Pore Structure Characterization by PMI Ultra Nano Porometer

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Introduction

Through Pore Characterization is an important parameter for filtration industry. Currently membrane researchers have to use multiple tools to characterize Micro, Ultra & Nanofiltration membranes and non-woven support base. Also conventional Capillary Flow Porometery is not suitable for hollow fibers as they tend to get damage when measured at high pressures. Liquid-Liquid Porometery is another technique which works at relatively low test pressure and doesn't damage the hollow fibre. The new Ultra Nano Porometer combines the benefits of our Capillary Flow Porometer and Liquid-Liquid Porometer conveniently into one product. The machine yields accurate and reproducible measurement of pore characteristics, considerably reduces test duration, and requires minimal operator involvement. The Ultra Nano Porometer is capable of measuring a wide variety of pore characteristics such as Mean pore size, pore distribution and liquid flow rate. The Porometer is also designed to calculate pore structure of materials having a wide spectrum of pore sizes from relatively large to relatively small.

Fig1 : PMI Ultra Nano Porometer

Principle

Liquid- Liquid Porometery Technique

A wetting liquid spontaneously fills the pores of the material. Two immiscible wetting liquids are selected. Liquid 1 with lower surface tension is used to fill the pores of the sample. Liquid 2 is added to the top of the sample and is pressurized to displace the first from the pores and flow through the empty pores. The flow rate of Capillary Flow Porometery A wetting liquid is allowed to spontaneously fill the pores in the sample and a non-corrosive gas is allowed to displace liquid from the pores. The gas pressure and flow rates through wet and dry samples are accurately measured. The gas pressure required to remove liquid from the pores and cause gas to flow is given by: Liquid 2 is also measured without wetting the sample with Liquid 1. The pore diameter is related to the surface tension of the two liquids. The flow rates yield pore distribution
and is given by:

Equation 1: $D = 4 \gamma_1 \cos \theta_1 / p$

Where, D = pore diameter
γ_1 = Interfacial surface tension of liquids
$\cos \theta_1$ = contact angle of liquid 1 on pore surface
p = differential pressure applied on the sample by liquid 2

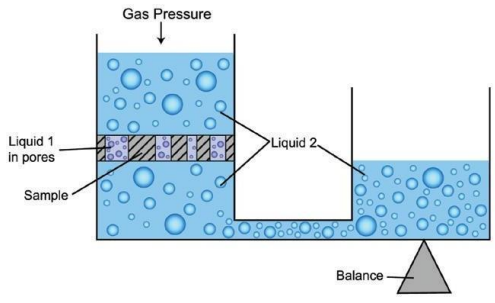


Figure 2: Liquid Liquid Porometry Principle

Pore distribution is expressed by the distribution function:

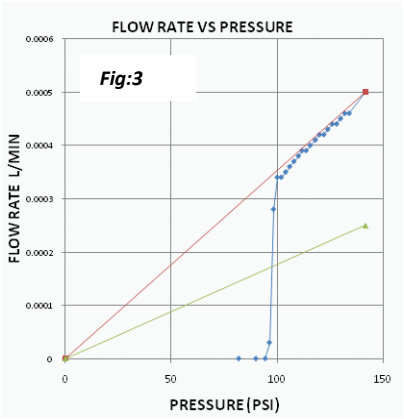
Equation 2: $f = -d[(fw/fd) \times 100] / dD$

where fw and fd are the flow rates through wet and dry sample at the same differential pressure. The distribution function is such that the area under the plot of distribution functions against pore diameter in any desired pore diameter range yields percentage flow through pores in the selected pore diameter

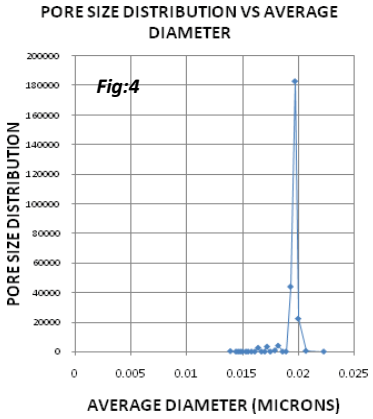
APPLICATION OF LIQUID-LIQUID POROMETRY FOR CHARACTERIZATION OF ULTRAFILTRATION MEMBRANES

