

Mindel S-1000 Based Asymmetric Membranes for O₂/N₂ Separation: Effect of Polymer Concentration

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Commercially blend of polysulfone (PSf) and acrylonitrile-butadiene-styrene (ABS) resin known as Mindel S-1000 was used to prepare flat sheet membranes for O₂/N₂ separation. The produced membranes were expected to inherit the excellent gas separation properties of polysulfone and strong mechanical properties of ABS. Asymmetric membranes were successfully prepared by a pneumatically-controlled casting machine with methanol as the second coagulation medium. Commonly use solvents for pure PSf and ABS; N-methyl-2-pyrrolidone (NMP) and a more volatile tetrahydrofuran (THF); were chosen in the dope formulation. The polymer concentration was varied between 20 to 23.5% to promote the formation of the desirable membrane morphology that affecting the gas separation performance. As the concentration increased, a more oriented membrane with denser skin layer was developed that was responsible for the slight improvement in gas separation factors with slight reduction in gases permeabilities. However, as the solution became too viscous due to the high content of polymer, solvent evaporation was hindered during the solvent-exchange process producing membranes with huge microvoids and thinner skin. To further promote the membrane skin formation, solvent ratio of the dope solution was manipulated. Membrane morphology analysis revealed that the increment of solvent ratio; reducing the volatile solvent, promoted the membrane porosity while decreasing the skin thickness. Thus, a significant loss of gas pair selectivity was observed as the permeability increased. In order to enhance the membrane performance and plugged any possible defects on the skin surface, the produced membranes were silicone coated. This step improved the membrane gas separation performance while retaining the same trend as the uncoated membranes. Due to the dispersion of rubber particles in ABS that contributed to the toughness of the polymer, the mechanical properties of PSf-ABS membranes were found to be high with comparable elasticity to other common polymeric membranes.

1. Introduction

Membrane-based gas separation is currently popular due to its inherent advantages over those more traditional methods. These include low capital and operating costs and ease of operation (Barbieri *et al.*, 2011). Since it does not require any phase transformation, membrane is a viable energy-saving alternative for gas purification (Clarizia, 2009). In addition, the membrane system is compact and simple, maintenance-free since there is no moving part, highly flexible that any additional membrane modules can be easily installed for future expansion and highly reliable and durable since it can withstand high pressure and temperature operation (Shekhawat *et al.*, 2003).

An important concern in membrane gas separations is to produce a membrane process that is economically feasible while maintaining a high permeability and selectivity with good mechanical and thermal stability (Kesting and Fritzsche, 1993). Since the last two decades until today, remarkable progress has been made in the development of high-performance polymers for gas separation. The

potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of the product. This means that both the permeability coefficient for the gas that is transported more rapidly and the selectivity should be as large as possible (Maier, 1998). Among the polymers that have been involved in gas separations included cellulose acetate, polysulfone, polyimides, polycarbonates, polyethersulfone and polysulfones. Glassy polymers such as polysulfone, polyimide and polycarbonate have been widely applied to the separation of gas mixtures such as oxygen/nitrogen and carbon dioxide/methane. Polysulfone has satisfactory gas permeabilities and acceptable permselectivities and it can be used with highly sorbing plasticizing gases (Marchese *et al.*, 2003). These properties and its relatively low cost had made polysulfone as a standard membrane material in gas separations.

On the other hand, polycarbonates membrane too, tend to have comparable permeabilities for light gases than analogous polysulfones, and both polymers have also comparable selectivities for O₂/N₂ and CO₂/CH₄ gas pairs (Stern, 1994). Polyimide is strongly affected by highly soluble penetrants, such as CO₂, plasticizing the polymer matrix. Nevertheless, a comparison of analogous polycarbonates and polyimides, for example, polycarbonate and 6FDA-IPDA or HFPC and 6FDA-6FpDA, lead to higher CO₂ and O₂ permeabilities and higher O₂/N₂ and CO₂/CH₄ selectivities for polyimides (Koros and Fleming, 1993).

