Development of defect-free asymmetric polysulfone membranes for gas separation using response surface methodology

A.F. Ismail*, P.Y. Lai
Membrane Research Unit, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

Received in revised form 15 February 2004; accepted 28 February 2004

Abstract
This paper reports the preparation of defect-free asymmetric membranes through the manipulation of membrane fabrication variables, including polymer concentration, solvent ratio (ratio of less volatile solvent to more volatile solvent), forced-convective evaporation time and casting shear rate. Main effects and interaction effects of these variables on membrane structure and performance were investigated by using factorial design and response surface methodology in order to optimize membrane formation process. According to the results of this study, an essentially defect-free skin layer with skin thickness in the range of 6590–11330 Å was prepared for asymmetric polysulfone membranes. Selectivity of these membranes was relatively higher as compared to conventional membranes; some of them even surpassed the intrinsic selectivity. Therefore, optimal processing conditions can be developed to prepare defect-free asymmetric membranes for gas separation.

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Keywords: Asymmetric membrane; Gas separation; Polysulfone; Phase inversion; Factorial design

1. Introduction
Performance of membrane-based gas separation process strongly depends on permeability and selectivity of membrane. Membrane with higher permeability leads to higher productivity and lower capital costs whereas membrane with higher selectivity leads to more efficient separations, higher recovery and lower power costs; indeed, membranes that simultaneously possess high values of selectivity and permeability would lead to the most economical gas separation processes. Hence, numerous studies and efforts were centered upon development of high performance membranes for gas separation process. In 1960, Loeb and Sourirajan successfully developed the first integrally-skinned asymmetric membranes [1,2]. An integrally-skinned asymmetric membrane consists of a very thin and dense skin layer (0.1–1 μm) overlaying on a thick and highly porous sub-layer (100–200 μm) with an average void size ranging from 0.01 to 1 μm), where both layers are composed of the same material and formed in a single operation [2–4].

The skin represents the actual selective barrier, while the sublayer serves only as a mechanical support for the skin, with negligible effects on separation.

In asymmetric membrane, density and mass transfer resistance of the skin layer is somewhat greater than that of the sublayer, therefore, permeability of asymmetric membrane does not depend on entire membrane thickness, but instead is inversely proportional to thickness of skin layer [2,5]. Hence, a high value of permeability can be achieved in asymmetric membrane with very thin skin layer. Generally, asymmetric membrane with skin thickness of approximately 1000–5000 Å is classified as ultrathin-skinned membrane; whereas hyperthin-skinned asymmetric membrane possesses a skin layer with thickness much less than that for ultrathins [6]. Both of them are specifically designed to achieve permeability of practical interest. However, development of thin-skinned asymmetric membranes would result in defects or pinholes on skin surface due to irregular packing of kinked polymer chains and incomplete coalescence of polymer molecules in skin layer [7,8]. Solution-diffusion mechanism of permeation through membrane materials is very slow compared to Knudsen diffusion or viscous flow that occurs through nonselective pores in membrane; thus a defective area plague on membrane surface can substantially
cause a dramatic loss in selectivity and prevent intrinsic selectivities from being achieved in very thin membranes. Consequently, for any given separation, there is usually a trade-off between permeability (skin thickness) and selectivity (skin integrity), where both parameters tend to exhibit a contradictory relation, representing a major problem in productions and applications of asymmetric membranes for gas separation process. Today, new challenges are directed towards development of defect-free and high performance asymmetric membranes for gas separation process, in which further insight and dramatic progress are being made.

According to earlier studies, dry/wet phase inversion process is one of the most versatile methods to produce high performance asymmetric membranes for gas separation. Asymmetric membrane formation process involves formulation of a homogenous multi-component solution that consists of a polymer, solvents (a less volatile solvent and a more volatile solvent) and a nonsolvent. The solution is tailored to be close to thermodynamic instability limit and approaching phase transition boundary. Membrane is cast at an appropriate shear; followed by a forced-convective evaporation for dry phase separation. A nascent skin layer is formed from a region with locally elevated polymer concentration due to a selective loss of highly volatile solvent from the outermost surface of freshly cast membrane. Underlying region beneath the nascent skin layer remains in a fluid state. The nascent membrane is then immersed in a coagulation bath for wet phase separation, where the bulk of the membrane structure is formed by counter-diffusion of solvents and nonsolvents and extraction of the remaining components occurs.

Polymer concentration and solvent ratio (the ratio of less volatile solvent to more volatile solvent), forced-convective evaporation time and casting shear rate have been identified as dominant fabrication parameters in controlling skin thickness and skin integrity, and thus causing substantial effects on separation properties of asymmetric membrane. Therefore, in this study, main effects and interaction effects of these variables on membrane structure and performance were investigated by using factorial design and response surface methodology in order to optimize membrane formation process.

2. Experimental

2.1. Materials

Dope used in this study consisted of polysulfone (PSf) (Udel-P1700) supplied by Amoco Chemicals, N,N-dimethylacetamide (DMAc), tetrahydrofuran (THF) and ethanol (EtOH) at appropriated composition, whereas tap water was used as a coagulation medium. Polysulfone was dried in an oven at 60 °C for overnight before use, while other organic chemicals were obtained in reagent grade purities and used as received.

