FABRICATION, CHARACTERIZATION, AND APPLICATION OF ELASTIC HYDROPHOBIC ELECTROSPUN FIBER MATS

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FABRICATION, CHARACTERIZATION, AND APPLICATION OF ELASTIC HYDROPHOBIC ELECTROSPUN FIBER MATS

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ABSTRACT

Electrospinning is a simple, effective, and versatile method to produce polymeric micro- and nanofibers. The electrospun fibers and fabrics are extensively used in a variety of fields such as filtration, biomedical engineering, energy storage, and catalysis. Specifically, electrospun nowoven fibrous media used as various types of filters function efficiently in filtration, separation, and purification applications. This dissertation studies the novel research of using elastic electrospun fiber mats as filter media for filtration and separation applications, which has not been discussed in literatures.

In this work, submicron elastic acrylonitrile-butadiene copolymer fibers were fabricated via electrospinning. Fiber morphologies and diameters were investigated. The surface wettability of the fiber mats were characterized by water contact angle, and the surfaces showed hydrophobicity. Fiber mats and yarns rolled from the mats were conducted uniaxial tensile tests to study their mechanical behaviors and it turned out different stress-strain performance, which was essentially due to the difference in fiber slippage and rearrangement mechanisms.

Air permeabilities of the stretched elastic fiber mats were evaluated when subject to air flow. As the fiber mats stretched, fibers shifted apart relative to each other such that the pores enlarged. The permeability/mat thickness values increased initially and then reached constant as a result of the pore structure change during stretch. Poly (vinyl pyrrolidone) (PVP) electrospun fiber mats were measured for bubble point and mean flow pore diameters to determine their dependence on fiber diameter and fiber mat basis weight.
Generally, pore sizes were smaller for a fiber mat of higher basis weight and for those composed of fibers of smaller diameters. More interestingly, the two characteristic pore diameters decreased initially and then reached minimum plateau as the basis weight increased.

The elastic fiber mats were built into different types of filter media to capture solid nanoparticles from air as well as remove dispersed water droplets from diesel fuel to inspect the filter performance in terms of penetration, separation efficiency, pressure drop, and overall Filtration Index. For the solid aerosol separation, particle penetration increased and pressure drop decreased when the elastic fiber mats stretched to give larger pores. For the water-in-diesel emulsion separation, better separation efficiencies were achieved by using filter media containing electrospun fiber mats of higher basis weight under lower emulsion face velocities.
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CHAPTER I

INTRODUCTION

1.1 Background and overview

Study on polymer nanofibers has been extensively conducted all over the world and is drawing more and more attention during recent years. Nanofibers can be fabricated in many ways, such as self-assembly\textsuperscript{12}, melt-blowing\textsuperscript{3}, electrospinning\textsuperscript{4}. Among these techniques, electrospinning is preferred due to its simplicity, effectiveness, and versatility. It takes advantage of electrostatic forces to generate continuous fibers from polymer solutions. A typical laboratory setup (Figure 1.1) consists of a high-voltage power supply, a syringe pump, and a collector. A polymer solution held in the syringe is fed by the syringe pump continuously through a needle to a drop on the end of the needle. The needle is charged to a high electrical potential relative to ground. The electrical charges induced in the droplet distribute across the surface of the drop\textsuperscript{5} and cause the drop to deform into a conical shape known as the Taylor cone\textsuperscript{6}. Once the electric charge repulsive forces overcome the surface tension of the solution, a fluid jet is launched from the drop towards a grounded collector. The jet stretches and elongates as it travels through the air due to the repulsive forces generated by the charges it carries. Solvent in the polymer solution in the jet evaporates and the jet solidifies into a fiber.
In 1990s, Reneker and his group conducted fundamental research\textsuperscript{7-9} on electrospinning, making it a globally popular topic since then. The number of scientific publications regarding electrospinning has been increasing tremendously in the first decade of the 21\textsuperscript{st} century (Figure 1.2). There are more than 200 universities and research institutes worldwide focusing on various aspects of electrospinning, from process basics to product applications (Figure 1.3).

Figure 1. 1 Laboratory Single-needle electrospinning setup.

Figure 1. 2 Number (n) of scientific publications and patents with the keyword “electrospinning” between year 2000 and 2015 (source: Google Scholar).
Electrospun nanofibers typically have small diameters and extremely high surface-to-volume aspect ratios. These fascinating properties make them excellent candidates in a broad range of applications (Figure 1.4) including filtration\textsuperscript{11–15}, catalysis\textsuperscript{16–19}, energy storage\textsuperscript{20,21}, and tissue engineering\textsuperscript{22–24}. Specifically for filtration and separations, electrospun fiber mats function effectively as depth or coalescence filter media in both air and liquid filtration processes. Nonwoven media of electrospun polymeric fibers possess high specific surface areas to capture tiny particles in aerosols through major capture mechanisms. The surfaces of the electrospun fiber mats are randomly arranged fiber structures. The polymers from which the fibers are fabricated may be hydrophobic by nature, but the surfaces of the nanofiber mats may be superhydrophobic due to the roughness of the surface according to Cassie-Baxter model. With enhanced surface hydrophobicity, the electrospun fiber mats are used as surface barrier filter media to remove tiny water droplets from organic liquids through surface coalescence mechanism.
The electrospinning of elastic polymers is also popular besides inelastic polymer materials. Elastomers are a class of polymers showing viscoelasticity. Current research trends include the electrospinning and characterization of the elastomeric fibers. Some interesting properties of elastomeric fiber mats include high tensile strength and surface hydrophobicity which make these fabrics excellent candidates for a broad range of applications such as protective clothing\textsuperscript{25}, scaffold\textsuperscript{26}, and insulation\textsuperscript{27}. Fong et al.\textsuperscript{28} found electrospun styrene-butadiene-styrene (SBS) triblock copolymer nanofibers to be elastic and birefringent with diameters around 100nm. Staining tests showed phase separations of styrene and butadiene blocks in the fibers. Hao et al.\textsuperscript{29} spun elastic mats of cis-1,4-polyisoprene smooth fibers and fibers with a bamboo-like morphologies ascribed to polymer chain entanglement and solvent properties. Feng et al.\textsuperscript{30} successfully electrospun elastic mats of styrene-isoprene-styrene (SIS) copolymer. Stress-strain measurements of the fiber mats revealed that mechanical performances were dependent upon the fiber size.
Commercially available HEPA and ULPA filters are commonly composed of glass micro and submicron fibers. The inner structures of the filter media are rigid, giving fixed filter-related properties, such as porosity, permeability, and pore size. Elastic electrospun fiber mats have not been studied for filtration and separation applications, however, they are of great interest since the fiber mat properties may vary as the local structures change due to stretching, leading to variable filter performance. This dissertation discusses the fabrication, characterization, and application of elastic electrospun acrylonitrile-butadiene copolymer fibers and fiber mats. Acrylonitrile-butadiene copolymer is an elastomer that is generally referred to as nitrile rubber (NBR). NBR has strength, elasticity, chemical resistance, and hydrophobic properties that make it useful for oil and fuel handling hoses, self-sealing fuel tanks, conveyor belts, seals, and roll goods\textsuperscript{31}. We anticipate that its properties will be useful when formed as submicron electrospun fiber mats for applications as filters.

1.2 Project motivation

The use of elastic electrospun fiber mats as filter media is not widely discussed in filtration and separation literatures. Since the mat structures can deform when stressed, their filtration performance is expected to change as the stress changes, potentially making these materials perform as “smart” filters that adapt to the changing applied pressure as the filter loads with particles. The purpose of this research is to explore the filtration performance of elastic acrylonitrile-butadiene copolymer electrospun fiber mats to better understand when and how such fabrics may be advantageous in filtration applications.
1.3 Hypothesis

When an elastic electrospun fiber mat is stretched, the fibers are expected to simultaneously suffer elongation and shift apart relative to each other to cause the pores to enlarge. As a result, the permeability of the fiber mats will increase, such that the fluids will flow through the medium more easily. Frazier air permeability test will be performed to evaluate the permeability values of the stretched fiber mats subject to air flow in order to investigate the relation between permeability and pore structure. When the fiber mats are used as filter media for aerosol separations, enlarged pores will favor the penetration of the particles through the fiber mats, therefore will result in decreased separation efficiencies. However on the other hand, the aerosols will penetrate the media with less restriction when passing through the larger, which will generate lower pressure drops across the fiber mats. To prove this hypothesis, the elastic fiber mats will be constructed as depth filter media to capture solid nanoparticles from air under both non-stretched and stretched states, to compare resulting separation efficiency, pressure drop, and overall Filtration Index. Besides elasticity, surface hydrophobicity of the fiber mats are expected to function in water-in-diesel emulsion separation when used as surface barrier filter media. Separation experiments will be done by removing dispersed water droplets from diesel fuel using a laboratory custom made setup.

1.4 Research objectives

This project is divided into three categories according to their natures which are also in time sequence. Objectives for each category are listed below.
1. Fabrication
   - Select suitable polymer material and solvent to prepare the solution system for electrospinning
   - Determine electrospinning conditions (feeding flow rate, voltage, tip-to-collector distance, etc.) to fabricate smooth fibers

2. Characterization
   - Evaluate the fiber morphologies and sizes
   - Inspect the surface wettability and mechanical performance of the fiber mats
   - Measure filter-related properties (porosity, permeability, pore size, etc.) of the fiber mats
   - Investigate permeability of elastic fiber mats under non-stretched and stretched conditions
   - Develop a descriptive empirical mathematical model to describe the behaviors of the fiber mat stretch subject to air flow

3. Application
   - Prepare depth filter media using the elastic electrospun fiber mats to separate solid nanoparticles from air
   - Compare filter performance of elastic electrospun fiber mats under non-stretched and stretched states in solid aerosol separation
   - Construct superhydrophobic surface coalescing filter media using the elastic electrospun fiber mats and test the mats for separation of dispersed water droplets from diesel
1.5 Dissertation outline

- CHAPTER I introduces the project overview, backgrounds, research motivations and objectives
- CHAPTER II reviews the literatures of electrospinning, surface wettability, material mechanics, filter-related properties, solid aerosol separation, particle capture, liquid-liquid coalescence filtration
- CHAPTER III describes the electrospinning of elastic acrylonitrile-butadiene copolymer fibers and characterizations of the fiber mats
- CHAPTER IV presents the permeability property of the stretched elastic fiber mats subject to air flow via Frazier Test
- CHAPTER V presents the filter performance of the elastic electrospun fiber mats under both non-stretched and stretched states in solid aerosol separation
- CHAPTER VI presents the electrospinning, pore characterizations, and solid aerosol filtration performance of poly (vinyl pyrrolidone) fiber mats
- CHAPTER VII presents the filter performances of the elastic superhydrophobic electrospun fiber mats used as surface coalescing barrier filter media for removal of dispersed water droplets from diesel fuel
- CHAPTER VIII presents the summary and conclusions of the research work
- CHAPTER VIII presents some suggestions for the future work on the elastic electrospun fiber mats
2.1 Electrospinning

2.1.1 Brief history of electrospinning

Electrospinning as a simple and versatile technology to produce fine fibers has been developing over 3 centuries until nowadays. In 1600, William Gilbert published his book *De Magnete* in regard to the study the electricity and magnetism. He noticed that when a piece of electrically charged amber was held close to a water drop sitting on a surface, the water drop deformed into a conical shape. This phenomenon was recorded as the first experimental observation of the deformation behavior of a liquid drop due to the external electrostatic field. In 1887, Boys designed and used an electrically charged dish to make fibers from several materials. In early 1900s, Cooley and Morton patented the use of electrospinning to electrically disperse fluids. Furthermore, Formhals obtained patents on process and apparatus of electrospinning for fabricating textiles between 1934 and 1944, showing the commercialization of electrospinning. In 1964, Taylor studied the deformation of an electrically conductive liquid drop placed in an electric field and described this phenomenon theoretically based on mathematical modeling. The cone shape was commonly known as “Taylor cone”. Starting from 1990, Reneker and research fellows conducted extensive research on the fundamentals of electrospinning of polymeric materials, which made electrospinning a popular topic in that decade. Since then,
study on various aspects of electrospinning has been carried out all over the world with the quantity of relevant research articles increasing rapidly year by year.

2.1.2 Mechanisms of electrospinning and electrospraying

Electrospinning is a technique that uses electrostatic forces to produce polymer fibers with diameters range from nanometers to micrometers using polymer solutions. A typical laboratory setup (Figure 2.1) consists of a high-voltage power supply, a syringe pump, and a collector. A polymer solution held in the syringe is fed by the syringe pump continuously through a needle to a drop on the end of the needle. The needle is charged to a high electrical potential relative to ground. The electrical charges induced in the droplet distribute across the surface of the drop and cause the drop to deform into a conical shape known as the Taylor cone. Once the electric charge repulsive forces overcome the surface tension of the solution, a wet jet is launched from the drop towards a grounded collector. The jet stretches and elongates as it travels through the air due to the repulsive forces generated by the charges it carries. Eventually, solvent in the jet evaporates and the jet solidifies into a fiber to accumulate onto the collector.

Figure 2. 1 Single needle electrospinning setup.
Electrospray is a process similar to electrospinning that generally happens when the polymer concentration and the resulting solution viscosity is relatively low\textsuperscript{41}. To have electrospinning occur, a critical solution viscosity is required to insure sufficient chain entanglement of the polymer molecules that leads fiber formation\textsuperscript{42}. At relatively low levels of polymer concentration, solution viscosities are low due to the lack of high degree of chain entanglement of the polymer molecules. As a strong voltage is applied to the pendent solution drop, the drop breaks down into tiny drops that deposited onto the grounded collector to form a dry polymer film after the solvent evaporates.

2.1.3 Electrospinning parameters

The morphology and structure of electrospun polymer fibers, especially fiber diameter, are directly dependent on three categories of parameter: solution, operation, and ambient condition. Thompson et al.\textsuperscript{43} conducted a comprehensive study to evaluate the effects of 13 parameters that affect the resulting fiber sizes. These parameters are classified into 3 groups based on the effect degrees and listed in Table 2.1. According to this study, it is recommended to focus on varying the parameters that cause relatively prominent effects in order to efficiently prepare fibers of desired size ranges.
Table 2. 1 Effects of the parameters on electrospun fiber size\textsuperscript{43}

<table>
<thead>
<tr>
<th>Strong effect</th>
<th>Moderate effect</th>
<th>Minor effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Initial jet radius</td>
<td>• Initial polymer concentration</td>
<td>• Vapor diffusivity</td>
</tr>
<tr>
<td>• Volumetric charge density</td>
<td>• Perturbation frequency</td>
<td>• Relative humidity</td>
</tr>
<tr>
<td>• Nozzle-collector distance</td>
<td>• Solvent vapor pressure</td>
<td>• Surface tension</td>
</tr>
<tr>
<td>• Initial elongational viscosity</td>
<td>• Solution density</td>
<td></td>
</tr>
<tr>
<td>• Relaxation time</td>
<td>• Electric potential</td>
<td></td>
</tr>
</tbody>
</table>

2.1.4 Electrospinning apparatus

During recent years, various electrospinning apparatus have been developed for different purposes, mainly to improve the production rate of the polymer fibers. These apparatus differ primarily in the nozzle that initiate the fiber jet and the collector used for fiber accumulation. Varabhas et al.\textsuperscript{44} constructed an electrospinning setup that employed a porous hollow tube as the solution reservoir. The hollow tube had holes drilled in series (Figure 2.2) to allow the polymer solution to flow outwards to generate multiple jets. Therefore, it provided higher production rate compared to single jet electrospinning. Wang et al.\textsuperscript{45} developed a conical wire-coil nozzle to hold the polymer solution for needleless electrospinning. A great amount of fiber jets launched from the wire surface (Figure 2.3) to yield a much higher productivity. Besides, the sizes of the fibers prepared from the wire-coil nozzle were smaller than that of the typical single-needle setup. Dosunmu et al.\textsuperscript{46} used a cylindrical tube with porous wall (Figure 2.4) to generate multiple jets in order to increase the fiber production rate. The tube wall made of tiny polyethylene particles possessed irregular pores for the polymer solution to flow through to form the jets. The average diameter of the fibers prepared using the porous tube was similar to that of the single-
needle setup, but the fiber diameter distribution was broader. Lu et al.\textsuperscript{47} designed a spinneret which was a rotary metallic cone to create numerous jets ejecting from the circumferential edge of the cone (Figure 2.5). The polymer solution injected onto the surface of the cone flew downwards to the edge due to gravity, and the whole cone surface was covered by the continuously-fed solution as the cone rotated. The electric field intensity at the sharp edge was strong enough to initiate the fiber jets to be collected on the collector placed underneath the spinneret. The authors concluded an impressively 1000 times higher production rate compared to the traditional electrospinning setup. The four example electrospinning devices listed above have a common point that they are all needleless, showing a trend of abandoning the traditional needle and employing novel spinnerets with either multiple pores as the solution outlets or sharp geometries to generated much more fiber jets to essentially improve the production rate. However, the sizes of the fibers produced from these needless nozzles are slightly different than the single-needle setup, which needs to be considered when the fiber sizes of the products are also important besides productivity.

![Figure 2.2 Holes drilled on the porous tube as outlets for the polymer solution to generate fiber jets\textsuperscript{44}.

Figure 2.2 Holes drilled on the porous tube as outlets for the polymer solution to generate fiber jets\textsuperscript{44}. 

13
Figure 2. 3 Fiber jet formation on wire coils. Air pressure drives the polymer solution to flow through the wall of the porous cylindrical tube to generate multiple fiber jets.
Figure 2. 5 Numerous fiber jets eject from the circumferential edge of the rotary cone that used as the spinneret\textsuperscript{47}.

It is widely known that the electrospun fibers align randomly when they are collected on a piece of metal sheet, e.g., aluminum foil. Whereas using an electrospinning device with a special collector, fibers with certain alignments can be produced. Katta et al.\textsuperscript{48} obtained axially aligned fibers by collecting the fibers using a copper wire-framed rotating drum (Figure 2.6). The fibers stretched perpendicular to the copper wires and spanned the gap between the wires as the drum rotated. Parallel-aligned fibers were formed at the beginning but the alignments became random as the fiber mat turned thicker after a certain electrospinning period. Pan et al.\textsuperscript{49} simultaneously electrospun polymer fibers using two oppositely placed needles (Figure 2.7) that charged to positive and negative voltages, respectively. The fibers carrying positive charge stuck to the ones carrying negative charge to form a yarn after they ejected from the needles. The yarns were uniaxially aligned on a rotating cylinder served as a collector. It was also found that the rotation speed of the cylinder affected the degree of the fiber alignment. Higher rotation speed turned out better alignment, but the fibers broke if the speed was too high.
Figure 2. 6 (A) Electrospinning setup with a rotating wire drum as the collector; (B) Rotating drum with parallel wires$^{48}$.

Figure 2. 7 Schematic of the electrospinning setup for preparation of aligned fibers on a rotating cylinder collector$^{49}$.

2.1.5 Spinnability of polymers

A polymer of high-enough molecular weight dissolved in a suitable solvent system yields sufficient molecular chain entanglements in the solution of certain polymer
concentration. Provided appropriate electrospinning conditions (voltage, feeding flow rate, needle-to-collector distance, etc.), fine electrospun fibers can be prepared. So far, a large number of polymers have been successfully electrospun into fibers. Huang et al.\textsuperscript{39} listed the electrospinning of 44 polymers in their review article. The table below summarizes the electrospinning parameters and resulting fiber sizes of some commonly used polymers.

Table 2. 2 Electrospinning of common polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Polymer concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylpyrrolidone\textsuperscript{50}, PVP</td>
<td>Ethonal, water</td>
<td>0.00006 M</td>
</tr>
<tr>
<td>Polypropylene\textsuperscript{51}, PP</td>
<td>Cyclohexane+Acetone+DMF (80/10/10, w/w/w)</td>
<td>5 wt%</td>
</tr>
<tr>
<td>Polyethylene oxide\textsuperscript{52}, PEO</td>
<td>Water+ethanol (60/40, w/w)</td>
<td>4 wt%</td>
</tr>
<tr>
<td>Polyacrylonitrile\textsuperscript{53}, PAN</td>
<td>DMF</td>
<td>9.9 – 14.8 wt%</td>
</tr>
<tr>
<td>Nylon 6\textsuperscript{54}</td>
<td>HFIP+DMF (95/5, w/w)</td>
<td>10 wt%</td>
</tr>
<tr>
<td>Polystyrene\textsuperscript{55}, PS</td>
<td>THF, DMF, toluene, etc</td>
<td>18 – 35 wt%</td>
</tr>
<tr>
<td>Polyvinylidene Fluoride\textsuperscript{56}, PVDF</td>
<td>DMF+actone (80/20, v/v)</td>
<td>15 wt/v%</td>
</tr>
<tr>
<td>Polyvinylidenefluoride-co-hexafluoropropylene\textsuperscript{57}, PVDF-HFP</td>
<td>Acetone+DMF (70/30, w/w)</td>
<td>16 wt%</td>
</tr>
</tbody>
</table>
Table 2.2 Continued.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Voltage (kV)</th>
<th>Feeding flow rate (mL/h)</th>
<th>Needle-to-tip distance (cm)</th>
<th>Average fiber diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylpyrrolidone(^{50}), PVP</td>
<td>20</td>
<td>0.1</td>
<td>15</td>
<td>100 – 700</td>
</tr>
<tr>
<td>Polypropylene(^{51}), PP</td>
<td>10</td>
<td>—</td>
<td>15</td>
<td>650</td>
</tr>
<tr>
<td>Polyethylene oxide(^{52}), PEO</td>
<td>8.5</td>
<td>—</td>
<td>15</td>
<td>Diameter range: 100 – 300</td>
</tr>
<tr>
<td>Polyacrylonitrile(^{53}), PAN</td>
<td>8 – 16</td>
<td>—</td>
<td>13 – 16</td>
<td>380 – 1670</td>
</tr>
<tr>
<td>Nylon 6(^{54})</td>
<td>20</td>
<td>—</td>
<td>25</td>
<td>Diameter range: 100 – 500</td>
</tr>
<tr>
<td>Polystyrene(^{55}), PS</td>
<td>10 – 20</td>
<td>4.2 – 6</td>
<td>12 – 35</td>
<td>Diameter range: 800 – 20000 (±10000)</td>
</tr>
<tr>
<td>Polyvinylidene Fluoride(^{56}), PVDF</td>
<td>5</td>
<td>0.3</td>
<td>10 – 20</td>
<td>172</td>
</tr>
<tr>
<td>Polyvinylidenefluoride-co-hexafluoropropylene(^{57}), PVDF-HFP</td>
<td>12</td>
<td>—</td>
<td>12</td>
<td>600</td>
</tr>
</tbody>
</table>

2.2 Wettability

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces. Wetting deals with the three phases of materials: gas, liquid and solid (Figure 2.8). To gauge wetting properties, a parameter named spreading parameter (\(S\)) is used, given by

\[
S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})
\]

where \(\gamma_{SG}\), \(\gamma_{SL}\) and \(\gamma_{LG}\) are the solid-gas, solid liquid and liquid gas interfacial surface tensions, respectively. When \(S > 0\), the liquid wets the surface completely (complete wetting); when \(S < 0\), there is partial wetting\(^{58}\).
2.2.1 Young’s equation

The wettability of a flat surface, expressed by contact angle (CA, $\theta$) of a water droplet, is given by Young’s equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$  \hspace{1cm} (2.2)

where $\gamma_{SV}$, $\gamma_{SL}$ and $\gamma_{LV}$ refer to the solid-gas, solid-liquid and liquid-gas interfacial surface tensions, respectively.

