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Characterization of Porosity in Porous Polymeric Implant Materials

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Dental and Medical Materials
Polymer Science and Standards Division
Washington, DC 20234

February 1982

Annual Report for Period October 1980 - September 1981

Prepared for:

Bureau of Medical Devices
Food and Drug Administration
Silver Spring, Maryland 20910

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CHARACTERIZATION OF POROSITY IN POROUS POLYMERIC IMPLANT MATERIALS

R. E. Dehl, W. G. Grant and J. M. Cassel

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

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ANNOUNCEMENTS

1. Certain commercial materials, instruments, and analytical laboratories are identified in this report in order to adequately specify experimental procedures. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the identified materials, instruments, or laboratories are necessarily the best available.

2. In our first Annual Report to the Bureau of Medical Devices, Food and Drug Administration, entitled "Evaluation of Methods of Characterizing the Porosity of Porous Polymeric Implant Materials: A Review of the Current Status of Porosity Measurements" (NBSIR 81-2212, February, 1980), we have inadvertently reproduced certain copyrighted materials. Pages 11 to 14 of this report consist of information contained in two copyrighted publications of the Richards Manufacturing Company (Refs. 18 and 20 in the Annual Report). We also acknowledge that the trade names Plasti-Pore® and TORP® are registered trade names of the same company, and Tilt-Top™ is a trademark of the company. We regret any inconvenience to the Richards Manufacturing Company resulting from these accidental oversights.

3. We also wish to call the reader's attention to one paragraph of Richards' Technical Publication No. 4240, "Plasti-Pore® Material Technical Information." On page three of this publication, under the heading "Biocompatibility," two statements are attributed to the National Bureau of Standards. These are as follows:

(1) "Because of the near total inertness of ultra high molecular weight polyethylene, the National Bureau of Standards (NBS)

has established it as the standard to which all other implant and tissue contact polymeric materials are compared."

(2) ". . . the NBS considers, by definition, UHMWPE to be the most inert implant material that can be used as a reference."

Neither of the above opinions (1) or (2) has ever been expressed or implied by any employee of the National Bureau of Standards. NBS has never performed or sponsored any research or tests which could lead to the above conclusions.

ABSTRACT

In this report, we describe the application of several methods of porosity characterization to two commercial polymeric implant materials, a porous polyethylene and a composite of polytetrafluoroethylene and carbon. In exploring the use of mercury porosimetry to determine interconnecting pore size distributions in the composite, we have found that, contrary to widespread belief, this rather soft and deformable material was not distorted by the mercury pressures required to measure its pore size distribution. The mercury intrusion technique indicated that the porous polyethylene has a narrower distribution of pore sizes than the composite. In the polyethylene and the composite, the weighted average interconnecting pore "diameters" were found by this technique to be, respectively, 30 μm and 50 μm. The average pore diameters were also estimated by measurement of specific surface area and pore volume. Assuming a spherical pore shape, the average pore diameters in polyethylene and composite were calculated to be, respectively, 60 μm and 25 μm. The accessible pore volumes of the materials were measured by three different techniques: a simple "apparent density" method, mercury intrusion, and bulk compression, the last for the composite only. For the polyethylene and composite we found pore volumes of about 45 and 70 percent, respectively.

I. INTRODUCTION

During the first half-year of this project, which was begun in May 1980, efforts were directed to a comprehensive search of the existing published literature pertinent to the characterization of porosity in porous materials, with emphasis on methods appropriate to polymeric porous solid materials used as surgical implants[1]. The following year's efforts, which are described in this report, involve experimental approaches to the measurement of the volume of accessible pores in porous implant materials, and the size and size distribution of such pores.

It is important to be aware that there is a fundamental difference between the measurement of pore volume and pore size for the porous implant materials, in that the pore volume is a well defined physical property of the materials, whereas the pore "size" is not. For this reason, it is proper to refer to the accuracy of experimentally derived pore volumes; however, the word "accurate" has no well-defined meaning when applied to the measurement of a poorly defined physical property such as size or "diameter" of objects having any shape other than circular. In order to give physical meaning to the term "size", as it applies to irregularly shaped objects such as the pores in manufactured porous materials, one must in general make some arbitrary assumptions about the shape of the pores, realizing that other equally arbitrary assumptions may lead to different "size" parameters.

A consequence of this dilemma is that there is no reason to believe that different methods of measuring pore "size" will produce comparable results. Every method either requires arbitrary assumptions about pore shape or contains no information about the shape, as in the case of certain optical image analyses. Certainly, pore shape is expected to have some effect on the rate of tissue ingrowth, and one feels intuitively that it should not be ignored. However, it is not clear that any particular shape best describes the irregular pores in the porous implant materials discussed in this report. It is clear that measured pore "sizes" or "diameters" of irregularly shaped pores should always be accompanied by a statement about how the numbers were obtained and what assumptions were made about pore shape.

The activities of the past year may be divided into six categories, as follows:

(1) Continuation of the acquisition of reprints and other information pertinent to the use of porous polymeric implant materials.

(2) Attendance by W. Grant and R. Dehl at a one-day seminar concerning surface area and porosity measurements, sponsored by the American Chemical Society and presented by the Quantachrome Corporation. Lectures and laboratory demonstrations were presented.

(3) Laboratory studies of three porous polymeric implant materials, using mercury porosimetry to estimate pore size distributions and intruded void volumes. A publication has resulted from the results of some of this work.

(4) Surface area measurements on two porous implant materials and estimation of the average pore diameters.

(5) Accessible void volume measurements by three different techniques.

(6) Correspondence with Dr. C. A. Homsy and others concerning our work and its possible application to current Draft Standards of the American Society for Testing and Materials (ASTM) for porosity characterization of implant materials.

Items (3) to (6) are discussed in the following Report. The reader should be reminded that the work described here is ongoing, so that extensions or modifications of the data may be necessary in the future.

II. VOID VOLUME MEASUREMENTS

As we have indicated above, the volume of accessible pores in the porous implant materials is a well-defined physical property and is, therefore, subject to measurement by one or more physical methods. In the following, we describe the application of three different void volume measurements to two commercial implant materials, a porous polyethylene[*] and a porous composite of polytetrafluoroethylene (PTFE) and carbon[**].

A. Apparent Density Method

The simplest way to measure the void volume of a porous material, if the density of its solid phase is known, is simply to weigh a sample of well-defined geometry and calculate the total volume of the specimen from its measured dimensions. The volume of the solid phase is calculated from its weight and density and subtracted from the total volume. The difference between the total and solid volumes is the void volume, which may be expressed as a percentage of the total.

Porous Polyethylene

A sample of porous polyethylene in the form of a disc, 5.4 cm in diameter and 1.0 cm thick, was used to determine the void volume by this method. Assuming the density of polyethylene in this "high density" material to be 0.94 to 0.96 g/cm^3, we determined the volume of pores to be 44 to 45 percent of the total. In the product literature furnished by the manufacturer of this material[2], the void volume is stated to be

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[*] Plastipore®, registered trademark of the Richards Manufacturing Company.

[**] Proplast®, registered trademark of Vitek, Inc.

"approximately 35 percent." Because we had only one sample of this material in the form of a regular geometrical shape, we can only report one value of the density. We were told by the manufacturer of this material that all of their porous polyethylene has the same porosity, from which we assume that our measured void volume is representative of the company's material, but we cannot as of this writing report a range of sample-to-sample or lot-to-lot variability. However, the value obtained here may be compared with our mercury porosimetry value, as reported below, for a sample derived from a different disc of material.

PTFE-Carbon Composite

The void volume of this material was determined from a rectangular block, 1.5 x 4.0 x 1.0 cm^3. The density of solids in this material is complicated by the fact that there are two solid components present, and the ratio of the two is unknown. According to handbook values, the density of graphitic carbon[3] is 2.25 g/cm^3 and the density of crystalline PTFE (amorphous form of PTFE never observed)[4] is 2.27 to 2.30. From these data, the density of solids would have to lie within the range 2.25 to 2.30. Using a value 2.27 g/cm^3 for the density of the composite, we calculate that 82 percent of the sample volume is due to the volume of pores. This value falls approximately in the middle of the range specified by the manufacturer (70 to 90 percent) in the package inserts accompanying this material.

As a routine check on the assumed value of the density of solids in the composite, we have measured this density and found it to be much less than the assumed value. Samples of the composite in the form of 10 mm thick block were compressed between smooth metal plates in a hydraulic press, and regular geometrical samples (circular discs and rectangles) were cut from the compressed sheets to measure the density directly from the sample weight and dimensions. While it was, of course, expected that the measured density would increase with increasing applied pressure, it was found that the density of a compressed sample remained unchanged, above the lowest pressure at which a measurable reading could be observed on the hydraulic pressure gauge, (about 3 x 10^6 Pa). In fact, the material is quite easily compressed simply by applying finger pressure, and it is not surprising that relatively low hydraulic pressure is required to drive out the remaining airspace.

After several measurements of the density, we concluded that, rounded to two significant figure accuracy, the density of solids in the composite is 1.4 g/cm^3. Using this value for the density, we calculated that void volume of the rectangular block of composite was 70 percent. This figure is only 5 percent greater than the value reported by Spector et al.[5] using an optical point counting technique. It is apparent that part of the discrepancy between measured and assumed densities can be accounted for by the fact that the carbon used in the composite was of the "pyrolytic" type[6], which according to Bokros et al.[7] has a density of 1.5 to 2.0 g/cm^3. However, this factor alone would not be sufficient to account for a composite density of 1.4. There is probably some included air trapped in the PTFE solids which lowers its apparent density somewhat. As of this writing, we do not feel that we have entirely accounted for the large discrepancy between measured and assumed densities.

As part of the procedure, one sample of the PTFE-carbon composite was sent to a commercial analytical laboratory[8] for elemental analysis of carbon, hydrogen, and fluorine. This analysis was intended to verify that the material was composed of the two solid materials PTFE and elemental carbon, and if so, to determine the weight ratio of the two materials. The following elemental analysis was determined:

% C -- 52.81

% H -- less than 0.01

% F -- 47.10

Since 99.91 percent of the total weight is accounted for in this analysis, the data are consistent with a PTFE-carbon composite with less than 0.1 percent of other elements present. By elementary stoichiometric analysis, these data indicate that the weight fractions of PTFE and carbon in the composite are, respectively, 0.62 and 0.38.

