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Microstructured hollow fibers for ultrafiltration

Pınar Zeynep Çulfaz[a], Erik Rolevink[a], Cees van Rijn[b], Rob G.H. Lammertink[a,*], Matthias Wessling[a]

[a] Membrane Technology Group, Faculy of Science and Technology, University of Twente, PO Box 217, 7500 AE, Enschede, Netherlands
[b] Aquamarijn Micro Filtration BV, Berkelkade 11, NL 7201 JE, Zutphen, Netherlands

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ABSTRACT

Hollow fiber ultrafiltration membranes with a corrugated outer microstructure were prepared from a PES/PVP blend. The effect of spinning parameters such as air gap, take-up speed, polymer dope viscosity and coagulation value on the microstructure and membrane characteristics was investigated. Fibers with maximum 89% surface area enhancement were prepared. The structured fibers and the round fibers spun under the same conditions had comparable (intrinsic) pure water permeability, molecular weight cut-off, pore size distribution and average skin layer thickness. This implies that the flow through the unit volume of the structured fibers will be enhanced compared to their round counterparts, while maintaining the same separation properties. A colloidal filtration method was used to determine the skin layer thickness. Structured fibers spun with a slow-coagulating polymer dope had varying skin thickness throughout the outer surface, which was dependent on the geometry of the fiber and was probably caused by varying local coagulation conditions around the structured outer surface of the fibers. A polymer dope with high coagulation value, on the other hand, resulted in a structured fiber with a homogeneous skin layer all along the surface.

1. Introduction

Hollow fiber membranes are commonly used in many membrane processes ranging from gas separation to microfiltration. The main advantage of this configuration over the flat sheet membranes is that it provides a high ratio of membrane area to module volume, and therefore higher productivity per membrane module. Hollow fiber membranes are produced by a spinning process in which the polymer solution is extruded through a spinneret into a nonsolvent bath. The membranes are formed via phase inversion and have an asymmetric structure with a thin separating layer on the inner surface, the outer surface or both [1,2].

To produce a hollow fiber membrane with high permeability, usually the first approach is to optimize membrane fabrication conditions (e.g. composition, temperature and flow rates of the polymer dope and the coagulant, air gap distance, take-up speed, etc.) [2–5]. Mostly, a thin skin emerges on the surface of the hollow fiber, having the desired separation properties. The remaining part of the fiber wall has only mechanical support function. It is difficult, however highly desirable, to increase the permeability of the skin layer [6]. Here, we propose to increase the productivity of a membrane by increasing the area-to-volume ratio of the membrane using corrugated surfaces. The use of corrugated surfaces is a common approach used to enhance heat transfer in heat exchangers. In recent years, this approach has also been used in membrane applications to enhance mass transfer rates. For certain fabrication conditions, the amount of membrane area that fits a certain volume can be increased by using corrugations, thereby increasing the productivity of the membrane module.

Most of the work done so far on corrugated membranes has focused on sheet-like membranes. To prepare the membranes several approaches have been followed such as pressing originally flat sheet membranes between structured dies [7–10] and casting the polymer solution on or between structured molds of millimeter or micrometer scale corrugations [11–13]. It has been shown that corrugated membranes enhance flow by both increasing the membrane area per volume and by disrupting the concentration polarization layer.

There are fewer studies on corrugated tubular or hollow fiber membranes. Broussous et al. reported the preparation of helically corrugated ceramic tubular membranes by adapting the extrusion process, which proved to improve the permeate flux in the microfiltration of bentonite suspensions [14,15]. The only report of fabrication of corrugated polymeric membranes has come from our group showing hollow fiber membranes with micrometer-scale corrugations for gas separation by combining silicon micromachining technology and the conventional hollow fiber spinning process [16]. The micro-engineered spinneret that was used contains a silicon insert with a structured opening. The polymer dope flows through this structured annulus instead of a round one and takes

* Corresponding author. Tel.: +31 53 4892063; fax: +31 53 4894611.
E-mail address: r.g.h.lammertink@utwente.nl (R.G.H. Lammertink).

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Table 1
Fiber spinning parameters.

Fiber	Polymer dope	Insert	Air gap (mm)	Polymer dope flowrate (mL/min)	Polymer dope velocity (m/min)	Bore liquid flowrate (mL/min)	Pulling speed (m/min)
S1	D1	Structured 1	5	10	4.0	6	7.0
S2	D1	Structured 1	12	10	4.0	6	7.0
S3	D1	Structured 1	32	10	4.0	6	7.0
S4	D1	Structured 1	58	10	4.0	6	7.0
S5	D2	Structured 1	5	5	2.0	3	5.0
S6	D3	Structured 1	5	5	2.0	3	5.0
S7	D4	Structured 1	5	5	2.0	3	5.0
S8	D1	Structured 2	5	5	2.7	3	3.5
S9	D1	Structured 2	5	5	2.7	3	7.0
S10	D1	Structured 2	5	5	2.7	3	13.0
S11	D1	Structured 2	5	5	2.7	3	23.5
S12	D5	Structured 1	5	5	2.0	3	5.0

the shape of the insert. Upon coagulation, the corrugated fiber forms. The microstructured and round fibers made in this study were shown to have similar intrinsic gas permeances, resulting in enhanced productivity in the structured fibers.

