Effect of polymer concentration on development of asymmetric polyethersulfone membrane for gas separation

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Abstract

Asymmetric polyethersulfone (PES) membranes were fabricated through a simple dry/wet phase inversion process. Casting solution developed in this study consisted of polyethersulfone, 1-methyl –2- pyrolidone (NMP) and distilled water. The casting solution was cast using pneumatically-controlled casting machine at constant shear rate and evaporation time. The membranes were characterized by gas permeation with pure O_2 and N_2 as test gases, while the cross section and surface layer morphologies were examined using Scanning Electron Microscopy (SEM). The results showed that the selectivity of the PES membrane increases with the increasing of polymer concentration. Polymer concentration has been identified as one of the most influential parameter in determining membrane performance as well as producing different morphology. Selectivity of these membranes was relatively higher compared to conventional membranes, some of them even surpassed the intrinsic. Thus, the selectivity of O_2/N_2 is approximately 7.95, at 32.67 wt % of PES concentration and it is believed that the parameter such as polymer concentration used strongly affects the membrane performance.

Keywords : Gas separation, phase inversion, asymmetric membrane, polymer, concentration

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1. Introduction

Membrane separation processes has become one of the emerging technologies, which undergo a rapid growth during the past few decades. Gas separation became a major industrial application of membrane technology only during the past 15 years, but the study of gas separation actually has begun long before that period [1].

Asymmetric membranes that are suitable for gas separation should have thin and dense skin layers supported by thick porous sublayers [2, 3, 4]. One of the major problems confronting the use of membrane based gas separation processes in a wide range of applications is the lack of membranes with high pressure-normalized flux and high selectivity. During fabrication, membrane formation process plays an important role and certain factors need proper attention in order to produce a good gas separation membrane [5].

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According to previous researchers, different type of nonsolvent additive [2; 6], shear rate [7, 8, 9, 10,12], polymer concentration [11, 12] and evaporation time [12, 13] are most important parameters understudied since these influence the membrane formation.

Polymer concentration has a strong correlation to viscosity and gives a big influent to the membrane performance [11, 12, 14, 15]. Increasing the polymer concentration of casting solution will formed a denser and thicker skin layer, resulting in a more selective but less productive asymmetric membranes for gas separation as described by previous researcher [12, 16]. The optimum polymer concentration of casting solution therefore has to be determined in order to achieve defect-free and ultrathin-skinned asymmetric membranes for gas separation. Referring to Teo et al, polymer concentration of about 25 wt.% to 50 wt.% in the casting solution is needed to achieve the resulting membrane with desirable separation factor and mechanical strength. Exceeding the optimum polymer concentration tends to form membrane with low selectivity and poor mechanical strength. A preferred range of polyethersulfone concentration is 25wt.%- 40wt.%. The optimum range is 25 wt. % to 35 wt. % [17]. Therefore, in this study, the influence of the polymer concentration will be discussed in order to develop an asymmetric polyethersulfone membrane with high performance.

2. Experimental

2.1. Materials

Polyethersulfone (PES) (Radel A300 from Amoco) with weight-average molecular weight of about 15000 Dalton was selected as membrane material in this study. 1-methyl-2-pyrrolidone (NMP, 99.7+ %), was the solvent supplied by MERCK and used as-received. The nonsolvent additive used was distilled water. Polydimethylsiloxane (Sylgard-184) obtained from Dow Corning Corp. was used as the coating material to seal the surface defects of the asymmetric membranes. n-Hexane was used as a solvent for the polydimethylsiloxane (Sylgard 184). The membranes were tested with oxygen and nitrogen gases.

2.2. Turbidity titration method

Turbidity titration method was used to determine the cloud point or the equilibrium thermodynamic data on ternary system (polymer / solvent / nonsolvent additive). Cloud point represents an approximate transition boundary beyond which demixing (phase separation) takes place, indicating that a casting solution has become thermodynamically unstable [19]. 100g of polymer solution (solvent + polymer) was titrated with nonsolvent additives until the cloud point is observed. Titration was conducted at temperature of $30^0C\pm2$ and 84% humidity, until permanent turbidity was detected visually. Each recorded data will represent the average reading of at least four samples.

