



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 of electrospun nanofiber membrane has a quadratic function relation with the air flow resistance; 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.

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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, electrospon nanofiber membrane is thinner and it can reach the nanometer level. As a result, the application of electrospon 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

$$\{x_k: k = 1, 2, \dots, N\}, \tag{1}$$

convert to M dimensional Euclidean space, as follows:

$$X_{(M,r)} = \{x_n, x_{n+\tau}, \dots, x_{n+(M-1)\tau}, n = 1, 2, \dots, N\} \tag{2}$$

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

$$C_M(r) = \frac{1}{N(N-1)} \sum_{i \neq j} \theta(r - |X_i - X_j|) \tag{3}$$

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

$$H(x) = \begin{cases} 1, & x > 0 \\ 0, & x \leq 0 \end{cases} \tag{4}$$

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 :

$$D(M, r) = \frac{d \ln C_M(r)}{d \ln r} \tag{5}$$

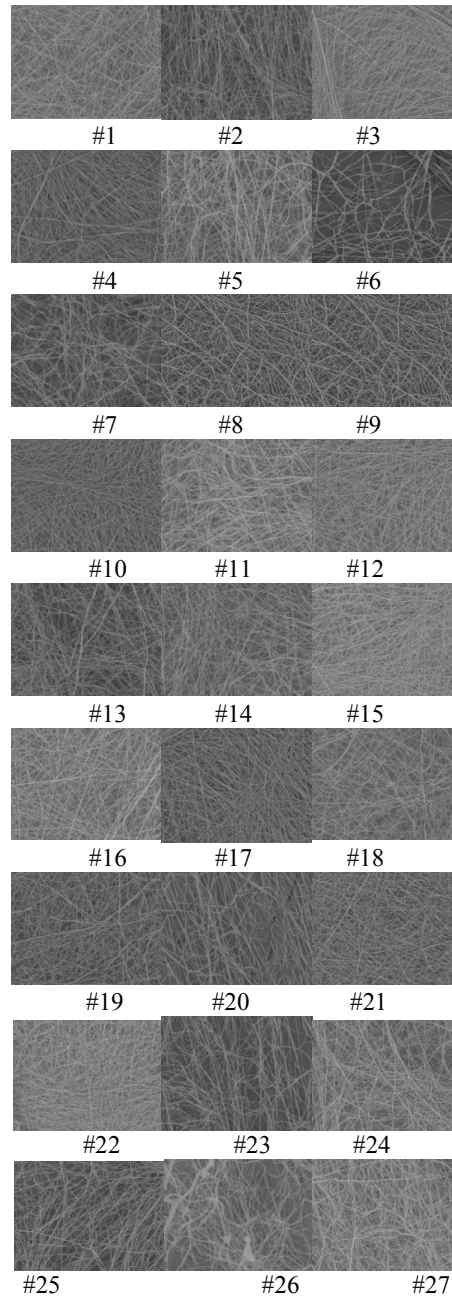
By selecting the appropriate M , the correlation fractal dimension can be obtained [9-10] : When the double log curve $\ln C_M(r) - \ln r$ is nearly linear, the sample is considered to have a fractal structure, and the slope of the line corresponding to the linear interval is D , namely the correlation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



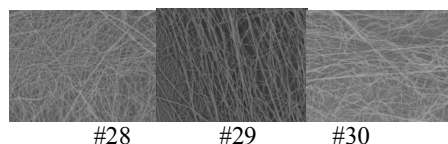


Fig. 1. Bmp images of 30 samples

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	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 $e^{1.6\alpha}$, where $\alpha=2.5029078750\dots$ (Feigenbaum's constant [13]):

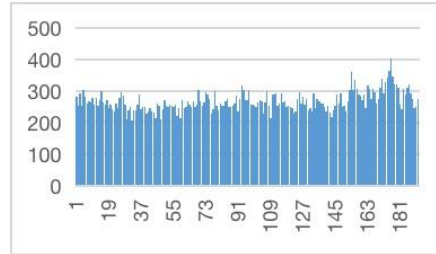


Fig. 2. The average pore distribution of sample 2

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.