B. Compression Method

In the current ASTM Draft Standards for porosity characterization of PTFE-Carbon composites (see Section IV) the suggested method for void volume measurement of this material is a "confined pressurization" technique. While the experimental details of this method are not given, the implication is that a sample is simply confined in such a way that it cannot spread out as it is compressed, so that the change in sample thickness is a direct measure of the void volume originally present. We did not confine the rectangular sample in our experiment, but we allowed it to spread out slightly, still retaining a regular geometrical shape. In this way, the change in sample volume could be observed directly. For one sample, we measured a void volume of 68 percent in this way, which is only 2 percent less than the value obtained by the similar apparent density method described above. As we have described them, both of these methods require the measurement of sample dimensions, and these are necessarily somewhat inaccurate due to small irregularities in the sample shape. Also, of course, the compression method requires that the void can be expelled quantitatively at pressures accessible with a hydraulic press. For materials less compressible than the PTFE-carbon composite such as porous polyethylene, it would undoubtedly be necessary to melt the material during compression in order to drive out all the air. For this material, it may be preferable to use a liquid uptake technique such as mercury porosimetry to measure the void volume, as we describe below.

C. Mercury Intrusion Method

Mercury intrusion porosimetry is a well-established technique for characterizing the porosity of porous materials (see Section IIIA). Both the pore size distribution and the void volume may be measured by this technique. The volume of mercury intruded into the sample is measured on a graduated dilatometer stem, thus giving a direct measure of the accessible void volume of the sample. In all of the work reported here, the mercury intrusion pressure was varied from 0-1 atmosphere (0 to 1.01×10^5 Pa).

Porous Polyethylene

From the shape of the mercury intrusion curve for this material, as shown in Fig. 1, it is apparent that most of the void volume was intruded at one atmosphere pressure. Two samples of the material were cut from the same circular disc for porosimetry analysis. If we assume that the density of solid polyethylene is 0.95, the void volumes for the two samples were calculated to be 42.6 and 45.6 percent. The average of these (44.1 percent) is within the range of values found above by the apparent density method for this material. It should be noted that this method, at least in principle, appears to be the most accurate of the three methods discussed here for determining the specific void volume (cm^3/g of sample), since both sample weight and void volume may be directly measured to three significant figures. The other methods contain unknown inaccuracies both in their total measured volumes, due to sample irregularities, and in their measured or assumed densities of the solid phase. For these reasons, the mercury intrusion method would appear to be the method of choice for measurement of specific pore volume. However, if one desires to express the sample void as a percentage of the total, it is necessary to measure or assume a density of the solid material which introduces possible errors not present in the specific void volume measurement.

PTFE-Carbon Composite

For the composite material, it is apparent from the mercury intrusion curve (Figs. 4 and 5), that the maximum applied pressure (1 atmosphere) was not sufficient to fill all of the void volume. Therefore, we would expect the measured void to be less than that found by the other two techniques. Indeed, assuming a density of 1.4 for the solids, we found an average void volume of 67 percent for five samples of the material, as compared with 70 percent measured by the apparent density method. If both figures are accurate, the implication is that 95 percent of the total void was filled with mercury at one atmosphere pressure. To complete the intrusion experiment, it will be necessary to increase the pressure above one atmosphere. These experiments will be performed during the next phase of our experimental work.

D. Summary

During our first year of experimental work, we have measured the void volumes of two porous polymeric implant materials, porous polyethylene and PTFE-carbon composite, in three different ways. The simplest method, which we have chosen to call the apparent density method, requires only the sample weight, total volume (which is determined by direct measurements on a regular-shaped specimen) and a knowledge of the density of the solid phase. The compression method measures the void directly by the changes in one or more linear dimensions of the solid as the sample is hydraulically compressed. The mercury intrusion method also measures the void volume directly by dilatometric observation of the mercury intruding the sample void as pressure is applied. Table I summarizes the results found by these three methods.

Table I: Void Volume Percentage in Two Porous Implant Materials

Method	Solid Density		Void %	
	PE[1]	Composite[2]	PE	Composite
Apparent Density	0.94-0.96	1.4	44-45	70
Compression	---	---	---	68
Mercury Intrusion	0.95	1.4	44	>67

---

[1] assumed

[2] measured

III. PORE SIZE

As we have discussed above, "size" is not a well defined physical property, when one speaks of irregularly shaped objects such as the pores in porous implant materials. Nevertheless, various methods are available for estimating the size of pores, given that this is a somewhat vague concept. A summary of the important direct methods for measuring pore size is given in a review article by Rootare[9]. The methods include optical microscopy, electron microscopy, gas adsorption and condensation, mercury porosimetry, water suction pressure measurement, and small angle x-ray scattering. Of these, gas adsorption and small angle x-ray scattering can only measure pore diameters of less than 100 nm (0.1 μm), and are therefore inappropriate to the pore size range (> 10 μm) which applies to porous implant materials. Electron microscopy, while providing a good picture of the structural morphology of materials, is not appropriate for quantitative analysis of pore sizes, because it presents a plane projection of three-dimensional features of the materials. In order to obtain information about the size of three-dimensional objects such as pores from a photograph, it is necessary to know that one is looking at a flat, two-dimensional cross section of the material. This may be accomplished by optical microscopic examination of polished, flat sections.

The water suction method depends on the fact that water suction pressure is related to the size of pore openings. This method only senses pores which are interconnected in such a way as to pass entirely through the material, and it does not give a measurement of the fraction of total pore volume having a given pore size. Therefore, it would appear to have little value for studying the pore size distribution of the porous implant materials. Of the above techniques, only optical microscopy and mercury porosimetry appear to have potential for studying the materials of interest to this project. In the following, we discuss the application of mercury porosimetry to this problem and compare results obtained in this way with an indirect method which depends upon measured values of specific pore volume and surface area. Future studies will compare both of these methods with optical microscopy measurements.

A. Mercury Intrusion Porosimetry

1. Theory

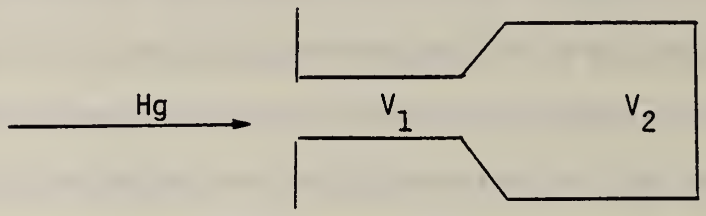
Mercury intrusion porosimetry is a well-established technique for measuring the pore size, size distribution, and void volume of porous materials. A number of articles have been written about the method[9-13] and the precautions which one should take in interpreting the data. The method depends upon some unique physical properties of liquid mercury, namely its non-wetting of surfaces and its high surface tension, which require high pressure to force the liquid into various pores. The diameter of an intruded pore and the pressure required to force intrusion are inversely related, and for cylindrical pores of circular cross-section the relation between applied pressure (P) and pore diameter (D) is given by the well known Washburn equation,

$$PD = -4\gamma\cos\theta,$$

where γ and θ are the surface tension of mercury, 484 dynes/cm (Appendix I, ref. 9), and the surface contact angle on the material of interest.

For cylindrical pores having non-circular cross-sections, the pore "diameter" is not defined, and the equation may be expressed in a more general form involving circumference and area of the cross-section. However, when one considers applying the porosimetry technique to materials having multitudes of irregular pore shapes, it becomes obvious that no equation can correctly describe the entire material or even one pore. For this reason, the usual method of treating mercury porosimetry data is to use the simplest (Washburn) equation, realizing that there is no obvious way to improve on it for a real system of irregular pores. The "average" pore diameters obtained in this way nevertheless provide a useful method for rough, semi-quantitative comparison of different porous specimens. In fact, the experimental plot of applied pressure vs intruded volume is itself a useful "fingerprint" of a material which can be used to distinguish one material from another and to see variations in pore size distribution for a given material.

It must also be considered that the mercury intrusion method has a built-in bias which is usually referred to as the "ink-bottle" pore effect. This effect is illustrated in the following diagram.



As mercury enters the narrow opening of this pore (V_1), the pressure required is governed by that opening. The entire volume of the pore (V_1+V_2) is measured as though it had the narrow entrance to V_1. In a pore pathway with many constrictions, the narrowest one governs the pressure required to intrude all the pore void beyond that point. For this reason, it is customary to indicate that mercury porosimetry measures "interconnecting" pore diameters rather than the true pore size distribution. However, two factors tend to minimize the errors introduced by this effect for the porous implant materials. First, because these materials have a very open network structure, mercury can often find its way into a large interior pore through several different routes, avoiding the narrowest constrictions in the pathway. The intruding liquid always takes the path of least resistance (largest diameter) when entering the porous structure, and it can enter from all sides of the sample at once. Second, remembering that the ultimate objective of this work is to be able to correlate measured pore "diameters" with the performance of the materials as tissue ingrowth media, it might be argued that the constrictions in the pores measured by mercury porosimetry are more important in governing the rate of tissue ingrowth than the larger pores between the constrictions.

In other words, it may be more meaningful to measure the interconnecting pore size distribution rather than the "true" distribution. In any case, it would not appear that the "ink bottle" effect should be regarded as reducing the usefulness of mercury porosimetry.

Another source of possible error in the Washburn equation is the choice of contact angle. Many workers use a constant value of this angle (usually 130° or 140°), realizing that most measured values have fallen in this range. It is possible to measure the contact angle with a goniometer instrument, and this measurement was performed on the composite material, as discussed below.

