Fractal Properties of Pore Distribution of Electrospun Nanofiber Membrane

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Authors’ contributions

This work was carried out in collaboration among all authors. Authors BC and CY designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors CR and SL managed the analyses of the study. Author LY managed the literature searches. All authors read and approved the final manuscript.

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Abstract

Due to the complex and chaotic characteristics of electrospun nanofiber membrane, fractal theory is a suitable mathematical framework. Using the fractal theory, Matlab and other computer software in Mathematics, the fractal properties of pore distribution of electrospun nanofiber membrane and the relationship between the fractal dimension and the physical properties of nonwovens are studied. Thirty samples were produced by using polyvinyl alcohol (PVA) on the DXES-01 automatic electrostatic spinning machine; BMP images of 30 samples were obtained by TM-1000 table scanning electron microscope; The scanning electron micro-scope images were grayed by digital image processing technology, and the average pore width of the samples was further calculated by Matlab software from the gray value matrix; G-P algorithm is used to calculate the fractal dimension of pore width distribution; The relationship between air flow resistance and the fractal dimension of pore width distribution of electrospun nanofiber membrane was analyzed. Finally, the correlation fractal dimension of the average pore width obtained is consistent with the fractal dimension of porosity obtained by Ting Wang under the meaning of the relative error less than 10% is the same.
Keywords: Electrospun nanofibers; average pore width; correlation fractal dimension; the fractal.

1 Introduction and Preparation

With the rapid development of nanotechnology, electrospinning technology [1-3] has attracted extensive attention as a manufacturing method of nanometer nonwovens. Compared with the traditional method, electrospun nanofiber membrane is thinner and it can reach the nanometer level. As a result, the application of electrospun nanofiber membrane is more extensive, and it is more difficult to study the properties of it.

Mandelbrot has proposed the concept of fractals at first in 1973. Fractal is a "shape" that has parts and a whole that are somewhat similar, and points out that the shape of objects in nature is mostly irregular and complex. In 1977, his works fractal: shape, opportunity and dimension and fractal geometry in nature were described in detail, which marked the birth of fractal theory [4,5].

The pore distribution of electrospun nanofiber membrane is complex and disordered, so it is very natural to use fractal theory as a tool to study its properties. On the basis of comparing various fractal definitions, aiming at the characteristics of pore distribution of electrospun nanofiber membrane, a fractal dimension -- correlation fractal dimension[6-8] defined on the basis of G-P algorithm was selected.

The concept of G-p algorithm and correlation dimension:

First, take such a system

\[ \{x_k: k = 1, 2, ..., N\} \]  \hspace{1cm} (1)

convert to M dimensional Euclidean space, as follows:

\[ X_{(M,t)} = \{x_n, x_{n+r}, ..., x_{n+(M-1)r}, n = 1, 2, ..., N\} \]  \hspace{1cm} (2)

And define the correlation function \( C(r) \) as

\[ C_M(r) = \frac{1}{N(N-1)} \sum_{i \neq j} \theta(r - |X_i - X_j|) \]  \hspace{1cm} (3)

Where, \( \theta(x) \) is Heaviside step function, namely

\[ H(x) = \begin{cases} 1, & x > 0 \\ 0, & x \leq 0 \end{cases} \]  \hspace{1cm} (4)

Where \(|\cdot|\) represents the distance between the state vectors \( X_i \) and \( X_j \) in Euclidean space.

When \( r \) is small enough, define a constant \( D(M, r) \) relative to \( M \) and \( r \) :

\[ D(M, r) = \frac{d \ln C_M(r)}{d \ln r} \]  \hspace{1cm} (5)

By selecting the appropriate \( M \), the correlation fractal dimension can be obtained[9-10]: When the double log curve \( \ln C_M(r) - \ln r \) is nearly linear, the sample is considered to have a fractal structure, and the slope of the line corresponding to the linear interval is \( D \), namely the correlation fractal dimension of the sample.

We will study the fractal characteristics of electrospun nanofiber membrane and its relationship with physical properties by using the correlation fractal dimension.
2 Experimental and Data Acquisition

2.1 Sample preparation and physical data acquisition

First of all, 30 samples of electrospun nanofiber membrane were prepared by using the DXES-01 automatic electrostatic spinning machine with PVA and using the method of orthogonal design to increasing the number of samples. The scanning electron microscope images of them are shown in Fig. 1.
The air flow resistance of each sample was measured with TSI8130 automatic filter, as shown in Table 1.

