Preparation and characterization of polyethersulfone hollow fiber nanofiltration membranes made from PES/NMP/PEG 400/WATER

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Abstract

The objective of this study is to develop nanofiltration hollow fiber membrane from a sophisticated multi component spinning dope. Polyethersulfone (PES) asymmetric nanofiltration (NF) hollow fibers membranes were prepared by a simple dry/wet phase inversion process from spinning solution consisted of N-Methyl-2-Pyrrolidone (NMP), Polyethylene-glycol (PEG 400) as polymeric additive and pure water as a non-solvent additive. These fibers have been produced from a newly developed spinning solution with a mass ratio of 21.34/31.22/10.2/7.24 (PES/NMP/PEG/water). The dope formulation was designed to be very close to its cloud point (binodal line) in order to speed up the coagulation of the nascent fibers so that the relaxation effect on molecular orientation is reduced. Sodium chloride solution was used to determine the rejection rate of the membranes. In order to achieve high performance NF membranes, the effects of shear rate on the separation performance of NF hollow fiber membrane were studied. Thus, different dope extrusion rate (DER) ranging from 2.0 to 3.5 cm^3/min were used to produce the fibers. The results are used to correlate the relationship between DER and the separation performance (rejection) of the membrane. Experimental results show a significant effect of extrusion shear on the rejection rate of the membranes. As the shear rate was increased, the rejection increased until a certain level, before the rejection decreases. Finally, the optimum shear rate was observed in this study and it was about 2.5 cm^3/min. In conclusion, we demonstrated that increasing the shear rate (DER) experienced by the spinning solution during membrane fabrication increased the molecular orientation and this had favorable effect on membrane rejection.

Keywords : Nanofiltration, polyethersulfone, hollow fiber membrane, shear rate and polyethersulfone

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1.0 Introduction

Recently, the research interests in the development of new and better asymmetric hollow fiber membrane with improve performance characteristics as well as good thermal, radiation and environmental resistance and stability has grown rapidly. Polyethersulfone (PES) has excellent thermal and mechanical stability as well as good chemical resistance [1]. Beside, PES can offer higher degree of chain rigidity because of its regular and polar backbone [2].

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Lately, Nanofiltration (NF) emerges to be a potential membrane-based separation process to be commercialized, its application is for liquid-liquid separations that uses asymmetric membrane. Despite impressive improvements in NF performances where phase inversion process conditions being the primary factor in determining high rejection values and high flux, the search for better membranes has always continued. Fabrication of a hollow fiber with a desirable pore-size distribution and performance is not a trivial process [3] and the fabrication hollow fiber membrane with a desirable performance for specific applications and the effect on hollow fiber membrane morphology and permeation properties reported in the literature often provide conflicting observations [4].

It has been recognized that molecular orientation will affect membrane selectivity and that orientation can be brought about by altering the rheological conditions during fabrication [5]. Ismail et al. [5] had stated that shear and elongation during spinning have been shown to affect the permeation performance of polysulfone hollow fiber membranes for gas separation and this was attributed to molecular orientation in the active layer. Rheological influence on phase inversion is an important area in the membrane production and performance, and yet it is one that has been neglected by membrane experties. But recently, more research has been focused on the effect of shear stress (shear rate) within the spinneret because it has been recognized that the dope rheology does play a very important role in the process of hollow fiber membrane formation.

Several membrane experts have been investigating and emphasizing the effect of shear stress on membrane performance. Chung and co-workers [7, 10, 12, 13] had studied the effect of shear stress within the spinneret on morphology and properties of hollow fiber membranes for gas and liquid separation. However, in membrane gas separation several researchers have shown that both permeability and selectivity increased with increasing dope extrusion rate [5, 14, 9, 11]. The increase in selectivity is due to enhanced orientation in the skin of dry-jet wet spun polysulfone hollow fiber. Ismail [15] also investigated the effect of shear rate on molecular orientation on skin layer of gas separation hollow fiber membrane by using plane-polarized infrared spectroscopy. The result suggested that there was an increased molecular orientation in the high sheared membrane that enhanced the gas selectivity.

Although an extensive series of research and developments have been studied in order to improve the properties of PES membranes, less research has been conducted on the fabrication and characterization of PES nanofiltration hollow fiber membranes for cyclodextrin enzymes separation. Therefore, this study attempt to investigate the effects of increased dope extrusion rate (DER) during spinning process in order to produce a newly developed polyethersulfone NF hollow fiber membrane. The focus is to understand the effect of rheological conditions on asymmetric NF hollow fiber characteristics and its separation performance. Membrane morphology and molecular orientation in the membrane active layer was investigated using Scanning electron microscopy.

2. Experimental

2.1. Material selection

Polyethersulfone (Radel A-300) was purchased from BP Amoco, USA with molecular weight of repeat unit 232.26 g/mol as the membrane-forming polymer. Solvent used is 1-Methyl-2-Pyrrolidone with analytical purity 99.7%, NMP and was purchased from Fluka, Germany and non-solvent used is water. Polyethylene Glycol 400, with molecular weight 380-420 was used as the polymeric additive for pore forming agent and were purchased from Fluka, Germany. Sodium Chloride (NaCl) was supplied by Merck, Germany. Three types of poly (vinyl)-pyrrolidone (PVP) from Merck, Germany, PVP K15 (average molecular weight 10 000), PVP K25 (average molecular weight 24 000), PVP K30 (average molecular weight 40 000) and cyclodextrin enzymes (average molecular weight 67 000) from Genetic Engineering Laboratory (2) , UTM were used to characterize the separation performance of fibers. Other organic solvents were reagent grade and uses as treated. For the pre-treatment process, non-solvent used were tab water and methanol at analytical grade. A two-component epoxy-potting compound was used in the potting of fiber modules.

