SMART SUPERHYDROPHOBIC MATERIALS

Adetoun Taiwo

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SMART SUPERHYDROPHOBIC MATERIALS

A Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical and Nuclear Engineering at Virginia Commonwealth University.

by

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Abstract

SMART SUPERHYDROPHOBIC MATERIALS

By Adetoun Oludara Taiwo, B.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University.

Virginia Commonwealth University, 2013.

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Superhydrophobicity refers to surfaces with extremely large water droplet contact angles (usually greater than 150°). This phenomenon requires a hydrophobic material with micro or nano-scale roughness. Superhydrophobic surfaces exist in nature (e.g. the lotus leaf) and can be produced synthetically. This project focuses on the development and characterization of superhydrophobic materials with tunable wettability (i.e. smart superhydrophobic materials). In this study, surfaces were prepared by electrospinning thin, aligned polystyrene fibers onto a piezoelectric unimorph substrate. Results showed electric field induced changes in substrate curvature, which produced corresponding changes in surface wettability. From experiments, an average change in water contact angle of 7.2° ± 1.2° with 90% confidence was observed in ~2μm diameter fiber coatings.
electrospun for 5 minutes with applied electric field. In addition, fiber coatings electrospun with equivalent deposition showed average electric field induced changes in WCA of 2.5° ± 0.92° for lower diameter fibers (~1µm) and 3.5° ± 1.37° for higher diameter fibers (~2µm) with 90% confidence.
CHAPTER 1 Introduction

Smart superhydrophobic materials can be defined through the lens of smart materials and superhydrophobic materials. Smart materials are ones whose properties can be altered with the initiation of a stimulus such as temperature, an electric field or a magnetic field; more details on these materials will be discussed later. On the other hand, a proper definition of superhydrophobic materials requires a basic explanation of the concept of hydrophobicity, which is discussed in the next section.

1.1 Superhydrophobicity

Hydrophobicity is a term that describes the wetting behavior of a material. A hydrophobic material is one that repels water and is difficult to wet while a hydrophilic material is one that is easily wettable. These expressions stem from the Greek root “hydro”, which means “water” and suffixes “phobos” and “philia” meaning, “fear” and “love” respectively. Hydrophobic and hydrophilic materials can be classified using a metric known as static contact angle (the angle a stationary liquid droplet makes with the interphase of the solid it sits on and surrounding vapor [1], [2], [3]). Specifically a droplet of water on a solid surface makes this angle with the solid where it interphases with air around it.

Water contact angle (WCA), which is defined the same as above but for water specifically, is measured using a device called a contact angle goniometer. By definition,
when the WCA of a material is below 90°, it is said to be hydrophilic. Conversely, hydrophobic materials have a WCA above 90°, and when the WCA for a material falls between 150° and 180° it is known as superhydrophobic and water droplets tend to bead on the surface of such a material.

![Figure 1.1: Criteria for hydrophobicity](image)

**1.1.1 History of superhydrophobic materials**

Several instances of superhydrophobicity were identified before the term was actually used in the literature. Around the 1900s and early 1920s, contact angles (CA) around 160° and above were observed on surfaces coated with soot and another with galena modified with steric acids indicates that research relating to superhydrophobic materials dates back to more than a century ago. A few decades later, Wenzel, Cassie and Baxter established the principles behind superhydrophobic behavior. Between
the 1940s and 1990s, research progressed slowly especially in connection with geometry effects on wetting behavior until 1996 when T. Onda et al. pioneered validation of artificial superhydrophobic surfaces.\[4, 6, 10, 11\] A year later, the term “lotus effect,” that describes the natural superhydrophobic property in lotus leaves, was patented by Neihus and Barthlott, which catalyzed research in the field as exemplified by the first critical review on superhydrophobicity by McCarthy et al. in 1999.\[4, 6, 12, 13\]

In the last couple of decades, significant research efforts have been channeled towards the creation of superhydrophobic materials using relatively simple and inexpensive means. Many of the techniques reported in literature involve microfabrication and chemical processes.\[6, 14, 15, 16\] Some specific techniques include etching,\[17\] chemical vapor deposition\[18\], thermal through-air bonding,\[19\] and two-beam laser interference.\[14, 16\] In recent times, superhydrophobic materials have become sought out for applications including anti-fog and anti-corrosion surfaces\[6\], self-cleaning\[20\], deicing\[21\], drag reduction\[20\], as well as medical devices.\[16\]

