

## FORMATION OF ASYMMETRIC POLYSULFONE FLAT SHEET MEMBRANE FOR GAS SEPARATION: RHEOLOGICAL ASSESSMENT

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**Abstract.** This study was focused on the effect of shear rate on asymmetric polysulfone membrane structure and gas separation performance. Flat sheet asymmetric membranes were formed using an optimized ternary casting solution. The asymmetric membranes with the molecular-oriented skin layer were prepared by a simple dry/wet phase inversion technique with forced convection using a newly developed pneumatically-controlled casting system. Experimental investigation was conducted focusing on different casting speed, thus representing different rheological conditions. Casting speed was varied from 5s to 60s, as known that varying casting speed would vary shear rate. Rheologically induced molecular orientation on the skin layer of membrane was measured using fourier transform attenuated total reflection spectroscopy (ATR-FTIR) to examine whether higher shear rate may induce anisotropy at the molecular level of the membrane. These rheological results were then correlated to the gas separation performance in four different pure gases. The results indicated that the highly sheared asymmetric membranes tend to exhibit greater molecular orientation in the skin layer. As the casting speed increased, the level of shear experienced on the membrane surface layer also increased, thus this was leading to greater molecular orientation in the skin layer. Hence, the gas selectivities of O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> significantly increase with an increase in the shear rate and were greater than that of the recognized intrinsic value.

**Keywords:** Polysulfone, asymmetric membrane, gas separation, rheological, shear rate

**Abstrak.** Kajian ini memfokuskan kepada kesan kadar ricih ke atas struktur membran asimetrik polisulfona dan prestasi pemisahan gas. Membran asimetrik kepingan rata dibentuk dengan menggunakan satu larutan pertigaan yang optima. Membran asimetrik yang mempunyai lapisan kulit bermolekul terhal disediakan melalui satu teknik fasa balikan kering/basah yang ringkas bersertakan olakan paksaan menggunakan sistem tuangan kawalan pneumatik yang baru dibangunkan. Ujikaji yang dijalankan juga menumpukan kepada perbezaan kelajuan tuangan yang mewakili keadaan reologi yang berlainan. Kelajuan tuangan dibezakan dari 5 saat hingga ke 60 saat, diketahui bahawa perubahan kelajuan tuangan boleh mengubah kadar ricihan. Halaan molekul teraruh secara reologi atas lapisan kulit membran diukur menggunakan spektroskopi jumlah pantulan terkecil jelmaan fourier (ATR-FTIR) untuk menguji sama ada kadar ricih yang tinggi berupaya mempengaruhi tak isotropi peringkat molekul pada membran. Keputusan reologikal ini juga dikaitkan kepada prestasi pemisahan gas dengan 4 jenis gas tulen yang berlainan. Keputusan menunjukkan bahawa membran asimetrik ricihan tinggi cenderung mempamerkan penghalaan molekul yang lebih ketara dalam

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lapisan kulit. Dengan peningkatan kelajuan, kadar ricihan pada lapisan permukaan membran juga ditingkatkan. Keadaan ini telah menyebabkan peningkatan penghalaan molekul yang lebih ketara dalam lapisan kulit. Oleh sebab itu, kememilhan gas  $O_2/N_2$  and  $CO_2/CH_4$  dipertingkatkan dengan peningkatan kadar ricih dan lebih ketara dibandingkan dengan nilai kememilhan hakiki.

*Kata kunci:* Polisulfona, membran asimetrik, pemisahan gas, reologi, kadar ricih

## 1.0 INTRODUCTION

Recently, gas separation membrane systems have received a lot of attention from both, industry and academia. This is due to the fact that there is a belief that membrane separation processes may offer high separation efficiency, simple operation, more capital, and energy efficiency as compared to the conventional separation processes in some applications.

The performance of asymmetric gas separation membranes is dependent on a thin and defectiveness skin layer. The phase inversion process of polymer precipitation has been widely studied [1-4]. At present advanced polymer solution enables effective membranes to be casted as flat sheets [5] and spun as hollow fiber [6]. Recently, research is on-going to enhance the permeability and selectivity of the polymeric asymmetric membrane in gas separation. Membrane materials with high permeability and selectivity, and advanced of fabrication technologies to produce membrane with a defect free ultrathin dense selective layer are the primary focuses for most membrane scientists. Significant progresses have been made in membrane materials, dope preparation, fabrication technology, and fundamental understanding of membrane formation. Many works have been published to study fiber morphology and separation performance as membrane fabrication techniques, quench conditions, air gap distance, effect of ternary systems (polymer, solvent and non-solvent), and others.

In addition to the phase inversion process, it has been recognized that rheological conditions during membrane fabrication will also affect membrane performance by altering molecular orientation [7,8]. In gas separation membranes, it has been acknowledged that molecular orientation in the active layer will affect selectivity [9,10]. This effects have been observed in the performance of ultrafiltration [11] and gas separation [12].

Spectroscopic techniques have been used to directly measure mechanically induced orientation of polymer molecules in flat sheet and hollow fiber membranes. This technique was used to probe the active layer of the gas separation membranes. It was shown that molecular orientation is intensified by increasing the shear rate during casting, hence there is a favorable effect on selectivity [13].