2.2. Formulation of spinning solution

The new spinning dope formulation for hollow fiber fabrication consists of polymer, polymeric additive, solvent and non-solvent. Newly designed dope-spinning solution consisting (by weight percent) of 21.34 % PES and was dissolved in a mixture of 31.22 % NMP, 10.2 % PEG 400 and 7.24 % water. The solution preparation temperature was maintained in the region of 50^{o}C and high-speed stirrer was used so as to enhance the dissolution of polymers. Then, when the polymer was completely dissolved, the dope solution was cooled, poured into a storage bottle and degassed to remove any micro bubbles.

2.3. Hollow fiber fabrication by dry/wet spinning process

Asymmetric polyethersulfone hollow fiber membranes for liquid separation were fabricated using a dry/wet spinning process with forced convection in the dry gap. The dope reservoir was at ambient temperature (27^{o}C $\pm$ 2) and was kept at 1 atm during the spinning process. On extrusion from the spinneret (spinneret dimensions: OD 600 μm/ ID 330 μm), the nascent fiber passed through a cylindrical forced convection chamber (length 9 cm, diameter 5 cm) that was flushed with 0.5 l/min of nitrogen gas. The whole spinning rig is shows in Figure 1.

A high-pressure syringe pump conveyed the bore fluid (BF) and the flow rate used was one third of the DER. Water was used as the BF. The spinning solution and BF was extruded through a spinneret die in order to form a nascent hollow fiber at the ambient temperature. The nascent fiber will pass controlled environment air gap distance before entering into the non-solvent coagulation bath and the washing treatment bath. Tab water at 14^{o}C $\pm$ 0.5^{o}C was used in the external coagulation baths. The bore coagulant

was tab water at ambient temperature. This equates to water activities of 1 respectively. At this water activity, fibers were spun at four level DER and hence at different levels of shear.

The stretch ratio (wind up speed/ extrusion speed) was fixed at 1 throughout the whole experiment. Then the fully formed fibers were collected onto a wind up drum of diameter 17 cm. Prior to testing, the membranes were subjected to a pre-treatment process so as to reduce the pore size of the membrane. After the spinning process, the fully formed fibers were steeped in water and methanol for solvent exchange; then dried at ambient temperature.

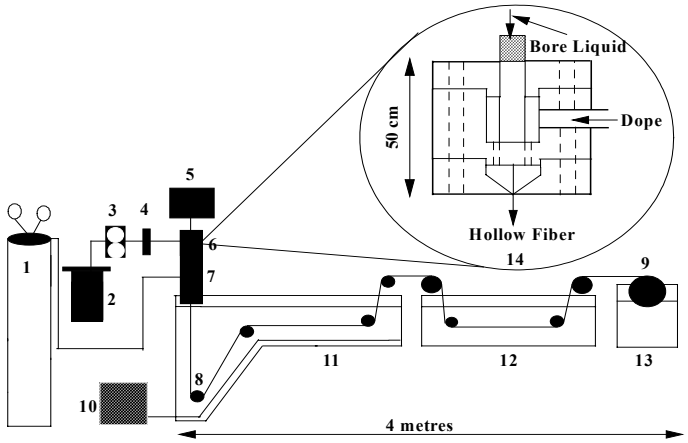


FIGURE 1: Schematic diagram of hollow fiber spinning system: (1) nitrogen cylinder; (2) dope reservoir; (3) gear pump; (4) on-line filter, 7 mm; (5) syringe pump; (6) spinneret; (7) forced convective tube; (8) roller; (9) wind-up drum; (10) refrigeration/heating unit; (11) coagulation bath; (12) washing/treatment bath; (13) wind-up bath; (14) Schematic spinneret

2.4. Characterization of nanofiltration hollow fiber membrane

Hollow fiber membrane must be potted into bundles consisting 15 fibers of approximately 26 cm before any other test should be done. This bundles size was selected because the surface area provided for by the 15 membranes will provide a representative average performance of a particular fiber spinning condition. Membrane modules 30 cm in length was prepared. Then, the fibers were carefully threaded through the tube sheet, top to bottom, until about 3 cm protruded from the bottom end of the silicone tubing. At the other end, the fibers were placed in the end cap and sealed with epoxy resin.

Distilled water was used to characterize the Pure Water Permeability (PWP) and was also used to prepare the feed solutions containing 1000 mg/l of the different solutes used. The experiment was carried out in a cross flow filtration set up. The feed solution was pumped into the shell side on the NF module and permeate liquid flowed out from the lumen of the fibers. For each batch of hollow fibers, a total of three bundles of fiber

are potted for testing. In this manner, test indicating the significance of the replicate error in comparison to the model dependent error can be performed. Flux was calculated by taking the average of three readings taken at a regular interval by noting the time taken to collect 10 ml or permeate for each condition. Thus, the average flux and solute separation data are reported.

A test rig as illustrates in Figure 2 was used in order to test the hollow fiber modules. The test cell will consists of an Hydra Cell pump with complete 1.5 HP gear motor with a maximum capacity of 8.5 gpm and head of 1000 psi, a 4 litre feed holding tank and the hollow fiber nanofiltration module. Beside, there is also a flow control valve in order to regulate the concentrate flow of the feed.A feed solution of sodium chloride, different polyvinyl-pyrrolidone at various molecular weights and an enzyme, cyclodextrin glycosyltransferase (CGT) was used.

