Effects of Feed Pressures on Permeability of Polycarbonate Membranes Prepared by Dry-Wet Phase Inversion Method

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ABSTRACT

Polycarbonate membranes were fabricated from casting solution using Dichloromethane and N-methyl-2-pyrrolidone solvents. The dope solution viscosities were determined to evaluate the critical polymer concentration required for membrane gas separation applications. Investigation on coagulation values were conducted to estimate the coagulant ratio required for the membrane fabrication. Among the coagulants used, water is found to be strong coagulant for the given polymer-solvent pair. For the dry-wet phase inversion method of membrane fabrication, the membrane casted from Polycarbonate-N-methyl-2-pyrrolidone solution led to asymmetric porous membranes, whereas the membranes casted form polycarbonate-dichloromethane solution resulted to a dense membrane. The performance of the membranes were tested for the permeability of carbon dioxide, methane and nitrogen gases at 24 oC with varying feed pressures 1-24 bars. The average CO2/CH4 ideal selectivity of the membranes tested were found to be 18.75 and 19.82 for both Polycarbonate membranes prepared from Dichloromethane and N-methyl-2-pyrrolidone solvents respectively, whereas the CO2/N2 selectivity were obtained to be 22.94 and 17.80. However, these selectivity decreases with the increase of the feed pressures.

INTRODUCTION

Polycarbonate (PC) is highly engineered thermoplastic polymers with unique properties. They are generally characterized by outstanding mechanical, optical and thermal properties and have a wide range of applications (L. Baumann et al., 2013). PC is also known for their dimensional stability. A mechanical property of PC is also higher than the other polymers such as the PP, PVC, PS(Shih-Hsiung 1997). PC is also suggested as one of the suitable materials for membrane preparation(Kim and Lee 2004).

Most PC membrane was prepared by either dry or wet phase inversion, which resulted to different types of membrane and morphology, the effects of solvent on morphology and performance of PC membranes were also reported.

The phase inversion or separation process is one of the common techniques used for the preparation of asymmetric membranes. Generally, phase inversion takes place if the stability of the polymer solution is altered. This consequently minimizes the free energy of the mixture, which leads the solution to separate in to two phases. There are three techniques commonly utilized to bring change in the stability of the polymer solution. These are accomplished either by temperature variation, solvent evaporation, or by mass exchange with non-solvent/coagulant bath(Marco Di, Ronaldo et al. 2002). The mass exchange with non-solvent bath is regarded as non-solvent induced phase separation, which is most popular technique used to prepare asymmetric membrane. A combined technique of solvent evaporation (dry phase) and mass exchange with coagulant bath (wet phase) is known as dry-wet phase inversion technique(Sennur 2006).

The present work was undertaken to study the effects of varying feed pressure on the performance of the membrane prepared by dry-wet phase inversion, and to determine their ideal selectivity.
Permeation Theory:

In gas permeation, the membrane material is responsible for the separation as it determines the permeability and selectivity to particular gas (Hacarlioglu, Toppare et al. 2003). The flux (mol m\(^{-2}\) s\(^{-1}\)) of gas transport through the membranes can be obtained using Fick’s first law (P. Luis et al. 2012),

\[
J_i = \frac{P_i}{l}(p_{x_i} - p_{y_i}) = \frac{D_i}{l}(c_{x_i} - c_{y_i}) \quad (1)
\]

where \(P_i\) is the permeability of gas component \(i\), \(l\) is the membrane thickness in cm, \(p_x\) and \(p_y\) are pressures on the feed and permeate side, \(x_i\) and \(y_i\) are the fractions of component \(i\) in the feed and permeate stream respectively, \(D_i\) is the diffusivity coefficient and \(c_{x_i}\) and \(c_{y_i}\) are the concentration of component \(i\) on the feed and permeate stream, respectively.

In membrane gas separation applications, permeance and permeability are commonly used as measures of gas transport rate. The permeance, \(Q\) (mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)) is defined as the flux per unit pressure difference between the two sides of the membrane. If the thickness of the membranes is known, the permeability coefficient, \(P\) (mol m\(^{-1}\) s\(^{-1}\) Pa\(^{-1}\)) is obtained by normalizing the permeance by the unit thickness of the separation layer. In short, the permeance and the permeability can also be determined as:

\[
Q = \frac{Q_{STP}}{A_l \Delta P} \quad (2)
\]

where \(Q\) is the permeance of the membrane in (cm\(^3\) (STP) cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\)), \(A_l\) is cross-sectional area of the membrane (cm\(^2\)), \(\Delta P\) is the pressure difference between two sides (cmHg) and \(Q_{STP}\) the volumetric flow rate (cm\(^3\) (STP)/s). And the permeability \(P\) of the membrane at given thickness is given as:

\[
P = Q_{STP}A_l \Delta P \quad (3)
\]