1.1.2. Existence of Superhydrophobicity in Nature

Numerous cases of superhydrophobic behavior are found in nature and have motivated researchers to duplicate this phenomenon artificially (depicted in Figure 1.2 below - the surface on the right is a modified cotton fabric). As mentioned above, a popular example of a naturally occurring superhydrophobic material is the lotus (Nelumbo nucifera) leaf, which is equipped with hierarchical surface projections (epicuticular wax crystals) responsible for its characteristic superhydrophobicity and low adhesion to water.\[11, 14, 20, 22\] When a lotus leaf is tilted, water droplets roll down the surface and collect
contaminant particles such as dust and spores along the way—this is due to the micro and nanoscale projections that provide roughness on the leaf surface.\textsuperscript{[10, 20, 23]} These projections reduce contact area and adhesion between dirt particles and the leaf surface, while increasing these same factors between the particles and water resulting from rain, dew or fog thereby enhancing easy roll-off of dirt from the surface of the leaf.\textsuperscript{[24, 25]} The probability of dirt roll-off depends on the fraction of tension at the interphase between water, the surface and contaminant particles.\textsuperscript{[25]}

![Figure 1.2: Picture (from left to right) showing a water droplet(s) on a lotus leaf and superhydrophobic surface.\textsuperscript{[26, 27]}

Rice (Oryza sativa) leaves are also similar natural superhydrophobic surfaces due to “epicuticular wax” and longitudinal indentations on their “micropapillae”.\textsuperscript{[20]} The Indian Cress (Tropaeolum majus) is another example of a water-repelling leaf species with microscopic surface roughness.\textsuperscript{[22]} Its roughness is on three different length scales, which include about one micron-sized wax crystals, wax crystal bundles about five microns apart and epicuticular cells of a few tens of microns. Butterfly wings (e.g. Blue Morpho didius) protect their body from water and contaminants via hierarchical scales that make their surface superhydrophobic.\textsuperscript{[20]} Absence of this mechanism would allow capillary forces to
prevent them from flying by making their wings stick together. \[28\]

Figure 1.3: Picture showing water striders floating on water \[29\]

In addition to flora listed above, superhydrophobicity also occurs in fauna such as some insects found in water. The mechanism adopted for gliding by water striders involves the superhydrophobic surface of their legs. \[28\] This feature prevents them from drowning. In addition, scientists have demonstrated that a bed of hairs sustains an air layer on the underside of some arthropods such as the water boatman. \[30\] This bed of hairs buoys their body to achieve superhydrophobicity.

1.1.3 Applications of superhydrophobicity in Science and Engineering

There are several applications for superhydrophobic materials in science and engineering. They could be applied as transparent superhydrophobic coatings for various uses including architecture, vehicle windows, eyeglasses, and optical windows for electronics. \[31, 32\] An application that mimics the superhydrophobic property of butterfly wings is that of a uniform inverse opal investigated by Z. Gu et al. Potential applications
for this material include adornment of the exterior of architectural structures, which serve both aesthetic and superhydrophobic purposes. \[32, 33\]

Superhydrophobic surfaces have the capacity to reduce drag in water as a result of a significant repulsion that limits the interaction of water at the interface. Consequently, a thin layer of air and a new condition between air and water occurs. \[9, 32, 34\] Drag reduction in superhydrophobic materials has undergone more in-depth study in recent years. \[11, 14, 20\]

In addition, superhydrophobic coatings offer a means for control of fluids as demonstrated in an experiment in which a water droplet is electrostatically manipulated on a superhydrophobic surface. \[32, 35\]

Understanding of the mechanism of water striders’ legs shows that coatings that mimic this structure provide additional support for objects that float or are immersed in water. \[32, 36\] Superhydrophobic coatings have also been found useful to help support force on objects placed on coated surfaces. In an experiment by X. Zhang and his group a superhydrophobic coating enhanced supporting force per centimeter beyond that provided by a regular hydrophobic coating on a surface. \[32\] The group believes this enhancement results from higher surface tension in the vertical direction because of the superhydrophobic coating.

In figure 1.4 below, a few applications of superhydrophobic materials are also depicted with pictures showing deicing (A), self-cleaning (B), repellent spray (C) and drag reduction (D). Picture (A) shows a superhydrophobic plate \[images (a), (d) and (g)\] not easily covered in ice relative to a hydrophilic surface \[images (b), (e) and (h)\] and vulcanized rubber \[images (c), (f) and (i)\]. \[21\] In picture (B), liquid droplets are beaded on
a fluorinated SiO$_2$ layer on a silicon wafer indicating superhydrophobic behavior. [37] A repellent spray is applied to the various surfaces shown in picture (C). [38] Picture (D) shows a superhydrophobic rib model patterned after the skin of a shark (Squalus acanthias). [14]

![Figure 1.4: Pictures showing various applications of superhydrophobic materials](image)

1.1.4 Fabrication Methods for Superhydrophobic Materials

A superhydrophobic material is created based on the influences of low surface energy (additional energy at the surface of a material relative to the bulk) and surface roughness. [11, 22] Hydrophobic materials have low surface energy; hence a combination of a rough surface applied to a hydrophobic material can be used to produce a
superhydrophobic material. In a particular study, changes in a material from hydrophilic to superhydrophobic were achieved by altering the roughness of its surface. In this study, Y. He and his colleagues used reactive ion etching and catalyzed etching to create both micro and nano scale pillars to bring about superhydrophobicity on a silicon surface. This points to the pivotal role that surface roughness plays in the fabrication of superhydrophobic materials.