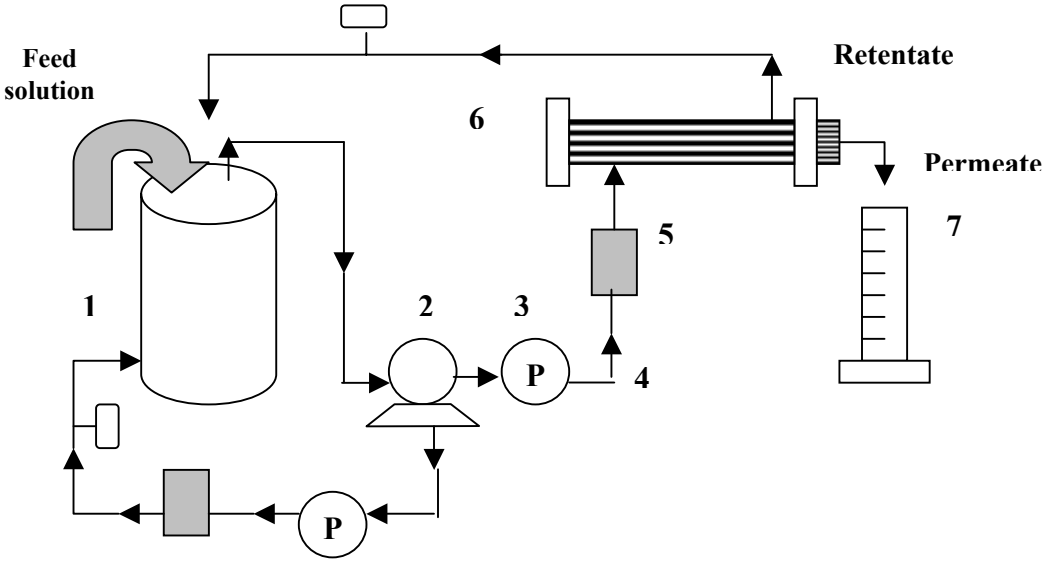


FIGURE 2: Testing rig for nanofiltration hollow fiber module; (1)Feed tank; (2) Pump; (3) Pressure gauge; (4) Control valve; (5) Flow meter; (6) Hollow fiber membrane module; (7) Measuring cylinder

The Molecular Weight Cut Off (MWCO) was constructed by measuring the separation values of PVP solutes of varying molecular weight. The feed solution was supplied to the hollow fiber module by the Hydra Cell pump, while the permeate (product) solution was discharged from the permeate (product) outlet which was open to the atmosphere. For nanofiltration characterization test, the suggestion feed pressure or the Trans-Membrane Pressure (TMP) suggested was 5-6 bar [16]. The feed pressure was brought to a gauge pressure of 75 $\pm$ 10 psig. The temperature of the feed solution was maintained at ($25^{o}C\pm2$) by means of a cooling system. The concentration measurement of sodium chloride at the feed and permeate solute were determined by the conductivity of solution and the measurement were done by using a digital conductivity meter (WTW Hand Held Meter model LF 330/set). The solute concentration of other solutions in the feed and or in the solution of permeate was determined using a Total Organic Carbon, (TOC-V Analyser, Shimadzu). The binary salt solution and other solute solution were

composed of 0.01 wt% NaCl and the concentrations of PVPs were 0.001 wt%. The percent (%) rejection, *R* and permeability (flux) of the membranes were calculated by this formula: -

$$\text{Retention or Rejection, } R\ (\%) = \frac{Cf - Cp}{Cf} \times 100 \quad (1)$$

$$\text{Permeability (Flux)} = V / (t \times A \times \Delta p) \quad (2)$$

Where *Cp* and *Cf* represent the solute concentration for permeate and the feed, *V*, *t*, A and Δp denoted for permeate volume, time, surface area of hollow fiber membranes and pressure gradient, respectively.

2.5. Scanning electron microscopy (SEM)

Hollow fiber membrane sample were immersed in liquid nitrogen and fractured. Here, the hollow fiber was snapped under liquid nitrogen, which gave a generally clean break. Then, the sample was sputtered with gold by using an ion-sputtering (Biorad Polaron Division) before viewed on a Scanning Electron Microscope (Phillips SEMEDAX; XL 40; PW6822/10) with potential of 10 kV under magnifications ranging from 500x to 5000x.

2.6. Fourier transform infrared spectroscopy (FTIR)

Plane polarized infrared spectra of membrane (parallel and perpendicular to shear direction) were determined by a diffuse reflectance infrared Fourier transform spectrometer (Nicolet Magna-IR 560). Samples of about 4 cm length were mounted at position with skin surface facing infrared beam and were rotated according to shear direction (either vertical or horizontal). Then, spectra of linear dichroism were obtained by straightforward subtraction of plane polarized infrared spectra perpendicular to shear direction from plane polarized infrared spectra parallel to shear direction. In any case, consistent results were obtained in several determinations, both with different samples and different occasions. The difference in background reflexivity between spectra recorded with different polarizations can be expected and had successfully opted to derive normalized based spectra by subtracting of one polarized spectrum to the other. The conclusion was based on the molecular orientation given on the relative intensity difference between IR absorptions in the linear dichroism spectra and not on the absolute signs of the dichroism.

3. Results and discussions

3.1. Effects dope extrusion rate (DER) on hollow fiber nanofiltration performance

Generally, it has been proven experimentally that the variation of data and results are contributed by the dope extrusion rate (DER). It is shown that a spinning solution

starts to exhibit significant chain entanglement at a critical polymer concentration. The fibers spun from this critical concentration exhibit theoretically the thinnest skin layer with minimum surface porosity.

The experimental data for pure water permeability (PWP) flux, flux of sodium chloride and the rejection of sodium chloride solution are shown in Table 3 and Table 4. From Figure 3 it is clearly observed that when DER is increased from 2.0 cm^3/min to 2.5 cm^3/min, the rejection rates of sodium chloride for all the spinning solutions was also increases but not the flux value for sodium chloride solution and PWP flux in Figure 4 and Figure 5. This means that as the dope extrusion rate increases, the molecular chains tend to align themselves better and pack more closely to each other, leading to a denser skin.

