

OPTIMIZATION OF FORMATION PROCESS IN DEVELOPMENT OF HIGH PERFORMANCE ASYMMETRIC MEMBRANES

Lal Ping Yean*, Ahmad Fauzi Ismail

Membrane Research Unit, Faculty of Chemical & Natural Resources Engineering,

Universiti Teknologi Malaysia, Locked Bag 791, 80990 Johor Bahru

Tel: 07-5505315, Fax: 07-5581463, E-mail: fauzi@fkkksa.utm.my

ABSTRACT

Selectivity and permeability of asymmetric membrane characterize its performance for gas separation process. Unfortunately, there is usually a trade-off between permeability and selectivity, thus representing one of the major obstacles to commercial application and production of membranes. Hence, serious compromises are required to achieve a defect-free skin layer with minimum thickness in order to avoid dramatic loss in the overall membrane selectivity by maintaining sufficient permeability. Structure and property of asymmetric membrane are intimately tied to its formation mechanism, where slight changes either in the solution recipes or processing parameters can greatly influence the resultant membrane. Specifically, preparation of high performance asymmetric membranes with defect-free and ultrathin skin layers has been performed through the manipulation of two fabrication variables, including solvent ratio and forced-convective evaporation time. Therefore, investigation of their effects was conducted by using factorial design, in which the main effects and the interaction effects of variables on membrane structure and performance were analyzed. Indeed, the interdependencies of these variables play a critical role in the production of defect-free and ultrathin-skinned asymmetric membranes. Based on the analysis of results, optimal processing conditions can be developed to produce high performance asymmetric membranes without the necessity of post-treatments.

Keywords: Asymmetric membrane, ultrathin-skin, defect-free, phase inversion, rheology

INTRODUCTION

Development of membranes that exhibit both a superior selectivity and a high permeability is important since large value of flux leads to higher productivities, smaller areas, and lower capital costs whereas higher selectivity leads to more efficient separations, higher recoveries, and lower power costs. Unfortunately, a reciprocal relation often exists between permeability and selectivity, where the early dense membranes tended to be rather thick in an attempt to avoid defects, thereby sacrificing productivity or flux. Hence, integrally-skinned asymmetric membranes developed by Loeb and Sourirajan in 1960's, produced fluxes that were an order of magnitude greater than those for the dense membranes, yet accelerated the progress of membrane-separation technology [1]. Nowadays, dry/wet phase inversion process is the most commonly used method for producing integral-skinned asymmetric membranes, which can be schematically represented in Figure 1 [2]. The basic procedure involves casting a multicomponent dope solution containing polymer, solvents (a more volatile solvent and a less volatile solvent) and nonsolvents (which is at the incipient state of stabilization) onto an appropriate substrate, followed by the interfacial dry phase separation process that requires a defined period for a selective loss of a highly volatile solvent from the solution, causes destabilization at the topmost surface of nascent membrane. The nascent membrane is then immersed in a nonsolvent coagulant, thus undergoing a wet phase separation, where the bulk of the membrane structure is formed and extraction of the remaining solvents and nonsolvents occurs. Recently, new attempts are implemented to develop a defect-free and ultrathin-skinned asymmetric membrane without requiring any additional post-treatments such as curing or coating by adopting proper modifications during membrane formation. Therefore, in this study, effects of solvent ratio of casting solution and forced-convective evaporation period during casting were investigated in detail.

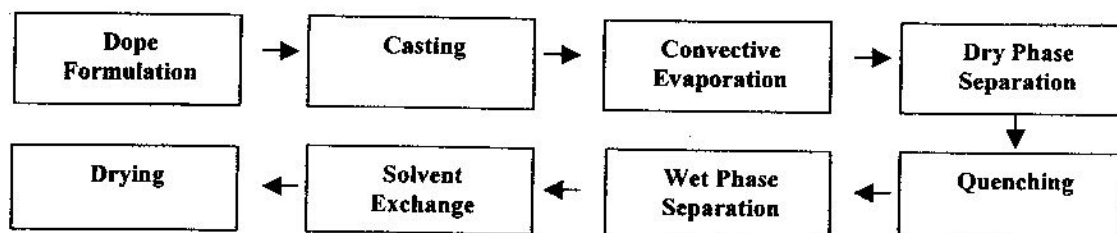


FIGURE 1 Schematic Diagram of Dry/Wet Phase Inversion Process

EXPERIMENTAL**Materials**

The dope used in the current study consisted of polysulfone (PSF (Udel-P1700)) supplied by Amoco Chemicals, *N,N*-dimethylacetamide (DMAc), tetrahydrofuran (THF) and ethanol (EtOH) at appropriatory specific composition, whereas tap water was used as the coagulation medium.

