

EFFECTS OF SHEAR RATE ON O₂/N₂ GAS SEPARATION PERFORMANCE OF MINDEL S-1000

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Abstract

Mindel S-1000, a commercial blend of Polysulfone and Acrylonitrile-Butadiene-Styrene (ABS), was chosen in this study as a membrane material for oxygen/nitrogen separation system. N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) were used as a solvent to prepare 21 wt% polymer dope solution. The membrane was fabricated using pneumatically-controlled flat sheet membrane casting system with dry/wet phase inversion method. The optimum casting shear rate for Mindel S-1000 membrane preparation was found to be in the range between 220.13 s⁻¹ to 440.27 s⁻¹ with a constant evaporation time of 15 seconds. As the membrane was cast at low shear rate, thicker skin layer and large pore radius tend to form. As the shear rate increased the support layer tend to be non-compact that caused increased in permeability but this does not thinning the skin layer significantly. Thus, the membranes prepared at higher shear rate enhanced the molecular orientation in the skin layer in which not only improving the selectivity of the membrane, the gas fluxes also increased. On the other hand, shear rate above the optimum value reduced the membrane thickness severely and this reduced it gas separation performance. At the optimum shear, oxygen/nitrogen selectivity for this membrane was found to be 4.86 with the oxygen and nitrogen pressure-normalized fluxes were 10.5 GPU and 2.2 GPU, respectively. This shows that Mindel S-1000 has great potential as membrane material for gas separation process.

Keywords: Asymmetric membrane, Mindel S-1000, Shear rate, Gas separation.

1. Introduction

Membrane-based gas separation is becoming increasingly popular due to inherent advantages over those more traditional methods such as cryogenic distillation,

Nomenclatures

| | |
|----------|--------------------------------------|
| A | Membrane effective surface area |
| l | Membrane skin thickness |
| P_i | Permeability coefficient for gas i |
| P_{ds} | Downstream pressure |
| P_{us} | Upstream pressure |
| Q_i | Volumetric flow rate of gas i |

Greek Symbols

| | |
|----------|------------|
| γ | Shear rate |
|----------|------------|

Abbreviations

| | |
|------|---------------------------------|
| ABS | Acrylonitrile-Butadiene-Styrene |
| NMP | N-methyl-2-pyrrolidone |
| PDMS | Polydimethylsilicone |
| SAN | Styrene-acrylonitrile |
| THF | Tetrahydrofuran |

adsorbent bed process and adsorption process. These include low capital and operating cost and ease of operation. Since it does not require any phase transformation, membrane is a viable energy-saving alternative for gas purification. In addition, the membrane system is compact and simple, maintenance-free 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 [1, 2]. A considerable progress has been made for the commercial use of membranes for gas separation, covering many existing and emerging applications.

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 [3]. 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 [4]. Criteria for selecting good membrane materials are complicated; nonetheless, durability, mechanical integrity at the operating conditions, productivity and separation efficiency are important stipulations that must be balanced against cost in all cases. 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 [5]. Koros and Mahajan [5] also proposed that the current status and the limitations faced by the available membrane materials are the difficulties to achieve high permselectivity with at least equivalent productivity and to maintain these properties in the presence of complex and aggressive feeds. In other words, the main problems to be overcome in using polymeric membranes are the loss in performance stability at high temperature, high pressure and the presence of highly sorbing components.

Mindel® S-1000 resin is an engineering thermoplastic. It is a blending of Polysulfone and Acrylonitrile-Butadiene-Styrene (ABS). This polymer offers a unique combination of high heat deflection temperature, steam and hot water resistance, autoclavability, outstanding electrical properties and excellent dimensional stability. Mindel® S-1000 is usually extruded into sheet, pipe and profiles. It is a known fact, polysulfone has been for many years an important membrane material for gas separations with satisfactory permeability and acceptable permselectivity [6]. ABS is a polymer with a dispersion of rubber particles in a matrix of styrene-acrylonitrile (SAN) copolymer resin. The rubber is usually polybutadiene. Since the rubber and the SAN copolymer are not mutually soluble, there are two polymeric phases. The role of the rubber phase is to provide toughness to these structural thermoplastics [7]. The main objective of this research is to develop a defect-free asymmetric membrane for gas separation from a novel polymeric membrane material, Mindel® S-1000 (Polysulfone-Acrylonitrile-Butadiene-Styrene). In addition, studies the effect of rheologically induced molecular orientation during membrane fabrication in order to enhance membrane separation performance.

