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Fundamental understanding of nano-sized zeolite distribution in the formation of the mixed matrix single- and dual-layer asymmetric hollow fiber membranes

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Abstract

We have revealed, for the first time, the evolution of nano-particle distribution and the mechanisms of nano-particle movement during the formation of single-layer and dual- membranes. Both single-layer and dual-layer mixed matrix hollow fibers have been fabricated using nano-size zeolite beta. It is found that three factors play important roles in determining the nano-particle distribution in the resultant fibers. They are (1) shear within the spinneret, (2) die swell when exiting from the annulus spinneret and (3) elongation drawing in the air gap region. The shear stress induced within the spinneret determines the initial particle distribution. As a result, the particle distributions in both wet-spun single-layer and dual-layer hollow fibers follow the parabolic shape of dope's axial velocity profile in the spinneret. Die swell flattens and levels off the particle distribution, while elongation stretch redistributes the particles to the outer surface with the aid of (1) moving outer surface inward and (2) the outflow of solvents during the phase inversion process. The particle redistribution phenomenon is significantly magnified and enhanced during the co-extrusion of dual-layer hollow fiber membranes with an outer layer made of mixed matrix materials. The proposed causes and mechanisms for particle distribution have been verified by the EDX line scanning spectra of silicon and SEM pictures. Preliminary gas separation data indicate that the outer mixed matrix layer of the as-spun hollow fiber membrane has a defective skin for Knudsen diffusion. Further post-treatment is needed to eliminate defects for gas separation.

Keywords: Mixed matrix membranes; Mixed matrix hollow fibers; Particle distribution; Dual-layer membrane; Shear and elongation effects

1. Introduction

Using selective polymeric membranes for gas separation is a promising process that can compete effectively with the traditional separation processes [1–7]. Efficient gas separation membranes are required to have both high permeance (production) and high selectivity (separation factor). Nowadays, many commercialized asymmetric membranes are still made by means of the Loeb and Sourirajan phase inversion process [8]. Compared with flat membranes, hollow fiber is more favored due to the following advantages: (1) a larger membrane area per volume and (2) good flexibility and easy handling in the module fabrication. The fabrication of single layer asymmetric membranes has been well studied in the literature [1–7].

Dual-layer hollow fiber membranes produced by the co-extrusion of two polymeric solutions represent a technology breakthrough in the hollow fibers fabrication [9–14]. It may provide a solution for the wide application of high performance but expensive materials; because it only uses them for the selective skin layer instead of the whole fiber. It is a simplified process for composite membrane fabrication compared to dip coating. By adjusting the dope viscosity and the

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porosity of the inner layer, the dual-layer hollow fibers can exhibit excellent pressure resistance compared to integrally skinned single-layer hollow fibers.

The intrinsic separation property of a membrane material is as important in determining the final membrane performance as the membrane fabrication technology. The considerable efforts in tailoring the polymer structures to improve the selectivity and permeability have identified several polymers with high separation properties [1–3,15,16]. However, the Robeson upper-bound trade-off curve of polymeric materials [17] has transferred the attention of the researchers partially to inorganic carbon molecular sieves and zeolites with high entropic and size selectivity, and more recently the mixed matrix materials integrating the advantages of molecular sieves and polymers [18–25].

To further expand the applications of mixed matrix materials for membrane applications, one must explore approaches to convert this unique material into useful forms, such as asymmetric flat membranes or hollow fibers. Some progresses have been made. Kulprathipanja et al. developed flat asymmetric membranes for the separation of monosaccharides and polysaccharide [21]. Kiyono et al. has fabricated the mixed matrix hollow fibers for ion exchange [26]. Work on mixed matrix hollow fibers for gas and hydrocarbon separations has also been carried out by Ekiner and Kulkarni [27], Koros et al. [28] and Miller et al. [29]. However, they were released in patents that are aimed at proprietary product development.

To our best knowledge, almost none of the above references reveals the basic science and engineering on the evolution of zeolite distribution during the hollow fiber spinning and teaches young membrane scientists on how to directly control particle distribution across the membranes. Therefore, there is a considerable motivation for us to investigate the formation process of hollow fibers made of mixed matrix materials for both single-layer and dual-layer ones. The particle is zeolite beta with size of around 0.3–0.5 μm; it is a self-synthesized molecular sieve in our lab. For the single-layer hollow fiber, the entire membrane is spun from a solution mixture of mixed matrix materials, while for the dual-layer hollow fiber, the nano-sized zeolite beta particles are added to the outer layer polymeric dope only. A comparison between the single layer and the dual-layer hollow fibers will be made to show the effects of flow behavior and air gap on zeolite distribution in the asymmetric hollow fiber membranes.

2. Experimental

2.1. Materials

Matrimid 5218 purchased from Vantico was the polymer used in this study. The polymer was dried in a vacuum oven at 110–120 °C for overnight before dope preparation; *N*-methyl-pyrolidinone (NMP) from Merck was used as solvent due to its low toxicity. Zeolite beta particles were added to the polymer solutions to form the mixed matrix single or dual-layer hollow fiber. The particles were synthesized in our lab and had an average diameter of 400 nm.

2.2. Dope preparation

The homogeneous polymer solutions were prepared according to the following procedure. The solvent was first stirred at 0–5 °C in an ice bath, followed by the addition of desired amount of polymers; then the temperature gradually increased to room temperature as the ice melted. The solution was agitated with the Eurostar power-control stirrer at a high speed for at least 24 h for the polymer to dissolve completely and homogeneously.

For the heterogeneous polymer solution containing nanoparticles, some modifications were made. First of all, the particles were dispersed to the solvent and stirred for at least 1 day at a high speed of about 400–500 rpm. This procedure forced the particles separate by the high shear rate. The other procedures were the same as for the homogeneous solutions. All the solutions were degassed in the stirring flask for 24 h first and then in the pump for another 24 h before spinning. Table 1 shows the compositions of dopes for the single-layer and dual-layer hollow fibers. The polymer solutions used for obtaining the outer layer and inner layer were referred to as solution OL and solution IL, respectively.

The rheological properties of all the polymer solutions were determined by using an ARES Rheometric Scientific Rheometer with a 25 mm cone-plate fixture under dynamic mode. The relationship between shear stress and shear rate of the dope solutions can be described by the expressions:

$$\text{SL and OL}: \quad \tau = 34.80|\dot{\gamma}|^{0.8572}$$

$$\text{IL}: \quad \tau = 66.87|\dot{\gamma}|^{0.4243}$$

2.3. Hollow fiber spinning

The single-layer hollow fibers were spun according to the procedure described in references [30,31], while the dual layers are described in references [9–12]. The details of the spinning conditions and parameters were summarized in Table 2. The as-spun fibers were taken by a drum and then cut into segments and rinsed in a clean water bath for at least 5 days to remove the remaining solvent. Solvent exchange was carried out by first using methanol three times, each time with 30 min, then *n*-hexane three times, each time 30 min. After being taken out from the hexane, the fibers were dried in the air at room temperature.

2.4. Characterization

The morphology of the resulting membranes was observed by scanning electron microscopy (SEM JEOL JSM-5600LV) or field emission scanning electron microscopy (FESEM JEOL JSM-6700LV). The samples for the SEM