Table 1. Air flow resistance of the sample

| No. | Needle-to-collector distance (cm) | Applied voltage (kv) | Volume flow rate (ml/h) | Concentration (wt%) | resistance (pa) |
|-----|----------------------------------|----------------------|------------------------|---------------------|----------------|
| 1   | 11                               | 15                   | 0.5                    | 12                  | 11.1           |
| 2   | 13                               | 15                   | 0.7                    | 12                  | 22.1           |
| 3   | 15                               | 15                   | 1                      | 12                  | 21             |
| 4   | 17                               | 15                   | 1.2                    | 12                  | 11.1           |
| 5   | 19                               | 15                   | 1.2                    | 12                  | 8.9            |
| 6   | 19                               | 15                   | 1.5                    | 12                  | 6.1            |
| 7   | 11                               | 18                   | 0.5                    | 12                  | 11.5           |
| 8   | 11                               | 18                   | 0.7                    | 12                  | 19.3           |
| 9   | 13                               | 18                   | 1                      | 12                  | 15.6           |
| 10  | 15                               | 18                   | 1.2                    | 12                  | 19.8           |
| 11  | 17                               | 18                   | 1.5                    | 12                  | 9              |
| 12  | 19                               | 18                   | 0.5                    | 12                  | 8.1            |
| 13  | 11                               | 20                   | 1                      | 12                  | 31.2           |
| 14  | 13                               | 20                   | 1.2                    | 12                  | 27.5           |
| 15  | 15                               | 20                   | 0.7                    | 12                  | 9              |
| 16  | 15                               | 20                   | 1.5                    | 12                  | 43.1           |
| 17  | 17                               | 20                   | 0.5                    | 12                  | 8.5            |
| 18  | 19                               | 20                   | 0.7                    | 12                  | 4.9            |
| 19  | 11                               | 23                   | 1.2                    | 12                  | 30.1           |
| 20  | 13                               | 23                   | 1.5                    | 12                  | 29             |
| 21  | 15                               | 23                   | 0.5                    | 12                  | 7              |
| 22  | 17                               | 23                   | 0.7                    | 12                  | 5.8            |
| 23  | 17                               | 23                   | 1.5                    | 12                  | 7.3            |
| 24  | 19                               | 23                   | 1                      | 12                  | 9              |
| 25  | 11                               | 26                   | 1.5                    | 12                  | 15.7           |
| 26  | 13                               | 26                   | 0.5                    | 12                  | 9.9            |
| 27  | 13                               | 26                   | 1                      | 12                  | 25.9           |
| 28  | 15                               | 26                   | 0.7                    | 12                  | 8              |
| 29  | 17                               | 26                   | 1                      | 12                  | 5.7            |
| 30  | 19                               | 26                   | 1.2                    | 12                  | 4.3            |

2.2 Calculation of the average pore width of sample

Taking sample 2 as an example, the BMP images of nanofibers were grayed successively, and the gray-value matrix was obtained by Matlab. We adopted the idea of Ting Wang and Ying Chen [13], and use 85% of the average gray value as the threshold value to transform the gray matrix into a 0-1 matrix, the number of 1 or -1 obtained by subtracting adjacent elements in each row of the 0-1 matrix, namely the number of pore or fibers in the row. Then, divide by the total length of the fiber pore (the sum of all zeroes for each row in the 0-1 matrix) to get the width of the average pore, or the average pore for short. Average the pore width of each
row to get the average pore of the sample. Because of too much data, the average pore data of each sample was obtained by taking one data every five. After obtaining the average pore data, multiply it by $e^{1.6a}$, where $a=2.5029078750...$ (Feigenbaum's constant [13]):

![Fig. 2. The average pore distribution of sample 2](image)

It is called the relative average pore distribution. The same method can be used to obtain the relative average pore distribution of other samples.

### 3 The Correlation Fractal Dimension Calculation of Samples

Using the relative average pore width sequence of each sample, Matlab [11,12] was used to calculate the correlation fractal dimension of the average pore width. Set M as 5, 10, 15, 20, 25, 30, 35, 40, and then observe the double log curves of its operation to determine the appropriate M value according to the curve characteristics. The appropriate interval is selected according to the criterion of long linear interval and good linearity, and the correlation fractal dimension is obtained by linear fitting on this interval. The double log curves of sample 2 are shown in Fig. 3.

![Fig. 3. Double log graphs corresponding to different M values](image)

It can be seen from Fig. 2 that when M=40, the collinearity of the curve is good and the collinearity range is longer. The interval [ln244, ln304] with good linearity corresponding to M=40 is selected for linear fitting to obtain the correlation fractal dimension of the sample. The double log curves of sample 2 are shown in Fig. 4.
The correlation fractal dimension is $D = 1.442937449$, the correlation coefficient is $R = 0.991458805$, and F test is $F = 6848.69888$. 

