A Novel Method for Measurement of Porosity in Nanofiber Mat using Pycnometer in Filtration

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ABSTRACT

Electrospun Polymer nanofibers have a wide range of applications including automotive air filters. Large surface area, small pores, flexible and adequate porosity are widely recognized as important parameters for improving the performance of the filter media and therefore measuring the porosity of the medium is extremely important. Porosity measurement techniques such as density based method, mercury porosimetry, capillary flow porometry, image analysis are relatively inaccurate and they have some disadvantages for measuring the porosity of the nano fibers. In the present study porosity measurement for nanofiber mat using pycnometer was explored. Pycnometer is generally used to measure the density of the solids of having volumes upto 150 cc. Volume of the nanofiber was measured by pycnometer and porosity is determined as fraction of the void in total volume of the fiber. Total volume is calculated from FESEM image thickness. Various advantages of pycnometry method when compared to other techniques were discussed based on the results of porosity measurements of nanofiber mats.

INTRODUCTION

Polymer nanofibers are important class of nanomaterials, widely investigated in recent years [1]. Scope of research on nanofiber filter media has increased significantly covering the applications for filtering of air, water, beverages, chemicals, oils, diesel, petrol, etc [2]. For automotive air filters, nanofibers were coated on standard filter media for improving the filtration efficiency and filter life with minimal rise of pressure drop [3, 6].

The nanofiber mat has extremely high specific surface area, adequate porosity and small pores due to their small diameters. The fiber size and morphology depends on various parameters involved in the preparation method. For example, in one of the most popular techniques like electrospinning, fibers are produced with the fiber diameter varying from nanometers to micron dimension. In this case, various parameters like concentration of the solution, applied electric voltage, and distance between the electrodes, deposition time, and rotation speed of the electrode, ambient temperature and relative humidity influences the fiber quality [1, 4].

Porosity is one of the important parameter in filter design and filter performance. Past studies have shown that the thickness and porosity of the nanofiber mats can be controlled by changing the deposition rate of nano fibers [5, 6].Adequate porosity and surface area of the nanofiber mat has turned nanofiber coatings as an important candidate for high performance filters. There are few methods for measuring the porosity such as conventional methods using apparent density and bulk density [7, 8], image analysis [9] and mercury porometer [10]. However, till date, an accurate estimation of porosity in these grades of materials (Nanofiber mat) is a difficult task. In this paper determination of porosity of the nanofiber mat by the pycnometer has been demonstrated for the first time. Novelty is determining the porosity by measuring volume by pycnometer and thickness by FESEM image. Though use of pycnometer for measuring the pore volume of porous materials may not be new but we believe that use of pycnometer for measurement of porosity of electrospun nanofiber mat in filtration is a new method. The advantage of pycnometry for the porosity measurement of nanofibers has also been discussed.

It is worthwhile to mention that porosity is a ratio of the volume of the fluid or void space in a filter medium to the total volume of the filter and as such it has no units and has values in the range of zero and one. A typical value of porosity for a sand filter is about 0.3 while it is in the range of 0.6 to 0.9 for various filtrations medium. Various general techniques available for characterization of porous materials are shown in *Table I* [11].

An alternative method using pycnometer has been reported by Stephani et al. [12] for measuring the porosity of the sinter products by measuring the thickness by micrometer. Whereas in this paper, pycnometer technique was applied to nanofibers.

TABLE I. Common methods used for measuring the porosity [11].

Method	Information yielded	Pore width range (nm)
Mercury porosimetry	Porosity , pore diameter and pore size distribution,	10 to 10000
Image analysis by FESEM,TEM	Porosity , pore diameter and pore size distribution	0.1 to 1000
Capillary flow porometry	Median pore diameter, pore size distribution and permeability	10 to 1000
Adsorption and condensation/BET	Pore size and pore size distribution of the fiber but not mat	0.1 to 10

Pycnometer generally measures the volume of the substance, and with the knowledge of mass of the material its density can be calculated. In this paper we have discussed the technique for porosity measurement in nanofiber mats (NFM) using pycnometer along with estimated porosity data for nanofibers produced by electrospinning when compared with conventional method [7, 8].

MATERIALS AND METHODS

Materials

Polyamide-6 of specific gravity 1.14, formic acid of 99% purity purchased from SRL, India and acetic acid glacial purchased from Fisher Scientific, India, were used for electro spinning of PA-6 nanofibers. Nanospider (Elmarco NS-500, Czech Republic) was used for synthesizing the fibers. Fibers were collected on the polypropylene fabric.

