A study on the performance and morphology of multicomponents hollow fiber ultrafiltration membrane

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Abstract

Multicomponent (Polysulfone/poly(vinylpyrolidone)–K30/N,N-dimethylacetamide) hollow fiber ultrafiltration membrane was spun using dry-wet spinning method. The membrane was produced at different shear rate. Permeation properties and separation tests were examined using pure water flux and sodium chloride solution of concentration 1g/L respectively. Membrane morphology and molecular orientation were observed and directly measured using scanning electron microscopy (SEM) and plan polarized infrared spectroscopy. Positive infrared dichroism was detected only in samples of highest shear membranes. This suggests that the polymer molecules become aligned under high shear. Permeation test using pure water showed that increasing shear rate increases flux. On contrary, percentage rejection using sodium chloride solution showed a decreasing trend in rejection with the increased in shear rate. Increasing shear rate during dope extrusion through spinneret in the spinning of hollow fiber ultrafiltration membranes will apparently decrease the skin layer thickness and thus increasing the flux and also enhances the molecular orientation in the skin layer which causes high percentage rejection which was in the range of 21% to 33% for transmembrane pressure of 6 bar. The results indicate that there is a strong correlation between extrusion shear rate and the membrane morphology thus affecting the flux and rejection of hollow fiber ultrafiltration membranes.

Key words: hollow fiber, ultrafiltration, extrusion shear rate and molecular orientation

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1. Introduction

Development of integrally skinned asymmetric membranes by Loeb and Sourirajan in 1960's was a major breakthrough in membrane technology. An integrally-skinned asymmetric membrane consists of a very thin and dense skin layer overlaying on a thick and highly porous sub-layer, which is normally formed by phase inversion process. Previous research into membrane formation has focused on the phase inversion process parameters, which generally influenced the general morphology of the membrane, such the skin layer thickness and surface porosity. These parameters eventually the determining factors for membrane separation performance [11].

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In addition to phase inversion, it has also been recognized that molecular orientation will affect membrane selectivity and altering the rheological conditions during fabrication can bring about that orientation. Shear during casting and spinning has been shown to affect the permeation performance of polysulfone membranes and this has attributed to molecular orientation in the active layer [11]. Shear-thinning properties of polymer solution are often suggesting a progressive alignment of polymer molecules under shear in flow direction. As a result, shear induced molecular orientation induces favorable effects on membrane properties. Shilton et al. also have shown that shear and elongation during spinning affect the permeation performance of ploysulfone hollow fiber membranes [23,24]. They used plane-polarized infrared spectroscopy to directly measure and confirm the presence of shear rate induced polymer molecule orientation in gas separation membranes [12,21].

Sharpe et al., has studied on the extrusion shear and forced convection residence time in the spinning of polysulfone hollow fiber membranes for gas separation (Sharpe et al, 1999). This study reveals that increasing shear would increase selectivity to levels greater than the intrinsic value for the amorphous membrane polymer. This may result of induced molecular orientation in the active layer. However, a critical shear rate existed beyond which selectivity deteriorated. This was attributed to the development of surface pores as the active layer thins. On the other hand, membrane spun at intermediate forced convection residence times exhibited the highest selectivities. Skin formation must be complete, but excessive residence time allows deleterious non-solvent encroachment from the lumen. The results indicate that if enhanced selectivity and high flux to be achieved, membranes should be spun at high shear rate and an optimized residence time in order to minimized surface defects, increase the critical shear rate, decrease active layer thickness and heighten molecular orientation [20].