2.3. Preparation of casting solution (Dope)

Apparatus for preparing the casting solution is shown in Figure 1. Polymer was first dried for at least 4 hours in a vacuum oven at a temperature of $150^{o}C$ in order to remove all absorbed water vapor. The polymer was then dissolved in NMP and nonsolvent additive. The solution was heated at $40-60^{0}C$ and stirred for about 4 to 6 hours to achieve complete homogeneity. Finally, the solution was kept in a storage bottle and was degassed by using ultrasonic bath to remove any traces of micro bubbles present in the solution.
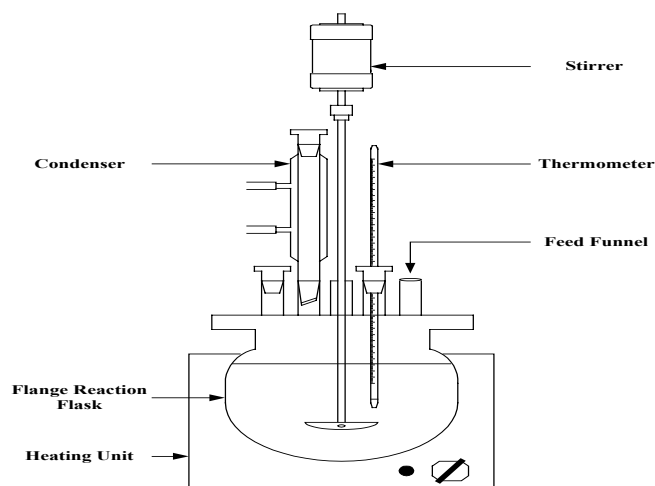

FIGURE 1: Dope preparation system

2.4. Measurement of casting solution viscosity

The viscosities of the casting solutions were measured with a Brookfield viscometer (model DV-III) using spindle number 3 at 2 rpm.

2.5. Membrane casting

Asymmetric polyethersulfone membranes were prepared according to the dry/wet phase separation process using a pneumatically controlled casting machine. The casting was carried out at constant evaporation time and shear rate. The procedure involves four different steps: (i) casting of homogeneous casting solution (ii) evaporation of solvent (iii) immersion in a nonsolvent bath and (iv) washing and drying of the membrane

The casting process was conducted at room temperature ($30^{o}C\pm2$) and approximately 84% relative humidity. A small amount of casting solution was poured onto a glass plate with a casting knife gap setting of $150\mu m$ and at an appropriate casting shear of 223.33 s^{-1}. During the casting process, forced convective evaporation was induced on membranes before being immersed into the coagulation medium. An inert nitrogen gas stream was blown parallel and across the cast membrane surface at a specified exposure time of 10 s. This will enable, a sufficient amount of the easily

volatized solvent to be evaporated. The glass plate together with the membrane was then immersed into the coagulation bath (compose of water as the coagulant medium). After the coagulation process completed, the membranes were transferred to a water bath for 1 day and finally, were washed with methanol for 1 day before being air dried for at least 48 hr at room temperature to remove any residual organic compounds.

2.6. Membrane coating

A 3 wt% coating solution was prepared by dissolving polydimethylsiloxane (Sylgard–184) in n-hexane. The membrane were cut into a circular disc of $13.5cm^2$ in area and the solution was slowly poured on to the top layer of the membrane for 5 min, before it was removed and allowed to cure at room temperature for 24 h.