In this study, flat sheet asymmetric membranes were casted at different shear rates in an attempt to induce molecular orientation, which would alter the separation performance of membranes. A unique dry/wet casting system was used with a particular forced convective evaporation technique in the dry phase inversion process for producing a dense skin layer on top of polymeric membranes. Here, we aim to decouple

membrane casting shear and forced convection evaporation time in the dry phase inversion process, in order to study the possibility of enhancing the selectivity of gas separation flat sheet membranes by varying the shear rates during the membrane casting process. The molecular orientation in the dense skin layer of membranes was examined by observing dichroism in the spectrum.

## 2.0 EXPERIMENTATION

### 2.1 Materials

The polysulfone, PSf, supplied by Amoco Chemical (USA) S.A under the trade name of “Udel Polysulfone P-1700”, is an amorphous, and hydrophobic polymer. Polysulfone is a high performance-engineering thermoplastic which resists degradation, good gas permeability and selectivity values, low cost, excellent thermal, chemical and mechanical properties, and has a widespread use as a commercial polymer. Polysulfone resin was first dried for at least 24 hours in a vacuum oven at a temperature of about 80°C before being used for solution making. N,N-dimethylacetamide (DMAc) and tetrahydrofuran (THF) were used as solvents for polysulfone membrane and supplied by MERCK-Schuchardt. The organic non-solvents used are methanol (MeOH) and ethanol (EtOH), which were also purchased from MERCK-Schuchardt. All liquid solvents were reagent grade and used without further purification. Tap water was used as a coagulation medium during phase inversion process. After the uncoated membranes were tested, they were coated with a highly permeable elastomeric silicone polymer (Slygard 184, Dow Corning). The purpose of this coating is to fill any surface pinholes or defect on the membrane surface. The coating was applied by flooding the membrane skin layer surface with 3%w/w solution of the silicone in n-hexane for 15 minutes. After coating, the membranes were placed in an oven at 60°C for 4 hours to allow curing, prior to the gas permeation testing.

### 2.2 Preparation of Asymmetric Flat Sheet Membranes

The flat sheet asymmetric membranes were produced using an optimized four multi-component dope solution containing polysulfone, N,N-dimethylacetamide, tetrahydrofuran; and ethanol [6, 14]. Water was used in the coagulation bath. The solutions were mixed in a round bottom reaction vessel stirred by motor driven stirrer under a temperature of 60°C for 8 to 10 hours until the polymeric solution become homogeneous. The homogeneous solution was then placed in an ultrasonic water bath to remove the particles and gas bubbles that may exist in the casting solution dope, prior to membrane casting process.

Asymmetric flat sheet membranes were prepared according to the dry/wet phase separation process. The polymer solution was casted on a clean glass plate using a unique pneumatically-controlled membrane casting system. The casting knife consists

of a steel blade, which rested onto two runners, arranged to form a precise gap between the blade and the glass plate. Polymer solution was spread by casting knife with a slit height of 150  $\mu\text{m}$  across the glass plate.

### 2.3 Gas Permeation Measurement

The pressure-normalized fluxes of the membranes were determined by a variable volume method using pure oxygen, nitrogen, carbon dioxide, and methane at room temperature of 28°C, using an upstream pressure of 1 bar. The material used for the construction was stainless steel 316, and the membrane specimens were supported in the cell on a porous stainless steel disk.

Once membranes were in the permeation cell, the pure gas, such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ , would permeate through the membranes with the input upstream pressure of 1 bar, respectively. The down-stream pressure was effectively atmospheric. Volumetric gas permeation rates were determined with a simple soap bubble flow meter. Both of the upstream and downstream sides were always purged with the test gas, prior to the permeation measurement.

The transport properties of the polysulfone asymmetric membranes reported in this study are the average of at least three membrane samples per data point.

The pressure-normalized flux  $(P/l)_{i/j}$  is calculated as below:

$$\left(\frac{P}{l}\right)_{i/j} = \frac{Q_{i/j}}{(\Delta p)(A)} \quad (1)$$

where  $Q_{i/j}$  is the volumetric flow rate of gas 'i or j' at a standard temperature and pressure,  $\Delta p$  is the trans-membrane pressure difference, and  $A$  is the membrane active surface area. Permeances are expressed in gas permeation units, GPU, where

$$\text{GPU} = 1 \times 10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{ sec cmHg}}$$

The pure gas selectivity is determined by taking the ratio of the pure gas permeances:

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \quad (2)$$

If the selectivity of an asymmetric membrane is essentially equal to that of the membrane material, measured at the same temperature and pressure difference, an apparent skin layer thickness,  $L$ , can be estimated using an equation as below:

$$L = \frac{P_i}{(P/L)_i} \quad (3)$$

where  $P_i$  is the permeability coefficient of gas  $i$  ( $\text{cm}^3\text{-cm}/\text{cm}^2\text{-sec-cmHg}$ ), determined from isotropic films of known thickness and,  $(P/L)_i$  is the pressure-normalized gas flux of an asymmetric membrane ( $\text{cm}^3/\text{cm}^2\text{-sec-cmHg}$ ). In this case, the apparent skin layer thickness were determined based on the polysulfone oxygen permeability coefficient  $1.06 \times 10^{-10} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{-s-cmHg}$ , respectively [5,15].