Wolf has studied the effects of shear on the phase separation of polymer blends and solutions for quite sometime (Wolf, 1984 and wolf, 1997). This work is of relevance to the membrane production but as yet, has not been invoked by membranologists. Shear can distort the phase diagram and hence alter precipitation thermodynamics considerably. Systems can gain or lose stability under shear depending on circumstances (wolf, 1997).
Wong et al. carried out a research on the determination of pore sizes and surface porosity and the effect of shear stress within a spinneret on asymmetric hollow fiber membranes [27]. This research shows that a high shear tends to eliminate surface pores of hollow fiber membranes, especially for big pores of Poiseuille flow. Contradicting with other findings, Wong et al. found that hollow fiber membranes spun with high shear rates apparently have thicker skin layer because of shear-induced chain orientation and packing. Shear reduces pores for Poiseuille and Knudson flows through two mechanisms, namely, shear-induced chain packing and orientation, and shear-induced pore deformation and transformation. The former tightens chains and reduces pore sizes to be suitable for Knudsen flow and solution diffusion, while the latter transforms or deforms big pores originally for Poiseuille flow to small pores suitable for Knudsen flow. They also reported for the first time, the mean pore size of the dense selective layer of hollow fibers for Knudsen flow as a function of shear rate [27].

In hollow fiber spinning, the pressurized viscous polymer solution extrudes through the conduit within a spinneret, thus it is subjected to various stresses. The highest shear stress usually occurs at the wall of the spinneret and may dramatically induce the molecular orientation of polymer chains at the outer surface of the nascent fiber. The influences of these stresses on the morphology of hollow fiber membranes and gas separation performance have been investigated in the past years [1,9,10,23,24].

Chung et al. have demonstrated the effect of shear rate on the outer surface morphology of polyethersulfone (PES) hollow fiber ultrafiltration (UF) membranes by an atomic force microscope (AFM). A digital instrument (DI) AFM was used to reveal the surface morphology of hollow fiber membranes prepared with varying shear rates from 1305 to 11, 066s^{-1}. A Tapping mode was operated for studying the polymeric membranes when AFM was applied to image the surface of a fiber in air. AFM images of the outer surface have revealed that the nodules in the outer skin appeared to be randomly arranged at low shear rates but formed bands that were aligned in the direction of dope extrusion when the shear rate increased. Both nodules sizes in the fiber spinning and transversal directions decreased with the increasing shear rate possibly because of chain disentanglement and thermodynamically favored. However, this result has not been reported so far. The analysis of AFM images showed that the roughness of the outer surface of hollow fiber UF membranes in terms of R_{ms}, R_a, and R_z decreased with an increase in shear rate. The pure water flux of the membranes was nearly proportional to the mean roughness resulted in lower separation of membranes. AFM data also imply that there was a certain critical value of shear rate around 3585s^{-1}, the roughness decreased significantly with an increase in shear rate below 3585s^{-1} and almost leveled off or in a much slower pace above this shear rate [8].

Aptel et al. studied the effect of shear rate on the properties of polysulfone hollow fiber ultrafiltration membranes. They reported that the water permeability of final fibers decreased but the rejection increased with an increase in the shear rate. They explained that the orientation was introduced into the polymer solution as it was extruded from the spinneret [1]. Porter reported that a tighter fiber with lower permeability and higher rejection would be resulted as the spinning solution velocity was increased because polymer molecules under shear flow tended to align themselves in the direction of. He concluded that the pores in the skin would be elongated as a result of the alignment of polymer chains when spinning solution velocity was increased [17]. Chung and coworkers investigated the effect of shear rate on morphology and properties of hollow fiber membranes for both gas and liquid separation [4,9,10,18,19]. They demonstrated that the orientation induced by shear stress within the spinneret could be frozen into the wet-spun fibers and might relax in the air gap region. Their results suggested that the hollow fiber membranes spun with enhanced shear had a lower permeability but higher separation due to greater molecular orientation induced in the high-sheared fibers. They also found that there was a certain critical value, when the dope extrusion speed was over this value, the final fiber performance would not be influenced significantly [18]. However, this research aimed to determine the morphology and performance of multicomponent polymer (PSF/PVP–K30/ DMAc) spun as hollow fiber ultrafiltration membrane and sheared at different shear rate using dry-wet spinning method.

