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Densification-induced hollow fiber membranes using crosslinked thermally rearranged (XTR) polymer for CO_2 capture

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ABSTRACT

Since thermally rearranged (TR) polymers were known as high gas permeable and processable materials, fabricating high performance hollow fiber (HF) membranes have been tried using them. However, an unexpected drawback emerged which is the gas productivity loss by thermal densification of skin layers during thermal treatment above their glass transition temperature (T_g). In this work, we used a recently reported crosslinked-TR (XTR) polybenzoxazole to develop a new class of high-flux TR hollow fibers by directly exploiting the thermal densification phenomenon. The TR temperature range (320–460 °C) and T_g (394 °C) were determined by thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The chain rigidity of the XTR polymer increased during an isotherm treatment at its T_g, suggesting a restricted densification. Surprisingly, the undesired pinhole-defects (pore diameter < 5 *nm*) on precursor fibers were perfectly healed after thermal treatment (> 400 °C), forming an ultrathin defect-free skin layer on thermally-densified XTR hollow fiber membranes. The pore-healed XTR hollow fibers exhibited an outstanding CO_2 permeance of ~2300 GPU and a CO_2/N_2 selectivity of 17.4 with a skin thickness of 103 nm.

1. Introduction

Over the past several decades, membrane technology for gas separation has been intensively researched due to its high energy efficiency, low operating costs, and small footprint [1,2]. It is now a proven unit operation in industrial scale production of high purity nitrogen, dehydration of natural gas, and purification of hydrogen gas, to name a few [3]. However, for more pressing separation challenges such as CO_2 capture (CO_2/N_2), membrane performance needs to be improved further to become economically feasible [2].

The efficiency of a gas separation process (*e.g.,* CO_2 capture) is largely dependent on the intrinsic performance of the membrane material itself, generally characterized by its gas permeability and selectivity [4–11]. More importantly, it is necessary to fabricate the materials in a hollow fiber form exhibiting a thin skin layer to maximize process productivity. Due to the second criteria, many novel materials with impressive intrinsic permeability and selectivity can only be used in lab-scale processes. The current consensus is to fabricate membranes with a defect-free ultrathin skin layer using a highly permeable material into a hollow fiber form [12] to obtain both high gas permeance and high packing density.

Thermally rearranged (TR) polybenzoxazole (PBO) is a glassy polymeric material that can be obtained by thermally treating a polyimide precursor with an *ortho*-functional group (*e.g.*, –OH) at high temperatures, resulting in a much higher gas permeability than conventional glassy polymers [13–26]. Notably, the TR precursor (polyimide) can be easily processed into a hollow fiber form exhibiting an asymmetric morphology with a skin layer, suggesting TR polymer as a promising candidate for gas separation applications. However, thermal treatment during TR process inevitably causes the substructure to collapse in hollow fibers, leading to increased skin layer thickness [27,28]. In the work of Kim et al., [27] the theoretical skin layer thickness of precursor fibers increased from 333 nm to 2.39 μm after a TR process step. Woo and Lee et al. [28] reported a similar densification in TR-copolymer (with imide group) hollow fibers.

Xu et al. [29] reported that the thermal densification phenomenon in asymmetric hollow fibers results from the increased polymer chain mobility near the T_g, collapsing small pores just beneath the selective

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