Table 2. Correlation fractal dimension of average pore distribution of 30 samples

| No. | Correlation dimension | Intercept of fitting line | Correlation coefficient | F test | Left end point of collinear interval | Right end point of collinear interval | M-value |
|-----|-----------------------|---------------------------|-------------------------|--------|--------------------------------------|----------------------------------------|---------|
| 1   | 1.495840727           | -8.641611365              | 0.947164025             | 448.1624686 | 304                                   | 330                                    | 35       |
| 2   | 1.442937449           | -8.204860069              | 0.991458805             | 6848.69888 | 244                                   | 304                                    | 40       |
| 3   | 1.537743878           | -8.675917722              | 0.974328110             | 1935.608702 | 232                                   | 284                                    | 30       |
| 4   | 1.46214790             | -8.112467211              | 0.946991332             | 357.2967875 | 244                                   | 265                                    | 35       |
| 5   | 1.624468238           | -8.987105480              | 0.976523379             | 4034.770128 | 347                                   | 445                                    | 20       |
| 6   | 1.555059522           | -11.26135497              | 0.992443985             | 111117.7883 | 492                                   | 1339                                  | 15       |
| 7   | 1.234365431           | -7.884254344              | 0.980479020             | 5424.509249 | 492                                   | 601                                    | 15       |
| 8   | 1.604770633           | -9.592653776              | 0.969725871             | 2306.26822 | 330                                   | 403                                    | 15       |
| 9   | 1.712486420           | -9.550290523              | 0.962615626             | 643.7286148 | 244                                   | 270                                    | 25       |
| 10  | 1.722798614           | -8.969877712              | 0.960642619             | 1171.593343 | 265                                   | 314                                    | 15       |
| 11  | 1.4619181645          | -9.091258849              | 0.985621047             | 6717.517291 | 284                                   | 383                                    | 30       |
| 12  | 1.450061511           | -8.619830077              | 0.961193321             | 2922.713716 | 284                                   | 403                                    | 20       |
| 13  | 1.397007462           | -8.090111174              | 0.960572695             | 1437.424874 | 270                                   | 330                                    | 25       |
| 14  | 1.651033607           | -9.745852433              | 0.976978755             | 3607.241671 | 244                                   | 330                                    | 20       |
| 15  | 1.472982426           | -8.641505401              | 0.971618558             | 3663.069283 | 257                                   | 365                                    | 15       |
| 16  | 1.133025970           | -6.45224860               | 0.941297660             | 513.123125  | 278                                   | 311                                    | 35       |
| 17  | 1.532052129           | -8.812485762              | 0.983796959             | 1275.053063 | 270                                   | 292                                    | 35       |
| 18  | 1.497045485           | -9.193017337              | 0.96881497              | 1217.313227 | 424                                   | 468                                    | 20       |
| 19  | 1.580897087           | -8.883748333              | 0.953541089             | 697.8294809 | 249                                   | 284                                    | 30       |
| 20  | 1.582398585           | -8.878926682              | 0.967175600             | 589.3028510 | 257                                   | 278                                    | 35       |
| 21  | 1.477796157           | -9.236937260              | 0.985808347             | 11808.87302 | 347                                   | 518                                    | 15       |
| 22  | 1.326070403           | -8.105746417              | 0.969056902             | 3037.786409 | 347                                   | 445                                    | 20       |
| 23  | 1.495447966           | -9.563095416              | 0.975193786             | 14388.36778 | 298                                   | 665                                    | 20       |
| 24  | 1.523309022           | -9.467649122              | 0.962211726             | 5423.669318 | 330                                   | 544                                    | 20       |
| 25  | 1.749428379           | -10.28484146              | 0.993132651             | 7375.44675  | 278                                   | 330                                    | 15       |
| 26  | 1.553981755           | -9.179152179              | 0.978150032             | 4208.065819 | 270                                   | 365                                    | 15       |
| 27  | 1.443057877           | -8.778185238              | 0.96190023              | 1918.762876 | 347                                   | 424                                    | 40       |
| 28  | 1.587684342           | -9.052362086              | 0.958611479             | 990.3039788 | 257                                   | 304                                    | 25       |
| 29  | 1.680042749           | -10.49292150              | 0.985090888             | 11695.86116 | 365                                   | 544                                    | 35       |
| 30  | 1.357785562           | -8.788310245              | 0.987431935             | 32919.46721 | 181                                   | 601                                    | 5        |
After the other samples are treated in the same way, we can obtain their correlation dimension, intercept of fitting line, correlation coefficient, F test and other data. The calculation results of the fractal dimension of the average pore of other samples are shown in Table 2.

4 Conclusion

In this paper, the correlation fractal dimension was selected as a tool to analyze the chaotic and disordered pore distribution of electrospun nanofiber membrane. The relationship between the correlation fractal dimension of the average pore width of samples and its resistance [13,14] is shown in Table 3.