2. Experimental

2.1. Materials

Asymmetric hollow fiber membranes for ultrafiltration were fabricated using dope consisted of 18% (w/w) polysulfone (udel-P1700, weight-average molecular weight 35400) supplied by Amoco Chemicals and 13% (w/w) poly (vinyl-pyrolidone) – K30. The solvent used to prepare the dope solution was 69% (w/w) N, N-dimethylacetamide (DMAc). The percentage composition were determined and adopted through titration, which was very close to the cloud point.

2.2. Membrane spinning

The dope reservoir was at ambient temperature (25 ± 2 ºC) during spinning. On extrusion from the spinneret (spinneret dimensions: OD 600µm/ ID 300µm), the fiber passed through a forced convection chamber (diameter 5cm, heights 9cm), which was flushed with 0.1 ml/min of nitrogen gas. The nitrogen was induced through a 0.25-inch (0.6cm) tube which abutted upon the chamber normal to the surface at mid-height. A 2mm clearance existed between the top of the forced convection chamber and the bottom plate of the spinneret and the water level in the first coagulation bath.

Tap water at 14 ± 0.5 ºC was used in the external coagulation bath and the bore coagulant used was distilled water. Hollow fiber were spun at various dope extrusion rates and hence at different levels of shear. The jet-stretch ratio (wind-up speed/ extrusion speed) was fixed at 1 throughout. The bore fluid injection rate was 1ml/min. After spinning, the membranes were steeped in water and then dried using methanol solvent exchange technique [15].

2.3. Spinning dope rheology and flow profile in spinneret

Previous rheological test have shown that in the range of shear rates experienced during spinning, the dope used in this work behaves as a shear thinning power law fluid: power law index 0.693, power law constant 43.1(Pa.s^n) [12,13]. The flow profile in the spinneret for the different dope extrusion rates can then be established by solving the flow equations for a power law fluid in a concentric annulus [21]. Table 1 summarizes the general spinning conditions.

Table 1
General spinning conditions

Spinning dope composition	18% (w/w) polysulfone 13% (w/w) poly(vinyl-pyrolidone) – K30 69% (w/w) N,N-dimethylacetamide
Spinning dope temperature	25 ± 2 ºC (Ambient temperature)
Spinning dope rheological properties	Power law index 0.693 Power law constant 43.1(Pa.s^n)
Spinneret dimensions	OD 600µm/ ID 300µm
Bore fluid coagulant	Distilled water
Bore fluid temperature	25 ± 2 ºC (Ambient temperature)
Dope extrusion rate	2.5 cm^3/min 3.0 cm^3/min 3.5 cm^3/min 4.0 cm^3/min
Forced convection flow rate	1ml/min
Forced convection gas	Nitrogen
External coagulant bath	Tap water
External coagulant bath temperature	25 ± 2 ºC (Ambient temperature)
Jet-stretch ratio (wind-up speed/ extrusion speed)	1:1

2.4. Permeation test

The fluxes of the membranes were measured in a cross flow filtration set-up. Pure water permeability and percent separation of sodium chloride solution were used to measure its performance. Pressure normalized flux and percentage rejection were calculated by

$$\left(\frac{P}{l}\right)_i = \frac{Q}{A\Delta p} \tag{1}$$

Where A is the membrane surface area, Q is the volumetric flow rate and Δp is the pressure difference.

$$R = \left(1 - \frac{C_i}{C_o}\right) \text{x } 100 \tag{2}$$

where R is the percentage rejection, C_i is the permeate concentration at any time and C_0 is the feed concentration.