As shown in Figure 3, increasing DER up to 2.5 cm^3 /min extrusion rate tend to enhance and improve separation performance of hollow fiber membrane. This is due to increased molecular orientation in the skin layer of the membrane. However, flux of pure water and sodium chloride as depicted in Figure 4 and Figure 5 of hollow fiber membrane was found to decrease with increasing dope extrusion rate, which was consistent with an increased skin thickness and decrease of surface pore size at the skin layer. These results were in agreement with the results reported by Chung *et al.* [13] and Qin *et al.* [7, 18].

The increasing trend in rejection value for sodium chloride does not continue once it reaches a certain critical point (maximum) at 2.5 cm^3/min as shown in Figure 3. As the dope extrusion rate was further increased, the rejection of sodium chloride solutes decreased for all dope solutions as shown in Figure 3. The nanofiltration membrane performance deteriorates, suggesting the existence of optimum shear level, which yields optimal membrane morphology for nanofiltration hollow fiber membranes.

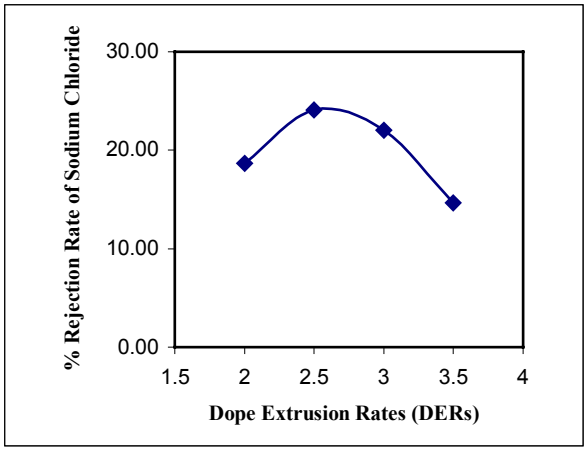


FIGURE 3: Effect of dope extrusion rate on pure water permeability for hollow fiber nanofiltration membrane

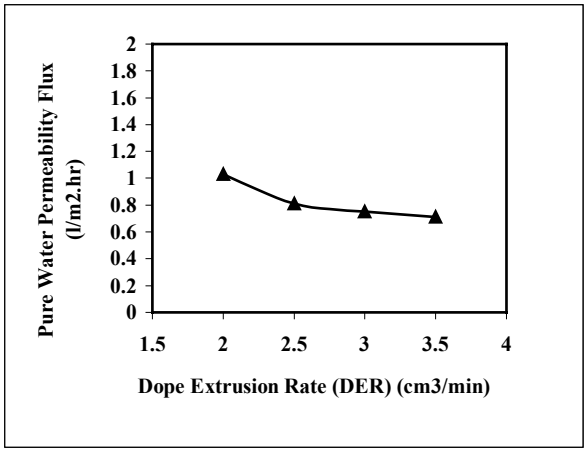


FIGURE 4: Effect of dope extrusion rate on sodium chloride rejection for hollow fiber nanofiltration membrane

The reduction in separation performance happened because of shear thinning behaviour of polyethersulfone spinning solutions, which also exhibited viscoelasticity properties, resulted in polymer molecules becoming more aligned at greater shear or dope extrusion rate. When the dope extrusion rate was further increased, the viscosity of the shear-thinning polymer solution was reduced. This is due to the reduction of chain entanglement and resulting in a looser skin structure. According to [17], shear-thinning materials may have high apparent viscosity with shear rate. This results were agreed with Chung [14] that membrane spun at a higher speed (shear rate) may show not only low rejection rate especially when the optimum shear is obtained but also lower flux rate because the reduction in chain entanglement and resulting in a looser skin structure.

In all cases, the same trend goes to the flux of sodium chloride and pure water permeability flux as in Figure 4 and Figure 5; for all the spinning solutions. This probably relates to the development of surface defects at the active layer skin. This interesting phenomenon had proven that the increase in the rejection rates are probably due to enhanced orientation in the membrane active layer.

Table 3
Rejection value of nanofiltration hollow fiber membranes

Dope extrusion rate (cm^3/min)	MWCO (Dalton)	Rejection of solutes (%)				
		NaCl	PVP 15K	PVP 25K	PVP 30K	CD 67K
2.0	45 360	18.64 ($\pm$ 4.6x10^{-1})	41.84 ($\pm$8.7x10^{-1})	51.45 ($\pm$5.5x10^{-1})	61.77 ($\pm$ 2.1x10^{-1})	70.58 ($\pm$ 2.4x10^{-1})
2.5	36 980	24.08 ($\pm$ 2.01)	46.52 ($\pm$7.3x10^{-1})	59.83 ($\pm$ 2.4x10^{-1})	68.42 ($\pm$ 6.2x10^{-2})	74.22 ($\pm$ 2.7x10^{-1})
3.0	50 670	22.01 ($\pm$ 9.0 x10^{-1})	44.85 ($\pm$8.4x10^{-1})	53.64 ($\pm$ 4.1x10^{-1})	57.57 ($\pm$ 2.6x10^{-1})	68.98 ($\pm$ 2.5x10^{-1})
3.5	44 410	14.66 ($\pm$ 6.0 x10^{-1})	37.95 ($\pm$2.1x10^{-1})	47.44 ($\pm$5.9x10^{-1})	55.55 ($\pm$ 7.2x10^{-1})	63.08 ($\pm$ 9.5x10^{-2})