If solution-diffusion is considered as the means of transport of the gases through the membrane, the permeability of a single gas \((P_i)\) can be described as the product of its solubility \((S_i)\) and diffusivity \((D_i)\) through the material (L. Zhao et al. 2008).

\[
P_i = S_i D_i \quad (4)
\]

The ideal permselectivity \((\alpha_{ij})\) is the ratio of the permeability of the more permeable gas \((i)\) to that of the less permeable gas \((j)\). Therefore, the ideal selectivity is can be calculated as (Matteucci, Yampolskii et al. 2006).

\[
\alpha_{i,j} = \frac{P_i}{P_j} = \frac{S_i D_j}{S_j D_i} \quad (5)
\]

Therefore, using the above equations, the performance of the membrane can be evaluated for the application of gas separation (Peter and Neil 2010).

Experimental:

Materials:

Bisphenol A Polycarbonate (PC) [M.wt 64 kg/mol, density 1.2gm/cm\(^3\)] was supplied by LG-Dow Polycarbonate Ltd. Solvents such as Dichloromethane (DCM), N-Methyl-2-pyrrolidone (NMP), and coagulants (non-solvents) such Methanol (MtOH), Ethanol (EtOH), 2-Propanol (PrOH), and 2-Butanol (BtOH) were purchased from Merck. Co. and used as received, and also double distilled water was used as coagulant.

Dope solution preparation:

PC pellets were first dried in an oven at 90 °C for 24 hrs to remove absorbed moisture. The dope solutions were prepared on weight basis with concentration of 3, 7, 12, 15, 18, 21 wt% PC in DCM; 3, 6, 9, 12, 15 and 18 wt% PC in NMP; in a sealed glass bottles. The solutions were stirred for 24 hrs with a hot plate magnetic stirrer to achieve homogeneous polymer solutions. These concentrations were prepared to determine their respective viscosities. Solutions of 16, 17, 18, and 19 wt% PC in DCM and NMP were prepared separately for membrane casting.

Viscosity Determination:

Viscosity of the dope solution prepared has a crucial role in determining the appropriate composition of the dope solution required for membrane casting. The appropriate composition of membrane casting solution can be obtained after determination of critical composition of polymer concentration with respect to their viscosities.
The viscosity of polymer solutions was determined by the Cannon-Ubbelohde viscometer. The procedure was adopted from ASTM D 445 and D 446.

2.4. Coagulation value determination:

The coagulation value is defined as the amount of coagulant in grams required to make 100 g polymer solution containing 2 g polymer become turbid (Dongliang, Li et al. 1993). Coagulant value corresponds to the coagulant tolerance of casting solution and hence faster liquid-liquid demixing rate to occur during the membrane making process. In other words, higher coagulation value shows the larger coagulant tolerance of casting solution which results delayed demixing.

The determination of coagulation value was performed by the titration of polymer solution prepared at the ratio of 1 g PC to 49 g solvent against the non-solvents such as double distilled water, MtOH, EtOH, PrOH and BiOH. The solvents used were DCM and NMP.

The polymer solutions prepared were sealed and stirred with magnetic stirrer over night, until the complete dissolution of PC with transparent homogenous solution was achieved. The solution was titrated at sealed condition with an air-tight rubber septum stopper by adjustable volume a micropipette, until the solution visually becomes turbid or cloudy. Thus, the quantity of the coagulant added was calculated from the coagulant volume added and its respective density. According to the definition, the coagulant value of the polymer solution for a given coagulant at a given temperature can be reported as the quantity in grams of coagulant and polymer solution used.

2.5. Membrane casting:

The procedure of membrane casting using the dry-wet phase inversion techniques is illustrated in the schematic diagram Figure 2. Dope solution was prepared as follows; desired quantity of a dried PC (at 90 °C in an oven) was dissolved separately in DCM and NMP, in sealed bottles with magnetic stirrer for 24 hrs to assure a complete dissolution. The dope solutions were put in ultrasonic vibrator (sonicator) for 3 hrs to remove any bubbles created during stirring step.

The Dope solution was then casted using doctor's blade (with a predetermined gap of 300 μm) on to a glass plate. A nitrogen gas was blown over the casted solution for the period of 10-15 sec with an immediate immersion into coagulation bath composed of water and EtOH at proportion of 3:1. The casted membranes were kept in coagulation bath for 12 hrs to ensure a sufficient mass exchange between the solvent and non-solvent. Finally, the membranes are dried in vacuum oven to remove any residual solvent and non-solvent.

2.6. Characterization and performance test:

The PC membranes were characterized with the VP-FESEM (Model SUPRA 55VPCarl Zeiss AG, Germany) for the study of the surface morphology, FTIR (Model Spectrum One/BX, Perkin Elmer Inc.) to study the effect of varying polymer composition and the performance tests were conducted in a four channel permeation cell shown in the Figure 3.

