

Application of Activated Carbon Mixed Matrix Membrane for Oxygen Purification

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Abstract— This study is performed primarily to investigate the effect of activated carbon on oxygen separation performance of polyethersulfone mixed matrix membrane. In this study, polyethersulfone (PES)-activated carbon (AC) mixed matrix membranes were fabricated using dry/wet technique. This study investigates the effect of polyethersulfone concentration and activated carbon loading on the performance of mixed matrix membrane in terms of permeability and selectivity of O₂/N₂ gas separation. The fabricated flat sheet mixed matrix membranes were characterized using permeation test, Field Emission Scanning Electron Microscopy (FESEM) analysis and Differential Scanning Calorimetry (DSC). It was found that the activated carbon loading affected the gas separation performance of mixed matrix membrane. PES- 1wt% AC membrane yielded 3.75 of O₂/N₂ selectivity, however 5 wt% of AC can produced 5 O₂/N₂ selectivity.

Keywords— mixed matrix membrane, activated carbon, gas separation.

I. INTRODUCTION

The use of membrane in gas separation has grown at a very rapid pace in recent times. Membranes are being used to separate gases from their mixtures by the differential permeation of the components through them. For examples, the separation of air into oxygen and nitrogen and the removal of volatile organic compounds from effluent streams. The membrane separation processes offer a number of advantages in terms of low energy requirements, low capital and operating costs and generally ease of operation. In general, membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. Koros et al. [1] described membrane as a structure which having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces. A membrane separation system separates an influent stream into two effluent streams known as permeate and concentrate. Permeate is the portion of the fluid that has passed through the semi-permeable membrane whereas the concentrate

stream contains the constituents that have been rejected by the membrane.

Polymeric membranes dominate the membrane separation field due to the fact that they are well developed and quite competitive in separation performance and economics. Since the separation of gas mixtures depends on the relative solubility and diffusivities of individual components within a particular membrane, no single membrane material is capable of successfully separating all gas mixtures. The choice of membrane material will be dictated by the nature of the gases mixture to be separated. Glassy polymers such as polysulfone, polyethersulfone, polyimide, and ethyl cellulose which are known to have high mechanical stability and desirable inherent transport properties at high temperature are more commonly used [2]. Lately, the relation between gas permeability and polymer structure has been a prime subject of investigation. However, experimental results for numerous glassy polymers indicate that a significant increase in both permeability and selectivity coefficients cannot be achieved simultaneously. Apart from the synthesis of new engineering polymers, gas separation membranes can be alternatively prepared by blending existing, suitably selected polymers. This method offers several advantages, as it can reconcile families of polymers with different separation properties, physicochemical characteristics, or even production costs in a simple and reproducible way.

Despite concentrated efforts to tailor polymer structure to affect separation properties; current polymeric membrane materials have seemingly reached a limit in the tradeoff between productivity and selectivity [3]. Pure polymer membranes are oftentimes shows several limitations as low selectivity, high temperature instability and swelling and decomposition in organic solvents. While carbon molecular sieves and zeolites recommend very attractive permeation properties with permeabilities and selectivities significantly higher than polymeric materials, processing challenges and high costs obstruct their industrial application [4]. Therefore, to obtain the high selectivity benefits of molecular sieving media as well as to counter the costly processing of purely homogeneous molecular sieving membranes, mixed matrix

membranes have been proposed as an alternative approach by incorporating these sieves into a processable polymeric matrix. This heterogeneous or hybrid membrane concept combines the advantages of each medium high separation capabilities of the molecular sieves and the desirable mechanical properties and economical processing capabilities of polymers [4]. Thus, in this research polyethersulfone-activated carbon mixed matrix membrane has been investigated for oxygen separation. To our knowledge, there is no documentation on the use of activated carbon as inorganic filler for mixed matrix membrane for oxygen separation.