There are several ways of generating superhydrophobic materials based on low surface energy and roughness. A material that is already hydrophobic can be roughened. Such materials include fluorocarbons, silicon compounds, and organic materials (e.g. polystyrene) and roughness can be applied to them through various methods such as casting, electrochemical polymerization and electrospinning. Conversely, a hydrophobic coating can be applied to an already rough surface. There are several methods used to create rough surfaces such as surface etching, electrical or chemical reaction, and chemical vapor deposition.

A few specific processes recorded in the literature will be highlighted as representatives of the multiple techniques used to fabricate superhydrophobic materials. An example previously mentioned was by Y. He and his colleagues, which used reactive ion and catalyzed etching. Micro and nano surface structures have also been made with zinc oxide (ZnO) nanoparticles on micropatterned substrates through surface modification with octadecylphosphonic acid (ODP). A superhydrophobic cotton fabric was prepared by multiple dip-coating cycles of TiO₂ and subsequent surface modification with n-octadecylthiol (ODT). Another example by J. Zhang and his colleagues
involves elongation of a polytetrafluoroethylene (PTFE also known as Teflon) sheet causing a distortion of the microstructure and production of a rough surface with a WCA as high as 165°. [41] This particular experiment highlights that a change in microstructure could produce excellent results in the attempt to create a superhydrophobic material. R. Asmatulu et al. [42] produced superhydrophobic fibers using electrospinning and included titanium dioxide and graphene based nanoparticles in the fibers to enhance superhydrophobicity. They also noted that electrospinning is potentially useful for tunable non-wetting behavior.

### 1.2 Electrospinning

#### 1.2.1 History of Electrospinning

The science that has directly influenced the development of electrospinning began over 200 years ago around the time the concepts of electricity and magnetism were beginning to be better understood. [43] Over a century ago, patents and experiments related to the distribution of fluid through an electric field [44, 45, 46, 47] were recorded. These paved the way for the patent by Anton Formhals in 1934, the first for electrospinning, as it is known today. [43, 48, 49] Several other patents for electrospinning have since been released [43, 50, 51, 52, 53, 54, 55, 56, 57, 58] however, it was not until 1995 that Jayesh Doshi and Darrel H. Reneker coined the name “electrospinning” for this process. [43, 59] Since this research was published, significant efforts have been focused on this process especially with the heightened interest in nanotechnology, as it has the capacity to produce micrometer (10^{-6}) and nanometer (10^{-9}) sized fibers. [42, 60, 61, 62] In the fields of science and technology
Electrospinning has become a sought-out option for applications including non-woven fabrics, tissue scaffolds, filtration media, and medical devices.

1.3 Objective of this Thesis

The aim of this project is to attempt to create a smart superhydrophobic material by tuning the wetting behavior of a hydrophobic substrate through a voltage-induced mechanical process. This process involves electrospinning of polystyrene (PS) fibers on smart substrates (piezoelectric unimorphs) and measurement of the contact angles made by water droplets on the fiber-coated substrate. Having a tunable system is valuable as it creates opportunity to interact with the material and can lead to progression from a simple model to a device.

There are several methods recorded in literature on how to develop superhydrophobic materials [11, 15, 32, 40, 41] that involve chemical processes. However, only a few methods have been developed that involve a change in microstructure through an adjustable mechanical process. The method described above [41] in which a Teflon sheet’s microstructure was changed by stretching is an example in which superhydrophobicity is achieved by an adjustable method. This technique also confirms how a change of microstructure could provide a means to adjusting the hydrophobicity of a material to achieve superhydrophobicity. Even though that experiment did not motivate this project, it confirmed the plausibility of the goal to tune wettability by mechanically changing surface microstructure. The work by R. Asmatulu et al. noted above [42] also provides support for a tunable approach involving the process of electrospinning for a superhydrophobic application.
In order to facilitate explanation of the approach for tuning via a piezoelectric unimorph applied in this work, a brief overview of smart materials and piezoelectricity will be covered in the next section.

1.4 Smart Materials and Piezoelectricity

Smart materials are a group of materials with unique properties that can be changed by the influence of an external stimulus. Examples of smart materials include magnetostrictive materials, piezoelectric materials, shape-memory polymers and alloys, and electrochromic materials. A piezoelectric material, PZT-5A, is used in this project specifically. A piezoelectric material is one that has the capacity to change its shape or dimensions in the presence of an applied electric field or one that produces an intrinsic electric charge on application of mechanical stress.