For the FESEM analysis, only morphology and mapping of the samples were conducted on the PC membrane of average thickness of 145 μm. Images of high magnification and ultra high resolution can be produced at different sample points. For the colourless samples, i.e., the membrane prepared from DCM solvent, was treated with liquid nitrogen and then SEM images were taken for both surface and cross-section.

FT-IR were also used as characterization tool, which uses infrared portion of the electromagnetic spectrum to characterize the material as molecules absorb specific IR frequencies that exactly match the frequency of the
chemical bonds present in the molecular structure. The data processing technique (Fourier Transform) converts the raw data into FTIR spectrum.

Performance tests were carried out with four channel permeation cell membrane gas separation system designed for flat plate membrane module. The schematic diagram of the system is presented in Figure 3. The membrane material was cut into 6 cm diameter and assembled with the permeation cells. For the given gas pressure, the flow rate and the pressures of permeate were recorded. Based on the data obtained, the permeability was calculated using Equation 3, and the ideal selectivity (permselectivity) can be determined using Equation 5.

![Figure 3: Schematic diagram for permeation cell set-up](image)

**RESULTS AND DISCUSSION**

Viscosities of the PC solutions were determined using Cannon-Ubbelohde viscometer, all measurements were carried in a water bath maintained at 24 °C, and the efflux time was recorded and multiplied by the given viscometer constant which gives to the viscosity of the polymer solution in mPa.s. The viscosities of the solutions are presented in Figure 4. One can see that at particular polymer concentration, the viscosity of solution composed of NMP solvent is higher than the one of DCM solvent. A tangent line can be drawn at the highest value of the viscosity and extended to the x-axis of the plot to determine the critical polymer concentration required for membrane gas separation application.

![Figure 4: Viscosities of PC solutions prepared from two different solvents](image)

![Figure 5: Coagulation value for PC, Solvent, and Water](image)
For this study, the critical polymer composition/concentrations are at the ranges of 16 and 18 wt%, thus these compositions are studied further to investigate their suitability for membrane gas separation applications.

The coagulation value determined for PC-solvent-water, as shown the ternary diagram, the PC-NMP have higher coagulation value, as compared to PC-DCM pairs when titrated using a double distilled water. This indicates that there is a delayed liquid-liquid demixing rate when the casted solution is put in a coagulation bath(Ywu-Jang, Jung-Tsai et al. 2013). This may lead to very porous and asymmetric membranes. The faster the liquid-liquid demixing rate, lower is the coagulation value, and hence the resulting membrane may lead to dense or semi porous membranes depending to how fast the demixing might takes place.

Generally, alcohols are also regarded as coagulants/non-solvents. They can be utilized in the coagulation bath according their coagulant power, or they can be mixed with distilled water at an appropriate coagulation ratio. Therefore, the coagulation value of alcohols for PC-DCM and PC-NMP pairs were also determined, and presented in Figure 6 and 7 respectively.

![Fig.6: Coagulation value for PC, DCM and Coagulant.](image1)

![Fig.7: Coagulation value for PC, NMP and Coagulant.](image2)

From Figure 6, for PC-DCM pairs, the coagulation value of EtOH is lower as compared to other alcohols studied. Thus, EtOH-DCM demixes at faster rate, or in the other words, faster will be the phase inversion, or transformation to solid membrane.

For the PC-NMP pair, BtOH has the lowest coagulation value, which may serve as the facilitator to a rapid phase inversion, once if the casting solution composed of PC and NMP.

Therefore, one can conclude that coagulation value is a characteristic to particular polymer-solvent pairs. The concept of coagulation value can be exploited in either ways; to slow down quick phase inversion, in an attempt to control porosity of membrane, or shorten the time taken for complete phase inversion; however, the applications of the either cases may vary.

The SEM images for the membranes analyzed show that the membrane casted using DCM solvents resulted in a dense membranes, this is because of the solvent evaporation step involved in the procedure, where nitrogen gas was blown for fraction of 10-15 sec, which obviously removed most of volatile solvents, before allowed to interchange with the non-solvents in coagulation bath. These membranes are shown in Figure 8 and 9 for both surface and cross-sectional views.
Moreover, the increase in concentration of PC in the membrane formed was more dense than the lower concentration, it can be concluded that from the cross-section view of SEM images, these membranes are good candidates for the gas separation application.

For those membranes casted from solution of PC and NMP, with 16 and 18 wt% PC in NMP, are shown in Figure 10 and 11 respectively. At higher resolution of magnification, the pore structure can viewed, viewing from the cross-section, most of the pores are of 2-3 μm size. The pores are not interconnected to each other to form pin holes, however the irregular structures of these pores may restrict their specific application of the membrane.

