

EFFECT OF P84 (BTDA-TDI/MDI) COMPOSITION TOWARDS THE PERFORMANCE OF THE DISK SUPPORTED CARBON MEMBRANE

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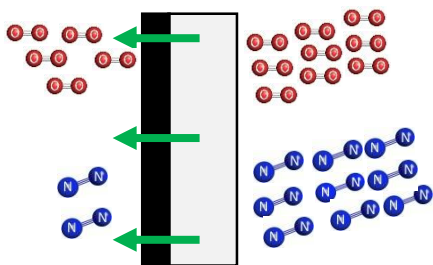
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Graphical abstract



Abstract

Carbon membrane has attracted researchers' attention as it is superior in terms of its gas separation performance. In this study, the composition of polymer precursor in the dope solution was investigated based on carbon membrane performance. P84 polyimide was chosen as the polymer precursor as it fulfils the requirement for carbon membrane properties. By varying the polymer precursor composition (6, 9, 12, and 15 wt.%), P84 was stirred in NMP solvent until homogenous solution was formed. Commercialised alumina disc was coated via spray coating method at 1 bar at room temperature. The disc supported polymeric membrane was carbonised at 700 °C under nitrogen (200 ml/min) with heating rate of 3 °C/min. The carbon membrane was analysed via SEM. Gas permeation tests were performed using pure O₂ and N₂ at 4 bar at room temperature. The selectivity of 3.7 was obtained using the disc supported carbon membrane for O₂/N₂. The optimum polymer composition in this study was obtained by 12 wt.% of P84.

Keywords: Carbon membrane, Disk Supported, Gas separation, Polymer Composition, Performance

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1.0 INTRODUCTION

In pursuing excellent and efficient gas separation performance of membrane technology, the polymeric membrane needs to be improved as it is well known for its disadvantages [1, 2]. One of the promising membrane technologies is carbon membrane that is fabricated by carbonising polymeric membrane beyond its decompose temperature [3]. These superior carbon membrane is known for its performance due to the presence of graphitic and turbostratic structure [4]. These structures will improve permeability and selectivity as the molecules of the gas is slightly different in their size. In order to enhance the result, P84 polyimide is

used as polymer precursor as polyimide family is known for their encouraging outcome. Based on previous studies, unsupported carbon membrane especially hollow fibre membrane were chosen for its high productivity due to its high surface area to volume ratio [5]. However, this type of unsupported carbon membrane suffers from brittleness that will reduce the capacity of the product.

Thus, several porous supports such as graphite, stainless steel, glass, and ceramic were recommended to overcome the mechanical problem [6]. In this report, porous alumina disc support was introduced in handling this obstacle. The presence of the support will not affect the membrane and the resistance of the support could

be negligible [7]. In addition, spray coating technique is applied in order to obtain thin membrane layer and to enhance the adhesion mechanism between membrane and porous support [8]. These mechanism is important as it will avoid the membrane from peeling off the porous support and reduces the defect on the membrane surface. Susanna and co-workers compared different coating techniques, which were spin and spray coating technique in order to evaluate the deposition technique on the device [9]. They reported that spray coating is an efficient method in comparison to the spin coating due to the losses in short density which make it not preferable.

The concentration of the polymeric solution is needed to consider to obtain thin uniform membrane layer with defect-free membrane. Commonly, low viscosity of the solution is required to make sure the solution is distributed uniformly on the porous support. The distribution of the polymeric solution is due to the mass air flow that contributed by the viscosity of the polymer concentration composition [10]. Differences in solution composition make the transport of P84 particle to be at different destination which contributes to the thickness of the fabricated carbon membrane.

Hence, the concentration composition of the P84 is a crucial issue that will directly determine the carbon membrane performance. Thus, the objective of this study was to investigate the optimum concentration composition of the polymer precursor P84 in order to obtain uniform defect-free thin layer carbon membrane. Four compositions of polymer precursor P84 were investigated and the viscosity of the composition were further discussed. The SEM images were compared between the polymeric and carbon membrane of P84.

2.0 METHODOLOGY

2.1 Materials

The commercial co-polyimide BTDA-TDI/MDI (P84) powder was obtained from Sigma Aldrich (CAS#: 58698-66-1). N-Methyl-2-pyrrolidone (NMP) purchased from Merck (Germany) was chosen as the solvent. Commercial support of porous alumina disc with a diameter of 47.0 mm, thickness of 1.0 ± 0.05 mm, and mean pore size of $0.14 \mu\text{m}$ was bought from Shanghai Gongtao Ceramics Co., Ltd.