2. Experimental

The mercury porosimeter used in this work* was equipped with a "macro" filling accessory, which allows the graduated penetrometer to remain in a horizontal position during the experiment. This facilitates reading the graduated stem and eliminates a large correction for the Hg head pressure when the sample is held in a vertical position. The sample chamber is first evacuated to a pressure less than 50 µm of Hg. One or two hours was usually allowed for evacuation, even though the manufacturer suggests a half-hour evacuation. It must be remembered that the mean free path of gas molecules in a porous matrix can be much less than that in a surrounding chamber, and it is essential for the gas to diffuse out of the sample before the mercury intrusion is begun. The filling device is then tilted to immerse the open stem of the penetrometer into a mercury pool. A small pressure, usually about 0.5 psi (3.5×10^3 Pa), is then admitted to the mercury chamber, causing the mercury to enter and fill up the penetrometer. At this point, the sample in the

---

*Model J5-7121-B, supplied by the American Instrument Co.

penetrometer is surrounded by mercury, but little if any has entered the porous matrix due to the very small applied pressure. The pressure is then increased in steps, and the volume of mercury entering the sample is read on the penetrometer stem, which can be interpolated to 0.001 cm^3. The total void volume which can be measured by our penetrometer is 0.2 cm^3, so that the sample specimens are typically quite small (< 0.1 g). Data were plotted, as is the custom, on semi-log paper with intruded volume on the ordinate and pressure on the abscissa.

The macro-filling device used in this work can only measure pressures by admission of air, up to one atmosphere. For higher pressure measurements, which will be needed to complete some of the mercury intrusion curves, it will be necessary to insert the penetrometer into the high pressure chamber and apply hydraulic pressure, which is transmitted to the sample by fluid. The volume of mercury intruded is measured by remote control rather than direct observation. These experiments will be performed during the next phase of our studies.

Samples of the porous materials were in most cases cut from as-received blocks or discs of the material, using a sharp surgical scalpel with removable blades. It was found that all of our materials could be cut without compressing the materials.

3. Porous Polyethylenes

Two samples of the porous polyethylene implant material were examined by mercury porosimetry, and their intrusion curves were very similar in shape. One of these is shown in Fig. 1. This curve is also very similar to one published by the manufacturer[2], who found that a majority of pores lay in the range of 18 to 35 μm diameter as calculated from the Washburn equation, using a 130° contact angle. According to

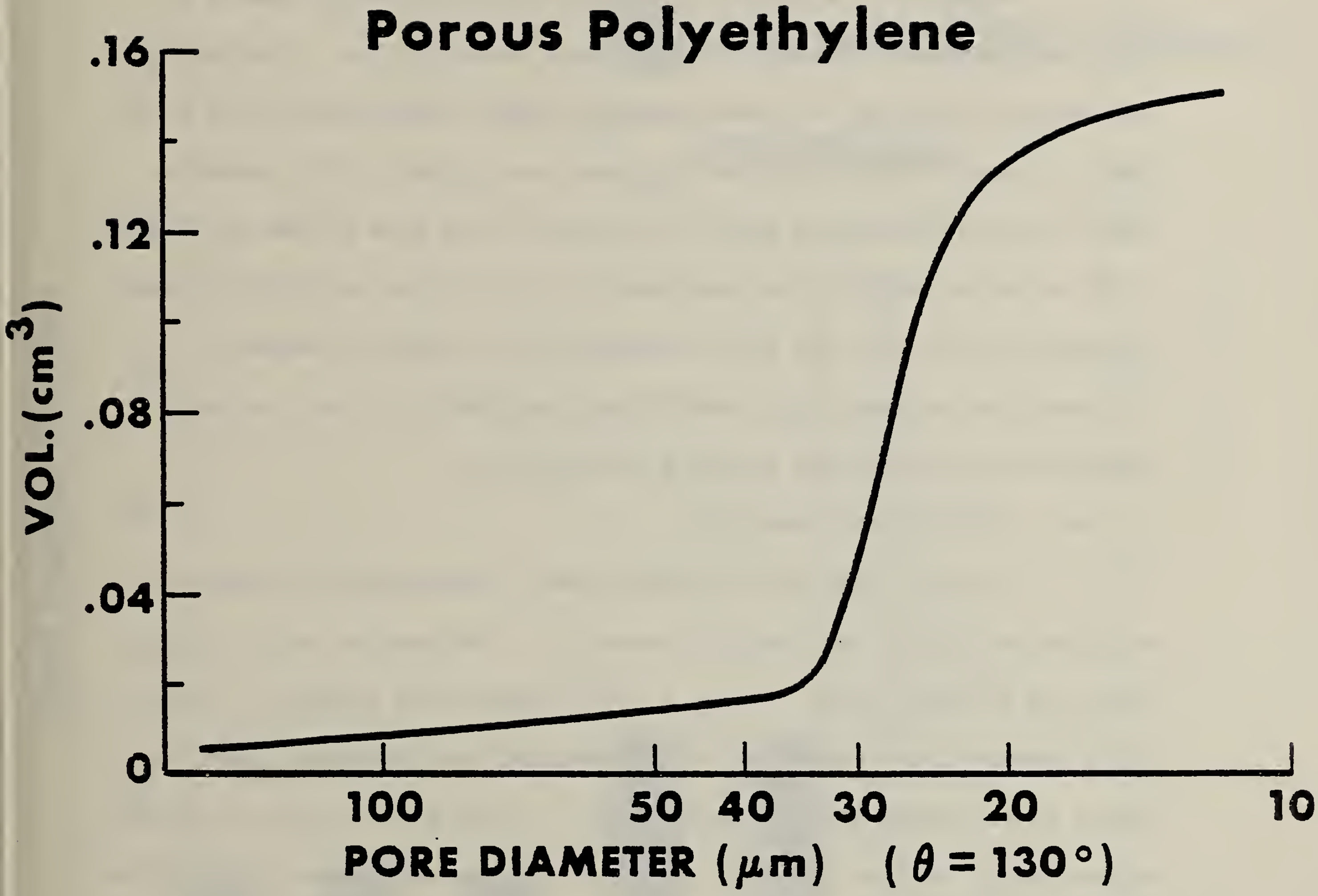


Figure 1. Mercury intrusion curve for Plastipore® porous polyethylene.

our curves, almost 80 percent of the total pore volume consists of pores in the range 20 to 40 μm, and we are therefore in good agreement with the manufacturer about the pore size distribution of this material. This distribution is plotted as a bar graph in Fig. 2, together with that of the PTFE-carbon composite.

Figure 3 is a mercury intrusion plot for another sample of porous polyethylene obtained from Glasrock Products, Inc. The pore size was not specified for this material, but simply designated "small pore size". Clearly the interconnecting pores are larger in this material than in the one discussed above, with most of the pore volume consisting of 50 to 100 μm pores. The porosimetry plots for the two polyethylenes illustrate quite well how this technique can distinguish between different porous materials, even without application of any assumed equation relating applied pressure to pore size.

4. PTFE-Carbon Composite

In Fig. 4 are shown three curves illustrating the effects of bulk compression of the composite material. The samples were sliced from a 10 mm thick block. Curve A, the uncompressed composite, clearly has a broader distribution of interconnecting pore diameters than the porous polyethylene illustrated in Fig. 1. From Fig. 2, it is seen that approximately half of the pore volume in the composite consists of 20 to 40 μm pores, with most of the remaining volume having larger than 40 μm pores, as calculated from Washburn's equation, using a 146° contact angle for mercury on the composite. The contact angle was measured on a compressed sample of the composite, using a commercial contact angle goniometer. The range of contact angles measured with this instrument

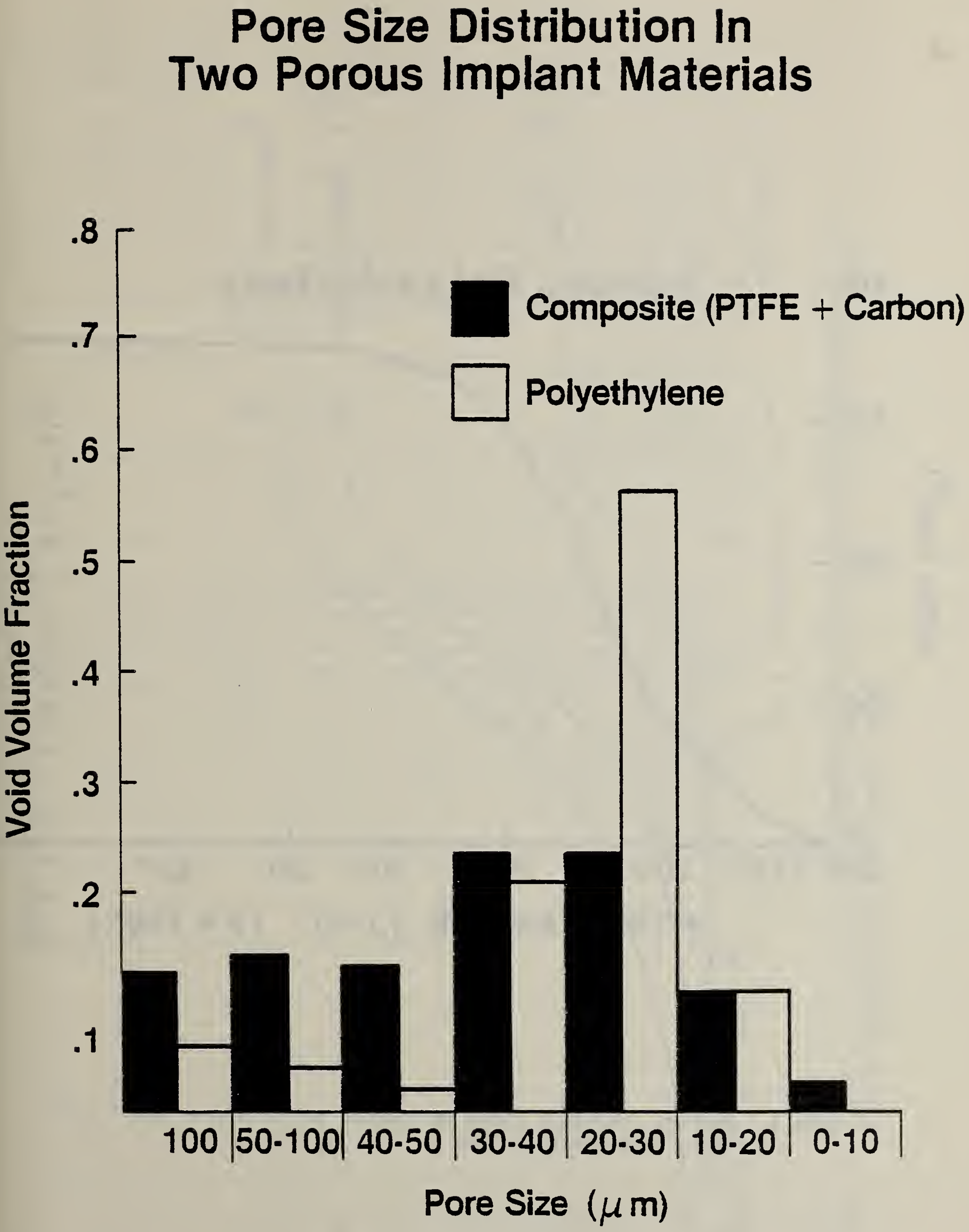


Figure 2. Pore size distribution in two porous implant materials.

