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# Transport properties of electrospun fibrous membranes with controlled anisotropy

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ABSTRACT

In-plane gas permeability measurements were performed on electrospun polyacrilonitrile fibrous mats. Samples were cast onto a drum rotating at various speeds in order to create materials with different degrees of fiber alignment. Permeability measurements were made in both parallel and perpendicular directions and large increases were seen for flow in the fiber direction as expected. Because these measurements were performed in-plane it was necessary to mechanically compress the samples during measurement. Tests were performed at several compressed thicknesses, but it was found that the samples did not compress uniformly so it was not possible to determine a unique Carman–Kozeny constant for the material. A methodology was developed by which the Carman–Kozeny constant was determined for each compression that produced a linear trend against compressed porosity. It was proposed that the true Carman–Kozeny constant for the material can be determined by extrapolating this trend to the value of the uncompressed porosity, and good agreement with the literature values was obtained.



## 1. Introduction

Transport phenomena in fibrous media are of great interest in many fields, ranging from filtration [1,2], tissue scaffolding [3,4], fuel cell [5] and flow battery electrodes [6], ion exchange materials [7], textiles [8] and so on. In many of these applications, the performance of the material is highly dependent on its structural properties, so great gains can be made by rationally designing their porous structures. Electrospinning is a very appealing technique for this purpose since it allows for a variety of novel material structures to be made with fairly simple adjustments to the production conditions. A number of reviews are available which give a thorough overview of the possibilities [9–12]. In particular, electrospinning can make arbitrarily large sheets, with very small fibers ( $<$ 50 nm), high porosity ( $>$ 95%), and controlled amount of fiber alignment [13]. Moreover, almost any polymer solution can be electrospun and no heating or processing of polymer melts is required, enabling the use of functionalized, biological or otherwise sensitive materials to be produced. This tremendous flexibility has led to an explosion in the use of electrospinning in many diverse fields.

Producing an optimized fibrous structure, by electrospinning or any other method, requires a solid understanding of the relevant transport phenomena occurring within it. The ability to properly characterize fundamental transport parameters of these materials is essential if one is to correlate material properties to performance, perform simulations of processes within them, or to apply quality control measures to their production. Measuring transport properties in fibrous media can be quite challenging however. Most established measurement protocols and modeling tools, such as those outlined by Dullien [14] for instance, were developed for the traditional suite of porous materials such as rock cores and sand packs. The study of fibrous materials invariably requires the development of custom-made, specialized techniques for numerous reasons. They are almost always quite thin (usually less than a few mm) which leads to a myriad of difficulties. For instance, it not at all trivial to measure their thickness (i.e. thinness) since the very act can compress them a significant proportion of the total thickness (with calipers for instance). Similarly, it is difficult to clearly define the boundaries of a sample since surface roughness can be a significant portion of the total domain. Furthermore, fibrous materials are typically flexible and compressible, which means that experimental devices need to control compression carefully and transport properties should ideally be measured as a function of compression. In fact, Choong et al. recently reported that their materials underwent compression from the drag of water flowing through them [15]. Finally, the fibers are usually oriented in the plane of the material and are often aligned in a preferred in-plane direction, meaning that transport processes are direction dependent thus all properties of interest must be

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measured as tensors. Fibrous materials also present a host of other differences from standard materials such as high porosity and inverted geometry (the solid phase in a fibrous material more closely resembles the pore space in a material like sandstone). One helpful feature of working with electrospun fiber mats is that, because they are (usually) manufactured, their chemical makeup and diagenetic history are controlled and well known, which can simplify some aspects of their analysis.

In the present work we present a methodology for measuring the in-plane components of the permeability coefficient tensor in electrospun fibrous mats. Despite similar values of fiber diameter and porosity between the tested materials, it proved nearly impossible to directly compare permeability values between samples. Permeability is such a strong function of both these parameters that even slight deviations lead to wide discrepancies. One of the main challenges of this project was to relate the permeability measured on different materials via some common indicator or metric. Typically the Carman–Kozeny constant is used for this purpose [16,17], but as will be discussed below this was not a straight-forward procedure for these unique materials. This work will outline the methodology and experimental protocols that were developed in order to extract meaningful Carmen–Kozeny constants from in-plane permeability measurements of electrospun materials with random and aligned fiber orientations as a function of mechanical compression. To our knowledge, this work is also the first to measure the in-plane components of the permeability tensor of electrospun nanofibrous materials. In most applications the flow is in the through-plane direction (e.g. filtration), but there are instances where in-plane flow occurs, such as flow battery electrodes. Moreover, any detailed 2D or 3D fluid dynamics models require knowledge of the full permeability tensor.