2.2. Preparation of asymmetric flat sheet membranes

Asymmetric polysulfone flat sheet membranes were prepared by casting solution generally consisted of polysulfone (polymer), N,N-dimethylacetamide (DMAc) (less volatile solvent), tetrahydrofuran (THF) (more volatile solvent) and ethanol (EtOH) (nonsolvent). Casting process was performed by using a pneumatically-controlled casting machine. Casting solution was cast on a glass plate with a casting knife with gap setting of 150 μm at an appropriate casting shear. The overall casting knife geometry is 265 mm length and 60 mm width. The shear rate experienced during casting were calculated from the following relationship:

Shear rate (\( \dot{\gamma} \)) = \( \frac{\text{Velocity of casting knife}}{\text{Membrane thickness}} \)

Casting was carried out at ambient atmosphere (30 °C and 84% relative humidity). Then, forced-convective evaporation was induced by blowing an inert gas stream across membrane surface for a certain period before immersion into an aqueous bath. Finally, the membrane was solvent-exchanged with methanol for 2 h and then air-dried for 1 day.

2.3. Gas permeation measurement

Gas permeation tests were performed with a permeation cell by using pure hydrogen (H\(_2\)) and nitrogen (N\(_2\)) as test gases. Circular membrane discs with an effective permeation area of 13.5 cm\(^2\) were used. Feed pressure was controlled at 1, 2, 3, 4 or 5 bar while permeate side was maintained at atmospheric pressure. Experiments were carried out at ambient temperature (30 °C). Gas permeation rates were measured by a soap bubble flow meter. Each set of data was determined as an average of three replicates. Gas permeation rate can be calculated by

\[
\frac{P_i}{L} = \frac{Q_i}{A \Delta p}
\]

where \( P_i \) is defined as pressure-normalized flux or permeability for gas \( i \). The common unit of pressure-normalized gas flux is GPU (1 GPU = 1 × 10\(^{-6}\) cm\(^3\) (STP) cm/cm\(^2\) s cmHg). \( Q_i \) is volumetric flow rate of gas \( i \), \( \Delta p \) the pressure difference across membrane, \( A \) the membrane effective surface area and \( L \) the membrane skin thickness. Selectivity (unitless) of asymmetric membrane can be determined by

\[
a_{ij} = \frac{P_j}{P_i} = \frac{(P_i L_j)}{(P_j L_i)}
\]

H\(_2\) and N\(_2\) permeability coefficients of a solution-cast polysulfone film at 25 °C have been determined to be 14.0 × 10\(^{-10}\) and 0.25 × 10\(^{-10}\) cm\(^3\) (STP) cm/cm\(^2\) s cmHg, respectively, corresponding to an ideal H\(_2\)/N\(_2\) selectivity of 56 [10].
Dense film values are useful for comparison to asymmetric values. In addition, finite structural details of asymmetric membrane, such as skin thickness, mean pore size and effective surface porosity can be deduced from gas permeation data, as being proposed by Marchese and Pagliero [10].

As shown in Fig. 1, asymmetric membrane consists of a very thin skin layer (labeled 1) supported on a relatively thick porous spongy region (labeled 3). Skin layer normally suffers from presence of surface pores or defects (labeled 2). Total gas flux through asymmetric polymeric membrane with defects is sum of permeation through polymeric material of skin layer and flux through defects. The former is exclusively predominated by solution-diffusion mechanism, while the latter occurs due to a combination of Knudsen diffusion, viscous diffusion and bulk flow. Relative contribution of each transport modes for a particular case depends on temperature and pressure conditions in pore. Equations for flow in porous media can only be approached by analogy with flow in capillaries. Carman suggested a general equation for permeability in capillaries with noncircular cross-sections, as follows [10],

$$P_{ij} = \frac{m^2 \bar{\rho}}{k_i q_i (\bar{p} - \bar{p}_0)} + \frac{4 m \eta i}{3 p_i q_i} \bar{\nu}_i. \quad (2)$$

The first term on right-hand side of equation is contributed by viscous flow term, where $m$ is mean hydraulic radius or mean pore size, $\eta_i$ the viscosity of permeant $i$, $\bar{p}$ the mean pressure given by $\bar{p} = (p_u + p_d)/2$, and $p_0$ the atmospheric pressure at which gas flux was measured. The last term is contributed by Knudsen flow, where $\bar{\nu}_i$ is mean molecular speed of permeant $i$, given by $\bar{\nu}_i = (8RT/\pi M_i)^{1/2}$, where $M_i$ is molecular weight of permeant $i$, $T$ the absolute temperature, and $R$ the gas constant.