2.5. Morphology study by SEM

Fiber samples were immersed in liquid nitrogen and fractured to obtain tidy cross-section of fibers and then deposited with gold in a sputter coater. After that, the samples were imaged and photographed by employing a scanning electron microscope (Philips SEMEDEX; XL40; PW6822/10) with potentials of 10kV in achieving magnification ranging from 250x to 5000x

2.6. Plane polarized IR spectroscopy

Plane polarized i.r. radiation has been recognized as a good probe of molecular orientation, because the preferred orientation of specific functional groups can be determined. The samples were mounted at the sample position with the outer skin surface facing the infrared beam and were rotated according to the shear direction. Thus, linear dichroism spectra were obtained by straightforward subtraction of perpendicular-polarized spectrum from parallel-polarized spectrum.

2.7. Principles of fiber spinning

Gravity will influence the minimum jet-stretch ratio achievable in the spin line during membrane production. Once set, the jet-stretch ratio determines the longitudinal velocity profile in the dry jet gap. Since the jet-stretch is maintained at 1 throughout this study, there can be minimal elongation or strain rate in the dry gap. Thus, the velocity of the extruded filament can be assumed constant in the spin line and equal to the extrusion speed [20]. In addition, lumen side coagulation starts immediately on extrusion and restricts any subtle die-swell/gravitational effects since mechanical integrity is immediately conferred on the hollow filament. In fact, no die swell has been detected in the laboratory during spinning of the dope. This is in line with rheological expectation. Previous test have shown that polysulfone solutions exhibit no detectable normal stress [24]. This is in turn, is consistent with the prior finding that polysulfone solutions are only moderately viscoelastic by virtue of measured Trouton ratios [22]. These rheological properties are not surprising for a low-molecular-weight polymer like polysulfone (molecular weight 35400 [25]).

Based on the above principles, the fiber velocity was calculated by dividing the dope extrusion rate by the cross-sectional area of the spinneret annulus. The residence time in the forced convection chamber was determined by dividing the chamber height by the fiber velocity [20]. Indeed, in their work, Sharpe et al. found that no significant variation in fiber dimensions were noticed which confirms that fixing the jet stretch at a value of 1 eliminates elongation or strain influences.

3. Results and discussion

3.1. Effect of shear on membrane performance

According to the experimental data shown in Table 2 and Figure 1, these results can be related to the rheological properties of the dope solutions. Since the dope used is shear thinning and exhibited viscoelastic by virtue of Troutan Rations suggesting that polymer molecules become more aligned at greater shear [13,21]. As shown in Figure 1, flux increases with the increase in extrusion shear during spinning process. Since the solution used in this study was shear-thinning, when shear rate increases it might cause a decrease in solution viscosity presumably due to chain entanglement losses in solution. In this case membrane might undergo an early demixing and precipitation to results in a porous and highly oriented skin layer [5,20] and thus causes a reduction in membrane percentage rejection. Furthermore, spinning membrane at high shear would pull the molecular chains or phase-separated domains apart and began to create slight imperfections (defects) in the skin layer [20]. As shown in Figure 2, membrane produced by high-shear ($235.8s^{-1}$) showed a pronounced positive linear dichroism, indicating that polymer backbone aligned in shear direction. On contrary, membranes produced by lower shear rates were dichroic in opposite directions (Figure 2). Increasing shear decreased active layer thickness and increased pressure-normalized flux [20].

Table 2
Permeability and selectivity of membrane with different shear rate

Module No.	DER (cm^3/min)	Shear s^{-1}	Feed Pressure (bar)	PWP (L/m^2hr)	NaCl Flux (L/m^2hr)	NaCl % Rejection
A1-1	2.5	147.8	6	0.24	0.32	33
A1-2	3.0	176.8	6	0.34	0.37	23
A1-3	3.5	206.3	6	0.41	0.52	24
A1-4	4.0	235.8	6	0.49	0.59	21

