A Novel Technique for Characterization of Membranes

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Abstract

The performance of membranes is governed by their pore structure. Pore structures of porous materials can be determined by a number of techniques. However, the novel technique, capillary flow porometry has a number of advantages. In this technique, the sample is brought in contact with a liquid that fills the pores in the membrane spontaneously. Gas under pressure is used to force the liquid from the pores and increase gas flow. Gas flow rate measured as a function of gas pressure in wet and dry samples yield data on the largest pore size, the mean flow pore size, flow distribution and permeability. Pore characteristics of a number of membranes were measured using this technique. This technique did not require the use of any toxic material and the pressure employed was low. Capillary flow porometry is a suitable technique for measurement of the pore structure of many membranes.

Introduction

In many applications membranes act as barriers to particles or organisms. The barrier characteristics of membranes are determined by the pore structures of membranes. The novel technique capillary flow porometry is capable of determining the relevant membrane properties that determine the barrier characteristics. In this paper the technique and its capabilities will be discussed.

Capillary Flow Porometry

Principle

The sample of the membrane is soaked in a liquid that fills the pores in the sample spontaneously. The pressure of a non-reacting gas on one side of the sample is gradually increased so as to empty the pores and allow flow of gas through the sample to increase (Figure 1).

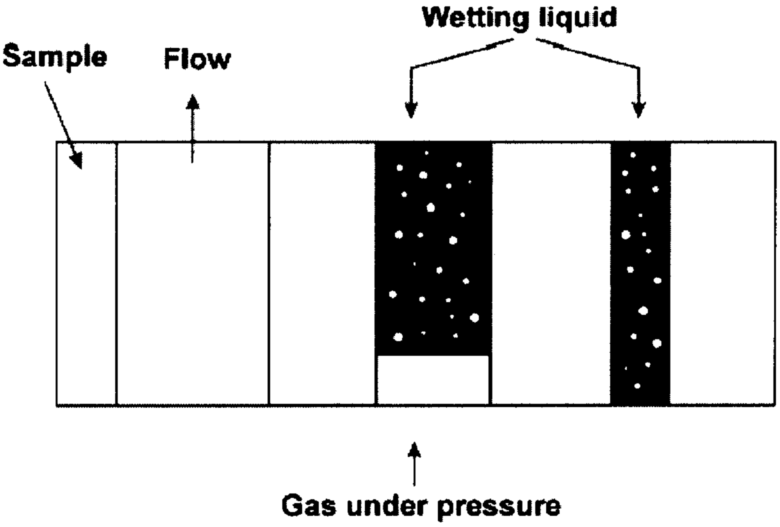
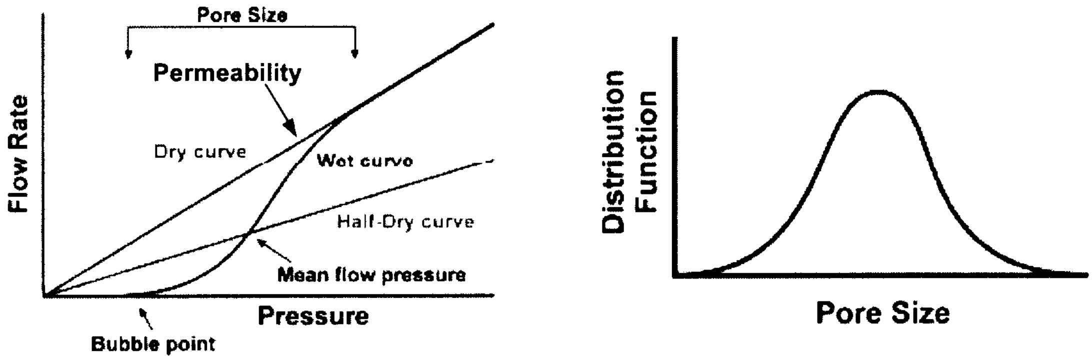


Figure 1. Illustration of the principle of capillary flow porometry

Flow rate as a function of pressure difference across the dry sample is measured. These data generate a dry curve (Figure 2). Similarly a wet curve is generated using the wet sample. A half-dry curve is calculated from the dry curve so as to give half of the flow rate of the dry curve at a given differential pressure. These data are used to compute various characteristics of the membrane.