GE ZeeWeed 20 nm Ultrafiltration Membrane

Figure 3 shows the measured wet and dry flow rates as a function of differential pressure for a 20 nm ultrafiltration membrane. The computed half-dry curve in the figure 3 gives half of the flow rate through the dry sample at the same differential pressure. Through Pore Throat Diameter: In this technique, a pore is detected when it is emptied and flow of wetting liquid-2 starts through the empty pore. A pore becomes empty when the pressure is sufficiently high to push wetting liquid-2 past the pore throat. Therefore, pore diameter computed from the measured differential pressure is the pore throat diameter. The mean flow pore diameter is computed using the mean fow pressure, which is the differential pressure at which half-dry curve and wet curve have the same flow. The mean flow pore diameter of the membrane was 0.020 µm. The largest through pore throat diameter (Bubble Point Pore Diameter) is computed from the pressure needed to initiate flow through the wet sample in the wet test.



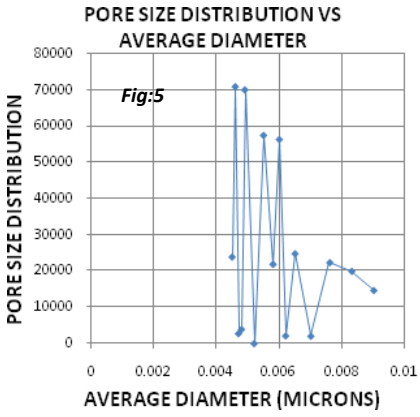
Pore Distribution: The pore distribution is given in terms of the distribution function (Equation 2). The distribution function computed from measured flow rates is shown in Figure 4. A very sharp distribution peak is observed.



Liquid Permeability: The measured dry curve in Figure 3 is the flow rate of liquid with increasing differential pressure. These data are used to compute liquid permeability after Darcy's law.

PALL 10 nm Ultrafiltration Membrane

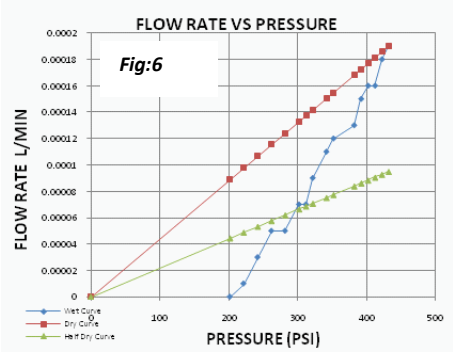
Figure 5 shows the measured wet and dry flow rates as a function of differential pressure for a 10 nm membrane from PALL Corporation. PALL is well known for making Ultrafltration membranes. The computed half-dry curve is also shown in the figure. The mean flow pressure and the bubble point are shown in the figure. The mean flow pore diameter was 0.0065 µm. The largest through pore throat diameter (Bubble Point Pore Diameter) was 0.009 µm. The pore distribution is given in terms of the distribution function (Equation 2). The distribution function computed from measured flow rates is shown in Figure 6. An unique distribution peak is observed.



Capillary Flow Porometery Technique

A wetting liquid is allowed to spontaneously fill the pores in the sample and a non-corrosive gas is allowed to displace liquid from the pores. The gas pressure and flow rates through wet and dry samples are accurately measured. The gas pressure required to remove liquid from the pores and cause gas to flow is given by:

Equation 3: D = 4 γ cos θ/p
Where,
D = pore diameter,
γ = surface tension of liquid
θ = the contact angle of liquid
p = differential gas pressure
From measured gas pressure and flow rates, the pore throat diameters, pore size distribution, and gas permeability are calculated.