1.4.1 Brief History of Piezoelectricity

Jacques and Pierre Curie discovered piezoelectricity in the late 19th century with the observation of the piezoelectric effect in crystals.\textsuperscript{[63]} This effect has to do with the production of positive charges on one side of a crystal and negative charges on its opposite surface in response to an applied mechanical stress such as bending.\textsuperscript{[63]} It was also confirmed that the inverse of this effect could result, in which an electric field applied to both sides of the material causes bending.\textsuperscript{[63]}

The Curie brothers classified crystals and suitable conditions for piezoelectricity in them through consideration of crystal symmetry and their previous studies on pyroelectricity (“ability of certain materials to generate an electrical potential when they
are heated or cooled). Another scientist, Voigt came up with the tensor (mechanical stress) equations that described the linear behavior of piezoelectric crystals. In addition, Max Born formulated theoretical crystal lattice calculations for the piezoelectric coefficient (change experienced by a piezoelectric material as a result of an electric field or polarization as a result of applied stress) in the 1920s.
CHAPTER 2 Theories of Superhydrophobicity, Electrospinning, and Piezoelectricity

2.1 Wetting Modes for Superhydrophobic Materials

Wetting behavior of materials has been explained by Young’s equation, which expresses the static contact angle of a droplet of water on a solid surface. The water droplet has three relevant phases of contact: solid, liquid and vapor phases each with its own associated surface tension that helps define the shape of the drop. [1, 10, 61] The equation is shown below:

\[
\cos \theta_V = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]

(1)

Where \( \gamma_{SV} \), \( \gamma_{SL} \) and \( \gamma_{LV} \) represent surface tension of the solid-vapor, solid-liquid and liquid-vapor interphases respectively. Young’s work helps highlight how reduction of surface tension of the solid helps improve static WCA but subsequent research efforts have also been made to incorporate the influence of roughness on wetting behavior. [61] Two major models of this phenomenon are the Cassie-Baxter and Wenzel models. [9, 18]

Cassie-Baxter explained that for a solid in contact with a liquid droplet, air could sit partially below the droplet in the spaces created by the rough surface, thereby causing a superhydrophobic behavior. [7, 9, 61] On the other hand Wenzel believes roughness increases the surface area as the water traces the pattern of the inconsistencies of the solid in contact with the drop thereby enhancing hydrophobic behavior. [7, 8, 61] Equations to describe these theories are shown below:
\[
\cos \theta^* = f (\cos \theta) + 1 - 1 \\
\cos \theta^* = r (\cos \theta)
\]

In the Cassie-Baxter equation, \( f \) represents the fraction of the solid in contact with the liquid while \( r \) represents the roughness of the surface in the Wenzel equation. \( \theta^* \) represents the measured contact angle and \( \theta \) represents the contact angle of the flat solid without additional roughness. The value of \( f \) is usually smaller than unity while \( r \) is typically larger than unity. \(^7\) These models are useful for describing the hydrophobic behavior of various materials including the surfaces of hydrophobic polymer fibers relevant to this project.

2.2 Electrospinning and Fibrous Polymer Coatings

There are several methods used to create non-woven fibers including drawing, extrusion, and electrospinning. Among these and various other methods recorded in the literature, electrospinning has the ability to effectively create fibers in the micro and nano range. This process has also recently been under significant scrutiny because it is relatively cheap and versatile for various applications including self-cleaning, medical and microfluidic devices. \(^{16}\)

Electrospinning is a process that creates thin fibers, which are deposited on a target surface with the aid of an electric field. \(^{59}\) Fibers are generated from viscoelastic materials including sol-gels, polymer melts and polymer solutions. \(^{62}\) The most commonly electrospun materials are polymers, substances made up of long chains of smaller subunits called monomers, which can be either natural (biopolymers) or synthetic polymers. Plastics are popular commercial polymers. The structure of polymers consists of monomers that
have been combined through the process of polymerization. Electrospinning is also useful for its easy scale-up potential, which in fact has been achieved in Nanospider™. Other benefits include its ability to apply a wide variety of coatings including hydrophobic polymer fibers to substrates of arbitrary geometry, and create aligned and controlled structures.

2.2.1 Electrospinning Process

Electrospinning involves three main components: the polymer fluid usually contained in a capillary such as a hypodermic needle, an electric field source and a collector, however, each setup has different variations. Sometimes there is a top-to-bottom arrangement of the needle and collector. They could also be arranged horizontally across from each other. Sometimes, the needle is held in place by an infusion pump that controls the release of the liquid. There also different kinds of collectors used including a grounded stationary metal screen [59], rotating collectors of different forms [48, 66, 67, 68, 69] as well as a shallow water bath collector (“electro-wet apparatus”) [48, 70, 71]. The type of collector used depends on the specific application. The needle is usually connected to an electric field source and the collector could either have the opposite of the charge passing through the solution or be grounded. In addition to electric charge, several parameters affect the process of electrospinning and will be discussed further later.

A solution contained in the needle/capillary is held in by surface tension. Without voltage, this solution would form a pendant drop at the tip of the needle. However, with the application of voltage, it goes from a hemispherical to a spherical shape. With increase in
voltage, the solution continues to bulge, with the maximum charge at the tip, which results in tapering into a conical shape called the Taylor cone.\textsuperscript{[59, 72, 73]} Eventually, a critical voltage value is reached where the electrostatic force overcomes surface tension of the fluid and a jet is released. This jet travels in air causing the solvent(s) to evaporate as the jet dries and is deposited on the collecting surface as a fiber.

