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Gas transport properties of electrospun polymer nanofibers

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Although the basic principles of gas flow through unidirectional fibers have been widely studied and well understood since the 1950s, questions arise when these principles are applied to electrospun polymer nanofibers. Classic theories based on orderly packed coarse fibers are inadequate in accounting for the influences of random fiber distribution and slip flow. In this work, a mechanistic model in terms of fiber volume fraction and fiber radius is presented to determine the through-plane permeability of electrospun nanofiber layers. The fibrous system is subdivided into a series of cells of orthogonal fibers with random volumes. A single factor is proposed to quantify the effect of randomness of fiber distribution on flow behaviors. When the fiber radius is comparable with the mean free path of air molecules, the slip flows in the nanoscale fibrous media are particularly explored. The solutions obtained are successfully validated through comparison with experimental and numerical results. It is demonstrated that the through-plane permeability of electrospun nanofibers is enhanced by the slip effect and randomly distributed fibers are more permeable than ordered structures.

1. Introduction

From particle filtration in air filters to the breathable property of protective clothing, through-plane flow past electrospun polymer layers is an essential phenomenon that has wide applications in scientific and industrial environments [1–12]. The unique nature of electrospun polymer fibers, including their much smaller fiber radius (normally in the 20–1000 nm range) and increased specific surface area, is accessible compared with currently commercial fibers [4]. One of the most important parameters for measuring the flow resistance or the species separation efficiency involved in those applications is permeability, which has been extensively explored over several decades. However, most classic models [13–17], cannot be directly applied to determine the permeability of electrospun fibrous mats. The assumption of the fibrous media as homogeneous, with orderly fiber alignments, appears widely in these models, but available electrospun nanofibers are always disorderedly and randomly distributed [9]. This variation can result in the predicted permeability differing from that in reality. Furthermore, the permeability of electrospun nanofibers is underestimated by existing models that generally assume a no-slip flow condition at the fiber surface, which is inaccurate when the fiber size is comparable with the mean free path of air molecules λ (e.g., $\lambda = 65$ nm for air in normal temperature and pressure) [18]. In fact, only the minorities of the air molecules near nanofibers collide with the fiber surface, while the rest of the molecules without contacting the nanofibers continue their principal flow motion with a slip velocity.

Among the efforts to model laminar gas flow through fibrous porous media, Darcy's law is the best-known equation, which linearly relates the volume-averaged velocity with the pressure gradient [19]:

$$\langle u \rangle = -\frac{K}{\eta}\nabla p, \tag{1}$$

where K is the permeability tensor of the medium, η is the fluid viscosity, ∇p is the pressure gradient and u is the flow velocity. The permeability tensor K lumps all the complex interactions between fluid flows and solid fibers. Darcy's law is generally valid for flow in the continuum region with pore size much larger than λ. As well, Darcy's law can be applied in the slip and transition regimes with Klinkenberg or Knudsen's correction when the pore size is comparable with λ [20]. However, Darcy's law does not work with the pore size much smaller than λ, as gas molecules flow with minimal interaction with neighboring molecules and the continuum

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assumption breaks down [20]. In this article, Darcy's law is employed to characterize the flow behavior in electrospun nanofiber mats, since the minimum fiber radius considered is comparable to λ.

Based on Darcy's law, Gibson et al. [4,21] measured the permeability to convective gas flow of electrospun nanofibers in terms of an apparent flow resistance with an automated dynamic moisture permeation cell. They found that the flow resistances of PAN and PBI electrospun nanofibers are around 3×10^8 m^{-1} and 3×10^9 m^{-1}, respectively [4,21]. Recently, Tsai and Kornev [22] developed a new characterization technique to determine the permeability of electrospun yarns using capillary liquids on complex conduits composed of yarn-in-a tube pairs.

In the context of permeability prediction, limited flow within a unit cell has been widely used to determine the flow behavior of circular fibers in a square array proper boundary conditions defined, exact solutions of permeability are available by solving Stokes equation [13–17,23], viz.,

$$-\nabla p + \eta \nabla^2 u = 0. \tag{2}$$

Here, Stokes equation is a linearized form of the Navier–Stokes equations in the limit of small Reynolds number, when the inertial forces and the applied body forces are assumed to be negligible.