Preparation of Casting Solution

The casting solutions used in the current study consisted of polymer, solvents and nonsolvent at appropriatory specific composition. Initially, solvents were fed into a flange reaction vessel, following by the required amount of polymer. The mixture was stirred at a high speed while its temperature had to be maintained at about 55°C. Finally, after the solution had become homogeneous, nonsolvent was poured into the vessel to mix with the solution. The whole mixing process took place for approximately 8 hours in order to get a completely homogeneous solution.

Preparation of Asymmetric Membrane

The casting solution was cast by a pneumatically-controlled casting machine on a glass plate with the aid of casting knife for a gap setting of about 150 μm . Then, an inert nitrogen gas stream was blown parallel across the as-cast membrane surface for a certain period to induce forced-convective evaporation prior to immersion into an aqueous bath and remained there for 1 day. Finally, the washed membranes were solvent-exchanged with methanol for 2 hours and then air-dried for 1 day. The whole process was carried out at ambient condition.

Gas Permeation Testing

Circular membrane discs with effective area of 13.5 cm^2 were cut and mounted in a stainless steel permeation cell. The gas permeation rates are determined by using pure gases such as hydrogen and nitrogen at various pressure gradients while the permeate side was opened to atmosphere. All experiments were performed at ambient temperature. Then, the volumetric flow rates of permeate were measured by a soap bubble flow meter. By measuring the flux for each gas, permeation rate and selectivity can be calculated by the following equations:

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{A\Delta p}, \text{ and} \quad (1)$$

$$\alpha_{ij} = P_i / P_j = (P/l)_i / (P/l)_j \quad (2)$$

where $(P/l)_i$ is pressure-normalized flux or permeability for gas i (1 GPU = $1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$), P_i is permeability coefficient for gas i , α is ideal separation factor or selectivity, Q_i is volumetric flow rate of gas i , Δp is pressure difference across membrane, A is membrane effective surface area and l is membrane skin thickness.

RESULTS AND DISCUSSION**Effect of Solvent Ratio on Membrane Structures and Separation Properties**

In dry/wet phase inversion process, the casting solution contains two types of solvents, a primary more volatile solvent and a secondary less volatile solvent, that allows finer control of solvent evaporation and polymer coagulation rates [2]. Upon evaporation of some of the volatile solvent, the outermost region of the nascent membrane will undergo a dry phase separation prior to immersion in the coagulant. Since membrane skin layer thickness and integrity are intimately related to solvent evaporation and the interfacial dry phase separated region, the ratio of less volatile solvent to more volatile solvent in the

casting solution, the "solvent ratio", is a crucial parameter for control of the dry/wet phase inversion process. As shown in Figure 2, a low solvent ratio could increase the solvent evaporation rate, causing a thicker and more concentrated outermost skin in the nascent membrane and thus increasing the selective skin thickness and denseness, thus resulting an increase in selectivity but a loss in permeability; and vice versa. On the other hand, a change in the solvent ratio can alter the kinetics of the wet phase separation process. The less volatile solvent is used to be thermodynamically better than the more volatile solvent, and therefore promotes an instantaneous liquid-liquid demixing process, while the other exhibits a delayed liquid-liquid demixing process, when both of them are exposed to the same quench medium. Qualitatively, membranes with a thin top layer of porous nodular structure and macrovoid-filled open cell substructure are often obtained under instantaneous liquid-liquid demixing process, while membranes having a dense, thick top layer, and a closed cell substructure are always formed by the delayed liquid-liquid demixing process [3]. Hence, a delicate balance must, therefore, be achieved to allow optimization of membrane skin thickness by including sufficient less volatile solvent to promote a rapid quench while providing sufficient more volatile solvent to maintain a defect-free skin layer.

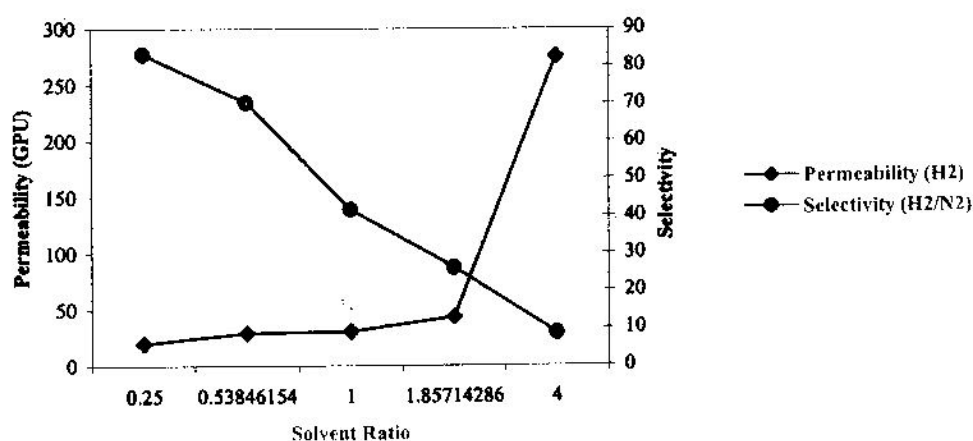


FIGURE 2 Effects of Solvent Ratio on Membrane Permeability and Selectivity

Effect of Forced-Convective Evaporation Period on Membrane Structures and Separation Properties