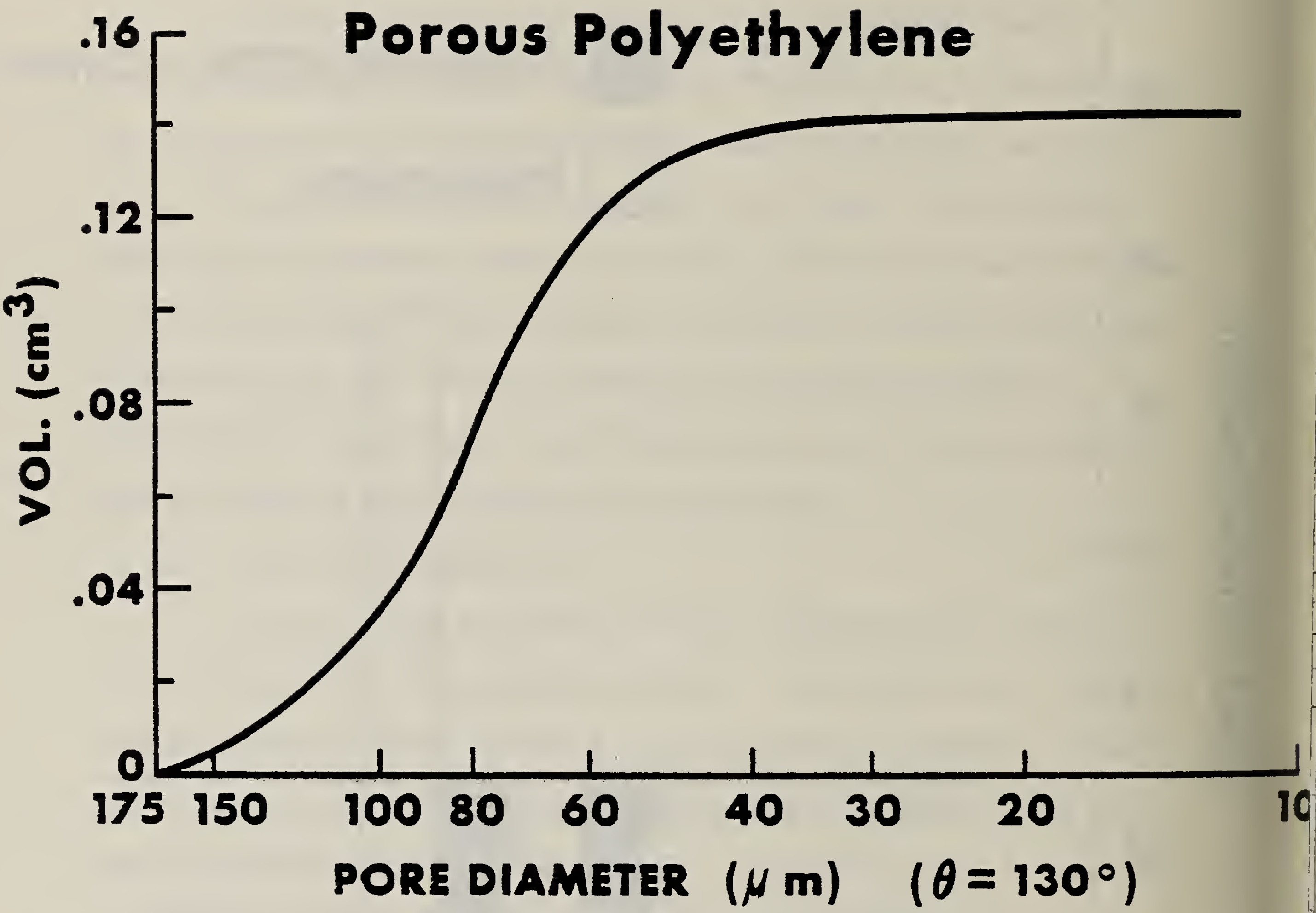


Figure 3. Mercury intrusion curve for porous polyethylene "small pore size" from Glasrock Corp.

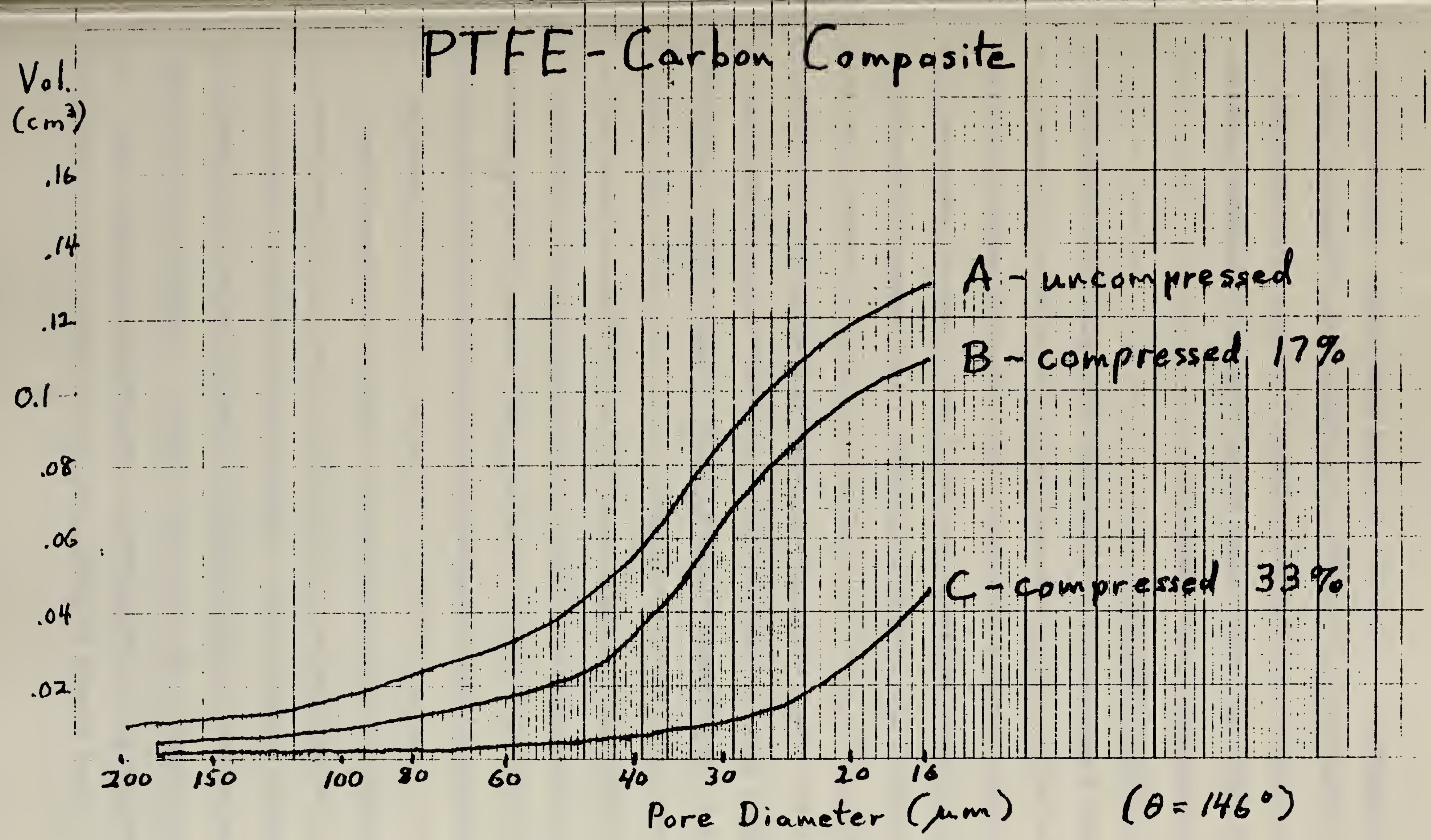


Figure 4. Effect of bulk compression on mercury intrusion curves of PTFE-carbon composite. Curves normalized to same sample weight.

was approximately 5°, with 146° representing an average. Even a 10° error in this angle (135° vs 145°, for example) only introduces a 13 percent error in the value of $\cos\theta$, so that it is not usually considered necessary, given the other unknown errors in using the Washburn equation, to make very accurate measurements of θ.

Effects of Sample Compression

Curves B and C in Fig. 4 illustrate the effect of bulk compression of this material on the observed mercury intrusion plots. All three curves in the figure are normalized to the same sample weight. By this procedure, it would be easy to see that B and C represent compressed samples, even if they were not so labeled. It is apparent that mercury porosimetry offers a convenient method of determining whether or not a sample of this material has been accidentally compressed. It is only necessary to have an intrusion curve for the non-compressed composite available. The corresponding curve for the "unknown" sample, normalized to the same weight as the known sample, will lie below the known sample curve if compression has occurred. From the difference between intruded volumes of the end point (plateau) of the intrusion curves, the amount of sample compression can be estimated. In this way, if the pore volume of the known sample was determined, one could discover whether the pore volume of a "compressed" block of this material falls within acceptable limits, as stated by the manufacturer. There are, of course, other methods of determining the accessible pore volume, as discussed above, but mercury intrusion is the only method discussed in this report which can determine the pore size distribution and pore volume simultaneously.

