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Chapter

The Porosity of Nanofiber Layers

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Abstract

Nanofiber layers have recently received lots of attention. These layers can be produced in various methods, but the most common is electrospinning. Therefore, this chapter focuses on the nanofiber layers from electrospinning. The porosity of nanofiber layers is a critical property. Several methods can be used to measure this value. Also, there are numerous methods for controlling and changing it. The porosity is an essential property for the application of nanofiber layers. Each application requires a unique set of porosities. As a result, measuring and controlling the porosity with high precision is critical for applying nanofiber layers. This chapter concentrated on porosity measurement and control methods and the importance of porosity in applications.

Keywords: nanofiber, porosity, electrospinning, nanofiber layers, porosity measurement methods

1. Introduction

In recent years, multifunctional properties for nanofibers derived from polymers, metal composites, and metal oxides have been expressed. Additionally, surface-modified nanofibers are simple and inexpensive to manufacture. It is due to the unique properties of nanofibers, which include high tensile strength, high specific surface area (surface area per unit mass), and porosity [1, 2]. The length-to-diameter ratio of nanofibers is high [3]. As a result, nanofiber properties are critical for high-performance filters, absorbent textiles, medical textiles, drug release, and many other applications [1, 4].

Electrospinning is a continuous method for producing nanofibers with diameters ranging from micrometers to nanometers. Layers with a high specific surface area, high porosity, and good mechanical properties can be produced using this method [5]. Electrospinning is a popular method for preparing scaffolds. Various electrospun nanofiber patterns are used to prepare layers with medical applications ranging from artificial skin to endocrine organs and from the nervous system to cardiovascular applications [6].

The porosity of electrospun layers varies depending on their application. In some applications, porosity is required less than usual, while in others, it is required more than usual. Therefore, there are various methods for achieving sufficient porosity.

The only way to prepare large-scale nanofibers is through electrospinning. The reason for this is the ease of control, high speed, low solution consumption, control of diameter and pores and fibers alignment, ease of the process, low cost, simple and
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reproducible fiber production process, and technological advances [7]. This process can use a wide range of polymers to obtain polymer fibers in the submicron range, which is difficult to achieve with traditional spinning methods [8]. Electrospinning is affected by various environmental and solubility parameters and processes. Two environmental parameters include temperature and relative humidity. Also, concentration, conductivity, molecular weight, and viscosity are the solubility parameters. The process parameter includes feeding rate, voltage, and needle distance to the collector. The diameter of fibers decreases with increasing temperature and increases with increasing humidity [6, 7]. The electrospun fibers had diameters ranging from 10 nm to 100 μm. Polymer solutions are most commonly used for electrospinning. However, in some cases, polymeric melts with higher direct current voltages can also produce fibers with diameters less than micrometers [6].

Electrospinning is an electrohydrodynamic process in which the liquid droplet is affected by electricity to make a jet (accelerated flow of liquid). It is then stretched and bent to form fibers or nanofibers with the main components of the high voltage supply, a power pump (in the form of a syringe), a spinner (typically a special subcutaneous injection needle with a tipless head), and a conductive collector. Power can be supplied in either a direct or alternating current. Surface tension causes the liquid to be removed from the filament during electrospinning, resulting in a hanging drop. As soon as the droplet is electrified, the repulsive force between the same surface loads reshapes it as a Taylor cone, ejecting a loaded jet. The jet is first drawn in a line (this occurs due to polymer tying in a polymer solution and prevents the jet from turning into droplets [9]), and then it undergoes rapid whipping movements due to bending instability (this occurs due to high surface load density [9]). The jet quickly solidifies as it is drawn to finer diameters, resulting in solid fiber deposition on the surface of the collector attached to the ground. Typically, the electrospinning process is divided into four consecutive steps:

1. Charging liquid drops and formation of Taylor cones or cone-shaped jets;
2. Drawing the charged jet along a straight line;
3. Jet thinning in the presence of an electric field and increasing electrical bending instability (also known as whipping instability); and
4. Freezing and collecting jets in the form of fibers or solid forks on the grounded collector [10].

