Materials Letters 143 (2015) 315–318

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Polymeric hollow fiber membranes prepared by dual pore formation mechanism

Yingbo Chen *, Xinping Hu, Xiaoyu Hu, Shifeng Zhang, Yufeng Zhang

School of Materials Science and Engineering, State Key Laboratory of Hollow Fiber Membrane Materials and Process, Tianjin Polytechnic University, Tianjin, 300387, China

ARTICLE INFO

Article history:
Received 25 September 2014
Accepted 3 December 2014
Available online 12 December 2014

Keywords:
Microstructure
Porous material
Hollow fiber membrane
Dual pore formation
Phase separation
Dye separation

ABSTRACT

Novel hollow fiber membranes were developed by dual pore formation mechanism. The formation mechanism of hollow fiber membranes spun through single orifice spinneret was explained by combination of foaming reaction and conventional non-solvent induced phase separation. Structure of the hollow fiber membranes was examined by scanning electronic microscopy and BET analysis. The hollow fiber membranes have excellent mechanical property and can be used for dyes separation. The highly tunable hollow fiber membranes possess promising applications in separation.

1. Introduction

Membranes have been widely used in numerous separation processes for their advantages of excellent combination of selectivity and productivity, energy or space saving. Among them, hollow fiber membranes (HFMs) are favored for a larger effective membrane area per unit volume of the separation device, good mechanical property and easy of handling in comparison to other types of membrane configuration [1,2]. Non-solvent induced phase separations (NIPS) are the dominant in preparation of HFMs, which allows for the conformation of various morphologies and physicochemical properties for various applications [3–6]. However, a coaxial spinneret and proper additives are needed for fabricating hollow fiber membranes with desired properties and morphologies [7,8]. The inner channel of the coaxial spinneret forms the bore of the hollow fiber membranes and makes the self-supported membranes have bad resistance to compression. Addition of these additives tends to create a spongy membrane structure by preventing finger-like macrovoid formation, enhancing pore formation, and improving pore inter-connectivity [9–13]. However, the additives usually result in deteriorating the mechanical strength of the hollow fiber membrane. Some novel NIPS processes have been developed to fabricate HFMs with better performance, [14–21] such as phase separation micromolding, honeycomb porous structure through 'breath figure' and self-assembly of block copolymers while NIPS.

In the present work, polymer foaming combined with NIPS was used to produce well-performed HFMs directly by pre-adding small amount of foaming agent and a single orifice spinneret. In this method, two processes occurred almost simultaneously. One process was the reaction of foaming agent to produce gas, and another process was the conventional NIPS in the presence of gas. These two processes were contributed to formation of the various pores in HFMs through different mechanisms, thus we called the method as dual pore formation mechanism. HFMs prepared by dual pore formation mechanism have better mechanical property than that of HFMs through conventional NIPS due to the absence of large amount of pore forming agent. Moreover, the single orifice process is much convenient compared to conventional NIPS process.

2. Materials and methods

Dope solutions containing 18 wt% polysulfone (PSf) (Solvay Advanced Polymers), varied amount of sodium borohydride ($NaBH_4$ 0.1–1.2 wt%), and dimethylacetamide (DMAc) were used to prepare the hollow fiber membrane. The PSf hollow fiber membranes were spun through a single orifice spinneret (1 mm inner diameter, horizontal to the water bath) directly into the coagulation bath (pH=1, 2 HCl aqueous solution or DI water) at extrusion rates of 0.1, 0.3, and 0.5 mL/min by a syringe pump. The hollow fiber membranes were kept in the coagulation bath. These prepared hollow fiber membranes were immersed in DI water for 24 h to remove the residual solvent in the membranes, and then immersed in 30 wt% glycerol aqueous solution for 24 h and dried in air at room temperature for 6 h. The HFMs were

* Corresponding author.
E-mail address: bocy2009@hotmail.com (Y. Chen).

http://dx.doi.org/10.1016/j.matlet.2014.12.023
0167-577X/

characterized using SEM, universal tensile machine and BET adsorption. the pure water flux and rejection of the HFMs were tested with home-made equipment. The details of the characterization and performance testing were described in supporting materials.

3. Results and discussion

Dual pore formation mechanism: The HFMs prepared by dual pore formation mechanism were much different from HFMs by conventional NIPS. They contained thin skin layer, finger-like pores, sponge pores and bore (Fig. 1a–c). However, their skin layer was very thin and dense (4 μm in thickness and 3.06 nm in average pore diameter) over the finger-like pores (40 μm). The thin skin layer and the short finger-like pores were formed soon after the polysulfone solution extruding to water followed by a fast NIPS process. After that, water diffused through the skin layer and finger-like pores, to react with sodium borohydride as well as to induce phase separation of the inner part polymer solution. Because of the formation of the dense skin layer, diffusion of water was slowed down, which made phase separation of polysulfone solution delay, and thus resulted in the sponge pores under the finger-like pores. At the same time, hydrogen gas was produced through water reacting with sodium borohydride. Hydrogen gas tended to diffuse into the polymer solution side, since the outer side was the solid dense skin layer. Initially, gas bubbles took the place of the polymer solution and formed macrovoids embedded in the sponge pores. Moreover, the gas bubbles contacting the polymer solution hindered contra-diffusion of the solvent and non-solvent, which further delayed phase separation of the polymer solution. More gas was produced with time and gathered to the center to form the bore of the HFMs. The process of HFMs in this work did not use bore flow solution, which brought a highly porous inner surface (Fig. 1d). The bore was not straight as that of HFMs from conventional NIPS. Many macrovoids connected the sponge pores and the bore (Fig. 1e and f).