Table 3. Relationship between correlation fractal dimension and air flow resistance of samples

| Source of variance | Sum of square | Degrees of freedom | Square | F       | Conspicuousness |
|--------------------|--------------|--------------------|--------|---------|-----------------|
| Regression         | SSR          | 2                  | SSR/2  | 15.79591077 | Extremely significant |
| Residual           | SSE          | 27                 | SSE/27 | 108.92559   | 5.74704825 |
| Sum                | Lxx          | 29                 |        |          |                 |

Matlab was used to fit Table 3, and the correlation fractal dimension of the average pore width of the sample has a quadratic function relation with its resistance, that is,

\[ y = -0.00076226660605591x^2 + 0.0288271256410095x + 1.3232485018709. \]  

(Where y is the correlation fractal dimension and x is the air flow resistance)

F test: After looking up the table, F_{0.99}(2,27)= 6.48851, F-test value: F=15.7959107696337, indicating an extremely significant relationship in Table 4.

Table 4. F checklist

| Source of variance | Sum of square | Degrees of freedom | Square | F       | Conspicuousness |
|--------------------|--------------|--------------------|--------|---------|-----------------|
| Regression         | SSR          | 2                  | SSR/2  | 15.79591077 | Extremely significant |
| Residual           | SSE          | 27                 | SSE/27 | 108.92559   | 5.74704825 |
| Sum                | Lxx          | 29                 |        |          |                 |

The fitting effect is shown in Fig. 5.
Therefore, the relationship between the fractal properties of the average pore width of electrospun nanofiber membrane and the air flow resistance is a quadratic function, and the correlation is significant. It can be seen from the relation diagram of correlation dimension and resistance that when the fractal dimension is about 19pa, the fractal dimension reaches the maximum. A new way to explore electrospun nanofiber membrane was established.

5 A Little Though

In this paper, We used the average pore width value as the basis to calculate the fractal. However, the results obtained were surprisingly consistent with the results of Ting Wang, Ying Chen etc.[13] under the meaning of the relative error less than 10%, as shown in Table 5.

The fractal dimension of the average pore width obtained is consistent with the fractal dimension of porosity obtained by Ting Wang etc.[13] under the meaning of the relative error less than 10%, this shows that it is reasonable to discuss the correlation fractal dimension.

Table 5. Comparison with fractal dimensions in [13] paper

| No. | Average pore width dimensions | Porosity dimension | Relative error |
|-----|-------------------------------|--------------------|---------------|
| 1   | 1.495841                      | 1.56139686         | 0.0438256     |
| 2   | 1.442937                      | 1.38839672         | 0.0377984     |
| 3   | 1.537744                      | 1.44812325         | 0.0582806     |
| 4   | 1.462115                      | 1.43159072         | 0.0208767     |
| 5   | 1.624468                      | 1.48468356         | 0.0860495     |
| 6   | 1.55506                       | 1.58022408         | 0.0161824     |
| 7   | 1.234365                      | 1.3369629          | 0.0831176     |
| 8   | 1.604771                      | 1.55601202         | 0.0303835     |
| 9   | 1.712486                      | 1.6217215          | 0.0530018     |
| 10  | 1.722799                      | 1.69049555         | 0.0187503     |
| 11  | 1.461982                      | 1.39038706         | 0.0489709     |
| 12  | 1.450062                      | 1.43218884         | 0.0123255     |
| 13  | 1.397007                      | 1.3597149          | 0.0265109     |
| 14  | 1.651034                      | 1.61659512         | 0.0208587     |
| 15  | 1.472982                      | 1.35311754         | 0.0813756     |
| 16  | 1.133026                      | 1.02169            | 0.098264      |
| 17  | 1.532052                      | 1.500271           | 0.020744      |
| 18  | 1.497045                      | 1.440925           | 0.037487      |
| No. | Average pore width dimensions | Porosity dimension | Relative error |
|-----|-------------------------------|--------------------|---------------|
| 19  | 1.580897                      | 1.544863           | 0.022794      |
| 20  | 1.582399                      | 1.509439           | 0.046107      |
| 21  | 1.477796                      | 1.39264            | 0.057623      |
| 22  | 1.326607                      | 1.322473           | 0.003116      |
| 23  | 1.495448                      | 1.412103           | 0.055732      |
| 24  | 1.523301                      | 1.559902           | 0.024028      |
| 25  | 1.749428                      | 1.662555           | 0.049658      |
| 26  | 1.553982                      | 1.41934            | 0.086643      |
| 27  | 1.443058                      | 1.557588           | 0.079366      |
| 28  | 1.587684                      | 1.447892           | 0.088048      |
| 29  | 1.680043                      | 1.59986            | 0.047727      |
| 30  | 1.357786                      | 1.428429           | 0.052028      |

**Competing Interests**

Authors have declared that no competing interests exist.

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