The Role of Porosity

A look at the application of porosimetry in reconstructive surgery and wound care biopolymers.

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The technique of mercury intrusion porosimetry (MIP) is well understood to be of value in the field of bioceramics and rigid high-density polyethylene porous surgical implants. One might be hesitant to use the same pressure-based technique on soft, deformable polymers e.g. polyhydroxyalkanoates (PHAs), chitosan, polylactic acid (PLA), polyglycolic acid (PGA) and their co-polymers (PLGA). However, since the pore sizes involved are typically quite large (usually above 100 microns[1]), the pressures involved are rather small (less than 10 psi). Furthermore, the pressure is applied "isometrically", not transversely as in bubble-point (permeametry) techniques, so the polymer will not rupture even if in sheet form. MIP is therefore a viable technique.

Craniofacial reconstruction is a typical application for porous biopolymers.

Thin Sheets or Regular Shapes

Nevertheless, if detailed pore size measurements are not required, but just a measurement of overall porosity, the analysis is remarkably straightforward. Pore volume need not be measured directly (by pore filling with mercury[2]) but can be calculated as the difference between bulk volume and "skeletal" volume. Bulk volume can be determined from consideration of geometric dimensions. Many biopolymers are formed as thin sheets or regular shapes. It is a therefore a trivial matter to take micrometer or caliper readings. Alternatively, and certainly for irregularly shaped pieces, bulk volume can be determined by Dry Powder Pycnometry. This technique entails measuring the increase in volume of a packed bed of powder when the sample is immersed in it, Archimedes style. One simply needs a powder, reasonably free flowing, whose particle size precludes it penetrating those pores connecting to the polymer surface.

Limited Only By Ones Imagination

Over the years a number of different materials have been employed: graphite [1], aluminum hydroxide [2], metal powders [2,3], rapeseed [4], glass beads [5,6]. The list of possible materials is only limited by one's imagination. To complete the testing a reproducible means of packing the powder, by tapping, is employed. The Autotap (Quantachrome Instruments, Boynton Beach, FL) is such a device. The powder and sample volumes are simply read from the graduations on the sample container. Both rapid and inexpensive, the Autotap (or its two-station sibling the Dual Autotap) is a valuable addition to any material development lab.

A Good Fit

The second half of indirect pore volume determination is the measurement of Skeletal Volume (true volume of polymer excluding pores—not the patient!). Nowadays this is normally achieved using a gas expansion pycnometer (dry, non destructive) rather than liquid displacement (solubility problems, solvent disposal etc). The one-sample Ultrapycnometer 1000 and the unique five-station Pentapycnometer (both Quantachrome Instruments) feature simple programming of automatic repeat measurements, balance and PC interfaces, and automatic printed report generation. The Ultrapycnometer is available in a special version, the UltraFoam Pycnometer, which additionally calculates open porosity and closed pore volume (as percentages). Already used for a number of years in non-surgical fields (packaging, insulation, wicking etc), the technology is well established and seems like a good fit to the objectives of the bio-materials community. ■

References

1. S. Davis, A. Dolle and E. Moreau (1988) *Prog. Batt. Sol. Cells*, **7**, 342-348
2. B. Buczek and D. Geldart (1986) *Powder Technol*, **45**, 173-176
3. A. Korta and J. Klinik (1975) *Chem. Anal*. **20**, 1079
4. Approved Methods of the American Association of Cereal Chemists, 10-05 Guidelines for Measurement of Volume by Rapeseed Displacement.
5. M. P. Hwang, and K.-I. Hayakawa, (1980) *J. Food Sci*, **45**, 1400-1402.
6. S. L. Wilkison and M. S. Robinson. (2000) *Meteorit. Planet. Sci.*, **35**, 1203-1213.

Footnotes

1. Wound dressings have considerably smaller pores.
2. ...although mercury is an excellent contrast medium to assist in visualizing pore shape and connectivity by X-ray tomography and/or confocal light microscopy.

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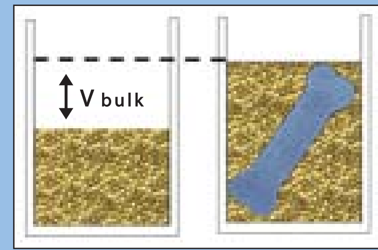

AUTHOR'S NOTE: DELVING FURTHER INTO V-BULK

The diagram shows the principle of simple Archimedes-style displacement in order to determine the bulk volume of a three-dimensional object. When using dry powder, the trick is to cause reproducible packing behavior of the powder around the sample. It is for this reason that the powder bed should be tapped until it reaches its maximum packing density (at the so-called "jamming transition"). External force supplied by a ram, or tamping, should be avoided so as not to compress a porous polymer.

Displacement of liquid mercury can also be employed. Non-wetting mercury will not enter a pore unless an external pressure is applied. In this case the determination is usually performed gravimetrically, using a mercury intrusion porosimeter to fill the sample holder (pycnometer) with mercury. The Gay-Lussac density-bottle principle is then used to calculate the sample volume from a series of weighings.

CALCULATIONS

1. $$\text{Porosity} = \frac{\text{Pore Volume}}{\text{Bulk Volume}} \times 100\%$$

and since

2. $$\text{Porosity} = \text{Bulk Volume} - \text{Skeletal Volume}$$

then

3. $$\text{Porosity} = \frac{\text{Bulk Volume} - \text{Skeletal Volume}}{\text{Bulk Volume}} \times 100\%$$

therefore

4. $$\text{Porosity} = 1 - \left(\frac{\text{Skeletal Volume}}{\text{Bulk Volume}}\right) \times 100\%$$

or

5. $$\text{Porosity} = 1 - \left(\frac{\text{Bulk Density}}{\text{Skeletal Density}}\right) \times 100\%$$