A SIMPLE AND PRECISE METHOD TO SIMULTANEOUSLY DETERMINE THE STRUCTURAL PARAMETERS OF NANOFIBROUS MATERIALS

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Abstract

It is necessary to precisely determine the structural parameters (i.e., porosity, thickness and fiber diameter) of nanofibrous materials. However, the currently used direct methods are either complicated or inaccurate. One of the indirect methods, inverse characterization, is the alternative to obtaining the structural parameters. The inverse characterization based on the airflow penetration behavior of nanofibrous materials is implemented in this work. The Kozeny-type and Ergun-type equations are selected as the models involved in the inverse characterization. An open-source MATLAB-based app is used to carry out the inverse characterization. The results show that the Kozeny-type equation is feasible for nanofibrous materials, and the results are more accurate compared with the values obtained with the help of the Ergun-type equation. The findings indicate that the airflow method is suitable for nanofibrous materials.

Keywords: *nanofibrous materials, inverse characterization, structural parameters, airflow*

1. INTRODUCTION

Nanofibrous materials have been extensively used for various applications in medicine, engineering, environment, and many other fields [1–6]. It is obvious that their structural parameters have a significant influence on the final properties. Thus, it is essential and meaningful to characterize the nanofibrous materials' structural parameters (i.e., thickness, porosity and fiber diameter). There are some widely used methods to directly determine these parameters [7]. For instance, the porosity of nanofibrous materials can be determined by the gas sorption and liquid intrusion methods [8]. Besides, the porosity can be obtained by applying the equation of $\phi = 1 - \rho/\rho_f$, where ρ_f is the fiber density, and ρ is the bulk density of the material [9]. The morphological methods are feasible to determine the fiber diameter and its' distribution, such as micro-CT (Micro Computed Tomography) and SEM (Scanning Electron Microscope) [10]. However, it is tricky to directly measure the thickness of nanofibrous materials due to the thin structure (e.g., < 0.05 mm). It is not easy to control the compression load to avoid a thickness decrease occurring in the thickness measurement by means of a vainer caliper. A common and relatively precise method is to use liquid nitrogen to treat nanomembranes to remain stable state during the preparation phase, and the thickness from SEM images was subsequently measured [5].

Except for the above-mentioned direct characterization method, indirect methods are alternatives to determine the structural parameters. Inverse characterization is one of the most popularly studied indirect methods. Inverse characterization estimates the structural parameters based on the acoustic properties or airflow penetration behavior by solving the inverse problems via the probabilistic or least-squares approaches [10]. The acoustical inverse method is able to estimate the fiber diameter, porosity, bulk density, tortuosity, viscous and thermal characteristic lengths [11,12]. In the inversion characterization process, model predictions initially fit measurements. Subsequently, the parameters that best describe the material will be found. A number of models applied to predict impedance and sound absorption of porous materials have been reported. Part of them is empirical models, which are widely

adopted to predict the acoustic properties of fibrous material. The empirical models are developed by regression methods based on a large number of experimental data from impedance and airflow resistivity measurements [13]. The semi-phenomenological models consider the frame of porous material as rigid. They are very useful and robust for sound propagation modeling in porous media. These models use four to eight non-acoustical parameters (e.g., porosity, tortuosity, airflow resistivity, viscous and thermal characteristic lengths) to calculate the dynamic density and dynamic bulk modulus. Consequently, the surface impedance and sound absorption coefficient are rapidly calculated. The application of the particle swarm optimization method on Johnson-Champoux-Allard and Garai models for porosity, tortuosity, airflow resistivity, thermal and viscous characteristic lengths estimation of jute fiber material has been reported [14]. An inverse numerical method was applied to deduce the basic characteristics of kenaf and polyester materials [15]. The most significant advantage of the indirect acoustical method is that it is able to simultaneously estimate several structural parameters. One of the main shortcomings of the acoustical method is that a specific device is required, i.e., an impedance tube. Moreover, it is not applicable to inversely characterize the structural parameter of nanofibrous materials since the acoustic properties (e.g., transmission coefficient and absorption coefficient) are complicated to be precisely measured in the impedance tube. In addition, the inversed porosity from the acoustical method is relatively inaccurate [10].