The most basic criteria that must be fulfilled by membrane materials are selectivity (or separation efficiency) and permeation rate (or productivity). The higher the selectivity, the more efficient the process, the lower the driving force (pressure ratio) required to achieve a given separation and therefore, the lower the operating cost of the membrane system. The higher the flux, the smaller the required membrane area and therefore, the lower the capital cost of the membrane system (Koros and Mahajan, 2000). Besides the membrane performance, other criteria for selecting good membrane materials that must be balanced against cost are membrane durability and mechanical integrity at the operating conditions.

Hence, Mindel S-1000, a commercially blend of polysulfone (PSf) and acrylonitrile-butadiene-styrene (ABS) resin, was chosen as the membrane material for this study due to the prominent gas separation performance of PSf that have been widely reported and strong mechanical property that ABS possesses due to the dispersion of rubber particles. Using this novel polymeric membrane material, the main aim of this paper is to investigate the effect of polymer content in the dope solution on membrane structures, gas separation performance and mechanical properties.

2. Experimental

2.1 Materials

Mindel S-1000 was supplied by Amoco Chemical (USA) was oven dried at 60 °C overnight prior to usage to remove any moisture. Analytical grade (AR) N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) supplied by Merck, Darmstadt, Germany were used as purchased. Tap water used as the coagulation medium and was temperature controlled at 25 °C and AR methanol was used as obtained as the second coagulation bath. An elastomer silicone polymer polydimethylsilicone (PDMS), Slygard 184 was from Dow Corning (USA) and AR *n*-hexane was chosen as the solvent the silicone coating solution.

2.2 Dope solution preparation and membrane fabrication

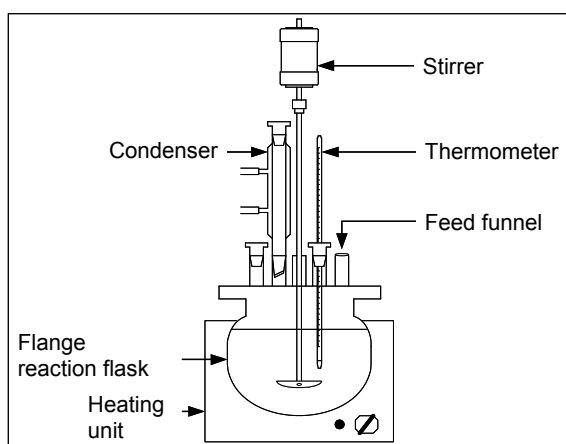


Figure 1: Apparatus for solution preparation

First, the solvents, NMP and THF were poured into the round bottom reaction vessel. The solvents mixture was then left to warm-up to a temperature of 45 °C. Then, the required amount of polymer, Mindel, was slowly added to avoid accumulation or agglomeration from occurring. This step is important to reduce the time required to dissolve the polymer. A stirrer was used for mixing. Figure 1 illustrates the system used for dope solution preparation.

The process continued until all of Mindel and mixture of NMP and THF were homogenous. The dope solution was left with the stirrer on for about 12 hours to ensure a completely homogenous solution was produced.

After that, the solution was poured into a clean bottle, and degassed using an ultrasonic bath from Branson Ultrasonics (USA) to remove trapped micro-bubbles prior to casting process. Four samples of

PSf-ABS solutions with various compositions (20.0 wt % to 23.5 wt %) were prepared by maintaining the solvent ratio (NMP/THF) to 1/1.

Table 1: Dope solutions with different polymer compositions

Composition of PSf-ABS (wt %)	Composition of less volatile solvent, NMP (wt %)	Composition of volatile solvent, THF (wt %)	Solvent ratio (NMP/THF)
20.00	40.00	40.00	1/1
21.00	39.50	39.50	1/1
22.00	39.00	39.00	1/1
23.50	38.25	38.25	1/1

Flat sheet configuration was selected for this study because it is a base of module in laboratory before commercialization in hollow fibre or spiral wound membrane module and it is easy to handle and fabricate. Casting process was performed using a pneumatically-controlled casting machine. Flat sheet membrane was prepared according to the dry/wet phase inversion technique. The solution was poured onto a clear, flat and smooth glass plate that was placed on the trolley. The solution was spread by pneumatic forced stainless steel support casting knife to form a uniform thickness layer.