**Note: ( ) = standard deviation value

Table 4
Flux value of nanofiltration hollow fiber membranes

Dope extrusion rate (cm^3/min)	Flux rate ($l/m^2.hr$)					
	Water	NaCl	PVP 15K	PVP 25K	PVP 30K	CD 67K
2.0	1.02 ($\pm$ 0.01)	0.83 ($\pm$ 0.01)	0.83 ($\pm$ 0.01)	0.78 ($\pm$ 0.01)	0.75 ($\pm$ 0.02)	0.71 ($\pm$ 0.01)
2.5	0.81 ($\pm$ 0.01)	0.77 ($\pm$ 0.01)	0.72 (0)	0.72 ($\pm$ 0.01)	0.69 ($\pm$ 0.01)	0.64 ($\pm$ 0.01)
3.0	0.75 ($\pm$ 0.01)	0.72 (0)	0.67 (0)	0.66 ($\pm$ 0.01)	0.64 ($\pm$ 0.01)	0.59 ($\pm$ 0.01)
3.5	0.71 ($\pm$ 0.01)	0.69 (0)	0.66 (0)	0.64 ($\pm$ 0.01)	0.61 ($\pm$ 0.01)	0.58 ($\pm$ 0.01)

**Note: ( ) = standard deviation value

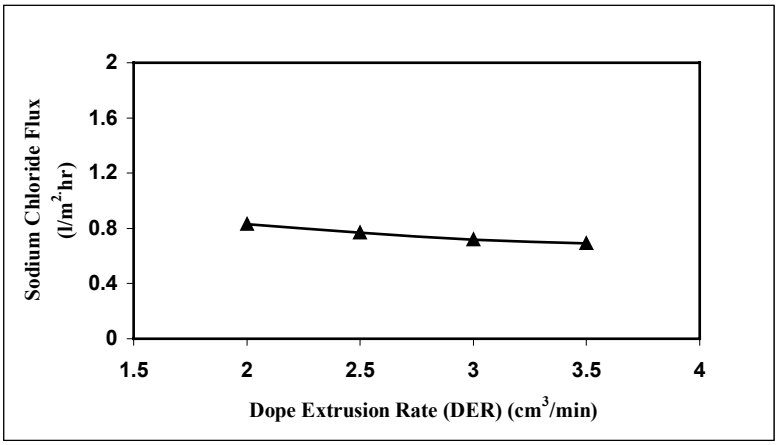


FIGURE 5: Effect of rejection and flux for sodium chloride solute on hollow fiber nanofiltration membrane

Thus, it is in agreement with result reported by [5, 14, 9, 11] that shear affects the phase inversion of the membrane active layer. Beside, the outer surface seems to reduce with increasing shear rate. The decrease in the active layer thickness with increasing shear may be a result of the way in which shear deformation interacts with the phase inversion process. From this research, it is suggested that the hollow fiber membranes spun with enhanced shear had a lower flux but a higher separation until a critical of level is achieved due to the greater molecular orientation induced in the high-sheared fibers.

3.2. Morphology of PES hollow fiber nanofiltration membranes

Asymmetric membranes, with thin skin layers to retain selectivity and porous sub layers to reduce permeation resistance and to offer proper mechanical strength, have been widely used to separate gaseous and liquid mixtures. A variety of asymmetric membrane structures, such as open cell sponge, closed cell sponge and macrovoid can be fabricated by the phase inversion method; and it is suitable for ultrafiltration process and can be employed as support layers for composite membranes [20].

The cross-sectional structures of the hollow fibers spun from different dope formulations by the dry/wet method were examined by Scanning electron microscope (SEM) as depicted in Figure 6. As illustrated in Figure 6 for PES/Poly (ethylene) glycol (PEG) blend, the cross-sectional structures of the fibers are similar displaying many small finger-like macrovoids from the inner edge to the external region. The length of the macrovoids can be diminished at higher polymer concentration.

From the SEM images for Figures 6, it shows that beneath the small finger-like voids, sponge-like structures were present for membrane with spinning solutions consists PEG as an additive. Specifically, there was an extremely well defined separating region

supported on a highly open-celled substrate containing not only small microvoids but also finger-like shape macrovoids.