It is well-known that the pressure drop between two sides of fibrous materials is related to the airflow velocity when the airflow goes through the material. And the relationship of pressure drop-airflow velocity depends on the materials' thickness, porosity and fiber diameter as well as the velocity of the airflow. The device based on the airflow method to measure fiber fineness (or diameter) has been commercially used for a long time [16,17], but this device is mainly used to get the micronaire value of cotton fibers and the fineness of wool fibers. Theoretically, it is possible to use the airflow method to characterize the structural parameters of nanofibrous materials by solving the inverse problem. Furthermore, the airflow penetration behavior of fibrous materials is much easier to be measured compared to the acoustic properties [18]. To the best knowledge of the authors, there has been little discussion about using the airflow method to simultaneously determine the structural parameters. Hence, we used the inverse characterization method to obtain the structural parameters of three nanofibrous samples based on their airflow penetration behavior. The inversely determining porosity, fiber diameter and thickness were compared with the directly measured values.

2. MATERIALS AND METHODS

2.1. Materials

Three nanofibrous materials with different fiber diameters, porosity and thickness were selected to carry out this study. The PVDF, PU and PA 4/6 nanofibrous membranes (samples J, K and L) were made by the electrospinning technique. The characteristics of the samples are demonstrated in Table 1.

Materials	Areal density (g/m^2)	Thickness (mm)	Bulk density (kg/m^3)	Porosity (%)	Average fiber diameter (μm)
PVDF Nanomembrane	5.93	0.022 ± 0.005	272.09	84.45	0.250 ± 0.068
PU Nanomembrane	30.91	0.134 ± 0.009	231.03	80.75	0.255 ± 0.072
PA 4/6 Nanomembrane	8.04	0.050 ± 0.013	159.32	86.50	0.374 ± 0.079

Table 1. The characteristics of the nanofibrous samples

PVDF: polyvinylidene fluoride, PU: polyurethane, PA 4/6: polyamide 46.

A square size specimen of each sample was cut into the size of 10 by 10 cm. Then the weight was measured on the digital balance. The areal density was subsequently obtained according to $\rho_{areal} = w/s$, where w is the weight of the specimen, and s is the sample area which is 100 cm^2. A thickness gauge (SOMET CZ sro, Bílina, Czech Republic) was used to measure the thickness of nanofibrous samples. A flat plastic film was placed between the test head and samples to avoid compression on the samples. The ImageJ software was subsequently used to read the dial for a result. Each sample has been measured ten times. As mentioned above, the porosity is obtained according to $\phi = 1 - \rho/\rho_f$. The fabric bulk density is easily obtained via dividing areal density by thickness. The samples' fiber density is obtained in the literature [19–21]. The Scanning Electron Microscope (SEM) was applied to get the microscopic images of the samples at the Technical University of Liberec, Czech Republic. A MATLAB-based image analysis tool, called SIMPoly, was used to semi-automatically get the fiber diameter and its standard deviation [22].

2.2. Methods

2.2.1. Determination of airflow-penetration behavior of nanofibrous materials

The airflow velocities under the 21 different pressure drops were measured on FX 3300 Textech Air Permeability Tester III at the Technical University of Liberec, and the test was conducted ten times for each pressure drop to ensure the reproducibility. The airflow velocity measuring range of the FX 3300 is 1 to 10000 mm/s. Owing to the results being inaccurate if the airflow velocity is too low (i.e., < 1 mm/s), the given pressure drop for nanofibrous samples ranges from 100 to 500 Pascal to ensure the accuracy of airflow velocity.

2.2.2. Models used in the inverse characterization

Two common models are selected to solve the inverse problem, which are the Kozeny and the Ergun equations [23,24]. These equations were initially developed for the media composed of sphere particles, the derivation of them was proposed to suit fibrous materials via changing the expression of particle diameter:

$$\Delta p = A\frac{(1-\phi)^2}{\phi^3}\frac{\eta h u}{(1.5d)^2}, \quad (1)$$

$$\Delta p = B\frac{(1-\phi)^2}{\phi^3}\frac{\eta h u}{(1.5d)^2} + C\frac{(1-\phi)}{\phi^3}\frac{\rho_{air} h u^2}{1.5d}, \quad (2)$$

where Eq. (1) is the Kozeny-type equation, and Eq. (2) is the Ergun-type equation, Δp is the pressure drop between two sides of the fibrous media, h is the media thickness, ϕ is the porosity of the media, η is the dynamic viscosity of the fluid which is airflow viscosity in the present study, u is flow velocity, d is the average fiber diameter, A is the Blake–Kozeny–Carman constant, B and C are respectively the coefficients of viscous effect and inertial effect in the Ergun-type equation.