(a) Pore diameter and permeability (b) Pore distribution

Figure 2. Characteristics measurable by capillary flow porometry

Equipment

The PMI Capillary Flow Porometer that was used in this study is shown in Figure 3. The sample chamber is shown in Figure 4.

Figure 3. The PMI Capillary Flow Porometer

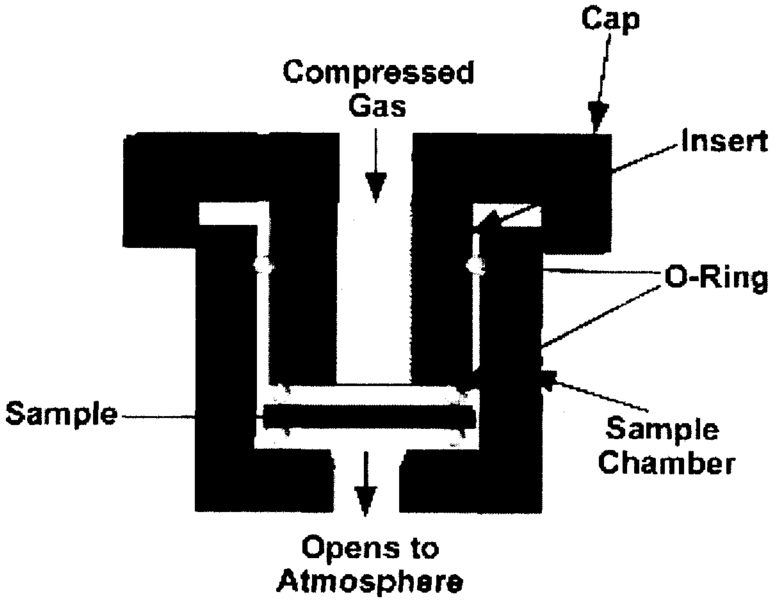


Figure 4. Sample chamber

The instrument uses state-of-the-art components, has many innovative designs and uses windows based software for data acquisition and reduction. The instrument has a built in internal computer for complete automation of its operations

Accuracy and Reproducibility

In order to test the accuracy of the instrument, diameters of circular pores etched in stainless steel discs and polycarbonate membranes were measured by Scanning Electron Microscopy and capillary flow porometry. The results shown in Table 1 demonstrate the exceptional accuracy of results obtainable by the PMI Capillary Flow Porometer.

Table 1. Pore diameters measured by SEM and PMI Capillary Flow Porometer

Material	SEM Pore diameter, µm	PMI Capillary Flow Porometer Pore diameter, µm
Stainless steel disc	81.7 ± 5.2	86.7 ± 4.1
Polycarbonate membrane	4.5 ± 0.5	4.6 ± 0.1

The high reproducibility of results obtained with the PMI Capillary Flow Porometer has been demonstrated by repeating measurements up to 32 times [1]. The results [1] in Table 2 demonstrate the reproducibility.

Table 2. Scatter in the largest pore diameters obtained from 32 repeated measurements.

Material	Scatter in pore diameter using wetting liquid:	
	Porewick	Silwick
Stainless steel disc	1.8 %	1.2 %
Nonwonen fibrous mat	0.2 %	1.5 %
Paper	1.7 %	1.1 %

Results and Discussion

Change of flow rate with differential pressure

Typical results obtained with a membrane is shown in Figure 5. Because a wetting liquid fills the pores spontaneously, the Solid/liquid interfacial free energy ($\gamma_{s/l}$) is less than the solid/gas interfacial free energy ($\gamma_{s/g}$). Displacement of liquid in the pore by the gas results in an increase in the solid/gas interfacial area. Hence, work done by the gas is equal to the increase in interfacial free energy. By considering energy balance, the relation between measured differential pressures and pore diameter can be derived [2].