As discussed in our first Annual Report[1], a controversy has existed concerning the application of mercury porosimetry to the composite material. Some workers have felt that the relatively soft and deformable material would be compressed by mercury pressure during the measurement, thus giving lower values of pore size and pore volume than were present in the "as-received" material. Because the composite is inelastic and easily deformed even by finger pressure, this concern was certainly a legitimate one. In order to determine whether sample compression occurs during the porosimetry experiment, in which the samples discussed in this report were only subjected to a maximum of one atmosphere pressure, we piled weights equivalent to 1.2 atmospheres pressure on top of a flat sample of the material in the form of 1 mm thick sheets. The mercury intrusion curves for this sample and for another sample not subjected to the compression treatment are illustrated in Fig. 5. The very small differences in the two curves are less than the difference between the uncompressed sheet and uncompressed block composite, (curve A of Fig. 4). In fact, sample-to-sample variations of either block or sheet composite are expected to be at least as great as the differences observed in Fig. 5.

The above findings for the PTFE-carbon composite have been written up, approved by the NBS Editorial Board (WERB), and submitted for publication as a Note to the Journal of Biomedical Materials Research. A copy of the latest revised edition of this manuscript is reprinted in Appendix I.

B. BET Method

It is possible to estimate an average pore diameter in a porous material from the measured specific surface area (S) and specific void volume (V) of the material. If one assumes for simplicity that all the pores are spherical in shape, the average pore diameter D is shown by simple geometry to be equal to 6 V/S. For other regular geometrical pore shapes, the diameter (or other linear dimension of the pore if its cross-section is noncircular) is also proportional to V/S, but the

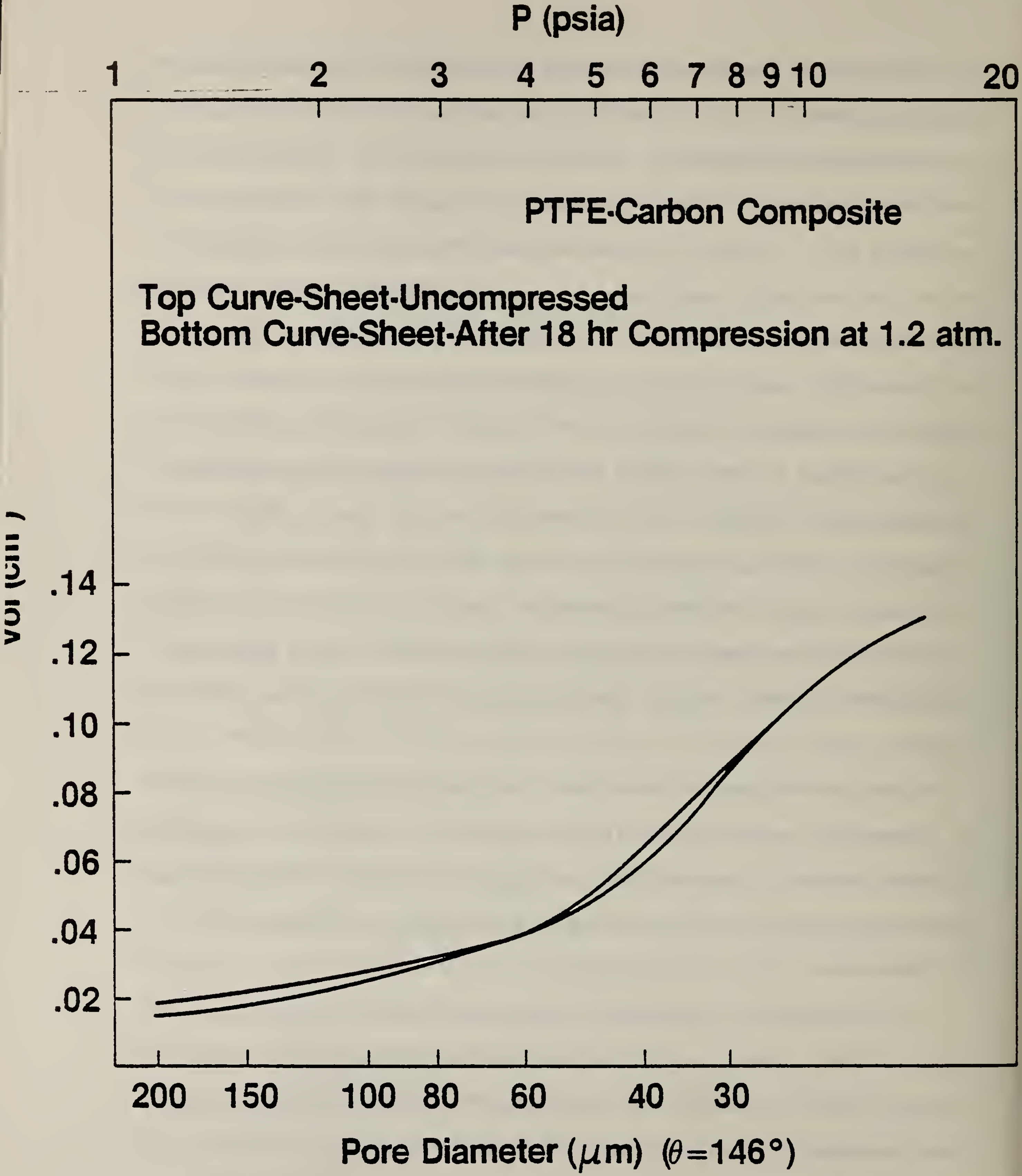


Figure 5. Mercury intrusion curves for PTFE-carbon composite, before and after compression at 1.2 atm.

proportionality constant varies with pore shape. This problem is discussed in more detail below. We have already measured the specific volumes of both the porous polyethylene and PTFE-carbon composite, as discussed in Section II. The specific surface area may be determined by a technique known as the BET method, named for its inventors, Brunauer, Emmett, and Teller[14].

1. Theory

The theoretical basis for the BET surface area measurement has been well described in textbooks. Two examples are Refs. 10 and 15. Only a brief summary will be given here. The method is based upon the adsorption of an inert gas (usually nitrogen) on a porous solid material. From the weight of the adsorbed gas and an assumed surface area covered by one molecule of gas, one may calculate the total surface area covered. This area, divided by the initial weight of the sample, gives the specific surface area of the material. In practice, the problem is complicated by the fact that the surface does not simply adsorb one monolayer of gas molecules and stop. The amount of gas adsorbed increases as the pressure is increased, and the BET theory uses Langmuir's kinetic arguments to describe how the weight of the desired first monolayer of gas depends upon the gas pressure, the total weight of gas adsorbed, and a constant parameter which expresses the ratio of molecular escape probabilities, related to the energies of adsorption, of the first adsorbed layer relative to all subsequent layers. The BET equation may be expressed as the following,

$$\frac{1}{W[(P_o/P)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \frac{P}{P_o} \qquad (1)$$

where W is the total weight of gas adsorbed, Wm is the weight in the first monolayer, P/P_o is the ratio of the applied gas pressure to the condensation pressure P_o, and C is a constant which describes the difference between the adsorption energy of the first layer and the following layers, all of which are assumed to be the same. In order to measure the surface area, one first plots the experimentally obtained quantity $\frac{1}{W[(P_o/P)-1]}$ vs P/P_o, to obtain a straight line having the slope

$$s = \frac{C-1}{W_m C} \tag{2}$$

and intercept

$$i = \frac{1}{W_m C} \quad . \tag{3}$$

The desired W_m is obtained by solution of these equations, to give

$$W_m = \frac{1}{s+i} \quad . \tag{4}$$

Usually, three points are sufficient to give a good straight-line plot. The sample surface area (S) is given by the expression

$$S = \frac{W_m NA}{M} \tag{5}$$

where N is Avogadro's number, A is the cross-sectional area of a gas molecule, and M is the molecular weight of the gas.

In summary, the purpose of the BET plot is to extract W_m, the desired monolayer weight of gas, from the observed total weight of adsorbate W. This adsorbed monolayer weight then tells us the total surface area covered by gas molecules, each of which is assumed to cover the same amount of surface area.

2. Experimental Results

One sample each of porous polyethylene and composite, the latter in the form of 10 mm thick block, were sent to a commercial laboratory[16] for 3-point BET surface area measurements. The results of these analyses are given in Appendix II. As indicated, the specific surface area of the polyethylene was found to be 0.083 m^2/g, while the composite had a much larger area, 0.39 m^2/g. The specific void volumes for the two materials were discussed in Section II. Using the expression $D = 6\ V/S$ to calculate the average pore diameters, we find that the average diameter for polyethylene is 61 μm, while the corresponding value for the composite is 25 μm.

It is interesting that these relative values of average pore diameters are reversed as compared with the average diameters measured by mercury porosimetry (p. 16). The BET polyethylene value is higher than the porosimetry value, and the composite BET value is lower than the porosimetry value, each by about a factor of 2. Considering the possible errors inherent in each method, it is perhaps only surprising that the two techniques are in as close agreement as they are. The errors in the mercury intrusion method have already been discussed in Section IIIA. The errors in the specific void volume, we feel, are small, as we discussed in Section II. The errors in the BET method are of two types: (a) errors in the assumptions needed to validate Eq. (1) and (b) assumption of an arbitrary "shape factor", which is necessarily inaccurate for an irregularly shaped pore, in the equation relating pore "diameter" to the ratio V/S. Each of these problems is discussed briefly below.

3. Assumptions in the BET Equation

The gas molecules are adsorbed to a surface by relatively weak dispersion forces, which are not necessarily constant over a given surface, or from one surface to another. In the BET theory, it is assumed that all molecules in the first layer have the same adsorption energy, and that all molecules in subsequent layers have an adsorption energy equal to the heat of liquefaction. Neither of these assumptions is likely to be true for a real system, although it has generally been found that in the range of relative gas pressure P/P_o near the value required for surface coverage ($W/W_m = 1$), the measured BET C-values usually give reasonable heats of adsorption[10]. There is also the problem that lateral interaction energies between adsorbed molecules increase with increasing surface coverage; however, this effect tends to be cancelled by decreasing energy of attachment to the surface with increasing coverage, assuming that higher energy surface sites are the first to be filled.

One may only speculate about the effects of these variables upon the experimental BET surface areas of the materials which we are studying. Certainly the composite would be expected to have quite different gas adsorption energies of its two component species. However, from the above arguments it is not clear that this two-component phenomenon would lead to greater inaccuracies in the measured surface area than in the case of the porous polyethylene, even though the latter is a chemically more homogeneous material.