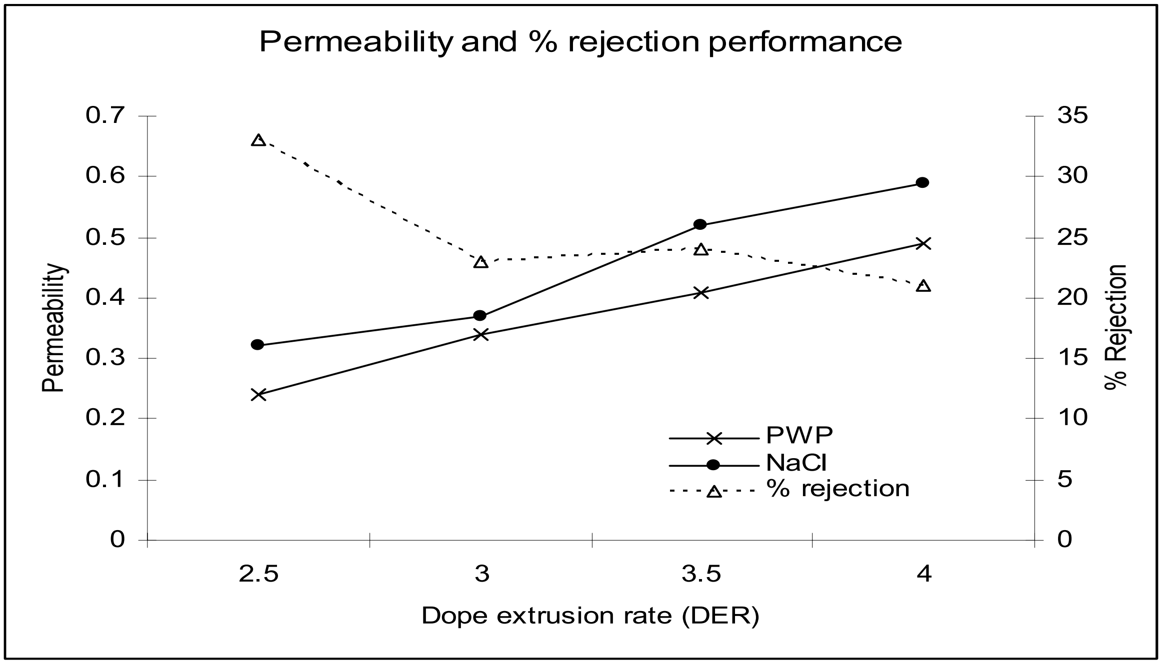


Figure 1: Relationship of permeability and percentage rejection with extrusion rate

