INTRODUCTION

Application of membranes in various fields of gas and liquid separation has got strong attention, recently [1,2]. Selectivity and permeability are two major factors which affect the successful utilization of membranes in these fields. These two parameters are defined as [3]:

\[ P = \frac{N}{\Delta P/l} \]  

\[ \alpha_{O_2} = \frac{P_{N_2}}{P_{O_2}} \]  

Correlation of Nitrogen Enriching Polymeric Membranes Performance Developed through Various Methods with their Morphological Structure Revealed via SEM

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ABSTRACT

Various phase inversion methods were applied to fabricate oxygen selective membranes out of polymeric materials such as polycarbonate (PC), ethylene vinyl acetate (EVA), and polyvinylchloride (PVC) that were dissolved in solvents like chloroform, tetrahydrofuran (THF), cyclohexanone, and dimethylformamide (DMF). Developed membranes were investigated using their permeability data and scanning electron microscopy (SEM) images. The more concentrated was the solution, the more homogeneous overall structure was obtained with smaller pores and more decreased gas diffusivity. Application of DMF as the solvent was found to be incorporated in the formation of larger porosity in the membranes. Less crystalline and hence more permeable membranes were made using volatile solvents such as THF. In casting 10% PVC solution in THF via the wet phase inversion method, micro-voids developed in the membrane and a non-homogeneous finger-type structure with porous skin was formed. Films with 28% vinyl acetate prepared by thermal phase inversion had a semi porous skin and a dense structure in the sub-layer. Results showed that EVA containing 28% vinyl acetate demonstrated the most appropriate permeability and selectivity for separation of oxygen-nitrogen gas mixtures.

Key Words:
membrane; polymer; gas separation; phase inversion.

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where, \( N \), \( \Delta P \), \( I \), \( P \), and \( \alpha \) are the flow rate of the passing gas through membrane in \( \text{cm}^3/(\text{STP})/\text{s.cm}^2 \), the pressure difference between the two side of membrane in \( \text{cmHg} \), the membrane thickness in \( \text{cm} \), the permeability coefficient of the considering gas in \( \text{cm}^3/(\text{STP}).\text{cm}/\text{s}.\text{cm}^2.\text{cmHg} \), and the ideal selectivity factor for two gases, respectively.

Prior to 1980 most manufactured membranes for gas separation were relatively thick and homogeneous dense films from polymeric materials such as thermoplastic derivatives of cellulose, polyethylene terephthalate and silicone rubber. Such thick and dense films introduced great mass transfer resistance leading to low flux and hence low separation efficiencies.

To overcome mass transfer problem, multi-layer membranes such as integrally skinned and substrate supported membranes have been developed till now [2]. In these membranes, a dense thin layer of polymeric material with high selectivity and low permeability lies on top of another layer(s) of low selectivity and high permeability which normally provides mechanical support. In integrally skinned membrane, the thin layer was essentially a structured skin developed on a body of thick polymeric film with a different morphological structure and density. In the composite multi-layer membranes however, the thin layer is supported by a highly porous substrate which may have been prepared in a totally different process [4].

Among the gas separation processes to be materialized by membranes, much attention has been devoted to nitrogen mixture purification in the past [3-15]. As an example, permeability and selectivity of the mixtures of \( \text{CO}_2 \) and \( \text{N}_2 \) through poly dimethyl siloxane (PDMS) membranes have been studied by Yeom et al. [5]

Ward et al. [6] have also prepared different membranes of block copolymers of diethyl siloxane and polycarbonate and found that prepared membranes from these copolymers could act as proper separators for \( \text{O}_2 \) and \( \text{N}_2 \) in gas mixtures. Huang and Ruan [7] prepared different membranes from polyurethane based on hydroxyl terminated poly butadiene and found that membranes which were prepared from cross-linked urethane showed better permeability and selectivity for oxygen gas than non-cross-linked polymers.

Membranes of polycarbonate and its derivatives have been studied for gas separation by different researchers [2,11,12].

In the majority of the research works reported in the literature, low or non-crystalline polymers have been used to develop proper membranes. This is primarily due to the fact that despite their enhanced mechanical properties, crystalline polymeric structures are not generally permeable and introduce high mass transfer resistances [2].