2. Experimental

2.1. Materials

Mindel® S-1000 which is polymer blend of Polysulfone and Acrylonitrile-Butadiene-Styrene (ABS) was supplied by Amoco Chemical (USA). Organic chemical, N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) were chosen as a solvent that supplied by Merck, Darmstadt, Germany. For the coagulation medium, water tap was used at controlled temperature 25 °C. An elastomer silicon polymer polydimethylsilicone (PDMS), Slygard 184 obtained from Dow Corning and n-hexane were used for coating.

2.2. Preparation of dope solution

Prior to the preparation of dope solution, Mindel® S-1000 (PSf-ABS) was dried overnight in a vacuum oven at about 60 °C. Based on the different composition of the required solutions, precise weighing was done on a digital electronic weight. The materials used to fabricate asymmetric membrane for gas separations in this study were Mindel, THF and NMP with different weight percentages. N-Methylpyrrolidone (NMP) and Tetrahydrofuran (THF) that were used were supplied by MERC-Schuchardt. All liquid solvents were reagent grade and used without further purification. Tap water was used as a coagulation medium in the phase separation process. The necessary equipment to be used in the casting solution preparation were first cleaned and dried. Firstly, 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. 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 produced. After that, the solution was poured into a clean bottle, and degassed using an ultrasonic bath from Branson to remove trapped micro-bubbles prior to

casting process. Sample of PSf-ABS solution with 21 wt% was prepared by maintaining the solvent ratio (THF/NMP) to 1/1 [8].

2.3. Preparation of flat sheet asymmetric membrane

Flat sheet configuration was selected because it is a base of module in laboratory before commercialization in hollow fiber or spiral wound membrane module and it is easy to conduct. Casting process was performed using a pneumatically-controlled casting machine [9].

Flat sheet asymmetric membranes can be prepared according to the dry/wet phase separation process with casting condition as stated in Table 1. Shear rate, γ experienced during casting was calculated by,

$$\gamma = v/g \quad (1)$$

Table 1. Flat sheet asymmetric membrane casting condition.

| Conditions | Value |
|--------------------------------------|---|
| Casting solution composition | 21 wt% of PSf-ABS, 31.6 wt% of N-methyl-2-pyrrolidone 47.4 wt% of Tetrahydrofuran |
| Casting knife gap distance | 150 μm |
| Casting temperature | Ambient temperature, 28°C |
| Casting speed | 5, 8, 10 and 15 seconds |
| Free standing duration | 5 s |
| Forced convection gas | Nitrogen |
| Forced convection residence duration | 15 s |
| Forced convection flowrate | 4 l/min |
| Forced convection temperature | 28 °C |
| First coagulant | Water/ 1 day / ambient condition |
| Second coagulant | Methanol/ 1 day / ambient condition |

2.4. Asymmetric membrane characterization

2.4.1. Pure gas permeability measurement

Gas permeation test was performed to obtain the pressure-normalized fluxes of the membrane. It measured by fixing a circular membrane sample (12.38 cm²) into a permeation cell. Pure hydrogen and nitrogen was used as test gases and pressure-normalized flux measured at ambient temperature and at a drop of 1 bar. 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. Intrinsic permeability and selectivity data of dense film were used as standard values for comparison with asymmetric membrane. Gas permeation rate can be calculated by:

$$P_i = \frac{Q_i l}{A \Delta p} \quad (2)$$

where P_i is permeability coefficient for gas i , Q_i is volumetric flow rate of gas i , A is membrane effective surface area and l is membrane skin thickness. Δp is

pressure different across membrane, which is given by $\Delta P = P_{us} - P_{ds}$, where P_{us} and P_{ds} are upstream and downstream pressure respectively. Selectivity (dimensionless parameter) of asymmetric membrane can be determined by relative permeability of components i and j .

$$\alpha_{ij} = P_i / P_j = (P/l)_i / (P/l)_j \quad (3)$$

2.4.2. Plane polarized infrared Fourier transform spectroscopy

Molecular orientation in the active layer of flat sheet membranes was directly and quantitatively measured using plane polarized reflectance infrared spectroscopy. Plane polarized infrared spectra of membrane (parallel and perpendicular to shear direction) were determined by a diffuse reflectance infrared Fourier transform spectrometer (OMNIC-Thermo Finningan by Research Instrument). The samples of membranes were mounted at the sample position with the outer skin surface facing the infrared beam and were rotated according to the shear direction (either vertical or horizontal). Then, spectra of linear dichroism were obtained by straightforward subtraction of plane polarized infrared spectra perpendicular to shear direction from plane polarized infrared spectra parallel to shear direction.