The surface is defined as hydrophobic with $CA > 90^\circ$ or hydrophilic with $CA < 90^\circ$. There are two types of contact angle: static and dynamic contact angles. Static CAs, obtained by sessile droplet measurements, are close to Young’s angles. Dynamic CAs are non-equilibrium and measured during the growth (advancing CA, $\theta_a$) and shrinkage (receding CA, $\theta_r$) of a water droplet. The difference between $\theta_a$ and $\theta_r$ is defined as contact angle hysteresis ($\Delta \theta$).
2.2.2 Superhydrophobic surface

A surface with water contact angle larger than 150°, accompanied with low contact angle hysteresis is defined to be superhydrophobic\(^60\). Superhydrophobic phenomena exist commonly in the nature\(^61,62\) (Figure 2.9). Artificial superhydrophobic surfaces are obtained as well, e.g., electrospun fibers\(^63,64\), films\(^65\), etc. A useful application of superhydrophobicity is self-cleaning\(^66–68\). Water drops sitting on a superhydrophobic surface present almost spherical shapes as the WCAs are fairly high. The water drops own mobility such that they can roll freely on the surface with low hysteresis values. Provided a substrate with a tilted angle, the mobile water drops roll across the surface following straight paths and therefore wash away the dust attached on the surface. Besides self-cleaning, superhydrophobic coalescence filters are used to remove tiny water droplets from water-in-oil emulsions\(^69,70\).

Water droplets get detained by the superhydrophobic surface of the vertically placed filter media as the emulsion passes through. As more and more water droplets accumulate on the surface, adjacent droplets coalesce to form bigger droplets. Big droplets further coalesce with smaller droplets nearby to grow. Once the water droplets achieve certain weights, they slide down vertically due to gravity such that water is gathered at the bottom of the filter media.

Figure 2. 9 Superhydrophobic phenomena in the nature: (a) Lotus effect, (b) water strider.
2.2.3 Superhydrophobic surface models

2.2.3.1 Wenzel model\textsuperscript{71}

Wenzel observed that roughness can improve wetting properties of a smooth material if a drop wets the surface in such a way that it follows the roughness features. In this model, the drop is in touch with the rough surface intrinsically (Figure 2.10). As a consequence, water drops adhere to the surface and lack mobility. The contact angle $\theta_w$ is given by

$$\cos\theta_w = r \cos\theta$$  \hspace{1cm} (2.3)

In equation 2.3, the roughness factor $r$ is defined as the ratio of the actual surface over the geometric surface.

$$r = \text{roughness factor} = \frac{\text{actual surface}}{\text{geometric surface}}$$  \hspace{1cm} (2.4)

![Figure 2.10 Wenzel model.](image)

2.2.3.2 Cassie-Baxter model\textsuperscript{72}

Cassie-Baxter model is considered when dealing with a heterogeneous surface. According to this model, the drop sits on the top of the rough surface, leaving the space underneath occupied by air (Figure 2.11). In this case, the water drop is in touch with both
the solid surface and the trapped air. Especially, air is treated as completely non-wetting and the WCA is 180°. The contact angle $\theta_c$ is calculated using

$$\cos \theta_c = \sum \phi_i \cos \theta_i$$  \hspace{1cm} (2.5)

where $\phi_i$ is the area fraction for each surface component and $\theta_i$ is the corresponding contact angle. Since the water drops sit on the top of the surface, they possess higher mobility compared to Wenzel model. Cassie-Baxter model is generally considered to describe superhydrophobic surfaces in which case the WCAs are high and the hysteresis values are low, such that the water drops can easily roll on the surface.

Figure 2. 11 Cassie-Baxter model.

2.3 Mechanics of materials

2.3.1 Fundamentals

Mechanical performances reflect the properties and behaviors of a material under stress. Generally, tensile stress-strain test is the most traditional method for evaluating relevant mechanical behaviors of a material. According to the types of generated stress-strain curves, materials can be classified into different categories, e.g., brittle, ductile, and
elastomeric. Brittle materials (e.g., glass) break with minor deformation at very low strains under tensile stress. For this type of material, the stress-strain curves are short and do not present a typical plastic region for some circumstances. Ductile materials (e.g., aluminum, copper) suffer significant plastic deformation and rupture at larger strains compared to brittle materials. Generated stress-strain curves own typical elastic as well as plastic regions connected by yield point, and eventually end at failure point. Elastomeric materials, also known as elastomers, are mainly rubbery products consist of polymers or copolymers of different types of polymers, such as natural rubber, butyl rubber, and nitrile rubber. Common rubbers and their components are listed in Table 2.3.

Table 2. 3 Common rubbers and their components.

<table>
<thead>
<tr>
<th>Rubber name</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber (NR)</td>
<td>cis-1,4-polyisoprene, trans-1,4-polyisoprene</td>
</tr>
<tr>
<td>Butadiene rubber (BR)</td>
<td>Polybutadiene</td>
</tr>
<tr>
<td>Chloroprene rubber (CR)</td>
<td>Polychloroprene</td>
</tr>
<tr>
<td>Butyl rubber (IIR)</td>
<td>Copolymer of isobutylene and isoprene</td>
</tr>
<tr>
<td>Styrene-butadiene rubber (SBR)</td>
<td>Copolymer of styrene and butadiene</td>
</tr>
<tr>
<td>Nitrile rubber (NBR)</td>
<td>Copolymer of acrylonitrile and butadiene</td>
</tr>
</tbody>
</table>

Elastomers characteristically own viscoelasticity as they are essentially composed of polymers. Viscoelasticity reflects both the viscous and elastic properties of an elastomer. When an elastomer undergoes the tensile stress-strain test, the molecules in the polymer chains of the elastomer migrate and rearrange relative to each as a response to the applied stress, showing the characteristic of viscosity. Under the cyclic stress-strain test (stress applied, then removed), the stress-strain curve presents looped-shape (Figure 2.12) in which case hysteresis is exhibited. The hysteresis loop is enclosed by the loading and
unloading curves and its area is considered as the energy loss as heat dissipation during deformation and recovery.

Figure 2. 12 Hysteresis loop.

Creep-recovery and stress relaxation tests are two typical tests of elastomers besides stress-strain test. For the creep-recovery test, a material is loaded with a constant mass (stress) and then removed, with strain monitored as time proceeds. An instantaneous strain is generated when the stress is applied at the very beginning. Strain continues to increase over time with a decreasing strain rate. Once the stress is removed, elastic recovery occurs and the strain instantaneously drops. Anelastic recovery follows the elastic recovery, in which case the strain slowly decreases until it becomes constant after a certain time length. Eventually the material possess permanent strain and therefore suffers unrecoverable deformation. The stress relaxation test is conducted by stretching a material to a certain strain and then holding that strain. The stress needed to keep the strain is inspected over time. For an elastomer, the stress is found to decrease over time due to the migration and rearrangement of the molecules in the material.
2.3.2 Uniaxial tensile stress-strain test

In the traditional uniaxial tensile stress-strain test, a material of length \( (L_0) \) and cross-sectional area \( (A_0) \) is uniaxially stretched by tensile force \( (F) \) applied on the two ends (Figure 2.13). The material elongates to length \( (L) \) along the stretch direction, and compresses transversely in the directions perpendicular to the stretch direction such that the cross-sectional area \( (A) \) decreases, which is known as the Poisson effect (Figure 2.13). The stress-strain test can be performed using a Universal Testing Machine (UTM), with values of stress and strain recorded by the instrument to give a continuous stress-strain curve for analysis. The stress-strain curve eventually ends when the material completely ruptures. A typical stress-strain curve containing elastic and plastic regions is used to illustrate some of these concepts (Figure 2.14). Concepts and definitions regarding the stress-strain behaviors of materials are given below.

![Figure 2.13 Poisson effect.](image)

\[ L \]
\[ L_0 \]
\[ A \]
\[ A_0 \]
\[ F \]
\[ \Delta L/2 \]
Figure 2. 14 Typical stress-strain curve.

(A) Elastic region

The material undergoes temporary deformation, and it is able to return to its original form when the applied tensile force is removed.

(B) Plastic region

Permanent deformation occurs and the material does not recover to the original form even though the load is removed.

(C) True stress

True stress \( (\sigma_T) \) is defined as the ratio of applied tensile force \( (F) \) to the actual cross-sectional area of the specimen \( (A) \). The cross-sectional area of the specimen changes over time during the tensile test (Poisson effect).

\[
\sigma_T = \frac{F}{A} \quad (2.6)
\]
(D) Engineering stress

Engineering stress ($\sigma$), also known as the nominal stress, is defined as the ratio of the applied tensile force ($F$) to the original cross-sectional area of the specimen ($A_0$).

$$\sigma = \frac{F}{A_0} \tag{2.7}$$

(E) True strain

True strain ($\varepsilon_T$), is defined as the natural logarithm of the ratio of final length ($L$) to the initial length ($L_0$), of the specimen.

$$\varepsilon_T = \log \frac{L}{L_0} \tag{2.8}$$

(F) Engineering strain

Engineering strain ($\varepsilon$), also known as the nominal strain, is defined as the ratio of the increment of specimen length ($\Delta L$) to the initial length of the specimen ($L_0$).

$$\varepsilon = \frac{\Delta L}{L_0} \tag{2.9}$$

(G) Young’s modulus

Young’s modulus ($E$), also known as the tensile modulus or elastic modulus, describes the elastic properties of a material by relating the stress and strain when the material is uniaxially stretched. It is defined as the ratio of engineering stress to engineering strain in the elastic region, and it is equal to the slope of the straight line through the original point.

$$E = \frac{\sigma}{\varepsilon} = \frac{F/A_0}{\Delta L/L_0} \tag{2.10}$$
(H) Yield point and yield strength

Yield point shows the end of elastic region and the start of plastic region. From this point, the material deforms plastically and permanently. Yield strength is the stress at the yield point.

(I) Ultimate tensile strength

Ultimate tensile strength (UTS) is the maximum stress a material can withstand during a tensile test. Graphically, it is indicated by the highest point of the entire stress-strain curve. UTS is an intensive property determined by the nature of the material, such that it is independent on the size or quantity of the specimen used for test.

(J) Rupture point

Rupture point is the termination of the stress-strain curve, at which the specimen breaks completely.

2.3.3 Tensile performance of electrospun fiber mats

Uniaxial tensile tests have been performed by a number of researchers to study the stress-strain behaviors of electrospun fiber mats. Lu et al.\(^7\) conducted uniaxial tensile test on a rectangular strips of the mat. The sample compressed transversely in the direction that was perpendicular to the stretch direction during elongation. Impressively, the POM fiber mat achieved a strain of 460% prior to rupture. The fiber morphology was investigated at different elongations using a SEM. The fibers aligned randomly initially, and started to arrange their orientations to align along the stretch direction as the sample elongated. Furthermore, the fiber diameters did not change at lower strains when the fibers were randomly arranged, in which case the
fibers primarily shifted relative to each other and did not suffer stretch themselves. However when the fibers mostly aligned along the stretch direction at higher strains, they experienced elongation and the fiber diameters decreased remarkably.

Park et al.\textsuperscript{74} performed cyclic tensile test on electrospun SBS/Ag fiber mats at multiple strains and obtained stress-strain loops with continuously-changed slopes. At lower strains ($\varepsilon \leq 0.4$), the fibers slipped to adjust their alignments to be straightened as a response to the stretch. The local stress in each single fiber was negligible and the fiber mats returned back to their original form when the applied tensile stress was removed. While at higher strains ($\varepsilon \geq 0.6$), straightened fibers suffered irreversible elongation such that the fiber mats ended up with permanent deformation. Shown on the graph, the stress-strain curves for greater strains starting from 0.6 failed to return back to the original point, indicating the existence of residual strains in the fiber mats. Huang et al.\textsuperscript{75} studied the influence of fiber morphology on the mechanical behavior of electrospun gelatin fiber mats. The electrospun fiber mats were fabricated from solutions of different polymer mass that resulted in fibers of different diameter ranges and morphologies. Tensile stress-strain tests showed that the mechanical performance depended upon both the fiber diameter and morphology. Fiber mats composed of finer smooth fibers exhibited higher tensile moduli and ultimate tensile strengths compared to larger fibers due to tighter cohesion between the fibers. However for the case of the smallest fiber diameter, there were beads on the fibers and their existence intrinsically changed the internal structure of the fiber mats. Consequently, fiber cohesion effect was weakened for this case, such that the tensile modulus and ultimate tensile strength were the lowest.
Uniaxial tensile test on a single fiber is still a challenge due to the difficulty of handling the ultra-tiny fiber. As a result, nonwoven media that consist of numerous fibers are conducted for test on macro-scale in order to study the performance of each single fiber on micro-scale. Generally, the elastomeric fibers in a nonwoven medium respond differently according to the stretch degree of the medium. During the initial stage, randomly aligned fibers rearrange their orientations to accommodate to the stretch, and barely experience stress. When most of the fibers are already aligned at high levels of stretch, single fibers start to elongate and reduce in diameters. In conclusion, the stretch process of an elastic nonwoven medium may contain different mechanisms for different stretch stages.

2.4 Filter-related characteristics

2.4.1 Porosity

Porosity ($\varepsilon$) is a measure of void spaces in a porous medium, and is defined as below

$$\varepsilon = \frac{V_{\text{Void}}}{V_{\text{Total}}}$$

(2.11)

where $V_{\text{Void}}$ is the volume of the void spaces and $V_{\text{Total}}$ is the volume of the porous medium. Table 2.4 shows typical porosity values of some porous media.
Table 2. 4 Typical porosity values.

<table>
<thead>
<tr>
<th>Porous medium</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica powder</td>
<td>0.013 - 0.051</td>
</tr>
<tr>
<td>Sandstone</td>
<td>0.05 – 0.3</td>
</tr>
<tr>
<td>Sand</td>
<td>0.25 - 0.5</td>
</tr>
<tr>
<td>Clay</td>
<td>0.4 – 0.7</td>
</tr>
<tr>
<td>Nonwoven filter medium</td>
<td>&gt; 0.9</td>
</tr>
</tbody>
</table>

Porosity can be measured in various ways. Vennat et al.\textsuperscript{76} measured the demineralized dentin porosity and got the pore size distribution by using mercury porosimetry. Deshpande et al.\textsuperscript{77} used image analysis to characterize the porosity in thermal spray coatings and confirmed this method as a straightforward, versatile, reliable and inexpensive way for porosity measurement. Farber et al.\textsuperscript{78} evaluated the porosity of granules by means of X-ray tomography. They also concluded that tomography provides accurate measurement of true pore size distribution while mercury porosimetry does not.

For a randomly packed nonwoven fiber mat, due to geometric similarity arguments, porosity is not a strong function of the fiber diameter but is a function of the fiber length to diameter aspect ratio. As the aspect ratio becomes large, the porosity becomes a constant. Specifically in the aspect of aerosol filtration, void spaces within a filter medium are as important as the solid fibers as they constitute the porous structures through which the continuous phase flows and provide space for the particles to accumulate on the fibers.

2.4.2 Permeability

Air permeability ($k$) is a property of a porous medium that considered as a measure of how easily a fluid passes through the medium (Figure 2.15). It is typically determined via Darcy’s law, which is given by
where $k$ is the permeability, $L$ is the thickness of the filter medium, $Q$ is the air volumetric flow rate, $\mu$ is the dynamic viscosity of air, $A$ is the cross-sectional area of the medium, and $\Delta P$ is the pressure drop. It can also be written in the following form at the continuum scale

$$q = -\frac{k}{\mu} \nabla p$$

where $q$ is the flux and $\nabla p$ is the pressure gradient.

Figure 2. 15 Darcy’s law.

Darcy’s law is valid only for slow, viscous flow and does not account for inertial effects. When dealing with high flow velocities in porous media, inertial effects are significant and should be taken into consideration. In this situation, inertial term is added and the equation turns out to be

$$\nabla p = -\frac{\mu}{k} q - \frac{\rho}{k_1} q^2$$
where $k_1$ is the inertial permeability. Table 2.5 shows typical permeability values for some porous media.

Table 2.5 Typical permeability values.

<table>
<thead>
<tr>
<th>Porous medium</th>
<th>Permeability, m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand and gravel</td>
<td>$10^{-12}$ to $10^{-9}$</td>
</tr>
<tr>
<td>Glass-fiber medium</td>
<td>$10^{-10}$ to $10^{-9}$</td>
</tr>
<tr>
<td>Fine sand</td>
<td>$10^{-16}$ to $10^{-12}$</td>
</tr>
<tr>
<td>Clay</td>
<td>$10^{-16}$ to $10^{-13}$</td>
</tr>
<tr>
<td>Sandstone</td>
<td>$10^{-16}$ to $10^{-11}$</td>
</tr>
<tr>
<td>Granite</td>
<td>$10^{-20}$ to $10^{-18}$</td>
</tr>
</tbody>
</table>

For nonwoven fibrous media, permeability can be either measured experimentally or calculated via simulation if an appropriate model is available. Happel and Kuwabara both developed their well-known models that describe air flow through a fibrous medium based on single fiber theories, to relate the pressure drop to flow velocity and fiber size. The two models considered different boundary conditions and the Kuwabara model was determined to give better results and can be used for predicting permeability when combined with Darcy’s law. Patel et al. conducted experiments to determine the permeability properties of PFMOP electrospun fiber mats of different fiber sizes and mat specific weights. The measured ratios of permeability/mat thickness were found to be strongly dependent upon the specific weight (mass of fiber mat per unit area) than the fiber size. Estimations of permeability/mat thickness calculated from the Kuwabara model were two to three orders of magnitude less than experimental results. This discrepancy was considered due to some model assumptions that were not in good match to the actual experimental conditions, such as medium properties and flow mechanisms.
2.4.3 Pore size

Pores are complex flow paths that are often multiple interconnected channels of varying internal dimensions in a porous medium. The properties of the pores are characterized by pore opening size besides porosity. Taking a porous filter medium that used to remove solid particles from air for example, pores are classified into three types\(^6\) (Figure 2.16): open pores, dead-end pores, and closed pores. Open pores are accessible for the flow such that the flow can penetrate and pass through the medium via these pores. Dead-end pores have an inlet but no outlet and do not contribute to the fluid flow but may contribute volume for retention of captured particles, if the particles can enter these pores. Closed pores are surrounded by solid phase and are not open to the flow, hence their presence does not contribute to the flow or the capture of particles, but may reduce the overall available space for fluid flow and thus restrict the flow and result in a higher pressure drop. Ideally a filter has open pores but no dead-end or closed pores.

![Figure 2.16 Pore structures in a medium: (a) closed pores; (b) dead-end pores; (c) open pores\(^6\).](image-url)
For a nonwoven electrospun fibrous medium, the porosity and pore size are closely related to the amount and packing of the fibers. As electrospun fibers are collected onto a grounded surface, they randomly cross over each other to pack and fill in the void spaces. The porosity and the pore sizes gradually reduce as more fibers accumulate to form a medium, and simultaneously the thickness of the medium increases. Eventually, when enough fibers have layered on top of each other, the fiber structure approaches a packed state that the porosity and pore sizes become constant and further addition of fibers only contributes to increasing the thickness of the medium.

Capillary flow porometry is a robust technique for evaluating the pore properties of a porous medium based on fluid-intrusion method. It contains bubble point test and subsequent tests to determine bubble point pore diameter, mean flow pore diameter, and overall pore diameter distribution. Initially, the porous medium saturated with liquid of low surface tension is placed horizontally in a sealed chamber (Figure 2.17), supported by the steel mesh with pores that much larger than those of the medium. Air pressure is introduced from the bottom into the chamber, attempting to flow through the wetted sample to come out as streams of bubbles. Once the air pressure is sufficiently high, the first and largest air bubble will be generated and its diameter is considered as the bubble point pore diameter. Generally, the smaller the largest pore, the higher the air pressure it requires. The bubble point pressure is inversely proportional to the radius of the pore and also is function of the properties of the wetting liquid. It is calculated using equation\textsuperscript{87}

\begin{equation}
P = \frac{2\gamma \cos \alpha}{r} \quad (2.15)
\end{equation}

where \(P\) is the air pressure, \(\gamma\) is the surface tension of the wetting liquid, \(\alpha\) is the wetting angle, and \(r\) is the pore radius.
As the air pressure continues to increase, on one hand, the air flow preferably passes through the larger pores, on the other hand, smaller pores start to become accessible for the air flow. The diameter of the newly detected pore keeps decreasing as the air flow increases until the smallest accessible pore is found. Beyond this point, further increase of air flow no longer helps discover new pores but increasing the flow amount through the detected pores. During this pore detection process, air flow through pores of a certain diameter range is recorded individually and then accumulated to be the total flow. Specifically, the diameter of the pore at which 50% of the total flow is accumulated is defined as the mean flow pore diameter.