## 2.4 Scanning Electron Microscopy (SEM)

Membrane dense skin thickness and porous substructure as well as other aspects of membrane morphology were determined by employing a scanning electron microscopic (SEM) technique. The specimen that was to be examined was chosen and cut into small dimension. Cross-section of the membrane was obtained by liquid nitrogen freeze fracturing, followed by gold sputtering (Biorad Polaron Division) before scanning on a Scanning Electron Microscope (Philips SEMEDAX; XL40; PW6822/10) with potentials of 10 kV under magnifications ranging from 500 to 5000x.

## 2.5 Spectroscopy

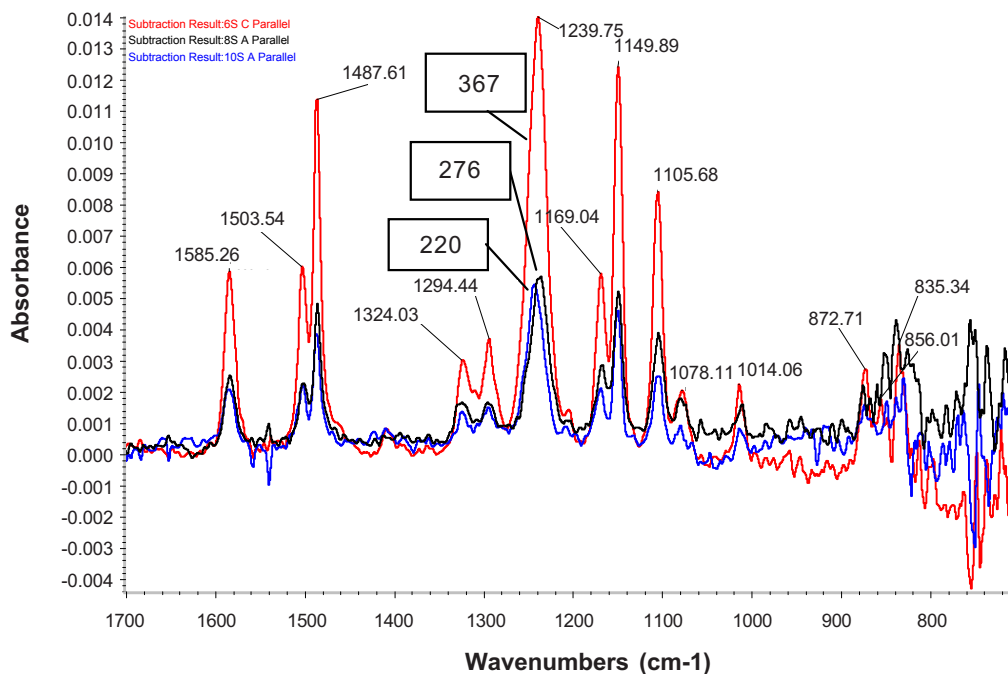
Molecular orientation in the active layer of flat sheet membranes was directly and quantitatively measured using the attenuated total reflection spectroscopy (ATR-FTIR). Pronounced infrared dichroism (difference in absorption between parallel and perpendicularly polarized light to the shear direction) indicates alignment of molecules, while the absence of dichroism shows that a sample has randomly oriented molecules. The IR spectra were recorded on a Magna IR-560 (Nicolet).

Membrane samples of approximately  $5 \text{ cm}^2$  cutting area were mounted at a position with skin surface facing the infrared beam and were rotated according to shear direction (either vertical or horizontal). Then, a spectra of linear dichroism were obtained by straightforward subtraction between the plane polarized infrared spectra perpendicular to shear direction and the plane polarized infrared spectra parallel to shear direction. The difference in background reflexivity between spectra recorded with different polarizations can be expected and we have 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 I.R. absorptions in the linear dichroism spectra, and not on the absolute signs of the dichroism.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Spectroscopy Analysis

Figure 1 is a combination of three normalized difference spectrums from three different shear membranes cast at low and high shear, respectively. All of the IR. spectrums are



**Figure 1** The normalized difference spectrum among the different shear rate ( $220\text{s}^{-1}$ ,  $265\text{s}^{-1}$  and  $367\text{s}^{-1}$ ) of polysulfone flat sheet asymmetric membrane

comparatively complicated having many strong bands in the “finger-print” region of the spectrum below  $1700\text{ cm}^{-1}$ . The different shear cast membranes exhibited dichroism in the infrared, but the highest shear membrane pronounced more effects in dichroism, suggesting it having greater molecular orientation.

