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MEMBRANE CHARACTERISATION: THE NEED FOR A STANDARD

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Biologists have been aware for at least 200 years that membranes in living creatures set up and maintain concentration differences between different regions of an organism, without which life could not occur. The search for synthetic membranes able to bring about useful separations in industry was a conscious attempt to mimic nature; early successes were limited, and industrial membrane technology has been a major development over the last 10 to 20 years. Now there are at least a dozen widely differing processes that use membranes to bring about separations.

When the liquid to be treated contains colloidal particles or aggregated molecular structures larger than about 0.01 μm in size, it is appropriate to think of it as a suspension rather than a solution. Such large particles undergo relatively minor Brownian motion and sediment appreciably, if rather slowly, under gravity. In order to separate them from the suspending liquid, which is usually a true solution and may contain molecular solutes, it is appropriate to think of filtration as an alternative to, for example, centrifugation.

Conventional filters made from compacted fibres or powders are available for removing particulates smaller than about 10 μm from liquid feeds. For this purpose, polymer technologists have developed techniques to cast films using a combination of solvent and precipitants that contain controllably small pores of fairly narrow size range. These 'membrane microfilters' are used extensively for the filtration of bacteria and colloidal particles and are coming up against increasing competition from a rapidly growing range of ceramic microfilters.

Methods of characterising the membranes are diverse and no standard exists between different manufacturers for the measurement of properties such as pore size and size distribution, pore shape, asymmetry, permeability and wettability. These properties, together with measured permeate flux decline and rejection data, are the ones that most affect the potential suitability of a membrane to a particular industrial application.

MEMBRANE STRUCTURE

Microfiltration membranes are available in a range of pore size ratings from 0.2 μm to 10 μm . Many of these membranes are produced in a variety of module configurations such as cartridges and tube bundles; they are also available in flat sheet format. Associated with the wide range of organic and inorganic membranes now available are a variety of manufacturing routes which impart different structural characteristics to the membrane.

The simplest pore geometry in a membrane is an assembly of cylindrical shaped pores of uniform dimension. These so-called track-etched membranes, such as Nuclepore PC and BioPore PC (Figure 1), are manufactured by exposing thin polymer films to a high energy radiation source. The particles damage the polymer matrix to create tracks. Subsequent etching by an acid (or alkali) of the polymeric material along the tracks creates uniform cylindrical pores with a narrow size distribution. To avoid excessive coincidence of pores in the film, the number density of pores tends to be low, leaving relatively large areas of impermeable polymer exposed to the feed stream and low membrane porosities of between 8 and 25%.

Cast membranes (such as Sartorius CN and Gelman Supor) are usually produced through a phase inversion process which allows a polymerisation reaction to occur under controlled conditions. By changing the reaction conditions, membranes of different pore size ratings can be formed; the

casting can be made on more permeable substrates to give the membrane improved mechanical integrity.

The surface of a typical cast membrane is shown in Figure 2, which indicates a structure quite different from that provided by the track-etching process. Cast membrane porosities are typically in the range 70 to 80%. Under some conditions, asymmetric microfiltration membranes (e.g. Domnick Hunter Asypor) are produced by the casting process where the pore sizes gradually increase through the membrane depth.

Stretching an extruded film of partially crystalline polymeric material, such as PTFE or polypropylene, in a controlled manner, forms a layered structure of inter-connected strands and the resultant membrane can be supported on a substrate. The porosity of these membranes is generally high (as may be gauged from Figure 3), with values up to 90% possible. More recently, inorganic microfiltration membranes, composed of materials such as alumina and zirconia, have become available. The Ceramesh membrane is an example and this is formed by dipping an inconel wire mesh into a zirconia slurry. The zirconia particles bridge the gaps between the constituent wires and the composite is sintered to produce the finished membrane. The large scale structure arising from the presence of the wire mesh is apparent in Figure 4, but within the mesh apertures there is also a small-scale granular structure, which endows the membrane with its filtering properties.

PORE SIZE AND DISTRIBUTION

Pore sizes and size distributions of microfiltration membranes can be measured using an automated bubble point tester such as the Coulter Porometer. These instruments use compressed air to displace a wetting fluid from the pores of a test specimen. As the air pressure is increased, the wetting fluid is displaced from progressively smaller pores and the total air flow rate through the membrane can be related to the pore size.

Unsoiled samples of membranes were tested in accordance with ASTM E1 294-89 to give the data shown in Table 1. Whilst 'track-etched' membranes exhibit fairly narrow pore size distributions around mean values close to the manufacturer's quoted ratings, most of the other membranes tested demonstrated mean pore sizes somewhat different from the quoted ratings. For instance, a 0.2 μm rated cast membrane such as Sartorius CN had an average mean pore size of 0.51 μm , and an 8 μm rated membrane of the same type had mean and maximum pore sizes of 3.6 μm and 5.8 μm , respectively.