2.2.3. Inverse characterization method

The general inverse determination procedure is shown in Fig. 1. In the inverse characterization method, the unknown structural parameters are assumed as random variables distributed according to the distribution based on the existing knowledge and the experience. Consequently, estimation of parameters can be obtained by using the optimization method in Matlab. The porosity, fiber diameter and thickness of fibrous materials are obtained by finding the minimum of the following equation:

$$f(x) = \sum_{i=1}^{n}\left(\Delta p_{Ergun} - \Delta p_{given}\right)^2, \quad (3)$$

where Δp_{Ergun} is the calculated pressure drop based on Eq. (1) or Eq. (2), and Δp_{given} is the given pressure drop during the airflow velocity characterization test.

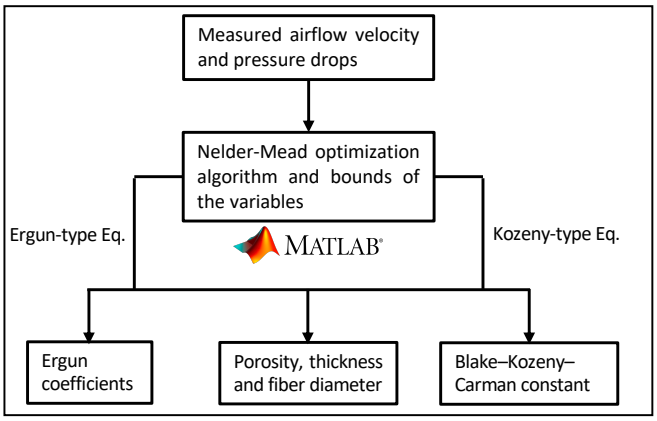


Fig. 1. Inverse characterization procedure of structural parameters determination of nanofibrous materials.

Besides, one MATLAB-based app, called AFDeter, was developed via APP Designer in MATLAB (Mathworks Inc.) to simply run and quickly get the structural parameter of both conventional fibrous materials and nanofibrous materials. The installation package of AFDeter is available on the GitHub website [25], a demo video of this app also can be found in the same repository. The screenshot of AFDeter's main interface with an illustrative example is demonstrated in Fig. 2.

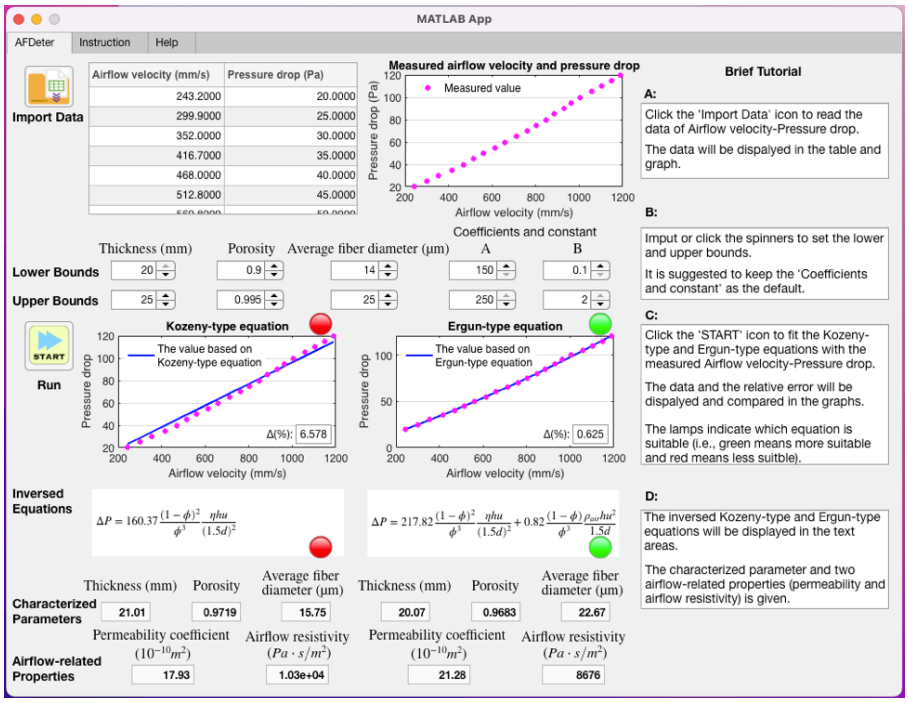


Fig. 2. The main interface of AFDeter and the illustrative example.