In this study, attention is paid to fabrication of membranes appropriate for oxygen/nitrogen separations. As low or non-crystalline polymers, commercially available polymeric materials such as polycarbonate (PC), ethylene vinyl acetate (EVA) with various vinyl acetate content and poly vinyl chloride (PVC) were used to develop proper membranes. Efficiencies of the developed membranes for oxygen/nitrogen separation were tested experimentally. Finally scanning electron microscopy (SEM) images were used to correlate membrane behaviour with its structural morphology.

### EXPERIMENTAL

#### Materials and Methods

Reagent grade chloroform, tetrahydrofuran, cyclohexane, and dimethyl formamide were obtained from Merck. Distilled water with 10 microsiemens conductivity was used as precipitant.

Polycarbonate (PC3022U, Triexfi), polyvinyl chloride (K70, Bandar Imam Co.), ethylene vinyl acetate with 28% vinyl acetate content (EVA101, Asia Polymer Corp.) and ethylene vinyl acetate with 18% vinyl acetate content (Exxon Chemicals) were used as polymeric materials. 99.9% Pure nitrogen and oxygen (Roham Gas Corp., Iran) were used in permeability measurements. The gas permeability Measurements were carried out according to ASTM D1434.

Solutions of polymers in solvents were prepared at controlled temperature under stirring. Different methods including dry, dry-wet and thermal phase inversion techniques were then used to prepare membranes from their solutions. 650 \( \mu \text{m} \) deep castings were made by pouring the solution into glass petri dish as well as forming the film via Doctor’s Blade on to glass mould [16]. In dry phase inversion, cast films were left to dry in room temperature for about 24 h and then transferred
to a vacuum oven to remove the remaining solvent. In dry-wet phase inversion however, samples were transferred to a distilled water bath after a primary short evaporation. In thermal dry phase inversion process, hot polymer solution was spread on glass surface in room temperature leading to a gel structure. In all methods, separated film was mounted on filter paper and dried at room temperature to develop a multi-layer membrane. Throughout the study, 3-4 films were made at each condition and reported data were the average of measurements made for them. Reproducibility and repeatability of the data were checked randomly in some occasions and a maximum variability of 20% demonstrated a fair level of reproducibility and repeatability in the experimentation. Detailed information of the fabricated membranes and their fabrication methods have appeared in Table 1.

For SEM micrography (Cambridge SEM instrument, Model S-360), samples were broken in liquid nitrogen and their surface were covered with a gold film with a thickness of 40 angstrom.

**RESULTS AND DISCUSSION**

Dry inversion method was used to fabricate membranes from solutions of 4, 5, and 6 % of PC in chloroform. Calculated data of permeability and selectivity coefficients of these films are presented in Table 2. Data presented for membranes cast in Petri dish show that by increasing concentration of polymer in the solution, gas permeability in the membrane decreases. This may be due to the inverse effect of concentration on the porosity. Porosity in turn may affect the rate of solvent evaporation from the film. Having said that, with a more concentrated solution, one may obtain a more homoge-