In this study we apply the same spinning method for the fabrication of microstructured hollow fibers for ultrafiltration. We report the effect of various parameters on the fiber structure and a thorough comparison of structured and round fibers spun under the same conditions with respect to their morphology and performance.

2. Experimental

2.1. Fabrication of the fibers

The hollow fibers were prepared from a PES-PVP blend. Polyether sulfone (PES) was purchased from BASF (Ultrason 6020), polyvinyl pyrrolidone PVP K30 ($M_w \sim 40$ kDa) and PVP K90 ($M_w \sim 360$ kDa) were purchased from Fluka. All polymers were dried in vacuum at 30 °C for 24 h prior to use. The solvent, N-methyl pyrrolidone (NMP) was purchased from Acros. The water used in preparing the polymer dopes was MilliQ water (18 MΩ cm). The polymer dopes were filtered through a 25 μm metal filter and degassed for at least 2 days before spinning. Spinning was done at room temperature. Water was used as the external coagulant, while the bore liquid was a mixture of 3% PVP K90, 19% H_2O and 78% NMP. After spinning, the fibers were washed in water for 24 h to complete the solvent–nonsolvent exchange. Then they were kept in a 4000 ppm NaOCl solution in water for 48 h. This treatment was followed by rinsing in water for an hour, and then putting the fibers in a 10% glycerol solution for 24 h, after which they were dried under ambient conditions.

The details of structured fiber spinning are described elsewhere [16]. In this study, two different structured inserts were used to spin structured fibers and a round insert was used to spin round fibers for comparison. Fibers were spun varying the air gap, the polymer dope composition and the take-up speed. The spinning parameters used in the fabrication of the structured fibers are shown in Table 1. The compositions of the different polymer dopes used are shown in Table 2. For the fibers spun with dope D1, round counterparts were also spun under the same conditions for comparison.

Table 2
Polymer dopes used.

Dope	% PES	% PVP K30	% PVP K90	% H_2O	% NMP
D1	20	5	5	5	65
D2	17	5	5	5	68
D3	14	5	5	5	71
D4	14	5	5	7.5	68.5
D5	17	5	5	7.2	65.8

2.2. Characterization of the fibers

2.2.1. SEM and FESEM analysis

The structure of the fibers was examined using Scanning Electron Microscopy (JEOL JSM 5600LV). To observe the pores on the skin surface on the outer side of the fibers and the cross-sections of the skin layer, Field Emission Scanning Electron Microscopy was used (JEOL 660T). For preparing the SEM and FESEM samples, the fibers were immersed in ethanol for a few minutes and then broken in liquid nitrogen. Prior to measurement, the fibers were sputtered with gold for SEM images and with platinum for FESEM images.

The perimeter and cross-sectional area of the fibers were measured from the SEM images using ImageJ software. For assessing the enhancement in surface area of the structured fibers, the convoluted perimeter of the fiber was divided by the perimeter of a circle passing through the middle of the fins and the valleys in the fiber.

2.2.2. Pure water permeability

The pure water permeabilities of the fibers were measured using MilliQ water with modules of fibers having a length of 30 cm (ca. 70–100 cm^2 membrane area) and under transmembrane pressure differences of 0.5 and 1.0 bars. Three modules were prepared for each fiber batch. Before measuring the pure water permeabilities, the fibers were washed with MilliQ water in cross-flow for approximately half an hour to remove the glycerol in the pores. The permeabilities reported for the structured fibers were calculated using the actual convoluted surface area. In other words, the intrinsic permeabilities of the membranes, in units of L/(h m^2 bar), are reported for both structured and round fibers.

2.2.3. Molecular weight cut-off

For measuring the molecular weight cut-off (MWCO) of the membranes a dextran mixture prepared using dextrans of 18, 75 and 250 kDa nominal molecular weight (PDI ≈ 1.5, as reported by the manufacturer) was used. The filtration was done in cross-flow mode with cross-flow velocities of 0.7–2.0 m/s and under transmembrane pressure difference of 0.15–0.25 bar. The filtration conditions for each fiber batch tested were such that the ratio J/k was smaller than 1, where J is the permeate flux and k is the estimated mass transfer coefficient in the boundary layer near the membrane surface. This choice of operating conditions minimizes concentration polarization and should yield data that is more representative of the membrane structure and independent of the filtration conditions [17,18]. Retentate and permeate samples were taken after 30 and 60 min of filtration and analyzed with Gel Permeation Chromatography (GPC) to determine the retention of each molecular weight. The dextran molecular weight whose retention is 90% was reported as the molecular weight cut-off.