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Tri-bore ultra-filtration hollow fiber membranes with a novel triangle-shape outer geometry

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ABSTRACT

The hollow fiber membrane with a multi-bore configuration has attracted much attention in recent years due to ease of potting during module fabrication and improved mechanical stability. The conventional multi-bore hollow fiber consists of seven or three bore channels and a round-shape outer geometry. In this work, novel tri-bore hollow fiber membranes made of Matrimid® and polyethersulfone (PES) materials with regular triangle-shape outer geometry have been fabricated. The fabricated membranes are advantageous in terms of uniform mechanical strength and enhanced permeation properties due to the evenly distributed membrane wall thickness. Experimental results suggest that the combined effects of rapid phase inversion, die swell, outer surface shrinkage and stress balance during the membrane formation are responsible for the unique membrane geometry. The micro-morphology, mechanical strength, pore size distribution and ultra-filtration rejection of the fabricated membranes were examined. We believe this work may provide useful insights for the fabrication of triangle-shape tri-bore membranes with other materials for various applications.

1. Introduction

In the past 40 years, polymeric membranes with the hollow fiber configuration have been widely used in various separation processes because this configuration has the advantages of high surface area, self-mechanical support, excellent flexibility and ease of handling during module fabrication [1,2]. The conventional hollow fiber membrane has a single-bore geometry. Over the past years, extensive studies have been performed in order to better understand the spinning process and to fabricate hollow fibers with higher performance for various applications [3–8]. However, there are increasing concerns about long-term stability and potting durability of the modules made from conventional single-bore hollow fibers. The capillary phenomenon which sucks epoxy into the membrane module often happens during the module potting [4,5,9,10]. Fine follow fibers also break and entangle one another during continuous operations, especially under shaking, aeration, backwash or mechanical cleaning [11,12]. For example, the clogging and breakage of fine ultra-filtration (UF) membranes have become the major difficulties in daily operation of membrane bioreactors (MBR) [13].

In recent years, a new generation of hollow fiber membranes with multi-bore configuration shows potential to overcome the drawbacks of conventional single-bore hollow fibers. Multibore® UF was the first commercial polymeric UF hollow fiber membrane that adopted this configuration with seven bore channels [14]. Very promising results were reported including an obvious reduction in energy consumption [15]. After the seven-bore hollow fiber, Hyflux launched another series of tri-bore UF hollow fiber membranes based on polyethersulfone(PES) and polyvinylidene fluoride(PVDF) materials. The molecular cut-off (MWCO) values of tri-bore PES and PVDF membranes are 150 k and 200 k Dalton, respectively [16].

Recently, Chung and his co-workers pioneered a series of seven-bore PVDF and polyacrylonitrile (PAN) membranes with various dimensions, configurations and pore sizes for membrane distillation (MD) and filtration applications [17–20]. In their works, the detailed formation mechanisms and spinning parameters were explored. The seven-bore MD hollow fibers fabricated from the optimized spinning conditions not only demonstrated high permeation fluxes and energy efficiency, but exhibited superior stability and robustness in long-term operation tests [18]. Credit to the superior mechanical stability, there was not a single fiber broken or damaged during all the experiments. Other groups also published related works with multi-bore membranes fabricated from the ethylene vinyl alcohol (EVOH) copolymer or PES polymer for applications including nanofiltration (NF) and UF [21,22].

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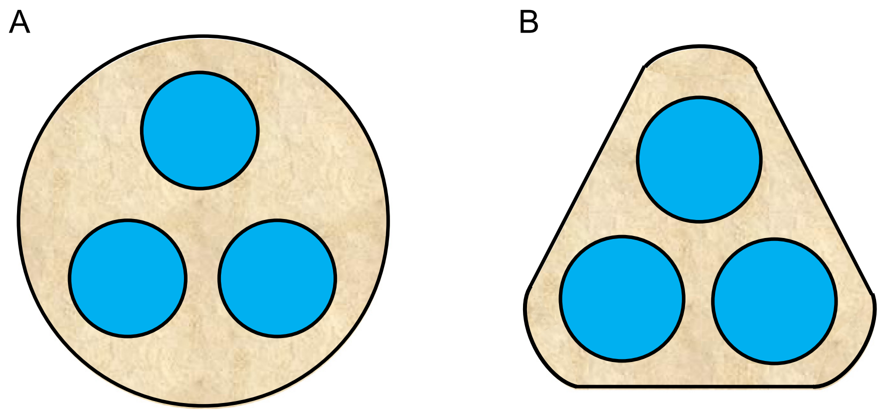

Fig. 1. Illustration of tri-bore hollow fibers with (A) round and (B) triangle outer geometries.