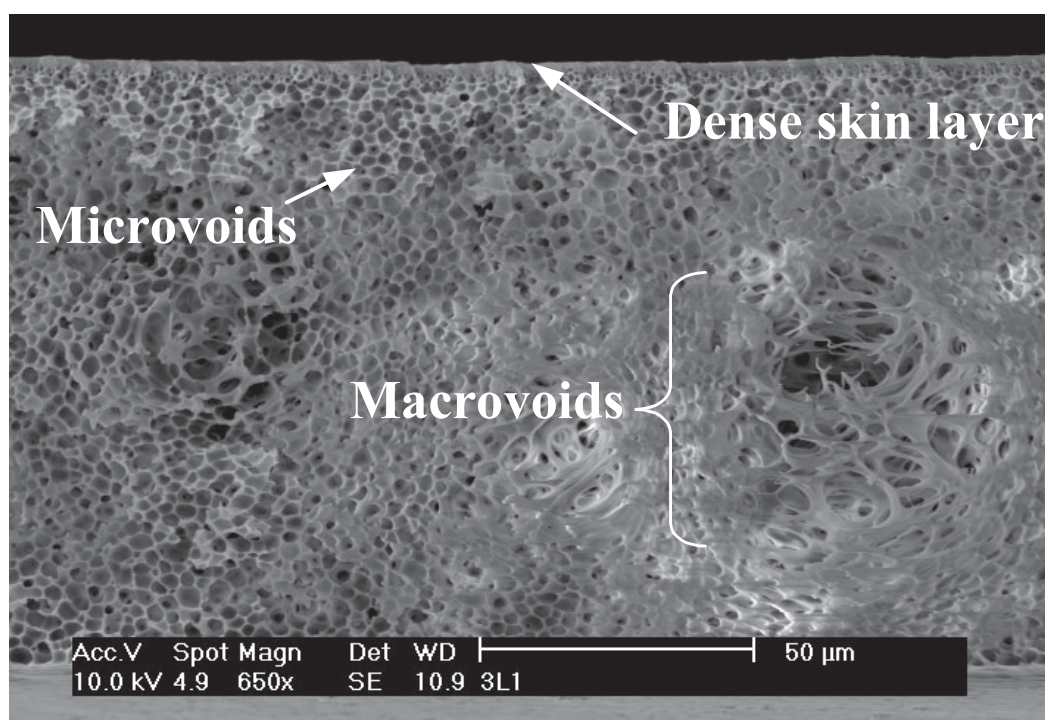
The polysulfone consists of a backbone made up of diaryl sulfone ( $\text{Ar-SO}_2\text{-Ar}$ ), diaryl ether ( $\text{Ar-O-Ar}$ ) groups pronounced strong absorption found at  $1150$  and  $1241\text{ cm}^{-1}$ . The band at  $1487$ , and  $1585\text{ cm}^{-1}$  belongs to vibration of the aromatic  $\text{C}=\text{C}$  in polysulfone molecule, while at  $1239\text{ cm}^{-1}$  it probably belongs to vibration of the  $\text{C-O-C}$  ether linkage. Besides that, there are two more strong absorption bands in the region associated with vibration of the sulfone group appear in  $1294$  and  $1324\text{ cm}^{-1}$ . Observation polarized IR spectra for membranes from Figure 1, it shows that the peak at  $1105$ ,  $1149$ ,  $1239$ ,  $1487$  and  $1585\text{ cm}^{-1}$  in the different spectrum for the high shear membrane is particularly more distinct, compared to the low shear membrane. The difference spectrum for low shear membrane has less distinct features corresponding to particular infrared absorptions, while higher shear membrane appears to be more dichroism as a result of differences in background reflectivity with parallel and perpendicularly polarized light.



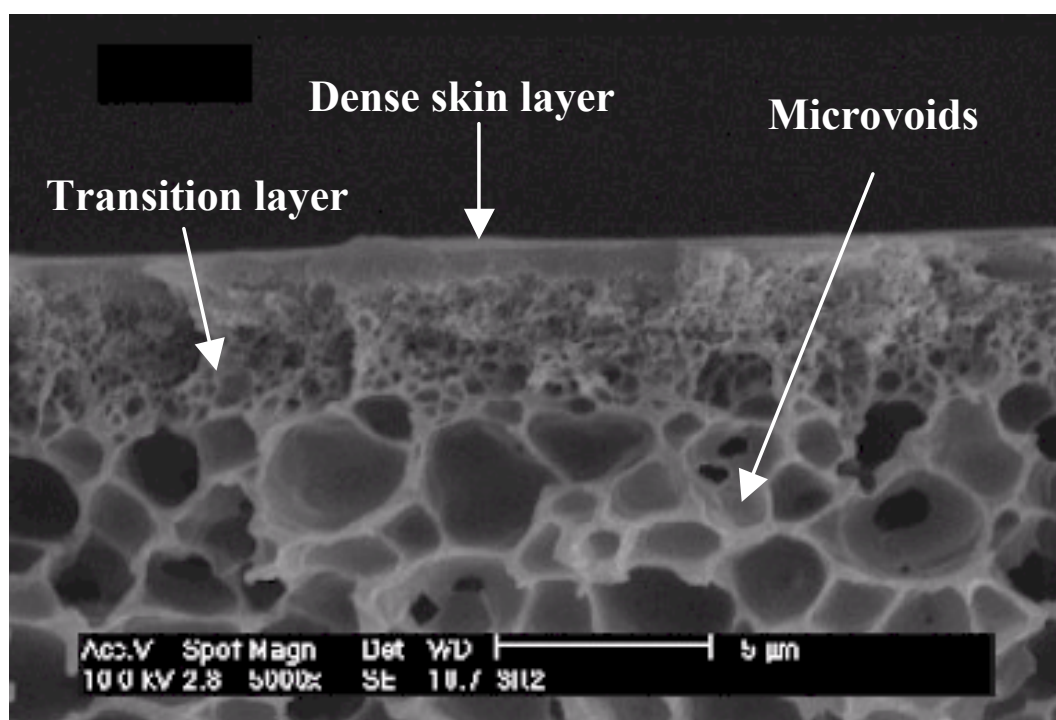
Here, we can conclude that the  $367\text{s}^{-1}$  shear membrane pronounced positive and the highest dichroism (absorption parallel to the shear direction > absorption perpendicular) indicating that the polymer backbone aligns more in the shear direction (greater molecular orientation) followed by  $267\text{s}^{-1}$ , and the lowest was  $220\text{s}^{-1}$  shear membranes. By using pneumatically-controlled casting system, it was clearly found that the orientation of polymer molecular in polysulfone membrane was significantly heighten as compared to the membrane fabricated using manually hand casting knife, as produced by Ismail [14].

