FILTRATIVE ENHANCEMENTS DUE TO GRADED MICROPOROUS MEMBRANE PORE STRUCTURE

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ABSTRACT

A primer on the three categories of membranes (microporous, ultrafilter, and reverse osmosis) used for filtration and separation applications are briefly compared and contrasted. The microporous membranes used for submicronic filtration are given greater emphasis. The important filtration parameters of retention, permeability and throughput are used to explain the advantages of a graded pore or asymmetric structure compared to conventional isometric microporous membranes.

Membrane Categories

In the realm of liquid filtration and separation technology devices, microporous membranes represent the high end or high performance segment. Historically, microporous membranes are used to remove suspended particles from fluid streams that are in the size range between 0.1 µm and 10 µm, and most preferably between 0.2 µm and 1.0 µm in size. Recent advances have extended the practical use of microporous membranes to sub 0.1 µm filtration levels('). Just below this pore size, ultrafiltration membranes become the device of choice. The tightest membranes are the reverse osmosis type where the separation of ionic compounds such as removing salt dissolved in water takes place.

Of the three types of membranes, microporous, ultrafilter (UP), and reverse osmosis (RO), the microporous are unique in that they rely primarily on the mechanical restraint of particles by discrete pores of selected size. Simply stated, they contain very small holes that are essentially at or smaller than the size of the desired particle size to be removed. The desired size pores or "holes" are "formed" in the membrane when it is made. The UP and RO membranes are made without "discrete" pores and are known as non-porous, dense or homogeneous films. They rely on the interstitial void spaces between the closely **packed chains** of polymer molecules of the semi-permeable membrane to separate dissolved species from the liquid phase.

Microporous Membranes are therefore primarily used to "filter" out solid particles that are suspended in a fluid stream; UF and RO membranes typically "separate" a dissolved species from a fluid. The objective of a UF separation may be to cull out a large protein of say 100,000 molecular weight, from another protein that has a molecular weight of say 75,000. RO separations are on the ionic scale involving aqueous salts, metal ions and some sugars, all of which are typically below 20 Angstrom units in size.

One can imagine that the "tightness" of the membranes increases as you move from Microporous to UF to RO. It is therefore much more difficult to "push" a liquid, say water, across a UP or RO membrane than a Microporous membrane. Microporous membranes typically operate under "transmembrane" pressures of less than 344.7 kPa (50 pounds par square inch, gauge, psig), while UF's may require up to 690 kPa, (100 psig) and RO's up to several thousand kPa. Partly because of the higher pressures required to operate UF and RO membranes, they are usually designed in devices that are flat and highly reinforced with supporting fabrics on either side of the membrane. These fabrics are important for enhancing flow distribution as well as for support and drainage.

The most common device for flat sheet UF's and RO's is a "jelly roll" spiral around a perforated center support tube. The other common device is a module that contains hundreds of tiny straw shaped "hollow fiber" UF or RO membranes (Microporous membranes can also be made into hollow fibers, but they will not be considered here). Because they can operate at much lower pressures, microporous membranes can be made in many more different shaped devices and configurations. One of the most common is the pleated cartridge configuration.

Likewise the UP and RO membranes will plug with contaminant very quickly if they are run in a "dead end" mode of flow. This means passing "all" of the fluid directly through the membrane from one side to the other. This is the normal mode of operation for the much more permeable microporous membranes. To extend the life of the UP and RO membranes they are run in a "crossflow" mode of operation. This means that the "dirty" fluid moves across the surface of the membrane, parallel to it. The driving force pressure on the fluid pushes some of it through the membrane (this is called the permeate), but much of the fluid continues its path across the top of the surface and eventually becomes a concentrated "reject" stream that flows out of the device. It may go to the drain or be recirculated back to the feedline, or both. The crossflow action serves to keep the upstream surface clean and prevent premature build up of blinding contaminants.

This crossflow design requires the use of additional piping and pumps and other equipment to accommodate the three fluid pathways of feed, reject (or concentrate), and clean permeate.
Some other differences in the structure and operation of the UF and RO membranes are mentioned below.

Microporous Membrane Types

Microporous Membranes can consist of a variety of materials made in a variety of different ways. The most common types are made of synthetic polymers. Others include inorganic membranes made of "ceramic" type materials that are sintered or fused together as a result of a combination of pressure and high temperature or with the use of an adhesive.

