Secrets of Longevity: How Membrane Properties Affect Long-Term Performance

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Key Takeaways

Given their life cycle cost and ability to meet more stringent water quality requirements, low-pressure membranes are increasingly replacing granular media filters.

Two important characteristics determine a membrane's service life: its physical strength and its permeability.

While there are many factors at play in membranes' long-term performance, the importance of their structural and morphological characteristics should be recognized.

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Low-pressure membranes (microfiltration and ultrafiltration) are increasingly replacing granular media filters because they can better meet more stringent water quality requirements and they are competitively priced given their life cycle. Once membrane filters are in place, system owners need to ensure their filters maintain acceptable performance through their service life. To this end, there are two important characteristics that determine a membrane's service life: its physical strength (including resistance to long-term wear and tear) and its permeability (especially long-term recoverability versus irreversible fouling).

Many design and operational factors contribute to overall membrane performance, and specific areas of research over the years have focused on improving pretreatment and cleaning to mitigate membrane fouling. One key aspect less explored is the role membrane properties themselves play in maintaining long-term performance. From a structural perspective, membrane properties can be defined as "macro-" structure and "micro-" structure. Macrostructure refers to the structural features of a membrane such as pore size, porosity, and membrane thickness. Microstructure, on the other hand, refers to characteristics such as homogeneity of void distribution and morphology of membranes and how those properties relate to membranes' operational performance.

While membrane pore size can be selected on the basis of separation needs, membrane porosity and thickness are characteristics that determine a membrane's physical strength.

Characteristics Affecting Membrane Performance

Membrane Macrostructure and Physical Properties

A low-pressure membrane is commonly likened to Swiss cheese; it is a sheet (or hollow fiber) with cylindrical pores, as depicted in Figure 1.

Assuming uniform pores, three parameters can be used to characterize the membrane: (1) pore diameter, d; (2) membrane thickness, δ; and (3) membrane porosity, ε (the ratio of areas occupied by pores, A_p, to total membrane area, A).

Schematic of a "Swiss-Cheese" Membrane

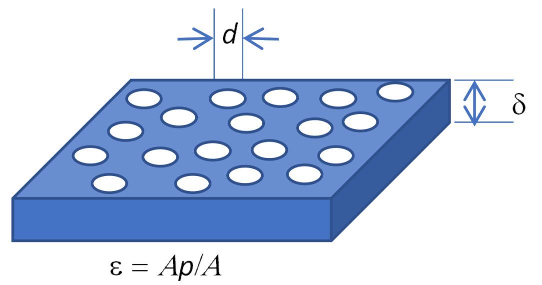


Figure 1

Assuming that the permeation through membrane pores is laminar flow, the permeation flow per unit membrane area, J, can be described by the Hagen-Poiseuille equation (Eq 1):

$$J = \frac{\varepsilon d^2 P}{32\delta\mu} \quad (1)$$

where P is the pressure differential across the membrane, and μ is the viscosity of the fluid.

If we consider an "ideal" membrane with d_0, δ_0, and ε_0 that can generate a maximum permeate flow J_0, then the ratio of the permeate J of any membrane to that of the referenced ideal membrane J_0 can be described as a function of the ratios of three parameters by the following equation (Eq 2):

$$\frac{J}{J_0} = \frac{\varepsilon}{\varepsilon_0}\left(\frac{d}{d_0}\right)^2\left(\frac{\delta}{\delta_0}\right)^{-1} \quad (2)$$

According to Eq 2, a membrane with higher permeation than another would theoretically be one with larger pore sizes and/or higher porosity or one that is thinner. While membrane pore size can be selected on the basis of separation needs, membrane porosity and thickness are characteristics that determine a membrane's physical strength and are not properties that are selected, per se. A more porous, open, and thin membrane favors high permeation, but it would be less sturdy, perhaps unable to withstand repeated mechanical stresses, and more amenable to chemical deterioration. In other words, membrane applications must balance membrane permeability and mechanical strength.

Applying classic continuum mechanics to analyze its behavior, a porous membrane can be approximated as a two-phase material—i.e., a solid phase of membrane medium and a liquid phase in the membrane pores. Per a 2012 report by Ragnar Larsson, this approach employs a two-phase homogenized model, as illustrated in Figure 2.

Unlike the simplified "Swiss cheese" model depicted in Figure 1 or the idealized two-phase model in Figure 2, actual low-pressure membranes are more likely to have a sponge-like structure consisting of an interconnected, three-dimensional network of flow channels, as described in the *Ultrafiltration and Microfiltration Handbook*.

Homogenizing a porous membrane in the idealized models relies on averaging the properties of a heterogenous material; therefore, the risk of material failure can be underestimated as the weakest region of a membrane would fail first, regardless of the "average" behavior of a membrane. Real membranes do not consist of homogeneous medium, meaning the relationships between membrane performance and bulk or average membrane macro properties may be inadequate for complex applications. Currently, the effects that microstructures in nonhomogeneous membranes have on membrane performance are not well understood.