Figure 2. Schematic of capillary flow porometry and bubble point test.

Besides experimental methods, mathematical calculation can also be used to estimate pore size. Fries et al.\textsuperscript{88} modeled the pores in a general porous medium as a bundle of capillary tubes in laminar flow with no-slip boundary and concluded porosity and permeability are related to the effective average pore radius ($R$) as
\[ R = \sqrt{\frac{8k}{\varepsilon}} \]  
\[(2.16)\]

where \( k \) and \( \varepsilon \) are the permeability and porosity of the medium, respectively. With equation 2.16, the effective average pore diameter of a porous medium can be calculated using known values of permeability and porosity.

2.5 Solid aerosol filtration

2.5.1 Single fiber efficiency

A solid aerosol is defined as a colloid of tiny solid particles in air. The solid particles can be separated from the air using different types of filter media, such as nonwoven fibrous media. During the separation process, upstream air flow carrying the solid particles passes through the filter media at a certain flow rate and a number of the particles are captured and loaded into the media. The remaining particles that are not captured penetrate the media to form downstream. The ratio of downstream particle amount to that of the upstream is defined as penetration \( (P) \), which is equivalent to unity subtract the overall filter separation efficiency \( (E) \).

The overall filter separation efficiency \( (E) \) of a fibrous medium is related to the single fiber efficiency \( (E_s) \) as

\[ E = 1 - e^{-E_s L_f d_f h} \]
\[(2.17)\]

where \( E_s \) is the single fiber efficiency, \( L_f \) is the total fiber length, \( d_f \) is the fiber diameter (single fiber theory assumes the fibers have the same diameter), \( h \) is the thickness of the filter medium.
Aerosol particles are captured mainly through three capture mechanisms: interception, inertial impaction, and Brownian diffusion, based on the particle dimension. Generally, smaller particles are more likely to be captured via Brownian diffusion, while larger particles favor the inertial impaction. Each individual capture mechanism corresponds to one type of single fiber efficiency. Assuming that the three capture mechanisms act independently, the total single fiber efficiency \( E_s \) is calculated as

\[
E_s = 1 - (1 - E_R)(1 - E_I)(1 - E_D) \tag{2.18}
\]

where \( E_R \) is the single fiber efficiency by interception, \( E_I \) is the single fiber efficiency by inertial impaction, and \( E_D \) is the single fiber efficiency by Brownian diffusion.

### 2.5.2 Particle capture mechanism

#### 2.5.2.1 Interception

Interception is the predominating mechanism for small particles when interacting with the fibers. The particles follow the air streamlines, and they are not subject to inertial effects, diffusive motion, or gravity. These particles carried by the air flow get captured by the fibers once they get in touch with the fiber surfaces (Figure 2.18). The single fiber efficiency for capture by interception, \( E_R \), is dependent upon the particle size. For the Kuwabara model, \( E_R \) is given by

\[
E_R = \frac{1}{2Ku} \left\{ 2(1 + N_R)\ln(1 + N_R) - (1 + N_R)(1 - c) + (1 + N_R)^{-1} \left( 1 - \frac{c}{2} \right) \right. \\
\left. - \frac{c}{2} (1 + N_R)^3 \right\} \tag{2.19}
\]

\[
Ku = -\frac{1}{2} \ln(c) - 0.75 + c + \frac{c^2}{4} \\
N_R = \frac{d_p}{d_f}
\]
where \( Ku \) is the Kuwabara constant, \( N_R \) is the dimensionless parameter describing capture by interception, \( c \) is the packing fraction, \( d_p \) is the particle diameter, and \( d_f \) is the fiber diameter. For electrospun nanofiber media, aerodynamic slip effect needs to be taken into account, and the equation becomes\(^{90}\)

\[
E_R = \frac{(1 + N_R)^{-1} - (1 + N_R) + 2(1 + 1.996Kn)(1 + N_R)\ln(1 + N_R)}{2 \left[ -0.75 - \frac{1}{2} \ln(c) \right] + 1.996Kn \left[ -0.5 - \ln(c) \right]}
\]

(2.20)

where \( Kn \) is the Knudsen number.

Figure 2. 18 Particle capture by interception mechanism.

2.5.2.2 Inertial impaction

Inertial impaction is the predominate mechanism for particles of large masses and inertias. As a particle of certain inertia carried by the air flow approach a fiber, it fails to timely adjust the abrupt change in streamline direction near the fiber, such that it continues along its original path and then hits the fiber surface (Figure 2.19). For inertial impaction, the dimensionless parameter is actually the Stokes number \((St)\), given by

\[
St = \frac{d_p^2 \rho U}{18 \eta d_f}
\]

(2.21)
where $\rho$ is the particle density, $U$ is the air velocity, and $\eta$ is the coefficient of viscosity.

At low Stokes numbers, the single fiber efficiency by inertial impaction is\textsuperscript{84}

$$E_I = E_R + (2\zeta)^{-2}Js$$  \hspace{1cm} (2.22)

where $J = (29.6 - 28e^{0.62})N_R - 27.5N_R^{2.8}$, with $0.01 < N_R < 0.4$ and $0.0035 < c < 0.111$ for Kuwabara model. At high Stokes numbers\textsuperscript{84},

$$E_I = 1 - \frac{\mu}{St}$$  \hspace{1cm} (2.23)

where $\mu$ is a constant that depends on the flow field.

![Particle capture by inertial impaction mechanism.](image)

Figure 2. 19 Particle capture by inertial impaction mechanism.

2.5.2.3 Brownian diffusion

Brownian diffusion is an efficient capture mechanism for small particles. Air molecules doing Brownian motion collide with the particles, causing these particles to move randomly (Figure 2.20). For this mechanism, Peclet number ($Pe$) that relating convective motion and diffusional motion turns out to be the dimensionless parameter, given by

$$Pe = \frac{2UR}{D}$$  \hspace{1cm} (2.24)
where $R$ is the fiber radius, and $D$ is the coefficient of diffusion. The single fiber efficiency for a simplified model is given by \(^{84}\)

$$E_D = 4.46\zeta^{-1/3}Pe^{-2/3}$$

(2.25)

When aerodynamic slip effect is taken into consideration, specifically for electrospun fibrous media \(^{91}\),

$$E_D = 2.27\zeta^{-1/3}Pe^{-2/3}\left(1 + 0.62\frac{KnPe^{1/3}}{\zeta^{1/3}}\right)$$

(2.26)

Figure 2. 20 Particle capture by Brownian diffusion mechanism.

2.5.3 Aerosol filtration by electrospun filter media

Nonwoven fibrous media fabricated by electrospinning possess high specific surface areas and small pores which are favorable for the tiny particle capture process through interaction mechanisms discussed above. High surface areas generally favor higher capture efficiencies by single fiber mechanisms and the small pores favor capture of smaller particles by straining mechanisms. Research on solid aerosol filtration by nonwoven fibrous media electrospun from various polymer materials have been conducted.

Podgorski et al. \(^{92}\) improved the filtration performance with respect to the most penetrating aerosol particles without greatly increasing the pressure drop by interlayering...
nanofiber and microfiber mats in a multilayer filter medium while maintaining certain mechanical strength. Zhang et al.\textsuperscript{93} and Ahn et al.\textsuperscript{94} electrospun Nylon 6 fibers of diameters lower than 200nm and conducted aerosol filtration tests to evaluate the filter media performance. They concluded that the Nylon 6 fibrous media performed better than common HEPA filters, making them promising candidates for applications requiring HEPA and ULPA filter media. Yun et al.\textsuperscript{95} tested PAN electrospun fibers as a filter medium to capture NaCl nanoparticles from air. Compared to commercial filters, less mass of electrospun filter media was needed to reach the same performance. The authors concluded that the penetration was strongly dependent upon the filter thickness, while the quality factor and single fiber collection efficiency were dependent on the fiber size. Li et al.\textsuperscript{96} prepared double-layered aerosol filter composites by electrospinning PVA nanofibers onto nonwoven PP fabrics to capture NaCl nanoparticles from air and compared their performance to commercialized HEPA filters. The separation efficiency got improved significantly by using the double-layered filter composites compared to only using PP nonwoven media without electrospun PVA nanofibers. Moreover, multilayered nanofiber filters composed of stacked single layered nanofiber mats of different thicknesses were also tested and showed even higher efficiencies exceeding 99.95\% which were comparable to commercialized HEPA filters. Compared the HEPA filters, these filter composites also demonstrated lower pressure drops and higher quality factors.
2.6 Water-in-oil emulsion surface coalescence filtration

2.6.1 Fuel contamination

Water contamination in diesel fuel affects the performance of engines in many ways such as lowering the fuel combustion efficiency, causing erosion on the engine parts, and generating pollutant emissions\cite{97,98}. Generally, water droplets of sizes larger than 100 µm can be removed by gravitational settling since the gravity forces acting on the droplets are sufficient to drive the droplets to settle. However for water droplets smaller than 100 µm, surface forces applied on the droplets by the diesel become significant to compete with the gravity forces such that the droplets suspend in the diesel to form emulsions, which are difficult for mechanical separations\cite{99}. For this specific water droplet size range, superhydrophobic barrier filters function effectively and efficiently through the mechanism of surface coalescence\cite{69,70,100}. Some commercialized fuel filters demonstrate separation efficiencies higher than 95\%\cite{101}.

2.6.2 Barrier filter media

Superhydrophobic barrier filter media take advantage of the surface wettability to facilitate the coalescence of the water droplets on the surface of the filter media. Superhydrophobic surfaces are defined as surfaces with water contact angles greater than 150° and with low hysteresis values\cite{65,102}, and have been used for the water-oil separation\cite{14,100}. Experimentally, superhydrophobic surface facing the upstream dispersions behave as a barrier when the dispersed water droplets try to pass through, and they are retained and collected on the surface to present spherical shapes with very high water contact angles. Coalescence occurs between two adjacent droplets to generate bigger
droplets. Bigger droplets continue to coalesce with more droplets nearby to form even bigger ones. For vertically positioned filter media, once the water droplets achieve certain weights, gravity overcomes the adhesion force applied the droplets by the surface, and drives them to slide downwards to the bottom of the media (Figure 2.21). During the sliding, these droplets keep growing as they further coalesce with other droplets that present on the pathways. The mechanism in addition helps accelerate the removal of the adherent water droplets from the surface and make the superhydrophobic surface fresh for upcoming water droplets.

![Figure 2.21 Surface coalescence of water droplets on a superhydrophobic surface.](image)

The surface barrier filter media perform in a different way compared to depth coalescing filter media that the water droplets are hindered by the surface rather than entering the filter media. Hence the passing of the droplets through the media is greatly lowered and the surface barrier filter media show better performance of higher separation efficiency. The clearance of the water droplets from the surface is a significant factor that affects the filter performance. Pressure drop can raise rapidly when the droplets completely
cover the surface to block the pores for the oil flow at the surface layer. Once the pressure drop achieves a certain level, it pushes the droplets to penetrate the media to enter downstream, causing the failure of the filter media. The water droplets break down into smaller droplets when they pass through the pores, which makes them more difficult to be removed from the oil.

Yang et al.\textsuperscript{103} induced mechanical vibration on superhydrophobic electrospun fiber mats to study the improvement of filter performance. Three configurations of vibration direction versus filter media positioning were selected and compared for separation performance. It turned out that filter media assisted with vibrations consistently yielded higher separation efficiencies than non-vibration cases. Under vibration, water droplets were more likely to get in touch to coalesce. Vibration also favored the sliding of the droplets on the superhydrophobic surface and further clearance of the droplets, helping fresh the surface for upcoming droplet collection.
3.1 Introduction

Electrospun submicron and nano-fibers have been studied and reported in literature for many polymer materials. To our knowledge, electrospun acrylonitrile-butadiene copolymer fibers have not been reported. Acrylonitrile-butadiene rubber (NBR) has strength, elastic, chemical resistance, and hydrophobic properties that make it useful for oil and fuel handling hoses, self-sealing fuel tanks, conveyor belts, seals, and roll goods\textsuperscript{31}. We anticipate that its properties will be useful when formed as submicron fiber mats for applications as filters, protective membranes, and elastic fabrics.

Elastomers are a class of polymers that have elastic properties. Current research trends include the electrospinning and characterization of the elastomeric fibers. Some interesting properties of elastomeric fiber mats include high tensile strength and surface hydrophobicity which make these fabrics excellent candidates for a broad range of applications such as protective clothing\textsuperscript{25}, scaffold\textsuperscript{26}, and insulation\textsuperscript{27}. Fong et al.\textsuperscript{28} found electrospun styrene-butadiene-styrene (SBS) triblock copolymer nanofibers to be elastic and birefringent with diameters around 100nm. Staining tests showed phase separations of styrene and butadiene blocks in the fibers. Hao et al.\textsuperscript{29} spun elastic mats of cis-1,4-polyisoprene smooth fibers and fibers with a bamboo-like morphologies ascribed to polymer chain entanglement and solvent properties. Feng et al.\textsuperscript{30} successfully electrospun
elastic mats of styrene-isoprene-styrene (SIS) copolymer. Stress-strain measurements of the fiber mats revealed that mechanical performances were dependent upon the fiber size.

This chapter discusses the electrospinning of acrylonitrile-butadiene copolymer fibers. Mechanisms of the fabrication process were studied based on the observations of the product morphologies. Characterizations were conducted to provide fundamental properties of the products, including fiber sizes and surface wettabilities. Furthermore, mechanical properties of the electrospun fiber mats were evaluated by conducting a uniaxial stretch on both flat mats and cylindrical yarns rolled from the mats.

3.2 Experimental description

3.2.1 Materials

Acrylonitrile-butadiene copolymer (33% Acrylonitrile, \( \rho = 0.98 \text{ g/cm}^3 \), Scientific Polymer Products, Inc, Ontario, NY) was dissolved in acetone (Sigma Aldrich, St.Louis, MO) to form solutions of five copolymer concentrations by weight as listed in Table 3.1. Inherent to the polymer as supplied are small talc particles some of which are visible in the SEM images described below. All solutions were stirred for 24 hours at room temperature to be homogeneous without further modification. The viscosities of the copolymer solutions were measured using a viscometer (DV2T, Brookfield Engineering Laboratories, Inc., Middleboro, MA).

3.2.2 Electrospinning

Using a typical single-needle electrospinning setup shown by Figure 3.1, the copolymer solution was loaded into a 5 ml syringe and fed by a syringe pump (New Era
Pump Systems, Inc., Farmingdale, NY) at a flow rate of 20 mL/h to a metallic needle. The needle was electrically charged to 20 kV using a high voltage power supply (Gamma High Voltage Research, Ormond Beach, FL) and grounded alumina foil served as the collector located 20cm underneath the needle tip.

Figure 3. 1 Single needle electrospinning setup.

Table 3. 1 Solution and processing parameters for electrospinning.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Concentration (wt %)</th>
<th>Viscosity (cP)</th>
<th>Voltage (kV)</th>
<th>Feeding flow rate (mL/h)</th>
<th>Drop-collector distance (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile-butadiene copolymer</td>
<td>Acetone</td>
<td>1%</td>
<td>0.85</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2%</td>
<td>1.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3%</td>
<td>3.83</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4%</td>
<td>7.81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5%</td>
<td>13.97</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2.3 Characterization

A scanning electron microscope (SEM, JSM5310, JEOL Ltd., Tokyo, Japan) was employed to observe the morphologies of the electrospun fibers. Fiber diameters were measured using the FibraQuant 1.3 software (nanoScaffold Technologies, LLC, Chapel Hill, NC) based on a length-weighted approach\textsuperscript{44}. For each concentration, multiple SEM images containing at least 150 fibers in total were analyzed to determine fiber diameter distribution, average diameter, and standard deviation.

The surface wettabilities of both the raw copolymer material and electrospun fiber mats were characterized by water contact angle (WCA) in air. WCA were measured using a Drop Shape Analyzer (DSA20E, Krüss GmbH, Germany) (Figure 3.2). To evaluate the intrinsic wettability of the raw material, the copolymer solution with concentration of 5 wt% was poured onto a standard glass slide. A thin copolymer film covering the glass slide surface was formed after the solvent evaporated completely. A water drop of 5 \( \mu L \) was placed on the film surface for WCA measurement. The shape of the sessile water drop was determined from the image captured by the DSA lens and further analyzed to determine the WCA. Water drops were measured at five randomly chosen distinct locations on the slide surface to obtain an average value. Similarly, copolymer fibers were electrospun directly onto a glass slide supported by the grounded aluminum foil to generate a thin fiber mat. Corresponding WCA values of the fiber mat were measured using the same experimental procedure.
Fiber mats (square shaped, 6 cm × 6 cm) (Figure 3.3a) of basis weights 10, 20, 30
\( \text{g/m}^2 \) prepared were from solutions of 5 wt\% polymer concentration. Both the flat fiber
mats and the yarns rolled from the mats were tested for tensile strength. The porosities of
the mats and yarns were calculated based on the mass balance using the expression

\[
\text{Porosity} = 1 - \frac{V_{\text{Fiber}}}{V_{\text{Mat/Yarn}}}
\]  

(3.1)

where \( V_{\text{Fiber}} \) and \( V_{\text{Mat/Yarn}} \) are the respective volumes of the fibers and the mat or yarn.

Mat thicknesses were measured using a micrometer at different locations to give
the average thickness used to calculate the mat volume. The diameters of the yarns were
measured at multiple points using a caliper to calculate the cross-sectional areas and
volumes of the yarns. The volumes of the fibers within the mats and yarns were determined
by dividing the mass of the fibers by the polymer density. Details were provided in Table
3.2.
Figure 3. 3 (a) Electrospun fiber mat; (b) Yarns rolled from the fiber mats.

The mats and yarns were uniaxially stretched until failure by the Instron 5567 universal testing system (100 N capacity, Instron, Norwood, MA) (Figure 3.4) to provide the stress-strain curves. Generally, to evaluate the tensile properties of vulcanized thermoset rubbers and thermoplastic elastomers, DIN 53504 S3A microdumbbell specimens (overall length = 45 mm, overall width = 9 mm, neck length = 25 mm, and neck width = 3 mm) are used and ASTM D 412-06a standard test methods are followed. According to the standard methods, the specimens are stretched at a rate of 500 mm/min, which is fast enough to avoid the disentanglement of the elastomer molecules. However for the fiber mats, a lower stretch rate, 10 mm/min, was selected to give the elastic fibers sufficient time to slip and rearrange during stretch for the study of the stress-strain behaviors and overall mechanical performance. The mats were cut to 2 cm in width for tests. The samples were clamped by the upper and lower grips to leave an initial sample length of 20 mm.
Table 3.2 Dimensions and porosity values of the mat and yarn samples of tensile tests.

<table>
<thead>
<tr>
<th>Basis weight (g/m²)</th>
<th>Mat thickness (mm)</th>
<th>Mat cross sectional area (mm²)</th>
<th>Yarn diameter (mm)</th>
<th>Yarn cross sectional area (mm²)</th>
<th>Mat porosity (%)</th>
<th>Yarn porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.043 ± 0.0027</td>
<td>0.85 ± 0.055</td>
<td>1.08 ± 0.026</td>
<td>0.92 ± 0.045</td>
<td>76 ± 1.5</td>
<td>47.8 ± 4.6</td>
</tr>
<tr>
<td>20</td>
<td>0.072 ± 0.0013</td>
<td>1.45 ± 0.025</td>
<td>1.34 ± 0.012</td>
<td>1.42 ± 0.024</td>
<td>71.8 ± 0.5</td>
<td>38.8 ± 1.4</td>
</tr>
<tr>
<td>30</td>
<td>0.092 ± 0.0083</td>
<td>1.84 ± 0.167</td>
<td>1.74 ± 0.015</td>
<td>2.39 ± 0.042</td>
<td>66.6 ± 2.9</td>
<td>33.5 ± 2.4</td>
</tr>
</tbody>
</table>

Figure 3.4 Instron 5567 universal testing system.

3.3 Idealized parallel fiber mats

An idealized parallel fiber model is used to relate the tensile strength of the fiber mats and to account for the void space in the mats and yarns. The fibers contribute to the strength of the mat but the void does not. The model gives a correction for calculating the cross sectional area over which the tensile force is applied when relating the tensile stress
to the strain. The model does not account for fiber-fiber junctions that may contribute to performance.

In this model, the mats and yarns are modeled as bundles of parallel arranged fibers \((\text{quantity } = n)\) of the same lengths \(L\), same diameters \(D_f\), and same cross-sectional areas, \(A_f\), with certain void spaces surrounding them. Figure 3.5 shows two configurations for the flat mats and the yarns.

![Schematics of the idealized fiber formation model](image)

Figure 3.5 Schematics of the idealized fiber formation model (3D view on the left, end view on the right. The flat mats (top) have dimensions of width \(W\), height \(H\), and length \(L\). The yarns (bottom) are characterized by the yarn diameter \(D\), and length \(L\).

