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Carbon hollow fiber membranes derived from PEI/PVP for gas separation

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ABSTRACT

Carbon hollow fiber membrane derived from polyetherimide (PEI) blend with polyvinylpyrrolidone (PVP) was prepared by pyrolysis under air and N_2 environment. The characteristics of the carbon structures and the gas separation properties of carbon hollow fiber membranes pyrolyzed at different temperatures were studied. The prepared membranes were extensively characterized using thermogravimetry analysis, scanning electron microscopy, and X-ray diffraction for its morphology, thermal stability and structure properties, respectively. Pure gases of different molecular size (CO_2, N_2 and CH_4) were used to determine the permeation properties of the carbon membrane. The permeance of the three gases decreased with increasing of pyrolysis temperature, however the selectivity of the gas pairs such as CO_2/CH_4 and CO_2/N_2 increased significantly. PEI/PVP is a promising carbon membrane precursor, which resulted in good separation performance for CO_2/CH_4 and CO_2/N_2. According to permeation data, it is confirm that the gas separation performance of prepared PEI/PVP-based carbon membranes significantly better than its polymer precursor.

1. Introduction

In 1980s, the developments in the field of gas separation by membranes were accelerated by the developments of synthetic polymeric membrane and became a commercial process on a large scale. During this period, significant progress were made in every aspect of membranology, including improvements in formation of membrane, chemical and physical structures, configurations, and applications [1]. Nevertheless, the utilization of polymeric membrane in rigorous environment has been restricted by their poor chemical and thermal resistance. The shortcomings of polymeric membranes have motivated the researchers to study other alternative materials for membrane separation in order to defeat the present challenges and competition in current separation technologies. Carbon membranes with excellent thermal and chemical resistances have come into the contest, where it exhibit high separation performance compared to their polymeric precursor membranes [2,3]. Most of the prepared carbon membranes are still in research stage due to the several factors such as low mechanical strength, high production cost, and vulnerable to adverse effect from expose to organic contaminants and water vapor. Thus, an extensively studies have been done by various research group around the world to produce high performance carbon membrane with excellent mechanical strength, acceptable cost, and long life membrane so that the membranes can be applied in industrial scale.

The separation properties of the produced carbon membrane largely depend on the type of their polymeric precursor. Several polymers that have been extensively studied are polyimides [4–13], polyetherimide (PEI) [14–19] and phenolic resin [20–23]. However, most of the polymer precursors used to fabricate carbon membranes are commercially expensive materials and even some of them are exclusively obtained at laboratory scale. Therefore, the works developed in this study focus on the use of relatively inexpensive and commercially available polymers as precursors of carbon membranes. In this work, PEI was selected as a starting material for carbon membrane fabrication, especially for its cost compared to other polyimide polymers, availability and polyimide-like structure. The early study on the preparation of carbon membranes from PEI was conducted by Fuertes and Centeno on 1998 [14]. A year later, Sedigh et al. [16,17] had prepared PEI-coated mesoporous tubular support for CO_2/CH_4 and H_2/CH_4 separation. After that, there was not much research involving the use of PEI as a precursor for carbon membranes applied in gas separation until in 2008, when Rao and coworkers [19] prepared their supported carbon membrane from PEI precursor. Even the studies on the structural morphology of PEI-based carbon hollow fiber membrane have reported by Coutinho and coworkers [18], but there is no permeation data and separation performance are measured. In the case of using PEI as precursor to the produced carbon hollow fiber membrane for gas separation, this article will be the first to report on the gas separation performance.

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Besides using pure polymer as precursors, an approach on the use of blend polymer has attracted many researchers in the preparation of carbon membrane. An early work regarding the use of polymer blend as a carbon material precursor was disclosed by Ozaki and coworkers [24]. Usually, the blended polymer was consisting of thermally stable polymer and thermally labile polymer. The pyrolysis of blended polymers led to the creation of two different porous carbon structures; larger pores derived from thermally labile polymer and microporous pores created from the thermally stable polymer. Kim et al. [25] successfully fabricated carbon membrane from PI/PVP blends by controlled pyrolysis. It is shows that the gas permeability through the carbon membranes was enhanced by the introduction of thermally labile polymer, which was PVP and decreased as the final pyrolysis temperature was increased. It is believed that the pore structure of the resultant carbon membrane can be controlled by the introduction of the thermally labile polymer in the precursor. Thus, in this work, PVP was used as a second polymer to produce PEI/PVP precursor polymer blends. An intensive study on the preparation of carbon membrane from PPO/PVP precursor have been done by Lee's group [26,27].