3. RESULTS

By means of the optimization algorithm, the coefficients of the Ergun-type equation and modified Blake–Kozeny–Carman constant of the Kozeny-type equation are obtained (see Table 2). The inversely obtained coefficients of the equations are different from the original values. This is because the shape of fibers is more like cylinders instead of the sphere shape. It indicates that the coefficients and the constant for every specific nanofibrous sample may need to be determined for accurate prediction.

Coefficients	PVDF Nanomembrane	PU Nanomembrane	PA 4/6 Nanomembrane
A	150.56	158.23	205.60
B	203.02	169.53	152.75
C	0.26	0.10	0.20

Table 2. The coefficients of the Kozeny-type and Ergun-type equations

The comparisons between the given pressure drops and the values from the Ergun-type and Kozeny-type equations, referred to as predicted values, are demonstrated in Fig. 3. It is found that both Ergun-type and Kozeny-type equations showed excellent predictions for nanofibrous samples. This is due to the high flexibility of the Ergun-type equation and the relatively low airflow velocity (i.e., 2 – 22 mm/s under 100 - 500 Pa pressure drop). The findings indicate that when the airflow velocity is relatively low (e.g., < ~400 mm/s), Ergun-type and Kozeny-type equations are suitable for pressure drop prediction for nanofibrous materials.

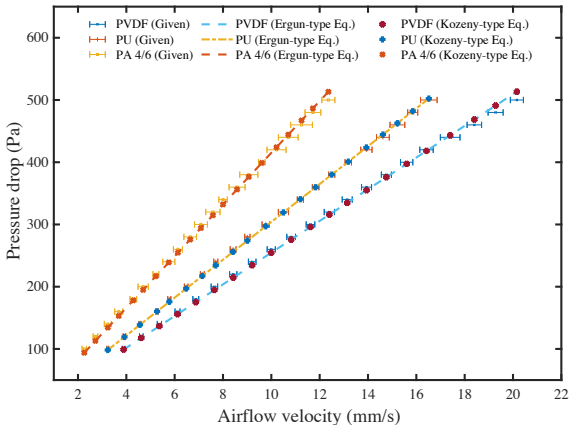


Fig. 3. Performance of the Kozeny-type and Ergun-type equations.

The screenshots of the AFDeter app for nanofibrous samples are illustrated in Fig. 4. It takes less than one minute to process one set of data if the data is valid. Warning messages will be given if the imported data contains a negative or zero value or the size of pressure drop and airflow velocity is unequal. The lamps are used to indicate the suitable equation and corresponding results, 'green' means more suitable while 'red' means unsuitable. In the app, the inversed equations, the inversed parameters and the comparison between given and predicted pressure drops are displayed.