Numerical factors $k_1$ and $k_2$ in Eq. (2) account for changes of pore shape; and $\delta$ the numerical factor for a particular system. Taking an average shape for pore or defect as more or less rectangular in commercial and asymmetric membrane, a typical constant value of $k_0$ should be 2.5 [10]. Experiments made by various investigators showed that $\delta/k_1q \approx 0.4$, $q = 2^{1/3}$, and $\delta/k_1 \leq 0.8$ in accordance with theoretical expectations [10]. Eq. (2) can now be written as

$$P_{ij} = 0.4 \frac{m^2 \bar{\rho}}{k_i q_i (\bar{p} - \bar{p}_0)} + 1.0667 \frac{m}{p_0} \bar{\nu}_i. \quad (3)$$

Introducing Eq. (3) in Eq. (1) leads to

$$K_i = \frac{P_{ij}}{l} + 1.0667 \frac{m}{l p_0 q_i} \bar{\nu}_i + 0.4 \frac{m^2 \bar{\rho}}{l i p_0 q_i^2} \bar{\nu}_i. \quad (4)$$

So, a plot of $K_i$ against $\bar{\rho}$ should give a straight line, where intercept, $K_{0ij}$ at $\bar{\rho} = 0$ and slope, $B_{0ij}$, are given by

$$K_{0ij} = \frac{P_{ij}}{l} + 1.0667 \frac{m}{l i p_0 q_i} \bar{\nu}_i, \quad (5)$$

$$B_{0ij} = 0.4 \frac{m^2 \bar{\rho}}{l i p_0 q_i^2}. \quad (6)$$

where $K_i$ is total effective permeability, $Q$, the total gas flux for permeant $i$, $A$ the total surface area of membrane, $P_1$ the intrinsic permeability of membrane material, $P_2$ the effective permeability characteristic of pore, $\varepsilon = A_2/A$ the surface porosity, $A$ the membrane effective surface area, $A_2$ the porous surface area, $l_i$ the skin layer thickness, $l_p$ the pore length and $q$ the tortuosity factor. $\Delta p$ the pressure difference across membrane, given by $p_u - p_d$, where $p_u$ and $p_d$ are upstream and downstream pressure of gas permeant, respectively.

Gas flow through pores occurs by a combination of Knudsen diffusion, viscous diffusion and bulk flow. Relative contribution of each transport modes for a particular case depends on temperature and pressure conditions in pore. Equations for flow in porous media can only be approached by analogy with flow in capillaries. Carman suggested a general equation for permeability in capillaries with noncircular cross-sections, as follows [10],

$$K_i = \frac{Q_i}{l} + 1.0667 \frac{m}{l p_0 q_i} \bar{\nu}_i + 0.4 \frac{m^2 \bar{\rho}}{l i p_0 q_i^2} \bar{\nu}_i. \quad (1)$$

where $K_i$ is total effective permeability, $Q_i$ the total gas flux for permeant $i$, $A$ the total surface area of membrane, $P_1$ the intrinsic permeability of membrane material, $P_2$ the effective permeability characteristic of pore, $\varepsilon = A_2/A$ the surface porosity, $A$ the membrane effective surface area, $A_2$ the porous surface area, $l_i$ the skin layer thickness, $l_p$ the pore length and $q$ the tortuosity factor. $\Delta p$ the pressure difference across membrane, given by $p_u - p_d$, where $p_u$ and $p_d$ are upstream and downstream pressure of gas permeant, respectively.

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where $K_i$ is total effective permeability, $Q_i$ the total gas flux for permeant $i$, $A$ the total surface area of membrane, $P_1$ the intrinsic permeability of membrane material, $P_2$ the effective permeability characteristic of pore, $\varepsilon = A_2/A$ the surface porosity, $A$ the membrane effective surface area, $A_2$ the porous surface area, $l_i$ the skin layer thickness, $l_p$ the pore length and $q$ the tortuosity factor. $\Delta p$ the pressure difference across membrane, given by $p_u - p_d$, where $p_u$ and $p_d$ are upstream and downstream pressure of gas permeant, respectively.
Pore size and surface porosity can be determined by using

\[ m = \sqrt{\frac{B_0 \eta_1 \rho_0 \varphi^2}{0.4\varepsilon}} \]  (7)

\[ \varepsilon = \frac{B_0 \eta_1 \rho_0 \varphi^2}{0.4\varepsilon^2} \]  (8)

In membrane-based gas separation process with relatively low operating pressure (or driving force) \( \bar{p} \approx 0 \), gas molecules tend to pass across porous area in skin layer (low resistance) by viscous flow rather than permeate through dense skin structure (high resistance). Besides that, compaction effects do not affect membrane exposed to low pressure driving force, so pore length is assumed the same as skin thickness. In this case, \( \varepsilon \approx 1 \) and \( \eta \approx 1 \), thus Eq. (7) can be rewritten as

\[ m = \sqrt{\frac{B_0 \eta_1 \rho_0 \varphi^2}{0.4\varepsilon}} \]  (9)

On the other hand, in membrane-based gas separation process with relatively high operating pressure (or driving force), gas transport is mainly contributed by gas flux through dense skin region. Furthermore, membrane exposed to high pressure driving force is affected by compaction effects, which tend to reduce pore length dramatically, therefore, pore length in more or less rectangular shape is assumed to be same as pore radius. In this case, \( \varepsilon \approx m \), thus Eq. (8) can be rewritten as

\[ \varepsilon = \frac{B_0 \eta_1 \rho_0 \varphi^2}{0.4m^2} \]  (10)

