Measuring Pore Size in the Walls of Hollow Fiber Membranes

Relevant for: through pores, hollow fibers, porometry

Hollow fiber and capillary membranes have a number of attractive properties such as flexibility, high surface area per unit volume, and unique packaging opportunities, which means they can be adapted to a variety of filtration applications. However, their physical form makes it challenging to measure the sub-micron size pores within the walls. A preparation procedure for measurement via capillary flow porometry and examples of different hollow fiber samples measured on the Porometer 3G series are reported.

1 Introduction

The excellent mass transfer properties of the hollow fiber construction (a relatively large lumen surrounded by a large area of a thin porous membrane wall) has led to it being utilized in numerous commercial applications in widely different fields such as medical (blood fractionation), water reclamation (purification and desalination), gas separation, and techniques using pervaporation. Other promising applications of this type of membrane are in the biochemical industry (bioseparation and bioreactors). Specifically, its beneficial features, compared with more traditional filtration and separation systems, are modest energy requirements, high volume efficiency, two modes of operation (*inside-out* and *outside-in*) and low operation costs. To a certain extent, these benefits are offset by more frequent fouling and initial capital expense.

The challenge faced by those needing to determine the pore size distribution through the walls is to find a technique which can functionally transfer a fluid radially through a narrow fiber; by comparison, measurements across a flat sheet are simple. The difficulty of analyzing hollow fibers has been overcome by a special preparation technique which involves sealing an individual fiber into a special sample holder and analyzing the pore size via capillary flow porometry.

2 Sample Preparation

The experimental setup for hollow fibers typically depends on the permeability or overall flow through the fiber. Fibers have nominal dimensions from 1 to 3 mm in diameter with wall thicknesses a factor lower. Typically, multiple–three (high flow fiber samples) to eight (low flow fiber samples)–hollow fibers from a batch are assembled together. Some samples that display high flow may require only a single fiber.

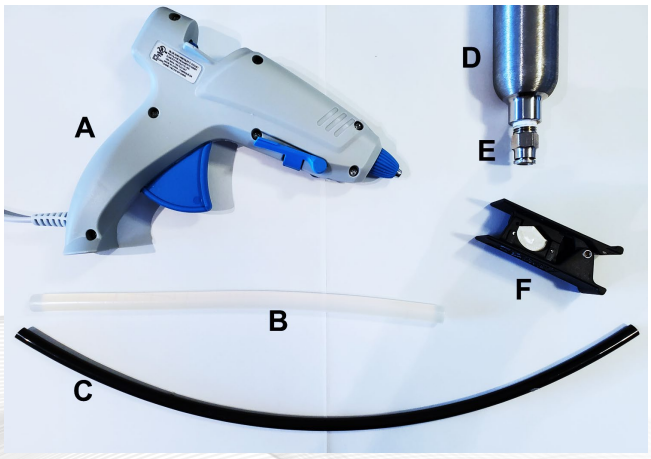

Figure 1: A hot glue gun; B glue stick; C nylon tubing; D external sample manifold; E push-in connector; F tube cutter.

To assemble the hollow fibers for an *inside-out* measurement requires non-permeable plastic tubing (nylon tubing), scissors, tube cutters, tweezers, pipettes, and a hot glue gun or epoxy for assembly (Figure 1). Assemble following the steps below:

1. Thread the hollow fibers into the plastic tubing with excess coming out of both ends.
2. Fill the interior part of the plastic tube with epoxy or hot glue taking caution not to melt the hollow fibers. Ensure enough glue/epoxy is used to seal the plastic tube's interior end completely and allow to dry/cure.
3. On the open end, glue/epoxy the ends of the hollow fiber to make a closed end (when forming a loop this step can be skipped).
4. On the initially glued side, clip the ends of the hollow fiber(s) flush with the plastic tube.
5. Submerge the whole sample in a test tube or suitable vial to completely wet the sample with Porofil or other wetting liquid. Allow the sample to wet for several minutes and pipette fluid over the sample as needed to completely wet the sample.
6. Remove the sample from the wetting fluid and allow excess fluid to drip off.
7. Insert the short ends of the fiber into the push-in connector of the external sample holder and ensure a clean seal (Figure 2). If there was glue on the outer side of the plastic tubing, it should be removed prior to the last step.
8. Perform the through pore measurement as any regular pore size run to determine the pore size distribution. Accurate length and diameter will be required for determining additional through pore related values.