Tensile force \(F\) acting on the mat or yarn is applied to the two ends of the fibers. The generated stress is therefore calculated on the basis of the total cross sectional area of the fibers that effectively sustain the tensile force, rather than the cross sectional area of the whole mat/yarn which includes the void areas. From Equation 3.1 the porosities of the mats and yarns are related to the cross sectional areas of the fibers and to the dimensions of the mats and yarns by
\[ \varepsilon_{\text{mat}} = 1 - \frac{V_{\text{fibers}}}{V_{\text{mat}}} = 1 - \frac{nA_f L}{LWH} = 1 - \frac{nA_f}{WH} \]  

(3.2)

\[ \varepsilon_{\text{yarn}} = 1 - \frac{V_{\text{fibers}}}{V_{\text{yarn}}} = 1 - \frac{nA_f L}{L \frac{\pi D^2}{4}} = 1 - \frac{4nA_f}{\pi D^2} \]  

(3.3)

Rearrangements of Equations 3.2 and 3.3 give

\[ nA_f = \begin{cases} 
WH(1 - \varepsilon_{\text{mat}}) \\
\frac{\pi D^2}{4}(1 - \varepsilon_{\text{yarn}}) 
\end{cases} \]  

(3.4)

The total cross-sectional area of the fibers \((A_{fT})\) is the summation of the individual cross-sectional area of each single fiber,

\[ A_{fT} = nA_f \]  

(3.5)

Substituting Equation 3.4 into 3.5 yields the equations for determining the total cross sectional areas of the fibers in terms of the cross sectional areas and porosities of the mats and yarns,

\[ A_{fT} = \begin{cases} 
WH(1 - \varepsilon_{\text{mat}}) = A_{\text{mat}}(1 - \varepsilon_{\text{mat}}) \\
\frac{\pi D^2}{4}(1 - \varepsilon_{\text{yarn}}) = A_{\text{yarn}}(1 - \varepsilon_{\text{yarn}}) 
\end{cases} \]  

(3.6)

The experimentally measured cross sectional areas and porosities of the mats and yarns of different basis weights are given in Table 3.2.

Tensile strength data are normally evaluated by plotting the stress versus the strain where the stress is calculated as the force over the cross sectional area of the sample. For the fiber mats and yarns it is expected that data for different basis weights will plot more consistently when \(A_{fT}\) is used to calculate the stress instead of the cross sectional areas of the mats and yarns.
3.4 Results and discussion

3.4.1 Morphology

Morphologies of the fibers electrospun from solutions of five solution concentrations were evaluated using SEM images. The SEM images showed a mechanistic transition from electrospraying to electrospinning with increase of solution concentration. Electrospraying is a process similar to electrospinning that generally happens when the solution concentration is relatively low\textsuperscript{41}.

In this work, the solution of 1\% concentration was so dilute that the jet divided into numerous independent tiny droplets characteristic of electrospraying instead of a contiguous jet. The solvent evaporated as the tiny droplets travelled to the grounded alumina foil, forming a dry copolymer thin film (Figure 3.6a). The process started to change to electrospinning for solutions of 2\% polymer concentration as fine fibers emerged, shown in Figure 3.6b. However the fibers contained polymer droplets as well as beads within the fibers, suggesting that the spinning parameters were still close to electrospray conditions and the electrospray mechanism may have contributed to a significant part of the product.

When the polymer concentration was increased to 3\%, the fraction of fibers in the product increased abruptly (Figure 3.6c). The concentrations of deposited polymer droplets and polymer fibers with beads was significantly less compared to the 2\% solution suggesting the electrospinning mechanism dominated the process. Figure 3.6d shows the presence of fewer beads for the 4\% solution than for the 3\% solution. The 5\% solution product shown in Figure 3.6e had smooth fibers with no beads. This indicated the minimum
solution concentration of 5% provided homogeneous fiber mats via the electrospinning mechanism alone.

The formation of drops and beads on fibers are dependent on the fluid properties, particularly the viscosity and surface tension. For polymer-solvent solution systems, the viscosity of the solution is highly dependent upon the weight concentration of the polymer. Both concentration and the consequent viscosity significantly determine whether electrospraying or electrospinning mechanism takes place\textsuperscript{105,106}. The viscosity of the prepared acrylonitrile-butadiene solution increased monotonously with the polymer concentration, as listed in Table 3.1. At relatively low levels of polymer concentration, solution viscosities were low due to the lack of high degree of chain entanglement of the polymer molecules. As a strong voltage was applied to the pendent solution drop, the drop broke down into tiny drops that deposited onto the grounded collector to form a polymer film after the solvent evaporated, showing the occurrence of electrospraying (Figure 3.6a). At higher polymer concentrations molecule chain entanglement increased the viscosity but also caused the molecules to stay connected as the jet launched causing the jet to be continuous instead of forming separate drops. The jet elongated as it traveled towards the collector due to the charge effect, and simultaneously the solvent evaporated, generating dry fibers (Figure 3.6c-e). Moreover, a transition mechanism occurred as a combination of electrospraying and electrospinning, in which case the product was composed of both droplets and fibers (Figure 3.6b).
Figure 3. 6 SEM images of the products prepared from solutions of different concentrations. 

(a) 1% polymer concentration, (b) 2%, (c) 3%, (d) 4%, and (e) 5%.
3.4.2 Fiber diameter

SEM images of the fibers spun from 3% - 5% polymer concentrations were analyzed for the fiber diameter distributions shown in Figure 3.7. For each case, at least 150 fibers were measured to insure adequate sampling of the fibers. Polymer beads that appeared in samples were excluded so that only fibers were taken into consideration in the measurements.

Fiber diameter ranges and average fiber diameters are listed in Table 3.3. Solution concentrations strongly affected the spinning process and consequently the fiber sizes. In this work, concentration was the only parameter varied, with all other conditions fixed. As the concentration increased, the bell-shaped distribution histogram became broader and shifted towards larger fiber diameters. Simultaneously, both the average and standard deviation of the fiber diameters increased. The average fiber diameters for all cases were less than 1µm, showing that the majority of the fibers were in the submicron scale.

<table>
<thead>
<tr>
<th>Concentration (wt %)</th>
<th>Fiber diameter range (nm)</th>
<th>Average fiber diameter (nm)</th>
<th>WCA (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>——</td>
<td>——</td>
<td>Water spreads</td>
</tr>
<tr>
<td>2%</td>
<td>——</td>
<td>——</td>
<td>Water spreads</td>
</tr>
<tr>
<td>3%</td>
<td>252 - 1384</td>
<td>718 ± 175</td>
<td>138.1 ± 1.43</td>
</tr>
<tr>
<td>4%</td>
<td>281 - 1789</td>
<td>840 ± 230</td>
<td>136.6 ± 1.01</td>
</tr>
<tr>
<td>5%</td>
<td>335 - 2183</td>
<td>964 ± 303</td>
<td>133.5 ± 1.24</td>
</tr>
<tr>
<td>Copolymer film</td>
<td>——</td>
<td>——</td>
<td>94.3 ± 1.18</td>
</tr>
</tbody>
</table>

Table 3.3 Fiber diameters and water contact angle values. The ± values represent one standard deviation of the fiber diameter distributions in Figure 3.7 and one standard deviation of at least five replicate measurements of the WCA. WCA was not measured for the 1% and 2% solutions because the water spread on the fiber mats.
3.4.3 Wettability

WCA were measured for mats fabricated from the polymer solutions that formed fibers. For the cases of 1% and 2% concentrations, a homogeneous film/fiber layer completely covering the glass slide could not be generated. The water drop was partially in contact with the surface of the glass slide, which affected the position of the drop. Consequently, the water drop sank and contacted the glass slide, then spread between the fiber layer and the glass slide surface. Therefore the WCA was not measured for these concentrations.
For higher concentration solutions the WCA could be measured. Example images of sessile water drops sitting on the copolymer film or fiber mat surfaces are shown in Figures 3.8. The sessile water drop on the film presented hemispherical shape. The average WCA of the film surface exceeded 90°, indicating that the raw material was intrinsically hydrophobic interpreted according to Wenzel model\textsuperscript{71}. Different than the copolymer film, the fiber mats were porous. The pores, being much smaller than the drops, resisted penetration of the liquid of the drop due to surface tension and hence were filled with air and not filled with liquid from the drop. This mechanism is described by the Cassie-Baxter model\textsuperscript{72} as an explanation for the increase in WCA.

The average contact angles are listed in Table 3.3 for the film and electrospun mats. The surfaces of the fiber mats were found to be hydrophobic with contact angles greater than 130°. The decrease in WCA with increase in solution polymer concentration from 3% to 5% corresponded with the increase in fiber diameters and decrease in bead concentrations in the mats. The differences in bead concentrations and fiber sizes affected the mat structural geometry, including pore sizes. The structural geometry effects are commonly referred to as surface roughness effects. It is possible that the separation of the co-polymer materials occurred as the materials were spun into fibers and beads. This later could affect the WCA but polymer separation was not directly observed in the samples that were evaluated. For the electrospun fiber mats, as the solution concentration increased, the mats turned more homogeneous, reducing the irregular beaded structures. As a consequence, the surface roughness effectively reduced corresponding to a decrease of the WCA.
3.4.4 Stress-strain tests

Uniaxial tensile tests on electrospun fiber mats have been performed by a number of researchers in similar ways. In this work, the flat fiber mats presented a series of response as the stretch proceeded (Figure 3.9). Initially, the mats elongated along the stretch direction, and the mats shrank along the direction perpendicular to the stretch direction which was attributed to the nature of elastic materials. The shrinkage phenomenon became more apparent at larger strains, especially at the middle region of the mats (Figure 3.9b). As the stretch continued and reached certain levels, certain regions of
the mats turned thinner and started to break at multiple locations within those regions (Figure 3.9c). The fibers among the rupture regions continuously shifted their orientations and further broke to accommodate to the on-going stretch (Figure 3.9d) such that the mats gradually ruptured. At the very end of the stretch process, it was observed that single fibers could elongate to remarkable extents (Figure 3.9e). Eventually the single fibers broke and the mats completely ruptured (Figure 3.9f).

Figure 3.9 A mat at different uniaxial stretch stages: (a) starting point; (b) stretch in progress (shrinkage phenomenon indicated by arrows); (c) mat starting to rupture
(indicated by the box); (d) continued mat rupture; (e) a single fiber (indicated by arrows) stretched before complete rupture; (f) complete rupture.

Example stress-strain curves for the samples of different basis weights are shown in Figure 3.10. The curves have ascending and descending regions. The curves are nearly on top of each other, from 0 to 1.2% strain, indicating that the stress-strain relation is largely independent of the mass of fibers and the mat porosity for this range of strain, as assumed in the idealized parallel fiber model. Interestingly, there are stress oscillations distributed on the curves mainly in the ascending region. The fiber mats were composed of randomly aligned fibers. As the mats were stretched, the fibers adjusted their positions and orientations (referred as ‘fiber slippage’) in response to the applied tensile force, and simultaneously, the individual fibers that aligned in the stretch direction were elongated. Significant fiber slippage may have occurred when many fibers simultaneously re-oriented, leading to the stress oscillations, either enhancing or weakening the mat strength. Moreover, the mats characteristically showed stress-strain curves with continuously declined slopes in the ascending region, rather than typical elastic and plastic regions.

The acrylonitrile-butadiene copolymer used to fabricate the fiber mats is an elastomeric polymer. At the microscale the molecules of viscoelastic polymers are known to migrate and rearrange relative to each other to accompany the applied stress, which reflects the viscous aspect of the property of viscoelasticity. For the elastomeric fibers, the degree of the migration and rearrangement of the polymer molecules and chains within the fibers increased as more fibers shifted to re-orient in the stretch direction and then experienced elongation, which caused relaxation of the stress on individual fibers. This
caused the rate of increase of stress relative to strain to slow, as shown by the decreasing slope of the stress-strain plot.

The fibers started to break when the elongations of the mats reached certain limits, at which the slopes of the stress-strain curves became zero or negative. In this region, the stress dropped rapidly with further increase in strain more fibers broke until the last single fiber ruptured. Eventually, the mats were completely ruptured and the curves ended.

Figure 3.10 Stress-strain curves for mats of different basis weights. There are stress oscillations distributed on the curves, primarily in the ascending region.

Yarns rolled from the flat fiber mats were also tested for stress-strain in the uniaxial tensile tests following the same experimental procedure. Example photos in Figure 3.11 show a yarn at different strains. The stress-strain curves of the yarns show high similarity compared to those of the mats by containing the ascending and descending regions (Figure 3.12). However for the yarns, the decrease in stress-strain slope showed abrupt drops in the stress curve but not the oscillations as did the fiber mat data in Figure 3.10, suggesting that
the mechanism of fiber slippage and may be different in the yarns than in the flat mats. According to Table 3.2, the porosities of the yarns were consistently lower than those of the mats for all the three basis weights, indicating the fibers within the yarns were packed more densely and hence the number of fiber-fiber contacts may be larger. It was also observed that the adjacent layers of fibers during rolling of the yarns stuck to each other. As a result of the above two factors, the mobility of the fibers relative to each other were more restricted in the yarns than the mats. Therefore, the effect of fiber slippage for the yarns may be reduced compared to the flat mats.

The increased fiber-fiber contacts give more strength to the yarns and restricts the movement of fibers during slippage. This may result in few fibers slipping simultaneously and hence causing a rapid drop in the stress-strain curve but not the over-shoot in strength of the oscillations in Figure 3.10. As the fibers took up the slack in the movement the stress resumed ascending after the sudden drops. The curves entered the descending region when critical portions of fibers broke, and the yarns gradually ruptured.
Figure 3. 11 A yarn at different uniaxial stretch stages: (a) starting point; (b) stretch in progress; (c) some fibers broken and a few fibers stretched further before complete rupture; (d) a single fiber (indicated by arrows) stretched before complete rupture; (e) complete rupture.

Figure 3. 12 Stress-strain curves for yarns of different basis weights. There are stress drops distributed on the curves in the ascending region.
Table 3.4 summarizes the tensile stress at maximum load (apex of the curve) for the mats and yarns of different basis weights. For both the mats and yarns, the maximum tensile strengths for different basis weights were close, indicating that the maximum tensile strength was independent on the amount of the fibers. Generally, maximum tensile strength is an intensive property of a certain value determined by the nature of the material. According to the idealized parallel fiber model, the maximum tensile strength is constant regardless the quantity of the fibers. Whereas in the actual fiber mats and yarns, the fibers were randomly aligned to generate more complicated formation compared to the idealized model. Consequently, there appeared small variations in the maximum tensile strengths for different basis weights. It was observed that the maximum tensile strengths for the yarns were 10 to 40% larger than those for the flat mats. When a yarn was rolled from a flat mat, the fibers wrapped around the central axis of the yarns, intrinsically formed a different fibrous structure than that of the mat, and adjacent layers of fibers in the yarn held together. As a result, the yarns were mechanically stronger as indicated by the greater maximum tensile strengths compared to the flat mats.

Table 3. 4 Results of the uniaxial tensile stress-strain tests. The ± values represent one standard deviation of at least three replicate measurements.

<table>
<thead>
<tr>
<th>Basis weight (g/m²)</th>
<th>Maximum tensile stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mat</td>
</tr>
<tr>
<td>10</td>
<td>0.48 ± 0.04</td>
</tr>
<tr>
<td>20</td>
<td>0.48 ± 0.02</td>
</tr>
<tr>
<td>30</td>
<td>0.51 ± 0.02</td>
</tr>
</tbody>
</table>
3.5 Conclusion

Electrospun acrylonitrile-butadiene copolymer fibers were produced. Electrospray occurred when the solution concentration was low. The solution became more spinnable into fibers as the concentration increased, and specifically, bead-free smooth fibers were generated at 5% concentration. As the solution concentration increased, both fiber diameter range and average diameter increased. Furthermore, raw copolymer material and electrospun fiber mats were characterized for their surface wettabilities. The copolymer material was hydrophobic intrinsically with a WCA near 90 deg. The electrospun fiber mats had WCA of about 130 deg due to surface roughness. Especially for the electrospun fiber mats, as the solution concentration increased, the mats turned more homogeneous, reducing the irregular beaded structures. As a consequence, the surface roughness effectively reduced corresponding to a decrease of the WCA. Uniaxial tensile tests on the mats and yarns gave similar stress-strain curves with ascending and descending regions. An idealized parallel fiber model was used to account for effects of porosity and mass of fibers. The resulting maximum tensile strengths of the fibers in the mats and yarns were similar for different basis weights, but variations occurred as the actual fiber formation was more complex than that of the model. Moreover, fibers in the yarns presented stronger mechanical strengths compared to the flat mats due to increased fiber-fiber contacts.
CHAPTER IV

PERMEABILITY EVALUATION OF STRETCHED ELECTROSPUN ELASTIC FIBER MATS SUBJECT TO AIR FLOW

4.1 Introduction

Elastic fiber mats are interesting since they deform (stretch) when stressed. When air passes through an elastic porous fiber mat the pressure drop causes the mat to increase surface area due to the stress. When stretched, the pores are expected to change size and to have an effect on the filter performance. The electrospun fibers also deform by increasing length and decreasing diameter. But the diameters of the fibers are so small compared to the mat size that the change in the fiber diameters is not expected to have a significant effect on the filter performance.

This chapter discusses the evaluation of permeability property of stretched electrospun elastic fiber mats subject to air flow. The fiber mats were placed upon a circular opening for air flow to pass through, making them to stretch into paraboloid shapes. The profile curves of the stretched fiber mats were observed by means of a customized transparent Plexiglas holder, and compared to the curves of the equation that derived from mathematical modelling. Permeabilities of the fiber mats under different stretched conditions were evaluated, and changes in permeability were concluded to be related to the pore properties.
4.2 Experimental description

4.2.1 Materials

Acrylonitrile-butadiene was dissolved in acetone to prepare solutions with copolymer concentrations of 5% by weight. The solutions were stirred for 24 hours at room temperature to be homogeneously mixed and then used for electrospinning directly without further modifications.

4.2.2 Electrospinning

The fiber mats were electrospun using the single needle electrospinning setup shown in Figure 3.1. The copolymer solution was fed at a flow rate of 20 mL/hr. A potential difference of 20 kV was generated by a high voltage power supply. The aluminum foil served as the collector was square-shaped (6 cm × 6 cm) and located 20 cm below the needle tip. Fiber mats of three basis weights: 15, 30, 45 g/m² were produced and tested. Details are listed in Table 4.1

<table>
<thead>
<tr>
<th>Table 4.1 Electrospinning conditions and fiber diameter data.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer</strong></td>
</tr>
<tr>
<td>Solvent</td>
</tr>
<tr>
<td>Concentration (wt %)</td>
</tr>
<tr>
<td>Voltage (kV)</td>
</tr>
<tr>
<td>Feeding flow rate (mL/hr)</td>
</tr>
<tr>
<td>Needle tip – to – collector distance (cm)</td>
</tr>
<tr>
<td>Fiber diameter range (nm)</td>
</tr>
<tr>
<td>Average fiber diameter (nm)</td>
</tr>
<tr>
<td>Standard deviation (nm)</td>
</tr>
</tbody>
</table>
4.2.3 Air permeability test

Experiments were performed to evaluate the permeabilities of the electrospun fiber mats of three basis weights using the Frazier air permeability tester (Frazier Precision Instrument Company, Inc., MD, USA) (Figure 4.1). The fiber mat was placed upon the circular opening of a transparent Plexiglas stage, and then the whole part was sealed using the upper and lower plates (Figure 4.2). As air flow of certain flow rates passed through, the fiber mat expanded downwards and presented bowl shapes, resulting in corresponding pressure drops and expanding depths (Figure 4.3). A series of flow rate and pressure drop combinations that leaded to different degrees of stretch was chosen, and consequent expanding depths were recorded. With all the parameters needed available, permeabilities of fiber mats under different stretch conditions were evaluated and compared.

Figure 4.1 Frazier Air Permeability Tester.
4.2.4 Transparent Plexiglas holder design

A custom-made transparent Plexiglas stage was machined to observe the stretch of the fiber mat as well as measure the expanding depths. A Plexiglas block (8 cm × 8 cm × 2.3 cm) was drilled a circular hole of 5 cm in diameter at the center (Figure 4.4). The inner curved surface and front side faces were polished to be sufficiently clear for observation. The sharp edge of the opening resulting from machining was rounded to be smooth (Figure
4.5) in case the fiber mats get cut and broken during expansion. On the front face, scale marks with a total range of 20 mm were carved starting from the upper horizontal edge downwards along the perpendicular bisector using a caliper. In this way, the stretched fiber mats were observed and the expanding depths were measured according to the scale marks.

Figure 4. 4 Transparent Plexiglas stage with scale marks on the front face.

Figure 4. 5 Polished inner surface and rounded edge.
4.3 Mathematical modeling

Mathematical modeling work (Appendix A) was done to study the profiles of the expanding fiber mats theoretically. Given the coordinates shown in Figure A4 in Appendix A, modeling results showed that the profiles (positive half where \( r > 0 \), axially symmetric for negative half) can be described by the equation:

\[
z = \left( r + \frac{1}{2k} \right) \sqrt{k^2 r^2 + kr} - \frac{1}{4k} \ln \left( 2kr + 2\sqrt{k^2 r^2 + kr} + 1 \right) + \frac{1}{4k} \ln \left( 2kR + 2\sqrt{k^2 R^2 + kR} + 1 \right) - \left( R + \frac{1}{2k} \right) \sqrt{k^2 R^2 + kR}
\]

(4.1)

where \( \Delta P \) is the pressure drop across the medium, \( E \) is the Young’s modulus of the fiber mat, \( L \) is the mat thickness, and \( R \) is the opening radius. The derived equation curves were compared to true fiber mat profiles to check if the modeling results describe the true profiles correctly.

An optical issue arose when doing the derived curve-true profile comparison. Due to the curvature effect caused by the inner curved surface of the hole, the object visually observed through the transparent front face was not the true shape of the object, such that the profiles of the expanding fiber mats observed got deformed compared to the true profiles. To verify the occurrence of this phenomenon, a paper card drawn with a set of curves of the derived equation passing two same endpoints was positioned parallel to the front face and then inserted into the hole along the central plane (Figure 4.6). The curves observed got squeezed obviously compared to true curves, especially the two sides with strongest curvature effect. Even though the observation was distorted in horizontal direction, the perpendicular bisector of the front face was not affected as there was no
curvature effect along this line with respect to the paper card. As a consequence, the depths of the curves read according to the scale marks were the actual depths. Analogically, the expanding depths of the fiber mats were measured in the same way directly and further used for permeability determinations.

Figure 4.6 Observation distortion caused by the curvature effect of the inner curved surface. The object observed got squeezed in horizontal direction.

