were left overnight for curing before tested. Then the permeation test was conducted by using permeation testing-rig as described previously by Ismail *et al.* [4].

In the permeation test system, the pure water flux were calculated by the equation (1)

$$J_w = \frac{V}{t \times A \times \Delta P} \quad (1)$$

Where V is the permeate volume (m^3), t is the time of permeate taken (sec), A is the surface area of the hollow fibre (m^2) and (P is the pressure gradient (Pa).

Natrium chloride (NaCl) were used for the measurement of solute rejection of the hollow fibre membranes. NaCl were used for the rejection experiment as a representative of inorganic ions to establish relationship on solute rejections with pure water permeation characteristics of the membranes, which discussed in the later section. Then membrane rejection percentage, R% is computed as in equation (2):

$$R\% = \left(\frac{1 - C_p}{C_f}\right) \times 100 \quad (2)$$

Where C_f and C_p is stand for solute concentration in feed and permeate respectively. The feed and permeate solute concentration were measured using digital conductivity meter (WTW handheld meter model LF330).

3.0 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM) Analysis

Three types of hollow fiber membranes from dope solution of PES/NMP/Water/PVPk10 (22/72/5/1) were fabricated at varied stretch. The dimensions of the fabricated membranes were summarized in Table 2. The inner and outer diameter of hollow fiber membranes were estimated via the SEM image. It must be mentioned here that an adequate hollow fiber diameter ratio of inside diameter (D_i) to outside diameter (D_o) of 0.5 has been suggested to have good strength properties [14]. So, all the fabricated fibers were agreed to this criterion.

The almost constant ratio implies that the radially inward velocity of the outer surface to the bore side is faster than that of the inner surface [15]. Radially inward velocity has been correlated with take up speed and fiber outer diameter [16]. Based on radial inward velocity, when take up speed increased, radial inward velocity also increased.

For hollow fiber spinning, the outer layer of the nascent fiber was influenced by external coagulant whereas inner cylindrical inner shell was influenced by the bore fluid. It was shown that the dimensions of the hollow fibers were affected by the take up speed. In Table 2, ratio of inside diameter (D_i) to outer diameter (D_o) of hollow fiber membrane would become closer to spinneret D_i/D_o (i.e. 0.5) due to higher take up. The higher take-up rate translates into a shorter contact time and solvent exchange between the bore fluid and the dope flow in the air-gap region. In addition, increasing take up would also increases dope flow which shrink the cross-sectional diameter of the dope flow and thus resulting a smaller inner hollow radius.

This is the reason for fiber JS0.83, where there were minimum or no stretch influence, and thus the solidification of fiber from outer surface slightly faster than inner surface, which produces the uppermost D_i/D_o ratio. In comparison, JS1.3 found to have a reduction of D_i/D_o which attributed to this phenomenon. This trend was also observed by several studies [15-19] especially when hollow fiber take up was higher than dope velocity. They also reveal that higher take up were not only reduces hollow fiber diameter but also resulting greater molecular orientation and reduces crumpling, which to some extend eliminate microvoids [19]. However at maximum limit depending on material properties, higher fiber take up speed would certainly break hollow fiber membrane during fabrication.

The variation thickness of the fiber wall (i.e difference of outer diameter, D_o to the inside diameter, D_i) could be correlated to the dual path of phase inversion influence during hollow fiber membrane formation. During hollow fiber spinning, the outer layer of the nascent fiber was influenced by external coagulant whereas inner cylindrical inner shell was influenced by the bore fluid. The fibers were fabricated at dry-wet condition of 5 cm air gap. So for dry-wet condition, the nascent fiber was driven into the air gap, where the dope experience delayed phase inversion as outer surface absorbed ambient moisture and formed a thin skin layer. Once a nascent fiber is driven into the air gap, the semi volatile solvent as NMP will evaporate immediately at the outer periphery of the fiber. This process increases the polymer concentration quickly at the outermost layer of the fiber and

Table 2 Physical dimension of the hollow fibers

Fiber No.	HF stretch ratio*	Wind up speed (cms^{-1})	D_i/D_o	Wall thickness (D_o-D_i) μm	Elongation draw ratio, Ø
JS0.8	0.83	19.7	0.538	272.75	1.09
JS1.0	1.00	23.6	0.531	218.25	1.74
JS1.3	1.25	29.5	0.515	249.20	1.39

*Wind up drum velocity (cm/s): extrusion velocity at spinneret nozzle (cm/s)

ideally vitrifies this layer to form a defect-free selective skin layer. At the air gap region also, occurrence of die swell of the dope when exiting spinneret also play an important phenomenon especially for short air gap [20] as used in this study. The die swell phenomenon allows the relaxation of dope polymer which create larger fiber diameter prior it immerse into water tank. An illustration of the hollow fiber formation via the excretion from spinneret towards air gap region is illustrated in Figure 1.