However, electrospun fibrous media are composed of fibers randomly located in horizontal planes (Fig. 1) and the above models based on ordered arrangements of fibers cannot provide accurate predictions of through-plane permeability. There have been several pioneering studies on gas flow in disordered fibrous media. In 2002, a statistical permeability model, based on the fractal (self-similar) characteristics of pores in random fibrous media, was presented in terms of the pore area fractal dimension and architectural parameters of the fibrous preform [24]. In 2006, Sobera and Kleijn [25] proposed a semi-analytical model of through-plane permeability as a function of the minimum inter-fiber distance, based upon the fact that most of the flow contribution or the pressure drop exists in the narrow slots formed between fibers. To characterize the randomness realization of fiber distribution, they proposed a dimensionless parameter as the ratio of the standard deviation to the mean value of the inter-fiber distance [25]. The parameter is zero for ordered arrays, and increases to unit for randomly located fibers with increasing permeability. Later, Hosseini and Tafreshi [18] numerically mimicked the microstructures of randomly layered electrospun nanofibers by a μ-randomness algorithm. Slip flow was particularly considered to occur at the fiber surface of generated electrospun nanofibers and a higher permeability was found, as compared to that predicted by classical models of ordered fibers [18]. Later, the ordered model of Kuwabara [13] was extended to predict the through-plane permeability of fibrous media based on random arrangements of cells composed of aligned fibers [26]. However, the correlation between randomness and permeability was not quantified, and the influence of slip flow on permeability has not been quantitatively realized and validated by experiments. Recently, Zheng et al. [27] analyzed the slip influence on permeability of porous media based on the fractal approach. They observed that the ratio of permeabilities with and without slip effect increases with porosity and the pore fractal dimension, but it decreases with the increase in the tortuosity fractal dimension [27].

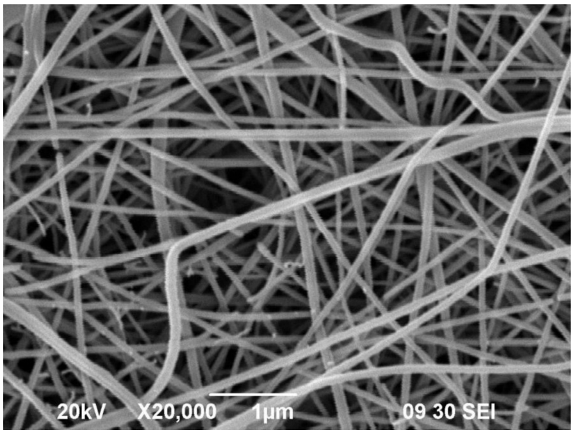

Fig. 1. An example of an electrospun fibrous mat.

From above discussions, it is clear that most theoretical models are established on the basis of parallel fibers. In a typical electrospun fibrous layer, however, the fibers are cross-wise located (Fig. 1). The current numerical simulations reveal that the in-plane fiber orientation has statistically negligible effect on the through-plane permeability [28]. This might be ascribed to that the fiber crosses in the medium cause an increase in flow resistance, whereas the enlarged pores between crossing fibers reduce the flow resistance; both mechanisms superimposed with each other lead to a close through-plane permeability between fiber alignments and crossing fibers. It is noted that the flow streams must be different between aligned and orthogonal fibers, though their permeabilities are close to each other.

Besides the experimental characterizations of transport properties for electrospun nanofibers [4,21,22], less studies have been carried out to theoretically predict the permeability. Therefore, there is a need of mechanistic model that can accurately determine the through-plane permeability of an electrospun polymer nanofiber layer as a function of randomness of fiber distribution and nanoscale influence, considering the above reviews. This study chooses a new representative cell of orthogonal fibers as the basic element to better characterize microstructures of the fibrous layer. The cells with random size and distribution will be used to simulate the real architectures of electrospun fibrous mats in the cubic space. Furthermore, the influences of randomness will be quantified by a simple parameter, and the analytical correlation between fiber radius and permeability will be analyzed after validation of the model by numerical and experimental results.

2. Model generation

In this work, the electrospun fiber layers are assumed to be macroscopically homogeneous and have a uniform porosity distribution. A typical representative schematic for fibrous media is an ordered array of unidirectional fibers, as shown in Fig. 2. Under the condition of a low Reynolds number (Reynolds number $<<$ 1), steady flow through the representative cell is governed by Stokes equation given in Eq. (2). Unlike macroscopic problems in mass, momentum, or energy transport as described by traditional continuum equations, the movements and interactions of the nanoscale entities tend to be random walks in the microscopic world. The continuum theory assumes that the average velocity of air molecules fully in contact with the solid boundary of a coarse fiber is zero. However, this assumption is not strictly correct for nanofiber, as its radius is comparable to or slightly larger than the mean free path of air molecules and only part of the air molecules can contact the nanofiber. As such, the molecules without colliding with the nanofiber generate a slip flow. For the flow around a fiber, when the partial slip occurs, the slip velocity is given by the widely used first-order Maxwell's slip boundary condition [17]:

$$u_s = \lambda \frac{\partial u}{\partial n}, \tag{3}$$