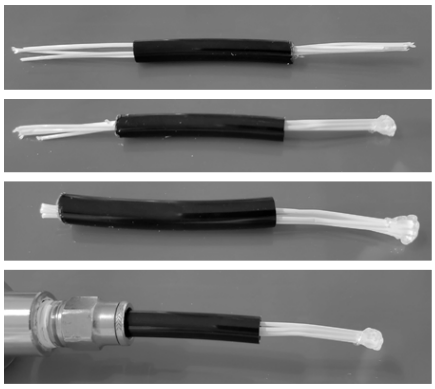

Figure 2: Set-up guide for performing inside-out measurements on a group of hollow fibers. Before inserting plastic tube into the external sample holder, cut the fibers flush with the plastic tube.

A single hollow fiber may be run in a "loop" configuration as shown in Figure 3. This configuration is recommended for samples that have a high flow rate and is prepared similarly to the step above, but both ends are glued into the nylon tubing.

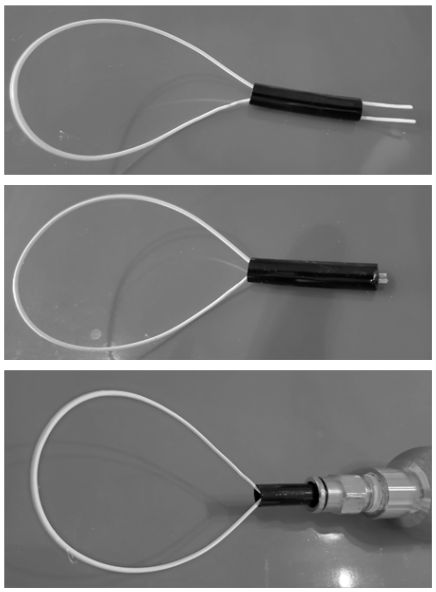

Figure 3: Set-up guide for performing inside-out measurements on a single hollow fiber that has been looped.

The setup to do *outside-in* measurements requires the set-up as shown in Figure 4. Again, insert the hollow fiber through the 3G fiber sample support and glue/epoxy the tapered end. After curing, close the ends of the hollow fiber that are above the tapered end with glue/epoxy to create the outside surface that is wetted prior to measurement (this step can be skipped for looped samples). Cut off the excess hollow fiber near the cylindrical end. Wet the sample and assemble the setup similar to a thin membrane except the O-ring is beneath the step on the fiber support (Figure 5).

Figure 4: Set-up guide for performing outside-in measurements on a group of hollow fibers.

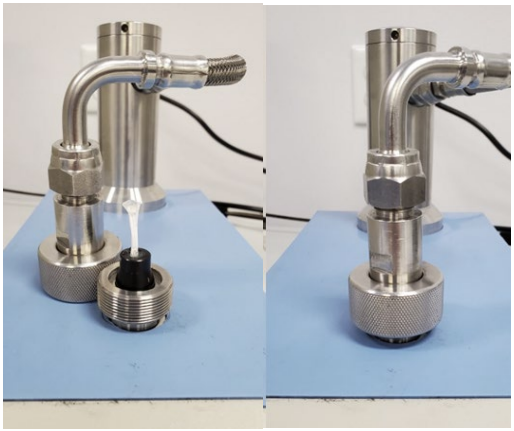

Figure 5: Guide for attaching the assembly for performing outside-in measurements to the Porometer 3G series.

3 Analysis and Results

Four samples of polymeric hollow fiber samples (HF1-4), each having an outside diameter of 1 mm and a wall thickness of 100 µm were prepared as above to be measured *inside-out*. Prepared samples were installed in an External Sample Manifold (Figure 6) in place of the usual sample holder assembly and block and analyzed on a Porometer 3Gzh using Porofil wetting fluid. The 3Gzh was equipped with both 10 and 200 ml/min sensors and both ranges were used. Up to 256 data points were measured over the selected pressure (pore size) range.

Figure 6: External sample manifold. The red arrow indicates the attachment point for the hollow fiber sample holder.

