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Preparation of polyaniline asymmetric hollow fiber membranes and investigation towards gas separation performance

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ABSTRACT

In this study, integrally skinned asymmetric hollow fiber membranes have been developed from emeraldine base form of polyaniline (PAni) for gas separation. High molecular weight PAni was synthesized in-house to provide the fresh supply of the polymer. The hollow fiber membranes were prepared using dry-jet wet spinning and the effects of air-gap distance on nascent fiber morphology, their gas permeation and mechanical properties were investigated. The spin-line stresses resulted in the molecular orientation of the polymer which had synergistic effect towards improving the gas performance of the PAni hollow fiber membranes. The induced molecular orientation also resulted in improvement in mechanical properties of the hollow fiber membrane. The use of volatile co-solvent, tetrahydrofuran (THF) assisted in the skin layer formation which showed a substantial improvement in the gas permeation performance of the hollow fiber as the time of evaporation was varied. Present PAni based hollow fibers showed a selectivity of 10.2 for O_2/N_2, 105.6 for H_2/N_2 and 7.9 for H_2/CO_2 with the H_2 and O_2 permeance of about 5.0 and 0.49×10^{-6} cm^3 (STP)/cm^2 s cmHg, respectively.

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1. Introduction

An important concern in membrane gas separations is to produce a membrane that is economically feasible while maintaining a high permeability and selectivity with good mechanical and thermal stability. Since the last two decades until today, remarkable progress has been made in the development of high-performance polymers for gas separation. The potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of the product. This means that both the gas permeability coefficient and the selectivity should be as large as possible. In order to cater for wide range of applications including oxygen enrichment system, carbon dioxide removal and even in the development of novel combined reaction separation system that involved relatively high temperature, study has been channeled in finding the suitable new material for membrane fabrication. For practical gas separation applications, hollow fiber is one of the modules that has been widely used commercially. A hollow fiber module consists of a bundle of very fine membrane fibers packed into a cylindrical housing or shell that provides the desired high packing density [1].

Besides ease of synthesis with economical monomer, polyaniline is thermally stable and chemically stable towards plasticizing gas, CO_2 [2–4]. In addition, polyaniline membrane possesses an added advantage over other polymeric membrane because it has the ability to alter the morphology and structure even once the membrane has been formed upon doping method. Ever since Anderson et al. reported the outstanding gas separation results, research on polyaniline as membrane material has been progressive [5]. They discovered a novel possible solution that enable to alter the membrane morphologies after being cast since polymeric membranes are always hard to predict and impossible to modify after casting especially to cater to a specific applications. Although Anderson's work was an act that is really hard to follow or even to repeat, the polyaniline has been an important material for gas separation membrane ever since. Later, Rebattet et al. followed the doping method by Anderson et al. with additional step of curing the membrane at 120 °C for 2 h prior to doping with strong acid. Although, they did not managed to improve or even replicate Anderson's work, they reported a remarkable selectivity of O_2/N_2 and CO_2/CH_4 of 14 and 78, respectively, with an increase of 15% for smaller gases fluxes and reduce the larger gases permeability by 45% [6]. Prior to Rebattet's work, Kuwabata and Martin had explored a wide range of factors including types of doping counterion, duration and temperature of membrane annealing as well as membrane doping level. They discovered that doping level is the most important factor in modifying the gas separation performance; as doping level increased from 13 to 38%, the selectivities

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