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Interfacial morphology between the two layers of the dual-layer asymmetric hollow fiber membranes fabricated by co-extrusion and dry-jet wet-spinning phase-inversion techniques

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ABSTRACT

The dual-layer asymmetric hollow fiber membranes were fabricated with Matrimid[®] 5218 as the functional material by using co-extrusion and dry-jet wet-spinning phase-inversion techniques. Different polymers polysulfone (PSf), polyethersulfone (PES) and polyetherimide (PEI), were used as support materials. Different organic solvents *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and dimethylformamide (DMF) were used as solvents in the inner layer spinning dopes. The precipitation order of the two layers was estimated from the cloud point curves for the respective systems. The purpose of this paper was to give out a method to control the interface structure of the dual-layer asymmetric hollow fiber membranes. The experimental result shows that if the inner spinning dope demixes prior to the outer spinning dope, dense skin will form both on the outer surfaces of the two layers, while if the outer spinning dope demixes prior to the inner spinning dope, the dense skin on the outer surface of the outer layer will prevent the formation of the dense skin on the outer surface of the inner layer. The skin morphology investigated by scanning electron microscopy (SEM) proves this result. The double dense skin structure of membranes increases the mass transfer resistance and decreases the gas permeance.

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1. Introduction

Membrane based gas separation process is dynamic and rapid growing due to low capital and operating costs, high energy efficiency and general ease of operation [1,2]. Current applications of membrane gas separation process include nitrogen enriched air, oxygen enrichment, natural gas separation, hydrogen recovery, the separation of volatile organic compounds, etc [1]. Some processes are at the stage of laboratory research, such as light olefin/paraffin separation [3–5], acid gas removal [6,7]. Membranes for gas separation include inorganic membranes, polymeric membranes and mixed matrix membranes [8,9]. The polymer membrane enjoys inherent advantages, such as low cost, desirable mechanical properties and matured technique. In fact, the vast majority of gas separation membranes used commercially are polymer-based, while only a few of them have been used to fabricate the commercial gas separation membrane for one reason or another [1]. Some polymers with excellent performances failed to commercial applications due to the fact that high cost of materials increases the invest cost [10,11]. One of promising methods to apply these expensive materials in gas separation membrane is to

fabricate the composite membranes by using the expensive material with the excellent gas separation performance in a very thin selective layer.

The technique of fabrication of dual-layer asymmetric hollow fiber membranes was invented by Du Pont [12] 30 years ago. This approach has practical value of lowering material costs for membrane fabrication [13] and allows the use of polymers that display excellent gas separation performance but poor mechanical properties [14–16]. And the dual-layer asymmetric hollow fiber membranes fabricated by this technique remain advantages of single-layer hollow fiber membranes: self-supporting structure, high active surface area-to-volume ratio, low resistance to gas flow, easy to fabricate and the ability to be operated at high pressure [17,18]. The dual-layer asymmetric hollow fiber membranes have been developed for gas separation [13–16,19–33], pervaporation [34–36], membrane distillation [37–39], nanofiltration [40] and fuel cell [41], etc. An ideal dual-layer asymmetric hollow fiber membrane for gas separation should have the following characteristics: (1) an ultra-thin and defect free dense skin in the outer layer, (2) delamination-free structure for long term use and high pressure endurance, and (3) low resistance in the inner layer and the interface between the two layers [20].

Some works have demonstrated the methods to fabricate the dual-layer hollow fiber membranes with an ultra-thin dense-selective layer for gas separation [14,19,33]. Some works focused

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on the morphology of the dual-layer hollow fiber membranes and fabrication the delamination-free dual-layer hollow fiber membranes [23,25–27,31]. Jiang et al. [35] revealed the importance of interface structure in overall membrane transport property for dual-layer asymmetric hollow fiber pervaporation membranes formed by co-extrusion. While few studies revealed the method to reduce the resistance between the two layers of the dual-layer asymmetric hollow fiber membranes. Yoshinaga et al. [29] found the decrease of the polymer concentration in the inner spinning dope improved the permeability. Widjojo et al. [20,23] reduced the substructure resistance by addition of Al₂O₃ nanoparticles into inner layer spinning dope. The nanoparticles produced large pores not only on the inner layer's outer surface but also on bulk. The nanoparticles also retained the porous structure morphology in the course of heating treatment. Jiang et al. reported that the coagulant temperature [24] and non-solvent (ethanol) [42] in inner layer affected the morphology of the outer skin of the inner layer.