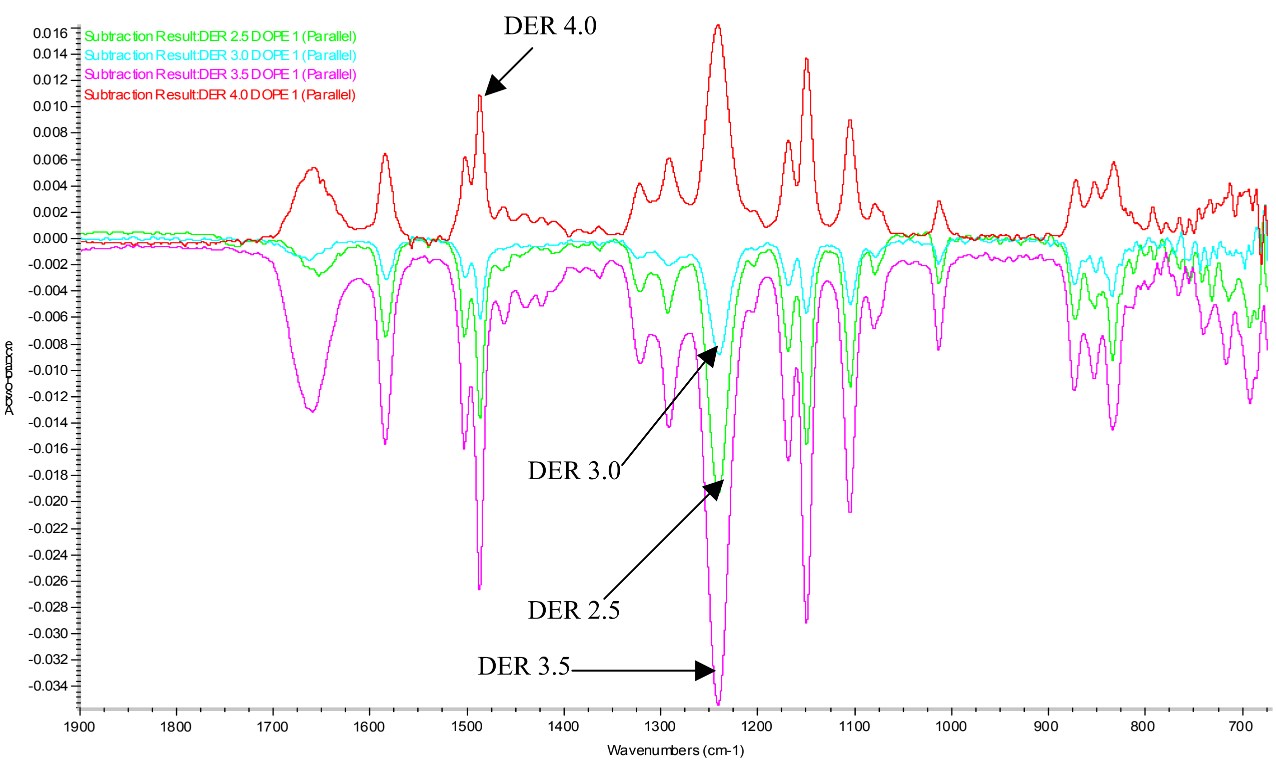
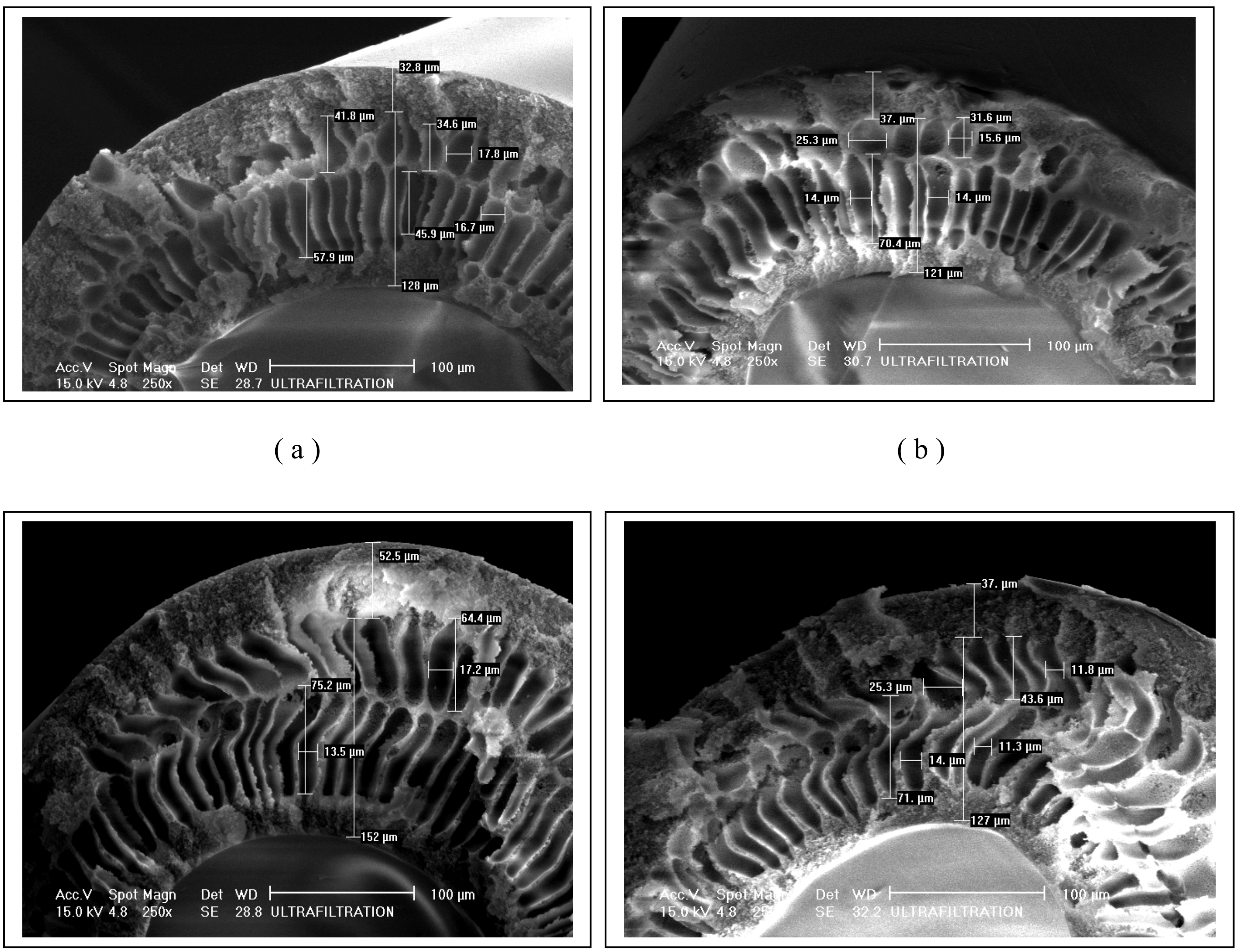