3. Result and Discussion

3.1. Effect of shear rate on plane polarized infrared spectroscopy of Mindel s-1000 asymmetric membrane

Molecular orientation in the active layer of flat sheet membranes was directly measured using plane polarized reflectance infrared spectroscopy because the preferred orientations of specific functional groups can be easily and clearly determined [10].

Figures 1 to 4 show the polarized infrared spectra for membranes cast a selected range of shear. All of the infrared spectra are comparatively complicated by having many strong bands in the 'finger-print' region of the spectrum below 3000 cm⁻¹. The different shear cast membranes exhibited dichroism in the infrared, but the membrane with shear rate of 275.17 s⁻¹ possessed the most pronounced effects in dichroism suggesting that it had the greatest molecular orientation.

The infrared spectra of polysulfone-ABS were dominated by absorption peaks characteristic of the benzene ring (aromatic group contributed by styrene) at 2953 cm⁻¹, the C≡N (nitrile group contributed by acrylonitrile) at 2352 cm⁻¹, the C₂H₃ (ethyl group) at 1768 cm⁻¹, the CH₃ (methyl group) at 1369 cm⁻¹, the CH=CH₂ (ethylene group contributed by butadiene) at 1431 cm⁻¹. As for the polysulfone, it consists of two main functional groups that are diaryl sulfone (Ar-SO₂-Ar) and diaryl ether (Ar-O-Ar) with strong absorptions at 1150 and 1235 cm⁻¹, respectively. The bands at 1491 and 1587 cm⁻¹ belong to the vibration of the aromatic -C=C in the molecule. The peak at the spectra for the high shear membrane was more distinct compared to the low shear membrane. Therefore, the degree of molecular orientation of the membranes at difference shear rates can be analysed by using the absorbance of the acetate functional groups.

This study also discovered that the further increase of shear rates beyond 275.17 s⁻¹ did not seem to cause further molecular orientation to take place

suggesting that a maximum molecular orientation was probably induced at the optimum shear. This by discovery is well supported by gas separation performance results and the membrane morphology that were discussed in the previous section.

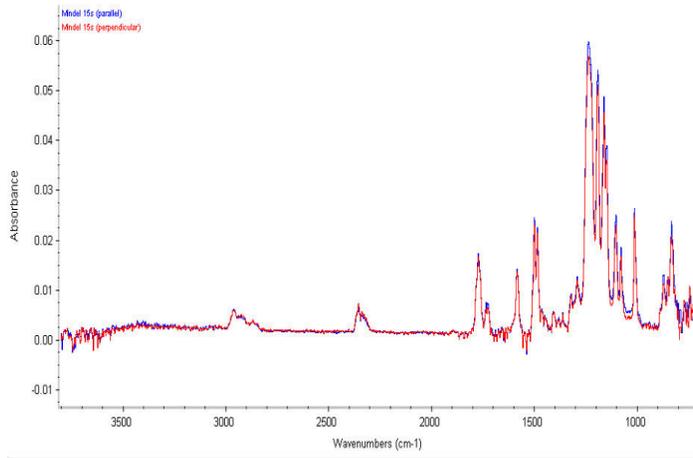


Fig. 1. Plane-polarized IR spectra of asymmetric Mindel S-1000 membrane at shear rate of 146.76 s⁻¹. The plane of the polarization of IR beam was perpendicular (red) and parallel (blue) to the shear direction.