The range of pore sizes found in the membranes widened considerably for the larger pore size ratings. As a consequence, there was a greater variation of measured pore size between different samples of the same membrane at the larger ratings. These latter findings perhaps indicate the difficulties experienced in manufacturing larger pore size membranes with 'tight', or even reproducible, size distributions.

In crossflow microfiltration tests, the relation between the larger membrane pores and the finer particles in the feed is important. When the particles in the feed are significantly larger than the membrane pores, little difference in flux performance or filtrate clarity can be observed over a range of feed suspensions and membrane ratings. However, when a significant proportion of the feed particles are near to, or smaller than the membrane pores, flux levels and filtrate clarity both deteriorate.

PERMEABILITY

The membranes were tested in a pressure driven permeameter to measure their permeability and 'clean water flux'. For each sample, the permeation rate for a given applied pressure was measured and this was related through Darcy's Law to give its permeability. All these tests were performed with double distilled water at 20°C. Table 2 compares some manufacturers' data with measured values obtained from permeation tests.

Comparison shows that the measured permeabilities, and hence clean water fluxes, are often somewhat different from those stated by the manufacturer. This is difficult to explain, though it should be noted that the manufacturers do not fully state test conditions and, in particular, at what temperature their permeation tests were performed. Whatever the explanation, there is a clear difference in the permeabilities between 'large' and 'small' pore size membranes. For instance, there are approximately two orders of magnitude difference in the permeabilities of 0.2 µm and 10 µm Nuclepore PC membranes.

Even though large differences in permeability and clean water flux can be observed, it would seem that their influence in microfiltration is often negligible. The fouling layers formed during the initial stages of filtration usually govern flux performance.

'WETTABILITY'

The technique used to evaluate the membrane wettabilities utilised a 400 frame per second camera and video system. A sample strip of fresh membrane was positioned in front of a zoom lens attached to the camera such that only the membrane 'edge' was visible. A droplet of the suspension (or fluid) to be tested was then placed on the membrane surface using a micro-syringe and pictures of the moving droplet/membrane interface recorded with the video system. In this way, it was possible later to examine the dynamic behaviour of the droplet and measure the contact angle at any time.

Table 3 shows the contact angle variation with time for double distilled water and several membranes of differing construction and materials of composition. With all the membranes tested, there was a fall in the measured contact angle with time, as the water in the droplet progressively penetrated the membrane pores and spread out over the surfaces. A sharp reduction of the contact angle with time is indicative of the lateral migration of fluid through the membrane structure being more rapid than its spreading over the surface.

Nuclepore PC membranes have no lateral connectivity between pores and hence an almost constant contact angle is observed. The magnitude and rate of change of the contact angle were dependent on the material properties of the membrane used and the coatings applied during their manufacture, and the initial contact angle gives an indication of the hydrophilicity of the fresh membrane. The more hydrophobic membranes tend to lead to lower filtration fluxes of aqueous solutions.

It would be helpful for used of microfiltration equipment if there were greater standardisation for the characterisation of membranes, and indeed, if international standards for testing and characterisation were to be developed.

TABLES AND FIGURES

| Membrane type | Rating (μm) | Max size (μm) | Mean size (μm) | Min size (μm) | Variance (μm^2) |
|---------------------------------|-----------------------------|-------------------------------|--------------------------------|-------------------------------|---------------------------------|
| Nuclepore PC | 10 | 18.97 ¹ | 10.26 ¹ | 7.92 ¹ | 3.18 |
| Nuclepore PC | 5 | 7.96 ¹ | 5.56 ¹ | 4.51 ¹ | 0.15 |
| Nuclepore PC | 1 | 1.49 ¹ | 1.26 ¹ | 1.04 ¹ | 0.0047 |
| Nuclepore PC | 0.2 | 0.38 ¹ | 0.35 ¹ | 0.28 ¹ | 0.00029 |
| Sartorius CN | 8 | 5.79 | 3.63 | 2.56 | 0.195 |
| Sartorius CN | 5 | 4.80 | 3.15 | 2.47 | 0.108 |
| Sartorius CN | 1.2 | 2.28 ¹ | 1.45 ¹ | 1.14 ¹ | 0.026 |
| Sartorius CN | 0.2 | 0.72 ¹ | 0.51 ¹ | 0.41 ¹ | 0.0019 |
| Pall Posidyne | 5 | 5.40 | 3.90 | 2.50 | 0.215 |
| Pall Posidyne | 1.2 | 3.16 ¹ | 1.94 ¹ | 1.40 ¹ | 0.095 |
| Pall Posidyne | 0.2 | 0.74 ¹ | 0.54 ¹ | 0.42 ¹ | 0.0052 |
| Gelman Supor | 0.8 | 1.93 | 1.22 | 0.91 | 0.035 |
| Gelman Supor | 0.45 | 0.99 | 0.70 | 0.58 | 0.0039 |
| Gelman Supor | 0.2 | 0.71 | 0.52 | 0.41 | 0.0028 |
| Gelman Versapor | 0.2 | 0.56 | 0.35 | 0.30 | 0.00037 |
| DH Asypor | 0.8 | 2.27 ¹ | 1.75 ¹ | 1.34 ¹ | 0.024 |
| DH Asypor | 0.2 | 1.03 ¹ | 0.75 ¹ | 0.59 ¹ | 0.0061 |
| BioPore PC | 0.4 | 0.71 | 0.54 | 0.45 | 0.0013 |
| DH Prepor | 1 | 10.59 | 3.59 | 2.44 | 0.52 |
| Gelman BioTrace NT | - ² | 0.36 | 0.26 | 0.20 | 0.00093 |
| Gelman Nylaflo | 0.45 | 0.56 | 0.49 | 0.37 | 0.0027 |
| Gelman Nylaflo | 0.2 | 0.46 | 0.34 | 0.24 | 0.0024 |
| Gelman TF | 1 | 1.27 | 1.00 | 0.78 | 0.0084 |
| Millipore Durapore ³ | 0.22 | 0.49 | 0.41 | 0.30 | 0.0027 |
| Millipore Durapore ⁴ | 0.22 | 0.47 | 0.40 | 0.29 | 0.0025 |