From Table 2, the membrane wall thickness observed thicker when fiber take-up velocity not equal to dope extrusion velocity. This is correlated to the membranes formation during the hollow fiber either stretch or die swell during free fall. When at free fall condition, wind up velocity <extrusion velocity, elongation induced by gravity in the air during dry-wet spinning is unavoidable but minimal. Moreover, die swell effect at dry gap region were also dominant causing the membrane thickness increase. The duration in the die swell region was more which cause the membrane wall is thicker and added with water penetration from the inner bore. At this elongation flow, there is a velocity gradient in the flow direction and affect the fiber diameter. If no shrinkage of fiber occurs, the formation will be uniformly across the fiber radius.

Whereas when take up speed was more the extrusion velocity (i.e stretch ratio of 1.3), the nascent fiber was stretch and promoted faster to the coagulant bath, reduces the die swell phenomenon and at the same time quench water bath which produces phase separation occurs in the underlying-skin layer region instantaneously, which expected to produce an open porous non-selective substructure. faster rate fiber take up, solidification at outer diameter experience shorter time period causing the limited growth of polymer-lean phase that resulting microvoids near outer surface.

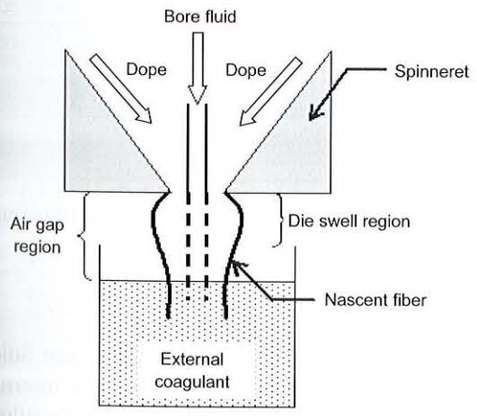


Figure 1 Illustration of die swell in hollow fiber formation at spinneret

Elongation draw ratio [15], was defined as ratio of cross section of spinneret to the cross section of the precipitated hollow fiber membranes. So, it can be reflected as the stretched out of fiber cross section with regards to the spinneret cross section. It is calculated as follows:

$$\phi = \frac{\left(D_o^2 - D_i^2\right)_{\text{spinneret}}}{\left(D_o^2 - D_i^2\right)_{\text{hollow fiber}}} \quad (3)$$

The elongation draw ratio of the fabricated hollow fiber membranes was found optimum when membrane stretch ratio of 1. Elongation draw ratio was found high when the take up velocity is equal to extrusion velocity as in JS1.0. This is because when the take up speed (cm/s) is equal to polymer extrusion velocity, the inward and outward coagulant is assumed to be equally balance and thus produces the least wall thickness compared to JS0.83 and JS1.3. As shown by fiber JS0.83, the elongation draw ratio is the lowest as fiber shrinkage is minimum. Whereas when fiber draw more than the dope extrusion, the fiber surface area ratio (elongation ratio) also increase and this suggest inward coagulation of fiber shell have more effect than the inner shell. When at high elongational stretch on nascent fiber cause the fiber wall shrink which induces radial outflow of solvents to both inner and external coagulant sides that withhold coagulants intrusion [15] that consequently produce thinner membrane wall. Consequently, for JS1.3, elongation draw ratio found lower than JS1 due to fiber shrinkage.

The morphology of the fabricated fibers was shown in Figure 2. The figure shows the cross-sectional structure of PES/Water/PVPk10 hollow fiber fabricated at increased take-up speed, i.e