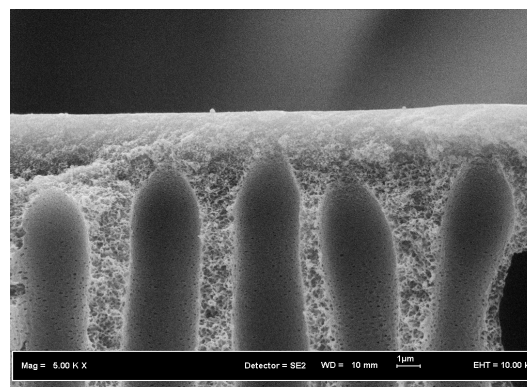
II. METHODS/THEORY

Polyethersulfone was supplied by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120 oC overnight before dope preparation; N-methylpyrrolidone (NMP) from Merck was used as the solvent due to its low. The inorganic filler molecular sieve involved was activated carbon purchased from Aldrich. In order to remove the adsorbed water vapour or other organic vapors, all activated carbon particles were dehydrated at 300 oC for 3 h before use. The polyethersulfone-activated carbon mixed matrix membrane was prepared by preparing the activated carbon solution. In this step, the solution was prepared by dissolving an amount of activated carbon in 1-methyl-2-pyrrolidone solvent, stirring continuously with stirrer during 4 hours at 298 K. Then, the corresponding amounts of Polyethersulfone were added into the solution under mechanical stirring at ambient temperature (298 K) during 12 hours. The solution was then placed in a vacuum oven to remove particles and gas bubbles that may exist in the casting solution. The PES-AC solution was poured onto a clear, flat glass plate. The plate was placed inside the plastic box. A stainless steel casting knife was used to spread the solution to a uniform thickness. The membrane film was then placed under a close environment in order to slow down the evaporation rate of the solvent from the film surface. The membrane film was then further dried after initial evaporation at temperature of about 100oC for about an hour followed by nitrogen purging for about an hour. After purging, the temperature increased to 200oC and left at least 12 hours in a vacuum oven to remove residual solvent. And lastly, the temperature was increased to 230oC for another 12 hours. Once the solvent has evaporated, the film is usually strongly adhered to the casting surface. A razor blade is use to carefully detach the edges from the casting surface.

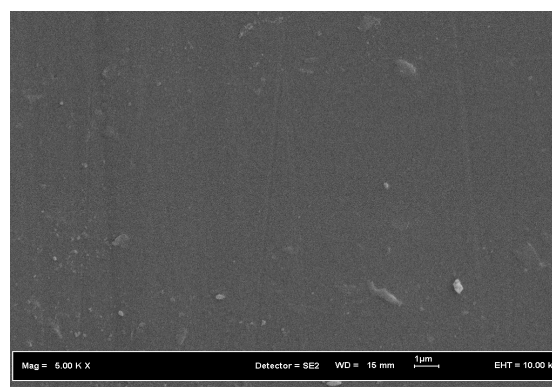
III. RESULTS AND DISCUSSION

The interface between a polymer matrix and inorganic filler plays an important role in the performance of mixed matrix membranes. Therefore, in this study, the feasibility of activated carbon (AC) as inorganic filler for fabricated polyethersulfone (PES) mixed matrix membranes was examined. Hence, the characterization and comparison of neat polyethersulfone and PES- AC would be further discussed.

In order to further investigate the effect of activated carbon as inorganic filler on the dispersion of activated carbon in mixed matrix membrane, careful FESEM inspections were carried out. The FESEM micrographs of the cross-sectional and the surface of the neat PES, PES- 1-10 wt% acticated carbon matrix membranes are shown in Figures 1-4. Figure 1-4 illustrates the partial cross-sectional area of representative neat PES membrane and PES-AC mixed matrix membrane; the Figure clearly reveals the presence of some macrovoids under the skin layer.



(a)



(b)

Figure 1: SEM picture of asymmetric polyethersulfone membrane at the: (a) cross section and (b) outer surface image layer.

Foremost, by referring to Figures 2-4, the differences in adhesion between PES with different concentration of AC can be successfully distinguished. The increasing of loading of AC in mixed matrix hollow fiber membrane caused the some agglomeration and ruptures on the surface of membrane as shown in Figures 3-4. The revealing of submicron gaps around the sieves may be formed due to poor adhesion between the polymer and activated carbon. As shown in Figure 2(a), the fabrication of 25 wt% PES-1 wt% AC shows good compatibility between activated carbon and PES phases since the formation of voids wasn't found; also, the activated carbon particles are distributed well. However, on the fabrication of 25 wt% PES-10 wt% AC, some area the activated carbon particles are not distribute well and shows

the existing of activated carbon agglomeration as presented in Figure 4 (b).