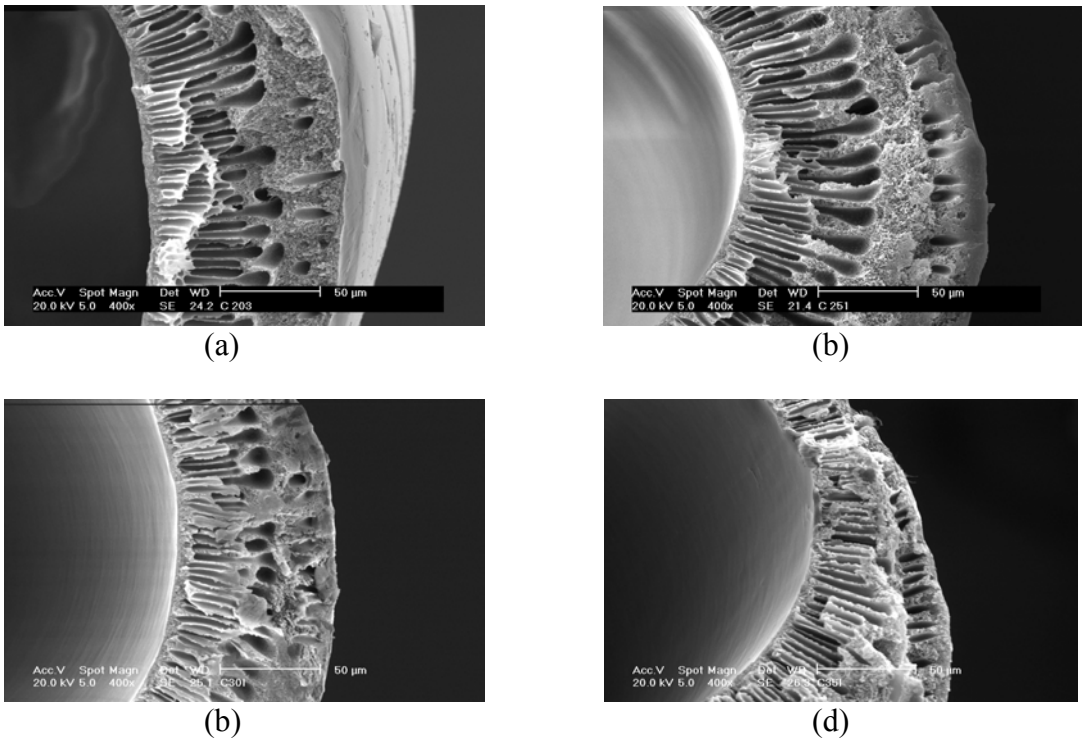


FIGURE 6: Partial cross section of hollow fiber membranes for PES/PEG blend (DS3) at 400 (a) DER 2.0 cm3/min (b) DER 2.5 cm3/min (c) DER 3.0 cm3/min (d) DER 3.5 cm3/min

The formation of the fiber structures shown can be attributed to mechanism of the coagulation process. In the dry/wet spinning process, water was initially in contact with the inner polymer solution. Phase separation occurred quickly on the inner edge and the inner skin was formed. The solvent concentration in the internal coagulant increased with time due to the outflow of solvent from the solution. Under the skin layer, a small amount of water penetrated into the solution and liquid-liquid phase separation occurred. During this process, water diffusion along the polymer-lean phase results in the growth of polymer-lean phase due to strong interaction between water and the polymer solution.

SEM images with spinning solutions consists of PEG and water as an additive, limited polymer-lean phase growth results in the membrane with small macrovoids near the outer edge. In the outer edge of the fiber, there exists the typical asymmetric structure (dense layer support with porous sub-layer). It is noted that the skin layer structure and its separation performance of the membrane is not related to the substrate. It was in agreement with Wang et al. [19]. When water was added into the polymer solution, the polymer coil in the solution was shrunk because water is a strong non-solvent for PES. Therefore, sufficient and suitable dry region is needed and rapid solifidication of the membrane and bigger pores formation can be eradicated. For the inner edge structure, fibers have thin finger-like structure with tiny macrovoids were observed when fast coagulation took place from both sides of the nascent fiber and the fast solidification

across the overall membrane wall restricted the growth of macrovoids in the polymer lean phase. This was due to the formulated spinning solutions that had small coagulation value and also the solvent mixtures of NMP and water was easily miscible with water as the coagulant.

It is observed that, the difference in cross-sectional structures is because of the different coagulation behavior between inner and outer surface even though water was used as the coagulant in both sides. The outflow of NMP from the external surface (inner edge structure) has little effect on the composition of external coagulant in the big water bath, a fast and nearly uniform coagulation prevailed which tends to form small and uniform pores beneath the external skin surface. However, in the tiny fiber bore, the fast outflow of the solvent, NMP altered the composition of the bore fluid and reduced the coagulation power. Thus, extended phase separation occurred prior to solidification and this could attribute the growth of polymer-lean phase resulting in the formation of bigger macrovoids at the inner edge structure.

3.3. Flux and separation performance on hollow fiber nanofiltration membranes

Flux and separation performance was characterized to further support the theory that increases the dope extrusion rate, the separation performance (rejection) of the produced membrane was found to increase as the outer skin layer is decreased.

From Table 3 and Table 4, it is clearly seen that the pure water permeability fluxes and fluxes of all particular solutes including cyclodextrin enzyme of the hollow fiber nanofiltration membranes decreases with an enhanced in dope extrusion rate (DER). The separation performance (rejection) for a particular solutes increases with increasing in DER, which means the selective skin of the final membranes becomes apparently thicker/denser. The present results indicates that pore size in the outer skin of the final nanofiltration hollow fiber membranes may decrease with increasing dope extrusion rate because smaller pore size of the final membranes results in better rejection for a solute solution and higher resistance for water permeation. The interesting phenomenon, reduction in fluxes and increment in separation performance can be observed for experimentally and the solutes separation performance for nanofiltration hollow fiber membranes are illustrates in Figure 7.

Figure 7 show there is a maximum rejection at DER 2.5 cm^3/min (critical shear), where it is the critical point of the rejection value observed in solute rejection (%) versus dope extrusion rate. Here, once the rejection reaches an optimum point, it decreases with increasing DER. It means that, as the DER increased, the lean polymer chain tend to align themselves better and pack more closely to each other leading to a denser skin. These results had confirmed that shear-induced molecular orientation occurred at enhanced dope extrusion rate. The same trend goes to all spinning solutions for solute rejection (%) versus dope extrusion rate.

From the results obtained it can be concluded that, increasing DER tend to enhance molecular orientation and improve separation performance of hollow fiber

membrane. This is due to increased molecular orientation in the skin layer of the membranes. Thus, at the same time the pure water permeability flux and flux of particular solutes was found to decrease, which was consistent with an increasing skin thickness and a decreasing of selective skin pore size

However, when the DER is further increased above the critical point at 2.5 cm^3/min, the rejection decreases slightly while the flux does not change significantly. Here, a decrease in viscosity had occurred because of the reduction in chain entanglement resulting in a looser selective skin layer.