Carbon membrane can be divided into two categories: unsupported and supported carbon membranes. Supported membranes have two different configurations: flat and tubular while unsupported membranes consisted of three configurations: flat sheet, hollow fiber, and capillary [28]. In supported carbon membrane preparation, the support material need to be coat several times with polymer solution and the dried membrane was tested with He and N_2 to insure that the layer was free of any pinholes. An ideal He/N_2 separation factor of 20–25 was used as the yardstick, indicating that a relatively defect-free selective layer had been prepared prior to heat treatment process [16]. In other cases, the cycle of polymer deposition-pyrolysis also needs to be repeat several times in order to obtain an almost defect-free carbon membrane [14,15]. Thus, self-supporting membrane without repeating polymer deposition and pyrolysis step such hollow fiber was chosen as a membrane configuration in this work. Carbon hollow fiber membrane are also more practical and suitable to be apply in industry due to low production cost, exhibit high separation efficiency, and high active surface area to volume ratio compared to other types of configuration.

To date, paper work regarding the systematic studies on the gas permeation properties of the derived carbon membranes from PEI/PVP using hollow fiber geometry is still not sufficient. Thus, the aim of this work is to focus on the use of PEI/PVP polymer blends as precursor of carbon hollow fiber membranes for gas separation application. The influence of the pyrolysis temperature on the permeation performances was investigated and the results were compared with their polymeric precursor membranes. To expand the knowledge on the transport characteristics of these carbon membranes, extensive pure gas permeation tests were performed at different feed pressure for N_2, CO_2 and CH_4 gases and the selectivity of CO_2/CH_4 and CO_2/N_2 separation were determined.

2. Experimental section

2.1. Materials and fabrication of PEI/PVP-based polymeric hollow fiber membranes (precursor)

A commercially available PEI, Ultem 1000 was chosen as main polymer precursor in this study. This polymer was blended with PVP (Fluka, K90). The polymer was dried overnight at 120 °C prior use. *N*-methyl-2-pyrrolidone (NMP) was used as the solvent of PEI/PVP to prepare the polymeric hollow fiber membranes. Polydimetylsiloxane (Sylgard-184) supplied from the Dow Corning was used as the coating material using *n*-hexane as a solvent. The asymmetric hollow fiber membranes were fabricated by a simple dry/wet spinning process. A dope was prepared by dissolving 6 wt.% of the PVP in a NMP at 80 °C. After that, 17 wt.% of the PEI was added to the dope. To prevent agglomeration, the powder form of PVP was gradually added followed by PEI pellets. The dope of PEI-based containing PVP was stirred for about 24 h to produce a completely homogeneous solution. At this stage, optical clarity of the solution was used for the assessment of polymer miscibility. Then, the homogeneous dope was degassed in ultrasonic bath (Branson Ultrasonics) for 24 h in order to remove the gas bubble present in the dope. The existence of gas bubble in the dope will stimulate the formation of poor polymeric hollow fiber membrane. The detail methods used in dry/wet spinning process have been described elsewhere [29]. The spinning conditions used in this study were listed in Table 1. The produced hollow fiber membranes were coated with a mixture of 3 wt.% silicone (Slygard 184, Dow Corning) and 97 wt.% *n*-hexane for 15 min to seal any defects present on the hollow fiber surface. After coating, the membrane was stored in a clean environment to allow curing. Finally, the polymeric hollow fiber membranes were ready for pyrolysis and testing.

2.2. Preparation of PEI/PVP-based carbon hollow fiber membranes

The heat treatment was carried out by placing the precursor membrane at the center of Carbolite (Model CTF 12/65/550) wire wound tube furnace with Eurotherm 2416CC temperature control systems as presented in Fig. 1. In the first step, the precursor membranes were heated to 300 °C under compressed air flow (200 ml/min) with a heating rate of 3 °C/min. At this stage, the membranes were held for 30 min and stabilized membrane was obtained. In second step, the temperature was increased to three different final pyrolysis temperatures (550, 650 and 800 °C) with the same heating rate and hold for 30 min under N_2 flow (200 ml/min). At last, the furnace was allowed to cool gradually to room temperature. The detailed heat treatment protocol is illustrated in Fig. 2. The nomenclature of resultant carbon hollow fiber membranes is given in the form of CM-pyrolysis temperature.

2.3. Characterizations of PEI/PVP-based polymeric and carbon membranes

Several characterization methods were used to study the carbon membranes fabricated at different pyrolysis temperatures. The weight loss of pure PEI and polymer blends PEI/PVP during heat treatment process was characterized by thermogravimetric analysis (TGA). The analysis was performed with a ramp of 10 °C/min at the temperature ranging from 50 to 900 °C. The outer surface and cross section morphologies of the precursor and carbon hollow fiber membrane were observed under JEOL JSM-5610LV scanning electron microscopy (SEM). The fiber samples were prepared by

Table 1
Dry/wet spinning conditions.

Spinning conditions	
Spinning dope temperature	25 °C
Spinneret dimensions	5.5×10^{-4} m (ID) 0.011 m (OD)
Internal coagulant composition	Distilled water
Internal coagulant temperature	25 °C
Dope extrusion rate (DER)	4.5 ml/min
Bore fluid injection rate	1.5 ml/min
External bath composition	Water
External bath temperature	25 °C
Air gap height	0.08 m