Homogenization of a Porous Membrane as a Two-Phase (V_s and V_f) Continuum

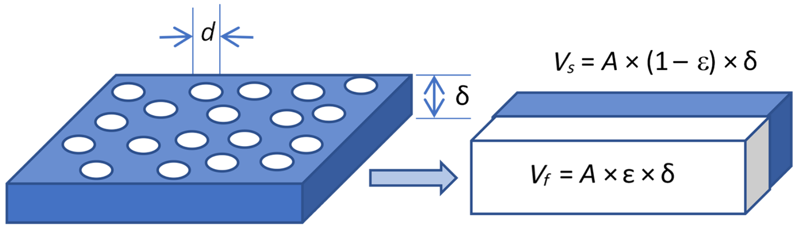


Figure 2

Membrane Microstructure and Physical Properties

Two important properties are used to characterize the microstructure of sponge-like, nonhomogeneous membranes: (1) void distribution and (2) crystallinity of medium.

Void Distribution

Voids within a membrane medium are formed during the manufacturing process. Depending on the material composition and manufacturing conditions, the void distribution within a membrane medium can be either homogeneous or heterogeneous. Figure 3 provides examples of structurally different membranes: Part A has a homogeneous distribution of voids throughout the cross-section of membrane walls; part B has a "fingering" structure: large voids in the middle section are surrounded by smaller voids at the edges of membrane walls.

Void distribution can influence the distributions of both fluids and stresses within the membrane medium. For the heterogeneous void distribution shown in Figure 3, part B, the "finger" portion of the membrane medium has macro voids so that the fluid flow encounters low hydraulic resistance. As a result, the overall hydraulic resistance from the membrane medium is lower, which enhances the membrane permeability. As shown in Figure 4, a heterogeneous void distribution leads to not only uneven flow distribution but also an uneven stress distribution.

One result of heterogeneous void distribution is the potential risk of stress in which certain regions of the membrane medium have significantly higher stress than others—e.g., at the edges of "fingers." In practice, membranes undergo filtration–backwash/air scrubbing cycles that bring repeated stress. Under this kind of cyclic stress, cracks are likely to develop first in regions where stress is concentrated, leading to crack propagation and eventually structural failure of the membrane.

Heterogeneous void distribution also leads to uneven flow distribution within the membrane medium, where the

Membrane Void Distribution: Homogeneous (A) and Heterogeneous (B)

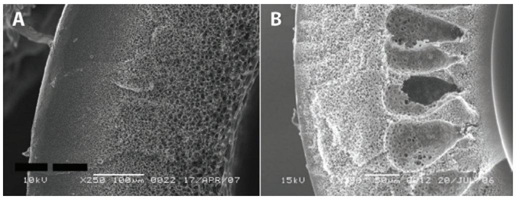


Figure 3

Stress Profile Across Membrane With Heterogeneous Void Distribution

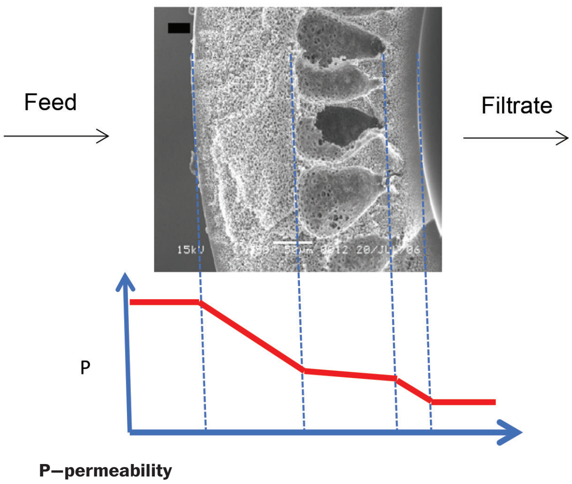
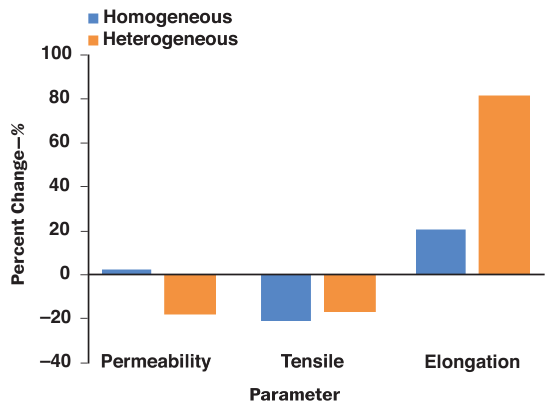


Figure 4

Comparison of the Impacts of Chemical Exposure on Membranes With Homogeneous and Heterogeneous Void Distribution



Exposure conditions: 2,000 mg/L NaOCl + 1% NaOH at 104 °F for seven days

Figure 5

regions with more voids tend to get preferential flow. When chemicals come into contact with this kind of membrane, e.g., during chemical cleaning, those regions are also more prone to exposure and degradation. Figure 5 illustrates the changes in membrane properties after chemical exposure for two membranes with different void distributions.