Instability of the jet due to electric charge results in random arrangement of fibers. However, various methods including the use of an alternating current (AC) field source, a negative ion source such as a corona assembly or a rotating collector help distribute charge thereby reducing instability and producing aligned fibers. It is important to know that completely or perfectly aligned fibers are difficult to obtain.

2.2.2 Electrospinning Parameters

Electrospinning parameters can be divided into three groups: solution parameters, ambient parameters and controlled parameters.\textsuperscript{[59]} Solution parameters include viscosity, concentration, and molecular weight. Ambient parameters include temperature, humidity and atmospheric pressure. Controlled parameters include infusion rate, spinning voltage and needle tip-to-collector distance.\textsuperscript{[74]}

Viscosity plays a significant role in the electrospinning process.\textsuperscript{[62, 75]} Solutions of low viscosity usually produce a combination of fibers with beads also known as bead-on-string. However, a sufficient viscosity can be reached where beads are eliminated and uniform fibers are collected. An important factor that affects solution viscosity is the weight concentration of polymer in the solution. Consequently, higher polymer
concentration increases the probability of fibers without beads and lower concentrations produce beads. However, with higher concentration of polymers, the viscosity is increased and the diameter of resulting fibers is larger in addition to possible formation of fiber bundles. [62, 75] Thinner fibers are produced at low viscosities. Also at very low viscosities or molecular weight, chain entanglement of the polymer is limited. As a result, the polymer breaks up into droplets rather than a continuous jet being formed. [75, 76] This occurrence, known as electrospraying is also influenced by the electric charge in the jet as it causes Raleigh instability. [76, 77] Electrospraying is useful in various applications however; the details are not covered in the context of this research.

It is a difficult task to isolate the impact of all the parameters that affect electrospinning as several of them work in tandem, such as concentration and viscosity as discussed earlier. [75] Experiments by Dietzel and his group using PEO have shown that an electric field influenced bead formation as fibers without beads were formed at 5.5kV while beads were observed for the same solution at 9kV. [75] They indicated that voltage at which the process was initiated affected the shape of the fluid at the capillary tip. As discussed above (section 2.2.1), applied voltage causes instability of the jet as charge passes through the polymer. This phenomenon often referred to as whipping instability, usually occurs a couple of centimeters beyond the tip of the cone and contributes to formation of random fibers. [62, 78] To reduce instability during spinning, several methods have been utilized such as increasing the speed of the rotating collector (drum), application of an AC voltage, and combination of a direct current (DC) bias with AC voltage. [78]
Most of the above techniques for reducing instability of the jet involve manipulation of its motion via regulation of the applied electric field. Other methods used involve near-field electrospinning using a tungsten electrode on a silicon based collector, conductive collector electrodes separated by an air gap with variable width, copper wires spaced evenly to form of a circular drum composed of a plexiglass disk, spinning on a water reservoir collector and subsequent drawing of the non-woven fiber web across the water prior to collecting the yarn, and a rotating collector consisting a Teflon tube with a negatively charged electrode underneath to facilitate deposition.

Figure 2.1: Illustration of Taylor cone and jet from polymer surface

2.3 Basics of Piezoelectricity

There are several materials that display piezoelectricity such as quartz, barium titanate (BaTiO₃), strontium titanate (SrTiO₃), zinc oxide thin films, tourmaline, lithium niobate, Rochelle salt and lead zirconate titanate (PZT) ceramics. Numerous naturally occurring piezoelectric materials, such as Rochelle salt show hardly noticeable evidence of the piezoelectric effect therefore, many piezoceramics such as PZT that have good
ferroelectric properties have been produced. In simple terms, ferroelectricity is a property possessed by a material that shows permanent electric polarization dependent on the amount of electric field applied. PZT ceramics are the most commonly used ferroelectric materials for various applications because of their exceptional mechanical and piezoelectric properties in addition to their capacity to be produced in different forms for transducer and actuation applications in their polycrystalline state.

In its natural state, PZT crystals have a crystal framework with unit cells that are symmetrical that is, the ions in the unit cell have “simple cubic symmetry”. Below Curie temperature they lose their symmetry as the ions in the cubic lattice are displaced; in other words polarization has occurred. Polarization in this case is a spontaneous process and individual crystals of the ceramic become piezoelectric when this occurs. There are several domains (groups consisting of unit cells with similar orientation) scattered around in a given material. This random location of “domains” around the material makes it difficult to observe the piezoelectric effect. However, the process of poling in which a uniform distribution of domains is elicited in the material through the influence of a high electric field remedies this challenge (see figures 2.2 and 2.3). A consequence of poling is that the ceramic has a residual polarization, which can degenerate if the maximum thermal, electrical or mechanical capacity of the material is overstepped.

