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Effect of pyrolysis temperature on gas permeation characteristics of poly(*p*-phenylene oxide) derived hollow fiber carbon membranes

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Abstract

Hollow fiber carbon membranes derived from poly(*p*-phenylene oxide) were subjected to different pyrolysis temperatures and their corresponding gas permeation characteristics were studied. Carbon membrane produced using pyrolysis temperature of 500°C was low in H₂, O₂, N₂ and CH₄ permeabilities, as well as H₂/N₂ and O₂/N₂ ideal selectivities. The highest permeabilities and ideal selectivities were obtained at 600°C. Different trend was shown by the CO₂ permeability which increased with pyrolysis temperature before decreased at 700°C. The CO₂/CH₄ ideal selectivity consistently increased with increasing pyrolysis temperatures.

Keywords: Poly(*p*-phenylene oxide), Hollow fiber, Carbon membrane, Pyrolysis temperature, Gas separation.

Introduction

Carbon membranes possess the capability of discriminating gas molecules with similar kinetic diameters such as O₂ and N₂ [1]. This feature has attracted many researchers to investigate and further develop the carbon membranes into commercially acceptance. Currently, the carbon membrane development focuses on finding new precursors and modification of the existing precursors. The precursors were mostly polyimides which is economically unattractive, thus non-polyimide polymers such as phenolic resin [2], cellulose acetate [3] and poly(furfuryl alcohol) [4] were extensively introduced. The current study reports interesting findings on the ideal gas separation characteristics of hollow fiber carbon membrane produced from poly(*p*-phenylene oxide) (PPO) using different pyrolysis temperature.

Methods

The hollow fiber PPO and carbon membranes were synthesized according to the previous work [5]. Heat treatments which were thermostabilization and pyrolysis, were applied to convert the PPO membrane into carbon membrane. The thermostabilization temperature was 240°C and held for 1 hour before proceeding to pyrolysis treatment at varied temperatures. A constant pressure/variable-volume system and a soap-bubble flow meter were used to measure the membrane flow rate. The membrane module was

open/close-ended in which gas was fed from the membrane bore side. The order of the feed was H_2 , N_2 , CO_2 , CH_4 and CO_2 to prevent strong adsorbing gases from influencing the measurement of the proceeding gases [6]. The morphology of the carbon membrane was captured using scanning electron microscope (SEM, Model Quanta FEG 450, FEI, USA).

Results and discussions

Fig. 1 (a–b) and (c–d) shows the cross-sectional morphology of PPO and carbon membranes, respectively. Both membranes exhibited homogeneous, symmetric, and nonporous structure. The PPO and carbon membranes were approximately 15.4 and 14.7 μm thick. The non-porous structure of the PPO membrane (PPOM) stemmed from the delayed phase inversion between the polymer solution and ethanol bore fluid and bath. The diameter and thickness of the membrane decreased after pyrolysis because of thermal shrinkage and decomposition. The change in surface morphology also suggested structure rearrangement during pyrolysis.

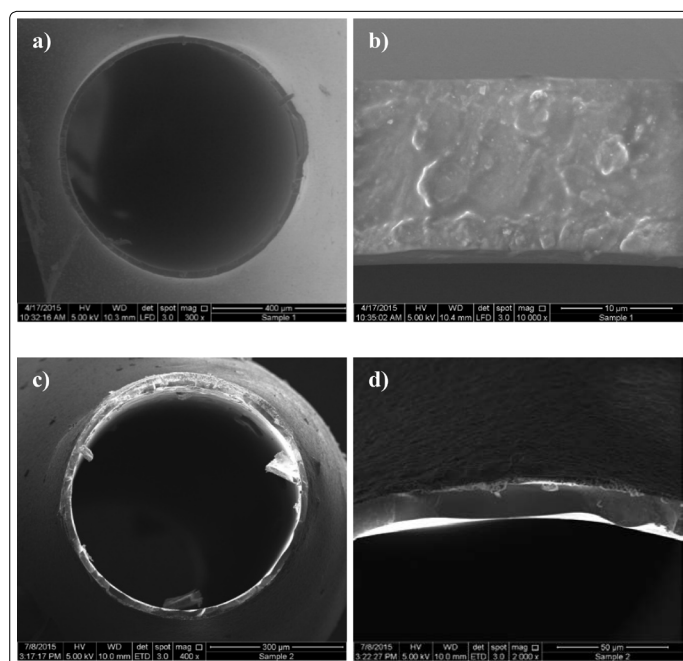


Figure 1. SEM images of cross-sectional views of PPO membrane (a, b) and carbon membrane (c, d)