4. Effects of Pore Shape

As in the case of mercury porosimetry pore size determinations, the pore shape as well as size must be taken into account in calculating pore sizes by the BET method. In the above calculation, we assumed for simplicity that all pores had spherical geometry. For a real porous material with irregularly shaped pores, such as the implant materials under investigation, it is pointless to attempt to approximate the real pore geometry with any specific regular pore shape. However, it is interesting to note the effect of pore geometry on pore sizes estimated by the BET method, because it gives one an idea of the range of pore sizes which can be calculated from the same BET data.

The equation used above to calculate the diameter of spherical pores by the BET method can be expressed more generally as

$$D = k\ V/S$$

where we define D to be either the diameter of a pore having a circular cross-section or the side length of the cross-section of a flat-sided pore. In the following table, we summarize the k values obtained for certain regular pore shapes having cross-section dimension D and pore length ℓ.

Table II: Shape Factors for BET Pore Size Calculations.

Pore Shape	k
Sphere	6
Circular cylinder, ℓ>>D	~4
Circular cylinder, ℓ=3D	4.7
Circular cylinder, ℓ=D	6
Cube	6
Rectangular tube, square cross-section, ℓ=3D	4.7
Triangular prism, ℓ=3D	7.6
Triangular prism, ℓ=D	9
Flat box, 10D x 10D x D	2.4
Flat box, very thin, thickness D	~2

From this brief sampling of pore geometries we observe a range of k values from 2 to 9. Our assumed spherical pore shape has a k value approximately in the middle of this range, but there is no assurance that this "average" value is best for any given porous material. It is apparent from published SEM photographs of the porous polyethylene and PTFE-carbon composite[1] that their pore morphologies are quite different, and it is, therefore, hardly to be expected that any assumed regular pore geometry will apply equally well to both of the materials.

In comparing pore sizes as measured by mercury porosimetry and BET methods, it should be remembered that the former method measures "interconnecting" pore diameters, which are necessarily somewhat smaller than the true pore diameters, whereas the latter method is not subject to this systematic error. One might therefore expect the BET method, if everything else were equal, to yield somewhat larger pore sizes than the porosimetry method. This expectation was realized for the porous polyethylene, but not for the composite. The reasons for this anomaly are not readily apparent; however, the above discussion is intended to show that quantitative comparison of pore sizes as measured by the two methods is a difficult matter.

IV. ASTM DRAFT STANDARDS FOR POROSITY CHARACTERIZATION OF PTFE-CARBON COMPOSITES

The ASTM Task Force F4.20.04.05 is presently drafting standards entitled, "Standard Specifications for Porous Composites of Polytetrafluoroethylene and Carbon for Surgical Implant Use." While the use of trade names in this document was specifically prohibited by the Task Force, the specifications apparently apply to one commercially available composite (Proplast®) having the properties indicated in the title above. The current draft standards were included in our Annual Report for 1980[1] on p. 17. In a telephone conversation with Dr. C. A. Homsy this year, he asked for our opinions about these draft standards, and our reply is given in Appendix III. A few additional comments may be added to this letter, as follows:

A. 4.4.1 "Volume Pores" - It would seem to be important to decide whether the primary objective of this specification is to verify that the void volume falls within the range given (70 to 85 percent) or whether it is to suggest a method sufficiently accurate to detect small differences between individual samples, as a quality control check on their porosity. The compression method of measuring void volume specified in this standard is described in Section IIB of this report. As we have indicated, this method may be subject to measurement errors which make it less accurate than some other methods. However, if the objective of this standard is merely to verify that the pore volume is within 70 and 85 percent, our experience indicates that the compression method is probably adequate to verify the specified volume range. The apparent simplicity of the method is an appealing feature, although one might wish for a more detailed description of the "confined pressurization" method named in this document, in order to ensure that different laboratories using this method will obtain equivalent results.

B. 4.4.2 "Pore Size Range" - In addition to the optical image analytical methods for characterizing pore sizes, recent work of this laboratory as indicated in Section IIIA indicates that mercury porosimetry is also a useful method for semi-quantitative analysis of pore sizes in this material. As discussed above, there are certain limitations inherent in this method, such as the fact that one measures only "interconnecting" pore diameters rather than the true pore size. However, the method is probably the most widely used one for rapid semiquantitative analysis of pore size distribution, and we would suggest that it be considered as at least a "fingerprinting" technique, to obtain pressure-volume plots characteristic of the material, and to determine whether or not the rather soft material has been significantly compressed due to accidental mishandling.

As stated in our letter of June 18 to Dr. Homsy (Appendix III), we feel that scanning electron micrographs (SEM's) should not be used for optical image analysis of pore sizes. These pictures provide a good impression of the structure and morphology of a porous material by projecting 3-dimensional rough surfaces onto a plane. However, one does not know exactly where to measure the pore dimensions in such a projection photograph. The standard technique for optical image analysis of the volume and size of the various phases in a multi-phase solid material involves measurements on smooth, planar surfaces by light microscopy[17]. Because of its very narrow depth of field, light microscopy is ideally suited to determine whether the surface is smooth and flat enough to permit quantitative measurements of the different phases present; nonplanar surfaces cannot be completely brought into focus. For a soft porous material such as the PTFE-carbon composite, it is necessary first to perfuse the sample with a nonviscous liquid, followed by cutting and polishing to achieve a flat surface. This method was used by Spector et al.[5] in their optical point-count analysis of pore volume in the PTFE-carbon composite. To date, we have not performed optical image analyses in this laboratory and thus cannot comment on their applicability to the composite material. Such studies will be pursued during the following year of this project.

V. SUMMARY

The activities of this project during the past year have involved the measurement of pore volume and pore size in two porous polymeric implant materials. Pore volume has been measured by three different methods, namely:

(1) "apparent density," which requires a knowledge of the macroscopic volume of the sample from its measured dimensions, and the density of solids in the material,

(2) bulk compression of the sample, from which the pore volume is measured directly from the ratio of sample dimensions before and after compression of the airspace in the material,

(3) mercury intrusion, which determines the void volume of the material by dilatometric measurement of the volume of mercury intruding the sample under pressure.

Only methods (1) and (3) were used to determine the void volume in porous polyethylene. Method (2) would require melting the material to allow all the air to escape. All three methods were used to determine the void volume in the porous composite of PTFE and carbon. For the two materials, the void volumes were found to be about 45 percent for the polyethylene and 70 percent for the composite.

Unlike the pore volume, pore "size" is not a well-defined physical property of materials when the pores are of irregular shape, as is the case for the porous implant materials. In general, it is necessary to make some arbitrary assumptions about the pore shape in order to relate the mercury intrusion pressure to pore size. In the case of mercury porosimetry, the simplest and most customary assumption is that the pores are circular cylinders. With this assumption, we have measured a weighted average pore diameter of 30 μm for the polyethylene and 50 μm for the composite. The pores measured by this technique are interconnecting pores, rather than the "true" distribution of pore sizes, due to the fact that constrictions in the diameter of a long pore determine the maximum measured diameter for that pore.

A major finding of this work was the discovery that, contrary to some widely held beliefs, the mercury intrusion technique can be used on the relatively soft and deformable PTFE-carbon composite without distorting the material. This finding enabled us to use the method on the composite material without fear that the results might be confounded by sample compression.

Another method was used to estimate the average pore "diameter" in the two porous materials. It also required an assumption of pore shape in order to calculate a pore size. First, we have measured the specific surface area (S) by the BET method, and the specific pore volume. With these measured quantitites, and assuming spherical pore shapes, we found the average pore diameters of the two materials to be 60 μm for the polyethylene and 25 μm for the composite. A discussion of the effects of pore shape on the calculated pore size is included in this report.

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Appendix I. Revised manuscript, "On the Characterization of Porosity in PTFE-Carbon Composite Implant Materials by Mercury Porosimetry."

ON THE CHARACTERIZATION OF POROSITY IN PTFE-CARBON COMPOSITE IMPLANT MATERIALS BY MERCURY POROSIMETRY

R. E. Dehl
Polymer Science & Standards Division
National Bureau of Standards
Washington, DC 20234

ABSTRACT

Questions have been raised about the use of mercury intrusion porosimetry to measure interconnecting pore sizes and void volumes in relatively soft and flexible materials such as porous implant composites of PTFE and carbon fibers. We have studied the effect of precompression of one such commercial composite on the mercury intrusion curves which cover all pore diameters greater than about 16 μm, the range of interest for tissue ingrowth applications. Prior compression by a pressure 20% greater than that encountered by the material during a mercury intrusion experiment did not change the ensuing pore size distribution curve, as compared with a noncompressed sample. Deformation of the material at higher pressures sufficient to decrease the sample volume inelastically by 17%, 33%, and 67% changed the shape of the mercury intrusion curves significantly, indicating that this technique can be used to detect prior deformation of an "unknown" sample. In the undeformed material, less than 15% of the total void as measured by mercury porosimetry consists of interconnecting pores > 100 μm in diameter and more than 50% of the void volume is composed of pores < 40 μm in diameter.

Key Words: Mercury porosimetry, PTFE-carbon composite, porous implant materials, pore size, pore volume.

It is important to establish reliable and reproducible procedures for characterizing the porosity of porous implant materials for several reasons. The manufacturers of such materials need to monitor their porosity during and after production to assure quality control. Surgeons who use the materials for implantation need to know that the porosity is appropriate to the particular tissue ingrowth situation, and other clinical researchers require that their tests be performed on materials well characterized with respect to porosity as well as other physicochemical properties in order to interpret their experimental results properly. Mercury intrusion porosimetry is a well established semi-quantitative method of measuring both the distribution of interconnecting pore sizes and the void volume of porous materials. However, because it is necessary to apply pressure to intrude Hg into the pores, concern has been expressed[1] about using this technique to characterize the porosity of relatively soft and deformable polymeric materials such as Proplast®, a composite of polytetrafluoroethylene and carbon fibers*. The purposes of this investigation were (1) to determine whether significant distortion of the PTFE-carbon composite occurs during a mercury intrusion experiment, and (2) to determine the extent to which macroscopic deformation of the material can be detected by the porosimetry technique. This study was restricted to the measurement of pore sizes in the range appropriate to tissue ingrowth. For soft tissue ingrowth, it has been reported[2] that pore diameters of at least 40-50 μm are needed, although at least one commercially available materials for soft tissue applications, a porous high density polyethylene[3] (not tested by the authors of Ref. 2) has most of its pores in the range 20-40 μm, as measured by mercury porosimetry.