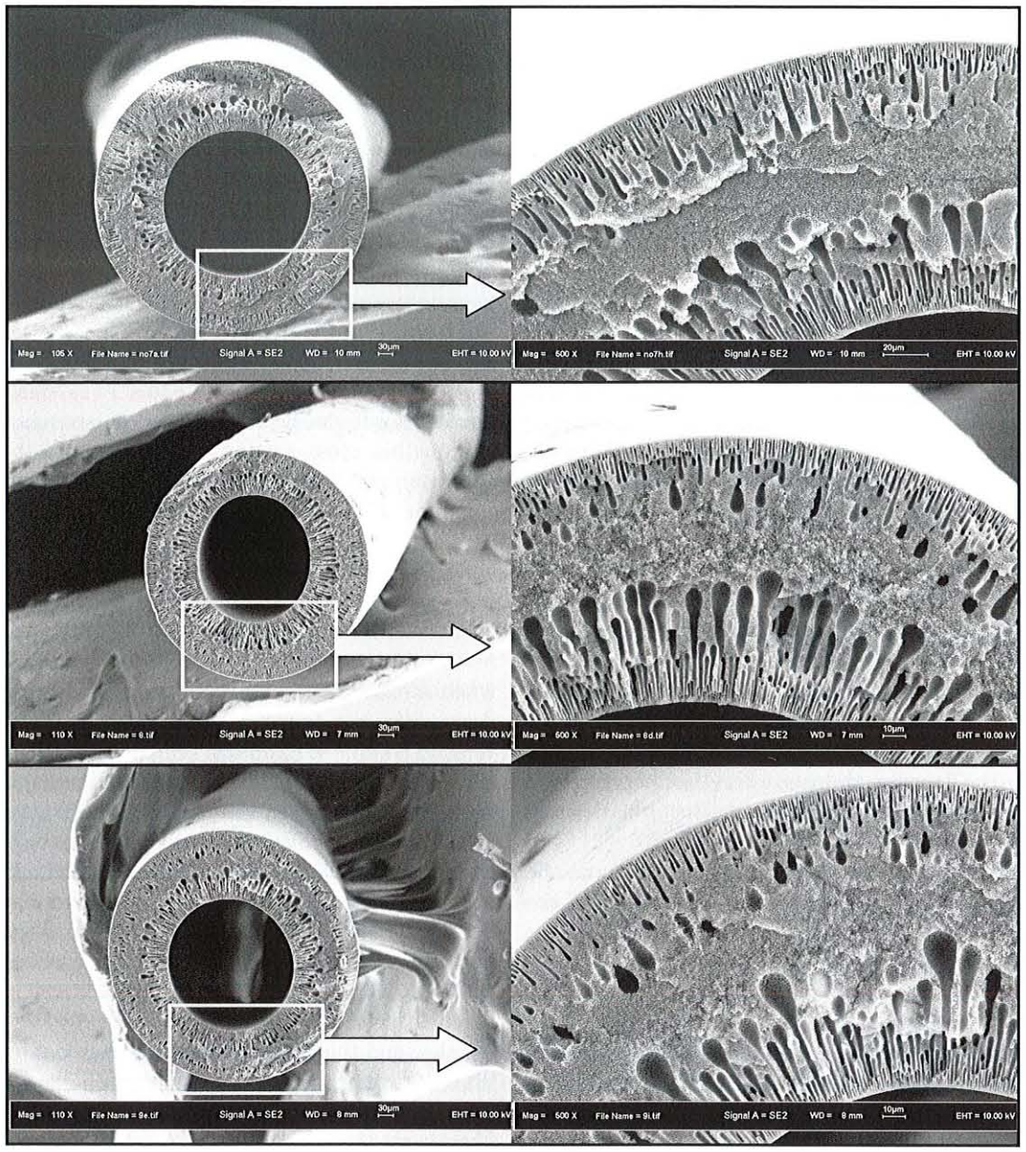


Figure 2 SEM cross section of hollow fiber membranes (a) JS0.8, (b) JS1.0, (c) JS1.3 (Magnification: 110× and 500×)

19.7, 23.6 and 29.5 cms^{-1}. During the hollow fiber formation for dry-wet process condition, water from the bore fluid is initially in contact with the inner polymer dope. At this point, phase separation occurs quickly on the inner edge, as a result of vitrification induced by the bore fluid. The solvent i.e NMP concentration in the internal coagulant increases with time due to the outflow of solvent from the dope. At the skin layer, small amount of coagulant of water infiltrate into the dope and thus produces liquid-liquid phase separation occurs. Water molecules diffuse along the polymer-lean phase due to the interaction between water and polymer dope. When reaching the water coagulation tank, the outer layer of the nascent fiber is immersed in the large amount of water makes it to undergo solidification.

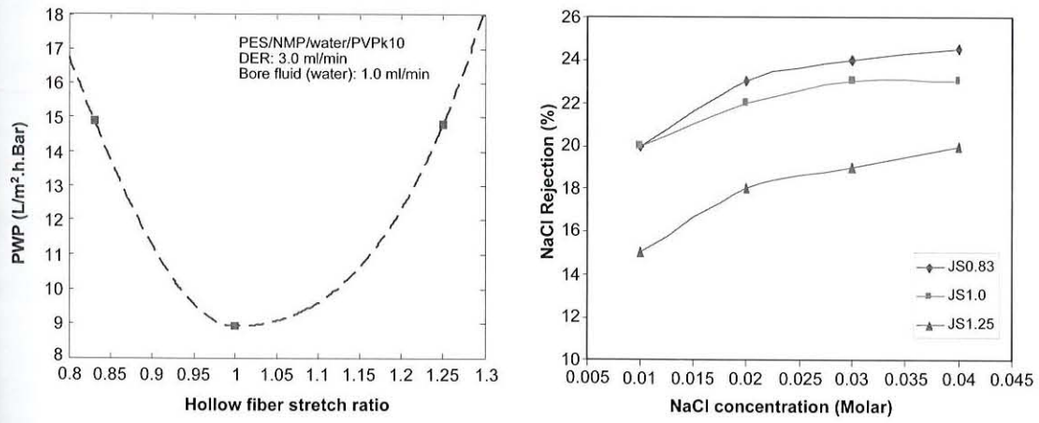
From the SEM cross section, inner fiber was more porous than the outer layer from the fingerlike microvoids formation. The fingerlike microvoids were found slightly longer at inner fiber. This is because the air gap has delayed the phase separation of the outer skin of the nascent fiber, whereas the phase inversion of the inner skin occurred immediately at the nozzle due to bore fluid in the spinneret. Yet a thin skin layer was formed at the outer fiber from the absorbed ambient moisture.