### 3.2 Morphology of Multi-component Polysulfone Asymmetric Membrane

Scanning electron photomicrographs of a typical asymmetric membrane structure are shown in Figure 2 at a magnification of 650, and Figure 3 at a magnification of 5000. The result of 22 wt.% dry/wet phase inversion polysulfone flat sheet asymmetric membrane has an outer relative dense layer and a porous substructure, which are



**Figure 2** Scanning electron photomicrographs of a flat sheet polysulfone asymmetric membrane prepared by dry/wet phase separation- cross-section under magnification of 650



**Figure 3** Scanning electron photomicrographs of a flat sheet polysulfone asymmetric membrane prepared by dry/wet phase separation- top structure under magnification of 5000

consistent with our expectation. These structure look very similar to those reported by Pesek and Koros [5], and Pfromm, *et al.* [10]. As shown in Figure 3, there is an extremely well-defined skin layer supported on a highly open-celled sponge-like structure that contained not only microvoids but also bulbous macrovoids. In the present case, the fine structure of the skin layer is believed to be formed during the dry phase separation by introducing forced convection residence duration of about 15 seconds. The microvoids and macrovoids are believed to be formed by the intrusion of nonsolvent during the wet phase separation.

### 3.3 Gas Separation Performance of Multicomponent Asymmetric Membrane

An optimum flat sheet casting solution for producing asymmetric polysulfone membranes was prepared according to the dry/wet phase separation process using a newly designed pneumatically-controlled flat sheet membrane casting system. The pure gas permeation properties of integrally-skinned asymmetric polysulfone membranes are shown in Table 1. The average selectivity of  $O_2/N_2$  of 10 randomly selected membrane samples was 4.78. The  $O_2/N_2$  selectivity of a solution-cast, dense



**Table 1** Permeation properties of aqueous quenched asymmetric polysulfone membranes prepared by dry/wet phase separation;  $t = 30^\circ\text{C}$ ,  $\Delta p = 1$  bar, casting solution: 22 wt% PSf, 31.8 wt% DMAc, 31.8 wt% THF and 14.4 wt% EtOH.

No. Memb..	Uncoated			Coated			Skin layer thickness (Å)
	$\text{O}_2$ Permea- bility (GPU)	$\text{N}_2$ Permea- bility (GPU)	Selecti- vity $\text{O}_2/\text{N}_2$	$\text{O}_2$ Permea- bility (GPU)	$\text{N}_2$ Permea- bility (GPU)	Selecti- vity $\text{O}_2/\text{N}_2$	
1	13.92	2.69	5.17	10.81	1.89	5.73	761
2	14.83	3.19	4.65	10.54	1.85	5.70	715
3	12.57	2.95	4.27	12.44	1.77	7.03	843
4	11.48	2.68	4.29	7.99	1.17	6.87	923
5	12.17	2.69	4.52	15.28	2.97	5.15	871
6	11.36	2.31	4.91	9.05	1.48	6.10	933
7	11.89	2.78	4.28	8.40	1.33	6.33	892
8	17.13	3.03	5.66	5.44	0.70	7.81	619
9	12.35	2.08	5.94	4.62	0.67	6.90	858
10	18.32	4.44	4.12	6.29	1.01	6.21	579
Mean	13.60	2.88	4.78	9.08	1.48	6.38	799
Mean*	19.3	—	6.0	—	—	—	615

\* Based on permeation properties of aqueous quenched asymmetric polysulfone membrane prepared by dry/wet phase separation [5].