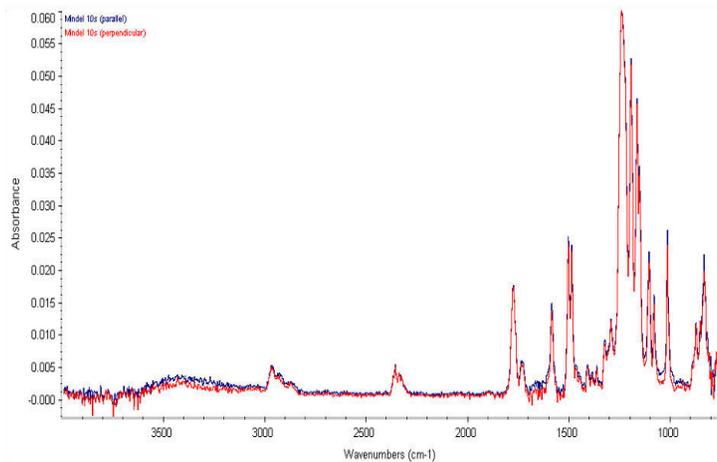


Fig. 2. Plane-polarized IR spectra of asymmetric Mindel S-1000 membrane at shear rate of 220.17 s⁻¹. The plane of the polarization of IR beam was perpendicular (red) and parallel (blue) to the shear direction.

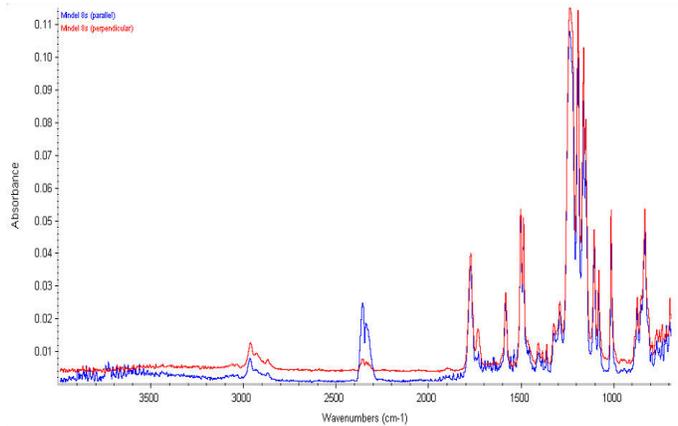


Fig. 3. Plane-polarized IR spectra of asymmetric Mindel S-1000 membrane at shear rate of 275.17 s^{-1} . The plane of the polarization of IR beam was perpendicular (red) and parallel (blue) to the shear direction.

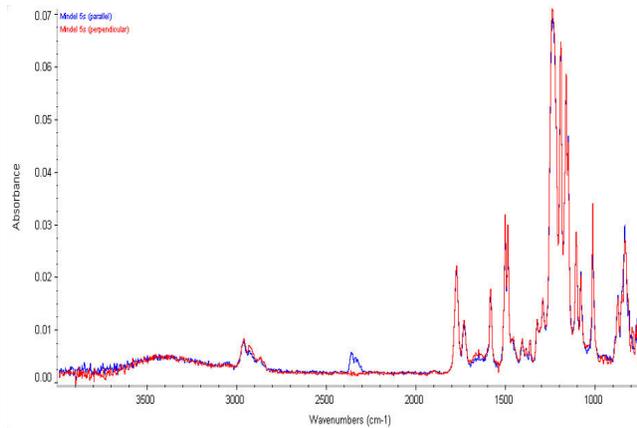


Fig. 4. Plane-polarized IR spectra of asymmetric Mindel S-1000 membrane at shear rate of 440.27 s^{-1} . The plane of the polarization of IR beam was perpendicular (red) and parallel (blue) to the shear direction.

3.2. Effect of shear rate on gas separation performance of Mindel S-1000 asymmetric membrane

Pressure-normalized flux and selectivity of asymmetric membrane were measured by using pure oxygen and nitrogen. Figure 5 shows the pressure-normalized flux of oxygen and nitrogen and oxygen/nitrogen selectivity. Even though it shows a fluctuation pattern for pressure-normalized flux of oxygen and oxygen/nitrogen selectivity, there is a critical point existed in each plot. However, the plot of pressure-normalized flux of nitrogen of Mindel S-1000 membrane versus shear rate decreased with increasing shear rate. According to experimental data, the critical shear rate was discovered to be around 275.17 s^{-1} .

In region prior to the critical shear rate (275.17 s^{-1}); formation of dense skin was mainly driven by conventional demixing and precipitation mechanism, which was

considered to be independent of shear rate. As shown in Fig. 5, the increase of shear rate enhances the molecular orientation in skin layer and, in turn, improving selectivity of asymmetric membrane [10-12]. However, casting membrane at an extremely high shear rate, especially over the critical shear rate (275.17 s^{-1}) had pulled the molecular chains or phase-separated domains apart and began to create slight defects in skin layer [13, 14]. Casting PSf-ABS membrane at the highest shear rate (440.27 s^{-1}) caused an abrupt deterioration in selectivity of oxygen/nitrogen.