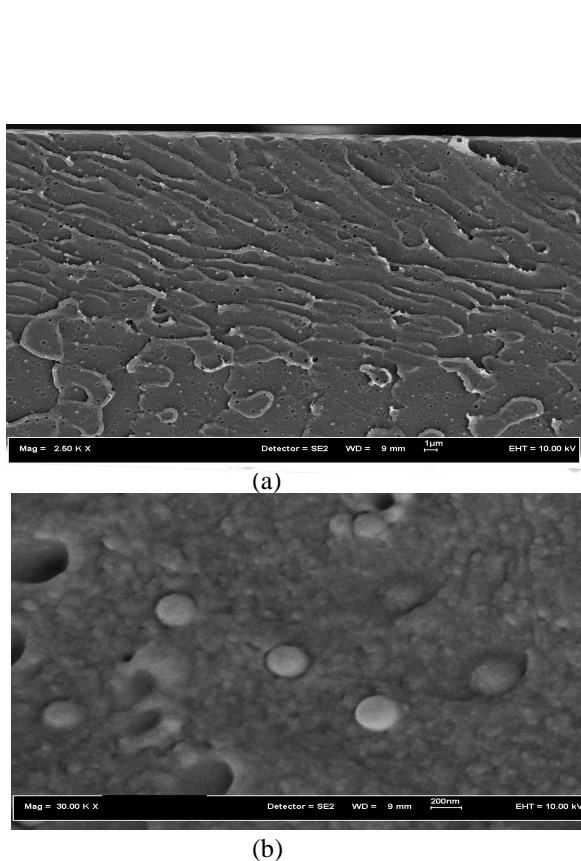
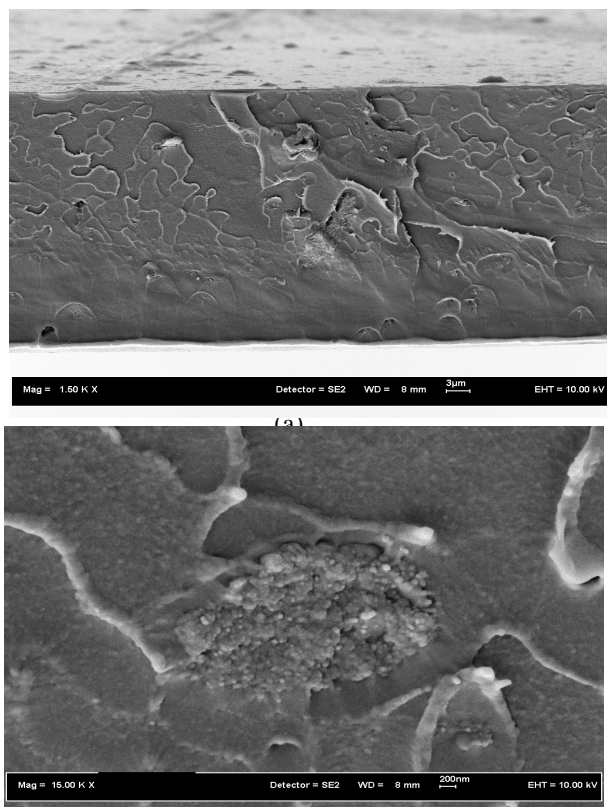
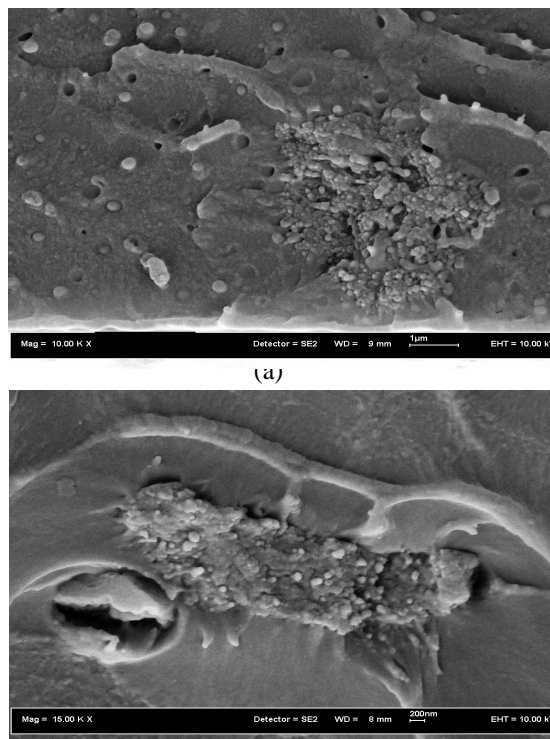


Figure 2: SEM picture of symmetric polyethersulfone-1 wt% AC membrane at the: (a) cross section and (b) outer surface image layer.



(b)
Figure 3: SEM picture of symmetric polyethersulfone-5 wt% AC membrane at the: (a) cross section and (b) outer surface image layer.



(b)
Figure 4: SEM picture of symmetric polyethersulfone-10 wt% AC membrane at the: (a) cross section and (b) outer surface image layer.