2.2 Methods

The polymeric membrane preparation was started by drying polymer precursor (P84) in an oven for one day at the temperature of $60 \text{ }^\circ\text{C}$ to eliminate the presence of water vapour. Various compositions (6, 9, 12 and 15 wt.%) of polymer precursor were applied in order to study the concentration effect towards the gas separation performance. Polymer solution

was prepared by stirring P84 in NMP until the polymer precursor was totally dissolved. The homogenous solution was sonicated to eliminate bubble that formed during the stirring process. The polymeric solution was coated on the porous alumina disc support by spray coating method at 1 bar pressure at room temperature. Carbon membrane preparation began when the polymeric alumina support was stabilised at $350 \text{ }^\circ\text{C}$ under nitrogen gas at 200 ml/min with heating rate of $3 \text{ }^\circ\text{C}/\text{min}$ for 30 minutes. Then the temperature was raised up to $700 \text{ }^\circ\text{C}$ under the same condition as stabilisation stage. The membrane was cooled down to room temperature naturally under N_2 . In this study, spray coating method was applied, where only one cycle of coating-carbonisation was adapted. Figure 1 illustrates the heat treatment profile of the fabricated carbon membrane throughout the study. The samples were designated based on P-composition for polymeric membrane: P-6, P-9, P-12, and P-15, and CM-composition for carbon membrane: CM-6, CM-9, CM-12, and CM-15.

The polymeric solution viscosity was determined using a viscometer (Brook Field). Scanning electron microscopy (SEM, JEOL JSM-5610LV) was used to observe the morphological structure of the membrane. The gas permeation properties were tested using pure gas of O_2 and N_2 .

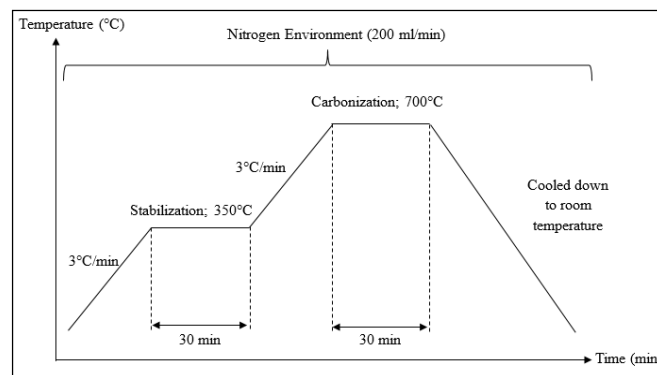


Figure 1 Heat treatment profile

3.0 RESULTS AND DISCUSSION

3.1 SEM

The SEM images represent the morphology of the P84-based polymeric and carbon membrane at 12 wt% composition. Figure 2 shows the cross section view of the P84-based polymeric and carbon membrane prepared at 12 wt%. A clear view of the presence of adhesion mechanism between membrane and support does not clearly seen in SEM images. The polymeric solution was cast on the glass plate and dried in an oven overnight, before proceeding to the carbonisation process. A dense structure was obtained for both membranes as shown in Figure 2.

The thickness of the polymeric membrane was thicker than carbon membrane at 13.6 and 11.5 μm , respectively. This was theoretically expected as polymeric membrane undergoes shrinkage process when being exposed to high temperature [11]. The surface view of the polymeric membrane shows smooth surface layer with several spots of defect formation, while carbon membrane formed a various size of pores on the surface view. In the range of 90 to 200 $^{\circ}\text{C}$, solvent residue and absorbed water was totally released, resulted in the non-smooth surface layer [12]. The absence of pore in the polymeric membrane tends to have high possibility of blocking the gas to permeate and increasing the mass resistance of the gases. While for carbon membrane, the presence of pores is due to the released of the heteroatoms and structure rearrangements that lead to a graphite-like structure carbon membrane [13]. These structures enhance the gas separation performance of the membrane as stated in Table 2.

The surface view of the carbon membrane shows several layer of pores that contain difference sizes of pores. The kinetic diameter size of O_2 (3.46) and N_2 (3.64) are hardly to distinguish and separate. The disordered sp^2 and hybridised condensed hexagonal sheets formed the amorphous structure make it possible to deal with the kinetic diameter size of the gas at the same time led to good gas separation [14]. The pore structure formation due to the packing imperfections between ordered regions after carbonising polymeric membrane is illustrated in Figure 3.

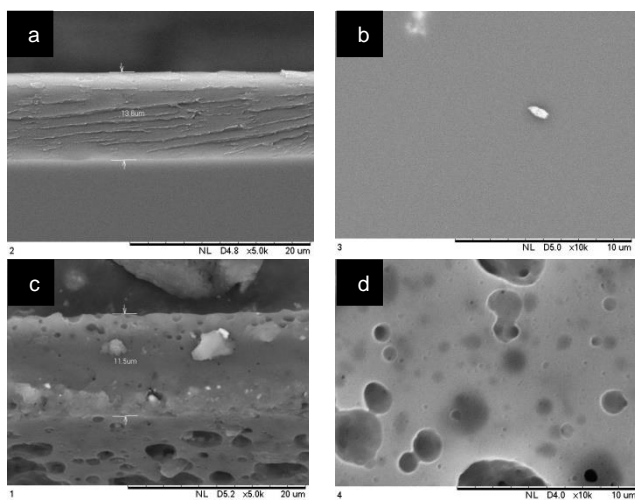


Figure 2 SEM cross section and surface view of 12 wt% P84 (a, b) P-12 (c, d) CM-12