Figure 2: The summary of perpendicular-polarized spectrum subtracted from parallel-polarized spectrum.

3.2. Effect of shear on membrane morphology

On the hand, dope formulation being very close to its cloud point (binodal line) would result in a membrane with a thin skin and high flux [19]. The electron micrographs of membranes cross-section are shown in Figure 3. As depicted in Figure 3, membranes developed in this study composed of dense skin layer with large fingerlike cavities extending from beneath the selective skin layer to the bottom surface of the membrane. This is in line with Cabasso et al. (1977), who states that the dry-wet spinning procedure of polysulfone is often accompanied by the formation of cavities and intrusion ("finger-like') cells within hollow fibers [3]. As shear increases, the fingerlike cavities merge from two to form one layer of large fingerlike cavity. The formation of macrovoids generally leads to less mass transport resistance [30]. Thus, this might be the cause of flux increase and decrease of rejection in the membrane spun at highest shear.



(a) (b)

(c) (d)

Figure 3: SEM of membrane cross-section
(a:147.4 s^{-1}; b: 176.8 s^{-1}; c: 206.3 s^{-1} ;d: 235.8s^{-1})

4. Conclusion

Extrusion shear rate has a significant effect on the performance of permeability and selectivity of ultrafiltration hollow fiber membrane. It is likely that shear affects the phase inversion dynamics of membrane precipitation as well as the orientation of polymer molecules in the active layer. It was found that pressure-normalized fluxes of asymmetric multicomponent membrane were increased with increasing shear because of the reduction in the skin layer thickness. On the other hand, it causes a reduction in the percentage rejection of sodium chloride solution. The results from plane polarized IR Spectroscopy showed a positive linear dichroism obtained from high sheared ($235.8s^{-1}$) hollow fiber ultrafiltration membrane, which indicates that polymer backbone aligned in shear direction. On contrary, membranes produced by lower shear rates were dichroic in opposite directions. In addition, SEM images showed that there are changes in the finger-like cavities. It can be seen that, as the extrusion shear increases, the two layers of finger-like cavities tend to merge to form one. Thus it can be concluded that extrusion shear can affect membrane morphology as well as membrane performance in multicomponent ultrafiltration membrane.

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