Comparing the two membranes prepared from different PC concentrations, 16 and 18 wt%, difference in pore sizes and porosity can be noticed. With the higher PC concentrations, the pore sizes at the surface are less
than 1 μm, however, at the cross section, the maximum pore sizes of 2 μm. Moreover, the porosity of the membrane has reduced much as compared with the membrane of 16 wt% PC.

Therefore, for the PC membranes prepared using the NMP solvent yielded to semi-porous surface layer, and porous substructure at 16 wt% PC, similarly at 18 wt% PC, dense surface with porous substructure.

Fig. 11: SEM images for PC membrane (18 wt% PC in NMP) a) Surface and b) Cross-section.

Visually the difference among the two membranes prepared by DCM and NMP, is the color of the membrane, it is colorless if the solvent of casting solution is DCM, and it is a white if the solvent of casting solution is NMP.

These differences of color in the membrane can be explained using FTIR results, which are shown in Figure 12 and 13 for polymer concentrations of 16, 17, 18, and 19 wt%. It is clear that as the polymer concentration increases, the percentage transmittance decreases, but in the case of the membranes prepared from PC-DCM, decrease in percentage transmittance is slight. However, in the case of membranes prepared from PC-NMP, although all the characteristic peaks exists, but there is a shift of peaks, with decrease in percentage transmittance. The characteristic peaks that corresponds to carbonyl functional group C=O are the ranges of 2000-600 cm⁻¹ (Coates 2000), which are exhibited in both cases.

Fig. 12: FTIR curves of PC membranes prepared from different PC-NMP concentrations.

Fig. 13: FTIR curves of PC membranes prepared from different PC-DCM concentrations.
The performance test was also conducted to determine the gas permeability of the membranes to \( \text{CO}_2, \text{N}_2 \), and \( \text{CH}_4 \) as well as to determine the ideal selectivity to \( \text{CO}_2 \). The effect of varying feed pressures on the performance of the membrane was also studied for pressures of 1-24 bars. The entire performance test was carried out at room temperatures. Membranes of 18 wt% PC are reported in Figure 13 for the effect of feed pressures.

For the membrane prepared from 18 wt% PC in DCM, the \( \text{CO}_2 \) permeability decreased with the increase of feed pressures. However, for gases such as \( \text{N}_2 \) and \( \text{CH}_4 \), the decrease in their permeability is very slight; this is due to the fact that, \( \text{CO}_2 \) has plasticization effect on the membrane at high pressure (Norman and Paul 2012). Since a single gas was used for the determination of the permeability, the average ideal selectivity or permselectivity (\( \alpha \)) over a wide range of feed pressures were calculated, and found to be 18.75 for \( \text{CO}_2/\text{CH}_4 \) and 22.94 for \( \text{CO}_2/\text{N}_2 \).

![Fig. 14: Permeability of PC membrane prepared from 18 wt% PC in NMP.](image)

![Fig. 15: Permeability of PC membrane prepared from 18 wt% PC in DCM](image)

For the membrane prepared using NMP solvent, higher values of permeability was obtained as compared to the one used DCM. This is due to the fact that the membrane is highly porous, where the diffusion of gases through the effective thickness of the membrane encountered less resistance. It can be also noticed that the permeability of \( \text{N}_2 \) increased slightly with the increase in feed pressures. The average ideal selectivity (\( \alpha \)) over range of feed pressures was found to be 19.82 and 17.80 for \( \text{CO}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{N}_2 \) respectively.

**Conclusion:**

The viscosities of the PC solutions were determined experimentally for wide range of concentration, to determine the critical polymer concentration required for the membrane gas applications. Studies on coagulation value of PC-DCM and PC-NMP pairs were also conducted to find out the extent of tolerance to coagulants, and determine the coagulation ratio, as the dry-wet phase inversion method was used to fabricate the membranes. The PC membrane prepared from two different solvents namely DCM and NMP were studied; Dry-wet phase inversion technique was used to cast the polymer solution in to a predetermined thickness of the membrane. From SEM images provided, the membrane produced from PC-DCM solution yielded to dense membrane,
whereas the membrane fabricated from PC-NMP solution yielded to porous asymmetric membrane. FTIR results showed to a major shift in the peaks that corresponds to the Bisphenol group for membrane casted from PC-NMP solution, and the percentage transmittance decreased with increase in PC concentrations. The performance test was conducted using four channeled permeation cell membrane gas separation system, it is found that the CO₂ permeability decreased with the increase of feed pressure, and a slight decrease in the permeability of CH₄. The ideal selectivity α(CO₂/CH₄) was obtained to be 18.75 and 19.82 for PC-DCM and PC-NMP membranes respectively, whereas α(CO₂/N₂) was 22.96 and 17.80 for PC-DCM and PC NMP membranes respectively.

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