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* Certain commercial materials and instruments are identified in this report to adequately specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or instrument identified is necessarily the best available for this purpose.

Bone ingrowth apparently requires pores larger than about 100 μm for optimum success[4]. It is also apparent from the published literature that porosity is only one of several variables governing the clinical success or failure of porous implant materials.

The usual starting point for interpretation of mercury porosimetry data is the Washburn equation[5] which is strictly applicable only to cylindrical pores with circular cross-sections. The Hg intrusion pressure and pore diameter are related by the equation

$$PD = -4\gamma\cos\theta,$$

where P is the pressure necessary to intrude Hg into a pore of diameter D, γ is the surface tension of Hg, and θ is the contact angle of Hg on the material of interest. For pore shapes other than circular cylinders, the cross-section "diameters" have been shown to differ by as much as a factor of 2 from the value predicted by the Washburn equation[6]. In a real system of irregularly shaped interconnecting pores such as the PTFE-carbon composite, this correction factor lies between 1 and 2, so that one measures an ill-defined and somewhat inaccurate "average" pore diameter. Regardless of this problem, however, pressure-volume plots obtained by mercury porosimetry provide a useful semi-empirical pore size distribution curve of a porous material. They can be used to establish a correlation with the success or failure of a material in implant applications and they provide a basis for comparing the relative porosities of different samples of the same material.

The contact angle θ of Hg on the material was found to be about 146° by the use of a commercial contact angle goniometer. This value agrees well with a reported value of 150° for the contact angle of Hg on PTFE[7], and with another value[8] (149°) for Hg on Proplast®. The surface tension of Hg _in vacuo_ at 25° was assumed[9] to be 484 dynes/cm.

As calculated from these values, the pressure range from 0-1.01 x 10^5 Pa (0-1 atmosphere) is sufficient to intrude all pores larger than about 16 μm, which covers the range of interest for all types of tissue ingrowth.

The manually operated porosimeter used in this work was a Superpressure® Model J5-7121-B supplied by American Instrument Co., equipped with a Macro-Filling accessory which keeps the Hg penetrometer in a horizontal position during the experiment and eliminates large corrections for the Hg head pressure. All measurements were performed in the pressure range from 0-1 atmosphere. Samples were cut with a sharp scalpel from a block of the composite material 6 mm in thickness and weighed before the intrusion experiment. Data points were taken sufficiently close together to give an accurate measurement of the shape of the intrusion curve.

A typical Hg intrusion plot for untreated Proplast® is shown as curve A in Fig. 1, for a pressure range from 6.9 x 10^3 Pa (1 psia) to one atmosphere (14.65 psia). (The lowest pressure at which significant intrusion occurred was typically about 1 psia.) Pore sizes shown on the plot were calculated from the equation above. In order to determine whether inelastic compression of the material occurs during the Hg intrusion experiment, one sample of Proplast® in the form of 1 mm thick sheet was placed under a weight equivalent to 1.2 x 10^5 Pa pressure (1.2 atmospheres) for 18 hours. After the treatment, the sample yielded an intrusion curve superimposable on that of an uncompressed sheet, indicating that insignificant inelastic deformation of the material occurred, due to the pressure treatment. The composite material is, in fact, quite inelastic and can be deformed by pressures well above one atmosphere. Curves B, C, and D were obtained by precompression of rectangular samples from 6 to 5 mm thick (B), from 6 to 4 mm (C) and from 6 to 2 mm (D). For quantitative comparison of the intrusion curve shapes for different samples, it is necessary to normalize the plots either by adjusting to the same end point, as for A and B in Fig. 1, or by adjusting all plots to the same sample weight, which will cause the curves of compressed samples to lie entirely below the uncompressed ones. Curves B, C, and D show significantly smaller fractions of pore volume attributable to large pores ($\gtrsim$ 50 μm), as compared with the uncompressed material. Even the relatively small reduction in total sample volume represented by curve B (17%) is enough to shift the curve well away from that of the uncompressed sample. It is apparent that the Hg intrusion curve for an "unknown" sample of this material can be used to determine whether or not significant compression of the sample has previously occurred.

For the uncompressed sample (A) it is apparent from the slope of the curve at the highest pressure that one atmosphere was not sufficient to intrude all of the pores. If we assume that all the void was intruded and use the calculated volume of solids present and the volume of Hg intruded to account for the total sample volume, we find that 78% of the total sample volume was intruded at one atmosphere pressure. This value falls well within the range 70-90% specified by the manufacturer of the material, and is only 4% less than the void percentage which we calculated for a rectangular block of the material, using the weight of the sample, the total volume, and the densities of PTFE and graphitic carbon. Thus, approximately 95% of the total void was apparently intruded by Hg at one atmosphere pressure. It is also apparent from curve A that only a small fraction ($<$15%) of the total void consists of pores greater than 100 μm.

in "diameter". Proplast® in sheet form has a mercury intrusion curve similar in shape to Curve A of Figure 1, but with a slightly higher fraction of pores (20%) of diameter 100 μm or greater. Because a small pressure ($<3.5 \times 10^3$ Pa) was used to fill the penetrometer containing the sample with Hg before intrusion measurements were begun, it might be argued that very large pores ($\gtrsim 400$ μm) were already filled with Hg before the first measurement was made. If this has occurred, the fraction of total void represented by such pores must have been extremely small because, as demonstrated above, essentially all of the expected void volume has been accounted for.

In summary, sub-atmospheric Hg intrusion porosimetry appears to be a useful method for characterizing PTFE-carbon composite implant material. It can provide an interconnecting pore size distribution curve which is sensitive to small macroscopic deformations of the material and therefore gives semiquantitative information about the mechanical history of the sample and/or deviations in the manufacturing process.

Contrary to earlier suggestions, mercury porosimetry apparently can be used on the PTFE-carbon composite implant material without fear of mechanically compressing it. In combination with a quantitative total void volume measurement such as the method used above or a liquid uptake measurement, this method can determine the fraction of total void represented by any interconnecting pore size range of interest.

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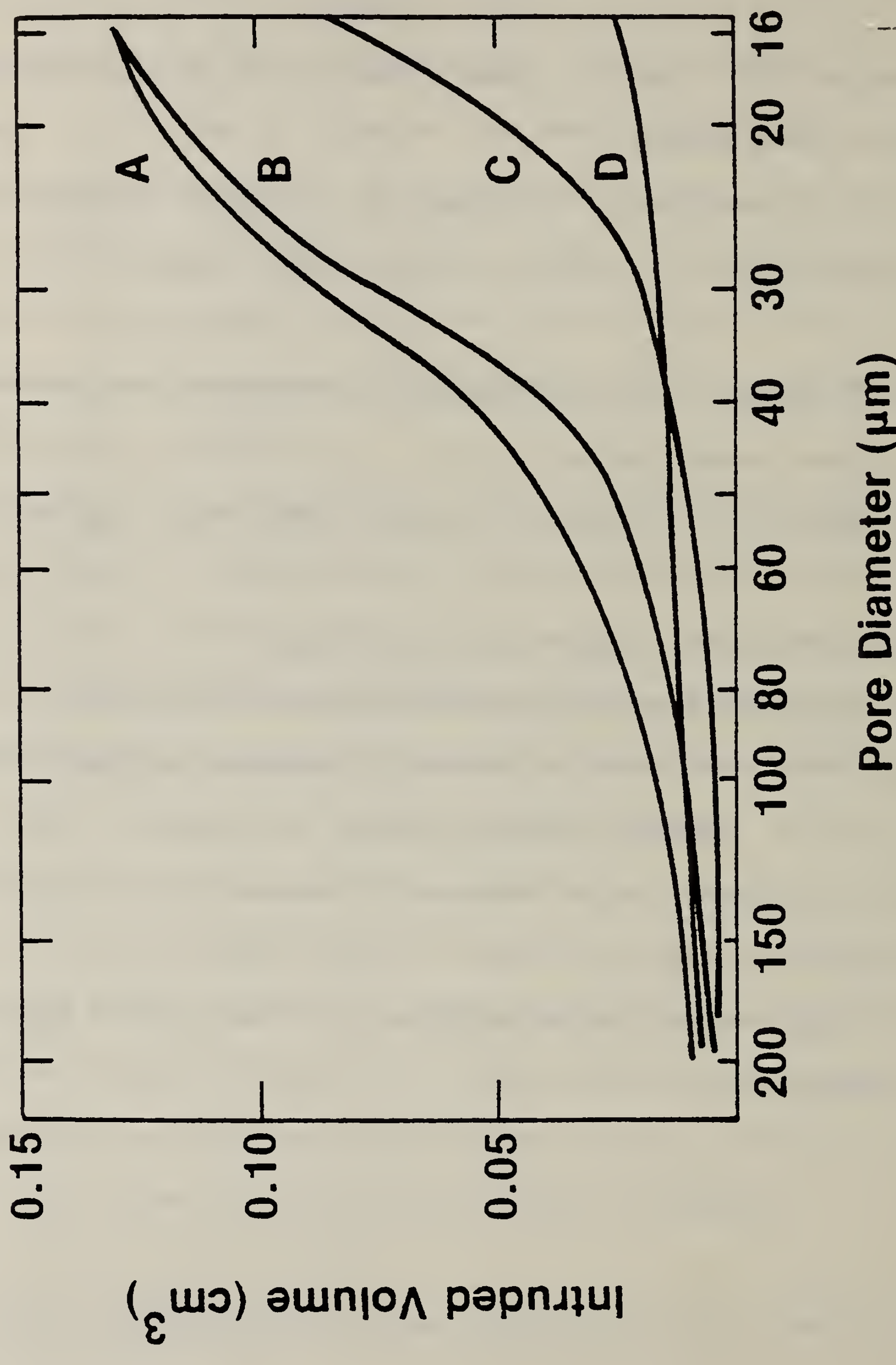
Figure Caption

Figure 1. Mercury intrusion curves for uncompressed Proplast™ (A), and for sample volumes compressed by 17% (B), 33% (C), and 67% (D).



