

PORE STRUCTURE OF NONWOVENS CONTAINING HYDROPHOBIC AND HYDROPHILIC CONSTITUENTS

Dr. Akshaya Jena and Dr. Krishna Gupta
Porous Materials, Inc.
20 Dutch Mill Road, Ithaca, NY 14850

ABSTRACT

Water intrusion porosimetry and mercury intrusion porosimetry were used to investigate pore structure characteristics of a nonwoven containing both hydrophobic and hydrophilic pores. For both hydrophobic pores and hydrophilic pores, it was possible to determine pore volume, pore volume distribution, and pore sizes with appreciable contribution to pore volume.

INTRODUCTION

Pore structures of nonwovens containing hydrophobic and hydrophilic constituents are complex because of the presence of hydrophilic and hydrophobic pores. Such structures are often found in many products such as pharmaceutical materials, health care products and outerwear. Surface treated media also contain hydrophobic and hydrophilic pores. During use of the media in biochemical applications, some of the pores appear to change their hydrophobicity. Therefore, determination of such pore structure is complicated.

There is no unique technique that can measure the pore structure characteristics of nonwovens containing hydrophobic and hydrophilic pores. In this investigation two techniques have been used to investigate the pore structure. Water intrusion porosimetry and mercury intrusion porosimetry have been used. It has been possible to characterize the complex pore structure of a nonwoven containing hydrophobic and hydrophilic pores.

TECHNIQUE

Water Intrusion Porosimetry

Water cannot flow spontaneously in to pores of hydrophobic materials because the water/solid surface free energy is greater than the gas/solid interfacial free energy. On application of pressure on water surrounding the sample, water intrudes into the pores because the work done on the system provides for the excess free energy required for replacement of the gas/solid interface by the water/solid interface [1]. The pressure and intrusion volume are measured. The intrusion volume gives pore volume. The pressure gives pore diameter computed using the following equations. Equating the net free energy change to zero [2].

$$p = - \gamma \cos \theta (dS/dV) \quad (1)$$

where γ and θ are surface tension and contact angle respectively of the liquid and dS is a small increase in water/solid surface area due to a small increase in water volume, dV in the pore. Because pore cross-sections usually change in an irregular manner along pore path, pore diameter is not defined. For any pore cross-section, pore diameter, D is such that:

$$\begin{aligned} (dS/dV)_{\text{pore}} &= (dS/dV)_{\text{cylindrical opening of diameter } D} \\ &= 4 / D \end{aligned} \quad (2)$$

From Equations 1 & 2:

$$D = - 4 \gamma \cos \theta / p \quad (3)$$

The water intrusion porosimeter used in this investigation is the PMI Aquapore shown in Figure 1. It was a fully automated windows based system that required very little operator involvement and yielded accurate and reliable results. Use of mercury and other toxic materials was completely avoided. The pressure required for the tests was much less than that required for mercury intrusion.



Figure 1. The PMI Aquapore used in this investigation.

Mercury Intrusion Porosimetry

Mercury is nonwetting for most materials. It does not flow spontaneously into pores. Pressure is applied on mercury for it to intrude into the pores. Mercury can intrude in to hydrophobic as well as hydrophilic pores. Pore diameter is obtained from intrusion pressure, surface tension of mercury and contact angle of mercury using Equation 3. Pore volume is computed from the intrusion volume.

RESULTS AND DISCUSSION

Hydrophobic Through and Blind Pores

In a material containing both hydrophobic and hydrophilic pores, water does not need to be pressurized in order to enter hydrophilic pores. These pores are spontaneously filled by water. Hydrophobic pores require water to be pressurized to enter these pores and the measured intrusion volume and pressure give hydrophobic pore volume and diameter respectively. Thus, hydrophobic through and blind pores can be determined by water intrusion porosimetry

Pore diameter: The pore diameters of through and blind hydrophobic pores calculated from intrusion pressure measured in the water intrusion porosimeter are shown in Figure 2.

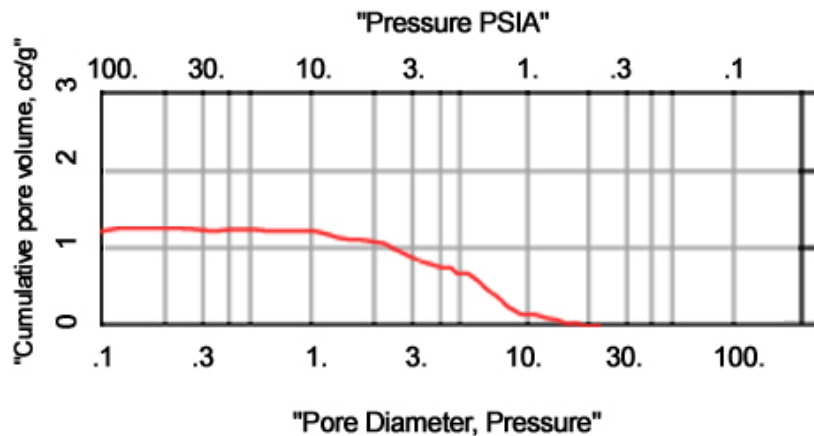


Figure 2. Hydrophobic through and blind pore diameter and cumulative volume measured by water intrusion porosimetry.