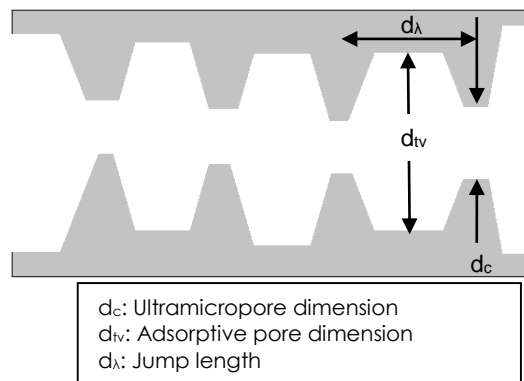


Figure 3 Idealized pore structure of carbon membrane [6]

3.2 Viscosity

As spray coating technique was applied in this study, it was important to determine its viscosity in determining its effects towards the adhesion mechanism and uniform distribution of the polymer solution on the porous surface. Theoretically, the spray coating is preferred compared to the dip-coating technique. During the spray coating, the applied pressure will strengthen the adhesion mechanism because it forces the polymeric solution to stick on the porous alumina support [9]. While dip-coating has less connection between the support and membrane that leads to peel off problem. These situations will stress the membrane to shrink and easily pull out from the support as it has less adhesion mechanism when undergoes heat treatment process. On the other hand, it is tough to distribute the high viscosity polymeric solution as it will form a spot that looks like agglomerate of P84 on the porous alumina disc support as a result of the mass flow velocity [10]. However, high viscosity value encourages good adhesion mechanism for the supported carbon membrane since it generates great coherent for the membrane layer. Table 1 shows viscosity of the polymeric solution at various concentrations of P84. A very huge difference is observed with the increased composition although the increase is just 3 wt%. CM-6, with the lowest viscosity, has high possibility to penetrate through the porous support in comparison to CM-12 and CM-15 that have almost 10 times cP values [8]. The dilute solution makes polymer solution easy to distribute but crucial in forming uniform layer, same goes to the high amount of viscosity solution. Thus, the optimum viscosity is 138 cP, obtained with 12 wt.% of P84.

Table 1 Viscosity of polymer solution at various concentration composition

Membrane	Viscosity (cP)
P-6	16.58
P-9	20.93
P-12	138.19
P-15	213.69

3.3 Gas Permeation

The gas permeation properties were tested using pure gas of O₂ and N₂ at room temperature with a feed pressure of 4 bar. The highest gas permeance was obtained at the lowest polymer precursor composition of 6 wt.%. While 12 wt.% of P84 obtained highest selectivity of O₂/N₂ of 3.73. The increasing P84 composition from 6 to 12 wt.% decreased the permeance but the selectivity was improved. Low composition of P84 gives low viscosity value that forms a dilute solution that is less preferable as it will easily penetrate deep through the porous alumina disc that results in high mass resistance and obtain non-uniform membrane layer [8]. However, high viscosity polymeric solution may not also be an option to obtain high gas separation. High viscosity solution will encourage the polymer precursor P84 to agglomerate when applied on the porous support. In high viscosity solution, the P84 will come out from the orifice unevenly due to the influence of the mass flow that is mainly consist of P84 [10]. Thus, sprayed polymeric solution may have blocked the path for the gas to pass through that results in high mass transfer resistance and low gas separation performance [15]. Based on the result obtained, when reaching 15 wt.% polymer precursor, the selectivity result was dropped.

Table 2 Gas permeation properties of carbon membrane of P84 at different composition

Membrane	Permeance (GPU)		Selectivity
	O ₂	N ₂	
CM-6	143.56	125.91	1.14
CM-9	102.11	69.95	1.46
CM-12	86.50	23.13	3.73
CM-15	91.56	43.46	2.11

Table 3 shows the gas separation properties of the polymeric and carbon membranes. The gas permeation result of the polymeric membrane was not as good as its surface view. The existence of amorphous and graphitic-like structure after the carbonisation process yields an almost four times better gas separation efficiency compared to polymeric membrane [16].

Table 3 Comparison of polymeric and carbon membrane

Membrane	Permeance (GPU)		Selectivity
	O ₂	N ₂	
P-12	11.09	13.97	0.79
CM-12	86.50	23.13	3.73

4.0 CONCLUSION

The disc supported carbon membranes were successfully prepared in a single step of spray coating-carbonisation method. The viscosity of various compositions of P84 played an important role where it influenced the distribution of the polymeric layer on the porous alumina support and at the same time gave impact towards the thicknesses and gas separation performance. The optimum composition was 12 wt.% of P84, with the highest O₂/N₂ selectivity of 3.73 at 4 bar feed pressure.

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