Appendix II. BET surface area analyses for Proplast$^{(R)}$ PTFE-carbon composite and Plastipore$^{(R)}$ porous polyethylene, obtained from Quantachrome Corporation.

QUANTACHROME CORPORATION
6 Aerial Way, Syosset, N.Y. 11791 • Phone: 516 935-2240

MULTIPOINT B.E.T. SURFACE AREA DATA SHEET

Date ____________

Operator ____________

Sample TEFlon & CARbON

Outgas Procedure 100°c/1½Hrs, He PURGE

Total Weight 13.5018 gms.

-Tare 12.8149

Sample Weight (W) 0.6869 gms.

Point	Adsorbate Flow (F_{ad}) ml/min	Carrier (F_c) ml/min	$P_{ad}=\frac{F_{ad}\cdot P_t}{F_{ad}+F_c}$	P/P_o	P_o/P	$(P_o/P)-1$	Calibration Volume (V_c) cc	X_c Grams $\times 10^{-4}$	Signal Area (A)	Calibration Area (A)cal	$X=\frac{(A)\cdot X_c}{(A)cal}$ $\times 10^{-4}$	$X[(P_o/P)-1]$ $\times 10^{-4}$	$\frac{1}{X[(P_o/P)-}$
I	.00104			.302	3.31	2.31	.070	2.41	625	688	2.19	5.06	1975
II	.00072			.209	4.77	3.77	.050	1.72	917	957	1.65	6.22	1607
III	.00029			.0844	11.9	10.9	.030	1.03	581	598	1.00	10.9	913.4
IV													
V													
VI													
VII													
VIII													

Ambient Pressure, P_a= 765.0 mmHg

Sample Pressure (above ambient), P_s= 0 mmHg

Total Pressure, $P_t= P_a+P_s$= 765.0 mmHg

Vapor Pressure (above ambient), P_g= .... mmHg

Saturated Vapor Pressure, $P_o= P_g+P_a$= 2.63 mmHg

Ambient Temperature, T = 248.4 °K

Molecular Weight of Adsorbate, M_a= 83.80 g

Adsorbate Cross Sectional Area, A_{cs}= 20.5×10^{-20} m^2

Calibration Gas Weight, $X_c=\frac{P_a M_a V_c}{6.235\times10^4 T}$ $= 3.446 \times 10^{-3} V_c$

PLOT $\frac{1}{X\left[(P_o/P)-1\right]}$ vs P/P_o

Slope, (S) 4916

Intercept, (I) 523

$X_m=\frac{1}{S+I}$ = 1.838×10^{-4} g

Corr. coeff. = 0.996

Total Surface Area (S_t)* $=\frac{X_m(6.02\times10^{23})A_{cs}}{M_a}$

*For N_2 $S_t= X_m(3.483\times10^3)$ m^2

S_t= 0.271 m^2

Specific Surface Area (S) = $\frac{S_t}{W}$

QUANTACHROME CORPORATION
6 Aerial Way, Syosset, N Y 11791 · Phone 516 935-2240

MULTIPOINT B.E.T. SURFACE AREA DATA SHEET

Date

Operator

Sample Porous Polyethylene

Outgas Procedure He purge @ 70°c./1½hrs.

Total Weight 14.8221 gms.

-Tare 14.3130

Sample Weight (W) 0.5091 gms.

Point	Adsorbate Flow (F_{ad}) ml/min	Carrier (F_c) ml/min	$Pad=\frac{F_{ad} \cdot P_t}{F_{ad}+F_c}$	P/P_o	P_o/P	$(P_o/P)-1$	Calibration Volume (V_c) cc	X_c Grams $\times 10^{-5}$	Signal Area (A)	Calibration Area (A)cal	$X=\frac{(A) \cdot X_c}{(A)cal}$ $\times 10^{-5}$	$X[(P_o/P)-1]$ $\times 10^{-5}$	$\frac{1}{X[(P_o/P)-1]}$
I	.00104			.302	3.31	2.31	.010	3.47	786	789	3.45	7.98	12540
II	.00072			.209	4.77	3.77	.010	3.47	569	749	2.63	9.93	10070
III	.00029			.0844	11.9	10.9	.005	1.73	354	384	1.60	17.4	5742
IV													
V													
VI													
VII													
VIII													

Ambient Pressure, P_a = 765.0 mmHg

Sample Pressure (above ambient), P_s = 0 mmHg

Total Pressure, $P_t = P_a + P_s$ = 765.0 mmHg

Vapor Pressure (above ambient), P_g = mmHg

Saturated Vapor Pressure, $P_o = P_g + P_a$ = 2.63 mmHg

Ambient Temperature, T = 298.4 °K

Molecular Weight of Adsorbate, M_a = 83.80 g

Adsorbate Cross Sectional Area, A_{cs} = 20.5×10^{-20} m²

Calibration Gas Weight, $X_c = \frac{P_a M_a V_c}{6.235 \times 10^4 T}$ $3.446 \times 10^{-3} V_c$

PLOT $\frac{1}{X[(P_o/P)-1]}$ vs P/P_o

Slope, (S) 31433

Intercept, (I) 3212

$X_m = \frac{1}{S+I} = 2.89 \times 10^{-5}$ g

corr. coeff. = 0.997

Total Surface Area (S_t)* $= \frac{X_m (6.02 \times 10^{23}) A_{cs}}{M_a}$

*For N_2, $S_t = X_m (3.483 \times 10^3)$ m²

S_t = 0.0425 m²

Specific Surface Area (S) $= \frac{S_t}{W}$

S = 0.083 m²/g

Appendix III. Letter from R. E. Dehl to C. A. Homsy concerning ASTM Draft Standard Specifications for porosity characterization of PTFE-carbon composite implant materials.

UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

June 18, 1981

Dr. Charles A. Homsy
6560 Fannin, Suite 2080
The Methodist Hospital
Houston, TX. 77030

Dear Dr. Homsy:

You asked for my opinions about the ASTM draft standards for porosity characterization of Proplast. I won't repeat the standards here, but will just comment on them.

4.4.1 "Volume Pores"- The compression method suggested for measuring void volume is not necessarily the most accurate, but considering the wide range of acceptable void (70-85%), it is probably quite adequate; it has the advantage of simplicity, which is always desirable for inter-laboratory data comparison. However, I don't agree that the mercury intrusion method is not appropriate also, and I suspect that it is somewhat more accurate than the suggested method. I'll try both and let you know the conclusion. Perhaps I should describe the mercury method. The evacuated sample is trapped inside a glass dilatometer under a pool of mercury. As pressure is applied, the mercury intrudes the pores and the volume intruded is measured on a graduated stem. If one applies sufficient pressure, all the void is eventually intruded, and it doesn't matter whether the sample compresses in the process or not. As shown in my recent manuscript, one atmosphere pressure is sufficient to intrude all but about 5% of the void in Proplast, and I suspect that 2 or 3 atmospheres will easily take up the rest. Our porosimeter operates up to 1000 atmospheres pressure, so I have little doubt of its ability to intrude all the void.

4.4.2 "Pore Size Range" - I think we agree that this problem is much more difficult than the void measurement. I looked up the "ten line intercept" method of analyzing surface composition referred to in Ref. (30). There are several variations of this general type of optical image analysis involving combinations of lines, grids, points, etc. The method looks quite good for the applications described in the article. However, several things bother me about applying this method to the SEM pictures of Proplast. I see a certain degree of arbitrariness in deciding exactly where the boundaries of a pore are in a material with such a complex morphology. Also, I'm not sure that analysis of porosity from a photograph is necessarily equivalent to analysis of the material itself, as by the porosimetry technique, for example. I can illustrate this problem by supposing that we see something in the photograph that looks like a large pore opening at the surface, but directly behind it is a "wall" with only narrow exits. The optical analysis would say that we have a 200 μm "pore", whereas tissue ingrowth is going to be constrained by the much narrower pores behind the opening. This type of difficulty makes me wonder whether optical measurements are directly related to the permeability of the material, which is certainly the critical aspect of "porosity" for tissue ingrowth.

Also, I'm not sure that SEM is preferable to ordinary light microscopy which could be used for the relatively large (μm) pores in Proplast. SEM "sees" 3-dimensional objects in focus, while light microscopy has a narrow depth of field. However, the 3-D SEM pictures may not be representative of a cross section of the material, and it seems essential to me to know that one is looking at a flat 2-dimensional surface in order to make quantitative measurements from the picture. The results of your independent laboratory which found only 57% void volume by the SEM technique seem to indicate that this method does not accurately measure pore dimensions. In this connection, I remind you that mercury porosimetry seems to measure void volume quite well.

I have not yet used optical analysis on the porous materials, but I will let you know if I come up with more definite conclusions.

Sincerely,

Ronald E. Dehl, Ph.D.
Dental and Medical Materials
Polymer Science and Standards Division

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

In this report, we describe the application of several methods of porosity characterization to two commercial polymeric implant materials, a porous polyethylene and a composite of PTFE and carbon. In exploring the use of mercury porosimetry to determine interconnecting pore size distributions in the composite, we have found that, contrary to widespread belief, this rather soft and deformable material was not distorted by the mercury pressures required to measure its pore size distribution. The mercury intrusion technique indicated that the porous polyethylene has a narrower distribution of pore sizes than the composite. In the polyethylene and the composite, the weighted average interconnecting port "diameters" were found by this technique to be, respectively 30 μm and 50 μm. The average pore diameters were also estimated by measurement of specific surface area and pore volume. Assuming a spherical pore shape, the average pore diameters in polyethylene and composite were calculated to be, respectively, 60 μm and 25 μm. The accessible pore volumes of the materials were measured by three different techniques, a simple "apparent density" method, mercury intrusion, and bulk compression, the last for the composite only. For the polyethylene and composite we found pore volumes of about 45 and 70 percent, respectively.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

porous implants, pore size, pore volume, PTFE-carbon composite, porous polyethylene.

13. AVAILABILITY

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