Polymeric membranes are usually made of a film of a single polymer, but some are "composites" made of a more open support layer and a functional membrane filter. Some of the more common polymers used to make membranes include polysulfone, nylon, cellulose acetate, polyvinylidine fluoride (PVDF), polypropylene, polycarbonate, and polytetrafluoroethylene (PTFE). The two main methods of manufacture include casting and stretching.(2) A few other methods also exist.

Most conventional membranes are made in a casting process. This generally starts with a dope or solution consisting of the polymer dissolved in a solvent. A very thin film of the polymer solution is formed and through the means of wet or dry processes the polymer is solidified into a controlled open colloidal type structure(phase-inversion process). The thin film layers are on the order of 150 μm (6 mils) in thickness. The distribution and size of the pores is controlled by varying important process parameters such as the amount of solvent, operating temperature, presence of pore former (nonsolvent), speed of casting, and exposure to air currents and/or quenching fluids.

Another method of membrane formation involves the controlled stretching of a dense plastic film such as polypropylene or PTFE. The film is stretched in all directions under varying temperature and pressure conditions such that a certain size distribution of "micro-tears" or pores are produced.

Another method for making a unique membrane structure involves the nucleation-track method. In this method, a very thin film (about 10 μm thick) of polycarbonate (or other suitable) material is bombarded with radiation. The irradiation contact sites leave a narrow track of damaged material which can be etched into straight through holes or pores in a subsequent operation.

Microporous Membranes as Filters

The characterization of a microporous membrane as a filter is based upon its performance in three areas:

a.) retention efficiency
b.) permeability
c.) throughput

These three parameters will be briefly examined comparing conventional isometric "straight-through" pore and asymmetric "graded pore" microporous membranes.

Retention efficiency is a measure of a filter's ability to remove selected sizes of particles. It is generally expressed as a percentage according to the following:

$$\%\ \text{Efficiency} = 100\ \frac{\{\text{Upstream Particles} - \text{Downstream Particles}\}}{\text{Upstream Particles}}$$

Microporous membranes are described as "absolute" rated. This means that they have removal efficiencies near 100% at their rated pore size. A membranes's ability to remove particles is a direct result of its morphology or pore structure. Most polymeric microporous membranes have a physical structure that has been described as sponge-like in appearance. The cross section consists of millions of interconnected channels or voids that are ultimately described as pores. The size of the pores does not vary much in this structure. In fact, microporous membranes are noted for their very narrow distribution of pore sizes that gives them the ability to provide sharp particle size "cut-off" performance. This means they can be used to remove all particles above a certain size, say 0.45 μm for example.

There are few oversized pores, and if they are present they can be easily detected by means of one of several non-destructive "integrity tests". These include, the bubble point test, diffusive flow test, and the pressure hold test.(3) Tested in this way prior to sale, it's possible for a membrane manufacturer to "guarantee" the absolute removal of particles. Such membranes are used to render pharmaceutical preparations sterile and safe for human injection. The ability to test and guarantee integrity is another way that microporous membranes differ from UF and RO membranes.

The pore structure is relatively uniform throughout the membrane from one side to the other. This is known as an "isometric" structure, i.e., pores on the top surface are about the same size as those in the middle and also on the bottom surface. Figure 1. shows a cross section of a 0.2 μm PVDF membrane at a magnification of 350X. This structure creates a positive barrier to particles larger than the mean pore size and explains why nearly all particle capture takes place on the membrane surface or to a depth of about 10 to 20% of the membrane. The maze of small pores and high surface area of the pore walls or interconnecting channels is also capable of removing particles smaller than the mean pore size with reproducible levels of efficiency if flow conditions are relatively stable. In fact, conventional isotropic membranes typically have mean pore sizes larger than their absolute rating!

An unconventional morphology for microporous membranes is an "anisotropic" , or highly asymmetric "graded pore size" structure. (Figure 2. shows a cross section of a highly graded pore 0.2 µm rated membrane of polysulfone. Magnification is 350x). Such membranes have a highly graded pore size from one surface to the other. For example, a 0.2 µm absolute rated highly asymmetric membrane can have pores on the top surface that are 10 µm to 20 µm in diameter, and exponentially decreasing pore sizes throughout the inner surface until a final pore size of 0.2 µm is reached at the bottom surface. This is an asymmetry ratio of between 50:1 and 100:1. Particle retention occurs on the membrane surface and throughout the depth of the membrane internal void structure.

It has been shown that the pore sizes of the small pores in a highly asymmetric membrane are typically smaller than those of similarly rated conventional isometric membranes.[4] See Table I for a comparison. Thus the asymmetric filter can remove particles of the rated size exclusively by means of mechanical sieving, and not have to rely on the more elusive and less reliable surface contact or adsorptive capture means in the face of changing fluid flow or other operating conditions.

