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# Permeability of electrospun fiber mats under hydraulic flow

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ABSTRACT

The hydraulic permeabilities of electrospun fiber mats are found to be functions of their compressibility. Hydraulic permeabilities of electrospun mats of bis-phenol A polysulfone (PSU) comprising fibers of different mean diameters, annealed at temperatures at and above the glass transition of the polymer, were measured for feed water pressures ranging from 5 kPa to 140 kPa. The electrospun mats experience a decrease of more than 60% in permeability between 5 kPa and 140 kPa, due to the loss of porosity, attributed to flow-induced compression. This behavior is explained using a simple model based on Darcy's law applied to a compressible, porous medium. Happel's equation is used to model the permeability of the fiber mats, and Toll's equation is used to model their compressibility. The permeation model accurately estimates the changes in solidity, and hence the permeability of the electrospun mats, over a range of pressure differentials.



## 1. Introduction

Electrospun fiber mats are promising for many filtration applications like coalescence filtration, depth filtration, etc., because of their high porosity ($>0.9$) and small inter-fiber distances (typically 0.1–10 μm), which provide high permeabilities and high separation efficiencies [1,2]. However, electrospun fiber mats are also highly compressible [3], hence their porosity decreases with increasing pressure. This compressibility of the mat can counter the benefits of high porosity in filtration applications. An understanding of the extent of the reduction in permeance upon compression for electrospun fiber mats is vital for evaluating their performance relative to other, commercial filtration membranes under conditions relevant for filtration processes. A typical operating pressure for an ultrafiltration process is 0.1 MPa [4].

The studies of liquid flow through compressible media are diverse. Biot [5,6] developed a theory for the consolidation of porous soil containing a viscous fluid; Mow et al. [7,8] studied the effects of compressive strain on the fluid permeability of articular cartilage. Zhu et al. [9] and Kataja et al. [10] modeled water permeation during wet pressing of paper. Jönsson and Jönsson [11,12] modeled filtration through compressible porous media as the gradual transformation of hydraulic pressure into mechanical stress on the porous solid. The main difference between the systems mentioned above is the structure of the porous network, which affects the expressions of permeability constant and compressibility. Here, we adopt the approach of Jönsson and Jönsson, combined with expressions for the permeability and compressibility of fibrous materials to describe the flux of water through electrospun mats.

The permeability of porous fibrous media has been studied extensively. Equations for permeability constants that account for the drag forces exerted on the liquid by the solid medium have been developed for flow through a 2-D array of cylinders that are aligned parallel [13,14] or perpendicular [13,14,15] to the direction of the flow, as well as through 3-D random arrays of cylinders [16]. Mao and Russell [17,18] included the effect of fiber orientation in both 2-D and 3-D arrays. Others have also studied the permeability numerically and developed the permeability equations empirically from experimental data [19,20,21]. Electrospun mats can be approximated as planar fibrous networks. From the review by Jackson and James [22], analytical permeability models for flow perpendicular to a 2-D array of cylinders developed by Happel [13] and by Spielman and Goren [16] fit the experimental data well in the solidity range ~0.05–0.3 (where solidity is defined as 1−porosity). Since Happel's model is simple, physically-based and does not involve implicit functions of permeability, Happel's equation is chosen for this work unless indicated otherwise.

The compressibility of electrospun mats can be described by a power-law equation that correlates the compressive stress ($\sigma_m$) applied to electrospun mats with the solidity ($\phi$) of the mats

$$\sigma_m = kE(\phi^n - \phi_0^n) \quad (1)$$

where $k$ is an empirical constant that accounts for variations in the length, contour, and other characteristics of the fiber segments

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between load-bearing contacts; $E$ is Young's modulus of the fiber; $\phi$ and $\phi_0$ are the solidity under compression and the initial solidity of the fibrous medium at zero stress, respectively; and $n$ is the exponent, which depends on the nature of the fiber network. We have previously validated Eq. (1) experimentally for electrospun fiber mats [3], and studied the effect of thermal annealing on compressibility of electrospun mats. For details of the derivation of Eq. (1), the reader is referred to the original work of Toll [23].

In this work we characterize the change in permeability of electrospun mats, which are highly compressible, under flow-induced compression, and explain this behavior through a simple combination of the foregoing analytical models. The details of the modeling framework are described in the following section.

## 2. Modeling of permeation

In Jönsson and Jönsson [11], the total pressure ($P_{tot}$) associated with fluid flow through a porous medium system is the sum of the hydraulic pressure ($P_h$) that drives the fluid flow through the porous medium, and the mechanical stress ($\sigma_m$) that deforms the porous medium. The mechanical stress arises from the drag of fluid on the interior surfaces of the medium as the fluid flows through it. The drag also results in the drop of the hydraulic pressure in the direction of the flow [13]. The mechanical stress on the fiber mat increases in the flow direction because the force propagates via the fiber–fiber contacts [23]. Therefore, the last layer of the porous medium in the flow direction experiences the largest compression, as shown qualitatively in Fig. 1. The $P_{tot}$ is equal to the trans-membrane pressure drop, $\Delta P$.