Figure 2.3 below shows the randomly oriented domains before polarization (a), the application of a high electric field causing poling (b) and the resulting permanent poling with the residual polarization in the ceramic (c).
Figure 2.2: Picture showing the orthogonal axes and poling direction of a piezoelectric material

Figure 2.3: Picture illustrating poling of a piezoelectric material (a) randomly oriented domains; (b) polarization by strong DC electric field; (c) residual polarization after electric field is removed

Figure 2.4: Plot showing polarization with respect to electric field i.e. poling curve/hysteresis curve
Some of the applications of piezoelectric materials include transducers for spotting submarines underwater \cite{65}, actuators and transducers in microphones and buzzers, dielectric material in ceramic capacitors, thermistor in heating systems, vibration sensors, shock accelerometers and atomic force microscope probes. \cite{85} PZT ceramics are the most commonly used piezoelectric materials for various applications because of their exceptional mechanical and piezoelectric properties in addition to their capacity for formation into different shapes for transducer applications in their polycrystalline state. \cite{85}
CHAPTER 3 Experimental Apparatus

The setup for electrospinning included an infusion pump (HARVARD apparatus PHD 2000), a DC power supply (TENMA 72-6615), a variable autotransformer (STACO Model 3PN1010B), high voltage amplifier (Matsusada precision Inc.), a two-phase Vexta stepping motor (Model PK268-02A) with an Immediate Motion Creator (IMC) software, a positioning system, a rotating collector, and a vibration isolation table. The polymer solution used in electrospinning comprised of polystyrene, toluene, and tetrahydrofuran (THF). Thunder® (FACE® international corporation) unimorphs were used as the substrate for electrospun fibers and these coatings were characterized using a Ramé-Hart goniometer, Nikon optical microscope and scanning electron microscope (Hitachi Su-70).

3.1 Electrospinning Set-up

The main set up for electrospinning used in this project included a voltage source, an infusion pump, a needle containing the polymer solution, and a grounded collector. As discussed previously (section 2.2.1), the kind of collector used helps determine whether fibers produced are randomly arranged or aligned on the substrate. A rotating collector was used which involved a moving drum and enhanced production of aligned fibers. The Immediate Motion Creator software controlled the process used to apply translational motion to the collector while a motor was used to produce high-speed rotation.
The choice of using a rotating collector, which produced aligned fibers for the purposes of this research, was important as the absence of a defined fiber arrangement complicates the process of detecting fiber spacing and other significant parameters that could influence wettability. Figure 3.2 below shows a scanning electron micrograph of random and aligned fibers of polystyrene.

![Figure 3.2: Random and aligned Polystyrene fibers](image)
Polystyrene, the focus material from which coatings were made in this research was chosen because it is one of the most thoroughly studied hydrophobic polymers with known physical properties and suitable processing parameters. It is also relatively cheap and easy to electrospin. Figure 3.3 below shows the molecular structure of polystyrene. In this figure, \( n \) represents the number of repeating units of the polymer. As shown, a polystyrene monomer consists of a straight hydrocarbon chain with a benzene substituent. The benzene ring gives polystyrene its characteristic hydrophobic behavior.

\[
\begin{align*}
\text{H}_2\text{C} & - \text{CH}_2 \\
\end{align*}
\]

Figure 3.3: Molecular structure of polystyrene

### 3.2 Electrospinning Solutions

Table 3.1: Table showing data for chemicals used

<table>
<thead>
<tr>
<th>Polymer/Solvent</th>
<th>Molecular Formula</th>
<th>Molecular Weight (M&lt;sub&gt;w&lt;/sub&gt;)</th>
<th>Density</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td>(C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>~350,000g/mol</td>
<td>1.06g/mL @ 25°C</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Toluene</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>92.14g/mol</td>
<td>0.87g/mL @ 20°C</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O</td>
<td>72.11g/mol</td>
<td>0.89g/mL @ 20°C</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>
3.3 Electrospinning Substrates

For the electrospinning process, two substrates were used. Nylon meshes were used for the preliminary observations while piezoelectric unimorphs were utilized in subsequent experiments.

3.3.1 Nylon Mesh

Nylon meshes with 1/2” micron diameter (Small Parts™, NYL filter 149) were used as substrates for polystyrene fibers for the preliminary observation of fiber morphology and determination of average fiber diameter with solution concentration.

3.3.2 Thunder Piezoelectric Unimorphs

The Thunder® unimorph substrates (Thunder® LI-1 model) used in this project are piezoelectric unimorphs. A unimorph is a composite material with one active layer and an inactive layer. In case of a piezoelectric active layer, applying electric field causes deformation in the form of bending. The inactive layer is usually non-piezoelectric and this type of setup allows for greater deformation than in piezoelectric materials by themselves. The Thunder unimorph consists of layers of Aluminum (Al) and lead zirconate titanate (PZT) on a stainless steel substrate held in place by an adhesive, an epoxy named LaRC-SI (Langley Research Center - Soluble Imide).[^89]