Because of their fine diameter, these layers have a high specific surface area, high porosity, and small pore sizes [11, 12]. If the fibers also have pores, the porosity and the specific surface area will also increase [10]. Femme and his colleagues demonstrated that increasing the diameter of the fibers increased the pore size [13]. This increase will cause a reduction in the specific surface area. Therefore, if high specific surface area, fine diameters, and large pores are required in applications, the pore size must be de-linked from the fiber diameter. Both theoretical models and experimental studies have shown that nanofiber diameter strongly affects the pore diameter with smaller nanofiber diameters resulting in smaller pores [11] (which will be discussed in the future). Higher pressure is also required for any fluid to enter the layer (higher surface tension) [8].

Smart layers, filtration membranes, fuel cells, batteries, wound dressings, sensors, catalysts, energy storage cells, electronics, and spintronics use electrospinning [1].
Drug delivery, tissue engineering, and protective textiles benefit from porosity and high specific surface area [4]. Because of their high porosity, good mechanical properties, and high-water permeability, electrospun membranes will be practical for air filtration and water purification [5]. Electrospun layers are used in multi-structural thin films, ultrafiltration, nanofiltration, reverse osmosis, and distillation membranes as porous protective layers. Today, distillation membranes are highly regarded. Multi-structural thin film membranes have three layers:

1. An upper layer that is very thin for filtration,
2. A middle layer that is a porous protective layer, and
3. The underlying layer that is a nonwoven textile [7].

For automotive air filters, nanofibers are coated on a standard filter environment to allow high efficiency and long filter life, which occurs with the lowest increase in pressure drop [12].

Electrospun nanofiber layers have a high specific surface area, controllable porosity, interconnective pores, microscale interstitial distance, and flexibility because of their various sizes and morphologies. Due to these advantages, they are appealing in applications [14]. However, because of electrospinning disadvantages, such as high voltage sources, it is necessary to use toxic organic solvents and low production rates [15]. Synthesis conditions (like high humidity) can affect nanofibers’ morphology, such as mesoporous fibers [16], resulting in a higher specific surface area of nanofibers that can improve their properties.

The amount of air, gas, or vacuum in a solid material is often expressed as the percentage of the nonsolid portion volume divided by the total volume (total solid and nonsolid volume) of a unit of matter [17]. Porosity is the fluid volume or space in the filter media to the total volume of the filter ratio. It has no unit, and its value can range from zero to one. One of the essential parameters in the design and operation of filters is porosity. Nanofiber layers have made nanofiber coatings the most important candidates for high-performance filters due to their porosity and sufficient surface area [12]. The membrane’s porosity, pore size distribution, and bending make it simple to pass steam through and collect steam as a filter outlet [9]. Previous research has shown that changing fibers’ sedimentation rate can control the nanofiber layer’s thickness and porosity. The pore space in the layer is related to the total porosity in the electrospinning layers [12].

Nonwoven materials have a pore structure, which is critical in their application. There can be three types of pores in a matter [18]. Closed pores are inaccessible, they also restrict the blind pores within the material and prevent fluid from passing through. Open pores are outwards and allow fluid to pass through, many nonwoven textile applications benefit from open pores. Their main characteristics are the largest pore diameter, pore distribution, high specific surface area, and gas permeability liquid passage. Through pores are pores which are in the entire thickness of the layer and the fluid can enter and then leave the layer through them.

1.1 Methods of changing the porosity of nanofibrous webs

Porosity can be created on the fibers and referred to as porous nanofibers. However, porosity can also be created between the fibers. The porosity that forms on the fibers can be reduced using the following methods:
1. Phase separation between polymer and solvent (breath figure) [10, 19];

2. Phase separation between polymer and nonsolvent [20];

3. Phase separation of the liquid section in polymer, nonsolvent, and solvent systems [21];

4. Collecting the nanofibers in a nonsolvent bath [21];

5. Selective removal of one phase of nanofiber [10]; and

6. Thermal degradation of one phase [22].

Many methods are used to increase the porosity of layers in which the porous scaffold structure is naturally placed together by adding the macroporous structure. This process is accomplished by aligning crystalline structures like ice or salt crystals parallel to the electrospinning. However, these methods increase cell penetration in the electrospun scaffold while preventing the actual pore effect defined by single fibers [10].

