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Formation of defect-free 6FDA-DAM asymmetric hollow fiber membranes for gas separations

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ABSTRACT

This paper reports the formation of defect-free 6FDA-DAM asymmetric hollow fiber membranes. 6FDA-polyimides are of great interest for advanced gas separation membranes, and 6FDA-DAM polyimide is a representative polymer in this family with attractive dense film properties for several potential applications. The work reported here for the 6FDA-DAM polyimide provides insight for the challenging fabrication of defect-free asymmetric hollow fiber membranes for this class of 6FDA-polyimides, which behave rather different from lower free volume polymers. Specifically, the 6FDA based materials show relatively slow phase separation rate in water quench baths, which presents a challenge for fiber spinning. For convenience, we refer to the behavior as more "non-solvent resistant" in comparison to other lower free volume polymers, since the binodal phase boundary is displaced further from the conventional position near the pure polymer-solvent axis on a ternary phase diagram in conventional polymers like Matrimid® and Ultem®. The addition of lithium nitrate to promote phase separation has a useful impact on 6FDA-DAM asymmetric hollow fiber formation. 6FDA-DAM phase diagrams using ethanol and water as non-solvent are reported, and it was found that water is less desirable as a non-solvent dope additive for defect-free fiber spinning. Phase diagrams are also reported for 6FDA-DAM dope formulation with and without the addition of lithium nitrate, and defect-free asymmetric hollow fiber membranes are reported for both cases. The effect of polymer molecular weight on defect-free fiber spinning was also investigated. Gas transport properties and morphology of hollow fibers were characterized. With several thorough case studies, this work provides a systematic guideline for defect-free fiber formation from 6FDA-polymers.

1. Introduction

Membrane separation technology offers energy-efficient, environmentally friendly and compact alternative to conventional gas separation technologies such as distillation, absorption and adsorption in applications, including air separation, hydrogen separation, and natural gas separation [1–3].

A few polymers, polysulfone, cellulose acetate, and polyimides, etc., have been used in commercial membranes [1–3], and there is significant interest in improving the current polymers for higher permeability, selectivity and stability. 6FDA-based polyimides offer high rigidity, and tunable transport properties, due to versatile co-monomer choices and resultant chemical structures [4–13]. For these materials, several polyimides have been investigated extensively for multiple applications. For example, due to the inhibited polymer chain packing and rigid backbone, 6FDA-DAM is one of the most permeable polyimides with moderate selectivity in some gas separation applications [14–16]. 6FDA-DAM is especially useful for butane isomers separation and other cases requiring high flux [4,7].

Besides optimizing the structure of polymers in conventional forms, seeking precursors to advanced materials able to overcome the polymer upper bound is another important direction [17–20]. Inorganic molecular sieves, mixed matrix membranes, and carbon molecular sieves are the most popular options for these advanced materials [21–24]. Mixed matrix membranes require polymers as the matrix, while carbon molecular sieve membranes are prepared from precursor polymers to achieve advanced performance. Due to their attractive intrinsic properties, 6FDA-polymers are often selected as matrix materials for mixed matrix membranes and precursor materials for carbon molecular sieves [7,15,25,26]. For example, 6FDA-DAM/ZIF-8 mixed matrix dense membranes provide excellent performance in propylene/propane separation, which is well above the polymer upper bound [15]. Nevertheless, the formation of defect-free mixed matrix hollow fiber membranes based on the 6FDA polymers has not yet been reported [15,27,28]. The formation of defect-free polymeric fibers is a key first step toward the successful fabrication of defect-free mixed matrix asymmetric hollow fiber membranes.

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In most previous studies with novel polymeric membranes, mixed matrix membranes, and carbon molecular sieve membranes, the focus is primarily upon the most basic membrane format—dense films. Partially, this is due to the ease of dense film membrane fabrication and less complexity compared to the asymmetric hollow fiber. In order to use these materials in a practical way, it is critical to form defect-free asymmetric hollow fiber membranes for large-scale applications [1,3]. Hollow fiber configurations provide the highest surface area to volume ratio, compared to other membrane configurations (plate and frame, spiral wound, etc.), and with a thin separation layer, the productivity can be maximized. Defect-free asymmetric fiber spinning is challenging, even with conventional polymers, and only a few advanced polymers have been reported in defect-free asymmetric hollow fiber form [29–39].