## 2. Literature review and background

The resistance to fluid flow through a porous material is described by Darcy's law:

$$Q = \frac{KA}{\mu L}\Delta P \tag{1}$$

where $Q$ is the volumetric flow of fluid, $\Delta P$ is the pressure drop across the domain of length $L$, $A$ is the cross-sectional area normal to the direction of flow, $\mu$ is the fluid viscosity, and $K$ is the permeability coefficient. $K$ is a fitting parameter that accounts for the pore scale structural properties of the medium such as pore sizes, grain or fiber sizes, void fraction, pore connectivity, tortuosity, and so on. It is possible to correlate the dependence of $K$ to the porosity and some characteristic size of a porous material. The most common relationship for this purpose is the well-established Carman–Kozeny equation:

$$K = \frac{d_f^2 \varepsilon^3}{16 k_{CK}(1-\varepsilon)^2} \tag{2}$$

where $d_f$ is the fiber diameter, $\varepsilon$ is the sample porosity and $k_{CK}$ is the so-called Carman–Kozeny constant. The value of $k_{CK}$ is a fitting parameter that accounts for the structure of the materials, so will have different values for granular and fibrous media for instance. In anisotropic materials, such as fibrous media, $k_{CK}$ has different values in each direction. The main advantage of correlating $K$ values using Eq. (2) is that $k_{CK}$ is constant for a given material or even class of materials, so that similar materials (e.g. nonwoven fibrous mats) all have the same $k_{CK}$ value regardless of porosity and fiber diameter. Tomadakis and Roberston [17] offer a good review comparing experimental data with numerical modeling results. They present several functions for correlating fibrous material properties with permeability, but the Carman–Kozeny model presented above provides the best balance of wide applicability and simplicity. Tomadakis and Roberston [17] provide predictions of $k_{CK}$ values for various fiber alignments; for fibers randomly oriented in the plane they suggest $k_{CK}$ of 4 (independent of direction); for fully aligned fibers they suggest a value of 2 in the fiber direction and 8 against the fibers. Although these values provide a useful benchmark for comparison, it must be remembered that these models all assume a uniform fiber diameter while real materials have a distribution of fiber sizes. A study with a similar theme was performed by Ho and Zydney [18] which characterized in-plane pore connectivity which one would also expect to strongly a function of anisotropy. It however did not take compression into account to the same degree as the Carman–Kozeny equation.

The growing use of nanomaterials in all realms of engineering has also impacted fibrous materials as well. Despite this rapid growth of interest in nanofiber mats, there have been relatively few studies that report fundamental transport properties in a universal way. The vast majority of studies report only the 'performance' of a material in its given application as a function of some key production parameter (e.g. solution concentration) or measured sample property (e.g. fiber diameter). For instance, numerous studies have reported on the use of electrospun membranes for capturing nanoparticles, but they focus largely on measuring capture efficiency [19,20] as a function of production parameters. In the cases where permeability to flow is considered it is often reported as some sort of pressure drop at a specific flow rate vs. a basic material characteristic (e.g. areal density or mat thickness) or production parameter (e.g. solvent concentration or duration of production) [21–24], which is usually insufficient to extract permeability. Others convert their pressure drop data to a permeability coefficient but do not take the final step of normalizing the permeability values for differences between samples [25,26]. Since these works were aiming to develop materials for specific applications it is understandable that they focus on reporting the relevant performance metrics; however, for the data to be more widely applicable (i.e. for use in modeling and optimization studies) it is necessary to report values in such a way that generalizations and comparisons between materials are possible. The recent paper by Choong et al. [15] illustrates this situation very clearly. They present flow vs. pressure data for a variety of electrospun materials which show very wide scatter. They then convert this data to a dimensionless permeability $K/d_f^2$ (which is equivalent to dividing Eq. (2) through by the squared fiber diameter term) vs. solid volume fraction $\phi$ (i.e. $1-\varepsilon$). All the apparently disparate data collapse onto a single line.

The goal of the present work was to study the fundamental permeability behavior of electrospun fibrous mats in an effort to measure generalized permeability data in the form of Carman–Kozeny constants. This mainly consisted of normalizing measured permeability coefficients for differences between materials and accounting for the abnormal behavior of the material. The present work undertakes a similar task to that of Choong et al. [15] but for in-plane permeability measurements. In addition, in this work the impact of fiber alignment on the in-plane components of the permeability tensor is measured.

## 3. Experimental techniques

### 3.1. Electrospinning

An electrospinning setup was designed and built in-house. The system consisted of a syringe pump (Harvard Apparatus, Pump11