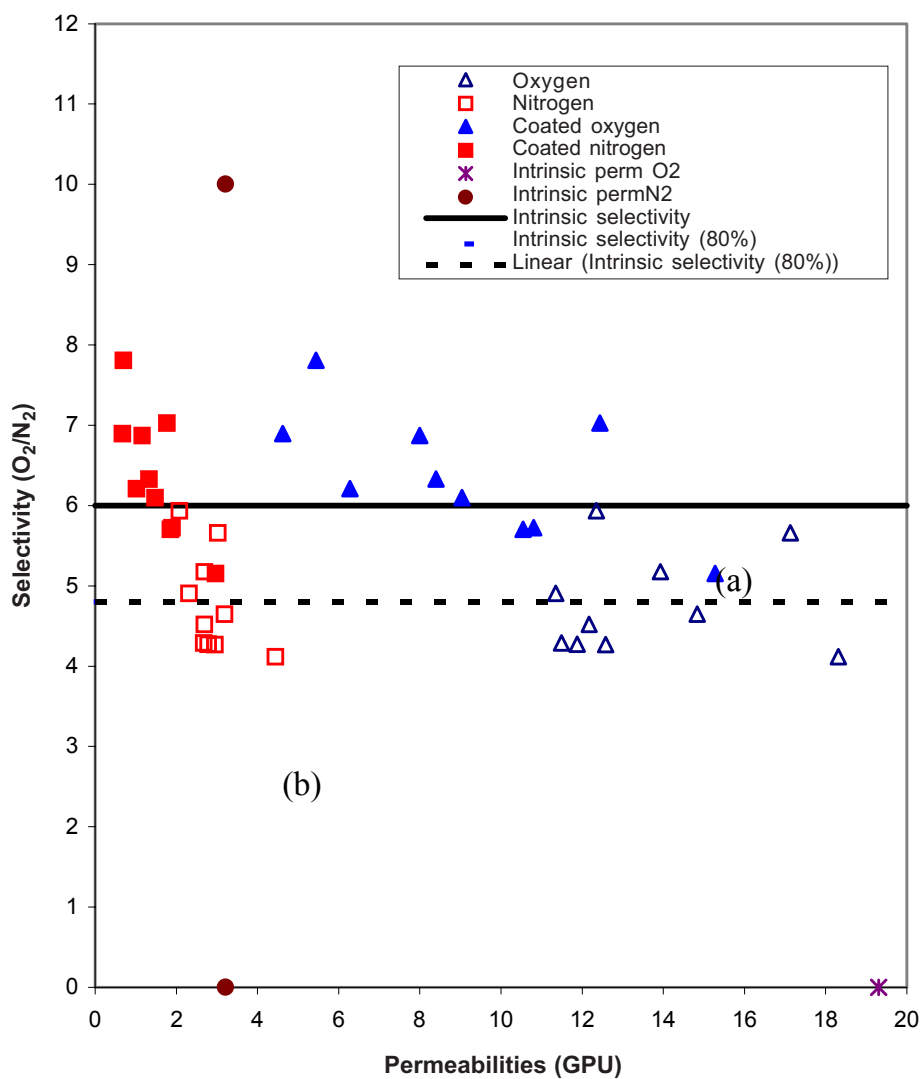
polysulfone membrane of a known thickness was determined to be 6.0, according to Pesek and Koros [5]. The experiment results showed that half of  $\text{O}_2/\text{N}_2$  selectivity of the asymmetric membrane samples was within 80% of the  $\text{O}_2/\text{N}_2$  selectivity of that of a solution-cast polysulfone film and were supported that the casting technique and equipment employed in the research were very reliable for preparing consistent quality membranes. The transport properties of the asymmetric membrane were predominantly determined by a solution/diffusion mechanism, as demonstrated. The skin layer of the cast membrane can be considered to be essentially defect-free and reflected a good degree of reproducibility, extremely thin selective skin layers. For those less than 80% of intrinsic selectivity value (at least >65% of intrinsic selectivity), the skin of asymmetric membrane was categorized as having a minor defect. It has been hypothesized that all of the asymmetric membranes contain some skin layer defects, due to incomplete coalescence of polymer in the skin layer during the membrane formation process. Therefore, the selectivities of the asymmetric membranes will always be lower, compared to those obtained for dense films.

The pressure-normalized  $O_2$  and  $N_2$  fluxes and  $O_2/N_2$  selectivities of the silicone-coated asymmetric membrane samples showed an average  $O_2/N_2$  selectivity of 6.38; hence, most of the results showed the permselectivity of the asymmetric membrane samples surpassed 80% of the  $O_2/N_2$  selectivity of that of a solution-cast polysulfone film after the additional post treatment (coating with silicone). Based on this observation, it can be said that the average molecular packing density in the asymmetric membrane skin layers was higher than that of the dense film [15]. The higher selectivities of the silicone-coated membranes provide an explanation that the gas transport of the uncoated membranes were partially influenced by flow through regions having pores or higher free volume (lower packing density) of the average polymer matrix in the skin layer.

Figure 4 shows the gas separation performance of integrally-skinned asymmetric membrane produced by new designed casting apparatus, compared to the results obtained by Pesek an Koros [5]. The triangle shape ( $\Delta$ ) represents the  $O_2$  permeability and the square shape ( $\square$ ) represents  $N_2$  permeability of produced membrane. Both of the gases permeabilities were slightly lower than results obtained by Pesek and Koros [5], but silicone coated membrane (solid) performed higher selectivity than the recognized intrinsic selectivity.