Table I - Summary of Pore Diameters Calculated Based on Several Different Methods (from Simonetti)

Method	APS	Nylon	PVDF
Mean Flow Pore Diameter, µm	0.099	0.180	0.144
Pseudomonas diminuta retention Pore Diameter, µm	0.2	0.2	0.2

APS - Asymmetric Polysulfone
Nylon - Conventional Nylon
PVDF - Conventional Polyvinylidine fluoride

Membrane permeability describes the ease or difficulty with which fluid such as water can pass through the structure. Equations describing the important variables and their relationship for measuring and predicting permeability are well documented in the literature.[5] Simply, with fluid parameters constant, flow resistance in a unit area of membrane depends upon the size and length of the restrictive flow channels or pores. For discussion, consider 0.2 µm rated membranes. A conventional isotropic membrane can be thought of as consisting of pores or flow channels that are about 0.2 µm in diameter and about 150 µm in length. A highly asymmetric "graded pore" size membrane would have a 150 µm long flow channel shaped more akin to a funnel with a large opening of about 20 µm and gradually tapering down to 0.2 µm for the last 10 µm of length. In the graded pore membrane, the greatest flow restriction of the 0.2 µm diameter flow channels is a fraction (< 1/10) of the length of that in the conventional membrane. Thus, even with slightly smaller diameter terminal pores, the flow resistance of a graded pore membrane is much less than that of a conventional non-graded pore membrane. Table II lists a comparison.

Table II - Permeability Comparison of Different 0.2 µm Membranes

Membrane	Filtration Time for 100 ml of Water ($10cm^2$)
Graded Pore Polysulfone	27
Charged Nylon	37.5
PVDF	40.5
Polycarbonate	52
Cellulosic	76

The throughput of a membrane is a measure of its service life. In other words, how long it will last before it becomes so plugged with trapped contaminant that flow through the membrane is unacceptably slow or requires too much pressure to maintain a desired flow rate. There are differences in expected life or throughput of graded pore and conventional membranes designs too. One can readily visualize that a hollow container such as a three dimensional bowl or bucket can hold more solid particles than a two dimensional flat plate. Likewise, a graded pore membrane uses its internal voids volume to hold contaminant as well as its surface. Various size particles ,large and small, can enter the large surface pores and settle into the membrane depth until sieve retained at the their appropriate cut off layer. A conventional membrane primarily uses only its surface to stop particles of all size greater than its restrictive surface pore sizes. Large particles captured on the surface can therefore block flow through a large number of surface pores, shortening the life of the membrane.

The highly asymmetric membrane contains over 75% voids volume. This entire internal volume is available for holding particles. As a result, even with an ultimately

tighter pore structure, asymmetric membranes can demonstrate significantly greater throughput of fluid before flow becomes too restricted.
Table III. is a comparison of membrane throughputs of both types of membranes.

Table III - San Diego Tapwater Filtration with 0.2 μm Rated Membranes (25mm Discs, 68.9 kPa [10 psi])

Membrane	Throughput Volume, ml
Graded Pore Membrane:	
Asymmetric Polysulfone	600
Conventional Membranes:	
Cellulose	300
Nylon 66	280
PVDF	210
Charged Nylon	200
Polycarbonate (Track Etched)	50

SUMMARY

A simple and brief explanation has been offered of the various categories of filtration and separation membranes. The microporous membranes were explored in more depth by outlining some of the performance differences of conventional isometric structures and those of more recently developed graded pore or asymmetric structures. It can be seen that the graded pore morphology provides the advantage of increased fluid flow rates and decreased clogging, while still permitting the absolute removal of small particles the size of the filter's absolute rating.

REFERENCES

1. Shucosky, A.C., *Filtration & Separation*, "High Flux Membrane Cartridge Filter", Vol 29, No.1, 1992.

2. Brock, T.,*Membrane Filtration: A User's Guide and Reference Manual*, 1st Ed., Science Tech, Inc., Madison, 1983, p.27.

3. Hofman, F., *Journal of Parenteral Science and Technology*, "Integrity Testing of Microfiltration Membranes, **38** (July/August): 148 (1984)

4. Simonetti,J., and Schroeder,H., *Fluid Filtration: Liquids, Volume II ASTM STP 975*, "Particle Retention of Submicrometer Membranes", P.R. Johnson and H.G. Schroeder, Eds., American Society for Testing and Materials, Philadelphia, 1986.