Figure 2 shows the permeabilities of H_2 , CO_2 , O_2 , CH_4 and N_2 for carbon membranes pyrolyzed at 500°C (CM500), 600°C (CM600) and 700°C (CM700) with heating rate and thermal soak time of 1°C/min and 15 mins, respectively. PPOM permeabilities was included for comparison purpose. The permeabilities of H_2 , O_2 , N_2 and CH_4 dropped significantly when the sample was pyrolyzed to 500°C. Similar trend was followed by their corresponding ideal selectivities of O_2/N_2 and H_2/N_2 . In contrast, the CO_2 permeability and CO_2/CH_4 ideal selectivity increased. As the pyrolysis temperature was increased to 600°C, all the gas permeabilities and ideal selectivities increased significantly. The ideal separation performances of the gases, except CO_2/CH_4 ideal selectivity, decreased again as the pyrolysis temperature was further increased to 700°C.

According to the values of permeabilities and ideal selectivities, particularly O_2/N_2 , of the hollow fiber carbon membrane, the transport mechanism of the gases was most probably dominated by the molecular sieving in which it suggested that the membranes possessed micropore structure with pore size less than 2 nm [7] [8]. When the thermostabilized PPO membrane was subjected to pyrolysis treatment, slow decomposition of the polymer structure took place. At the same time, thermal shrinkage and structural rearrangement also occurred. The amorphous structure originated from the thermostabilized PPO membrane gradually collapsed during the pyrolysis and chaotically rearranged as amorphous carbon.

At 500°C the decomposition was not sufficient to develop highly porous membrane structure and the newly-developed pores were constantly decreased in size due to the thermal shrinkage. The decomposition to thermal shrinkage ratio might have increased significantly at pyrolysis temperature of 600°C as suggested by the substantial increases of the gas permeabilities. The decomposition rate reduced as the decomposable structure of the membrane not much left, resulting the dominance of structural densification when the pyrolysis temperature was further increased to 700°C. The pores of carbon membrane might have collapsed and given away for the initiation of carbon graphitization which had higher density, tighter packaging and higher ordered structure [9].

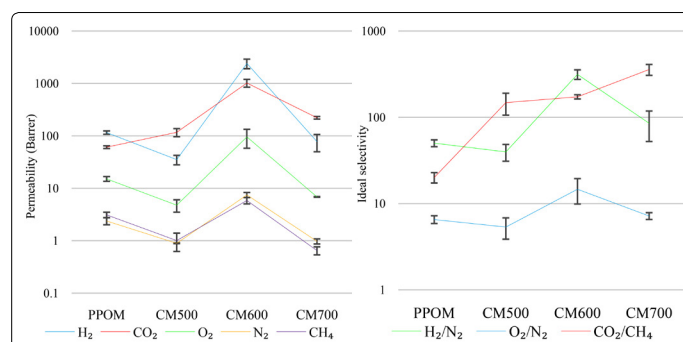


Figure 2. Permeabilities and ideal selectivities of PPO (PPOM) and PPO-derived hollow fiber carbon membrane (CM500, CM600 and CM700) prepared at different pyrolysis temperatures

The slightly higher CO_2 permeabilities than their H_2 counterparts as shown by the CM500 and CM700 indicated the presence of surface diffusion as one of the contributing transport mechanism besides molecular sieving effect. The lower H_2 permeability on both membranes indicated that the resistance into the membrane was high most probably due to smaller openings than that of CM600. At the same time, this pore resistance also accelerated the accumulation of the highly adsorbable CO_2 at the narrow opening which eventually provided suitable environment to produce surface diffusion effect that increased the CO_2 permeability.

The affinity between the CO_2 and carbon membrane pore wall suggested that kinetic diameter was not the sole factor in determining the magnitude of the gas permeabilities, but also the affinity of the diffusing molecules towards the carbon membrane pore wall [10]. This affinity is originated from the

van der Waal's forces produced by quadrupole moment of the symmetrical CO₂ that established weak attraction towards the carbon pore walls which occupied with delocalized electrons from its turbostratic structure.

Conclusion

The morphology of the PPO-derived hollow fiber carbon membrane was dense, homogenous, thin and symmetric. Each stage of pyrolysis temperature has significant impact on the PPO-derived carbon membrane structures. The highest permeabilities and ideal selectivities were obtained at 600°C. In exception of CO₂ permeability and CO₂/CH₄ ideal selectivity, all permeabilities and ideal selectivities were very low when pyrolysis temperature of 500°C was used. The transport mechanism through the carbon membranes was highly affected by molecular sieving and surface diffusion. The surface diffusion transport mechanism was highly dominating when the carbon membranes possessed very small pore sizes.

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