Several defect-free fiber spinning attempts have been performed by previous researchers on 6FDA-polymers. Wallace et al. started the exploration of asymmetric hollow fiber membrane formation based on 6FDA-DAM/DABA (4:1) polyimide [40]. Omole et al. formed defect-free PDMC (1,3-propanediol monoesterified cross-linkable) (3:2) polyimide asymmetric hollow fiber membranes [41]. Chen et al. successfully spun defect-free asymmetric 6FDA-DAM/DABA (3:2) polyimide hollow fiber membranes [42]. Chung et al. developed 6FDA-durene asymmetric hollow fiber membranes [38]. Ren et al. developed nearly defect-free 6FDA-ODA/NDA hollow fiber membranes [43]. Niwa et al. formed defect-free 6FDA-6FAP hollow fiber membranes [39]. Liu explored dual-layer fiber spinning of 6FDA-DAM polyimide on a cellulose acetate support [44]; however, these membranes are not truly defect-free based on lower butane isomers selectivity as compared to the dense film intrinsic value. The formation of defect-free 6FDA-DAM asymmetric hollow fiber membranes, therefore, remains as a very new and challenging topic.

In this paper, 6FDA-DAM fiber spinning is studied in detail to understand why it is challenging. The dope formulation was investigated carefully through several case studies. The effect of the solvent system, the addition of phase separation assistant and polymer molecular weight were evaluated. The knowledge presented here is useful for future endeavors in the formation of defect-free fibers for polymeric membranes, mixed matrix membranes and carbon molecular sieve membranes.

2. Background

Asymmetric polymeric hollow fiber membranes can be fabricated via a dry-jet/wet-quench spinning process [29,30,33–35], as illustrated in Fig. 1. The key spinning parameters are listed in Table 1. During a spinning run, dope (polymer solution) and bore fluid are coextruded from a spinneret into an air gap ("dry-jet") and then immersed into an aqueous quench bath ("wet-quench"). The "dry-jet" step produces the dense skin layer while the "wet-quench" step forms the porous support structure.

Optimization of dope composition, which is comprised of polymer, solvents and non-solvents, is a key to success [29,31,33,34]. A good dope must be "spinnable" (form a fiber upon exiting the spinneret without breaking), and have the potential to form a defect-free skin. Sufficient viscosity is the first factor required to create a spinnable dope. Polymer molecular weight and polymer concentration are key parameters for achieving sufficient viscosity to allow polymer extrusion and take-up as fibers [35,45]. Ternary phase diagrams are constructed via the cloud point technique [29,30], and potentially useful dope compositions should be in the one-phase region and be close to the binodal line. The dope formulation, together with spinning conditions, should drive the outermost region of the nascent fiber to the vitrified region without crossing the two-phase region, since entering the two-phase region may introduce defects in the skin layer. Optimization of the dope formulation step requires several iterations to achieve the desired fiber properties.

Qualitative dope composition trajectories during a spinning process are shown in Fig. 2. Before spinning, the phase boundary (binodal line) is established and the evaporation of volatile components in the dope in the air gap causes the outermost region of the composition to approach the vitrified region, so a dense skin can be formed on the outer layer of fibers. In the water quench bath, non-solvent water diffuses into the polymer solution and induces phase separation in the underlying porous support to provide mechanical strength during the phase separation step. In this way, a desirable asymmetric morphology, a dense layer on top of a porous substructure, is formed.

The hollow fiber configuration is formed by the extrusion of a bore fluid along with the dope. The bore fluid is a neutral fluid which occupies space and can be simply removed during solvent exchange and drying steps.

3. Experimental

3.1. Materials

The structure of 6FDA-DAM is shown in Fig. 3, and it is lab-synthesized via condensation of dianhydride 6FDA with

Table 1
Key parameters in a dry-jet/wet-quench hollow fiber spinning process.

Dope composition	Air gap height	Quench bath temperature
Bore fluid composition	Take-up rate	Quench bath composition
Dope/bore fluid flow rate	Spinning temperature	Humidity

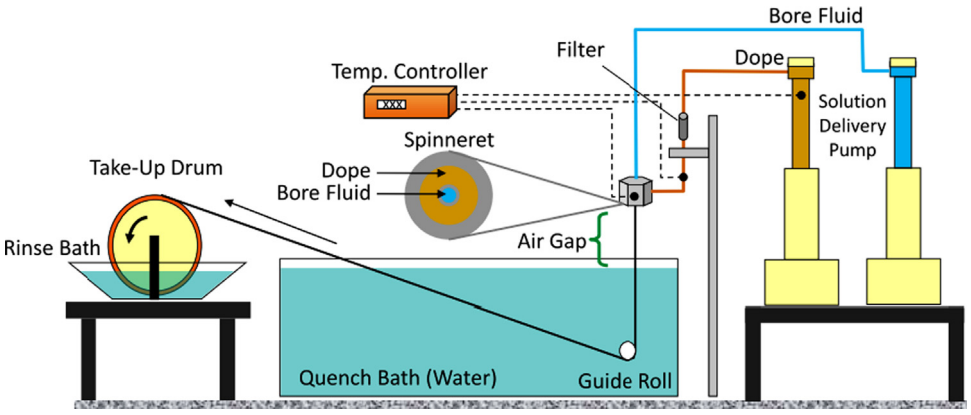

Fig. 1. Schematic of the dry-jet/wet-quench spinning process for asymmetric hollow fiber membrane fabrication.