4.4 Results and discussion

In the Frazier air permeability experiments, the fiber mats expanded remarkably to present bowl shapes as air flow passed through. Series of photos of the stretched fiber mat of different basis weights are shown in Figure 4.7, 4.8, and 4.9. Expanding depths \( (H) \) at different pressure drops \( (\Delta P) \) are listed in Table 4.2. The reading accuracy was 0.5 mm. For all the three basis weights, the fiber mats expanded more and turned out greater expanding depths as the air flow increased (Figure 4.10). Fiber mats of higher basis weights
contained more fibers such that they were denser and owned higher strengths. Consequently, they expanded less compared to fiber mats of lower basis weights as denser fiber mats held higher pressures and this resulted in slighter expansions.

Figure 4. 7 Fiber mat (15 g/m²) stretch at different pressure drop conditions: (a) 12.5 Pa; (b) 25 Pa; (c) 50 Pa; (d) 75 Pa; (e) 100 Pa; (f) 125 Pa; (g) 150 Pa; (h) 175 Pa; (i) 200 Pa.
Figure 4. 8 Fiber mat (30g/m²) stretch at different pressure drop conditions: (a) 12.5 Pa; (b) 25 Pa; (c) 50 Pa; (d) 75 Pa; (e) 100 Pa; (f) 125 Pa; (g) 150 Pa; (h) 175 Pa; (i) 200 Pa.

Figure 4. 9 Fiber mat (30g/m²) stretch at different pressure drop conditions: (a) 12.5 Pa; (b) 25 Pa; (c) 50 Pa; (d) 75 Pa; (e) 100 Pa; (f) 125 Pa; (g) 150 Pa; (h) 175 Pa; (i) 200 Pa.
Table 4. 2 Fiber mat expanding depths at different pressure drops for different basis weights.

<table>
<thead>
<tr>
<th>Basis weight, g/m²</th>
<th>∆P, Pa</th>
<th>12.5</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>125</th>
<th>150</th>
<th>175</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>H, mm</td>
<td>4.7</td>
<td>5.8</td>
<td>7.3</td>
<td>8.8</td>
<td>10.2</td>
<td>11.8</td>
<td>13.8</td>
<td>15.3</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>Standard deviation, mm</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.6</td>
<td>0.8</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>30</td>
<td>H, mm</td>
<td>3.2</td>
<td>4.2</td>
<td>5.5</td>
<td>6.8</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>10.8</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>Standard deviation, mm</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>45</td>
<td>H, mm</td>
<td>2.3</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Standard deviation, mm</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 4. 10 Expanding depth (H) versus Pressure drop (∆P) for different basis weights.

Curves of the derived equation and parabolas with three intercepts (-5 mm, -10 mm, and -15 mm) that pass through the same end points (-25 mm, 0) and (25 mm, 0) were drawn on two paper cards of same size (Figure 4.11). Visually, the equation curves and the
parabolas were similar while the later were more smooth. The two paper cards were inserted into the holder hole and then compared to the observed fiber mat profiles that also pass through the same end points and nadirs (Figure 4.12). For all the three sets of curves, multiple points with certain r-coordinates were selected, with corresponding z-coordinates read according to the scales. The coordinate points were plot in Figure 4.13. Complete coordinates of the points are listed in Appendix B. For points of same r-coordinates, differences between the z -coordinates of the equation curves/parabolas and the profiles were considered as the errors. The sums of squares ($SS$) for error were calculated and compared to evaluate which kind of curve described the observed profiles more accurately (Table 4.3).

Figure 4. 11 (a) Curves of derived equation, and (b) parabolas drawn on two separate paper cards.
Figure 4. 12 Observations of distorted true profiles, equation curves, and parabolas with different intercepts through the transparent stage.

Figure 4. 13 Coordinate points of the observed distorted profile curves with different intercepts.
Table 4. 3 Data summary of Sums of squares for error.

<table>
<thead>
<tr>
<th>Intercept</th>
<th>SS, Equation curve</th>
<th>SS, Parabola</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5 mm</td>
<td>16.08</td>
<td>5.68</td>
</tr>
<tr>
<td>-10 mm</td>
<td>15.38</td>
<td>6.08</td>
</tr>
<tr>
<td>-15 mm</td>
<td>75.94</td>
<td>2.78</td>
</tr>
</tbody>
</table>

For the cases of two greater intercepts, the equation curves roughly described the observed profiles with moderate SS values (16.08 and 15.38). However, the SS value (75.94) for the lowest intercept case was so large that it suggested the equation curve points highly deviated from the observed profile points, and therefore it was not a reliable approximation of the observed profile. On the other hand, the SS values (5.68, 6.08, and 2.78) for the parabolas were much smaller for all the cases, indicating that the parabolas represented the observed profiles more accurately. By examining the plots in Figure 4.13, it was also found that the parabola points located closer to the observed profile points compared to the equation curve points, graphically showing that the parabolas were better approximations. Based on the above analysis regarding the curves under curvature effect, it is reasonably concluded that the true fiber mat profiles can be represented by appropriate parabolas. The parabolas were revolutionarily integrated with respect to vertical axis to calculate for the surface areas of the generated paraboloids, which were considered as the surface areas of the expanding fiber mats for permeability calculations. The pressure drops across the fiber mats were controlled at low levels (lower than 0.5 inches of water) to ensure the laminar flow pattern of the air flow. Expanding depths at pressure drop values that were not directly provided in Table 4.2 were calculated using the equations of the trendlines that pass through the known points. The points were fitted to second-order polynomials with all R-squared values approaching 1 (Table 4.4).
Table 4. Fitted equations for calculating expanding depth ($H$) values given pressure drops for different basis weights.

<table>
<thead>
<tr>
<th>Basis weight, g/m²</th>
<th>Fitted equation</th>
<th>$R$-squared value</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>$H = -2 \times 10^{-5} \Delta P^2 + 0.0662\Delta P + 3.9843$</td>
<td>0.9973</td>
</tr>
<tr>
<td>30</td>
<td>$H = -9 \times 10^{-5} \Delta P^2 + 0.064\Delta P + 2.509$</td>
<td>0.9994</td>
</tr>
<tr>
<td>45</td>
<td>$H = -8 \times 10^{-6} \Delta P^2 + 0.042\Delta P + 1.885$</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

Permeabilities of the fiber mats were evaluated by Darcy’s law:

$$\frac{k}{L} = \frac{Q\mu}{A\Delta P}$$ (4.2)

where $k$ is the permeability, $L$ is the thickness of the filter medium, $Q$ is the air volumetric flow rate, $\mu$ is the dynamic viscosity of air, $A$ is the cross-sectional area of the medium, and $\Delta P$ is the pressure drop. Here consider two basic cases to better understand the permeability properties of porous media: packed bed and fluidized bed. A typical packed bed can be an empty cylinder of certain volume filled with packing materials (e.g., spherical particles), generating internal porous structures (Figure 4.14). Pressure drops occur as fluids of certain flow rates pass through the media, which are correlated by Darcy’s law. Blake-Kozeny equation\textsuperscript{110,111} and Burke-Plummer equation\textsuperscript{112} are used to describe the performance of a packed bed for laminar flow ($Re < 1$) and turbulent flow ($Re > 1000$), respectively.

Ergun\textsuperscript{113} comprehensively unified the two separate equations in one that covers a continuous range of Reynolds number including the transition region ($1 < Re < 1000$). The Ergun equation is in good agreement with experimental data for a wide flow range. It can be written in the following specific form indicating pressure drop as function of flow rate.
\[
\Delta P = \frac{150\mu L(1 - \varepsilon)^2}{D_p^2 \varepsilon^3 A} Q + \frac{1.75\rho L(1 - \varepsilon)}{D_p \varepsilon^3 A^2} Q^2
\] (4.3)

where \( \Delta P \) is the pressure drop across the bed, \( \mu \) is the dynamic viscosity of the fluid, \( L \) is the bed length, \( \varepsilon \) is the porosity of the bed, \( \rho \) is the fluid density, \( D_p \) is the effective particle diameter, \( A \) is the cross-sectional area of the bed, and \( Q \) is the volumetric flow rate of the fluid. For a certain packed bed as well as fluid type, dimensional and physical parameters are fixed, such that the coefficients of the two flow rate terms are constant. In the range of low fluid flow rate (low Reynolds number, laminar flow), second-order term is negligible compared to the linear term. In this case, Ergun equation reduces to Blake-Kozeny equation, and the pressure drop is proportional to the flow rate, which turns out that ratio \( k/L \) is constant regardless the increase of flow rate referring to Darcy’s law (Figure 4.15). Whereas for high levels of flow rate (high Reynolds number, turbulent flow), second-order term becomes more dominant over the linear term, making the linear term negligible. Ergun equation turns into Burke-Plummer equation, in which case pressure drop increases more quickly with the growth of flow rate, and therefore ratio \( k/L \) starts to decrease as flow rate further increases (Figure 4.15). Moreover, as the bed length is constant, it is concluded that the permeability of the bed keeps constant initially and then gradually decreases with the increase of flow rate.
A packed bed becomes a fluidized bed once the filled particles that are no longer restricted to a certain volume and start to behave like fluid when driven by the fluid flow that passes through upwards from the bottom (Figure 4.16). The fluid requires certain flow rate to fluidize the particles, known as the minimum fluidization\textsuperscript{114}. Prior to fluidization, the fluidized bed acts exactly as a packed bed with same permeability-related behaviors. Once the particles are completely fluidized and the bed operates at steady state, a force balance regarding the particles can be derived as following:
\[ \text{Gravity} - \text{Buoyant force} = \text{Pressure drop} \times \text{Area} \] \quad (4.4)

\[ F_{\text{Gravity}} - F_{\text{Buoyancy}} = (P_0 - P_L)A \] \quad (4.5)

\[ \rho_p (1 - \varepsilon_f)AL_fg - \rho (1 - \varepsilon_f)AL_fg = \Delta PA \] \quad (4.6)

\[ \Delta P = (\rho_p - \rho)(1 - \varepsilon_f)L_fg \] \quad (4.7)

Substituting Equation 4.7 into 4.3 yields the modified Ergun equation for fluidized bed

\[ (\rho_p - \rho)g = \frac{150\mu(1 - \varepsilon_f)}{D_p^2 \varepsilon^3 A} Q + \frac{1.75\rho}{D_p \varepsilon^3 A^2} Q^2 \] \quad (4.8)

where \( \varepsilon_f \) is the porosity of the fluidized bed, \( g \) is the gravitational acceleration. The total mass of the fluidized particles is constant given by

\[ m_{\text{particles}} = \rho_p AL_f (1 - \varepsilon_f) \] \quad (4.9)

The density of the fluid phase is considered either constant (for liquids) or negligible (for gases compared to solid particles) such that the right hand side of Equation 4.7 is constant for a fluidized bed under steady state operation. Consequently, the generated pressure drop across the bed holds constant, which means further increase in fluid flow rate will only result in the increase in the bed height. Applying Darcy’s law to this situation shows that ratio \( k/L \) increases proportionally as fluid flow rate increases (Figure 4.17).
Figure 4. Performance of pressure drop and permeability/length at different flow rates for a fluidized bed. The filled particles start to fluidize at a certain flow rate.

In this work, values of ratio $k/L$ instead of $k$ were determined in order to investigate the relevant permeability properties as it was difficult to accurately measure the thickness of the ultrathin fiber mats, particularly when the fiber mats were stretched. Plot of permeability/thickness versus flow rate is shown in Figure 4.18.
For all the three basis weights, the pressure drop across the fiber mat as well as the expanding depth increased as the air flow increased. For each basis weight, as the air flow increased, the $k/L$ ratio increased initially and then reached plateau. The increase of the ratios demonstrated the increase of the permeabilities assuming the change of the fiber mat thickness was negligible during expansion. The electrospun fiber mats were essentially porous media with irregular pores resulting from the entanglement and crossing of the fibers. As the fiber mat expanded, the elastic fibers at the central part of the mat stretched and shifted to move farther from each other such that the pores got enlarged. The pore enlargement directly made it easier for the air flow to pass through and therefore led to greater permeabilities. When the air volumetric flow rate reached certain high values to generate remarkable fiber mat expansions, the pores distributed at the central part continued to expand. While on the other hand, pores in the section of the fiber mat that close to the circular margin started to elongate and turn into shuttle shape as one end of the marginal fiber mat ring was fixed to the holder and the other end was free to move such
that it stretched similarly to uniaxial stretch, different than the unconstrained stretch at the central portion. In this way, the open areas of the pores diminished due to the shape change as the stretch proceeded. In consideration of the pore narrowing in the marginal region and the pore expansion in the central region that happened simultaneously, the total area of the pores open for air flow held constant afterwards. Therefore, it turned out that the ratios as well as true permeabilities became constant and no longer changed with further increase of flow rate.

It was also found that the permeability/thickness values of the fiber mats of 15 g/m² were consistently greater than those of higher basis weights. During the fiber collection process, the fibers tended to pack uniformly spanning across the collection area as they accumulated. The electrospun fibers accumulated on the aluminum foil to form a fiber mat of certain thickness. For a certain area of collector, as the basis weight increased, more fibers were collected and crossed to generate smaller pores, which directly yielded lower permeability values. However, once the packing of the collected fibers reached the limit for that specific thickness, further accumulated fibers started to pile up in height. In this condition, the sizes of the pores among the fiber mat somehow achieved minimum and no longer decreased with further fiber accumulation. Based on this analysis, pore sizes reached minimum starting from 30 g/m² such that the permeabilities for 30 and 45 g/m² were close while smaller than those for 15 g/m².

4.5 Conclusion

Acrylonitrile-butadiene copolymer fibers of 960 nm in diameter were electrospun to prepare elastic fiber mats of different basis weights. In the air permeability test
experiments, the fiber mats stretched and expanded to show bowl shapes as air passed across. According to the analysis of sum of squares for error, the profiles of the expanding fiber mats were found to be more similar to parabolas than the curves of the equation that derived from mathematical modelling, all with same end points and nadirs. As the flow rate of the downward air flow increased, pressure drops rose and the fiber mats expanded downwards more deeply. The resulting permeability/thickness values and true permeabilities increased at first and then reached constant after certain degrees of fiber mat expansion, which was attribute to the change of the pore opening under different fiber mat expansion conditions. Furthermore, the permeability/thickness values of the fiber mats of lowest basis weight were larger than those for higher basis weights due to the mechanism of fiber accumulation and packing during collection.
CHAPTER V

FILTRATION PERFORMANCE OF ELASTIC ACRYLONITRILE-BUTADIENE COPOLYMER ELECTROSPUN FIBER MATS IN SOLID AEROSOL SEPARATION

5.1 Introduction

Solid particles dispersed in aerosols can be efficiently separated from the continuous gas phase using conventional high-efficiency particulate air (HEPA) filters and Ultra Low Penetration Air (ULPA) filters that are typically composed of microfibers. HEPA filters remove solid particles of 0.3 µm and larger in diameter achieving separation efficiencies above 99.97%, and ULPA filters remove from air at least 99.999% of airborne particles of size 100 nm or larger. Novel nonwoven media of electrospun polymeric fibers typically possess high specific surface areas and small pores which are favorable for the particle capture process through interaction mechanisms of interception, inertial impaction, and Brownian diffusion. High surface areas generally favor higher capture efficiencies by single fiber mechanisms and the small pores favor capture of smaller particles by straining mechanisms.

The filter-related properties (permeability, porosity, pore size, etc.) are unchangeable once an inelastic electrospun fiber mat composed of rigid fibers is formed. However for an elastic fiber mat, fiber mat stretch changes the inner pore structures and resulting permeability as discussed in chapter IV, such that the filter-related properties are variable. This chapter focuses on the study of solid aerosol separation performances of elastic electrospun fiber mats under both stretched and non-stretched conditions. Elastic
fiber mats of different basis weights were electrospun from acrylonitrile-butadiene
copolymer solution. A capillary flow porometer was used to evaluate the filter-related
properties of the fiber mats, including bubble point and mean flow pore diameters, and
permeability. The elastic electrospun fiber mats were tested to capture NaCl nanoparticles
from an air stream under conditions in which the mat was restricted from stretching and
under conditions in which the mat was allowed to stretch due to the pressure drop of the
flow gas passing though the mat.

5.2 Experimental description

5.2.1 Materials

Acrylonitrile-butadiene copolymer was selected for its elastic properties. The
copolymer was dissolved in acetone to prepare solutions with copolymer concentrations of
5% by weight. The solutions were stirred for 24 hours at room temperature to be
homogeneous. The solutions were directly used for electrospinning without further
modifications.

5.2.2 Electrospinning

The single needle electrospinning setup shown in Figure 3.1 was used to fabricate
the fiber mats. The copolymer solution was fed at a flow rate of 20 mL/hr. A potential
difference of 20 kV was generated by a high voltage power supply. The aluminum foil
served as the collector was located 20 cm below the needle tip. Fiber mats of five basis
weights of 10, 20, 30, 45, and 60 g/m² were produced and cut to 6 cm × 6 cm squares mats
for testing. Details of the electrospinning parameters are summarized in Table 5.1.
Table 5. 1 Electrospinning conditions and fiber diameter data.

<table>
<thead>
<tr>
<th>Co-Polymer</th>
<th>Acrylonitrile-butadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Acetone</td>
</tr>
<tr>
<td>Concentration (wt %)</td>
<td>5</td>
</tr>
<tr>
<td>Voltage (kV)</td>
<td>20</td>
</tr>
<tr>
<td>Feeding flow rate (mL/hr)</td>
<td>20</td>
</tr>
<tr>
<td>Needle tip – to – collector distance (cm)</td>
<td>20</td>
</tr>
<tr>
<td>Fiber diameter range (nm)</td>
<td>335 – 2183</td>
</tr>
<tr>
<td>Average fiber diameter (nm)</td>
<td>960</td>
</tr>
<tr>
<td>Standard deviation (nm)</td>
<td>303</td>
</tr>
</tbody>
</table>

5.2.3 Characterization

The pore properties of the electrospun fiber mats of different basis weights were evaluated in terms of bubble point pore diameter, mean flow pore diameter, and pore diameter distribution using a capillary flow porometer (CFP-1500AEX, Porous Materials, Inc., Ithaca, NY, USA). Air permeabilities of the fiber mats were also measured using the porometer. In these tests the fiber mats were placed upon a supporting steel mesh that prevented the mats from stretching and deforming as air flowed the fiber mats. The pore openings of the steel mesh were sufficiently small to restrict the fiber mats from significant stretching. Blank tests with the steel mesh but no fiber mat confirmed the pressure drop across the steel mesh was zero and therefore did not contribute to the measured pressure drops of the fiber mats.
5.2.4 Filter holder design

To test the stretched and non-stretched fiber mats a custom-made filter holder was fabricated. The holder was composed of two Plexiglas plates, one on top of the other, with a 5 cm-diameter hole through the centers of the plates. The test media were clamped between the two plates as indicated in Figure 5.2. To prevent the fiber mats from stretching during the non-stretched mat experiments while aerosol flowed through the mats, a squared piece of polypropylene mesh (square 1mm mesh opening, Spectrum Laboratories, Inc.) was placed under the fiber mats as a support (Figure 5.3).
For experiments with stretched mats, two hemispherical bowl-shaped steel meshes (approximately square weave openings about 3 mm on edge) of different curvatures (centerline depth = 6 mm, 12 mm) (Figure 5.4) were machined to fit into the 5 cm diameter hole in the bottom plate of the filter holder, as shown in Figure 5.5. The polypropylene mesh was not used and the fiber mats were allowed to expand and stretch due to the aerosol flow pressure drop to the pre-determined hemispherical shapes. Therefore, the stretched...
fiber mats presented the same shapes as the curved meshes and did not stretch further. The polypropylene mesh and bowl-shaped steel meshes were highly permeable compared to the fiber mats such that they caused no effect on the separation process and the filtration performances were attributed to the fiber mats.

Figure 5. 4 curved steel meshes with different degrees of curvature (centerline depth=6, 12mm).

Figure 5. 5 A steel mesh assembled into the hole of the bottom plate.
5.2.5 Solid aerosol separation

The electrospun fiber mats were tested as filter media to separate solid particles from air flow to measure their filtration performance. An automated filter tester (model 8130, TSI Inc., Shoreview, MN) was used to generate solid aerosols containing sodium chloride (NaCl) nanoparticles of diameters between 25 and 100 nm with an average diameter of 75 nm\(^{117}\). A schematic of the filter tester is shown in Figure 5.7. A movable pneumatic cylinder clamped the filter holder in place during the experiments (Figure 5.8a). A pressure transducer measured the pressure drop across the fiber mat due to the flow of the aerosol through the medium. Two photometers measured the quantities of the particles in the upstream and downstream aerosol to give the penetration defined by

\[
Penetration = 1 - E = \frac{C_{\text{out}}}{C_{\text{in}}}
\]

where \(E\) is the separation efficiency, \(C_{\text{out}}\) and \(C_{\text{in}}\) are the particle number concentrations of outlet and inlet flow streams.
Figure 5. 6 Automated filter tester TSI 8130.

Figure 5. 7 Schematic of the TSI automated filter tester.
Pressure drop and penetration for each individual experiment run were measured and provided by the tester. The volumetric flow rate of the aerosol was fixed at 3 L/min for all experimental runs. This flow rate was high enough to cause the fiber mats stretch and contact the curved steel meshes (Figure 5.8b, c), such that they were under the same stretch conditions for comparison. The filter efficiency and pressure drop were combined into a single measure of performance, the Filtration Index (FI), that simultaneously accounts for both the separation efficiency ($E$) and the magnitude of the pressure drop ($\Delta P$), as defined by\textsuperscript{118}

$$FI = \frac{-\ln(1 - E)}{\Delta P} \quad (5.2)$$

Ideally the preferred filter medium has a greater Filtration Index when it performs with a high separation efficiency while maintaining a lower pressure drop.