Pore diameter normally changes along pore path. As the pressure increases, water enters narrower parts of the pore and the diameter of the narrower parts is measured. Therefore, this technique measures all the diameters associated with pores along their lengths. This is illustrated in Figure 3.

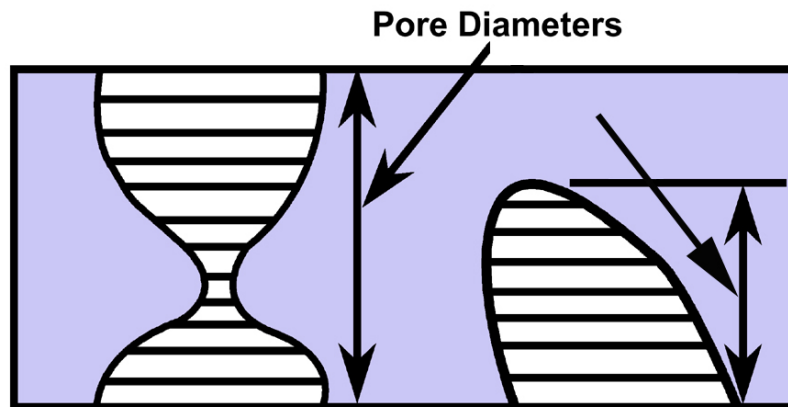


Figure 3. Pore diameters measurable by intrusion porosimetry.

Pore volume: The cumulative volume of hydrophobic through and blind pores is shown in Figure 2. As expected, the cumulative pore volume increases with increase in pressure and approaches a constant value indicating the absence of smaller pores. The total pore volume is 0.116 cc/g.

Pore volume distribution: The hydrophobic pore volume distribution over pore diameter is expressed by the following distribution function, f_v .

$$f_v = - (d V / d \ln D) \quad (4)$$

where V is pore volume and D is pore diameter. The distribution function is shown in Figure 4. The area under the curve in any pore diameter range gives the pore volume of the pore in that range. Pores with appreciable volume are in the range of 3 to 20 μm . The diameter of pores with maximum contribution to pore volume is 9.175 μm .

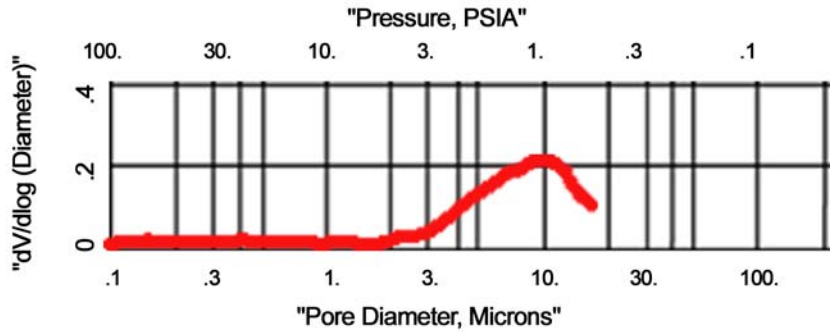


Figure 4. Distribution of volume of hydrophobic through and blind pores over pore diameter.

Hydrophilic Through and Blind Pores

Mercury is non-wetting for hydrophilic as well as hydrophobic pores. Therefore, mercury under pressure intrudes the hydrophilic and hydrophobic pores. Intrusion pressure and volume give through and blind pore diameters and volumes respectively of both hydrophilic and hydrophobic pores. Figure 5 shows the cumulative pore volume and diameters of hydrophobic and hydrophilic through and blind pores measured by mercury intrusion porosimetry.

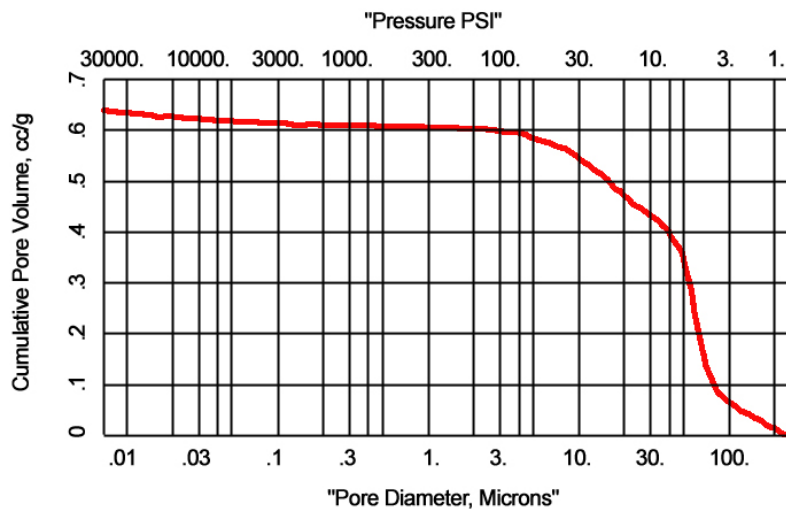


Figure 5. Cumulative pore volume and diameter of hydrophobic and hydrophilic through and blind pores measured by mercury intrusion porosimetry.