Effects of fabrication conditions on structure of HFMs: The structures of the HFMs prepared by dual pore formation mechanism were highly tunable. A bore-free fiber membrane can be fabricated by dual pore formation mechanism with higher extrusion rate of the polymer solution (Fig. 2c) or slower foaming reaction (less $NaBH_4$ (Fig. 3a) or higher pH of quench bath (Fig. 4c)). These results demonstrated that formation of bore highly depended on competition between foaming reaction and phase separation. Gas gathering formed the bore before

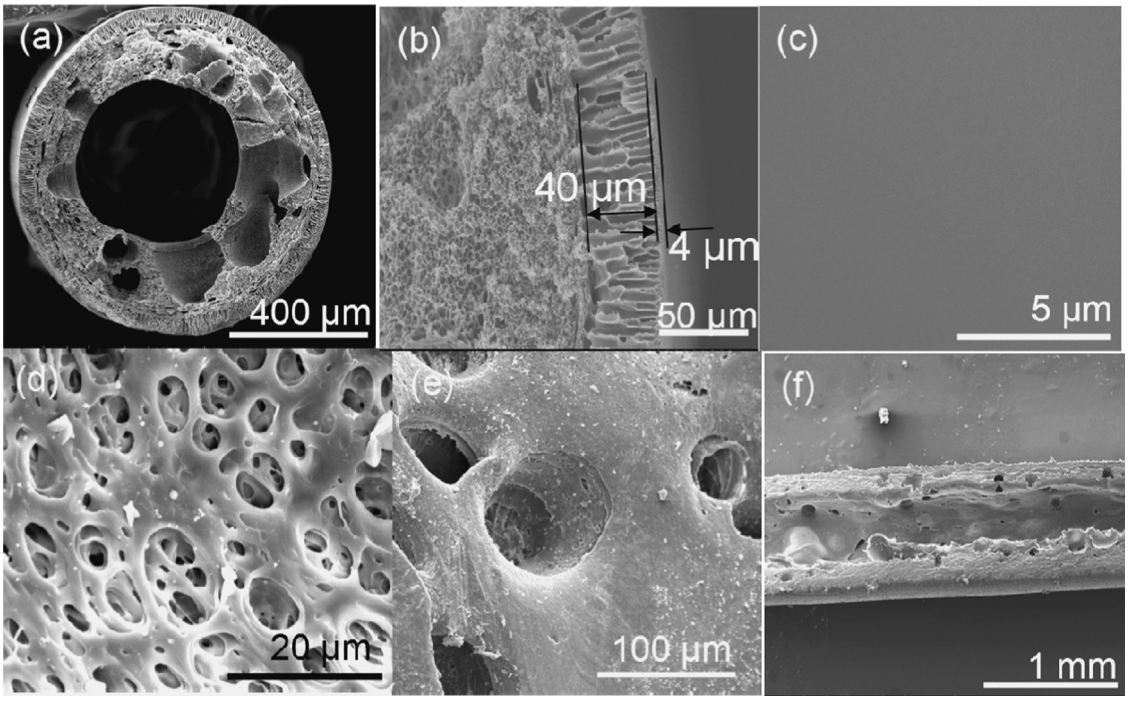

Fig. 1. SEM images of HFM prepared by dual pore formation mechanism. (a) whole-all cross section, (b) out parts of cross section, (c) out surface, (d) inner surface, (e) inner surface with macrovoids, and (f) longitudinal section.

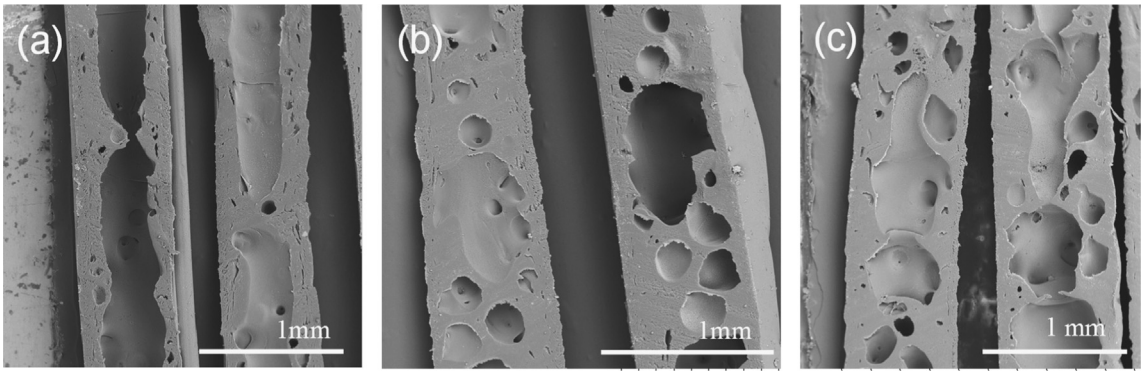

Fig. 2. SEM images of hollow fiber membrane with 0.1 wt% $NaBH_4$, and different extrusion rates. (a) 0.1 mL/min, (b) 0.3 mL/min, and (c) 0.5 mL/min.