Fiber collection on a rotating axis is a technique for modifying porosity and pore size independently of fiber diameter. Porosity decreases as axis speed increases due to increased layer density. At the same time, the diameter of the fibers decreases slightly [10].

1.2 Performing a final treatment

In this case, one of the components must be water soluble while the other is not. The pore size of a fiber changes when it is dissolved in water. It has been demonstrated that dissolving a component in water causes the pore size to increase exponentially. The effect on cell penetration is minimal in this condition, but the significant fiber removal from the layer affects the mechanical properties. Another person demonstrated that this work doubled the size of the pores and completed penetration into the cell, whereas previous work only affected penetration into the surface cell [23].

Of course, numerous methods exist for modifying pore size and porosity independent of the fiber diameter [24]. According to studies, the diameter of the fibers strongly influences the diameter of the pores and the porosity. The smaller diameter of the fibers, the smaller the pores. However, for some applications, it is appealing to combine the increased specific surface area provided by fine fibers with large pores for cell or fluid transport. For this purpose, the increase in pore size should be made independent of the fiber diameter.

To this end, two different polymers can be purposefully mixed during electrospinning. Then, one of these polymers is selectively dissolved, increasing the void volume and the pore size. The layer is created for this purpose by electrospinning two polymers from two unique devices (side-by-side arrangement). This configuration can result in high output.

The resulting fibers are layered on top of one another but are not intentionally mixed. The tendency of the resulting fibers to prevent material mixing in the case of side-by-side charged jets can be explained simply by the electrostatic repulsion of materials with the same charge. For this purpose, one can use the core/shell or side-by-side arrangement with a spinning machine and various other arrangements. In this case, the spinning conditions for both polymers cannot be independent.
Moreover, both polymers must be solvent-soluble, and the applied voltage must be the same [11]. A simple arrangement can spin two polymers with different solvents and applied voltages. Each material has its unique spinneret and voltage supply. Because the charged droplets are evenly spaced on the grounded collector, no electric field is applied to the rotating collector, and no electric field is observed. The collector rotates fast enough to mix the different fibers. However, it cannot make arranged or non-isotropic layers. Two electrosprinning units are placed facing each other with a collector. Each machine's electrosprinning parameters are controlled independently. The fibers are mixed by the collector connected to the ground to form a non-woven layer [11].

By performing an end treatment on the two-dimensional (2D) layer, three-dimensional foam can be obtained. A suspension of short fibers is frequently obtained by shearing and homogenizing the layer in a liquid (usually water or ethanol depending on the solubility of the nanofibers). After drying and cooling, a super elastic three-dimensional (3D) super light nano fiber foam is obtained. This foam has a low density and extremely high porosity. A cross-linking agent is required to increase the interaction between these short fibers [10]. Fiber collection engineering is a straightforward method for directly assembling nanofibers in three dimensions by engineering the aggregate [10]. Another method for creating 3D foams is to immerse the two-dimensional layer in a sodium borohydride aqueous solution. When this material is rapidly hydrolyzed in water, hydrogen gas passes through the 2D layer under applied pressure, separating the nanofibers and forming a 3D structure [25]. Furthermore, dry ice causes the same process by producing carbon dioxide; however, this method does not require water usage. The porosity is significantly high with this method [10].

The last three methods are for creating a 3D sponge with an irregular structure that lacks topographical cues. The materials required for these methods are exceptional. To overcome this limitation, the gas sponge method, which employs borohydride to create a very regular 3D sponge, employs a non-axially regularized layer [10].