5. Purchas, D., *Solid/Liquid Separation Technology*, 1st Ed., Uplands Press, Croudon, 1981, p. 89.

4 of 5

254

ILLUSTRATIONS

Figure 1. Cross section of a conventional isometric pore structure PVDF membrane rated at 0.2 μm. Magnification is 350X.

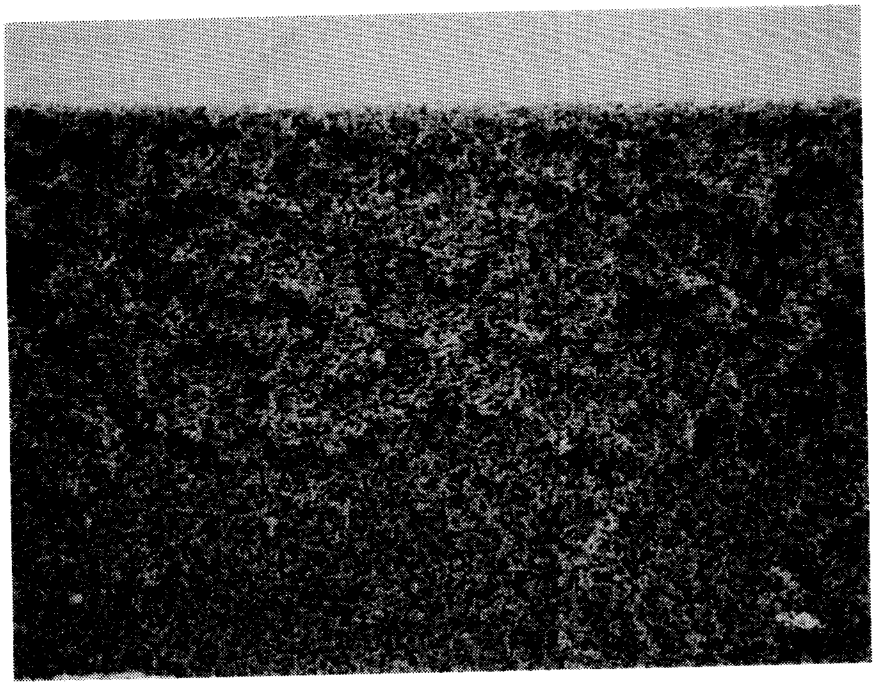
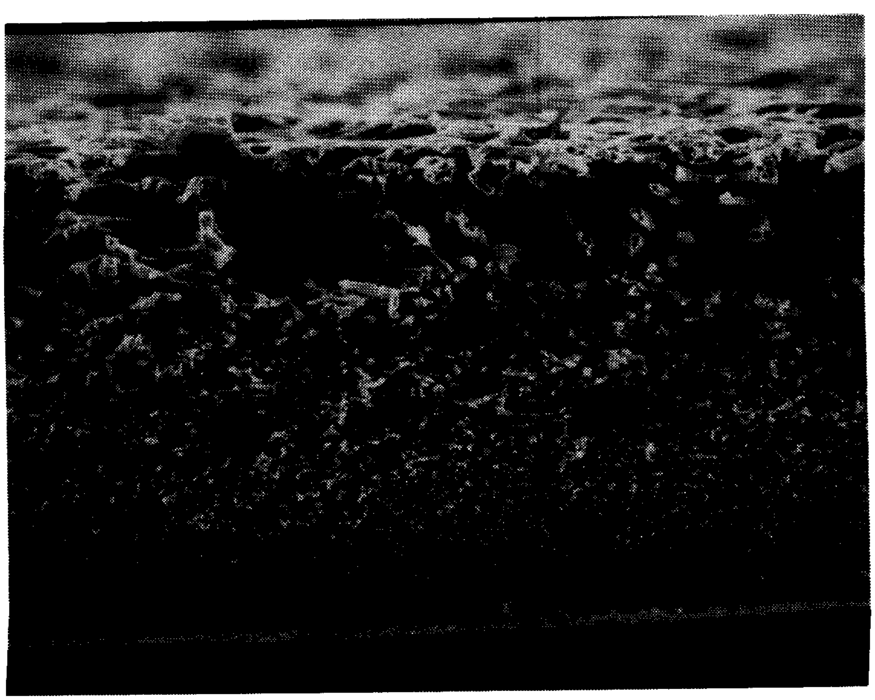


Figure 2. Highly asymmetric "graded pore" polysulfone membrane. Magnification 350X.



24