Skin thickness is calculated by gas permeation data obtained from two different gases, \( A \) and \( B \). Expression for skin thickness can be obtained from Eqs. (5) and (6), stated as

\[ I = \frac{P_{iA} - P_{iB} \rho C}{K_{iA} - K_{iB} C} \]  (11)

3. Results and discussion

Simulation and analysis of experimental data by a complete 2\(^4\) factorial design was systematically conducted using Statsoft Statistica (Version 5.5A), to examine effects and interactions of polymer concentration (A), solvent ratio (B), shear rate (C) and evaporation time (D) on permeability of hydrogen and selectivity of hydrogen/nitrogen for polysulfone membrane, within an empirically selected range of high (+) and low (−) levels based on preliminary screening experiments, as summarized in Tables 1 and 2. A set of sixteen runs representing every combination of four factors at each level was performed in a random order corresponding to response (total of three replicates). Treatment combinations are usually represented by lower case letters, where high (+) level of any factor in treatment combination is denoted by presence of corresponding letter, and low (−) level of any factor in treatment combination is denoted by absence of corresponding letter. By conventional, \( (1) \) is used to denote all factors at low (−) level. Therefore, any effects represented by single letters are main effect and

<table>
<thead>
<tr>
<th>Runs</th>
<th>Signs</th>
<th>Treatment combination</th>
<th>Level of factors</th>
<th>Response: pressure-normalized flux, ( \frac{P_i}{\varphi} ) (GPU)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>22 0.54 254 15</td>
<td>−−−−</td>
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</tr>
<tr>
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<td>−+−−</td>
<td>16.60 17.54 12.74 15.63</td>
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<tr>
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<td>c</td>
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<td>++−−</td>
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<td>−−−−</td>
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<td>−+−−</td>
<td>17.00 41.32 15.27 24.53</td>
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<tr>
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<td>g</td>
<td>22 1.00 381 15</td>
<td>++−−</td>
<td>17.84 14.50 19.75 24.03</td>
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<td>h</td>
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<td>++−−</td>
<td>16.27 14.63 5.60 12.17</td>
</tr>
<tr>
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<td>i</td>
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<td>−−+−</td>
<td>11.61 11.61 8.43 10.55</td>
</tr>
<tr>
<td>10</td>
<td>j</td>
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<td>−+−−</td>
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<tr>
<td>11</td>
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<td>+−+−</td>
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<td>15</td>
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<td>13.70 16.83 11.86 14.13</td>
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<tr>
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<td>p</td>
<td>22 1.00 381 18</td>
<td>+++−</td>
<td>22.10 19.71 27.36 23.06</td>
</tr>
</tbody>
</table>

- Polymer concentration, \( PC \) (wt.%).
- Solvent ratio, \( SR \) (wt.%/wt.%).
- Shear rate, \( \gamma \) (s\(^{-1}\)).
- Evaporation time, \( t \) (s).
Table 2
2^4 factorial design (selectivity of membrane)

<table>
<thead>
<tr>
<th>Runs</th>
<th>Signs</th>
<th>Treatment combination</th>
<th>Level of factors (high level: +; low level: −)</th>
<th>Response: selectivity, α (dimensionless)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A^a B^b C^c D^d Replicates Average</td>
<td>A^a B^b C^c D^d</td>
<td>I</td>
</tr>
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<td>1</td>
<td>(1)</td>
<td>22 0.54 254 15 − − − −</td>
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<td>a</td>
<td>26 0.54 254 15 + − − −</td>
<td>37.40 75.42 80.31 64.45</td>
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</tr>
<tr>
<td>3</td>
<td>b</td>
<td>22 1.00 254 15 − + − −</td>
<td>49.90 29.03 28.11 35.68</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ab</td>
<td>26 1.00 254 15 + + − −</td>
<td>39.58 60.97 40.13 54.33</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>c</td>
<td>22 0.54 381 15 − − + −</td>
<td>72.60 44.34 75.66 64.20</td>
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<tr>
<td>6</td>
<td>ac</td>
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</tr>
<tr>
<td>7</td>
<td>bc</td>
<td>22 1.00 381 15 − + + −</td>
<td>49.90 29.03 28.11 35.68</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>bc</td>
<td>26 1.00 381 15 + + + −</td>
<td>39.58 60.97 40.13 54.33</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>d</td>
<td>22 0.54 254 18 − − − +</td>
<td>70.39 61.65 69.96 64.20</td>
<td></td>
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<tr>
<td>10</td>
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<td>26 0.54 254 18 + − − +</td>
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<tr>
<td>11</td>
<td>bd</td>
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<td>56.29 29.67 63.40 49.79</td>
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<tr>
<td>12</td>
<td>abd</td>
<td>26 1.00 254 18 + + − +</td>
<td>41.08 58.79 54.35 51.41</td>
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<tr>
<td>13</td>
<td>cd</td>
<td>22 0.54 381 18 − − + +</td>
<td>70.68 60.61 82.17 71.15</td>
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<tr>
<td>14</td>
<td>acd</td>
<td>26 0.54 381 18 + − + +</td>
<td>131.00 44.48 81.26 85.58</td>
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<td>15</td>
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<td>22 1.00 381 18 − + + +</td>
<td>56.30 50.46 56.78 54.51</td>
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<tr>
<td>16</td>
<td>abcd</td>
<td>26 1.00 381 18 + + + +</td>
<td>81.21 27.64 72.60 60.49</td>
<td></td>
</tr>
</tbody>
</table>

a Polymer concentration, PC (wt.%).