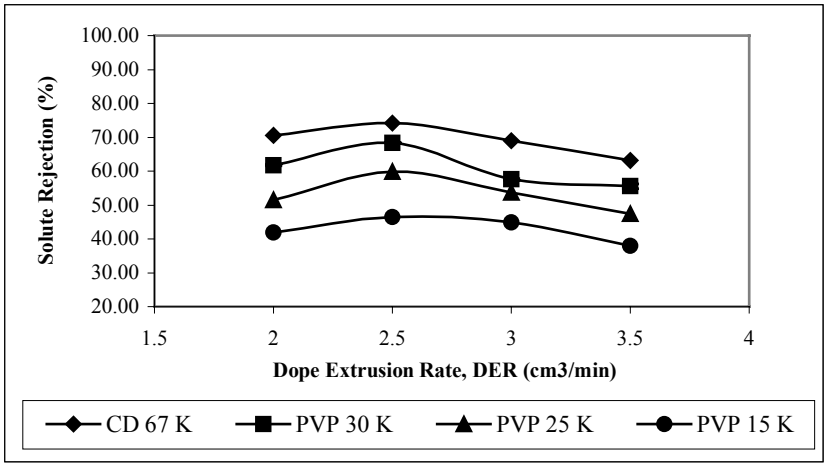


FIGURE 7: Effect of DER on separation performance of hollow fiber NF membranes

At this stage, the DER may not apparently result in significant impact on the flux and rejection of final nanofiltration hollow fiber membranes. Furthermore, hollow fiber membrane at extremely high shear, over the critical point (3.5 cm^3/min), pulled molecular chains or phase-separated domains apart and began to create slight imperfections (defects) in the skin layer [9]. Figure 7 demonstrated that membrane at the highest dope extrusion rate (3.0 – 3.5 cm^3/min) caused deterioration in rejection of particular solutes and disproportionately decreased in permeability value (flux).

The MWCO rating of a NF can vary widely depending upon the operating parameters, field of applications and chemical interaction or surface forces that occur between the test solute and the membrane. The MWCO profiles for hollow fiber NF membranes were constructed by
measuring solute separation for various PVP solutes and cyclodextrin enzyme solution of different molecular weight ranging from 30 000 to 51 000 Dalton. It can be seen that the rejection of a particular solutes increased with increases in molecular weight of PVP and cyclodextrin enzyme solutes and the profile are not sharp but gradually diffused for all spinning solutions. The MWCO measured for these membranes were measured to be around 36 000 to 50 000 Dalton and the overall MWCO values are listed in Table 3.

3.4. Plane polarized IR spectroscopy

Shear induced molecular orientation in membranes has been shown to enhance selectivity and has been directly measured using plane-polarized Fourier Transform Infra-Red Attenuated Total Reflection (FTIR-ATR) [8, 14]. It can be seen that, there was substantial orientation of polymer molecules in the flow direction when polymer solution was subjected to shear in the spinneret. Thus, upon subjecting the extruded filament to rapid coagulation, the orientation structure was frozen into the solid polymer.

Molecular orientation, which is mechanically induced on asymmetric membrane by varying shear rate experienced during casting, can be directly measured using spectroscopy. A preferential alignment of randomly coiled chain molecules in an anisotropic sample leads to a difference in absorption of plane-polarized infrared spectra between parallel and perpendicular directions. This phenomenon was known as linear dichroism. Therefore, relative intensity of linear dichroism indicates degree of molecular orientation in sample. Pronounced infrared dichroism shows alignment of molecules, whereas absence of infrared dichroism shows randomly oriented molecules. Chemical structure of polyethersulfone was shown in Figure 8, while infrared bands of functional groups in polysulfone were given in Table 5.

Figure 9(i) and Figure 9(ii) illustrates the polarized spectrum for membranes spun at low and high shear. It can be seen that the entire infra red spectrum is comparatively complicated with many strong bands in the 'finger print' region of the spectrum below 3800 cm^{-1}. The results obtained show that different DER during membranes fabrication exhibited dichroism in the infrared region but the highest DER membranes pronounced more effects in dichroism suggesting that having greater molecular orientation.

The polyethersulfone consist of a backbone made up of diaryl sulfone or aromatic sulfone (Ar-SO_2-Ar) and aromatic ether (C-O-C) groups, which show strong absorption at around 1290-1150 and 1245 cm^{-1}. Aromatic ether band is six member ring belong to acyclic ether. The bands at around 1225-1200 cm^{-1} and 1075-1020 cm^{-1} are belonging to the vibration of vinyl ethers group for asymmetric and symmetric respectively.

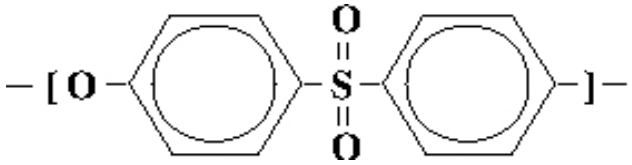


FIGURE 8: Monomer unit of polyethersulfone (PES)