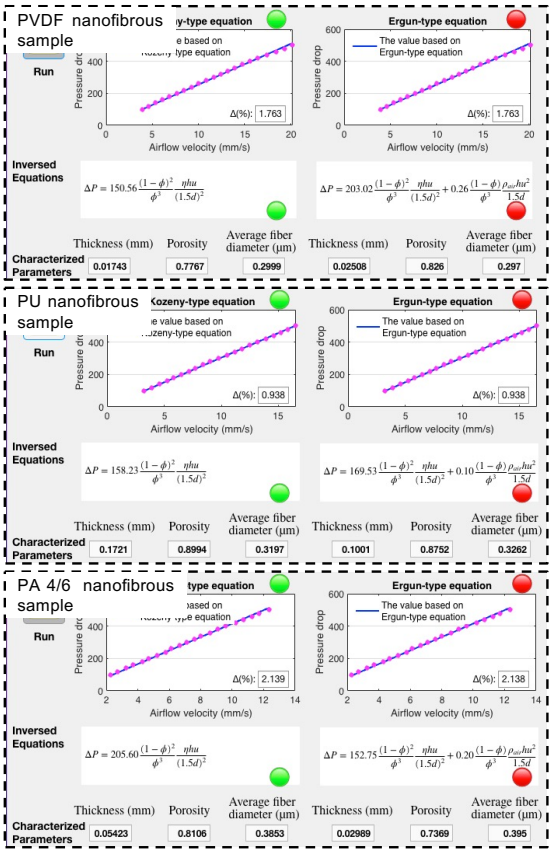


Fig. 4. The screenshots of the AFDeter app for inverse characterization of nanofibrous materials.

The inversely determined thickness, porosity and average fiber diameter are compared with the measured values in Fig. 5.

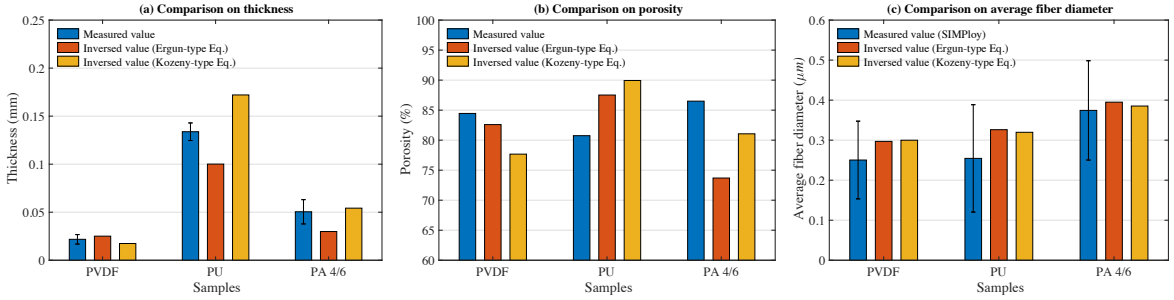


Fig. 5. Comparison of the inversely determined thickness, porosity, average fiber diameter and the measured values.

4. DISCUSSION

It is considered that the Kozeny-type equation is more feasible for nanofibrous materials compared with the Ergun-type equation, since in the former equation, the pressure drop is linearly related to the airflow velocity (see Eq. (1)) and they are quadratically related in the latter one, and the airflow velocity of nanofibrous samples are relatively low (i.e., < ~20 mm/s) (see Fig. 3). In Fig. 5, it can be seen that the difference between the Ergun-type equation and the Kozeny-type equation on thickness is more significant compared with porosity and average fiber diameter. The Kozeny-type equation has better

thickness determination on thickness compared to the Ergun-type equation. For the average fiber diameter, the Kozeny-type equation is more reliable. Although the Ergun-type equation has better performance for the PVDF and PU nanofibrous samples on porosity characterization compared with the Kozeny-type equation, the relative difference is not significant between these two equations. For example, the relative difference of the Ergun-type equation on porosity ranges from 2.2 % to 14.8 %, while it ranges from 6.29 % to 11.38 % for the Kozeny-type equation. In summary, it can be stated that the Kozeny-type equation is more suitable for structural parameters characterization for the nanofibrous samples.

5. CONCLUSIONS

This work studied the application of inverse characterization on nanofibrous materials based on their airflow penetration behavior. The FX 3300 Air Permeability Tester III was used to measure the velocity of airflow penetrating the nanofibrous samples under the pressured drop in a certain range (i.e., 100 – 500 Pa). The Ergun-type equation and the Kozeny-type equation were applied to compare the experimental airflow velocity-pressure drop relationship. The optimization method was conducted in a MATLAB-based app to inversely determine the structural parameters, the coefficients of the Ergun-type equation and the Kozeny-type equation. This study shows that the Kozeny-type equation is more feasible for nanofibrous materials compared with the Ergun-type equation. The Kozeny-type equation is able to accurately characterize the nanofibrous materials. Considering the uncertainties during the direct measurements, it can be stated that the inverse characterization method on nanofibrous materials based on their air penetration behavior is feasible. The MATLAB-based app (i.e., AFDeter) is convenient and easy to operate for the characterization of nanofibrous materials.

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