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Concentration (%)</th>
<th>Polymer</th>
<th>Solvent</th>
<th>Casting in/on</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-P-6</td>
<td>6</td>
<td>PC</td>
<td>Chloroform</td>
<td>Petri dish</td>
</tr>
<tr>
<td>PC-P-5</td>
<td>5</td>
<td>PC</td>
<td>Chloroform</td>
<td>Glass</td>
</tr>
<tr>
<td>PC-P-4</td>
<td>4</td>
<td>PC</td>
<td>Chloroform</td>
<td>Glass</td>
</tr>
<tr>
<td>PC-g-6</td>
<td>6</td>
<td>PC</td>
<td>Chloroform</td>
<td>Glass</td>
</tr>
<tr>
<td>PC-g-4</td>
<td>4</td>
<td>PC</td>
<td>Chloroform</td>
<td>Glass</td>
</tr>
<tr>
<td>PVC-C-6</td>
<td>6</td>
<td>PVC</td>
<td>Cyclohexanone</td>
<td>Glass</td>
</tr>
<tr>
<td>PVC-C-4</td>
<td>4</td>
<td>PVC</td>
<td>Cyclohexanone</td>
<td>Glass</td>
</tr>
<tr>
<td>PVC-D-6</td>
<td>6</td>
<td>PVC</td>
<td>DMF</td>
<td>Glass</td>
</tr>
<tr>
<td>PVC-D-4</td>
<td>4</td>
<td>PVC</td>
<td>DMF</td>
<td>Glass</td>
</tr>
<tr>
<td>PVC-T-10</td>
<td>10</td>
<td>PVC</td>
<td>THF</td>
<td>Glass</td>
</tr>
<tr>
<td>PVC-T-7</td>
<td>7</td>
<td>PVC</td>
<td>THF</td>
<td>Glass</td>
</tr>
<tr>
<td>PVC-T-4</td>
<td>4</td>
<td>PVC</td>
<td>THF</td>
<td>Glass</td>
</tr>
<tr>
<td>EVA-28-4</td>
<td>4</td>
<td>EVA (28%)</td>
<td>Hot chloroform</td>
<td>Glass</td>
</tr>
<tr>
<td>EVA-18-7</td>
<td>7</td>
<td>EVA (18%)</td>
<td>Hot chloroform</td>
<td>Glass</td>
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<tr>
<td>EVA-18-5</td>
<td>5</td>
<td>EVA (18%)</td>
<td>Hot chloroform</td>
<td>Glass</td>
</tr>
<tr>
<td>EVA-18-4</td>
<td>4</td>
<td>EVA (18%)</td>
<td>Hot chloroform</td>
<td>Glass</td>
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<tr>
<td>EVA-18-2</td>
<td>2</td>
<td>EVA (18%)</td>
<td>Hot chloroform</td>
<td>Glass</td>
</tr>
</tbody>
</table>
neous overall structure with smaller pores. In contrast, diluted solutions would develop into more heterogeneous membranes with larger pore sizes.

Transversal SEM photographs of membranes produced by 4 and 6% solutions are shown in Figures 1 and 2, respectively. These figures show that the membranes have asymmetric graded density with maximum density in their skin layer. In accordance with the above hypothesis, it may also be observed that with increasing concentration of polymer in casting solution, more homogeneous membrane is developed.

These observations explain why membranes developed from 4% solutions demonstrate a relatively similar selectivity but much greater flux when were compared with the membranes developed from 6% solution.

It is interesting to note that discussions made about the effect of solution concentrations on the membrane permeability fails in the case of glass moulding using the Doctor’s Blade instrument. The relevant results in Table 2 show that in this case, the more concentrated solutions have been led to more permeable membranes. In the analysis of data collected in this case, one should be careful about the effect of Doctor’s Blade on the characteristic features of the produced membrane. This may be explained by noting to the influence of a moving object in a fluid. Due to the no-slip-condition principle in fluid mechanics, a solid moving object in a fluid develops a velocity gradient in the fluid cross-section such that fluid is differentiated into layers (lamina) gliding on top of each other. Therefore, a field of shear stress is developed that could stretch polymer chains along the flow. Consequently, Doctor’s Blade movement results in partial alignment and/or stretching of the polymer chains. This in turn may result in a more ordered structure affecting the d-spacing of the chains.

Despite the fact that polymers have flexibility in the solution, rapid solvent evaporation may hinder the structural revamping of the chains specially at the solution/air interface. If this argument is true, the operator/blade performance will be a subjective extra parameter affecting the morphology and hence the membrane permeability in the glass mould casting protocol. It is obvious that a non-systematic set of data could be obtained due to the more degrees of freedom in this case and a method should be developed to

![Figure 1. Transversal SEM of the membrane manufactured from 6% PC in chloroform in petri dish.](image1)

![Figure 2. Transversal SEM of the membrane manufactured from 4% PC in chloroform in petri dish.](image2)