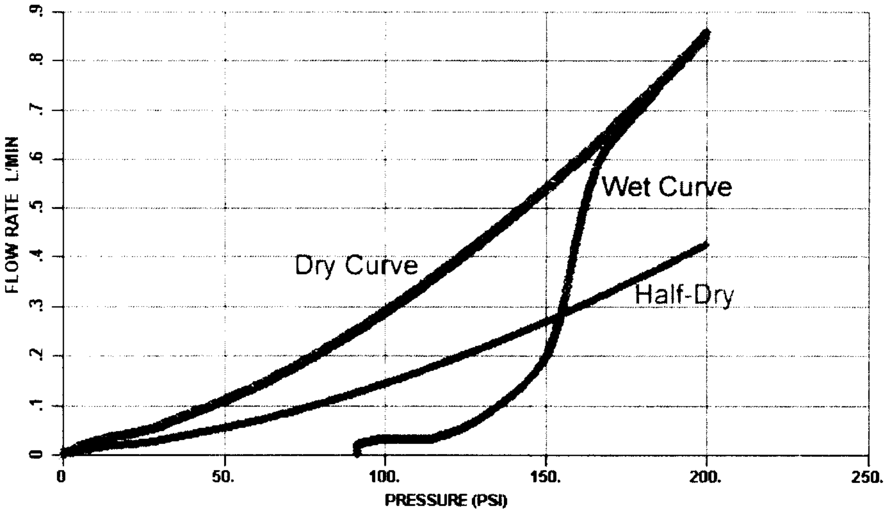


Figure 5. Change of flow rate with differential pressure for membrane #4.

The constricted pore diameter

The pores normally have irregular cross-sections and their size changes along pore path. We, therefore, define pore diameter at a given location in the pore as the diameter D of a circular opening such that its perimeter to area ration is the same as that of the pore at the specified location. Expressing the relation between surface tensions, $\gamma_{s/g}$, $\gamma_{s/l}$ and $\gamma_{g/l}$ in terms of contact angle, θ the energy balance equation yields the following relation [2].

$$D = 4\gamma_{l/g} \cos\theta / p$$

D = pore diameter
p = differential pressure
$\gamma_{l/g}$ = liquid/ gas surface tension

The contact angle θ has been shown to be close to zero for low surface tensions wetting liquids [1].

The presence of a pore is detected when gas starts flowing through the pore. Because differential pressure is inversely proportional to pore diameter, pressure must be increased to displace liquid in a pore up to the most constricted part of the pore, where the differential pressure requirement is maximum (Figure 6). Once this maximum differential pressure is reached, the gas removes liquid from the remaining part of the pore without requiring further increase of its pressure. Thus, the differential pressure that causes flow through the pore corresponds to the constricted part of the pore and the pore diameter calculated from the differential pressure is the diameter of the pore at its most constricted part.

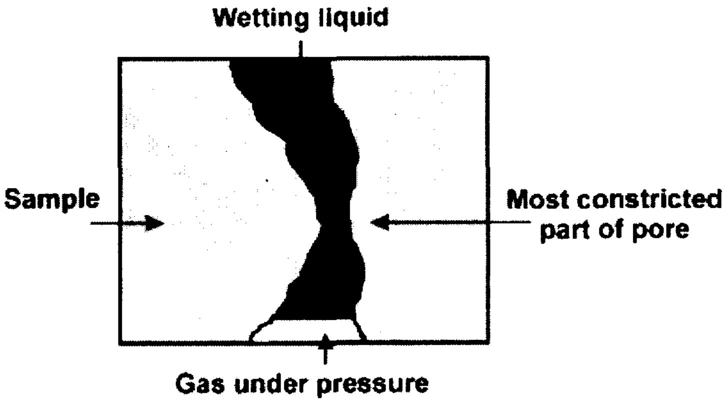


Figure 6. Constricted pore size

Constricted pore diameter determines the barrier characteristics of the pore. Capillary flow porometry is the only technique that is capable of measuring constricted pore diameter.

The largest pore diameter (Bubble point pore diameter)

With increase in differential pressure, the wet sample initially does not allow any gas to pass through, because its pores contain liquid. When the pressure reaches a value sufficient to open empty the largest pore, it is the first pore to open up and allow gas to flow. Thus, the pressure at which gas flow is initiated is used to calculate the largest pore diameter. The data in Figure 7 illustrates the procedure. The data on four membranes are listed in Table 3. Pore diameters in the range of 0.073 – 27.123 μm were easily measurable.