APPLICATION OF CAPILLARY FLOW POROMETRY FOR CHARACTERIZATION OF LARGE PORE NON-WOVEN MATERIAL

Here the non-woven material was wetted with Galwick having surface tension of 15.9 dynes /cm. Since the material has large pores, a small pressure is required to measure the pore size distribution. The PMI Ultra Nano Porometer not only measures very small pores, but also measures the large pores accurately. Figure 7 shows the measured wet and dry flow rates as a function of differential pressure for a non-woven fabric. The half-dry curve in the figure 7 gives half of the flow rate through the dry sample at the same differential pressure. Through Pore Throat Diameter: In this technique, Bubble point (largest pore) is detected when first flow is noticed. As the pressure increase the small pores start getting empty.
A pore becomes empty when the pressure is sufficiently high to push wetting liquid past the pore throat. Therefore, pore diameter computed from the measured differential pressure is the pore throat diameter. The mean flow pore diameter is computed using the mean flow pressure, which is the differential pressure at which half-dry curve and wet curve have the same flow. The mean flow pore diameter of the non-woven was recorded at 14 µm at pressures below 1 PSI whereas the bubble point was recorded as 40 µm at pressure as low as 0.2 PSI

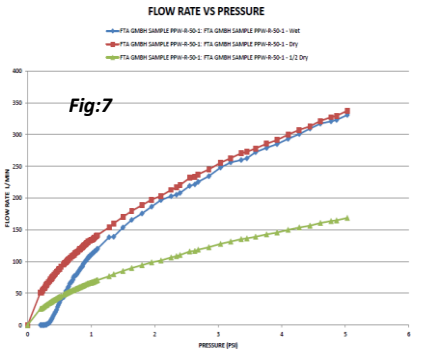


Fig:7

Pore Distribution: The pore distribution is given in terms of the distribution function (Equation 2). The distribution function computed from measured flow rates is shown in Figure 8 and Pore distribution histogram in Figure 9.

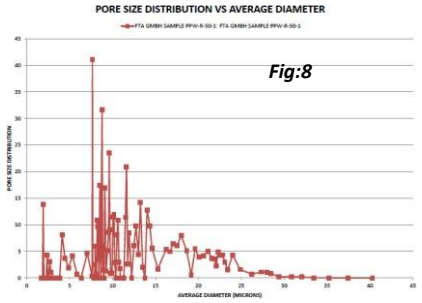


Fig:8

SUMMARY AND CONCLUSIONS

PMI Ultra Nano Porometer provides capabilities of both techniques i.e. Liquid- Liquid and Capillary Flow Porometery in a single platform. The Ultra Nano Porometer covers wide range of materials in the Nano/Ultra/Micro filtration range for through pore characterization.

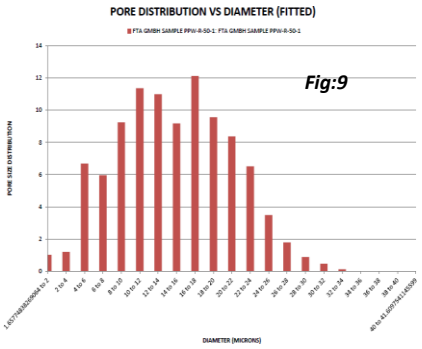


Fig:9

The following are the advantages of Liquid-Liquid Porometery over the widely prevalent Capillary Flow Porometery have been discussed and summarized here:

1. Lower pressures are required to measure to the same pore sizes.
2. Lesser energy is used for characterization of same material
3. An Liquid-Liquid Porosity test is much faster than a Capillary Flow Analysis.
4. Much lower pore sizes can be characterized with a Liquid-Liquid Porosimeter. Standard measurements can be as low as 2 nm.
5. Liquid-liquid Porometery does not cause structural distortion and membrane damage, since much lower pressures are used.

REFERENCES

Liquid-liquid porometer: H. Shi, F. Liu, and L Xue, “Fabrication and characterization of antibacterial PVDF hollow fibre membrane by doping Ag-loaded zeolites”, J. Membr. Sci., 437, 205 – 215 (2013)

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