As Figure 5 shows, these two membranes exhibited very different behavior following extreme chemical exposure: the permeability of the homogeneous membrane changed little, while its physical properties (tensile strength and elongation) had moderate changes (within ±20%). On the other hand, the permeability and tensile strength of the heterogeneous membrane experienced moderate change, while elongation of the membrane increased drastically, to 80%, indicating that the membrane became much softer and deformed easily under stress.

Crystallinity

Another important morphological property of polymeric membranes is crystallinity. Most polymeric membranes are semi-crystalline materials that consist of two phases: a crystalline phase consisting of dense and orderly packed polymer chains, and an amorphous phase consisting of loosely, randomly packed polymer chains.

According to the 1998 book *Fundamentals of Polymers*, the crystallinity of a polymer, defined as the volumetric or mass ratio of two phases, significantly affects its physical properties and thus also the long-term performance of membranes made from it. The volume fractions of each phase, the shape of crystals and their size distribution, the orientation of polymer chains, and how the crystalline regions connect with amorphous regions in the membrane medium all contribute to the macroscale physical properties of a membrane, including permeability, brittleness, and the rate of environmental degradation.

The major implications of crystallinity for a polymer's properties are summarized as follows:

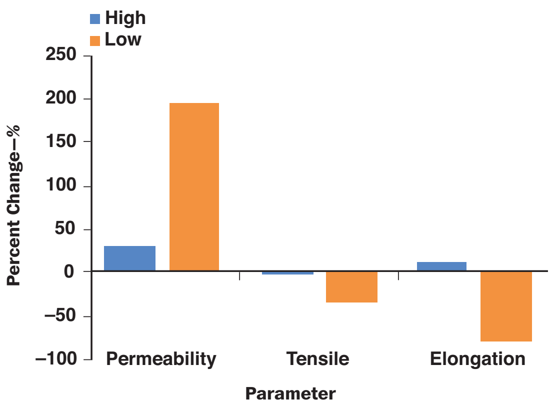
- Higher crystallinity generally enhances tensile strength by distributing the stress more evenly, but with reduced elasticity.
- In a polymer, crystalline structures can retard crack propagation, which is a prelude to failure. As described in *Fatigue of Engineering Plastics,* the crack growth rate of an amorphous polymer can be an order of magnitude higher than that of a semi-crystalline polymer. Crystalline polymers not only dissipate energy when

they deform, they can also reform into a crystalline structure that is exceedingly strong.

- Crystalline structures can limit the diffusion of solvent and nonsolvent into and through a polymer—per the 1991 book *Diffusion in and Through Polymers*—which is important in terms of the polymer's chemical stability. Practically, chemical degradation of polymers is most likely diffusion-limited.
- Crystalline structures in polymers can slow the reaction kinetics of chemical degradation. The attack of a chemical reagent on an amorphous structure generally occurs more readily than on a crystalline structure per *Elements of Polymer Degradation*.

Figure 6 compares the impacts of chemical exposure on two membranes with different degrees of crystallinity. For the membrane with higher crystallinity, chemical exposure moderately increased the permeability but had little change in physical properties. On the other hand, for the membrane with low crystallinity, chemical exposure resulted in a drastic increase in permeability (almost 200% increase) along with significant decreases in tensile strength (by 37%) and elongation (by 82%).

Comparison of the Impacts of Chemical Exposure on Membranes With Different Degrees of Crystallinity



Exposure conditions: 2,000 mg/L NaOCl + 1% NaOH at 104 °F for seven days

Figure 6

Conclusions

The low-pressure membrane systems used in water treatment plants are typically designed for 20 years of life with one or more membrane replacements, and those replacement events often determine the financial viability of the overall operation. While many factors contribute to the long-term performance of membranes, the importance of their structural and morphological characteristics should be recognized.

As this article explains, high-performance membranes need to balance permeability and mechanical strength. One solution to accommodate these conflicting demands is to produce a membrane microstructure with a high degree of homogeneous porosity, which enables it to distribute the stress more evenly and avoid localized stress concentration. In addition, membranes for the water industry need to have the proper degree of crystallinity to provide mechanical stability and resistance to chemical attacks but must be elastic enough to absorb and dissipate any mechanical stress applied during the various stages of operations. Data from long-term operations of multiple membrane plants demonstrate that those characteristics contribute to a membrane's longevity.

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AWWA Resources

- Consider Reverse Osmosis and Nanofiltration Membranes for Water Treatment. Broley W. 2016. *Opflow.* 42:8:20. https://doi.org/10.5991/OPF.2016.42.0048.
- Maintain Your Membranes to Know When to Replace Them. Walker T. 2015. *Opflow.* 41:8:26. https://doi.org/10.5991/OPF.2015.41.0049.
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