[^89]: The piezoelectric layer is PZT while Aluminum is the non-piezoelectric layer.[^89] The elastic modulus (ratio of stress to strain) and coefficient of thermal expansion (degree of expansion of material per change in temperature) of the PZT and Aluminum layers are unequal, which accounts for the curvature of the unimorph. [^89] Without any external force,
there is a prestress on the composite and Aluminum is in a state of tension while PZT is in a state of compression. [89] This property facilitates the relatively large deflections achieved in these unimorphs. In natural state, a PZT ceramic only deforms by about 0.1% of its original dimensions but when used in a composite such as the Thunder® unimorph, it usually generates better deformation. [90, 91, 92]

![Diagram showing bending due to mismatch in coefficient of thermal expansion between composite layers](image)

Figure 3.4: Picture showing bending due to mismatch in coefficient of thermal expansions between composite layers

The reason for this increase in deformation is that when combined in a composite form, deformation is more noticeable due to bending of the other layers by virtue of bonding with PZT. It is quite similar to the behavior of a bimetallic strip in which two metals with uneven coefficients of thermal expansion are bonded together. Due to their fixed connection, the strip with the highest coefficient of thermal expansion is forced to bend upon heating to an increased length in the direction of the other strip. Figure 3.4 above shows this behavior in the unimorph. Note that three layers are shown in the figure to represent the Thunder unimorph with a top layer of Aluminum and a bottom layer of stainless steel. Figure 3.5 below shows the layers that make up the Thunder® unimorph.
Figure 3.5: Picture showing layers of the Thunder Unimorph \[89\]

Figure 3.6: Picture from left to right showing unimorph at zero, positive and negative voltage \[89\]

At zero volts, the piezoceramic is in a compressive state of prestress while the substrate is in tension giving the unimorph an upward curvature. \[89\] On application of positive voltage the piezoceramic shrinks, and the unimorph appears flatter while the piezoceramic domes, giving the unimorph a more pronounced upward bend when negative voltage is applied. \[89\] In the manufacturing process, the aluminum, stainless steel and PZT layers are bonded together then placed in a vacuum oven. \[93, 94\] After cooling, the setup is placed in an autoclave at high temperature and pressure then left to cool at ambient temperature. Due to strong bonding between layers, the uneven thermal coefficients between Aluminum (Al) and the ceramic layer results in curvature as both layers oppose one another putting Al in tension and PZT in compression during cooling. \[89, 93\] Hence, the
strength of the adhesive provides the characteristic prestress that the unimorph possesses, as well as sturdiness. After cooling, a high electric field applied to the unimorph makes the adhesive break down electrically allowing for a connection between electrodes. When an electric field is applied across the thickness of the unimorph in such a way that it sits on a flat surface with Aluminum facing up, the positive electrode is Aluminum while the stainless steel back end serves as the negative electrode.

![Figure 3.7](image)

Figure 3.7: Figure showing diced cross sections of a Thunder wafer, (a) End View and (b) Midsection

The arrangement of the layers is shown in Figure 3.7 above. Note that the picture shows a Thunder TH-6 model with different dimensions for the main purpose of illustrating the general arrangement. In this figure, the “bottom metal layer” indicated represents the stainless steel layer in the case of the Thunder® LI-1 model used in this project. This model has a 0.425mm thick PZT ceramic layer with a total thickness of 0.679mm. The layer of stainless steel is slightly longer than the PZT layer however; the PZT and aluminum layers are equally long. The wafer is poled in the “3” or “Z” direction i.e. the axis about which the wafer expands and contracts when voltage is applied along or against the direction of poling. Opposite contraction or expansion occurs along the XY-plane due to contraction and expansion in the orthogonal “Z” plane along which
the unimorph is poled. This secondary effect causes the displacement of the wafer to occur in the negative Z-direction from rest (flattening) due to positive voltage. The directions are shown relative to the position of the unimorph in figure 3.5 below.

Figure 3.8: Figure showing a THUNDER® LI-1 wafer

The displacement of the unimorph decreases with increasing bias voltage. The plot below (figure 3.9) shows the behavior of the unimorph at positive bias values ranging from 0-500V. To create the plot, a unimorph with electrodes connected across its thickness was placed underneath a laser sensor (NAIS microlaser sensor LM 10). The top end (Al) was connected to the positive electrode while the bottom end (steel) was connected to the negative electrode. Each of the electrodes was connected to the corresponding terminal on a high voltage power supply (Test Driver™, TD-2). The initial position of the unimorph, which corresponded to a voltage value displayed on the meter of the sensor was measured and recorded. The amplifier was used to apply bias voltage steadily and the new position (displacement values in volts read off the display of the sensor and converted to millimeters) for each bias voltage value was recorded. Each volt on the sensor represented 2.0106mm of displacement. The relationship between voltage and displacement of the unimorph as depicted in the plot is linear.
3.4 Characterization Instruments

3.4.1 Scanning Electron Microscope

A Scanning Electron Microscope (SEM) creates images of samples by focusing a beam of electrons on a portion of the sample. At high voltage, electrons are extracted from the tip of the scanning probe and voltage is kept as low as possible to prevent damage to the sample. The tip is kept very pure by means of an ultra high vacuum system under which the SEM is operated. There is a difference of thirteen orders of magnitude between the pressure of the vacuum pump of the machine and ambient pressure.