The forced convection residence duration was fixed at 15s. After an additional of free standing time around 5 sec, the nascent membrane was removed from the glass plate by quenching immediately and smoothly into an aqueous bath at room temperature (28 °C) and remained there for about 30 minutes. Finally, the washed membranes were immersed in water (non-solvent coagulant for the wet phase inversion) at an ambient condition for 24 hours, followed by immersing them in methanol for one more day. Later, the produced membranes were air dried at room temperature for another 24 hours. The membranes were then further dried in a vacuum oven at a temperature of 60 °C for another day before storing them in sealed plastic bags prior to testing.

2.3 Preparation of silicone-coated asymmetric membrane

The produced membranes were later coated with a mixture of 3 wt% silicone (with curing agent) and 97 wt% n-hexane. The ratio of silicone to curing agent was 10. The asymmetric membranes prepared were dried in a vacuum oven for about 24 h at a temperature of 60 °C. Then, the membranes were dipped in the coating solution for about 30 min. This is to ensure that the membrane surface was well covered by the mixture of silicone and curing agent. The silicone was further cross-linked by keeping the coated membrane in an oven at 60 °C for another 24 h.

2.4 Asymmetric membranes characterization and testing

2.4.1. Pure gas permeability measurement

Circular membrane discs were cut and mounted on a porous support in a stainless steel, cylindrical membrane test cell and tightened using a rubber O-ring as previously reported by Kusworo *et al.* (2008). Prior to testing, the permeation cell was checked for any possible leakage and the system was totally flushed with test gas. Gas permeation rates were measured by using pure gases of oxygen and nitrogen from compressed gas cylinder at a controlled pressure of 1 bar. Experiments were carried out at ambient temperature of about 28 °C. Volumetric gas permeation rates were determined with a local design soap-bubble flow meter. Each set of data was determined as an average of three replicates. The detailed calculations of gas permeability and gas pair separation factor were as presented in Hasbullah *et al.* (2011).

2.4.2. Characterizations of the flat sheet asymmetric membranes

In order to examine the morphology of the surface and cross-section of membrane samples, they were fractured cryogenically in liquid nitrogen and mounted on sample stubs with double-surface tape. After the samples were gold-sputtered with coating machine, the gold-coated samples were examined using the Philips XL40 SEM with voltage of 20 kV.

The membrane mechanical properties were determined using a tensile machine LRX, Lloyd Instruments with a crosshead speed of 50 mm/min at room temperature (24 ±1°C) and relative humidity of 75±1% according to ASTM D882. The membranes were cut into 1 inch by 6 inch for the test. For each concentration, ten samples were tested and the average values were calculated.

3. Results and discussions

3.1 Effect of polymer concentration on membrane gas separation performance

Four different polymer concentrations (20.0 wt %, 21.0 wt %, 22.0 wt % and 23.5 wt %) of Polysulfone-ABS ternary system dope solutions were prepared with THF and NMP as solvents. Asymmetric membranes later were fabricated according to dry/wet phase separation using pneumatically-controlled flat sheet membrane casting system. Table 2 shows that both coated and uncoated membranes display a same trend. The mean pressure-normalized flux (P/l) of oxygen decreases while the mean selectivity (α) of O₂/N₂ increases as the polymer concentration of Mindel S-1000 was increased from 20.0 wt % to 23.5 wt % at a constant NMP/THF solvent ratio of 1/1.

According to Pesek and Koros (1993), the additions of more polymers to the casting solution increased its viscosity and tend to promote more selective but less productive membranes in the absence of offsetting casting conditions or other solution components changes. In other words, although these membranes were prepared under identical conditions, it can be easily seen that the transition layer thickness increases with the increasing polymer concentration. Therefore, it revealed an increased in the selective skin layer thickness and caused low porosity in membrane structure as the polymer concentration increased. The increase of the skin layer would promote the separation factor while reducing the gas permeability.