Figure 5. 8 (a) Separation experiment in progress; (b) curved steel mesh in the filter holder before the fiber mat stretched; (c) curved steel mesh with the stretched fiber mat in contact with the mesh.
In the stretched condition the surface areas of the bowl-shaped stretched fiber mats were larger than the non-stretched mats. Since the masses of the fiber mats were constant then the basis weights decreased as the surface areas increased. The calculated basis weights of the stretched fiber mats under different stretch conditions are listed in Table 5.2.

Table 5.2 Resulting basis weights of the stretched fiber mats.

<table>
<thead>
<tr>
<th>Initial basis weight (g/m²)</th>
<th>Resulting basis weight (g/m²)</th>
<th>Centerline depth = 6 (mm)</th>
<th>Centerline depth = 12 (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9.5</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>18.9</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>28.4</td>
<td>24.4</td>
<td></td>
</tr>
</tbody>
</table>

5.3 Results and discussion

5.3.1 Pore size and permeability

Bubble point pore diameters and mean flow pore diameters of the fiber mats were measured by the porometer. In the bubble point test, a porous medium is placed horizontally on a supporting steel mesh that is completely wetted by a liquid of low surface tension. Pressurized air is introduced into the chamber above the test sample. The pressure is gradually increased until the first air bubble passes through the medium. The pressure necessary to produce this bubble is used to theoretically calculate the corresponding bubble point pore diameter.\(^7\)

As air pressure is gradually increased above the bubble point pressure more pores open and contribute to the total air flow rate. By calculating the pore sizes corresponding to the pressures and measuring the total air flow rates at each pressure, the pore size distribution is determined by the porometer. Eventually all of the pores become open and contribute to the air flow and further increase in pressure causes a linear increase in flow.
The pore diameter corresponding to flow rate that is one-half of the flow rate that resulted in the total open pores is referred to as the mean flow pore diameter.

The bubble point and mean flow pore diameters of the fiber mats of different basis weights are listed in Table 5.3. As the basis weights increased, both the bubble point and mean flow pore diameters decreased. This is consistent with our expectation that the increase in the amount of electrospun fiber caused more fiber cross-over that decreased the pore size. Increasing the amount of the electrospun fibers essentially caused higher degree of the fiber crossings, yielding narrowed pores between the fibers. The plot in Figure 5.9 shows that the pore diameters did not decrease proportionally as the basis weight increased. As mentioned in the introduction section, a limit will be reached once the packing of the fibers gives the most densely packed medium as well as smallest pores. For the electrospun fiber mats, the limit was approximately achieved at the basis weight of 45 g/m², since which the pore sizes became fairly constant.

Table 5.3 Summary of pore size and permeability data. The ± values represent one standard deviation of at least three replicate measurements.

<table>
<thead>
<tr>
<th>Basis weight (g/m²)</th>
<th>Bubble point pore diameter (microns)</th>
<th>Mean flow pore diameters (microns)</th>
<th>Permeability/thickness (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.729 ± 0.472</td>
<td>4.762 ± 0.171</td>
<td>1.56E-08 ± 1.10E-09</td>
</tr>
<tr>
<td>20</td>
<td>3.319 ± 0.075</td>
<td>2.228 ± 0.474</td>
<td>5.70E-09 ± 9.53E-10</td>
</tr>
<tr>
<td>30</td>
<td>2.681 ± 0.191</td>
<td>1.255 ± 0.156</td>
<td>3.76E-09 ± 1.85E-10</td>
</tr>
<tr>
<td>45</td>
<td>1.873 ± 0.074</td>
<td>0.628 ± 0.099</td>
<td>9.64E-10 ± 5.59E-11</td>
</tr>
<tr>
<td>60</td>
<td>1.633 ± 0.2</td>
<td>0.618 ± 0.099</td>
<td>9.22E-10 ± 1.56E-11</td>
</tr>
</tbody>
</table>
Figure 5.9 Bubble point and mean flow pore diameters of fiber mats of different basis weights. The data points are the average values of at least three replicate measurements and the error bars represent one standard deviation. For some of the data points the error bars were smaller than the plot symbol.

Example pore diameter distributions were shown in Figure 5.10. Due to physical limitations of the porometer (operating gas pressure) the plots were truncated at the smallest pores. The plots show the pore size distributions were non-Gaussian (not symmetric), having extended tails towards larger pore sizes. The pore diameter distribution tended to shift toward smaller pores as the basis weight increased.
Permeability as a measure of the ability of a porous medium that allows a fluid to pass through, is intrinsically related to the properties of the pores. Due to the difficulty of accurately measuring the thicknesses of the ultrathin fiber mats that required for determining the permeabilities, permeability/thickness ($k/L$) values were considered to describe the performance of permeability, and calculated based on Darcy’s law by

$$\frac{k}{L} = \frac{Q \mu}{A \Delta P}$$  \hspace{1cm} (5.3)

where $k$ is the permeability, $L$ is the thickness of the fiber mat, $Q$ is the air volumetric flow rate, $\mu$ is the air viscosity, $A$ is the cross-sectional area of the fiber mat, and $\Delta P$ is the pressure drop. $k/L$ values for fiber mats of different basis weights are listed in Table 5.3. Similar to the behavior of pore diameters, $k/L$ values became smaller as the basis weight increased, indicating that the permeabilities would be lower for denser fiber mats assuming...
that the thicknesses of the fiber mats were close. Starting from basis weight of 45 g/m², $k/L$ values turned minimum and stayed fairly constant afterwards.

5.3.2 Solid aerosol separation

NaCl nanoparticles were effectively captured by the electrospun fibers in the filter tests. The captured nanoparticles (white dots) uniformly distributed on the surface of the randomly aligned fibers, shown in an example SEM image in Figure 5.11. It was also observed that there were particle clusters composed of many individual nanoparticles.

![SEM image of the electrospun fibers with captured NaCl nanoparticles and particle clusters (white dots).](image)

As the fiber mats stretched to be semispherical, they stretched to yield larger surface areas compared to the circular opening of the same circumference. In our previous work\textsuperscript{119}, we concluded that the fibers among the fiber mats slipped relative to each other as a response of uniaxial tensile stretch. Lu et al.\textsuperscript{73} conducted similar uniaxial tensile tests and found that the fibers among a fiber mat adjusted their orientations without diameter change.
at lower strains, while at higher strains the diameters of the fibers decreased after most of the fiber aligned along the stretch direction. In the solid aerosol separation experiments, the fiber mats stretched in the manner of resulting in a more complex 3-D stretch compared to the simple uniaxial stretch, and fiber slippage still occurred during the stretch. As the fiber mats stretched, it was primarily occurred that the fibers shifted apart from each other to cause the pores to enlarge.

Experimental results of pressure drop and penetration for fiber mats of different basis weights at different stretch conditions are presented in Figure 5.12 and 5.13, respectively. For the two highest basis weights (45 and 60 g/m²) tested under stretch conditions, the fiber mats were not sufficiently permeable for the aerosol flow such that they ruptured when stretched by the flow. Therefore, the results were not provided for these experimental configurations.

For a certain pole depth, fiber mats of higher basis weights possessed smaller pores as well as lower permeabilities, such that they caused greater resistance to the aerosol flow, leading to higher pressure drops according to Darcy’s law. Moreover, these fiber mats containing more fibers had larger fiber surface areas that exposed to the flow. Hence the carried particles were more probably to contact with the fibers and to be further captured. On the other hand, pore among the fiber mats of higher basis weights were narrowed, which restricted the flow of the particles through the mats and augmented the probability of contact and capture. Consequently, penetrations of the particles decreased and the separation efficiencies improved. Besides basis weight, fiber mat stretch also affected the filtration performance. As the fiber mats of a certain basis weight stretched, pores among
the mats enlarged due to the fiber slippage. Enlarged pores favored the pass of the aerosol flow such that the pressure drop reduced and the particle penetration increased.

Figure 5. 12 Pressure drops for different basis weights and pole depths. The columns show the averages values of at least three measurements and the error bars represent one standard deviation.

Figure 5. 13 Penetrations for different basis weights and pole depths. The columns show the averages values of at least three measurements and the error bars represent one standard
deviation. The penetrations for the fiber mats of 60 g/m$^2$ basis weight were nearly zero, and the bar is too small to appear on the plot.

Filtration Index ($FI$) values for all the experimental cases were calculated using EQ. (1) and plotted in Figure 5.14. For the fiber mats of basis weight 10, 20, 30, and 45 g/m$^2$, the $FI$ values were low and in narrow range of 3.5 to 5.5 kPa$^{-1}$ as the penetrations were remarkable. However for non-stretched fiber mats of 45 g/m$^2$, the $FI$ values (7.21 kPa$^{-1}$) were the highest attribute to the achievement of lowest penetrations (0.448%) which approached to zero, even though the pressure drops for this case were the highest (0.751 kPa). Therefore decreasing the penetration caused a significant raise of the $FI$ values, especially when the penetrations were at low levels. For a certain basis weight, the $FI$ values of the fiber mats at three different stretch conditions were close. Penetrations increased and pressure drops decreased simultaneously as the fiber mats stretched to cause the changes of the pores, such that the $FI$ values somehow remained constant, indicating that fiber mat stretch did not significantly influence the final $FI$ values.
Figure 5. 14 Filtration Index values for different basis weights and pole depths. The columns show the averages values of at least three measurements and the error bars represent one standard deviation.

The use of elastic electrospun media in solid aerosol separation is novel to this application as most of the commercialized products are rigid and inelastic (e.g., pleated filter media). For these conventional media, their separation properties are unchangeable once they are formed and further function in various situations. Whereas for the elastic fiber mats tested in this work, different stretch conditions led to different pore properties and resulting filtration performance. On one hand, stretched fiber mats with enlarged pores caused less resistance to the aerosol flow and resulted in lower pressures, which is favorable to the separation process. While on the other hand, more particles penetrated the mats through the enlarged pores, bringing drawbacks at the same time. Therefore, the two factors need to be considered comprehensively before applied in relevant fields.
5.4 Conclusion

Elastic acrylonitrile-butadiene copolymer fibers were electrospun to prepare fiber mats of different basis weights. The fiber mats were characterized by pore diameter and permeability, and were tested for their performance in separating solid nanoparticles from aerosol under both non-stretched and stretched conditions. Fiber mats of higher basis weights yielded smaller bubble point and mean flow pore diameters, as well as lower permeability/thickness values (lower permeabilities assuming the thicknesses of the fiber mats were close). NaCl nanoparticles carried in the aerosol were effectively captured by the fibers. Fiber mats of higher basis weights possessed smaller pores for aerosol flow and larger fiber surface areas for particle capture, such that higher pressure drops and lower penetrations were obtained. Moreover, fiber mat stretch leading to pore enlargement also affected the filtration performance. As the fiber mats stretched, internal pores turned bigger to favor the passing of the aerosol flow. As a consequence, pressure drop decreased while penetration increased. Filtration Index values were calculated based on the measured pressure drops and penetrations. It was found that for fiber mats of a certain basis weight at different stretch conditions, the $FI$ values were close. Moreover, the fiber mats of 60 g/m$^2$ had the highest $FI$ values (7.21 kPa$^{-1}$) and lowest penetrations (0.448%).
CHAPTER VI

SOLID AEROSOL FILTRATION BY ELECTROSPUN POLY (VINYL PYRROLIDONE) FIBER MATS AND DEPENDENCE ON PORE SIZE

6.1 Introduction

Filter performance of a filter medium depends upon many parameters including porosity, pore size, fiber size, and filter thickness. Electrospun fiber mats tend to be very thin and their thickness is difficult to measure accurately. Therefore for thin fiber mats, the basis weight (mass per mat area) is a more robust and convenient measure for investigation of filter media performance. From common experience, the pore openings of an electrospun fiber mat are known to vary significantly with the fiber size and with the basis weight for low basis weight fiber mats. As the basis weight increases, the pores within the fiber mat gradually approach a minimum plateau.

This chapter focuses on the evaluation of the pore characteristics and solid aerosol filtration performance of electrospun poly (vinyl pyrrolidone) fiber mats. To evaluate the effects of fiber diameter and basis weight on filter performance, poly (vinyl pyrrolidone) fibers of three average diameters (287, 883, and 1709 nm) were electrospun to form nonwoven fiber mats of six basis weights (5, 10, 15, 22.5, 30, and 45 g/m²). The fiber mats were tested for capillary flow porometry and used as filter media to separate dispersed NaCl nanoparticles from air.
6.2 Experimental description

6.2.1 Materials

Poly (vinyl pyrrolidone) (PVP, average Mw ~ 1,300,000, Sigma Aldrich, St.Louis, MO) was dissolved in ethanol (200 proof, Decon Laboratories, Inc., King of Prussia, PA) to prepare solutions with polymer concentrations of 10%, 15%, and 20% by weight. All solutions were mildly stirred for 12 hours at room temperature to be homogeneously mixed and then electrospun without any further modifications.

6.2.2 Electrospinning

Fiber mats were fabricated using the typical single needle electrospinning setup shown in Figure 3.1. Each polymer solution was loaded into a 5 ml plastic syringe and fed by the syringe pump at a flow rate of 2 mL/h. The metallic needle was charged by a high voltage power supply to generate a potential difference of 25 kV between the needle tip and grounded aluminum foil that served as the collector. The aluminum foil was square-shaped (6 cm × 6 cm) and located 20 cm underneath the needle tip. Details regarding the electrospinning are listed in Table 6.1.

<table>
<thead>
<tr>
<th>PVP Conc. (wt %)</th>
<th>Solvent</th>
<th>Voltage (kV)</th>
<th>Flow rate (mL/h)</th>
<th>Tip-collector distance (cm)</th>
<th>Fiber diameter range (nm)</th>
<th>Average fiber diameter (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>ethanol</td>
<td>25</td>
<td>2</td>
<td>20</td>
<td>112 - 574</td>
<td>287</td>
<td>70</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>471 - 1266</td>
<td>883</td>
<td>132</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>873 - 2628</td>
<td>1709</td>
<td>318</td>
</tr>
</tbody>
</table>
6.2.3 Characterization

Morphologies of the electrospun fibers were observed using a scanning electron microscopy (SEM, TM3000 & TM3030 Plus, Hitachi, Japan). SEM images were analyzed by FibraQuant 1.3 software to measure the fiber diameters based on a length-weight approach\textsuperscript{44}. For each concentration, at least 150 fibers were measured to determine fiber diameter distribution, average fiber diameter, and standard deviation.

For each concentration, PVP fiber mats of six basis weights (5, 10, 15, 22.5, 30, and 45 g/m\textsuperscript{2}) were prepared and tested in the capillary flow porometer to characterize the pore properties including bubble point pore diameter, mean flow pore diameter, and pore diameter distribution.

6.2.4 Solid aerosol separation

Filtration experiments were performed using the TSI automated filter tester to evaluate the performances of the electrospun fiber mats in terms of flow resistance and total particle penetration (penetration is defined as outlet-stream concentration divided by inlet-stream concentration whereas efficiency is defined as 1 minus penetration). The PVP fiber mats were challenged with an aerosol of sodium chloride (NaCl) nanoparticles in a size range between 25 and 100 nm with mean diameter of 75 nm\textsuperscript{117}. Each experimental run was performed for 10 s at an aerosol flow rate of 20 liters/min (face velocity of 0.17 m/s). Experiments were run in triplicate to calculate average and standard deviation of performance properties. The PVP fiber mats were characterized by their penetration and the pressure drop.
A custom-made filter holder was fabricated to hold the PVP fiber mat samples. The holder had a top plate (14 cm × 14 cm × 0.3 cm) and bottom plate (14 cm × 14 cm × 2.3 cm) machined of Plexiglas as indicated in Figure 6.1. Both plates had a 5 cm diameter hole for the aerosol flow. The PVP fiber mat sample was placed on a polypropylene (PP) mesh that supported the fiber mat. The PVP fiber mat samples and PP mesh were placed covering the 5 cm hole and sandwiched between two Plexiglas plates. The assembled plates and test samples were positioned onto the base of the TSI Filter Tester. The polypropylene mesh was highly permeable compared to the fiber mat test samples and blank tests (no PVP fiber mat) showed the PP mesh had nearly zero pressure drop and 100% penetration, meaning the PP mesh did not contribute to filter performance when testing the PVP mats.

Figure 6.1 Exploded 3D schematic of the filter holder assembly.
6.3 Results and discussion

6.3.1 Fiber morphology and diameter

All three electrospinning solution produced smooth fibers as shown in the images in Figure 6.3. The fibers were randomly aligned with irregular shaped porous structures. Fiber diameter distributions are shown in Figure 6.4. The concentration of the polymer in the electrospinning solution mainly affected the fiber diameter distribution. As the polymer concentration increased, the fiber diameter range became broader and the average diameter increased significantly.
Figure 6. 3 Example SEM images of the electrospun fibers fabricated from solutions of different PVP concentrations: (a) 10%; (b) 15%; (c) 20%.

Figure 6. 4 Fiber diameter distributions for different polymer concentrations. The average fiber diameter increased as the solution concentration increased.
6.3.2 Fiber mat pores

The capillary flow porometer was used to determine the bubble point pore diameter (largest pore diameter), mean flow pore diameter, and pore diameter distributions. In the bubble point test, air pressure was applied to one side of a PVP fiber mat saturated with a liquid of low surface tension. The air pressure was gradually increased until the first air bubble passed through the mat. The air pressure that produced this bubble was used to calculate the effective largest pore diameter, the bubble point pore diameter, as given by the theoretical expression

\[ P = \frac{2 \gamma \cos \alpha}{r} \]  \hspace{1cm} (6.1)

where \( P \) is the air pressure, \( \gamma \) is the surface tension of the wetting liquid, \( \alpha \) is the wetting angle, and \( r \) is the pore radius.

Equation (6.1) gives the pressure required overcome the surface tension force that prevents an air bubble from penetrating a cylindrical pore of radius \( r \). At pressures above the bubble point pressure, the air flows through pores of smaller sizes. The air volumetric flow rate of air through the fiber mat is related to the size of the pores and the number of pores of that size. The pore size distribution is calculated from the pressure and flow rate data. The air pressure is increased until no new pores are detected. The pore diameter corresponding to the pressure at which 50% of the flow is due to larger pores and 50% due to smaller pores is defined as the mean flow pore diameter.

Figures 6.5 and 6.6 show plots of the bubble point and mean flow pore diameters for the PVP fiber mats of different average fiber diameters and basis weights. The plots in show the bubble point diameters and mean flow diameters decreased as basis weights increased and reached a minimum plateau at about 30 g/m² basis weight. During the
electrospinning process, the collected fibers initially contribute to random mat formation and new fibers cross over large pore spaces thus reducing the pore sizes as fiber mass increases. However, eventually as more fibers are collected the fibers begin to support each other in the mat thickness direction and fewer large pores are exposed to new fibers to cause reduction of pore size. A point is reached where the fibers no longer decrease pore sizes but increase the thickness and the strength of the mat. This means that the pore sizes decrease but gradually reach a minimum plateau and become constant as basis weight increases while all other properties such as fiber diameter are constant. The mats with larger fibers had larger pores. The minimum plateau bubble point diameters were approximately 1.5~2 times the size of the average fiber diameters. The mean flow pore diameters roughly about half the size of bubble point pore diameters.

Figure 6. 5 Bubble point pore diameters for different average fiber diameters and basis weights. The data points are the average values of at least three measurements and the error bars represent one standard deviation. For some of the data points the error bars were smaller than the plot symbol.
Figure 6. Mean flow pore diameters for different average fiber diameters and basis weights. The data points are the average values of at least three measurements and the error bars represent one standard deviation. For some of the data points the error bars were smaller than the plot symbol.

Example pore diameter distributions are shown in Figure 6.7. Due to physical limitations of the porometer (operating gas pressure) the plots were truncated at the smallest pores that the instrument was capable of detecting with reasonable accuracy. The plots show the pore size distributions were non-Gaussian (not symmetric), having extended tails towards larger pore sizes. Pore size distributions tended to shift towards larger pore sizes as average fiber size increased (observed when inspecting the plots from the left to right). Pore size distributions tended to shift toward smaller pores as the basis weight increased (observed when inspecting the plots top to bottom).
Figure 6. 7 Example pore diameter distributions for different average fiber diameters and basis weights.

6.3.3 Filter performance

The PVP fiber mats were tested in the capture the NaCl nanoparticles in the filter tests. The high surface areas of the electrospun mats and the small pore diameters have high potential for capture of nanoparticles by interception and Brownian diffusion mechanisms. An example SEM image of a fiber mat after a filter test in Figure 6.8 shows captured particles as white dots distributed on the fibers. The white dots do not appear on the SEM images (Figure 6.3) prior to the filter tests.

![SEM image of the fibers with captured NaCl nanoparticles](image)

Figure 6. 8 SEM image of the fibers with captured NaCl nanoparticles (white dots).

Pressure drop and penetration data are plotted in Figures 6.9 and 6.10, respectively. For fixed fiber diameters, the pressure drop increased rapidly as the basis weight increased, due to the effects of decreasing pore size and increasing amounts of fiber. As the basis
weight approached 30 g/m² and the pore sizes reached minimum plateau the pore sizes became constants and the rate of increase of pressure drop with basis weight (slope of the pressure drop versus basis weight) reduced. At the basis weights greater than 30 g/m², the pressure drop is expected to be proportional to mat thickness according to Darcy’s law

$$\frac{\Delta P}{L} = \frac{Q\mu}{Ak}$$

(6.2)

where $k$, the permeability, is dependent upon the fiber structure (pore size, fiber diameter, etc.). Here, $L$ is the thickness of the medium, $Q$ is the fluid volumetric flow rate, $\mu$ is the fluid viscosity, $A$ is the cross-sectional area of the medium, and $\Delta P$ is the pressure drop.

The smaller pore sizes increase the capture efficiency by the straining mechanism when pores are smaller than the particle size. Mechanisms such as diffusional capture also increase efficiency, for particles smaller than the pores, as the diffusional distance decreases for smaller pores. Furthermore, capture efficiency increases as the total surface area available for capture increases. At a fixed mass of fibers, smaller fibers have larger surface areas than larger fibers, hence mats of smaller fibers have higher capture efficiencies and smaller penetrations. These mechanisms are consistent with the trends in the penetration in Figure 6.10. At a fixed basis weight the mats of smaller fibers had less penetration and as basis weights increased the penetrations decreased. The 287 nm fiber mats had nearly zero penetration for basis weights of 15 g/m² and larger.
Figure 6. 9 Pressure drops for different average fiber diameters and basis weights. The columns show the average values of at least three measurements and the error bars represent one standard deviation.