b Solvent ratio, SR (wt.%/wt.%).

c Shear rate, γ (s⁻¹).

d Evaporation time, t (s).

Those represented by multi-letters are interaction effects [11]. Treatment combinations are reported in “standard order” by introducing one factor at a time, with each new factor being successively combined with those that precede it. Overall effects of a particular individual parameter at selected operating conditions of other parameters, on membrane performance were illustrated explicitly. Furthermore, fine structural details (skin thickness, mean pore size and surface porosity) deduced from gas permeation data for polysulfone membrane were shown in Table 3. Fig. 2 shows some representative of electron micrographs of membrane cross-section with different shear rate prepared in this study.

Table 3
2^4 factorial design (fine structural details of membrane)

<table>
<thead>
<tr>
<th>Runs</th>
<th>Signs</th>
<th>Treatment combination</th>
<th>Level of factors (high level: +; low level: −)</th>
<th>Response: skin thickness l (× 10⁻⁵ cm), mean pore size m (× 10⁻⁸ cm), surface porosity ϵ/q² (× 10⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A^a B^b C^c D^d Replicates Average</td>
<td>A^a B^b C^c D^d</td>
<td>Skin thickness l (× 10⁻⁵ cm)</td>
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<td>(1)</td>
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<td>2</td>
<td>a</td>
<td>26 0.54 254 15 + − − −</td>
<td>10.68</td>
<td>4.02</td>
</tr>
<tr>
<td>3</td>
<td>b</td>
<td>22 1.00 254 15 − + − −</td>
<td>7.39</td>
<td>4.41</td>
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<tr>
<td>4</td>
<td>ab</td>
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<td>9.76</td>
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<td>c</td>
<td>22 0.54 381 15 − − + −</td>
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<td>2.83</td>
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<td>ac</td>
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<td>3.21</td>
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<td>10.14</td>
<td>2.56</td>
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<tr>
<td>10</td>
<td>ad</td>
<td>26 0.54 254 18 + − − +</td>
<td>11.33</td>
<td>2.10</td>
</tr>
<tr>
<td>11</td>
<td>bd</td>
<td>22 1.00 254 18 − + − +</td>
<td>8.15</td>
<td>2.85</td>
</tr>
<tr>
<td>12</td>
<td>abd</td>
<td>26 1.00 254 18 + + − +</td>
<td>9.91</td>
<td>2.64</td>
</tr>
<tr>
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<td>9.76</td>
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</tr>
<tr>
<td>14</td>
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<td>9.83</td>
<td>1.65</td>
</tr>
<tr>
<td>15</td>
<td>bcd</td>
<td>22 1.00 381 18 − + + +</td>
<td>6.59</td>
<td>1.85</td>
</tr>
<tr>
<td>16</td>
<td>abcd</td>
<td>26 1.00 381 18 + + + +</td>
<td>9.69</td>
<td>1.77</td>
</tr>
</tbody>
</table>

a Polymer concentration, PC (wt.%).

b Solvent ratio, SR (wt.%/wt.%).

c Shear rate, γ (s⁻¹).

d Evaporation time, t (s).
Contrast constants which is the value used for coding the level of factors and effects which is the response when factors goes from its low level to its high level, associated with each treatment combinations were determined by using a table of plus and minus signs, as illustrated in Tables 4 and 5. Sums of squares (SS) for effects can be computed from

$$SS_{AB...K} = \frac{1}{n^2} (\text{contrast}_{AB...K})^2$$

where \( n \) is number of replicates and \( k \) the number of factors.
Table 4
Contrast constants and effects for 2\(^4\) factorial design (permeability of membrane)

<table>
<thead>
<tr>
<th>Treatment combinations</th>
<th>Contrast constants and effects of treatment combinations</th>
<th>Total response: pressure-normalized flux, ( \frac{P}{l} ) (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>Signs</td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>(1)</td>
<td>−</td>
</tr>
<tr>
<td>2</td>
<td>a</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>b</td>
<td>−</td>
</tr>
<tr>
<td>4</td>
<td>ab</td>
<td>+</td>
</tr>
<tr>
<td>5</td>
<td>c</td>
<td>−</td>
</tr>
<tr>
<td>6</td>
<td>ac</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>bc</td>
<td>−</td>
</tr>
<tr>
<td>8</td>
<td>abc</td>
<td>+</td>
</tr>
<tr>
<td>9</td>
<td>d</td>
<td>−</td>
</tr>
<tr>
<td>10</td>
<td>ad</td>
<td>+</td>
</tr>
<tr>
<td>11</td>
<td>bd</td>
<td>−</td>
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<tr>
<td>12</td>
<td>abd</td>
<td>+</td>
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<tr>
<td>13</td>
<td>cd</td>
<td>−</td>
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<td>14</td>
<td>acd</td>
<td>+</td>
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<tr>
<td>15</td>
<td>bcd</td>
<td>−</td>
</tr>
<tr>
<td>16</td>
<td>abcd</td>
<td>+</td>
</tr>
</tbody>
</table>