¹average value; ²described by the manufacturer as 'optimised for maximum performance';
^{3,4}hydrophobic and hydrophilic samples, respectively

Table 1: Membrane pore sizes.

| Membrane type | Rating (μm) | Thickness (μm) | Permeabilities (m^2) | |
|---------------------------------|-----------------------------|--------------------------------|---------------------------------|-----------------------|
| | | | Manufacturers | Measured |
| Nuclepore PC | 10 | 10 | 6.0×10^{-14} (est) | 1.1×10^{-14} |
| Nuclepore PC | 5 | 10 | 4.8×10^{-14} | 9.4×10^{-15} |
| Nuclepore PC | 1 | 11 | 6.0×10^{-15} | 1.5×10^{-15} |
| Nuclepore PC | 0.2 | 10 | 4.8×10^{-16} | 2.7×10^{-16} |
| Sartorius CN | 8 | 140 | 1.8×10^{-13} | 1.2×10^{-13} |
| Sartorius CN | 5 | 140 | 1.3×10^{-13} | 6.7×10^{-14} |
| Sartorius CN | 1.2 | 140 | 7.5×10^{-14} | 4.6×10^{-14} |
| Sartorius CN | 0.2 | 130 | 4.7×10^{-15} | 5.0×10^{-15} |
| Pall Posidyne | 5 | 135 | 4.7×10^{-14} | 7.3×10^{-14} |
| Pall Posidyne | 1.2 | 135 | 1.9×10^{-14} | 3.0×10^{-14} |
| Pall Posidyne | 0.2 | 150 | 3.0×10^{-15} | 3.5×10^{-15} |
| Gelman Supor | 0.8 | 150 | 3.6×10^{-14} | 2.6×10^{-14} |
| Gelman Supor | 0.45 | 150 | 1.3×10^{-14} | 8.6×10^{-15} |
| Gelman Supor | 0.2 | 150 | 8.0×10^{-15} | 6.7×10^{-15} |
| Gelman Versapor | 0.2 | 185 | 7.9×10^{-15} | 7.0×10^{-15} |
| DH Asypor | 0.8 | 165 | 8.5×10^{-15} | 7.6×10^{-14} |
| DH Asypor | 0.2 | 175 | 6.0×10^{-14} | 2.8×10^{-14} |
| BioPore PC | 0.4 | 30 | - | 8.7×10^{-16} |
| DH Prepor | 1 | 520 | 2.6×10^{-13} | 8.4×10^{-14} |
| Gelman BioTrace NT | - ¹ | 130 | not stated | 1.5×10^{-15} |
| Gelman Nylaflo | 0.45 | 125 | 4.8×10^{-15} | 4.4×10^{-15} |
| Gelman Nylaflo | 0.2 | 125 | 2.4×10^{-15} | 2.2×10^{-15} |
| Gelman TF ² | 1 | 180 | 2.0×10^{-14} | - |
| Millipore Durapore ² | 0.22 | 120 | 2.6×10^{-15} | - |
| Millipore Durapore | 0.22 | 120 | 2.0×10^{-15} | - |
| Ceramesh | 0.1 | 170 | | 2.8×10^{-16} |

Table 2: Membrane permeabilities.

| Membrane | Rating (μm) | Contact angle at $t = 0 \text{ s}$ ($^\circ$) | Angle at $t = 10 \text{ s}$ ($^\circ$) | Angle at $t = 30 \text{ s}$ ($^\circ$) |
|---------------|-----------------------------|----------------------------------------------------|---------------------------------------------|---------------------------------------------|
| Nuclepore PC | 0.2 | 53 | 51 | 49 |
| Sartorius CN | 0.2 | 31 | <5 | <5 |
| Pall Posidyne | 0.2 | 42 | - | - |
| DH Asypor | 0.2 | 53 | 45 | 34 |
| DH Asypor | 0.8 | 84 | 45 | 36 |

Table 3: Membrane contact angles.