The Differential Scanning Calorimetry has been done to indicate whether the activated carbon as inorganic filler and PES as polymer matrix were indeed miscible by observing the glass transition temperatures of the blend composition. The T_g for each membranes was determined from the heat flow versus temperature curve using an onset method. The influence of loading of activated carbon on the glass transition temperature of PES-AC mixed matrix membranes are tabulated in Table 1. As shown in Table 1, the glass transition value, the loading AC have increased the glass transition temperature T_g . This can be seen in the effect of T_g for AC. The increasing of T_g in PES-AC is because of the strong interaction between the PES matrix and activated carbon membrane which reduce the matrix mobility which will express itself in a shift of T_g [5] and beside that the diffusion of small molecules can be retarded under high temperature. It can also be seen that compared with neat PES polymer, the T_g of the mixed matrix membranes increased about 3 °C with the incorporating only 1-5 wt% activated carbon into the matrix. This phenomenon indicates that the mobility of polymer chains is reduced due to the restriction effect of carbon

nanotubes. This result is in agreement with the previous study [6]. However, the glass transition temperature for PES-10 wt % activated carbon was lower than neat PES. This phenomenon indicated that the agglomeration and ruptures was occurred on the PES-10 wt% AC and was caused the adhesion of PES as polymer matrix and AC as inorganic filler was weak. The result is in agreement with the Figure 4.

TABLE 1
COMPARISON OF GLASS TRANSITION TEMPERATURE FOR MIXED MATRIX MEMBRANE

Mixed Matrix	
Membrane	Glass Transition Temperature of Mixed Matrix Membrane (°C)
Neat PES	215.67
PES-1 wt % AC	215.85
PES-5 wt% AC	218.43
PES-10 wt% AC	213.47

In order to evaluate the performance of the mixed matrix membrane, the fabricated membranes were tested for O₂/N₂ gas separation. The permeability and selectivity for tested gases of O₂/N₂ obtained for different activated carbon loading were tabulated in Table 2. From Table 2 shows that the permeability of O₂ is higher than N₂ for all combinations of mixed matrix membranes as well as pure PES membrane. This is because of the kinetic diameter of O₂ is smaller than N₂, which is kinetic diameter for O₂ and N₂ is 3.46 and 3.64, respectively. Activated carbon play a role of a molecular sieve in PES-AC mixed matrix membranes which facilitates the permeation of the smaller molecules, but hinders that of larger molecules. The permeability of O₂ and N₂ for mixed matrix membranes is higher compare to pure PES membranes. As mentioned before, the permeability of O₂ and N₂ are higher because of the existing of activated carbon as a filler phase in mixed matrix membranes. Activated carbon with high porosity will lead to very good permeation performances. As a result, the selectivity of pure PES membrane for O₂/ N₂ gas separation also lower compared to mixed matrix membrane.

It also shows that the permeability of O₂ and N₂ for the combination of 10 wt% AC-PES mixed matrix membrane is the highest compare to 1 wt% AC-PES and 5 wt% AC-25 wt% PES. However, the selectivity of 10 wt% AC-PES has lower than 1 wt% and 5 wt % of activated carbon. It might because of the formation of the voids and agglomeration in 10 wt% AC-PES mixed matrix membrane which is lead to a high permeability of O₂ and N₂.

By referring to the Figure 3, the activated carbon particles are distributing well and less formation of voids. Here, we can say that it might be the formation of voids in 10 wt% AC-PES mixed matrix membrane are higher which lead high permeability of O₂ and N₂. The selectivity of O₂/N₂ gas separation is increasing due to the increasing of activated carbon loading. Therefore, the best combination of AC-PES

mixed matrix membrane for O₂/ N₂ gas separation is 5 wt% AC-PES which achieve 5.

TABLE 2
EFFECT OF ACTIVATED CARBON CONCENTRATION ON THE GAS SEPARATION PERFORMANCE OF POLYETHERSULFONE-AC MIXED MATRIX MEMBRANES

Membrane	Single gas permeance (GPU)		Selectivity O ₂ /N ₂
	O ₂	N ₂	
Neat PES	1.77	0.64	2.76
PES-1wt%AC	3.25	0.86	3.78
PES-5wt%AC	4.2	0.84	5
PES-10wt%AC	2.94	1.68	1.76

IV. CONCLUSIONS

In this study, the polyethersulfone (PES) with activated carbon for the use of fabricating mixed matrix membrane for oxygen enrichment. Based on the experimental results and analysis, the following conclusions can be made.

- The FESEM for the cross-sectional and surface area images of mixed matrix membrane films indicated that the loading of activated carbon below 10 wt% at total solid dispersed well in the polymer matrix. The surface ruptures are occurred on the activated carbon mixed matrix membrane might be due to the agglomeration of activated carbon at high loading.

- The PES-activated carbon membranes had increased the permeability and selectivity of oxygen and nitrogen gas and the O₂/N₂ selectivity.

- The activated carbon has been potentially as inorganic filler for mixed matrix membrane for the future oxygen enrichment membrane.

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