Contrast constants

-59.31 109.36 49.03 93.30 10.18 38.42 0.42 113.56 -11.36 -11.75 -2.89 13.60 14.57 38.78

Effects

-2.47 9.56 -2.04 3.05 0.42 0.60 0.02 -4.70 -0.56 -0.47 -0.12 -0.55 -1.27 -0.61 -1.42
Table 5
Contrast constants and effects for 2^4 factorial design (selectivity of membrane)

<table>
<thead>
<tr>
<th>Treatment combinations</th>
<th>Contrast constants and effects of treatment combinations</th>
<th>Total response selectivity, α (unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>1 (1)</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>2 A</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>3 B</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>4 Ab</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>5 c</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>6 ac</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>7 bc</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>8 abc</td>
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<td>+</td>
</tr>
<tr>
<td>9 d</td>
<td>−</td>
<td>−</td>
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<tr>
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<td>−</td>
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<tr>
<td>11 bd</td>
<td>−</td>
<td>+</td>
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<tr>
<td>12 abd</td>
<td>+</td>
<td>+</td>
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<tr>
<td>13 cd</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>14 acd</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>15 bcd</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>16 abc</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Contrast constants 208.61 −496.13 −61.62 199.48 35.34 80.02 −36.36 167.54 20.35 −51.98 −76.27 −81.09 −19.46 −32.78 72.78

Effects 8.69 −20.67 −2.57 8.31 1.47 3.33 −1.51 6.98 0.85 −2.17 −3.18 −3.38 −0.81 −1.37 3.03
Table 6
ANOVA table (permeability)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares (SS)</th>
<th>Degree freedom (DF)</th>
<th>Mean square (MS)</th>
<th>F-tests value (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>73.28</td>
<td>2.03</td>
</tr>
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<td>B</td>
<td>249.16</td>
<td>1</td>
<td>249.16</td>
<td>6.83</td>
</tr>
<tr>
<td>AB</td>
<td>50.09</td>
<td>1</td>
<td>50.09</td>
<td>1.37</td>
</tr>
<tr>
<td>C</td>
<td>111.92</td>
<td>1</td>
<td>111.92</td>
<td>3.07</td>
</tr>
<tr>
<td>AC</td>
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<td>1</td>
<td>2.15</td>
<td>0.06</td>
</tr>
<tr>
<td>BC</td>
<td>4.20</td>
<td>1</td>
<td>4.20</td>
<td>0.12</td>
</tr>
<tr>
<td>ABC</td>
<td>0.00</td>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>D</td>
<td>265.62</td>
<td>1</td>
<td>265.62</td>
<td>7.28</td>
</tr>
<tr>
<td>AD</td>
<td>3.83</td>
<td>1</td>
<td>3.83</td>
<td>0.10</td>
</tr>
<tr>
<td>BD</td>
<td>2.60</td>
<td>1</td>
<td>2.60</td>
<td>0.07</td>
</tr>
<tr>
<td>ABD</td>
<td>0.17</td>
<td>1</td>
<td>0.17</td>
<td>0.00</td>
</tr>
<tr>
<td>CD</td>
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<td>1</td>
<td>3.66</td>
<td>0.10</td>
</tr>
<tr>
<td>ACD</td>
<td>19.50</td>
<td>1</td>
<td>19.50</td>
<td>0.53</td>
</tr>
<tr>
<td>BCD</td>
<td>4.42</td>
<td>1</td>
<td>4.42</td>
<td>0.12</td>
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<td>ABCD</td>
<td>31.34</td>
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<td>0.86</td>
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<tr>
<td>Error</td>
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<td>32</td>
<td>36.49</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1989.47</td>
<td>47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Every effect as well as their sum of squares has single degree of freedom. Total sum of squares (SS$_{T}$) for all effects with total degree of freedom of $n^2 - 1$ is given according to:

$$SS_T = \sum \sum \sum \sum z^2_{ijkl} = \frac{1}{n^2}$$

where $\sum \sum \sum \sum z^2_{ijkl}$ denotes total sum of squares for all factors at each levels and replicates, while $z_{ijkl}$ is sum of all responses and $n^2$ is total number of data points. Then, sum of squares for error is obtained by

$$SS_E = SS_T - SS_A - SS_B - SS_AB - SS_ABC...K$$

which is assigned as $2^k(n - 1)$ degree of freedom. Note that there must be at least two replicates ($n \geq 2$) in order to determine sum of squares for error if all possible interactions are included in $2^k$ factorial designs. Then, mean squares can be determined by dividing sum of squares for each effect with their degrees of freedom [11,12].