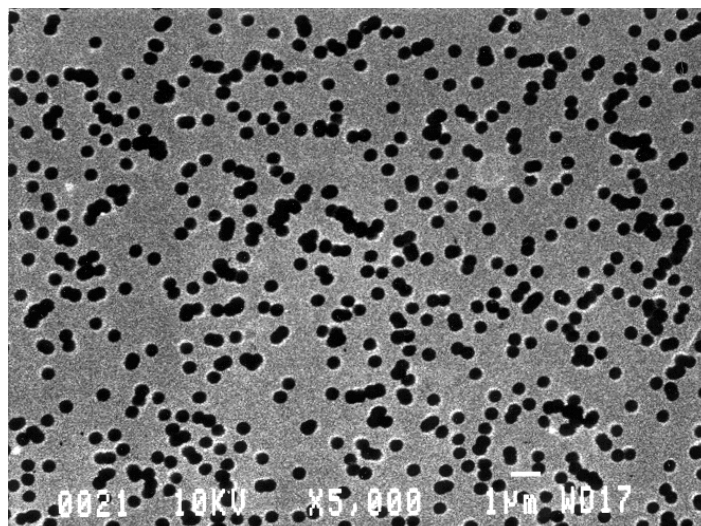


Figure 1: The topography of a 0.4 µm rated BioPore PC membrane.

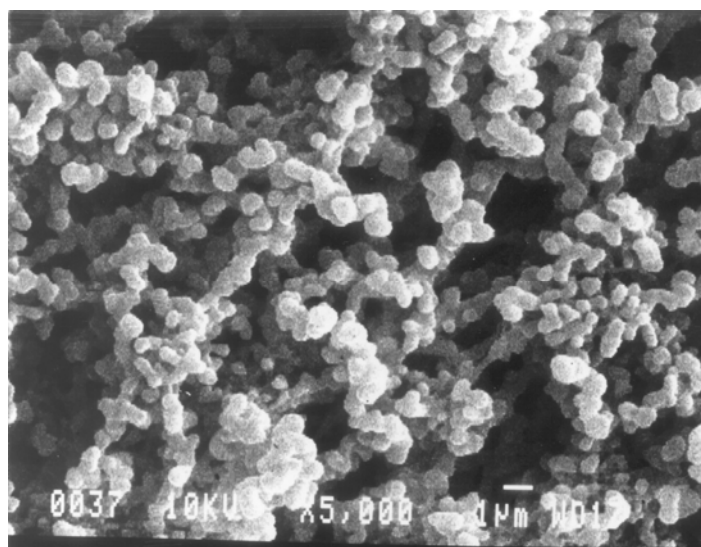


Figure 2: The topography of a 0.8 µm rated Gelman Supor membrane.

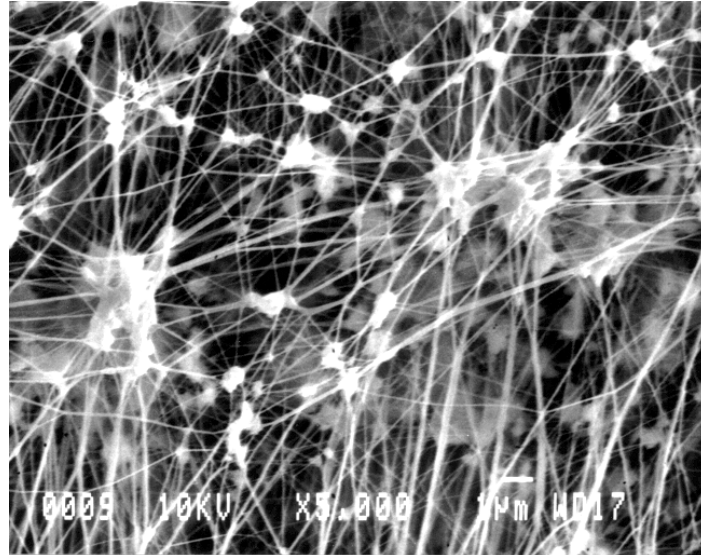


Figure 3: The topography of a 1 µm rated Gelman TF membrane.



Figure 4: Surface features of a 0.2 µm rated Ceramesh membrane.