In our previous work [22], the experimental result indicates that the composition of the spinning dope plays an important role in the structure of the interface between the two layers of the dual-layer asymmetric hollow fiber membrane. In this study, a commercial polyimide, Matrimid[®] 5218 was used as the outer layer material. Matrimid[®] 5218 has permeation properties near the O₂/N₂ upper bound and excellent mechanical strength [43,44], and has been used to fabricate high performance membranes [11,44,45]. The compositions of the inner spinning dopes were adjusted by using different polymer, different solvent and different non-solvent content. And the effect of the composition of the inner spinning dope on the structure of inner layer outer skin for the dual-layer asymmetric hollow fiber membranes was

investigated. The objective of this paper was to show that the composition of the inner layer spinning dope influenced the precipitation order of the inner and outer layers and then determined the interface structures.

2. Experimental

2.1. Materials

Matrimid[®] 5218 (Vantico, USA) was used as the outer layer material. Table 1 summarizes the typical permeation properties of Matrimid[®] 5218 [43]. Polysulfone (Amoco, USA), polyethersulfone (Jilin Hi-Tech material Co., Ltd, PR China) and polyetherimide (General Electric, USA) were selected as the inner layer materials because of excellent mechanical property and low cost. The chemical structures of polymers are shown in Fig. 1. The polymers were dried at 100 °C under vacuum for 12 h before use. *N*-methylpyrrolidone (NMP, purity 99.8%, Tianjin Kermel Chemical Reagent Development Center, PR China) and tetrahydrofuran (THF, purity 99.0%, Tianjin Kermel Chemical Reagent Development Center, PR China), dimethylformamide (DMF, purity 99.5%, Tianjin Kermel Chemical Reagent Development Center, PR China) and *n*,*n*-dimethylacetamide (DMAc, purity 98.0%, Tianjin Fuyu Fine Chemical Co., Ltd, PR China) were selected as polymer solvents to prepare the spinning dopes. The solvents were dehydrated with 4 Å molecular sieves (Dalian Hongda Chemical Co., Ltd, PR China) in glass solution bottles before use. Methanol (MeOH, purity 99.5%, Shenyang Chemical Reagent Factory, PR China) and *n*-hexane (Purity 98.0%, Tianjin Fuyu Fine Chemical Co., Ltd, PR China) were used for the solvent change. The gases, N₂ and O₂, with purities of 99.9% (Ka Na Science Technology Development Co., Ltd, PR China) were used as-received.

2.2. Fabrication of the dual-layer asymmetric hollow fiber membranes

The spinning dopes were prepared by mixing polymers, solvents and non-solvents in three-neck flasks at 40 °C, until the polymers were dissolved completely. The homogeneous dopes were poured into dope jars and degassed for at least 24 h before use. The spinneret

Table 1

Typical permeation properties of Matrimid[®] 5218.

Permeability of pure gases (Barrer ^a)		Ideal selectivity
P_{O_2}	P_{N_2}	O ₂ /N ₂
1.32–1.34 ^b	0.185 ^b	7.2 ^b

^a 1 barrer = 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹.

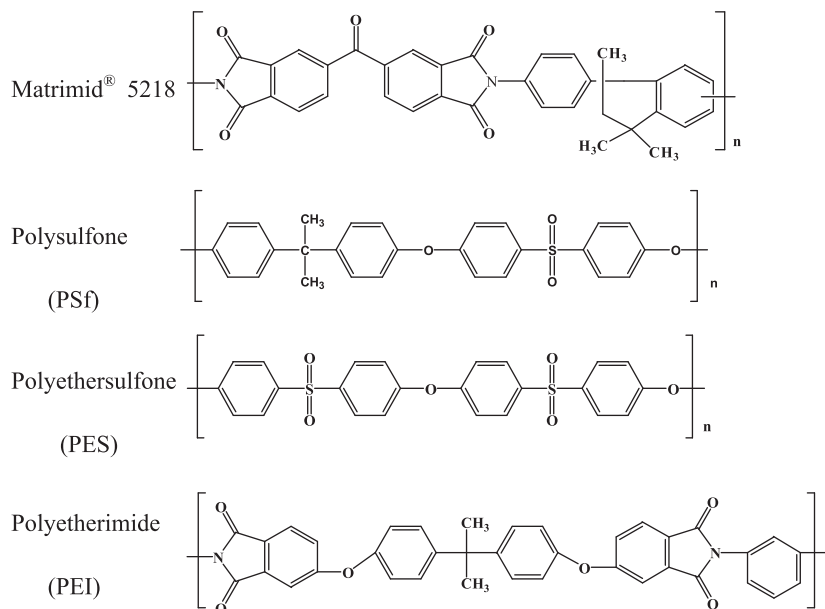


Fig. 1. Chemical structures of Matrimid[®] 5218, polysulfone, polyethersulfone, and polyetherimide.

^b Pure gas permeation measurement for O₂ and N₂ at 500 psi, 25 °C.

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