Measurement data from flow vs. pressure for wet and dry runs for all four samples are shown in Figure 7. The mean flow pore sizes were calculated in the usual manner: at the pressure intersection of half the dry flow data with the wet flow curve. These values and the bubble point values are presented in Table 1. The pore size distributions were calculated from the measured pressure assuming a zero degree contact angle. Number distributions were calculated based on the internal geometric surface of the sample fibers (from gross dimensions). These distributions are shown in Figure 8 and Figure 9.

Table 1: Capillary flow porometry measurement results for four hollow fibers.

	HF1	HF2	HF3	HF4
Maximum Pore Size (µm)	0.4604	1.1132	0.7506	0.5173
Mean Flow Pore Size (µm)	0.2384	0.9801	0.1547	0.1828
Minimum Pore Size (µm)	0.1460	0.7503	0.0905	0.1076
Bubble Point Pressure (bar)	1.39	0.57	0.85	1.24
Bubble Point Flow Rate (l/min)	0.1407	0.0647	0.0080	0.0518

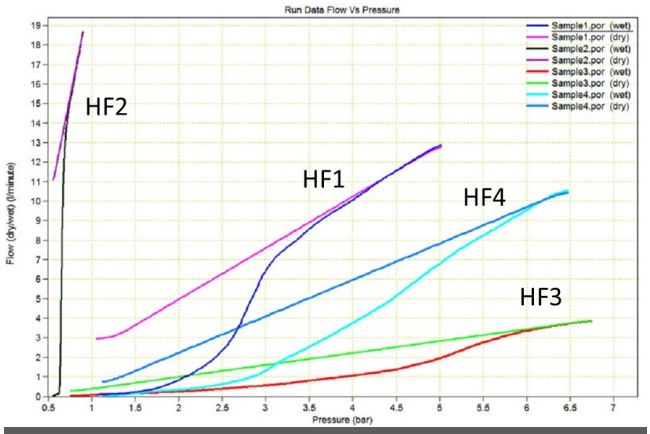

Figure 7: Measured wet and dry flow vs. pressure curves. Differences between samples are clearly evident.

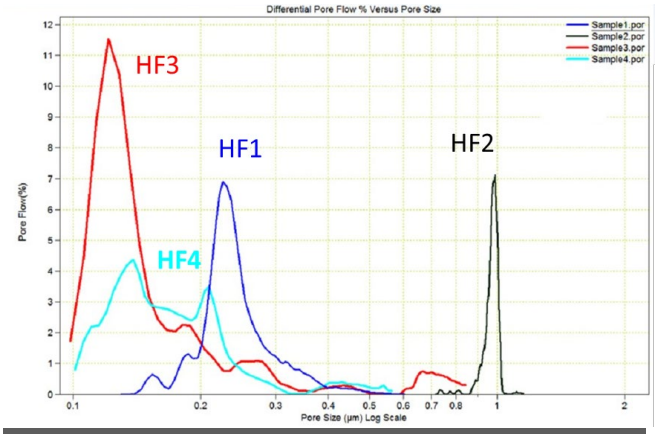

Figure 8: Differential percent flow vs. pore size. Differences between sub-micron pores are highly resolved.

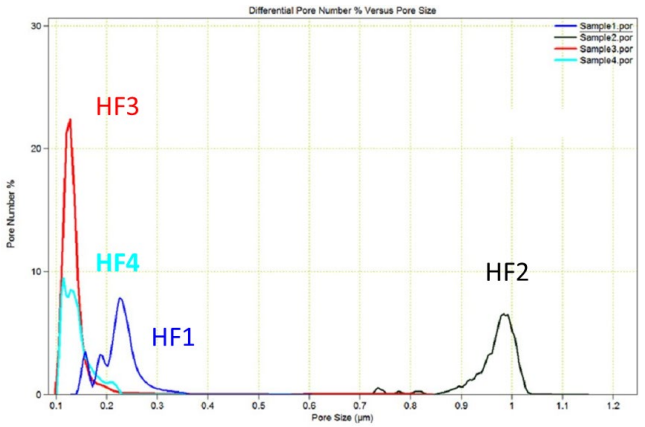

Figure 9: Differential pore number percent area vs. pore size. Some similarities between samples HF3 and HF4 are seen.

4 Conclusions

A successful sample preparation technique for measurement of hollow fiber membranes has been shown and employed to demonstrate the sub-micron resolution of the Porometer 3G series on these types of difficult samples. The ability to measure pore size distributions in the membrane wall of a single hollow fiber is of significant value to manufacturers and users of these materials.

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