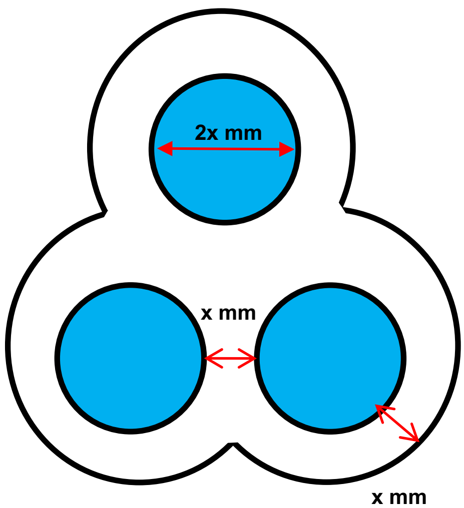

Fig. 2. The bottom view of a three needle blossom spinneret.

As illustrated in Fig. 1A, the shape of current multi-bore hollow fibers consists of a round-shape outer geometry. The main drawback of this geometry is the non-uniform wall thickness. The thinner part of the membrane wall suffers as the mechanically weak point while the thicker part generates additional mass transfer resistance. Therefore, we aim to fabricate a novel tri-bore hollow fiber with round-shape bore channels but a triangle-shape outer geometry. As demonstrated in Fig. 1B, the proposed geometry exhibits a much more uniform wall thickness, which could balance the mechanical strength and reduce mass transfer resistance. In addition, it is anticipated that very different behaviors in module fiber packing, flow distribution and inorganic/organic fouling may be observed when using these triangle hollow fibers [15,23,24]. Two different materials, namely, Matrimid® and PES, were chosen to demonstrate the technology. We believe this work may provide useful implications towards tri-bore membranes with better performance, improved resistance in harsh operation environments and easy module preparation.

2. Experimental

2.1. Materials

Commercially available Matrimid® 5218 and Radel® A PES were purchased from Vantico Inc. and Solvay Advanced Polymer, L.L.C., GA, respectively. N-methyl-2-pyrrolidone (NMP, $>99.5\%$), ethylene glycol (EG, $>99.0\%$), diethylene glycol (DEG, $>99.0\%$) and polyethylene glycol 400 (PEG400, Mw=400 g mol^{-1}, $>99.0\%$) were used as the solvent and additives in the fabrication of hollow fiber membranes. A mixture of glycerol (Industrial grade, Aik Moh Paints & Chemicals Pte. Ltd, Singapore) and water (50/50 wt%) was used to post-treat the as-spun hollow fibers. Polyethylene glycols (PEG, Mw=20,000 g mol^{-1}, and Mw=12,000 g mol^{-1}, Mw=10,000 g mol^{-1}, Mw=6000 g mol^{-1}, Mw=1000 g mol^{-1}, Merck) were used to characterize the molecular weight cut-off (MWCO) and mean pore size of the hollow fibers. The deionized (DI) water was produced by a Milli-Q unit (Millipore) with a resistivity of 15 MΩ cm.

Table 1
Spinning conditions of tri-bore Matrimid® hollow fiber membranes with different dope flow rates.

Membrane ID	TBF1	TBF2	TBF3
Dope composition (wt%)	Matrimid®/EG/NMP: 16/17/67		
Dope flow rate (ml min^{-1})	5	4	3
Bore fluid (wt%)	NMP/DEG/H_2O: 10/25/65		
Bore flow rate (ml min^{-1})		4	
External coagulant (wt%)	IPA/water: 60/40		
Air gap (cm)		3	
Take up speed		Free fall	

2.2. Spinneret design and hollow fiber membrane fabrication

The tri-bore hollow fiber membranes were fabricated via a dry-jet wet phase inversion spinning process by a specially designed tri-bore spinneret with a blossom geometry, as shown in Fig. 2. The tri-bore spinneret had three needles, which distributed uniformly within the spinneret. Certain distance between channels was employed to avoid the potential intra-bore crossing of nascent fibers resulting from die swell phenomena. It should be noted that this geometry was designed not to fabricate a tri-bore membrane with a blossom geometry. The main purpose was to ensure a uniform extrusion gap for the polymer dope and also to generate enough shear stress when the dope was extruded. Similar phenomenon was reported by Cufaz et al., where the circular fiber can be obtained even a micro-structured irregular spinneret was used [25]. Owing to the polymer chain relaxation and die swell effect, the nascent fiber was expected to exhibit a smoother outer surface, i.e., round shape [20,26]. Other proprietary know-hows and patented designs were also applied to achieve a more uniform distribution of dope solutions at the spinneret outlet [18].

In order to effectively control the phase inversion during membrane formation and obtain the desirable membrane structure and morphology, the dual-coagulation bath spinning technology was applied. The details of the dual-bath spinning process