Polymer solution with concentration 13 wt. % was prepared by dissolving PA-6 in a magnetic stirrer of acetic acid and formic acid in 2:1 ratio and was stirred for three hours at room temperature. The solution was electrospun by NanoSpider NS500 at an applied voltage of 60 kV. A schematic of the Nanospider setup is shown in *Figure 1*. The distance between the wire electrodes and collector electrode was maintained at 100 mm with rotating electrode speed of 5 rpm and deposition rates of 0.6, 0.4, 0.23 gram per square meter (GSM). Here after nanofiber mat (NFM) is specified with GSM. FESEM microstructure of 0.4 GSM fiber mat on the standard filter media is shown in *Figure 2*. The rotating wire electrode, partially immersed in the polymer solution carries the droplets, which are ejected as nanofibers and are collected as a mat on the standard commercial filtration medium or on a polypropylene substrate at the counter electrode. Thus 0.6, 0.4, 0.23 GSM fiber mats are coated on the standard filter medium or polypropylene fabric by Nano spider equipment. Microstructures of 0.6, 0.4, 0.23 GSM are shown in *Figure 3*.

Methodology

Nanofiber was coated on 20 x 30 Sq. cm size substrate and the coated fiber was peeled off from the substrate manually with utmost care in order to ensure the peeled off weight and coated weight is same so as to avoid any error in volume of the fiber while peeling off. The peeled off Nanofiber mat was placed in the container of the pycnometer of AccuPyc1330, Micromeritics, U.S. Helium gas was used for measuring the fiber volume using the pycnometer. Helium Pycnometer working principle is based on the gas law [13]. Schematic diagram of pycnometer is shown in *Figure 4*. In the pycnometer the volume is determined by measuring the change in

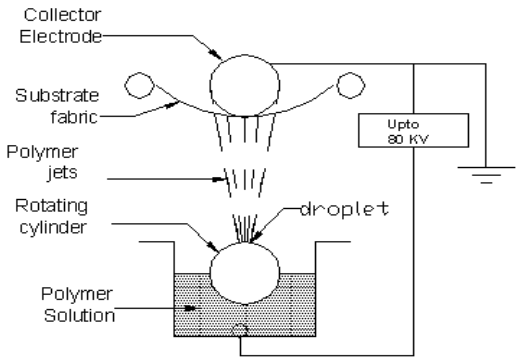

FIGURE 1. Schematic diagram of nano spider.

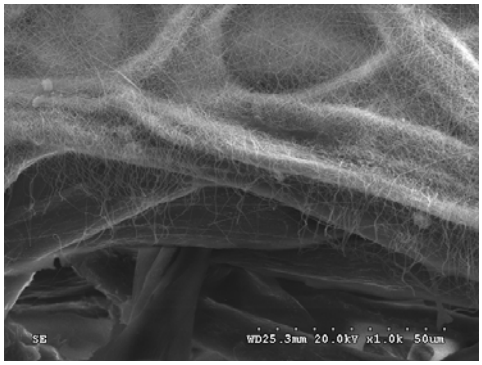

FIGURE 2. Nano fiber coated on the filtration medium.

pressure experienced by fluid due to displacement of fluid in constant volume by the sample to be tested. As shown in *Figure 4*, initially chamber 1 is empty with atmospheric pressure P_1 and chamber 2 is with pressure P_2. Chamber 1 with volume V_1 of known calibrated volume and let chamber 2 volume be V_2 and nanofiber mat volume be V_F . P_1 is equal to zero as gauge pressure of atmosphere is zero.

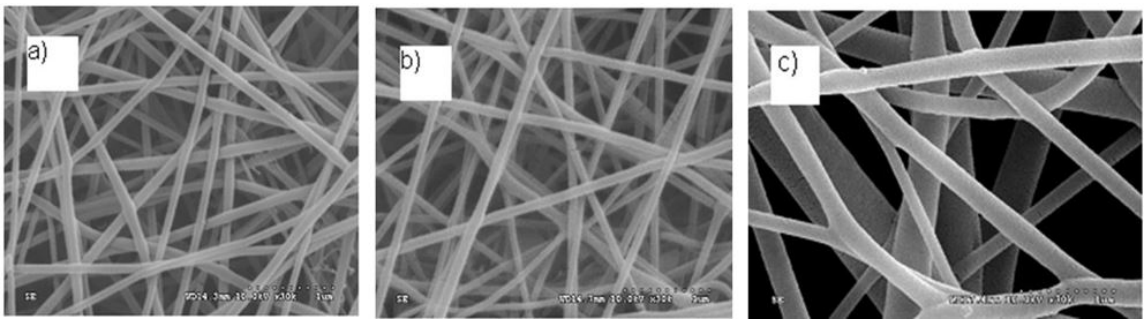

FIGURE 3. Microstructure of nano fiber of a) 0.6 GSM, b) 0.4 GSM, c) 0.23 GSM.

