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Facile fabrication of reinforced homoporous MF membranes by in situ breath figure and thermal adhesion method on substrates

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ABSTRACT

Homoporous membranes are promising for size-sieving filtration, but their prospect is restricted by the lack in mechanical strength. A facile and low-cost route based on in situ breath figure and thermal adhesion method is proposed to fabricate the reinforced homoporous MF membranes in this research. The substrates specific to this route are fabricated by PVDF coating and then ice sealing on nonwoven fabrics. On the tailor-made substrates, the porous film is formed as usual by the breath figure method, and then immobilized on the substrate conveniently by PVDF melting. Acetone is introduced into the casting solution with intent to accelerate solution spreading on ice surface and facilitate micron-scale water droplets floating down to the solution film, so that the resistance layer could be formed thinner and abundant in perforated pores to attain high water permeation flux. Four usually used homoporous membrane materials, i.e., PSF, PES, PPO and PEI, have succeeded in membrane fabrication. FE-SEM images reveal that membrane pores are perforated and homogeneous with controllable size, again the homoporous layer is tightly adhered on substrate. Water permeation, particle sieving and regeneration tests indicate that the reinforced homoporous membranes made by this novel method are practicable for high-resolution separation under moderate pressure and long-time service.

1. Introduction

The micro- and nano-scale particle materials possess unique size-dependent properties, which have promising applications in many fields [1–4]. However, the general strategies can only synthesize particles with wide size distribution. In this instance, the high-resolution separation has been one of the crucial procedures for preparing particles with uniformed size and intensive performance [5–8].

Uniformed porous membranes have attracted extensive attention for high-resolution separation [9–14]. Many approaches, e.g., track etching, anodization, micro-fabrication and self-assembly, are attempted for preparing perforated and uniformed porous membranes [15–18]. Hereinto, self-assembly is a promising alternative to fabricate ultrathin perforated membranes, with the advantage to achieve high-resolution separation with high flux and low flow resistance [19–22]. In comparison to the other self-assembly routes, the breath figure-driven templating strategy can be inexpensive with common engineering plastics as film matrix, e.g., polystyrene (PS), polysulfone (PSF), cellulose acetate (CA) [23–28], and the prepared membranes possess highly uniformed pores on the micrometer scale for size-sieving separation [29–32].

In order to meet the mechanical strength for pressure-driven filtration, the ultrathin porous medium fabricated by breath figure method should be cautiously transferred from the dense substrate onto the porous support [33–36], although some literatures have stated that the integral preparation coupling breath figure method and phase inversion can construct self-supported membranes [37–40]. It is unfortunate that the ultrathin porous film might be cracked or wrinkled in transfer process, due to the structure and the material inherent nature, which is disadvantageous to both separation performance and mechanical durability [41]. Again, the interfacial adhesion between the size-sieving film and the supports is another critical procedure, because the back flushing should be frequently conducted to migrate fouling and make membrane serviceable durably [42,43].

How to make the porous supports adaptive for breath figure means and cohesive to the size-sieving film is critical to achieve the transfer-free strategy. Referring to the substrates usually used for breath figure method, the porous supports should be pore-blocked and flatted with the gutter layer [44,45]. In this instance, the highly diluted polymer solution can be reserved on the substrate surface for porous film

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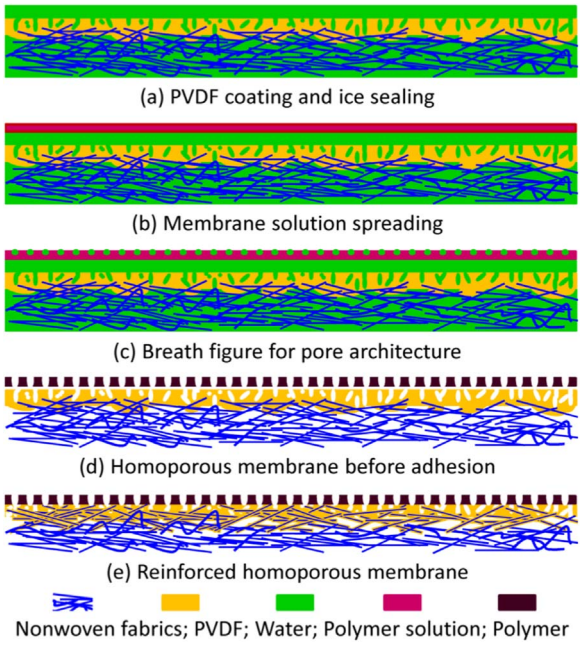

Fig. 1. Schematic microstructure and evolution of reinforced homoporous membranes.

fabrication. In addition, the gutter layer should be removable so that the pores can be perforated in the composite membranes after removing the gutter layer. Much more, it is expected that the gutter layer material could be retained partially between the supports and the size-sieving film as the adhesive to stick them together tightly.