Volume of hydrophilic pores: Mercury intrusion porosimetry gave 0.652 cc/g as the volume of hydrophilic and hydrophobic pores. Water intrusion porosimetry yielded 0.116 cc/g (17.8 %) as the volume of hydrophobic pores. Hence, the volume of hydrophilic pores is 0.536 cc/g (82.2 %).

Diameters of hydrophilic pores: Figure 5 shows the diameters of hydrophilic and hydrophobic pores. These diameters extend to much larger values compared with the pore diameters of hydrophobic pores (Figure 2). Therefore, hydrophilic pore diameters are expected to be much larger than the hydrophobic pore diameters.

Distribution of hydrophilic pore volume: The pore volume distribution (Equation 4) of hydrophilic and hydrophobic pores derived from the data in Figure 5 is shown in Figure 6, The distribution function shows two peaks at about 60 μm and 18 μm .

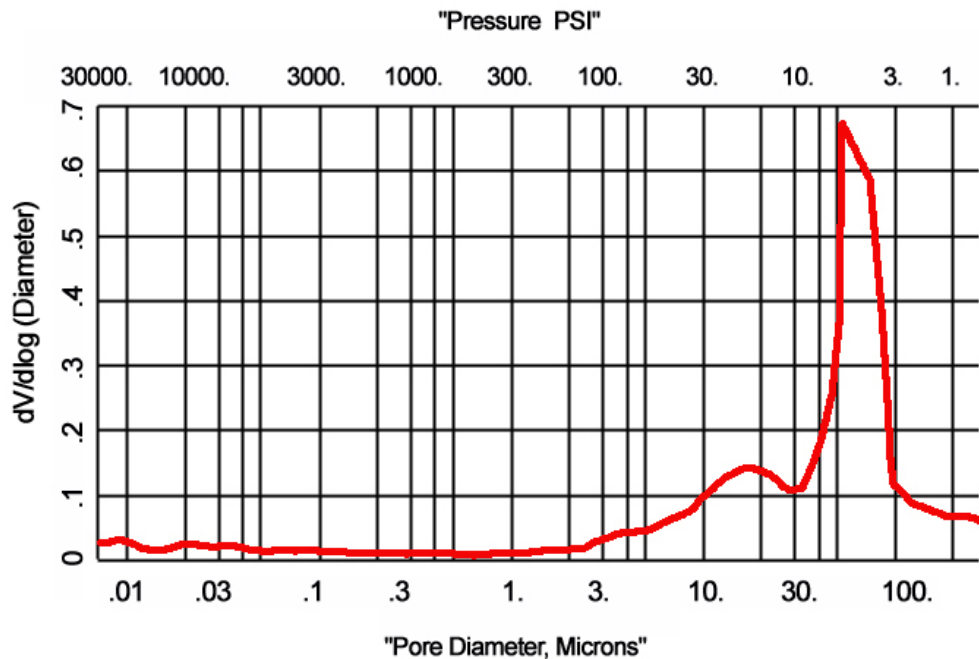


Figure 6. Distribution of hydrophilic and hydrophobic pores

The distribution function for hydrophobic pores (Figure 4) is symmetric around the peak value of 9.175 μm . Subtraction of pore volume distribution of hydrophobic pores from that of hydrophobic and hydrophilic pores results in a single peak corresponding to the distribution of hydrophilic pores (Figure 7). The small mismatch may be attributed to changes in contact angle and surface tension. The hydrophilic pore distribution has a maximum at 60 μm and pores having appreciable pore volume are in the range of about 20 –150 μm .