2.7. Membrane characterization methods

2.7.1. Gas permeation test

The pressure-normalized fluxes of the membranes were determined by using pure oxygen and nitrogen gases with purity 99.99%. Membranes were cut into a circular disc of $13.5cm^2$ in area. These experiments were carried out at ambient temperature ($30\pm2\,^oC$) at pressure drop of 1,3 and 5 bar. Rate of gas permeation were measured by using a soap bubble flow meter. The pressure–normalized fluxes, $(P/l)_i$ of pure gases such as oxygen and nitrogen is calculated by:

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta p_i A}$$

where P/l is defined as pressure-normalized flux for gas i (permeability coefficient divided by effective skin thickness)($cm^3(STP)/cm^2.s.cmHg$), Q_i is the volumetric flow rate of gas i (cm^3/s) at STP, Δp_i is the membrane pressure drop (cmHg), and A is the membranes surface area (cm^2). The common unit of pressure-normalized flux is GPU.

$$GPU = 1X10^{-6} \frac{cm^3(STP)}{cm^2 - \sec - cmHg}$$

Membrane selectivity, α_{ij} with respect to any gases, i and j, is the ratio of pressure-normalized fluxes,

$$\alpha^i_j = \frac{(P/l)_i}{(P/l)_j}$$

2.7.2. Scanning electron microscope (SEM)

Membrane morphology (cross-section and surface layer) was examined using a scanning electron microscope technique. A small piece of the tested membranes were cut and conditioned in liquid nitrogen to leave an undeformed structure and

mounted on sample stubs. The samples were then coated with gold by sputter coating under vacuum (Biorad Polaron Divison). The morphologies were then view with scanning electron microscope (Philips SEMEDAX; XL40; PW6822/10) with potentials of 20 kV under magnifications ranging from 300Xto 10000X.

3.0   Results and discussion

3.1 .   *Effect of polymer concentration on casting solution*

The optimum polymer concentration for casting solution had to be determined in order to achieve defect-free and ultrathin-skinned asymmetric membrane for gas separation. The increasing of polymer concentration in casting solution formed a dense and thicker skin layer, resulting in a more selective but less productive asymmetric membrane for gas separation [12, 16]. The preparation of polyethersulfone membrane required the casting solution to be as close as possible to the state of phase separation. All of the compositions were obtained using turbidimetric titration measurement. Results for turbidimetric titration are listed in Table 1. The values of polymer concentration after titration were identified less than values before titration. Most of the polymer concentrations after titration were identified in the optimum ranges which are suggested by Teo et al. [17]. Increased the polymer concentration is required less amount of nonsolvent additive (NSA). Table 2 shows the calculated solubility parameter difference of the various components understudied. From the calculation, the solubility parameter difference between polymer and nonsolvent additive ($\Delta\delta_{NSA-p}$), water has the biggest differences indicative of weak interaction. The weak interaction between water and polyethersulfone ($\Delta\delta_{NSA-p}$) promote the formation of big polymer aggregates. The relationship between viscosities of casting solutions with polymer concentrations is shown in Table 3. Pesek and Koros show that the addition of more polymers in the casting solution increased it viscosity [16]. The result obtained in this study was similar to a previous researcher. Therefore, polymer concentration and viscosity were identified having a significant effect on the flat sheet membrane casting due to solubility parameter differences.

Table 1
Composition of casting solution with different polymer concentration

Before Turbidimetric Titration			
Component	Solution Composition (wt.%)		
	CS1	CS2	CS3
Polyethersulfone(PES)	25	30	35
1-methyl-2-pyrrolidone	75	70	65
After Titration using Water as Nonsolvent Additive			
Component	Solution Composition (wt.%)		
	CW1	CW2	CW3
Polyethersulfone(PES)	23	27.74	32.62
1-methyl-2-pyrrolidone	68.9	64.72	60.58
Water (H_2O)	8.1	7.54	6.8

Table 2

Solubility parameter difference for studied systems

Components	Solubility Parameter Difference (a - b)	Solubility Parameter Difference (c - b)	Solubility Parameter Difference (a - c)	Solubility Parameter Difference (c - d)
Water[a] -PES[b]	33.85	-	-	-
NMP[c]-PES[b]	-	2.97	-	-
Water[a] -NMP[c]	-	-	35.48	-
NMP[c]-Methanol[d]	-	-	-	15.38
NMP[c]-Water[d]	-	-	-	35.48