The flux of water ($J$) through an electrospun mat, which is a fibrous porous medium, can be described by Darcy's law:

$$J = -\frac{K}{\mu}\frac{dP_h}{dz} \qquad (2)$$

where $K$ is the permeability constant, $\mu$ is the dynamic viscosity of water, and $dP_h/dz$ is the hydraulic pressure gradient through the thickness of the mat. The negative sign is due to the convention used in this work, where $z=0$ at the inlet of the mat. Since the sum of $\sigma_m$ and $P_h$ is constant ($\sigma_m = P_{tot} - P_h$), we can rewrite Eq. (2) in terms of $\sigma_m$.

$$J = \frac{K}{\mu}\frac{d\sigma_m}{dz} \qquad (3)$$

The permeability constant for a highly porous fibrous medium has been derived analytically for flow around a cylinder by Happel [13]

$$K = \frac{D^2}{32\phi}\left(-\ln\phi + \frac{\phi^2 - 1}{\phi^2 + 1}\right) \qquad (4)$$

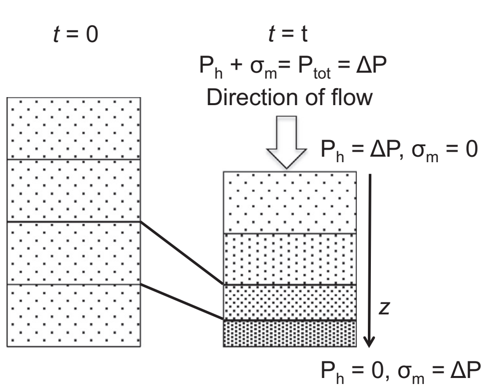


**Fig. 1.** Schematic of deformation of an electrospun mat under pressure driven flow. The density of the dots represents qualitatively the degree of compaction (solidity) [11].

where $D$ is the fiber diameter. Eq. (1) was used to account for the compression of the electrospun mat.

Given the basis weight and pressure drop across the membrane, we make an initial guess for flux ($J$) and integrate Eqs. (5) and (6) from $\phi = \phi_0$ and $\sigma_m = 0$ at $z = 0$ to $\sigma_m = P_{tot}$. From the profile thus obtained for $\phi(z)$, the error in basis weight can be determined, and the value for flux iterated until the correct basis weight is obtained.

$$\frac{dz}{d\sigma_m} = \frac{K}{J\mu} \qquad (5)$$

$$\frac{d\phi}{d\sigma_m} = \frac{1}{nkE\phi^{n-1}} \qquad (6)$$

During an experiment, the flux ($J$) and the trans-membrane pressure drop ($\Delta P$) were measured, from which the permeance, defined as $J/\Delta P$, was computed and compared to that predicted by the model. To convert permeance to permeability, it is also necessary to know the mat thickness during flow; the mat thickness, and thus permeability $K$, was obtained by application of the model. It should be noted that both $\phi$ and $K$ are average values in this case, since the mat deforms nonuniformly in the through-plane direction during testing, as indicated by Fig. 1.

## 3. Experimental

### 3.1. Materials

Bisphenol-A-polysulfone (PSU), purchased from Sigma Aldrich, is a glassy amorphous solid at room temperature, with a glass transition temperature of 188 °C, as measured by Differential Scanning Calorimetry (DSC, TA Q100). N,N-dimethyl formamide (DMF) was obtained from Sigma-Aldrich and used as received, as solvent for preparing the PSU solutions for electrospinning. Formic acid (FA) was added to some solutions in small amounts to modify their electrical properties, to allow some control of fiber diameter. Cellulose acetate microfiltration (MF) membrane with a nominal pore size of 3 μm and thickness of (167 ± 2) μm (measured using Agilent UTM as described in Section 3.5) was purchased from Millipore (SSWP02500) and used as received.

### 3.2. Fabrication

A vertically aligned, parallel plate setup was used for electrospinning, as described elsewhere [24]. The top plate was 15 cm in diameter and charged with a high voltage supply (Gamma High Voltage Research, ES40P) to a voltage in the range of 10–30 kV. The grounded bottom plate, which also served as the collector for the fiber mat, was a 15 cm × 15 cm stainless steel platform. The tip-to-collector distance was varied from 25 to 35 cm by adjusting the height of the bottom plate. The polymeric solution was loaded into a syringe attached by Teflon tubing to a stainless steel capillary (1.6 mm OD, 1.0 mm ID) that protruded 21 mm through the center of the top plate. A digitally controlled syringe pump (Harvard Apparatus, PHD 2000) was used to control the flow rate of the polymer solution in the range of 0.005–0.02 mL/min.

### 3.3. Post-processing

The as-spun mats were annealed thermally in a furnace (Thermolyne Industrial Benchtop Furnace, FD1545M) to strengthen the electrospun mat, as previously reported [24]. The mats were held in plane during the annealing process by draping over a petri dish that is 10 cm in diameter. The PSU mats were annealed at