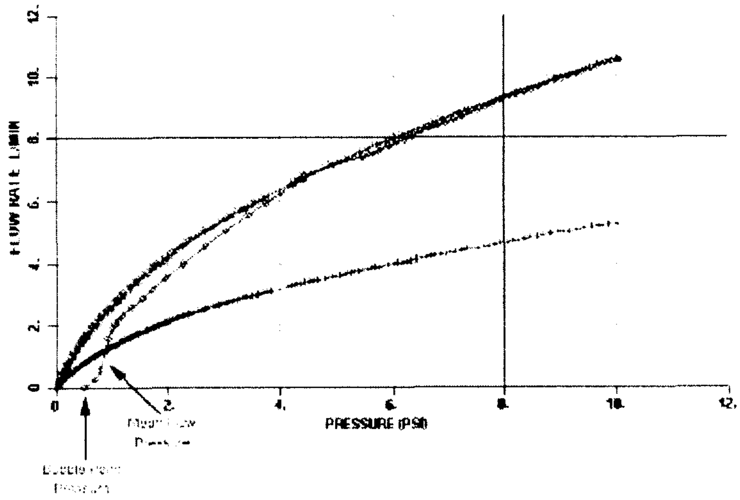


Figure 7. Variation of flow rate with pressure for membrane #3 showing bubble point pressure and mean flow pressure

Table 3. Bubble point and mean flow pore diametersof four membranes

Membrane	Bubble point Pore diameter, μm	Mean flow pore pore diameter, μm
Membrane, #1	27.123	14.714
Membrane #2	17.914	3.812
Membrane #3	13.544	7.668
Membrane #4	0.073	0.043

The mean flow pore diameter

The mean flow pore diameter is calculated from the mean flow pressure corresponding to the point of intersection of the wet curve and the half-dry curve. Mean flow pore diameter is such that 50 % of the flow through dry sample is through pores larger than the mean flow pore. Figure 6 illustrates the procedure and Table 3 lists the values.

Flow distribution over pore diameter

We define the distribution function, f in the following equation.

$$f = -d(F_w / F_d)_p / dD$$

where $(F_w / F_d)_p$ is the ratio of flow through wet and dry samples at the same differential pressure. Figures 8 and 9 give the distributions in two membranes. The distribution function is such that the flow through pores in a given range is given by the area under the curve in the same range. Membrane #1 has a single sharp peak. The second membrane shows a bimodal distribution. We also note that most of the pore diameters are close to the mean flow pore diameter

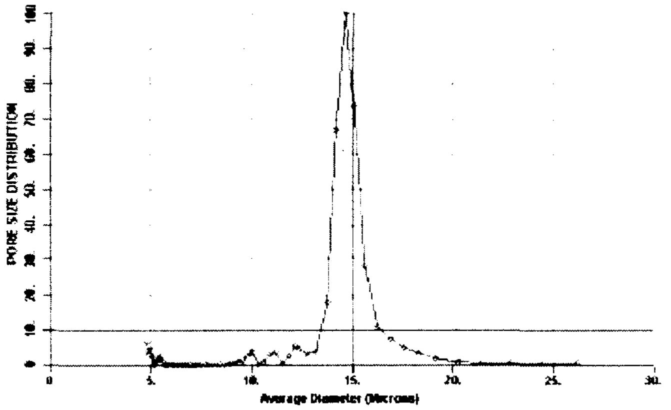


Figure 8. Pore size distribution for membrane #1

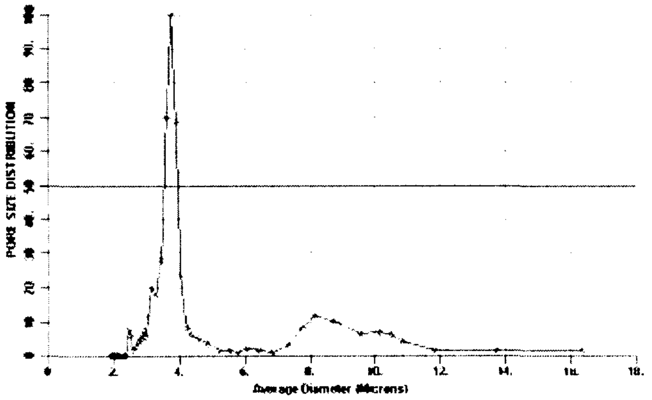


Figure 9. Pore size distribution membrane#2

Cumulative flow distribution

The percentage cumulative flow distribution is defined as 100x$(F_w/F_d)_p$. Figures 10 and 11 show the data on the two membranes, #1 and #2. The pore distribution characteristics are also obvious from the cumulative flow distribution plots.