Subsequently, appropriate procedure for analyzing a complete $2^k$ factorial design is based on analysis of variance, which is summarized in ANOVA Tables 6 and 7, to identify significance of effects or interactions of factors on a response. F-test is always constructed by dividing mean squares for each effect by mean square error,

$$F = \frac{MS_{Effect}}{MS_{Error}}$$

Then, calculated values of $F$ are compared with critical values of $F_0$ at 95% confidence limit, which are provided in

Table 7
ANOVA table (selectivity)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares (SS)</th>
<th>Degree freedom (DF)</th>
<th>Mean square (MS)</th>
<th>F-tests value (F)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>906.59</td>
<td>1.50</td>
</tr>
<tr>
<td>B</td>
<td>5128.09</td>
<td>1</td>
<td>5128.09</td>
<td>8.51</td>
</tr>
<tr>
<td>AB</td>
<td>79.09</td>
<td>1</td>
<td>79.09</td>
<td>0.13</td>
</tr>
<tr>
<td>C</td>
<td>828.99</td>
<td>1</td>
<td>828.99</td>
<td>1.38</td>
</tr>
<tr>
<td>AC</td>
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<td>1</td>
<td>26.02</td>
<td>0.04</td>
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<td>BC</td>
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<td>1</td>
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</tr>
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<td>D</td>
<td>584.77</td>
<td>1</td>
<td>584.77</td>
<td>0.97</td>
</tr>
<tr>
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<td>0.01</td>
</tr>
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<td>0.09</td>
</tr>
<tr>
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<td>121.20</td>
<td>0.20</td>
</tr>
<tr>
<td>CD</td>
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<td>136.96</td>
<td>0.23</td>
</tr>
<tr>
<td>ACD</td>
<td>7.00</td>
<td>1</td>
<td>7.00</td>
<td>0.01</td>
</tr>
<tr>
<td>BCD</td>
<td>22.39</td>
<td>1</td>
<td>22.39</td>
<td>0.04</td>
</tr>
<tr>
<td>ABCD</td>
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<td>110.36</td>
<td>0.18</td>
</tr>
<tr>
<td>Error</td>
<td>19288.91</td>
<td>32</td>
<td>602.78</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>27467.09</td>
<td>47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3. Pareto chart for 2^4 factorial design (permeability of membrane).
Fig. 4. Pareto chart for 2^4 factorial design (selectivity of membrane).
statistical tables. A great difference between $F$ and $F_0$ shows that a particular effect is relatively significant. Significances of effects and interactions of factors on a response can also be shown in a Pareto Chart (Figs. 3 and 4), where dominating effects that are likely to be most important and influential can be diagnosed.

Results based on assessment of $2^4$ factorial designs showed a number of trends as highlighted in the following statements:

1. In general, main effects of polymer concentration (A), solvent ratio (B), shear rate (C) and evaporation time (D) were more dominant than their interaction effects with respect to both permeability and selectivity of membrane over a selected range of operating levels.

2. However, importance of various interaction effects could not be neglected. Note that insignificant of interaction effects did not necessarily mean that these particular factors were unimportant; but just implied that interactions among them had little influence on responses.

3. Except for main effect of shear rate (C), which was positive for both permeability and selectivity of membrane, other main effects of polymer concentration (A), solvent ratio (B) and evaporation time (D) showed opposite signs with respect to permeability and selectivity of membrane over operating range of exploration. This phenomenon was consistent with trade-off relationship of permeability–selectivity that an increase in permeability through a single effort was often accompanied with a decrease in selectivity, or vice versa. Hence, optimal performance of membrane can normally be directed to either permeation flux or separation factor, but seldom both. Nevertheless, one cannot simply conclude whether an interaction effect affected performance of resultant membrane positively or negatively without performing statistical analysis because any individual factors that involved in interactions must be considered jointly. Obviously, contribution of each factor must be finely balanced to achieve optimum membrane properties.

4. Main effects of solvent ratio (B) and evaporation time (D) had the strongest influence on permeability of membrane, while main effect of solvent ratio (B) appeared to be a dominant factor responsible for selectivity of membrane. Interestingly, four-way interaction effect of factors (ABCD) was prominent for both permeability and selectivity of membrane as compared to the rest of other interaction effects.
Furthermore, an empirical study on the relationship between responses and input variables over a selected region of interest was carried out using response surface methodology (Figs. 5–12). Second-degree model (in two dimensions) and contour plots were fitted to give a functional relationship of system. Interrelationship among fabrication parameters, including polymer concentration, solvent ratio, evaporation time and shear rate, induced substantial effects on membrane properties and structures. Nevertheless, in some instances, presence of antagonistic and competing effects opposing against each other, would lead to controversy in membrane formation process. Therefore, serious compromises were necessary to achieve defect-free and high selectivity asymmetric gas separation membranes.