In the initial operation valve is opened and two chambers are brought to equilibrium state pressure P_3. Eq. (1) shows the equilibrium condition of initial operation.

$$P_3(V_1+V_2) = P_2V_2 \quad (1)$$

In the second operation, filter sample is kept in chamber 1 and chamber 2 has pressure P_4. When the valve is opened, equilibrium pressure P_5 is attained and corresponding equilibrium condition is shown in Eq. (2).

$$P_5\left(\left(V_1-V_F\right)+V_2\right) = P_4V_2 \quad (2)$$

Eq. (3) is obtained by solving Eq. (1) and Eq. (2), which gives nanofiber mat volume V_F

$$V_F = V_1 - P_3V_1 (P_5 - P_4) / P_5(P_3 - P_2) \quad (3)$$

Thus by operating the pycnometer two times and measuring the gauge pressures P_2 ,P_3 , P_4 , P_5 with known volume V_1, the volume of the nanofiber V_F can be obtained and this volume V_F can be used for estimating the porosity using the following relation

$$Porosity = 1 - \frac{Volume\,(V_F)\ of\ NFM\ by Pycnometer}{Total Volume\,(Length \times Width \times Thickness)}$$

Here, Length and width are 30, 20 cm, respectively and the thickness of the mat was measured by SEM image. An average thickness of 3.4 µm, 3 µm and 2.1µm was estimated from 10 image readings from each 30 cm length and 20 cm width mats of 0.6, 0.4 and 0.23 GSM, respectively. So by measuring the thickness of the mat by SEM and volume by pycnometer, porosity was estimated and results were compared with the estimated values obtained by conventional method [7, 8]. Conventional method was discussed in the results & discussion section.

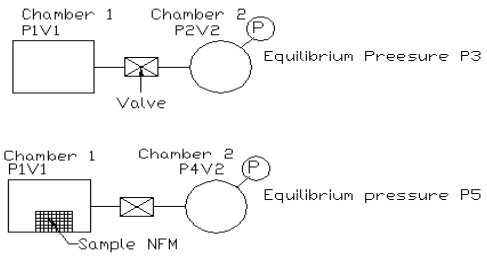

FIGURE 4. Schematic diagram of Pycnometer without and with sample.

TABLE II. Porosity data estimated by pycnometer and Conventional measurement.

Sample name	Mass of the sample, mg (M) ±0.1	Thickness (average) by micro-structure, µm ±0.05	Total Volume by dimensions, cc (V)	Solid Volume (average) by pycnometer, cc ±0.005 (V_F)	Porosity By Pycnometer ($1-V_F/V$)	Porosity by Conventional Measurement .[7,8] {1-((M/V) / Bulk density)}
0.6 GSM Nanofiberma t	38.20	3.4	0.2040	0.04947	0.7575	0.8300
0.4GSM Nanofiber mat	25.09	3.0	0.1800	0.04057	0.7746	0.8777
0.23 GSM Nanofiber mat	14.16	2.1	0.1260	0.02340	0.8140	0.8964
PP fabric	--	--	1.7300	0.62016	0.6415	--
Standard Filter media	--	--	1.5096	0.37920	0.7488	--

RESULTS AND DISCUSSION

Figure 2 shows Nanofiber coated on standard filter medium. As discussed in the above section, Nanofiber coating on the filter medium improves the filtration efficiency and dust holding capacity of the filter [3] provided coating porosity should be adequate enough to avoid the pressure drop. Very thin coatings are required for improving the filter performance. Accurate measurement of porosity is very useful in design of thin fiber coating so that required GSM of coating can be coated on the filtration medium for the minimum pressure drop due to coating. Generally in conventional measurement [7,8] porosity is estimated with the following relation.