Scaffold porosity is affected by electrospinning conditions, and fibers with varying fiber diameters made from various polymers can be produced in a controlled and reproducible manner [26–28].

Applying photoinduced thiol-ene cross-linking reactions to the electrospun layer is a versatile and efficient method for tuning the porosity of the nanofiber's web. Aside from preventing the polymer cold flow and freezing the structure obtained by electrospinning, the photocuring step finely controls the morphology of the nanofiber layers [29].

Electrospun porous nanofibers loaded with photocatalytic particles can increase the particle contact area with light, shorten the electron transfer path, and improve photocatalytic activity, which has applications in pollutant degradation [24].

Porosity can be calculated using the formula with the nanofibers' pore size and diameter [5].

2. Application of reducing and increasing layer porosity

An example of electrospinning layers with typical porosity and low porosity obtained by electrospinning with two pumps is examined. A wide lumen with no leakage necessitates blood flow in the lumen of a scaffold with no vessel leakage. An important parameter to consider is the size of the pore. If the pore size is too small, it prevents penetration into the cell. On the other hand, if it is too large, blood leakage
occurs. According to research, the performance of double-layered scaffolds inside and outside the body, with one layer with low porosity (62%) and another with high porosity (81%), is also placed in the conduit or external coating. A comparison of vascular scaffolds made of a single layer of nanofibers with high porosity, with two-layer scaffolds that significantly reduce blood leakage, reveals that a layer with low porosity is required. Also, when a multilayered vascular scaffold is made, leakage is possible. The blood level should be low and cell penetration should be done well. Cell infiltration from the connective tissue surrounding the scaffold was also concluded to be greater than flowing blood [10]. It is necessary to compactly place fibers with a very small diameter to achieve a layer with low porosity. In general, a two-pump electrospinning machine is required for this lumen. This is done to keep the two polymer solutions from mixing. The transfer is continuous in these layers, and the layers are not separated. Less electrospinning time is required to produce a layer with less porosity. The electrospinning conditions of each layer are different from the others [30]. Therefore, in some applications, a layer with low porosity and small pore size is required, whereas other common electrospun layers are suitable. Of course, in some applications, it is necessary to make an ultra-porous layer with large pore size and fine fibers to transport cells or fluid [11]. A layer with high porosity and good protection is required in some applications, such as wound dressing. Wound dressing permeability against oxygen, control of water vapor exit, and fluid passage occur due to high porosity in the layer of nanofibers, resulting in wound healing [17].

3. Porosity measurement methods

Electrospun polymeric nanofibers have broad applications, such as automobile air filters. High specific surface area, small pores, flexibility, and sufficient porosity are essential for improving the filter media performance, so measuring porosity is critical. Porosity affects several material properties, such as sorption capacity and mechanical, thermal, and electrical properties [31]. For example, porous materials can store and transport gas. Their porosity affects hydrate formation and gas-storage capacity [32]. Also, the quality of the dental composite depends on its degree of porosity [33, 34], so measuring the porosity by the most accurate method is very important. Porosity measurement methods such as the density method, mercury porosimetry, image analysis, and capillary flow porometry are relatively inaccurate methods, and all have disadvantages for measuring the porosity of nanofibers. Another way to measure porosity is by expanding gas, which works with helium gas. To date, accurate porosity measurement in nanofiber layers has been challenging.

3.1 Density method

The overall porosity is obtained following the conventional method per the following equation [8]:

\[
Total\ Porosity = 1 \ - \ Layer\ Density
\]

In this equation, the material density relates to the material from which the layer is obtained. Also, layer density is calculated by dividing weight by layer volume. This method is a good alternative when there is no access to the right equipment because it
is convenient and fast. Samples should be prepared carefully, and dimension measure-
ments should be accurate to achieve precise accuracy. A micrometer was used to
obtain the samples’ thickness, and the diameter of the samples was used to obtain
the sample size [8, 35]. This method causes many errors in the actual porosity [36].
Of course, this method is suitable for nanofiber layers that cannot withstand high
pressure [37].