It was predicted that the pore size in the spongy-like matrix increased and elongated macrovoids decreased with increasing polymer content in the dope and this explained the low porosity in membrane's structure. This phenomenon is probably due to the increased difficulty of diffusion of non-solvent in the forming flat sheet and hence, the time for nucleation and growth increased (Chung *et al.*, 1999). As the spongy-like matrix increases, it will decrease the productivity of oxygen as the porosity decreased in the substrate. PSf-ABS concentration also plays a significant role in the morphology of the flat sheet bottom surface, which would be further revealed in the next section.

Table 2: Effect of polymer content on membrane O₂ and N₂ separation performance

Polymer concentration (wt%)	(P/l) O ₂ uncoated (GPU)	(P/l) N ₂ uncoated (GPU)	α O ₂ /N ₂ uncoated	(P/l) O ₂ coated (GPU)	(P/l) N ₂ coated (GPU)	α O ₂ /N ₂ coated
20.0	191.56 (21.67)	202.02 (26.02)	0.95 (0.03)	4.70 (0.72)	4.24 (1.93)	1.26 (0.44)
21.0	11.33 (1.45)	8.12 (1.97)	1.43 (0.22)	1.45 (0.61)	0.56 (0.32)	2.73 (0.43)
22.0	65.10 (5.40)	59.60 (11.88)	1.12 (0.21)	2.97 (2.24)	2.01 (1.59)	1.50 (0.04)
23.5	46.67 (9.12)	41.82 (8.23)	1.12 (0.12)	2.26 (0.87)	1.38 (1.02)	2.20 (1.36)

() is the value of the standard deviation

Table 2 also displays the membrane coating effects on O₂ gases permeability in four different of polymer concentration. From the table, it can be observed that all the coated membranes exhibit lower pressure normalized fluxes in oxygen compared to the uncoated membranes. The uncoated membrane exhibited relatively high pressure-normalized fluxes of oxygen. On the other hand, it can also be observed that all the coated membranes exhibit higher selectivity compared to the uncoated membranes. The uncoated membrane exhibited relatively low selectivity suggesting that these membranes consisted with some pores or imperfections. Results obtained for coated membranes showed that the silicone rubber had successfully blocked the membrane defects on the selective skin and repaired the membrane imperfections and allowed substantial increase in permselectivity.

In this study, the membranes with 21.0 wt.% showed an average O₂/N₂ selectivity of 2.73 after coating with silicone; the average selectivity for the uncoated membrane is 1.44. Polysulfone membrane is the best comparison since Mindel S-1000 is a novel material and there is no intrinsic data available. So, both the average selectivities are below polysulfone membrane intrinsic selectivity that is about 6 (Robeson, 1991; Robeson, 1999). However, this gives some an indication that Mindel has huge potential for further improvement in future by exploring other factors that influence the Mindel based membrane development.

3.2 Effect of polymer concentration on membrane morphology and structure

Figure 2 illustrates scanning electron microscope (SEM) images at magnification of 400x of the cross section and dense layer morphology of dry/wet phase inversion Mindel S-1000 asymmetric membranes cast with four different polymer concentrations. It can be seen that the porosity of the membranes are decreasing while the skin layer thickness increasing with increasing polymer content in the solution from Figure 2A to 2C.