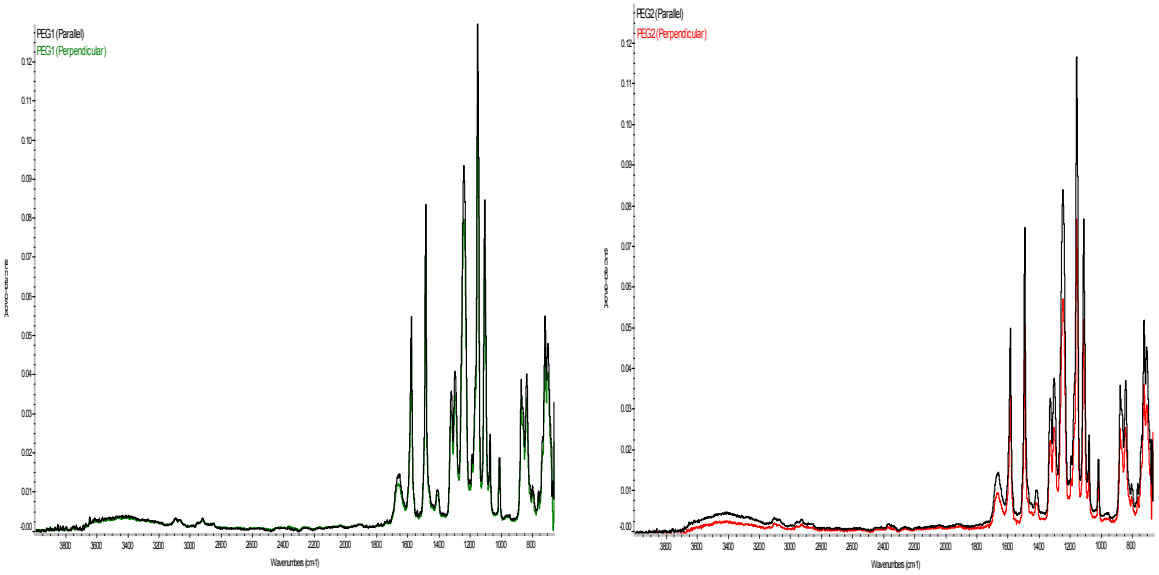
In addition, the aromatic C=C in polyethersulfone molecule (also from vinyl ether group) show strong absorption at 1660-1610 cm^{-1}, also from the vibration of the ether lingkage group. There is also another strong absorption band in the region at 1350 -1300 cm^{-1} or 1160-1120 cm^{-1} associated with vibration of the sulfur oxygen bonding which belong to the sulfone group. It can be observed that, higher shear membrane appears to be

more dichroism as a result of difference in background reflecting with parallel and perpendicularly polarized light.

Figure 10 shows a combination of two normalized spectrums from two different sheared (DER) membranes; they are at 2.0 and 2.5 cm^3/min. The 2.5 cm^3/min spun membranes showed the highest dicroism (absorption parallel to the shear direction < absorption perpendicular) in Figure 10. From these results it was clearly found that the orientation of polymer molecule in polyethersulfone membrane were significantly emphasized and discussed.

Table 5
Infrared bands of functional groups in polyethersulfone (PES)

Assignment	**Wave Number $\bar{\nu}$ (cm^{-1})**	**Description**
Ar-SO_2-Ar	Strong absorption 1290-1150	Aromatic sulfone group
Ar-O-Ar	strong absorption 1245 aliphatic ether 1150-1085	Aromatic ether band (six member ring belong to acyclic ether)
	1225-1200 (asymmetric) or 1075-1020 (symmetric)	vinyl ethers
	Strong absorption 1660-1610	Vinyl ethers, C = C
S = O	Strong absorption 1350-1300 or 1160-1120	Sulfur oxygen bonding



(i) (ii)

FIGURE 9: Plane-polarized infrared spectra parallel and perpendicular to shear direction for SS3 (a) low shear (DER) and (b) high shear (DER)

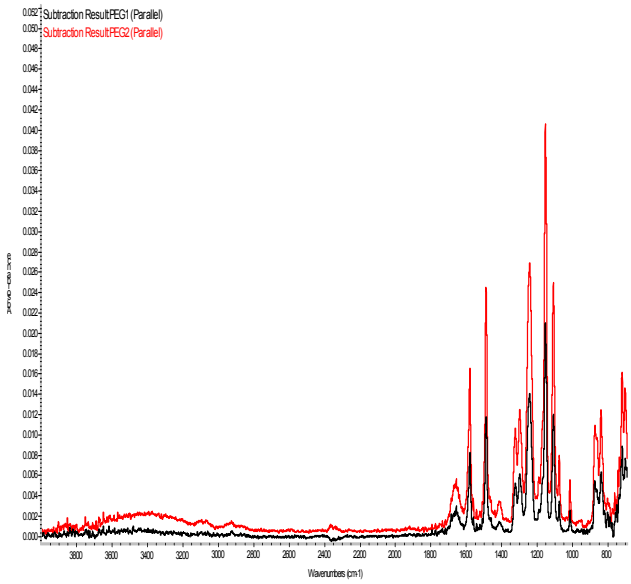


FIGURE 10: Linear dichroism spectrum for membrane spun from SS3 (substraction of parallel to perpinducular)

4. Conclusion

For this present study, we have investigated the effect of Dope Extrusion Rate (DER) on the nanofiltration hollow fiber membranes. The present results indicate that pore size of the outer skin of the final nanofiltration hollow fiber membranes may be decrease with increasing DER because smaller pore size of the final membranes results in better rejection for a solute and higher resistance for water permeation. CD enzymes were chosen for this characteristics test as to investigate the membrane performance with the enzyme solution. From this present study, we have successfully demonstrated that our membranes gave reasonable sodium chloride rejection at low-pressure application. The differences in morphology between the nanofiltration hollow fibers membranes spun at different DER was observed using Scanning Electron Microscope (SEM). In this study, we proposed that as the shear increased, the rejection of particular solutes were increased. It might result in that the final membranes become apparently denser/thicker. In addition, we found that when the shear increased, PWP flux, sodium chloride flux, PVP flux and CD flux decreases. Critical shear was observed at 2.5 cm^3/min extrusion rate, below which the rejection of fibers increased until a certain level while the flux decreases. In addition, there were no changes for the flux values. As a consequence, it was clearly found that the orientation of polymer molecule in polyethersulfone membrane were significantly discussed by directly measured using plane-polarized Fourier Transform Infrared Spectroscopy Attenuated Total Reflection (FTIR-ATR). As a consequence, from the results obtained it was possible to separate the CD enzymes by nanofiltration hollow fiber membranes proposed in this paper.

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