$$NFM\ ApparentDensity = \frac{NFM\ Mass}{NFM\ Area \times NFMThickness}$$

$$Porosity = 1 - \frac{NFM\ ApparentDensity}{BulkDensity}$$

In conventional method the mat thickness is measured with micrometer as the fiber mats are relatively thick for biomaterial applications and total volume (V) is calculated as product of area and thickness. In case of thin NFM for filter applications, micrometer reading gives large error due to the soft nature of the fibers and thickness is close to or less than the least count of the micro meter. It is felt that, porosity with conventional method gives inaccurate values due to the following three reasons. 1) Thickness error by micrometer but in the present paper that was overcome by taking the thickness with SEM even in the conventional method also 2) Pore volume is neglected but it cannot be neglected for highly porous mats and 3) There may be variation in taking the material density. Hence calculated density does not represent the true density of the nanofiber mat. While conventional method gives large errors in the density measurements, other methods also suffer from issues such as hydrophobicity, chemical reactivity and fiber damage during the measurements, pycnometer method was demonstrated. Pycnometry overcome the above issues as the gas used is helium which is chemically inert and small atomic size for easy penetration into pores and does not cause any damage to the fibers. The volume measured by this method is more accurate than other methods, and the porosity values with reasonable accuracy can be obtained if the thickness is measured by SEM rather than micrometer**.** *Table II* shows the results of volume obtained from dimensions (V) as well as by pycnometry (V_f), thickness by microstructure image, porosity by pycnometer and porosity by conventional method. The thickness of the fiber mats of different GSM which was measured from SEM images are shown in *Figure 5.*

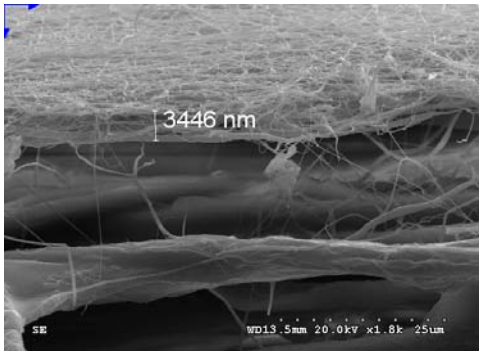

FIGURE 5. SEM images of the cross section of the nanofiber mats of 0.6 GSM on filter medium indicating its thickness.

Estimated porosity of nanofiber mat of different GSM by conventional method [7, 8] is shown in the *Table II* for comparison. In the results of *Table II* porosity by conventional measurement [7, 8] is higher than the pycnometer method, which is due to the fact that as discussed above, fiber mat is highly porous, volume measured for conventional method by dimensions is a total volume which is greater than the actual volume of the mat (Actual volume = Total volume - Pore volume), so density calculated in conventional method from dimensions and mass of the fiber mat does not represent the true density. Due to this reason porosity by conventional method is higher than the pycnometer method. The conventional method gives over estimated porosity than the actual porosity**.** To choose the right GSM coating for minimal pressure drop the accurate estimation of porosity is required. Usually, very thin coatings (low GSM) on standard filter media are necessary to have minimum pressure drop and high filtration performance. An example of 0.4 GSM coated conventional commercial filter media is shown in *Figure 2*. It is very clear that the regular micron size fibers with large pores are uniformly covered with very thin layer of nanofibers which improve the filtration performance without causing any significant pressure drop. In such nanofiber coatings it is difficult to measure porosity by conventional methods. As discussed above, we believe that pycnometer method provides logically and experimentally better accuracy than conventional method [7, 8] and proving the degree of accuracy with other proven methods is future scope of this paper. Pycnometry is simple and reliable method for such measurements. We have even tried to measure the porosity for 0.2GSM sample. However, in this case we had to use polypropylene as the substrate as such a thin film could not be peeled off from the conventional commercial grade substrate. The porosity of the fiber mat could be measured after peeling it off the substrate. The fibers coated on these substrates are thicker in diameter indicating that substrate also influences the fiber dimensions.

As shown in the *Table II* the fibers with 0.2 GSM shows higher porosity compared to other GSM because as density decreases, porosity increases as these properties (mass, volume and porosity) are related [14]. Thus it is believed that porosity by pycnometer will provide accurate porosity as the volume measured by the pycnometer is accurate. This is because it considers even micro and meso pores and also helium gas can diffuse into the micro pores due to its small atomic size. To ensure the accuracy of the volume measurement of this method, volume of the specified mass of PA-6 granules is also measured by pycnometer to calculate the density of granules and the density value of 1.14 is well in agreement with the manufacturer's specification, which validates the effectiveness of the pycnometer porosity data.

CONCLUSION

We have demonstrated, for the first time, that pycnometry is a simple and reliable method for estimating the porosity of electrospun nanofibers even for the thin coatings necessary for the regular filter media for high performance applications. The advantages of the method include (1) minimum damage to the fibers, (2) chemically inert, (3) measurement of total porosity including micro and meso pores due to the ease of penetration of helium gas, and (4) independent of direction of medium as the static pressure is applied. Measurement of the porosity by pycnometry allows the design of the coating structures suitable for filter media with minimum pressure drop for practical applications.

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