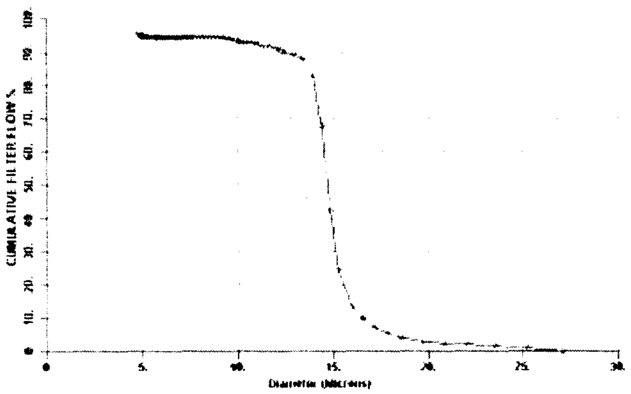


Figure 10. Cumulative flow distribution membrane #1

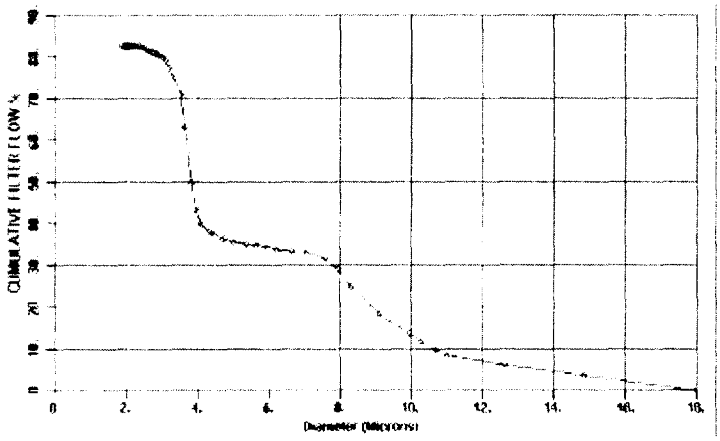


Figure 11. Cumulative flow distribution membrane #2

Gas permeability, liquid permeability and envelope surface area

Gas permeability in any desired commercial unit is computed from the dry curve. The instrument can be fitted with suitable attachments so that liquid permeability is also measurable. Gas flow rate is related to surface area, because it offers resistance to the flow of gases through porous media. The gas flow rate is used to compute the envelope surface area,

Advantages of capillary flow porometry

1. Very high pressures are not required. Chance of the sample getting damaged is very small.
2. Test is performed at ambient temperatures.
3. No toxic material is used.
4. Sample is reusable because it is not damaged or contaminated.
5. No special and expensive gases or gas mixtures are required.
6. This technique measures only the through pores that are responsible for flow.

Conclusions

1. The PMI Capillary Flow Porometer can measure pore sizes in membranes accurately. In this study sizes down to 0.073 microns were easily measured. The instrument is capable of measuring pore diameters down to 0.013 microns.
2. Largest pore size could be measured.
3. Mean flow pore size could be measured.
4. Bimodal and unimodal distributions could be detected.
5. Both sharp as well as broad pore size distributions could be measured.
6. Flow was primarily through pores having diameters close to the mean flow diameter
7. The samples did not get damaged during the test. They could be repeatedly used.
8. The technique has many operational advantages.

References

(1) Vibhor Gupta and A. K. Jena, Advances in Filtration and Separation Technology American Filtration & Separation Society, 13b (1999), 833.
(2) A. K. Jena and K. M. Gupta, Journal of Power Sources, 80 (1999), 46