Table 2. Permeability and separation properties measured at 5 bar transmembrane pressure.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>$P_{O_2}$ (barrer)$^a$</th>
<th>$P_{N_2}$ (barrer)</th>
<th>$\alpha_{O_2}^{N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-P-6</td>
<td>0.89</td>
<td>0.329</td>
<td>2.71</td>
</tr>
<tr>
<td>PC-P-5</td>
<td>4.8</td>
<td>3.7</td>
<td>1.30</td>
</tr>
<tr>
<td>PC-P-4</td>
<td>6.92</td>
<td>3.99</td>
<td>1.73</td>
</tr>
<tr>
<td>PC-g-6</td>
<td>2.6</td>
<td>0.313</td>
<td>8.31</td>
</tr>
<tr>
<td>PC-g-4</td>
<td>1.12</td>
<td>0.141</td>
<td>7.94</td>
</tr>
<tr>
<td>PVC-C-6</td>
<td>0.258</td>
<td>0.0491</td>
<td>5.25</td>
</tr>
<tr>
<td>PVC-C-4</td>
<td>-</td>
<td>0.133</td>
<td>-</td>
</tr>
<tr>
<td>PVC-T-4</td>
<td>2.073</td>
<td>1.11</td>
<td>1.87</td>
</tr>
<tr>
<td>EVA-28-4</td>
<td>6.2</td>
<td>2.2</td>
<td>2.82</td>
</tr>
<tr>
<td>EVA-18-7</td>
<td>-</td>
<td>3.33</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ $1$ barrer $= 10^{-10}$ cm$^3$(STP).cm/s.cm$^2$.cmHg
standardize the procedure.

Polymeric membranes manufactured from 4% solutions of PVC in DMF showed high diffusivity for both gases apparently because of high porosity developed in these membranes. This is consistent with the available experience for many cases that DMF has been used as an agent for producing porosity in membrane production [17]. As illustrated in Figure 3, the SEM verifies the highly porous structure of these films. In accordance with this observation, experimental measurements show very high permeability and low selectivity of these films which cancels out their eligibility to be applied in gas separation.

Table 2 may be used to make a comparison between selectivity and permeability factors of membranes prepared from 4% solutions of PVC in cyclohexanone and THF via dry phase inversion method. Comparison of these two films shows that the THF produced membrane that possesses a greater nitrogen permeability. One possible explanation as to this observation may be based on the differences between the volatility of these solvents. The normal boiling points of THF and cyclohexanone are 65.9 and 155.4°C, respectively. Consequently, it is expected that upon drying volatile solvent leaves the cast membrane much quicker. In the general knowledge regarding crystallization, it is believed that at increased rates of crystallization, less organized smaller crystals are developed. Therefore, the more volatile THF was expected to evaporate more quickly and we noticed that the applied polymers were semi crystalline, which this could lead to a less crystalline and hence more permeable membrane.

Other explanations to describe the above observation may be given by focusing on the events at the membrane surface as follows:

- A comparison between molecular relaxation and rate of evaporation suggests that in volatile solvents, quick evaporation could lead to microvoids at the membrane surface resulting in increased permeability.

- Quick evaporation from the surface results in a dry skin layer. The stress field developed because of this phenomenon could lead to the evolution of microcracks at the surface and hence increased permeability.

Referring to Figures 4 and 5, it may be realized that in the case of cyclohexanone, a more homogeneous dense structure prevails across the membrane. While, in the case of THF, a less dense structure has been formed in the membrane body. Moreover, some craze type patterns may be observed in the THF system. Therefore the SEM micrographs verify the speculations made as to the effect of solvent volatility on the mem-

![Figure 3. Transversal SEM of the membrane manufactured from 4% PVC in DMF on glass.](image)

![Figure 4. Transversal SEM the membrane manufactured from 4% PVC in cyclohexanone on surface of glass.](image)

![Figure 5. Transversal SEM of the membrane manufactured from 4% PVC in THF on glass.](image)
brane permeability.