* a-nonsolvent additive   b-polymer   c-solvent   d-coagulant

Table 3
Viscosity of various casting solutions

Polymer Solution	Polymer Concentration (wt %)	Viscosity (cPs)
CW1	23.00	370.00
CW2	27.74	1406.00
CW3	32.62	3852.00

3.2.   Effect of concentration on membrane performance

Table 4 shows the summary of separation properties of uncoated and coated membranes based on N_2 and O_2 for pressure-normalized flux and selectivity with respect to polymer concentration. All of the uncoated membranes seem to exhibit higher pressure-normalized flux but less of selectivity. This is probably due to the pores (defects) and the enhancement of free volume in the ultrathin skin layers. Skin layer pores are defined here as passageways that allow communication between upstream and downstream side of the membrane by a Knudsen or viscous flow

process [20]. Wang et al. revealed that, the extremely high pressure-normalized fluxes of gases through the membranes were due to the surface porosity. The gas transport through these membranes were predominantly determined from the combination of Knudsen flow (pore size>10^2-10^0nm) and Poiseuille flow mechanism [2] and not fully by solution diffusion. According to Wang [18], the O_2 /N_2 intrinsic selectivity value of polyethersulfone dense film was determined to be 6.1. The results showed that, the selectivity of the uncoated asymmetric membranes is much lower when compared to the intrinsic value. The selectivity and the pressure-normalized flux of those uncoated membranes show fluctuation occurring when the polymer concentration increased.

Table 4
Separation properties of uncoated and coated membranes at different polymer concentration

Solution	Uncoated Pressure-normalized Flux GPU		Selectivity	Coated Pressure-normalized GPU		Selectivity
	(P/l)N_2	(P/l)O_2	(P/l)N_2	(P/l)O_2	(P/l)O_2	(P/l)N_2
CW1	727.36	620.14	727.36	7.01	16.11	2.30
	756.53	695.36	756.53	4.90	13.29	2.71
	249.06	207.60	249.06	5.43	11.65	2.15
	93.48	98.85	93.48	5.82	12.21	2.10
	172.76	185.59	172.76	5.71	11.84	2.07
	172.00	187.37	172.00	6.23	12.58	2.02
Mean	361.86±298.63	332.49±255.83	361.86±298.63	5.85±0.72	12.95±1.66	2.2±0.26
CW2	25.65	32.53	25.65	2.26	11.90	5.26
	6.60	17.84	6.60	1.62	12.02	7.41
	14.44	28.25	14.44	1.49	11.12	7.45
	31.11	42.43	31.11	1.39	10.56	7.61
	6.43	15.03	6.43	1.67	11.79	7.07
	90.95	82.99	90.95	3.69	16.61	4.50
Mean	29.20±31.86	36.51±24.86	29.20±31.86	2.02±0.87	12.33±2.17	6.55±1.33
CW3	86.04	94.89	86.04	1.18	9.40	7.99
	55.69	73.56	55.69	1.01	9.59	9.54
	39.78	45.56	39.78	1.78	10.86	6.11
	6.96	20.00	6.96	0.86	7.23	8.42
	46.08	42.02	46.08	1.64	9.19	5.60
	50.37	64.61	50.37	1.19	11.98	10.03
Mean	47.49±25.56	56.77±26.43	47.49±25.56	1.28±0.36	9.71±1.61	7.95±1.79