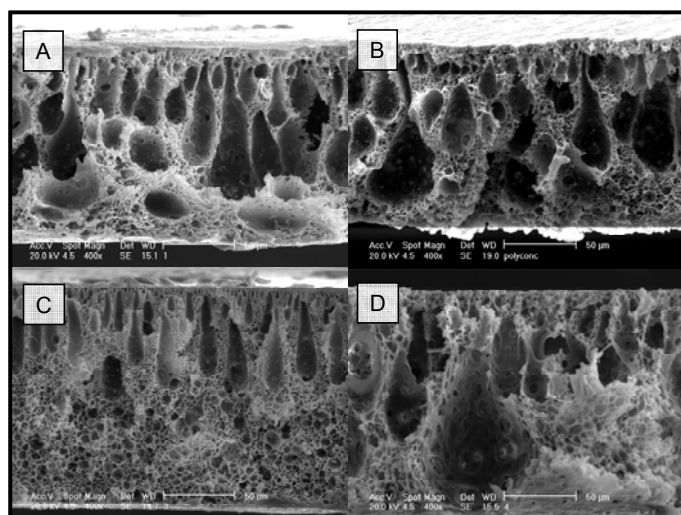


Figure 2: SEM of Mindel S-1000 asymmetric membrane with various polymer concentrations of: (A) 20.0 wt%; (B) 21.0 wt%; (C) 22.0 wt% and (D) 23.5 wt%

Hachisuka *et al.* (1996) suggested that asymmetric membranes prepared using a low polymer concentration tends to have finger voids or very porous structures. This explained the reduction in pressure-normalized flux of oxygen and the increment in the selectivity O_2/N_2 as the polymer concentration of PSf-ABS in the solution increased. However, as the dope solutions tend to be so viscous with the increment of polymer, it hindered the easiness of the solvent to vaporize during the solvent exchange process. Thus, at polymer concentration of 23.5 wt% (Figure 2D) more and bigger microvoids existed as compared to those in Figure 2C. This morphology is coherent to the gas separation performance results that showed asymmetric membrane prepared with 21.0 wt% of polysulfone-ABS possessed the optimum flux and selectivity.

Figure 2C also displays the SEM images of dense surface, bottom surface, cross-section and dense layer morphology of dry/wet phase inversion polysulfone-ABS asymmetric membranes cast with polymer concentration of 21 wt%, 39.5 wt% NMP and 39.5 wt% THF that exhibited the highest selectivity of O_2/N_2 among the four concentrations. These structures have an outer relative well-defined skin layer supported on a highly porous open-celled sublayer containing not only microvoids but also bulbous and finger-like macrovoids, while the outer surfaces are dense with invisible defects. These are consistent with early expectation and similar to those found in the aqueous quenched studies by Pinnau and Koros (1993).

3.3 Effect of polymer concentration on membrane mechanical properties

Table 3: Average values of Mindel S-1000 asymmetric membranes mechanical properties

Polymer concentration (wt%)	Strength at break (N/m)	Modulus (MN/m)	Elongation at break (%)
20.0	595.98	32.19	17.25
21.0	509.16	24.88	13.58
22.0	532.13	43.08	14.12
23.5	848.17	399.72	23.85

Table 3 exhibits the mechanical properties of the prepared membrane including the strength at break (N/m), modulus and elongation at break (%) increase with the increasing of polymer concentration. This was probably due to the denser structure of the membrane as previously explained in detail. As the

polymer content in the filmstrip increase, the interaction or bonding between the molecules are good, and therefore produces compact and strong mechanical properties membrane. As a result, when the tensile test was done on different polymer concentrations, membranes with 23.5 wt % of PSf-ABS have the highest value on strength at break, elasticity modulus and percentage of elongation at break. However, the other polymer concentration of membranes had reasonably strong mechanical properties as well.

4. Conclusion

This study revealed that Mindel S-1000 asymmetric membranes were able to be fabricated by manipulating the dope solution formulation with phase inversion method. Varying the polymer concentration had influenced the structures and transport properties of the resultant membranes quite significantly. Even though the produced membranes with 21.0 wt% as the best concentration, had relatively low selectivity, this preliminary data can be a starting point for future improvement and development of Mindel-S1000 based asymmetric membrane for fluid separation application. This is due to the very promising mechanical properties of the currently produced membranes which is highly desirable for the commercial separation process applications and also the interesting trend of the morphology that contributed to the strength and gas permeation properties. Based of this finding, other factors such as the casting parameters should be pursued in the future in order to improve the membrane further.

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