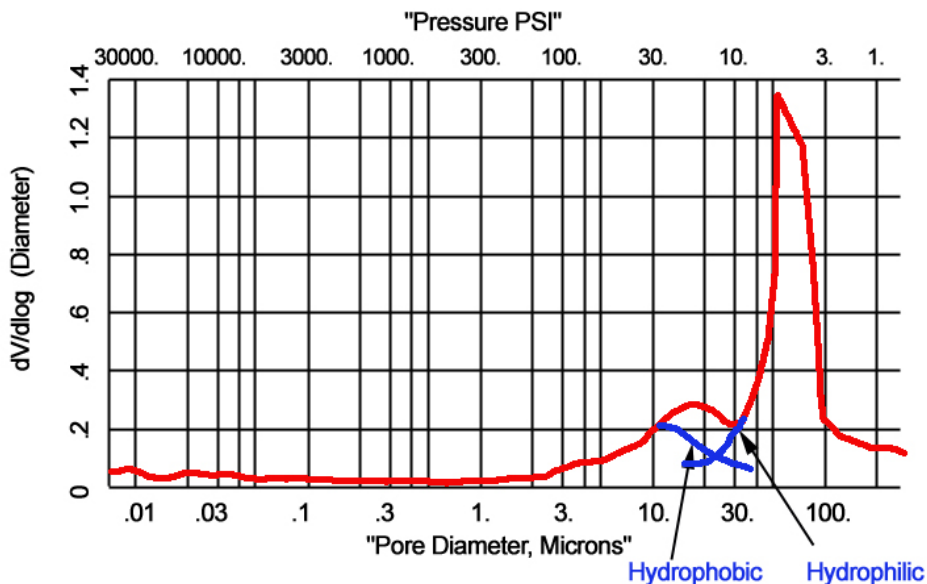


Figure 7. Distribution of pore volume of hydrophilic pores.

Pore structure

The measured and derived characteristics of hydrophobic and hydrophilic pores are listed in Table 1. Although intrusion porosimetry measures pore diameters and pore volumes, some of the pore diameters in complex pore configurations are not measurable. For example, the diameters of wider parts of pores accessed through narrower paths cannot be measured (Figure 8).

Characteristics	Pores	
	<i>Hydrophobic</i>	<i>Hydrophilic</i>
<i>Volume</i>	0.116 cc/g (17.8 %)	0.536 cc/g (82.2 %)
<i>Diameters contributing maximum to volume</i>	9.175 μm	60 μm

*Diameters contributing
appreciably to volume*

3 – 20 μm

20 – 150 μm

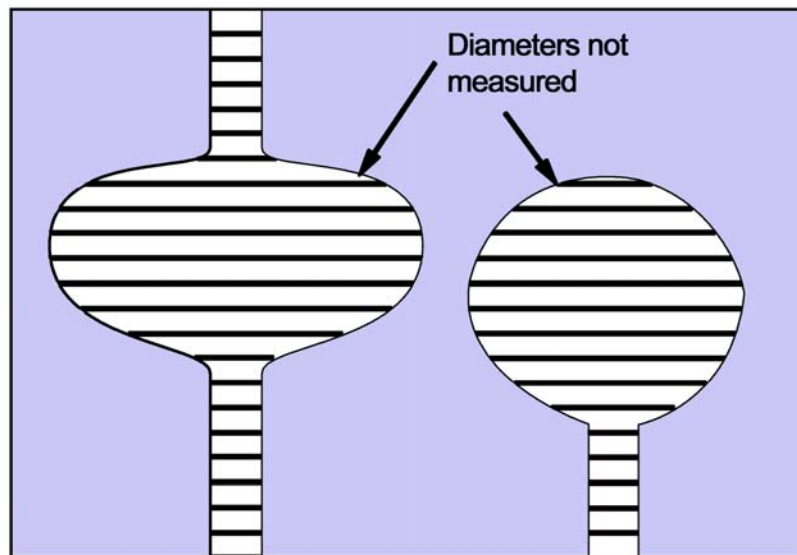


Figure 8. Examples of pore configurations in which some of the pore diameters are not measurable.

The fibrous paper-like material that was tested contained large hydrophilic pores of 60 μm diameter constituting 82.2 % of its pore volume. The much smaller hydrophobic pores had diameter of 9.173 μm and constituted only 17.8 % of the pore volume. It is postulated that the interfiber pores are the large hydrophilic pores and the intrafiber pores are the much smaller hydrophobic pores.

SUMMARY AND CONCLUSION

1. A partially hydrophobic and partially hydrophilic fibrous material was characterized by
Water Intrusion Porosimetry
Mercury Intrusion Porosimetry
2. The results were analyzed to obtain pore structure characteristics of hydrophobic and hydrophilic pores
3. The volume of hydrophobic pores was only 17.8 %. These pores had very small mean pore diameters of 9.175 μm .
4. The volume of hydrophilic pores was 82.2 %. These pores had much larger mean pore diameter of 60 μm .

5. This investigation suggests the importance of water intrusion porosimetry for measurement of hydrophobic pore structure characteristics.

References

1. K. Denbigh, *The Principles of Chemical Equilibrium*. Cambridge University Press, 1968.
2. Akshaya Jena and Krishna Gupta, 'Characterization of Pore Structure of Filter Media, *Fluid/Particle Separation Journal*, Vol. 14, No. 3, 2002, pp. 227-241.