All of the uncoated membranes exhibited a poor O_2/N_2 selectivity. None of the sample could surpass the O_2 /N_2 intrinsic selectivity value of polyethersulfone dense film. This is probably due to the existent of defects at the surface layer. Therefore, to obtain high performances polyethersulfone membrane, surface layer should be coated using silicone rubber. Asymmetric membranes usually contained few defects which are attributed to the incomplete coalescence of the nodule aggregates of the composed skin layer. From Table 4, membranes with silicone coating exhibited better performance compared to uncoated membrane. The membranes prepared from dopes labeled CW3 (32.62 wt. % of PES) show high selectivities, but low pressure-normalized flux. The flat sheet membranes prepared from the casting solutions, CW2 (27.74 wt. %) and CW1 (23 wt. %) however exhibited high pressure-normalized fluxes but low selectivity, especially for membranes prepared from CW1. Most of the coated membranes (CW3) exhibited high selectivity either surpasses the polyethersulfone intrinsic selectivity. Therefore,

coating reduced the pressure-normalized flux thus enhanced the membrane selectivity by caulking the pinholes or defects on the membrane outer dense layer.

By increasing the polymer concentration, it was observed that the skin layer thickness is increased, while both mean pore size and surface porosity decreased. As can be observed in Table 5 and Figure 2, active skin layer thickness increased from 398.95Åto 538.32Å while both mean pore size and surface porosity decreased from $0.071x\ 10^{-8}$ to $0.043\ x\ 10^{-8}$ and from $0.78\ x\ 10^{-4}$ to $0.42\ x\ 10^{-4}$, respectively. Therefore, the separations of gases through membranes were influenced by active skin layer thickness, pore size and surface porosity of the membrane.

Table 5

Fine structural details of membranes at different polymer concentration

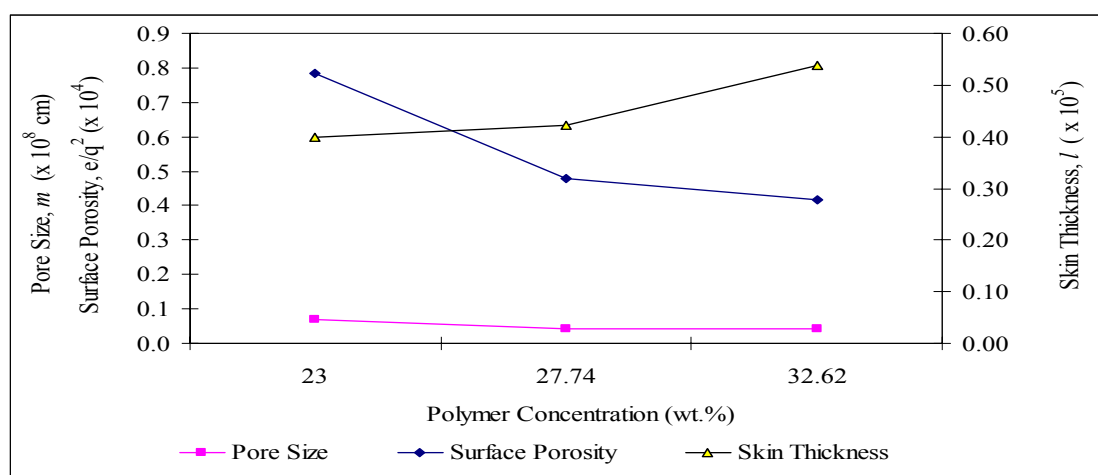| Polymer Solution	CW1	CW2	CW3
Skin Layer Thickness	398.95Å	422.32Å	538.32Å
Surface Porosity	$0.88\ x\ 10^{-4}$	$0.63\ x\ 10^{-4}$	$0.36\ x\ 10^{-4}$
Pore Size	$0.078x\ 10^{-8}$	$0.060x\ 10^{-8}$	$0.0375\ x\ 10^{-8}$

FIGURE 2: Surface porosity, pore size and active skin layer thickness versus polymer concentration

3.3. *Effect of polymer concentration on morphologies of uncoated and coated membranes*