3.2 Mercury method

This method is frequently used to characterize structures with nonwoven pores.
Mercury is not very destructive to soils because the surface free energy between
mercury and soil is more sizable than between gas and soil. Mercury does not enter
the pores. However, it can enter with force. Pressure is needed to enter mercury into
the pore, obtained by the pore diameter. The measurement of injectable pressure
and intrusive volume obtains the diameter and volume of blind and open pores. In
this method, mercury enters the pores with compulsion and pressure, the volume of
mercury is penetrated, and the pressure is measured. This method only reveals the
volume of pores and the diameter of blind and open pores. Here, the essential charac-
teristics are no longer measured.

Additionally, this method requires high pressure, which can significantly damage
the pore structure of nonwoven materials. Mercury is used in this method, which
harms one’s health and pollutes the environment. The pressure applied in mercury
porosity is slightly higher than 0.5 to 60,000 pounds per square inch. Biological
materials that can be compressed or degraded at high pressures must be analyzed with
relatively quantitative pressures, or a correction for compression capability should be
applied to experimental measurements. The pressure is obtained as per the following
equation:

\[
\text{Pressure} = \frac{2}{\text{Pore Diameter}}
\]  

(2)

Open porosity (obtained by the mercury measurement method) is obtained from
the following equation:

\[
\text{Open Porosity} = \text{Mercury Penetration} - \frac{\text{Total Volume}}{\text{Layer Volume}}
\]  

(3)

Finally, the closed porosity, which cannot be calculated by mercury porosity, is
determined by the following equation [38]:

\[
\text{Close Porosity} = \text{Total Porosity} - \text{Open Porosity}
\]  

(4)

This method obtains the average pore diameter, size distribution, and total vol-
ume fraction of pores [19, 39]. It should be noted that mercury is expensive and toxic.

However, it should be noted that this method is generally a liquid penetrating
method that can be used with Vaseline. In this case, the layer is weighed and remains
in Vaseline at room temperature with a mechanical stirrer for one day to allow the
liquid to penetrate the volume of the layer. The surface of the samples was then dried
and weighed again to obtain the weight of the penetrated Vaseline. Measurements are performed on five samples, and porosity is obtained from the following relationship:

\[ \text{Porosity} = \frac{\text{Total Vaseline Volume}}{\text{Volume of layer}} \]  

(5)

The Vaseline volume is derived from the division of primary and secondary Vaseline mass differences. The layer volume was obtained from the total Vaseline volume and the volume of fibers. Fibers’ volume is derived by dividing the primary mass by the density of the polymer of the layer manufacturer [8].

3.3 Liquid intrusion method

The fluid intrusion method can also achieve open porosity. This method is derived from the method for calculating the pore diameter. First, the method for calculating pore size is investigated. This method provides the most detailed information about the structure of the pores within the layer and is appropriate for testing the polymeric nanofiber layer. The general rule is that a liquid with a lower surface energy than the sample with gas is used to fill the pores of the sample. A decrease in the system’s free energy causes pores to fill spontaneously. Gas can transport liquid through pores, and the gas increases the free energy of the surface, allowing the free energy of the surface to be moved from the low-level free energy between the sample and the liquid to the high-level free energy between the sample and the gas.

If the sample is simply dropped into the liquid and removed, the porosity can be calculated using the fluid displacement method as shown below. After removing the saturated layer from the liquid, the residual liquid volume and open porosity are calculated using the following equation [38]:

\[ \text{Porosity} = \frac{\text{residue liquid volume}}{\text{Initial Volume}} \]  

(6)

However, according to some sources, this liquid should not cause the layer to accumulate and swell [40].

3.4 Scanning electron microscopy images

Various computer software programs analyze this method to determine porosity, particularly pore size. Samples of various sizes are used for statistical analysis. Finally, they shoot and analyze the porosity and pore size in layers using industrial shears. In short, isotropic incision information is obtained and reconstructed into two-dimensional images, which are then written and analyzed to create 3D photographs and to obtain few morphological details.