Physical processes occur during forced convective evaporation step are of utmost important for skin layer formation made by dry/wet phase inversion process and has been acknowledged as a crucial element in the production of defect-free, ultrathin-skinned asymmetric membranes. To induce "dry" phase inversion in the cast membrane, the casting formulations must be altered to include sufficient volatile solvent and nonvolatile solvent to cause the solution to be essentially at the point of incipient phase instability. During the evaporation-induced "dry" stage of the process, an inert gas stream passes over a properly formulated casting solution having a starting composition almost at the binodal boundary for a certain period. Sufficient volatile solvent is lost to drive the outside few microns of the as-cast nascent membrane into a phase-separated structure. This process becomes apparent instantaneously by the formation of a fine haze on the surface of the nascent membrane. Hence, the evaporation of volatile solvent from an initially homogeneous single-phase polymer solution leads to the formation of a turbid two-phase solution, as a precursor step in the dry/wet phase inversion process for asymmetric membrane formation [4, 5]. Results of this study as shown in Figure 3 had discovered that the skin layer is getting thicker while the skin porosity becomes lessen due to prolonged evaporation period during casting, causing those membranes to be lower in permeability but higher in selectivity. On the contrary, the opposite case held for the membranes that exposed to shorter evaporation period during casting.

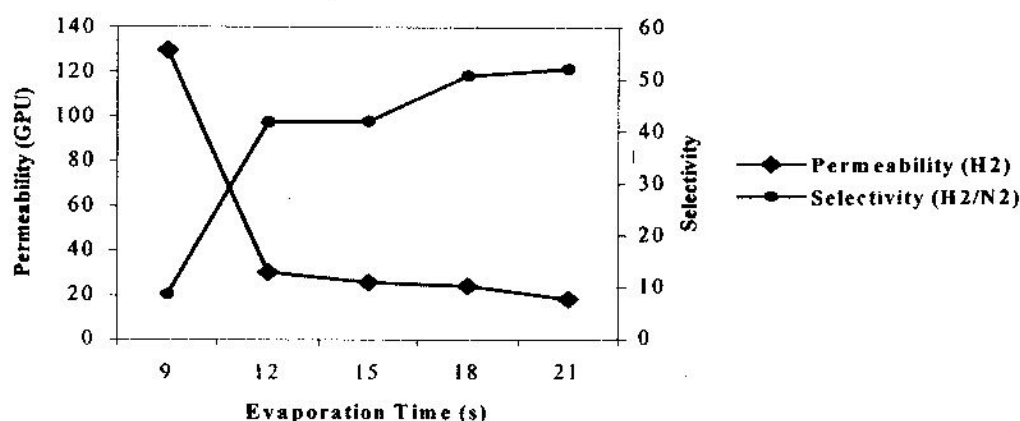


FIGURE 3 Effects of Evaporation Time on Membrane Permeability and Selectivity

2⁴ Factorial Design

A complete 2⁴ factorial design was carried out to examine the effects and interactions of the four major fabrication variables including polymer concentration, solvent ratio, forced-convective evaporation period and casting shear rate. The factors were chosen because of their relevance to integrity and thickness of asymmetric skin layer during membrane formation. The factors under consideration of 2⁴ factorial design were each assigned as A, B, C, and D, and were examined at two levels, high (+) and low (-). The 16 runs, representing all combinations of the four factors, were performed in a random order with the response (permeability or selectivity of membrane). The high level of any factor in the treatment combination was denoted by the corresponding lower case letter, and the low level was denoted by the absence of the corresponding letter. By conventional, (1) was used to denote all factors at the low level [6]. Therefore, the effects represented by single letters were main effects and those represented by multileters were interaction effects. The contrast constants and effects associated with each treatment combinations for the factorial design can be determined by using a table of plus and minus signs. Subsequently, analysis of variance was conducted to analyze a factorial design. Finally, significance of factors and interactions can be shown in a Pareto Chart (Figure 4 and Figure 5). Based on this analysis, we notice that the main effects of these fabrication factors were more dominant than their interaction effects. Besides that, solvent ratio and evaporation time had the strongest influence on selectivity and permeability of asymmetric membrane. Therefore, in order to develop high performance asymmetric membranes, the solvent ratio and forced-convective evaporation period have to be properly controlled, as described in previous sections.