Figures 3 to 6 illustrate the morphologies of uncoated and coated membranes. Both the uncoated and coated membranes displayed similar cross sectional with a long finger like macrovoids from the skin layer to the support region. The length of the macrovoids diminished from lower to higher polymer concentration as illustrated in Figures 3(a) to 3(c) and Figures 5(a) to 5(c) respectively. A large long finger-like macrovoids could be clearly seen in Figure 3(a) for low polymer concentration whereas a much smaller macrovoids in Figure 3(c) for high concentration. Analysis on the cross section of these membranes revealed that a thin dense skin layer with

highly porous substructure appeared for both coated and uncoated membrane. Figures 4(a) to 4(c) and Figures 6(a) to 6(c) illustrate the top surface layer of uncoated and coated membranes. The top surface layer of coated membranes was smooth compared to uncoated membranes. Defects were not observed on the surface layer of coated membrane whereas visible on the uncoated membranes although 6000X magnification were used.
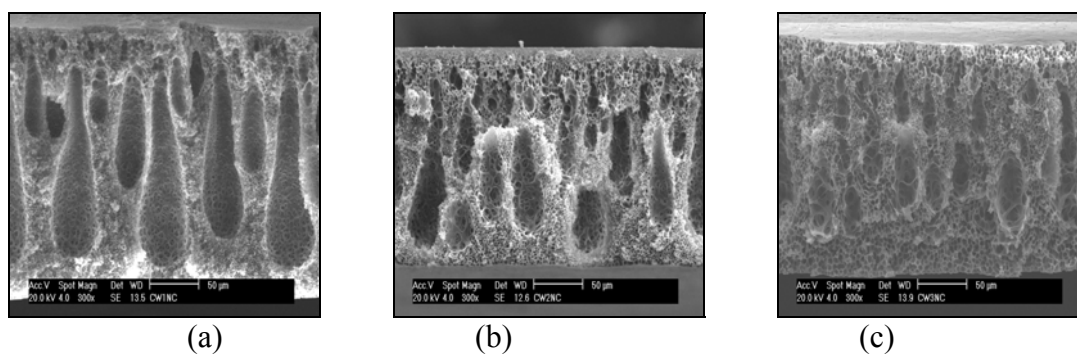

(a)   (b)   (c)

FIGURE 3: SEM cross section of uncoated membrane micrographs at different polymer concentration at magnification 300X. (a) 23wt.% (b) 27.74 wt.% and (c) 32.62 wt.%
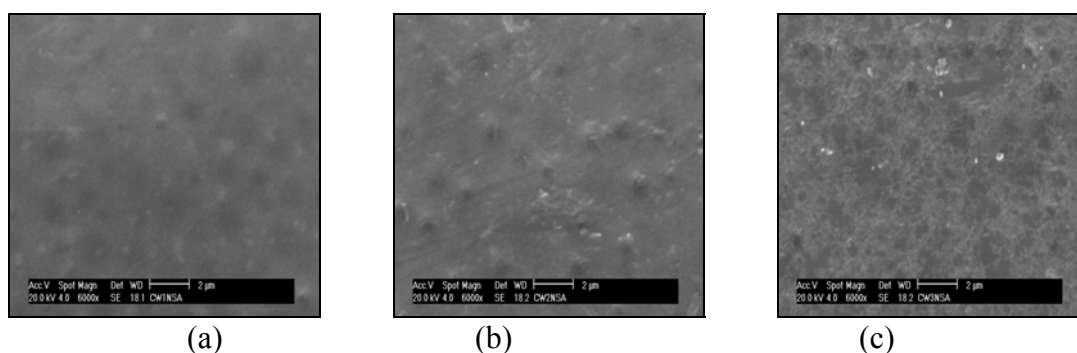

(a)   (b)   (c)