As stated above, there was a decrease in pressure-normalized flux of nitrogen (slow gas) through the Mindel S-1000 membrane. However, there was a disproportionate increase of pressure-normalized flux after the critical shear rate (275.17 s^{-1}). The decrease in the pressure-normalized flux can be explained by the rheological behavior of the polymeric solution dope as it was cast during early stage of membrane fabrication process. It is believed that, the molecular chains of the viscous solution experiencing higher shear rate tend to align themselves much better than those experienced lower shear rate, and this enhanced orientation that caused the polymer molecules to pack closer to each other [9]. However, oxygen (fast gas) that has a small kinetic diameter (3.46 \AA) and light molecular weight (32.0 g/mol) compared to nitrogen (3.64 \AA and 28.01 g/mol). As shown in Fig. 5, there was an increase in pressure-normalized flux of oxygen (fast gas) with increasing shear rate. Effective solution-diffusion polymeric membrane has no continuous passages but rely upon thermally agitated motion of the chain segments comprising the polymer matrix to generate penetrant-scale transient gaps in the matrix, thereby allowing diffusion from the upstream to the downstream face of the membrane [15]. Therefore, the oxygen undergoes random jumps, but because of a higher concentration at the upstream face than the downstream face, a diffusion of a high flux occurs towards downstream face.

Therefore, the optimum shear rate for preparing high performance Mindel S-1000 membrane was found to be in the range between 220.13 s^{-1} and 440.27 s^{-1} with the oxygen/nitrogen selectivity for these membranes varied between 1 and 4.86 with oxygen pressure-normalized flux range of 4.12 GPU to 10.51 GPU. At critical shear rate of 275.17 s^{-1} , the polysulfone-ABS membrane exhibited good selectivity of 80% of pure polysulfone membrane intrinsic selectivity value. Enhanced molecular orientation may enable membrane selectivity to be elevated beyond the recognized intrinsic value of the polymer. Therefore, a reasonably high pressure-normalized flux of oxygen and high selectivity as the best performance of Mindel S-1000 membrane was successfully produced from this study.

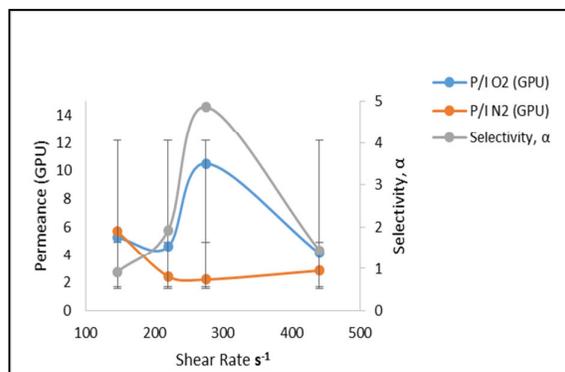


Fig. 5. Nitrogen and oxygen pressure flux and O_2/N_2 selectivity vs shear rate.

4. Conclusion

From the research conducted, the effect of shear rate on molecular orientation and gas performance was analysed. Based on the result of this study, a number of conclusions were drawn as follows:

- The membrane with shear rate of 275.17 s⁻¹ has more pronounced effects in dichroism suggesting greater molecular orientation and the membrane selectivity was found to be the best proving that higher molecular orientation would enhance separation performance.
- The critical shear was determined to be around 275.17 s⁻¹. Increasing shear rate enhanced molecular orientation in skin layer and, in turn, improving selectivity of asymmetric membrane. Casting the PSf-ABS membrane at a higher shear rate of 440.27 s⁻¹ had caused an abrupt deterioration in the selectivity of oxygen/nitrogen.
- Combined effects of fabricating conditions and rheological factor had successfully developed a defect-free asymmetric Mindel S-1000 membrane for gas separation. At an optimum shear rate (275.17 s⁻¹) and an ideal dope solution with polymer concentration of 21 wt% and solvent ratio of 0.67, the gas separation performance was optimized. Oxygen pressure-normalized flux (10.51 GPU) and oxygen/nitrogen selectivity (4.86) of this membrane surpassed 80% of the intrinsic selectivity.

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