Figure 6. 10 Penetrations for different average fiber diameters and basis weights. The penetrations were essentially zero for the 287 nm fiber mats at 22.5, 30, and 45 g/m² basis weights, and the 883 nm fiber mats at 30 and 45 g/m² basis weights, and the bars are too small to appear on the plot. The columns show the average values of at least three experiments and the error bars represent one standard deviation.
The overall performance of a filter must take into account both the penetration and the pressure drop. To assess the overall performance of the filter media in one numeric quantity, the Filtration Index \((FI)\) was calculated using the definition\(^{118}\)

\[
FI = \frac{-\ln\left(\frac{C_{out}}{C_{in}}\right)}{\Delta P}
\]

(6.3)

where \(C_{out}\) and \(C_{in}\) are the outlet-stream and inlet-stream particle concentrations, respectively. The ratio \(\frac{C_{out}}{C_{in}}\) is the penetration, and \(\Delta P\) is the pressure drop across the filter media. A medium with low penetration and low pressure drop is desired and has a higher Filtration Index value.

Calculated \(FI\) values for the filter test data are plotted in Figure 6.11. The \(FI\) values were in a narrow range between 7 and 11 kPa\(^{-1}\). Specifically, fiber mats of 45 g/m\(^2\) basis weight with an average diameter of 883 nm had the highest \(FI\) value (10.2 kPa\(^{-1}\)) as they gave one of the lowest penetrations (0.245\%) as well as fair pressure drops (0.606 kPa). Overall, the narrow range of the \(FI\) values suggest that \(FI\) does not distinguish well enough between the performances hence selection or design of a filter medium should be based on the penetration or the pressure drop, depending on the application for these fiber mats.

The filtration tests were conducted up to five runs for each sample and did not consider the effects of particle loading on the life time performance of the PVP fiber mats. Experimentally, the pressure drop tended to increase and the penetration tended to decrease when the same PVP fiber mat sample was tested multiple times. These trends in the performance are may be due to the aggregation of the NaCl nanoparticles into the pores of the mats that restricted the pore space for gas flow and thus increased the pressure drop. The restricted pores could increase the straining mechanism to capture particles and the
particles themselves may serve as collectors via mechanisms of Brownian diffusion and interception to increase the capture efficiency and reduce the penetration. This topic should be explored in future work.

Figure 6. 11 Filtration Indexes for different average fiber diameters and basis weights. The columns show the average values of at least three measurements and the error bars represent one standard deviation.

6.4 Conclusion

In this work, poly (vinyl pyrrolidone) fiber mats of three average fiber diameters were prepared via electrospinning. For each average fiber diameter, fiber mats were prepared in six basis weights to evaluate the effects of fiber diameter and pore size on filtration performance. The bubble point and mean flow pore diameters decreased as basis weight increased and reached a minimum plateau at 30 g/m² basis weight. The minimum plateau bubble point pore diameters were approximately 1.5~2 times the average fiber diameters of the mats. As filters, the PVP fiber mats effectively captured NaCl
nanoparticles from an air stream with the best separation efficiencies of 99.89%. The pressure drop and particle penetration were influenced significantly by both the fiber diameter and the basis weight, as both significantly determined the pore structures inside the filter media and the total effective surface area exposed to the aerosol flow. In general, as basis weight increased and as the fiber diameter decreased the penetration decreased and the pressure drop increased. The fiber mats of 45 g/m² basis weight and average diameter of 883 nm had the highest Filtration Index (10.2 kPa⁻¹). The mats of 45 g/m² basis weight and average diameter of 287 nm had the least penetration (0.11%).
WATER-IN-DIESEL EMULSION SEPARATION USING SUPERHYDROPHOBIC ELECTROSPUN ACRYLONITRILE-BUTADIENE COPOLYMER FIBER MATS

7.1 Introduction

Water-in-diesel emulsions are defined as mixtures of diesel fuel (continuous phase) and water droplets (dispersed phase). The dispersed water droplets are mostly in a size range of 0 to 100 µm. As a result of the balance of surface forces and body forces, the droplets suspend in the diesel fuel and they can’t be removed via physical separations, such as gravity settling. In this case, filter media with superhydrophobic surfaces demonstrate effectiveness. On a vertically positioned superhydrophobic surface with high water contact angle and low hysteresis, tiny water droplets coalesce to form larger droplets when they get into contact. Once the droplets achieve certain weights, gravity forces will drive them to slide off the surface, in which way water is removed from the emulsion.

In this chapter, the filter performance of superhydrophobic electrospun acrylonitrile-butadiene copolymer fiber mats in separating dispersed water droplets of sizes less than 100 µm from diesel fuel is presented. Copolymer fiber mats of different basis weights were electrospun onto glass fiber mats to prepare double-layered composite filter media. The filter media were challenged at different face velocities. Separation efficiency, pressure drop, and overall Filtration Index were determined to evaluate the filter performance.
7.2 Experimental description

7.2.1 Materials

Nonwoven glass fiber mats (Hovomat EX grades) were provided by Hollingsworth & Vose Company and used as received. Acrylonitrile-butadiene copolymer (33% Acrylonitrile, Scientific Polymer Products, Inc, Ontario, NY) was selected to fabricate the superhydrophobic fiber mats via electrospinning. The copolymer was dissolved in acetone (Sigma Aldrich, St. Louis, MO) to prepare solutions with copolymer concentrations of 5% by weight. The solutions were stirred for 24 hours at room temperature to be homogeneous. The solutions were directly used for electrospinning without further modifications. Ultra low sulfur diesel (ULSD) was purchased locally and used as received. Deionized water was used to generate dispersed water droplets.

7.2.2 Electrospinning

Electrospun acrylonitrile-butadiene copolymer fiber mats of different basis weights were fabricated using the single needle electrospinning setup shown in Figure 3.1. The copolymer solution was fed at a flow rate of 20 mL/hr. A potential difference of 20 kV was generated by a high voltage power supply. A glass fiber mat (9 cm × 9 cm) served as the collector was located 20 cm below the needle tip. Copolymer fiber mats of three basis weights of 10, 20, and 30 g/m² were directly electrospun onto the glass fiber mats to form double-layered composites referred to as C10, C20, and C30, respectively. Details of the electrospinning parameters are summarized in Table 7.1.
Table 7. 1 Electrospinning conditions, fiber diameter data, and surface wettability.

<table>
<thead>
<tr>
<th>Co-Polymer</th>
<th>Acrylonitrile-butadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Acetone</td>
</tr>
<tr>
<td>Concentration (wt %)</td>
<td>5</td>
</tr>
<tr>
<td>Voltage (kV)</td>
<td>20</td>
</tr>
<tr>
<td>Feeding flow rate (mL/hr)</td>
<td>20</td>
</tr>
<tr>
<td>Needle tip – to – collector distance (cm)</td>
<td>20</td>
</tr>
<tr>
<td>Fiber diameter range (nm)</td>
<td>335 – 2183</td>
</tr>
<tr>
<td>Average fiber diameter (nm)</td>
<td>960 ± 303</td>
</tr>
<tr>
<td>Water contact angle in diesel (°)</td>
<td>165.6 ± 2.12</td>
</tr>
</tbody>
</table>

7.2.3 Characterization

The morphologies (Figure 7.1) of the glass fibers were observed using the SEM. Fiber diameters were measured via FibraQuant software (Figure 7.2) to provide fiber diameter distribution and average fiber diameter. Surface wettability of the electrospun copolymer fiber mat was evaluated in a diesel environment using the Drop Shape Analyzer (DSA). The glass slide as well as the attached electrospun fiber mat were completely submerged in a diesel container for water contact angle measurement. The water contact angles were greater than 150°, indicating that the surface was superhydrophobic (Figure 7.3).
Figure 7.1 SEM image of the glass fibers.

Figure 7.2 Diameter distribution of glass fibers. The average fiber diameter is 5.876 µm.
Figure 7. 3 A sessile water drop on the electrospun copolymer fiber mats in diesel. The water contact angle is about 165°.

Pore diameter distributions, bubble point pore diameters, mean flow pore diameters, and permeability/mat thickness values of the glass fiber mats and electrospun copolymer fiber mats of different basis weights were determined by the capillary flow porometer and the results are summarized in Table 7.2. The characteristic pore diameters and permeability/mat thickness values for the glass fiber mats composed of big microfibers were larger than those for the electrospun fiber mats composed of tiny fibers, showing that the pore sizes were related the fiber sizes. For the electrospun fiber mats, these properties decreased as the basis weight increased. Glass fiber mats and double-layered composites were measured for porosity using a custom made pycnometer\cite{120} (Figure 7.4) based on ideal gas law as shown in Table 7.3. The porosities of the glass fiber mats and the composites exceeded 90% and the values were close, meaning that addition of the electrospun fibers did not significantly change the porosities of the composites.
Table 7. 2 Bubble point (BP) and mean flow (MF) pore diameters of the glass fiber mats and electrospun copolymer fiber mats.

<table>
<thead>
<tr>
<th>Media type</th>
<th>Glass fiber mat</th>
<th>Electrospun fiber mat (10 g/m²)</th>
<th>Electrospun fiber mat (20 g/m²)</th>
<th>Electrospun fiber mat (30 g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP pore diameter, µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>123.28 ± 2.56</td>
<td>6.729 ± 0.472</td>
<td>3.319 ± 0.075</td>
<td>2.681 ± 0.191</td>
</tr>
<tr>
<td>MF pore diameter, µm</td>
<td>63.08 ± 7.71</td>
<td>4.762 ± 0.171</td>
<td>2.228 ± 0.474</td>
<td>1.255 ± 0.156</td>
</tr>
<tr>
<td>Permeability/mat thickness (k/L), m</td>
<td>4.86E-07 ± 6.61E-08</td>
<td>1.56E-08 ± 1.1E-09</td>
<td>5.7E-09 ± 9.53E-10</td>
<td>3.76E-09 ± 1.85E-10</td>
</tr>
</tbody>
</table>

Figure 7. 4 Custom made pycnometer for porosity measurement.

Table 7. 3 Porosities of the glass fiber mats and composites.

<table>
<thead>
<tr>
<th>Media type</th>
<th>Glass fiber mat</th>
<th>C10</th>
<th>C20</th>
<th>C30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, %</td>
<td>0.91 ± 0.021</td>
<td>0.9 ± 0.017</td>
<td>0.93 ± 0.0058</td>
<td>0.92 ± 0.021</td>
</tr>
</tbody>
</table>
7.2.4 Filter holder assembly

A filter holder (Figure 7.5) consisted of four squared Plexiglas plates (10 cm × 10 cm × 2.3 cm) was used to hold the filter media. The two outer plates had a fitting at the center to be connected to tubes for the emulsion flow. The two inner plates were drilled an opening of 6 cm in diameter and used as upstream and downstream chambers to hold the emulsion of certain volume. The filter media were clamped between the inner plates. A piece of circular steel mesh of the same diameter as the chamber opening was stuck into the opening of the downstream chamber, and served as a support to prevent the filter media from deforming due to the emulsion flow. Two vents were installed onto the top of the two inner plates to eliminate the air bubbles accumulated inside the chambers. A pressure transducer was in place to measure the liquid pressures of inlet and outlet flow to determine the pressure drop across the filter media. The assembled filter holder is shown in Figure 7.6.
Figure 7.5 Exploded 3D schematic of the filter holder assembly.

Figure 7.6 Filter holder assembly.
7.2.5 Water-in-diesel emulsion separation

Figure 7.7 shows the schematic of the separation experiment. 3 gallons of ULSD and 27 mL of deionized water were added in the reservoir tank to make the emulsion. The mixture was agitated by a stirrer to break the water into tiny droplets. A 3500 rpm centrifugal pump circulated the emulsion from the bottom of the tank back the top. The circulation was run for 30 min to stabilize the water droplet size distribution prior to the separation experiments. Besides circulation, a portion of the emulsion was pumped to flow into the upstream chamber for separation. Circulation and mild agitation were maintained to keep the sizes of the water droplet in upstream constant during each separation experiment. The average diameters of the dispersed water droplets in the upstream were kept in a range from 35 to 45 µm for all the experimental runs. Each separation experiment was run for a total of 40 min to ensure the system reached steady state. The filter media were challenged by the emulsion flow at two face velocities: 0.5 and 1 cm/min. Face velocity ($FV$) is defined as the volumetric flow rate ($Q$) divided by the effective filter surface area ($A$), given by

$$FV = \frac{Q}{A}$$

(7.1)
Samples were obtained from upstream and downstream sampling points to measure the size distributions of the water droplets in the emulsion using a particle counter (AccuSizer 780, Particle Sizing Systems, Port Richey, FL, sensor range: 2 – 1000 µm) (Figure 7.8). The measurement range of the AccuSizer sensor was 2 to 1000 µm. As a result, water droplets of sizes smaller than 2 µm were not detected and this could lead to slight variance in experimental results. The size distributions denoted the number counts of the water droplets of different sizes. The separation efficiency ($E$) was calculated to evaluate the separation performance of the filter media. It is defined as the percentage of water removed by the filter media on the basis of the water contained in the upstream, determined by

$$E = \frac{C_{\text{upstream}} - C_{\text{downstream}}}{C_{\text{upstream}}}$$

(7.2)
where \( C_{\text{upstream}} \) and \( C_{\text{downstream}} \) are the mass concentrations of the water in upstream and downstream. The mass concentrations were calculated based on the particle counter data by

\[
C = \sum N_i \frac{\pi}{6} a_i^3 \rho_{\text{water}}
\]  

where \( N_i \) is the number count of the water droplets per cubic centimeter of emulsion of diameter \( a_i \), \( \rho_{\text{water}} \) is the density of the water. Besides separation efficiency, pressure drops across the filter media were also measured using a pressure transducer (PX-750 pressure transmitter, OMEGA Engineering, INC., Norwalk, CT). The filter media in presence to remove the water droplets were barriers for the upstream emulsion to flow freely, due to which a pressure drop was generated. Generally, higher pressure drop requires greater more power input to the pump to main the emulsion flow at a certain flow rate for separation task. Therefore, filter media yielding lower pressure drops are preferred for filtration and separation applications in order to save energy cost. The comprehensive performance of the filter media was characterized by the Filtration Index \((FI)\) taking into consideration of both separation efficiency and pressure drop, defined by

\[
FI = -\frac{\ln(1 - E)}{\Delta P}
\]  

In general, a filter medium with a higher \( FI \) gives better performance.
7.3 Results and discussion

A contrast between the water-in-diesel emulsion entering and leaving the filter media is shown in Figure 7.9. The emulsion was turbid prior to separation and became clearer afterwards. Dispersed water droplets were effectively removed from the upstream by the superhydrophobic double-layered filter media and the water was collected at the bottom of the upstream chamber (Figure 7.10). The superhydrophobic surface as a barrier prevented the water droplets from penetrating and the droplets collected on the surface presented nearly spherical shapes as illustrated in Figure 7.3. Once two adjacent droplets got in touch, they coalesced to merge into a bigger droplet. The bigger droplet continued to coalesce with nearby droplets to grow size. When the droplets achieved certain weights, gravitational force overcame the drag force applied by surface, such that the droplets slid downwards along the surface of the vertically placed filter media to gather at the bottom. In this way, the dispersed water droplets were removed.
Figure 7. 9 Water-in-diesel emulsion changed from turbid to clear after passing through the filter media.
Figure 7.10 Collected water at the bottom of the upstream chamber after an experimental run.

Separation efficiencies of the superhydrophobic double-layered filter media at different face velocities exceeded 70%, showing that the filter media effectively removed water droplets (Figure 7.11). The best separation efficiencies obtained were above 95% by the composites with electrospun fiber mats of 30 g/m² basis weight (C30), at the face velocity of 0.5 cm/min. At a certain face velocity, the separation efficiency enhanced as the basis weight of electrospun fiber mat increased. As shown in Table 7.2, the pore sizes
of the electrospun fiber mats decreased as more fibers were collected. The narrowed pores in the electrospun fiber mats restricted the passing of the water droplets of sizes greater than the pore sizes. Therefore the filter media with more electrospun fibers yielded higher separation efficiencies. Even though the glass fiber mats possessed much larger pores to favor the penetration of the water droplets compared to the electrospun fiber mats, they only served as a support and their presence did not influence the coalescence and separation occurred on the superhydrophobic surface. Face velocity also affected the separation performance. The separation efficiencies lowered at higher face velocity. On one hand, at a higher face velocity, water droplets in the upstream were more likely to be carried by the emulsion to penetrate the filter media such that they had shorter time to attach onto the surface to coalesce. On the other hand, upstream flow of higher face velocity applied larger drag force on the droplets that were already collected on the surface. As a result, the coalesced droplets had a chance to decompose into smaller droplets, which could possibly penetrate the filter media through the pores and enter back into the downstream, causing the separation efficiency to drop.
Figure 7.11 Separation efficiencies of the double-layered filter media with electrospun fiber mats of different basis weights at different face velocities. The plotted values are the averages of three measurements and the error bars represent one standard deviation.

Pressure drops across the filter media are plotted in Figure 7.12. The pressure drop values lie in a broad range of 2 to 10 kPa. At a certain face velocity, pressure drop increased with the basis weight of the electrospun fiber mat. With more electrospun fibers collected, pore sizes and permeability/thickness values became smaller such that the ability of the filter media to allow the emulsion to pass through reduced. For the same type of filter media, pressure drops were greater at higher face velocity. According to Darcy’s low, for a single-phase fluid flow, the pressure drop changes proportionally with the volumetric flow rate of the fluid. However for the emulsion which was essentially a multiphase flow, coalescence occurred on the surface contributed a new mechanism to the whole process. Some of the collected water droplets blocked the pores at the surface for emulsion flow, generating
additional pressure drop. Consequently, the pressure drop did not vary proportionally with the face velocity.

Figure 7.12 Pressure drops of the double-layered filter media with electrospun fiber mats of different basis weights at different face velocities. The plotted values are the averages of three measurements and the error bars represent one standard deviation.

Filtration Index (FI) values were calculated using Equation 7.4 to assess the comprehensive performance of the filter media (Figure 7.13). FI values decreased with both the basis weight of the electrospun fiber mat and the face velocity. According to Equation 7.4, a higher separation efficiency associated with a lower pressure drop leads to a greater FI. Whereas as the basis weight of the electrospun fiber mat increased, separation efficiency and pressure drop increased. Compared to the improvement of separation efficiency, the increment of pressure drop played a more important role in determining the
such that the $FI$ eventually turned out to decrease. Increase in face velocity caused disadvantage on both the separation efficiency and pressure drop as illustrated in Figure 7.11 and 7.12, resulting in lower $FI$ values.

![Image of Filtration Index values](image)

**Figure 7.13** Filtration Index values of the double-layered filter media with electrospun fiber mats of different basis weights at different face velocities. The plotted values are the averages of three measurements and the error bars represent one standard deviation.

Example upstream and downstream water droplet size distributions for all the six experimental cases are shown in Figure 7.14. The water droplets in the upstream had an average size of about 45 µm. After separation, the water droplet size distributions shift towards smaller sizes, showing that larger droplets were removed by the filter media. For the downstream size distributions, there is a trend that the quantity of smaller water droplets increases while the distribution shifts to smaller sizes. The filter media of C30 at a face
velocity of 0.5 cm/min yielded the highest separation efficiencies of about 96% corresponding to the leftmost size distribution (pink triangle dots) with the largest amount of water droplets in a size range of 5 to 15 µm. For this case, water droplets of sizes larger than 25 µm were completely removed, however more droplets of smaller sizes were generated. A comparison between the upstream emulsion and purified diesel fuel is shown in Figure 7.15.

Figure 7. 14 Example upstream and downstream water droplet size distributions. Average sizes of the water droplets in upstream were maintained in a range of 35 to 45 µm.
Figure 7. 15 Comparison between the upstream emulsion and downstream purified diesel fuel. The separation efficiency was about 96%.

7.4 Conclusion

Double-layered composites composed of hydrophilic glass fiber mats and superhydrophobic electrospun acrylonitrile-butadiene copolymer fiber mats were used as surface barrier filter media to remove dispersed water droplets from water-in-diesel emulsion. The separation performance was dependent on both the basis weight of the electrospun fiber mats and the face velocity of the emulsion. Composites with electrospun fiber mats of higher basis weights and smaller pores showed higher separation efficiencies, higher pressure drops, and lower overall $FI$ values. Increment of face velocity of the emulsion leaded to worse filter performance by raising pressure drops, lowering separation efficiencies and overall $FI$ values. Water droplets of larger sizes were removed while droplets of smaller sizes were generated after separation. The best separation efficiencies
were above 96%, accomplished by the filter composites containing electrospun fiber mats of 30 g/m\(^2\) basis weight, at a face velocity of 0.5 cm/min.
CHAPTER VIII

CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

The objectives of this research were preparation, characterization, and filtration application of elastic electrospun fibrous media. These objectives were achieved by electrospinning acrylonitrile-butadiene copolymer fiber mats, characterizing fundamental properties (fiber morphology and size, mechanical performance, surface wettability, and filter-related parameters), using the fiber mats as filter media for aerosol separation and water-in-oil emulsion separation. Hypotheses were applied and studied. These hypotheses were proven by experiments, as summarized below.