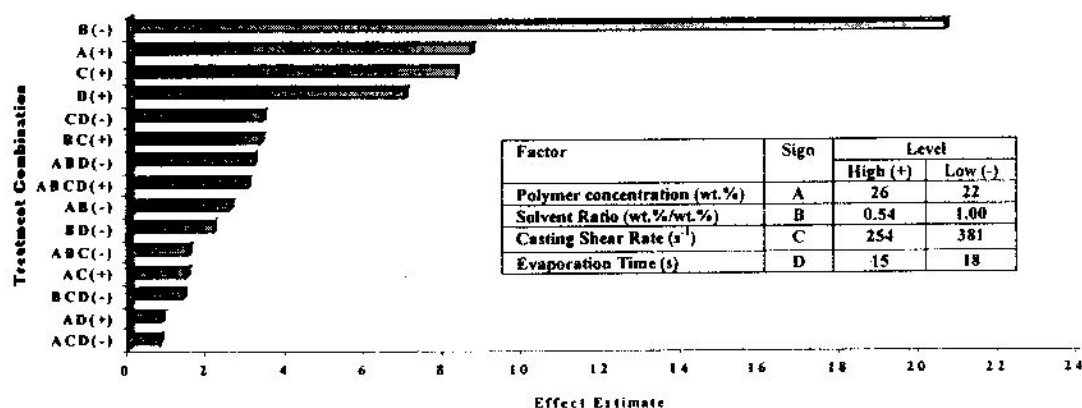


FIGURE 4 Pareto Chart for Selectivity of Asymmetric Membrane

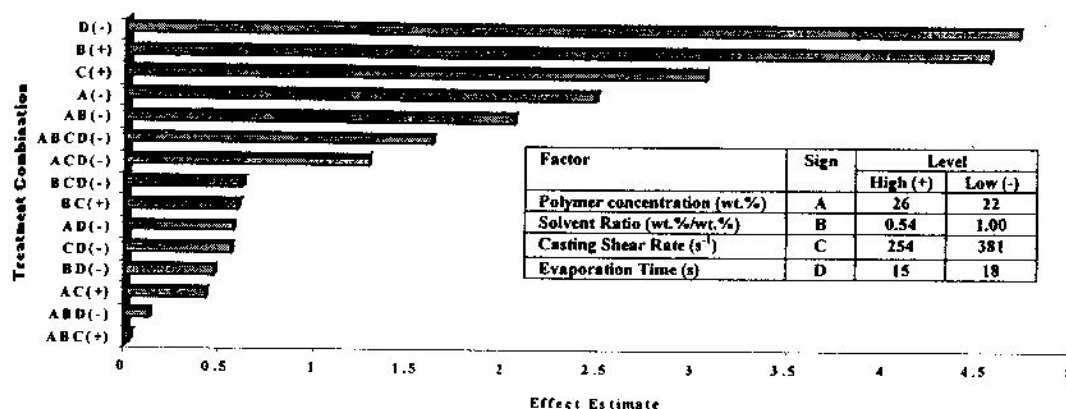


FIGURE 5 Pareto Chart for Permeability of Asymmetric Membrane

CONCLUSION

Asymmetric membranes are preferentially applied in gas separation processes because of their high efficiency. Structure and property of asymmetric membrane are intimately tied to its formation procedures during dry/wet phase inversion process. According to the results of this study, casting membrane from a solution with lower solvent ratio that was exposed to prolonged evaporation period would result in a more selective but less productive membrane, while casting membrane from a solution with higher solvent ratio that was exposed to shorter evaporation time would produce a high value of permeance but a relatively low degree of selectivity. Furthermore, analysis of factorial design had also reconfirmed that the main effects of solvent ratio and forced-convective evaporation period were more dominant than the other fabrication factors. Therefore, a delicate balance must be made in combination of these variables during formation of defect-free and ultrathin-skinned asymmetric membranes.

NOTATION

A	Membrane effective surface area (cm ²)
Q_i	Volumetric flow rate of gas i (cm ³ /s)
l	Membrane skin thickness (cm)
Δp	Pressure difference across membrane (cmHg)
P_i	permeability coefficient for gas i (Barrer = 10^{-10} cm ³ (STP).cm/cm ² .s.cmHg)
$(P/l)_i$	Pressure-normalized flux or permeability for gas i (GPU = 1×10^{-6} cm ³ (STP)/cm ² .s.cmHg)
α	Ideal separation factor or selectivity (unitless)

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