Increasing solvent ratio could decrease skin thickness while increase surface porosity, leading to a high value of pressure-normalized flux but a relatively low degree of selectivity (Figs. 5 and 8). An increase of polymer concentration resulted in a denser and thicker skin layer, leading to an improved selectivity and a significant flux loss (Figs. 5 and 8). Therefore, simultaneous adjustment of polymer concentration and solvent ratio would offset limitations brought by both parameters. Hence, a desirable solution viscosity and coagulation rate could be maintained in order to achieve...
defect-free and high performance asymmetric membranes for gas separation. A similar interpretation had been studied and exploited most by Pesek and Koros [9].

Physical events occurring during dry phase inversion may considerably affect membrane formation process. Basically, skin layer of asymmetric membrane is generated from a dry phase-separated region during solvent evaporation [9,13]. Therefore, structure and properties of skin layer were closely related to solvent ratio and evaporation time. As shown in Figs. 6 and 11, decreasing solvent ratio or increasing evaporation time would cause an increase in amount of evaporated solvent from membrane and thus enlarged dry phase-separated region with higher polymer concentration. As a result, a decrease in surface porosity and an increase in skin thickness would form a low flux yet selective asymmetric membrane; or vice versa. However, demixing and precipitation of dry phase-separated structures also depended on polymer concentration.

Casting of a shear-thinning and viscoelastic polymer solution induced molecular orientation in skin layer,
which could heighten asymmetric membrane selectivity [14–16,19,23]. Hence, fluid properties (dope rheology) as well as casting conditions became imperative in controlling degree of molecular orientation and enhancement of selectivity in asymmetric membrane. Dopes with higher polymer concentration exhibited more shear-thinning behavior and slow relaxation process than those with lower polymer concentration [17]. Nascent skin layer cast from the former solution could be instantaneously precipitated during dry phase inversion to yield asymmetric membrane with highly oriented structures as compared to those cast from the latter solution. Furthermore, aggressiveness of forced convection conditions caused by lower solvent ratio or longer evaporation time would lead to a smooth and efficient preprecipitation of oriented nascent skin. Therefore, shear-induced molecular orientation was locked into skin layer before relaxation could occur [18]. As a result, an increase of selectivity was corresponding to simultaneously increasing shear rate, polymer concentration and evaporation time, or decreasing solvent ratio, as depicted in Figs. 9, 10 and 12.

In addition, the pressure-normalized flux was also found to increase with increasing shear rate. This may relate to
an increase in molecular orientation at higher shear. Furthermore, an increase in molecular orientation induced at the skin layer resulted in higher free volume in the skin layer and this resulted in this phenomenon of increasing pressure-normalized flux with increase shear rate [19,20]. As a result, the combined effects of phase inversion and rheological factors had successfully developed defect-free and high selectivity asymmetric membranes for gas separation. Experimental data of this study reflected a high degree of reproducibility (93.75%). An essentially defect-free skin layer with effective thickness in the range of 6590–11330 Å was prepared for asymmetric polysulfone membranes produced in this study; some of them even surpassed the generally recognized intrinsic selectivity (Tables 1–3).

Selectivity of asymmetric membrane, preferably above the intrinsic value for corresponding dense film, was attributed to a more oriented molecular packing density in skin layer of asymmetric membrane than in dense film [21,22]. Chen et al. employed pore flow model in an attempt to explain selectivity levels beyond those described by solution diffusion mechanism [23]. Chen postulated that when pore size was around kinetic diameter of the larger penetrates, that species would scarcely be accommodated in pore. Friction against movement of that species significantly caused an extremely high surface viscosity and in turn minimized transport of the larger penetrates. Under these circumstances, membrane became highly selective towards the smaller penetrates. Therefore, enhancement of membrane selectivity beyond the intrinsic value was possible when pore flow prevailed. Robeson had also addressed this phenomenon, where super-selective membrane could even approach Robeson upper bound region [24].

4. Conclusion

The results presented here show that defect-free asymmetric membranes can be prepared by optimizing dope formulations and preparation conditions in membrane formation. Polymer concentration and solvent ratio (ratio of less volatile solvent to more volatile solvent) of casting solution, forced-convective evaporation time and casting shear rate were identified as dominant fabrication parameters in controlling skin thickness and skin integrity, and thus substantially influenced separation properties of asymmetric membrane. According to analysis of 2k factorial designs, main effects of these fabrication parameters were more dominant than their interaction effects with respect to both permeability and selectivity of membrane over a selected range of operating conditions. The optimized parameters obtained in this study are: polymer concentration: 22–26%, solvent ratio: 0.54–1.00 wt %/wt %, shear rate: 254–381 s−1, and evaporation time: 15–18 s. Main effects of solvent ratio and evaporation time had the strongest influence on permeability of membrane, while main effect of solvent ratio appeared to be a dominant factor responsible for selectivity of membrane. As a conclusion, correlation of rheological aspects with primary phase inversion conditions had successfully developed defect-free asymmetric membranes for gas separation process. Essentially defect-free skin layers with effective thickness in the range of 6590–11330 Å were prepared for asymmetric polysulfone membranes. Selectivities achieved by these membranes were even surpassed the generally recognized intrinsic selectivity for corresponding dense films.

References