Due to obvious reasons, in wet phase inversion, viscosity of solution must be so high that withstand various stresses exerted on the cast film upon immersion. This requirement was fulfilled in casting 10% PVC solution in THF. In order to avoid the undesired quick interaction between the solvent and non-solvent system, after casting, samples were maintaining for 3 minutes in ambient conditions and then transferred into water bath. SEM of whole cross section of manufactured samples are presented in Figure 6 and its skin face SEM is shown in Figure 7. It may be understood that these membranes have a non-homogeneous finger-type structure with porous skin. Existence of micro-void in these samples can be clearly observed. These micro-voids may be probably due to high solubility of THF in water and a high concentration profile between the solution and the surrounding water bath in the two phases. This could cause a high potential for diffusion of water in solidifying solution [2]. It is obvious that this morphology is not suitable for gas separation and hence permeability and selectivity tests were not run for them. Instead, these films may be suitable for micro and/or ultrafiltration.

Permeability coefficients and selectivity factors calculated for oxygen and nitrogen in EVA films with 28% vinyl acetate prepared by thermal phase inversion are also presented in Table 2. Results show that these films have the same selectivity but 30 to 40 % more permeable as compared with reported EVA films with 45% vinyl acetate prepared via milling process [18].

Morphology of the developed EVA film is presented in Figure 8. This SEM micrograph provides some information as to development of the skin layer and a dense structure in the sub-layer similar to latex. The skin structure apparently develops at the air/solution interface which is formed at later stages and a much lower temperature. This structure does not develop at the glass/solution interface. The structure developed at the air/solution interface may be investigated by X-ray diffraction (XRD) test later on.

Films were also fabricated out of hot chloroform with various contents of EVA with 18% of vinyl acetate. Due to high shrinkage however, permeability tests were not possible in most cases. In the best condition, a 7% solution produced film with measurable permeability. Comparing of this measurement with that obtained from 28% vinyl acetate containing EVA shows that greater vinyl acetate content leads to smaller

Figure 6. Total transversal SEM of the membrane manufactured from 10% PVC in THF on glass.

Figure 7. Transversal skin SEM of the membrane manufactured from 10% PVC in THF on glass.

Figure 8. Transversal SEM of the membrane manufactured from 4% EVA in chloroform on glass.
nitrogen permeability. Noticing the active acetate group in vinyl acetate, a stronger interaction may be imagined between the polymeric chains when a larger content of this residue is present in the system. Aside from this, it should be noted that in the 18% vinyl acetate case, a larger non-polar ethylene fraction prevails. Considering the solution-diffusion mechanism governing the transfer of non-polar nitrogen through this membrane, a stronger affinity and hence permeability is expected in this case. Therefore, the trend observed in this study does not seem to be peculiar at all.

CONCLUSION

Polymer concentration in the solution was found to have a direct effect on the characteristic features of the cast membranes. In general, by increasing concentration of polymer in the solution, gas diffusivity in the membrane decreased apparently due to the inverse effect of concentration on the porosity and consequently on the rate of solvent evaporation from the film. By a more concentrated solution, a more homogeneous overall structure with smaller pores was obtained.

In accordance with the available experience, application of DMF as the solvent was found to incorporate a large porosity in the developed membranes. Less crystalline and hence more permeable membranes were made using volatile solvents such as THF and in some occasions craze type patterns might be developed in these systems.

In casting 10% PVC solution in THF via the wet phase inversion method, a non-homogeneous finger-type structure with porous skin was developed. Moreover, the development of micro voids probably due to high solubility of THF in water and a high concentration profile between the solution and the surrounding water bath in the two phases was verified via SEM. The obtained membrane was not found to be suitable for gas separation but probably suitable for micro and/or ultrafiltration.

Permeability coefficients and selectivity factors for EVA films with 28% vinyl acetate prepared by thermal phase inversion showed that these films have the same selectivity but 30 to 40% more permeability compared with reported EVA films with 45% vinyl acetate prepared by milling process. The SEM micrographs revealed a semi porous skin and a dense structure in the sub-layer. The skin structure apparently developed at the interface of solution and the glass surface which was at a much lower temperature.

Films fabricated out of hot chloroform with various contents of EVA with 18% of vinyl acetate showed strong shrinkage tendency. A stronger interaction may be imagined between the polymeric chains when a larger content of this residue and hence greater vinyl acetate content was shown to lead to smaller nitrogen permeability in the produced membranes.

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