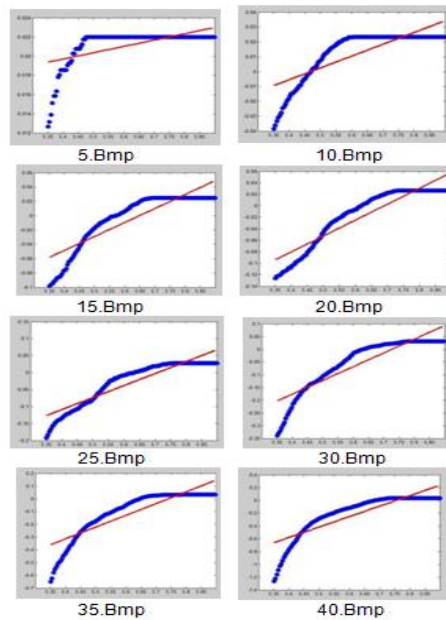


Fig. 3. Double log graphs corresponding to different M values

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 $[\ln 244, \ln 304]$ 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.

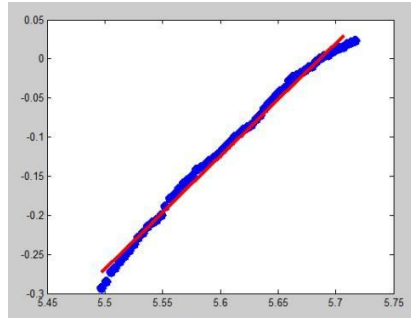


Fig. 4. Double log curves for sample 2 corresponding to M=40

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	1.462114790	-8.112467211	0.946991332	357.2967875	244	265	35
5	1.624468238	-9.897105480	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	-9.869877712	0.960642619	1171.593343	265	314	15
11	1.461981645	-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	3607.241617	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	0.965881497	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	1.326607043	-8.105746417	0.969056902	3037.786409	347	445	20
23	1.495447966	-9.563095416	0.975193786	14388.36778	298	665	20
24	1.523300922	-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	-9.052362686	0.955611479	990.3039788	257	304	25
29	1.680042749	-10.49292150	0.985009088	11695.86116	365	544	35
30	1.357785562	-8.788310245	0.987431935	32919.46721	181	601	5

The correlation fractal dimension is $T=1.442937449$, the correlation coefficient is $R=0.991458805$, and F test is $F=6848.69888$.

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

1	11.1	1.4958407270	16	43.1	1.1330259740
2	22.1	1.4429374490	17	8.5	1.5320521290
3	21	1.5377438780	18	4.9	1.4970454853
4	11.1	1.4621147902	19	30.1	1.5808970877
5	8.9	1.6244682380	20	29	1.5823985850
6	6.1	1.5550595228	21	7	1.4777961576
7	11.5	1.2343654310	22	5.8	1.3266070436
8	19.3	1.6047706330	23	7.3	1.4954479666
9	15.6	1.7124864202	24	9	1.5233009227
10	19.8	1.7227986140	25	15.7	1.7494283790
11	9	1.4619816459	26	9.9	1.5539817552
12	8.1	1.4500615110	27	25.9	1.4430578779
13	31.2	1.3970074620	28	8	1.5876843423
14	27.5	1.6510336070	29	5.7	1.6800427490
15	9	1.4729824267	30	4.3	1.3577855620

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,

$$y = -0.000762226660605591x^2 + 0.0288271256410095x + 1.3232485018709. \tag{6}$$

(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		
Sum	Lxx	29			

The fitting effect is shown in Fig. 5:

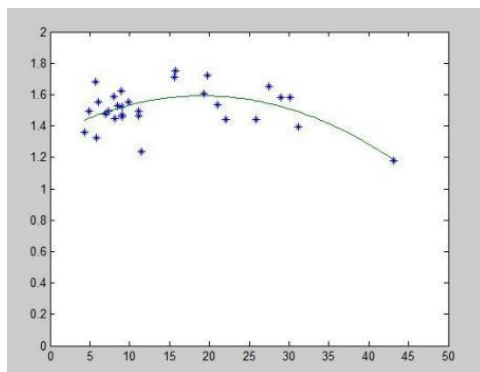


Fig. 5. Air flow resistance and correlation dimension

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	1.35997149	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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