### 3.4 Effect of Shear Rate on Permeability

The effects of shear rate toward the permeabilities of  $O_2$ ,  $N_2$ ,  $CO_2$ , and  $CH_4$  gases were analyzed for the uncoated and coated membranes. Table 2 shows the results of uncoated and coated membrane samples. The results shows that the increase in the shear rate results in the decrease of the permeabilities of all the tested gases for the lowest shear compared to the highest shear membrane. The uncoated membranes generally exhibited high pressure-normalized flux in the low shear membrane. The decrease of the permeabilities can be explained by the rheological behavior of the polymeric solution dope as it cast by the casting knife during the early stage of membrane fabrication process. It was believed that the molecular chains of the viscous solution experienced in higher shear tend to align themselves much better than those experienced in lower shear, and this enhanced orientation will cause the polymer molecules to pack closer to each other, as suggested by Chung and Xu [16]. By introducing a short forced convection evaporation time, lower free volume or a tighter dense oriented structure was pre-precipitated instantaneously at the outer surface of the membrane in dry phase inversion process. Nevertheless, the amorphous chain mobility will be restricted in the solid membrane structure, which is necessary for the opening of a transient molecular scale passageway into which, the gas molecule or penetrant can jump. Subsequently, the transport gases through the free space within the polymer network will be hindered, and inevitably this will lead to a lower permeance. As a result, the apparent dense layer thickness is increased with the increase



**Figure 4** Permeation properties of aqueous quenched asymmetric polysulfone uncoated and coated membranes prepared by dry/wet phase separation;  $t = 30^\circ\text{C}$ ,  $\Delta p = 1$  bar, casting solution: 22 wt% PSf, 31.8 wt% DMAc, 31.8 wt% THF and 14.4 wt% EtOH. (a) Horizontal solid line: Intrinsic selectivity value of dense polysulfone film = 6.0; (b) Horizontal dash line: 80% of intrinsic permselectivity of  $O_2/N_2$ ; (c) Vertical solid line: Mean  $O_2$  permeability obtained by Pesek and Koros [5]; (d) Vertical dash line: Mean  $N_2$  permeability obtained by Pesek and Koros [5].

**Table 2** Effect of shear rate on pressure-normalized flux of uncoated and coated membrane samples (forced convection residence time kept constant at 15s)

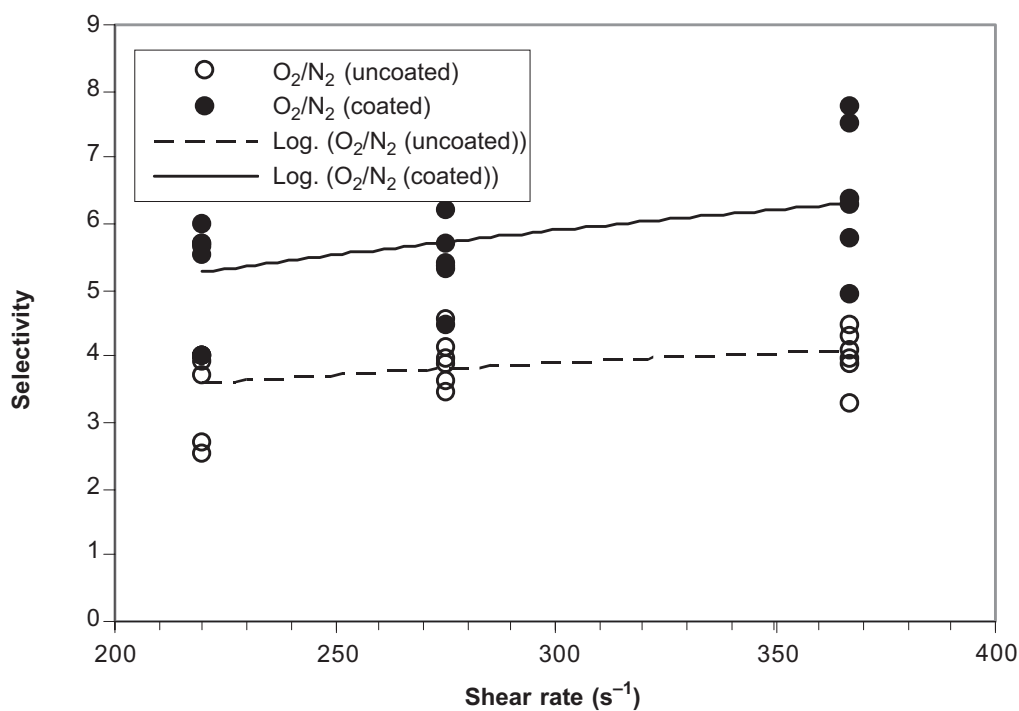
Shear rate	Uncoated				Coated				Skin layer (Å)
	O <sub>2</sub> , (GPU)	N <sub>2</sub> , (GPU)	CO <sub>2</sub> , P/1 (GPU)	CH <sub>4</sub> , (GPU)	O <sub>2</sub> , (GPU)	N <sub>2</sub> , (GPU)	CO <sub>2</sub> , (GPU)	CH <sub>4</sub> , (GPU)	
220s <sup>-1</sup>	19.81	6.10	51.50	5.86	6.30	1.15	8.91	0.61	805
275s <sup>-1</sup>	14.58	3.75	20.955	1.86	2.31	0.43	11.70	0.42	843
367s <sup>-1</sup>	13.30	3.34	17.515	0.92	5.88	0.98	6.00	0.15	929

in the shear rate, as illustrated in Table 2. The average apparent skin layer thickness of the high shear membranes was less than 1000 Å.