FIGURE 4: SEM surface layer of uncoated membrane micrographs at different polymer concentration at magnification 6000X. (a) 23wt.% (b) 27.74 wt.% and (c) 32.62 wt.%
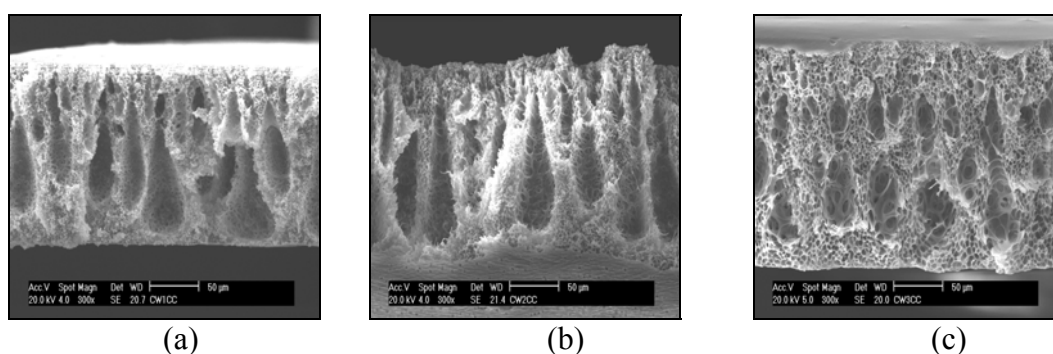

(a)   (b)   (c)

FIGURE 5: SEM cross section of coated membrane micrographs at different polymer concentration at magnification 300X. (a) 23wt.% (b) 27.74 wt.% and (c) 32.62 wt.%
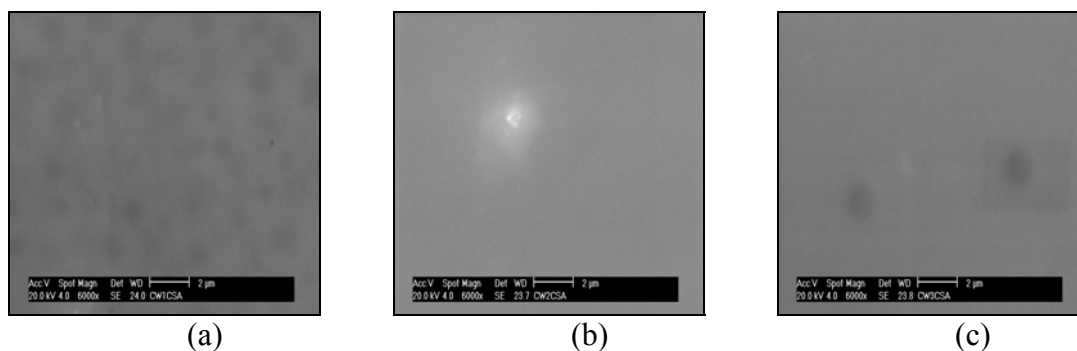
<center>(a)　　　　　　　　　　　(b)　　　　　　　　　　　(c)</center>

FIGURE 6: SEM surface layer of coated membrane micrographs at different polymer concentration at magnification 6000X. (a) 23wt.% (b) 27.74 wt.% and (c) 32.62 wt.%

4　　Conclusion

Polymer concentration was identified havinga significant effect on the flat sheet membrane due to the solubility parameter differences. All of the uncoated membranes exhibited a poor O_2/N_2 selectivity, probably due to the pores (defects) and the enhancement of free volume in the ultrathin skin layers. Silicone rubber coating was successful increasing the membrane selectivity. The PES membrane with the best combination of pressure-normalized flux and selectivity of O_2/N_2 was prepared from solution containing polymer concentration of 32.62 wt%. It exhibited an average O_2 pressure normalized flux of 9.71 GPU (0.0523 Barrer) and O_2/N_2 average selectivity of 7.95. It could be considered as defect-free because the selectivity of O_2/N_2 was found to be greater than 80% of intrinsic O_2/N_2 of dense polyethersulfone membrane film. These effects are found to influence the structure of the active layer thickness, pore size and surface porosity. The results clearly suggested that when polymer concentration increases, the active layer thickness also increases while the pore size and surface porosity decreases. Hence, polymer concentration in casting solution has been identified as one of the most influential parameter in determining membrane performance.

Acknowledgements

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