It was observed that fingerlike formation at inner bore for JS0.8 and JS1.3 seems shorter than JS1, although for all the three membranes, the bore fluid flowrate was the same (i.e 1.0 ml/min). As all the membranes undergo initial solidification at inner bore, larger and longer micropores was observed. The instantaneous demixing at inner bore produces similar trend of microvoids fingerlike observed from SEM. The numbers of fingerlike formation appeared larger and longer in JS1 indicating of an optimum duration for water diffusion. Whereas JS0.8 had longer time compared to JS1, and thus slower rate for NMP-solvent outward diffusion produced the fingerlike as shown. While for JS1.2, the pull up effect has been dominant which cause the solvent diffuse outward slightly faster than water penetration, and thus producing shorter fingerlike structure than JS1.

The SEM of the hollow fiber reveals the number of microvoids fingerlike structure in JS1 were less and smaller than JS0.8 and JS1.3. Approximately 33°m length fingerlike structure at outer fiber for JS1 while 49°m and 42°m for JS0.8 and JS1.3. The reduction for JS1 suggested the domination of die swell incident in JS0.8 during air gap. Whilst, quick immersed at coagulation bath for JS1.3 had induced 5.9 second faster towards instantaneous demixing than JS1 toward end hence produced longer fingerlike morphology.

3.2 Effects of Jet Stretch on Membrane Flux and Ionic Solute Rejection

Prior to the NaCl permeation test, the pure water permeability (PWP) of the membranes was first conducted and the results are shown in Figure 3(a). The experimental data shows the effect of hollow fiber stretch to casting solutions towards



(a) (b)

Figure 3 (a) Pure water performance (PWP) at increasing membrane stretch for PES/NMP/Water/PVPk10 and (b) Sodium chloride rejection at increasing concentration for the three types membrane stretch

its pure water permeation rates. When take up speed slower than the extrusion rate, PWP becomes decreasing whilst at certain point, it reach the minimum permeation rate and continued to increases when fiber wind up faster than the dope extrusion rate. This corresponds with fiber elongation draw ratio where less elongation cause high permeation rate. Moreover, the SEM morphology depicts the outer layer for JS1 were found less and smaller than JS0.8 and JS1.3.

In the view of ionic rejection properties of the membranes, the membranes which less stretch have resulted better rejections performance than the membranes had been stretch. This is shown in Figure 3(b). As expected, JS1.25 have a high permeation rate and thus producing lesser sodium rejection performance than JS1 and JS0.8. This phenomenon occur because larger pore membranes unable to retain smaller molecules as it easily passes through membranes and withdrawn at permeates. However, for the case of JS0.8, the separation performance was found high although the permeation rate was higher than JS1. This could be attributed to the dense outer layer from the delayed solidification during air gap region which also having longer fingerlike structure at both inner and outer layer of the hollow fiber.

4.0 CONCLUSION

By using the phase inversion process with dry-wet spinning, PES hollow fibers were fabricated at varied stretch conditions. The membranes were stretch at increased take up speed, which includes less stretch (extrusion rate less than take up rate), equally stretch (extrusion rate equal to the take up rate) and further stretch (extrusion rate more than the take up rate). The morphology study reveals the effect of membrane stretch towards the hollow fiber physical properties by observation morphologies changes at inside and outside fiber. The SEM morphology explains the formation process which corresponds to separation performance. Considering from the insight of water performance, experimental data suggest that membrane stretch during membrane formation promotes higher water permeation. It was found that the sodium chloride rejections were found higher for membranes when fabricated at relaxed or less-stretched process. Thus we concluded that, the fabrication of membranes at higher stretch will increase permeation rate but reduces the separation performance. Whereby, not only high permeability membranes produced but also gives high rejection properties at low jet stretch.

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