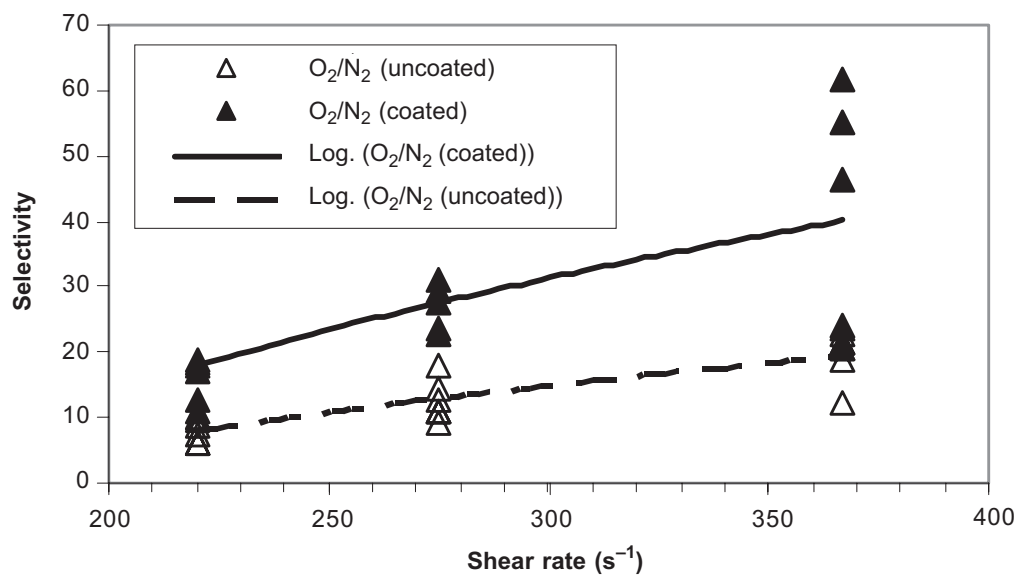
### 3.5 Effect of Shear Rate on Selectivity

From Figures 5 and 6, we observed that there was a trend of increasing selectivities with an increase in the shear rate. Figure 5 shows the selectivity of O<sub>2</sub>/N<sub>2</sub> and Figure 6 shows the selectivity of CO<sub>2</sub>/CH<sub>4</sub> in three different shear rates. It can be seen that all of the gas pair selectivity generally exhibit solution diffusion mechanisms in both of the uncoated and coated membranes. In the higher sheared membranes, the selectivities of both gas pairs studied are solely contributed to the solution diffusion mechanism because all of the selectivities observed are higher than those calculated from the inverse square root ratio of the molecular weights of the desired gas component to the undesired gas component. Even though the selectivities achieved were greater than those associated with Knudsen diffusion through pores in the skin layer, they were still far below the recognized intrinsic selectivity for polysulfone. Thus, with higher shear and higher orientation in the polymeric matrix, the effect of the chain mobility restriction will cause a size-dependent reduction in mobility of gases, leading to a higher selectivity.

Only a few gas pair selectivities from the lowest shear uncoated membrane giving poor solution diffusion mechanism. This can be said that the solution-diffusion separation is based on both of solubility and mobility of the penetrants in which, the thermally agitated motion of chain segments generates penetrant to diffuse across the membrane surface, as suggested by Koros *et al.* [17] and Chung *et al.* [16]. The poor selectivities suggest that surface pores or imperfections prevail and these membrane are not practically useful and need coating to heal the surface imperfections [14]. The coated results are more pertinent as they represent membrane performance. Coating reduced the pressure-normalized fluxes and greatly enhanced the selectivities of the membranes. The coated membranes exhibited great selectivities for high shear membranes either surpass or exceed the polysulfone intrinsic selectivity value of 6.0



**Figure 5** Effect of shear rate on the  $O_2/N_2$  selectivity of uncoated and coated membrane samples (forced convection residence time kept constant at 15s)



**Figure 6** Effect of shear rate on the  $CO_2/CH_4$  selectivity of uncoated and coated membrane samples (forced convection residence time kept constant at 15s)

for  $O_2/N_2$  and 28 for  $CO_2/CH_4$  at  $365s^{-1}$  sheared membranes. Enhanced molecular orientation may enable membrane selectivities to be elevated beyond the recognized intrinsic value of the polymer.

#### 4.0 CONCLUSION

The spectroscopy analysis provided evidence to suggest that the high shear rates on casting led to greater molecular orientation. The normalized different spectrum showed that high shear membrane ( $367s^{-1}$ ) pronounced positive and the highest dichroism (absorption parallel to the shear direction > absorption perpendicular). This indicated that the polymer molecular chain was aligned in the shear direction. Casting shear rate has a significant effect on the gas separation performance of asymmetric polysulfone flat sheet membrane. The increase in the shear rate caused in the decrease of the permeabilities of all the tested gases for high shear membranes. Higher shear tend to align the polymer molecular chains, causing the polymer molecules to be packed closer to each other, resulting in low permeability, but high selectivity. Silicone coating post treatment enhanced the selectivities of the membranes greatly. The coated membranes exhibited greater selectivities for high shear membranes, some of the values even surpass the polysulfone intrinsic selectivity value of 6.2 for  $O_2/N_2$  and 28 for  $CO_2/CH_4$ . This suggested that silicone rubber had successfully plugged the pores that were present at the membrane surface-active layer or repaired the membranes imperfections.

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