Elastic acrylonitrile-butadiene copolymer fibers were prepared via electrospinning. Morphologies of the product were highly dependent on the copolymer mass concentration of the solution. Copolymer droplets and beaded fibers were formed by electrospraying at lower concentrations, while beaded-free smooth fibers were generated at higher concentrations. The electrospun fiber mats showed surface hydrophobicity, and the hydrophobicity reduced as the copolymer concentration increased to yield more homogeneous surface structure and lower surface roughness. Uniaxial tensile tests on the electrospun fiber mats and yarns rolled from the mats gave similar stress-strain curves with ascending and descending stages, however fibers in the yarns presented higher mechanical strengths compared to the mats due to more fiber-fiber contacts.
It was hypothesized the fiber mat stretch would cause the fibers to rearrange to enlarge the pores in the media and therefore result in greater air permeabilities. This hypothesis was proved by means of Frazier Air Permeability Test. In the air permeability test, the elastic electrospun fiber mats placed upon a circular opening stretched to present bowl-shapes as air passed through. A descriptive empirical mathematical model yielded an equation approximately describing the profiles of the stretched fiber mats subject to air flow, while the profiles were found to be more similar to parabolas. The fiber mats of different basis weights stretched downwards more deeply as the air flow rate increased. Fiber mats of lower basis weights stretched more easily and presented more remarkable stretch compared to higher basis weights. The permeability/thickness values increased initially and then reached constant after certain degrees of stretch, resulted from the changes of the pore structures due to stretch. Moreover, fiber mats of higher basis weights contained larger amount of fibers, such that the fibers were more densely packed to give narrowed pores. Therefore, the permeability/thickness values were smaller than those of lower basis weights.

It was hypothesized that pore enlargement due to stretch would influence the filtration performance of the fiber mats by raising particle penetration and reducing pressure drop. Aerosol separation experiments were conducted to prove this hypothesis. The elastic electrospun fiber mats were tested for filter performance in solid aerosol separation under both non-stretched and stretched conditions. The fiber mats effectively captured nanoparticles from air flow, and showed the best separation efficiencies of about 99.5%. The filter performance was evaluated through penetration, pressure drop, and overall Filtration Index. It was found that both the basis weight and the stretch condition
affected the performance. The pores within the fiber mats turned smaller as the basis weight increased, resulting in improved nanoparticle capture and higher pressure drops. As the fiber mats stretched, fibers shifted apart relative to each other to generate enlarged pores, favoring the passing of the aerosol flow and leading to greater particle penetrations and lower pressure drops.

Besides acrylonitrile-butadiene copolymer, poly (vinyl pyrrolidone) (PVP) was also used to prepare electrospun fibers of different diameter ranges and fiber mats of different basis weight. The fiber mats were investigated for pore sizes and solid aerosol separation. Pore sizes of the fiber mats were related to both the fiber diameter and basis weight. The characteristic pore diameters (bubble point pore diameter and mean flow pore diameter) decreased as the basis weight increased, and reached a minimum plateau at 30 g/m². This experimental phenomenon was related to the fiber packing mechanisms during the electrospinning process. It was also found that the minimum plateau bubble point pore diameters were approximately 1.5 ~ 2 times the average fiber diameters. Separation performance (penetration and pressure drop) were also significantly influenced by fiber diameter and basis weight that essentially determined the effective surface for particle capture as well as pore structures. Generally, fiber mats of larger basis weights composed of smaller fibers yielded lower particle penetrations and higher pressure drops. The fiber mats efficiently removed solid nanoparticles from air with the best separation efficiencies of 99.9%.

It was hypothesized that a superhydrophobic fiber mat would be a barrier for water to pass through such that dispersed water droplets contained in a continuous phase flow would attach onto the surface to coalesce and then be removed. To prove this hypothesis,
the acrylonitrile-butadiene copolymer fibers were electrospun onto glass fiber mats to prepare double-layered composites that used as filter media to remove dispersed water droplets from diesel fuel. The surface of the electrospun fiber mats were superhydrophobic in diesel such that the water droplets could not penetrate. The separation performance was determined by both the basis weight of the electrospun fiber mat and the face velocity of the emulsion flow. Composites with electrospun fiber mats of higher basis weights possessed smaller pores, therefore they showed higher separation efficiencies and higher pressure drops. Increase in face velocity resulted in worse filter performance by reducing separation efficiencies and raising pressure drops. The best separation efficiencies exceeded 95%, achieved by filter composites containing electrospun fiber mats of highest basis weight at the lowest face velocity.

8.2 Future work

The results of this work suggest several future research questions.

1. Chemistry of the copolymer material and the electrospun fibers needs to be further studied, including the examination of creep, melting, etc. It is also interesting to perform crosslinking to the electrospun fiber mats to see how the mechanical properties change.

2. SEM analysis needs to be conducted on uniaxially and three-dimensional stretched fiber mats to observe the changes of the fiber and pore structures as an extension research of the work described in Chapter III and IV, respectively.

3. For the uniaxial tensile tests described in Chapter III, the fiber mats and yarns ruptured near the locations where the samples were clamped. Variations in stresses can occur
4. The descriptive empirical mathematical model needs to be improved to describe the profiles of the stretched fiber mats more accurately. To do this, old assumptions should be more carefully checked for their effectiveness, and new assumptions can be incorporated in the model.

5. Surface wettability of the fiber mats under stretched condition should be investigated. It is expected that stretch will affect the fiber and pore structures at and then lead to changes in surface structures. Water contact angle can be evaluated and compared for fiber mats at different stretch conditions.

6. For the solid aerosol separation experiments presented in Chapter V, higher aerosol volumetric flow rates or face velocities can be selected to inspect how the separation performance of the fiber mats changes.

7. In Chapter VI, the minimum plateau bubble point pore diameters of the PVP electrospun fiber mats were about 1.5 ~ 2 times the fiber diameter. In the future, more polymers should be used to produce fibers of different diameters. Fiber mats composed of fibers of different size ranges prepared from different polymer materials will be measured for characteristic pore diameters to study the relation between minimum plateau bubble point pore diameter and fiber diameter. Dimensionless analysis can help to derive a correlation that can apply to different kinds of polymer in relating the two parameters.

8. The barrier filter composites described in Chapter VII effectively removed water droplets from diesel by taking advantage of surface superhydrophobicity.
interesting to use only the electrospun fiber mats without glass fiber mats and to check the separation performance, while the fiber mats must be mechanically strong enough to withstand the emulsion flow without the support of the glass fiber mats.

9. The water-in-diesel emulsion separation performance of the elastic electrospun fiber mats under stretched condition should be investigated to study the influence of the change of the pore structures, similar to the research described in Chapter VII.
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APPENDICES
MATHEMATICAL MODELING OF PROFILES OF THE STRETCHED FIBER MATS SUBJECT TO AIR FLOW

Mathematical modeling work which can be used to theoretically predict the responses of the fiber mats subject to air flow was done. Results of the permeability tests (chapter IV) will be compared to the model for consistency check. In the modeling, a fiber mat is placed upon a circular opening with edge sealed. As air flows through, the fiber mat tends to stretch and present different shapes. The goal of this modeling work is to describe the profiles of the expanding fiber mat given specific air flow rates and pressure drops.

Consider a uniaxial stretch applied on an elastic object of cube shape. As shown in the picture, the material compresses transversely in y and z directions as it gets stretched in x direction, which is called the Poisson’s effect (Figure A1).

Figure A.1 Poisson’s effect.
Poisson’s ratio $\nu$ is defined as the negative ratio of transverse strain to axial strain,

$$\nu = -\frac{d\varepsilon_{\text{trans}}}{d\varepsilon_{\text{axial}}} = -\frac{d\varepsilon_y}{d\varepsilon_x} = -\frac{d\varepsilon_z}{d\varepsilon_x}$$  \hspace{1cm} (A1)

where $\varepsilon_{\text{axial}}$ is the axial strain, $\varepsilon_{\text{trans}}$ is the transverse strain.

Referring to the cube shown in Figure A1, $\Delta L$ is the increased length in $x$ direction due to stretching force, and $\Delta L'$ is the corresponding decreased length in $y$ and $z$ directions. For very small values of $\Delta L$ and $\Delta L'$, the first order approximation yields

$$\nu \approx \frac{\Delta L'}{\Delta L}$$  \hspace{1cm} (A2)

According to the theory of linear elasticity, the constitutive equation for describing Hooke’s Law is

$$\mathbf{\sigma} = \mathbf{C} : \mathbf{\varepsilon}$$  \hspace{1cm} (A3)

where $\mathbf{\sigma}$ is the Cauchy stress tensor, $\mathbf{C}$ is the fourth-order stiffness tensor, and $\mathbf{\varepsilon}$ is the infinitesimal strain tensor.

Specifically, for isotropic homogeneous media, the constitutive equation is written as

$$\sigma_{ij} = \lambda \delta_{ij} \varepsilon_{kk} + 2 \mu \varepsilon_{ij}$$  \hspace{1cm} (A4)

where $\sigma_{ij}$ are the components of the Cauchy stress tensor $\mathbf{\sigma}$, $\varepsilon_{kk}$ and $\varepsilon_{ij}$ are the components of the infinitesimal strain tensor $\mathbf{\varepsilon}$, $\delta_{ij}$ is the Kronecker delta, $\lambda$ is Lame’s first parameter, $\mu$ is the shear modulus.

$\lambda$ and $\mu$ can be determined in terms of Poisson’s ratio $\nu$ and Young’s modulus $E$,

$$\lambda = \frac{E\nu}{(1 + \nu)(1 - 2\nu)}$$  \hspace{1cm} (A5)

$$\mu = \frac{E}{2(1 + \nu)}$$  \hspace{1cm} (A6)
A fiber mat is placed upon the circular opening of a block and then clamped using two plates with center holes for sealing (Figure A2). Air flows downwards through the medium, causing the fiber mat to stretch and present arc shapes that vary with the air flow rate (Figure A3). This process is modeled mathematically based on the background theories and assumptions in order to calculate for the equations that describe the fiber mat profiles.

![Figure A. 2 Exploded 3-D view of fiber mat assembly.](image)

Figure A. 3 Schematic of fiber mat stretch due to air flow.
Assumptions were made as below to simplify the mathematical modeling:

1. The fiber mat is homogeneous and isotropic;
2. The edge of the fiber mat is perfectly sealed (no leaks);
3. The edges of the two disks that in touch with the fiber mat are round and smooth such that the mat will not be cut, which avoids potential air leak;
4. Air flows in the normal directions of the curved mat surface;
5. The change in fiber mat thickness is negligible such that the thickness is constant.

Assuming the change in thickness is negligible, the fiber mat only stretches along the curved surface, such that Poisson’s ratio is zero,

\[ \nu = 0 \]  \hfill (A7)

\[ \lambda = \frac{E \nu}{(1 + \nu)(1 - 2\nu)} = 0 \]  \hfill (A8)

\[ \mu = \frac{E}{2(1 + \nu)} = \frac{E}{2} \]  \hfill (A9)

Recall constitutive equation for isotropic homogeneous media

\[ \sigma_{ij} = \lambda \delta_{ij} \varepsilon_{kk} + 2\mu \varepsilon_{ij} \]  \hfill (A10a)

\[ \sigma_{ij} = 2\mu \varepsilon_{ij} \]  \hfill (A10b)

There is no shear for the fiber mat stretching, hence,

\[ \sigma_{ij} = 0 \text{ for } i \neq j \]  \hfill (A10c)

As a result, only \( \sigma_{rr} \), \( \sigma_{zz} \), and \( \sigma_{\theta\theta} \) remain.

As the fiber mat thickness is constant, \( \sigma_{zz} \) is related the pressure drop across the mat while not the material properties.

The stress in \( \theta \) direction is zero due to symmetry, thus
\[ \sigma_{\theta\theta} = 0 \quad (A11a) \]

Finally, \( \sigma_{rr} \) is the only term left and

\[ \sigma_{rr} = 2\mu \varepsilon_{rr} \quad (A11b) \]

Now consider an arbitrary point (A) on the mat surface for evaluating a force analysis (Figure A4). Taking advantage of symmetry, \( T \) is the tangential force in the plane of the fiber mat acting on a circle centered on the z-axis and with a radius \( r \),

\[ T = \sigma_{rr} \cdot 2\pi r L = 2\mu \varepsilon_{rr} \cdot 2\pi r L = 4\pi r L \mu \varepsilon_{rr} \quad (A12) \]

where \( L \) is the mat thickness.

The component of \( T \) in \( z \) direction, \( T_z \), is balanced with vertically downward force \( F_z \) that due to the pressure drop

\[ F_z = \Delta P \cdot \pi r^2 \quad (A13) \]

\[ T_z = T \cdot \sin \varphi = 4\pi r L \mu \varepsilon_{rr} \cdot \sin \varphi = \Delta P \cdot \pi r^2 = F_z \quad (A14) \]

\[ \varepsilon_{rr}(r) = \frac{\Delta P r}{4\mu L \sin \varphi(r)} \quad (A15) \]

where \( \varepsilon_{rr} \) and \( \sin \varphi \) are both functions of position \( r \).

Figure A. 4 Force analysis of a point on the fiber mat.
Define \( r \) as the unstressed flat mat length and \( s \) as the corresponding stressed curved mat length, hence

\[
s = r(1 + \varepsilon_{rr})
\]  
(A16)

Approximate the curve as a straight line, then

\[
\cos \varphi = \frac{r}{s} = \frac{r}{r(1 + \varepsilon_{rr})} = \frac{1}{1 + \varepsilon_{rr}}
\]  
(A17)

\[
\varphi = \cos^{-1} \left( \frac{1}{1 + \varepsilon_{rr}} \right)
\]  
(A18)

Substituting Equation A18 into A15 yields

\[
\varepsilon_{rr}(r) = \frac{\Delta Pr}{4\mu L \sin \left( \cos^{-1} \frac{1}{1 + \varepsilon_{rr}(r)} \right)}
\]  
(A19)

Consider a small increase along the fiber mat surface shown in the red box (Figure A5), then

\[
\Delta s^2 = \Delta z^2 + \Delta r^2
\]  
(A20)

\[
ds^2 = dz^2 + dr^2
\]  
(A21)

\[
ds = \sqrt{dz^2 + dr^2}
\]  
(A22)

\[
\frac{ds}{dr} = \sqrt{1 + \left( \frac{dz}{dr} \right)^2}
\]  
(A23)
Recall Equation A16

\[ s = r(1 + \varepsilon_{rr}) \]  

(A16)

Take derivative of \( s \) with respect to \( r \)

\[ \frac{ds}{dr} = 1 + \varepsilon_{rr} + r \frac{d\varepsilon_{rr}}{dr} \]  

(A24)

Combination of Equation A23 and A24 yields

\[ \sqrt{1 + \left(\frac{dz}{dr}\right)^2} = 1 + \varepsilon_{rr} + r \frac{d\varepsilon_{rr}}{dr} \]  

(A25)

\[ 1 + \left(\frac{dz}{dr}\right)^2 = \left(1 + \varepsilon_{rr} + r \frac{d\varepsilon_{rr}}{dr}\right)^2 - 1 \]  

(A26)

\[ \frac{dz}{dr} = \sqrt{(1 + \varepsilon_{rr} + r \frac{d\varepsilon_{rr}}{dr})^2 - 1} \]  

(A28)
Equation A19 and A28 are the intermediate equations used to further derive the final equation that describes the fiber mat profile. Due to the complexity, Equation A19 is solved numerically instead of analytically to get the relationship between $\varepsilon_{rr}$ and $r$. With $\frac{\Delta P}{4\mu L}$ as a positive constant, a list of $r$ values is input into the equation to calculate for the corresponding $\varepsilon_{rr}$ values. The two lists of values are used for generating the plot of $\varepsilon_{rr}$ vs. $r$ and then running the regression analysis. Both plot and regression analysis suggest an almost straight line through the original point $(0, 0)$ with a certain slope ($k > 0$) that is related to the pre-specified constant, and the relation is written as

$$\varepsilon_{rr} = k \cdot r$$  \hspace{1cm} (A29)

Take derivative with respect to $r$

$$\frac{d\varepsilon_{rr}}{dr} = k$$  \hspace{1cm} (A30)

Substitute Equations A29 and A30 into A28

$$\frac{dz}{dr} = \sqrt{1 + k \cdot r + r \cdot k^2} - 1 = \sqrt{(2kr + 1)^2 - 1} = \sqrt{4k^2r^2 + 4kr}$$  \hspace{1cm} (A31)

Integration of Equation A31 gives

$$z = \left( r + \frac{1}{2k} \right) \sqrt{k^2r^2 + kr} - \frac{1}{4k} \ln \left( 2kr + 2\sqrt{k^2r^2 + kr} + 1 \right) - \frac{\ln 4k}{4k} + C$$  \hspace{1cm} (A32)

where $C$ is the constant.

Apply the boundary condition: $z = 0$ at $r = R$ to calculate for $C$

$$C = \frac{1}{4k} \ln \left( 2kR + 2\sqrt{k^2R^2 + kR} + 1 \right) + \frac{\ln 4k}{4k} - \left( R + \frac{1}{2k} \right) \sqrt{k^2R^2 + kR}$$  \hspace{1cm} (A33)

Substitute the constant into Equation A32 to get the final analytical solution
\[ z = \left( r + \frac{1}{2k} \right) \sqrt{k^2 r^2 + k r} - \frac{1}{4k} \ln \left( 2 k r + 2 \sqrt{k^2 r^2 + k r} + 1 \right) \]

\[ + \frac{1}{4k} \ln \left( 2 k R + 2 \sqrt{k^2 R^2 + k R} + 1 \right) - \left( R + \frac{1}{2k} \right) \sqrt{k^2 R^2 + k R} \]

(A36)

Symmetry occurs at \( r = 0 \) (\( z \) axis). The whole curve passes through end points \((-R, 0)\) and \((R, 0)\), and vertex \((0, \frac{1}{4k} \ln(2 k R + 2 \sqrt{k^2 R^2 + k R} + 1) - \left( R + \frac{1}{2k} \right) \sqrt{k^2 R^2 + k R})\) and shows similarity compared to a parabola that passes through the same points.
Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>C</td>
<td>Fourth-order stiffness tensor</td>
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<td>E</td>
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<td>F</td>
<td>Force</td>
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<td>L</td>
<td>Fiber mat thickness</td>
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<td>P</td>
<td>Pressure</td>
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<td>ΔP</td>
<td>Pressure drop across the fiber mat</td>
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<td>R</td>
<td>Circular opening radius</td>
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<td>T</td>
<td>Tangential force along the fiber mat</td>
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Greek symbols

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## APPENDIX B

### LISTS OF THE COORDINATES OF THE SELECTED POINTS ON CURVES

Table B. 1 Coordinates of the selected points on the curves with an intercept of -5 mm.

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Table B. 2 Coordinates of the selected points on the curves with an intercept of -10 mm.

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<th>Parabola</th>
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Table B. 3 Coordinates of the selected points on the curves with an intercept of -15 mm.

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APPENDIX C

DATA SUMMARY OF THE FRAZIER AIR PERMEABILITY TESTS

Pressure drop ($\Delta P$), expanding depth (H), surface area (A), volumetric flow rate ($m^3$/h), and permeability/mat thickness (k/L) value data for the stretched fiber mats of different basis weights subject to air flow.

Table C. 1 Data summary for the stretched fiber mats of basis weight 15g/m$^2$.

<table>
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<tr>
<th>$\Delta P$, Pa</th>
<th>H, mm</th>
<th>A, mm$^2$</th>
<th>Q, $m^3$/h</th>
<th>k/L, m</th>
</tr>
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<tbody>
<tr>
<td>25</td>
<td>5.83</td>
<td>2067</td>
<td>1.44 ± 0.13</td>
<td>1.40E-07 ± 1.24E-08</td>
</tr>
<tr>
<td>30</td>
<td>5.95</td>
<td>2071</td>
<td>2.05 ± 0.17</td>
<td>1.66E-07 ± 1.39E-08</td>
</tr>
<tr>
<td>37.5</td>
<td>6.44</td>
<td>2089</td>
<td>3.05 ± 0.15</td>
<td>1.96E-07 ± 9.68E-09</td>
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<tr>
<td>45</td>
<td>6.92</td>
<td>2107</td>
<td>3.96 ± 0.16</td>
<td>2.10E-07 ± 8.55E-09</td>
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<tr>
<td>50</td>
<td>7.33</td>
<td>2124</td>
<td>4.51 ± 0.14</td>
<td>2.13E-07 ± 6.46E-09</td>
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<tr>
<td>52.5</td>
<td>7.4</td>
<td>2127</td>
<td>4.76 ± 0.17</td>
<td>2.14E-07 ± 7.82E-09</td>
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<tr>
<td>55</td>
<td>7.56</td>
<td>2133</td>
<td>4.99 ± 0.11</td>
<td>2.14E-07 ± 4.74E-09</td>
</tr>
<tr>
<td>60</td>
<td>7.88</td>
<td>2147</td>
<td>5.39 ± 0.15</td>
<td>2.10E-07 ± 5.84E-09</td>
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<tr>
<td>62.5</td>
<td>8.04</td>
<td>2154</td>
<td>5.71 ± 0.25</td>
<td>2.13E-07 ± 9.34E-09</td>
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Table C. 2 Data summary for the stretched fiber mats of basis weight 30g/m$^2$.

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<th>$\Delta P$, Pa</th>
<th>H, mm</th>
<th>A, mm$^2$</th>
<th>Q, $m^3$/h</th>
<th>k/L, m</th>
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<td>37.5</td>
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<td>0.78 ± 0.04</td>
<td>5.17E-08 ± 2.65E-09</td>
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<td>1.68 ± 0.03</td>
<td>8.21E-08 ± 1.66E-09</td>
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<tr>
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<td>2.62 ± 0.10</td>
<td>1.01E-07 ± 3.71E-09</td>
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<td>3.50 ± 0.05</td>
<td>1.12E-07 ± 1.66E-09</td>
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<td>4.16 ± 0.04</td>
<td>1.12E-07 ± 1.00E-09</td>
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<tr>
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<td>2153</td>
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<td>1.10E-07 ± 9.93E-10</td>
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<td>5.19 ± 0.08</td>
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<td>125</td>
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<td>2199</td>
<td>5.82 ± 0.12</td>
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Table C. 3 Data summary for the stretched fiber mats of basis weight 45g/m².

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<td>37.5</td>
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<td>7</td>
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<td>5.19 ± 0.10</td>
<td>9.89E-08 ± 1.99E-09</td>
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