In the present work, a facile and low-cost technique is presented to prepare the composite substrate in response to the requests above. In detail, the commercial nonwoven fabrics are successively coated with the low-melting-point polymer for adhesion and flatted with thin ice for pore-blocking. With the melting point much lower than the other frequently used membrane materials, polyvinylidene fluoride (PVDF, 172 °C) is selected as the adhesion material. Several common engineering plastics with high melting point, e.g., polysulfone (PSF, 280 °C), polyethersulfone (PES, 360 °C), polyetherimide (PEI, 275 °C), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, 368 °C), are attempted for fabricating the homoporous membranes on the specific substrates. The membrane synthesis scheme, together with the schematic membrane microstructure, have been shown in Fig. 1. Based on the conveniently modified nonwoven fabrics, the transfer-free strategy is succeeded in fabricating size-sieving membranes.

2. Experimental

2.1. Materials and reagents

PET nonwoven fabric with high thermal stability was purchased from Ahlstrom (Helsinki, Finland). PVDF in powder form was provided by Dongyue Group (Shandong, China). PSF (Udel P-3500) and PES (Radel A-200) in pellet form were purchased from Amoco Performance Products. PPO in powder form was provided by Institute of Chemical Engineering (Beijing, China). PEI (Ultem 1000) in pellet form was purchased from SABIC Innovative Plastics Inc. All these polymer materials were dried in a vacuum oven at 110 °C for 10 h prior to be used. N-methyl-2-pyrrolidone (NMP), dichloromethane, chloroform and acetone (analytical grade) were purchased from Kemiou (Tianjin, China) and directly used without further purification. Commercial microfiltration membranes were obtained from ANOW (Hangzhou, Chain) for comparison. The nominal pore size is 1.5 μm. Two kinds of silica microsphere particles, synthesized by hydrothermal method, were purchased from Aladdin (Shanghai, China) for the size sieving test. Their mean sizes are about 0.5 μm and 1.8 μm, respectively.

Table 1
Details about the polymer solutions for homoporous membrane fabrication.

Sample code	Polymer	Solvent	Composition/wt%		
			Polymer	Solvent	Acetone
M-1	PSF	CH_2Cl_2	2.0	98.0	0.0
M-2	PSF	CH_2Cl_2	2.0	95.0	3.0
M-3	PSF	CH_2Cl_2	2.0	93.0	5.0
M-4	PPO	$CHCl_3$	0.5	96.5	3.0
M-5	PES	CH_2Cl_2	0.5	96.5	3.0
M-6	PEI	CH_2Cl_2	1.5	95.5	3.0

2.2. PVDF coating and ice sealing for porous substrates

Nonwoven fabrics were scrubbed by acetone to remove stains before the use. Coating solution was prepared by dissolving PVDF (6.0 wt%) in dehydrated NMP. The solution would be evenly spreading on the fabrics with the thickness no more than 50 μm using a casting machine. Nonwoven fabrics after solution coating were immediately immersed into the deionized water for coagulation. Subsequently, the coated nonwoven fabrics would be washed in the stirred coagulation bath for 24 h to fully remove the solvent NMP. In the end, PVDF-coated nonwoven fabrics were directly transferred from the bath into the refrigerator at − 20 °C, and they should be flatted and fixed horizontally on the thick glass for freezing and ice sealing. The microstructure of the substrates was schematically shown in Fig. 1.

2.3. Reinforced homoporous membrane fabrication

The polymer solutions for homoporous membrane fabrication were prepared with the compositions listed in Table 1. Hereinto, the polymer concentration was directly referring to the experimental data in literature [40,43,45–46]. Considering that the solvents were immiscible with water, acetone was added after solving polymer pellets or powder thoroughly in the solvent to accelerate solution spreading on the ice surface. Acetone concentration in the PSF solutions were changed to analyze its action. On the basis, the appropriate dosage was directly adopted for the other membrane casting solutions.

Homoporous membrane fabrication was carried through in the humidification system assembled in the laboratory, as shown in Fig. 2. In this home-made batch system, only one spray nozzle is used to distribute the moist nitrogen. It is appropriate to tailor the PVDF-coated substrate with diameter close to 25 mm. Nevertheless, the reinforced homoporous membrane could be fabricated with much larger area while multiple nozzles are arranged in matrix with the pitch distance no more than 20 mm. In the case that nine nozzles are employed, the sample could be enlarged into 60 mm × 60 mm.

Membrane fabrication process and conditions are expounded as follows. Nitrogen was humidified with the relative humidity close to

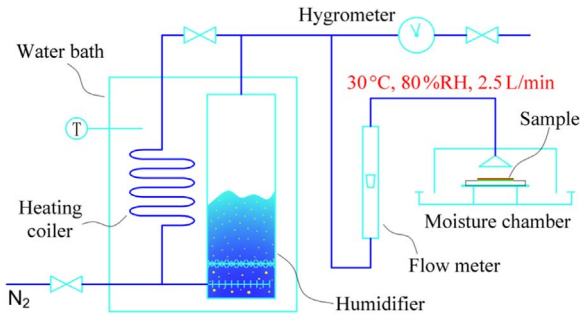

Fig. 2. Humidification system assembled for homoporous membrane fabrication.