Surface porosity is calculated using scanning electron microscopy images by dividing the free area by the total area of the sample. For the fiber area, the average diameter is used [8].

\[ \text{Porosity} = \left( \frac{\text{Total sample area} - \text{total fiber area}}{\text{total sample area}} \right) \times 100 \]  

(7)
3.5 Gas expansion

In this method, the solid density is measured using a volume of 150 cc. The volume of nanofibers can be calculated using a density meter and porosity based on the ratio of empty space volume to total volume. The total volume of the image thickness was determined by scanning electron microscopy (SEM). The use of a density meter to calculate pore volume is not novel, but it is new for determining the porosity of nanofiber layers via filtration. The density meter measures volume; however, the density can be calculated using the sample’s mass. The helium gas density meter is in accordance with the gas law. In this device, the volume is measured by the amount of fluid pressure change, resulting in the displacement of the sample in a constant volume. This method begins with one chamber (chamber 1) that is initially empty and has atmospheric pressure. As a result, the first chamber’s confusing pressure is zero. Chamber 1 have pressures and volumes of $P_1$ and $V_1$. The pressure and volume of the second chamber are $P_2$ and $V_2$, respectively. In the initial state, the valve is open and the two chambers are at equilibrium pressure $P_3$, so the equilibrium equation is written as follows:

$$P_3(V_1 + V_2) = P_2V_2$$

(8)

Next, the sample is placed in chamber 1, and the pressure of the second chamber is set to $P_4$.

$$P_5((V_1 - V_f) + V_2) = P_4V_2$$

(9)

As a result, the volume of VF nanofibers can be obtained by setting up the density meter twice and measuring the pressure of $P_2$, $P_3$, $P_4$, and $P_5$ with the specified volume of $V_1$. Also, the volume of fibers can be calculated as porosity with the following equation:

$$VF = V_1 - P_3V_1(P_5 - P_4)P_5(P_3 - P_2)$$

(10)

$$\text{Porosity} = 1 - \frac{\text{Total Fiber Volume}}{\text{Total Web Volume}}$$

(11)

This method has less porosity than the traditional method and has advantages over the others mentioned previously. The density of polyamide 6 chips was measured to control the accuracy of this method.

1. The minimum damage to the fibers,

2. Chemical entry,
3. In this method, meso- and micropores are both measured, and

4. Using another medium is not required due to applying static pressure on the layer [12].

The nanofiber layer’s porosity is an important property, and any application requires specific porosity [41]. All of the porosity measurement methods that were discussed had drawbacks. Methods based on liquids had more difficulty creating the sample, resulting in changes in structure and measurement errors. In addition, non-wetting liquids can damage the structure due to the need for pressure, which can change the structure and even damage the layer. The density method also has errors due to the need to measure dimensions, and a scale with appropriate accuracy is required. Of course, SEM images can be used to accurately measure dimensions. However, there are some issues to consider. The thickness of the layers is not uniform because the dimensions are too large, so the error increases. On the other hand, many methods are incapable of measuring the pore size of the pores, which are much smaller than the pores of nanofiber layers. SEM images are two-dimensional with layers stacked together. To consider pores the best method is nano-computed tomography (nano-CT) [36, 42, 43], but this device is not widely available. Its advantages include measuring pore size by machine and operator, providing completely accurate information about layer structure, and being very precise. Nanofiber imaging with micro-computed tomography (micro-CT) scanners is not possible due to the limitation of not being visible at distances less than 200 μm.

4. Conclusions

Methods for measuring and controlling porosity, as well as the importance of porosity in applications, are discussed in this chapter. The best method for measuring the porosity of the nanofiber layers was introduced as nano-CT. The focus of future work will be on controlling the porosity for various applications and making electrospun layers suitable for new applications. In addition, new porosity-controlling methods may be introduced in future works.

Conflict of interest

The authors declare that they have no competing interests.
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