The SEM used in this project is a Hitachi Su-70 model. It has two main apertures namely, the anode and objective apertures. The electron beam releases electrons of two major types on samples. Backscattered electrons are dependent on the morphology and
chemical composition of the sample. These are not desirable for Nanoscale applications. Secondary electrons however are good for such applications and undergo an inelastic scattering. Special upper and lower detectors help the machine to obtain images using secondary electrons at 1nm resolution without compromising topographical details. This state of the art equipment makes it possible to measure fiber diameter, the spacing between fibers, and observe general morphological features. The fibers are seen to have a cylindrical cross-section under the SEM. Figure 3.10 below shows the picture of the scanning electron microscope model used for the experiments in this project.

![Hitachi SU-70 Scanning Electron Microscope](image)

**Figure 3.10: Hitachi SU-70 Scanning Electron Microscope**

### 3.4.2 Optical Microscope

Another method used to observe fibers is optical microscopy (OM). An optical microscope (Nikon Eclipse model LV100D-U) was used to investigate morphological details of fibers.
3.4.3 Contact Angle Goniometer

Water contact angles are measured using a Ramé-hart contact angle goniometer (Model 100-25A, see Figure 3.11). The picture (Figure 3.11) below shows a Ramé-hart goniometer. This device makes measurements by assuming the water droplet is spherical or elliptical in shape. [99] It also has the ability to capture images of droplets from the same position repeatedly, which enhances precision in WCA measurements. Measuring drops of superhydrophobic surfaces with a Ramé-hart goniometer (Model 100-25A) is facilitated by a software package, DROPimage Advanced and is a simple process.

During experiments, a drop is dispensed with an Automated Dispensing System that requires care to avoid disturbance and potential distortion of its shape. [99] The goniometer is equipped with a high-resolution camera that allows for a clear and magnified view of the droplet. Pictures of water droplets are taken with a dark contrast to promote visibility. Focus knobs on the device can be used to ensure that the drop is in focus. The DROPimage software automatically generates a profile of the drop and contact angle lines that can be observed, adjusted and used to measure left, right and mean contact angles. [99]

Figure 3.11: Ramé-Hart Goniometer [100]
CHAPTER 4 Experimental Section I: Fiber Morphology

Experiments were performed to observe wetting behavior of fibers on piezoelectric unimorph substrates produced from polystyrene dissolved in toluene and tetrahydrofuran (THF). The metric used to determine hydrophobicity of coatings was the water contact angle. The process of electrospinning was chosen to generate the polymer coatings and mechanical tuning of hydrophobicity induced by an electric field was applied on piezoelectric unimorph substrates. This set of experiments involved a series of tests to show how hydrophobicity is influenced by electrospinning variables.

Polystyrene pellets with weighted average molecular weight (Mw) ~350,000 amu from Sigma Aldrich were dissolved in 70:30 solvent ratio consisting of toluene and THF respectively. Complete dissolution was achieved in three to four days spontaneously or via mixing with a stirring rod. Aligned fibers were electrospun from 18%, 20% and 25% by weight of polystyrene solutions on nylon substrates to gain preliminary knowledge of their morphology. Scanning electron micrographs (shown in figure 4.1 below) of these samples were obtained and compared. Afterwards, these categories of fibers were also spun on Thunder® TH-7R unimorph substrates. Electrodes were soldered unto unimorph substrates before spinning, but in a few cases soldering was done after spinning but the time of soldering had no important effect on the experiments.
4.1 Electrospinning Procedure

Unimorphs were properly secured to the rotating drum of the electrospinning setup using electric tape. The electrospinning setup used was made up of a cylinder also known as the rotating drum, or collector. This cylinder is 6.5 inches long and contains 6 faces with each face 1 inch away from the face parallel to it. The cylinder is mounted on a lathe (microlathe II, Model 4500) and rotated 1200 rpm through a belt linked to an AC motor (Marathon Electric, CAT No. S102 Model AVJ4817D2042L). The Immediate Motion Creator software (IMC SCX10) was utilized to generate translational motion of the collector.

On the left side of the collector axis was a needle (1” stainless steel blunt needle, 27G with luer polypropylene Hub) connected to a 1cm³ plastic syringe held in place by an infusion pump (Harvard Apparatus PHD, 2000). This pump controlled solution flow at different infusion rates. The needle was placed 7.5cm-10cm away from the axis of the collector. A positive voltage was applied to the electrospinning needle by a Matsusada Precision Inc. High Voltage amplifier (Model AMT-10B10-LCS). Aligned fibers were spun on the unimorph substrates with their alignment perpendicular to connection points of the electrodes.

4.2 Fiber Diameter and Beads

Fiber diameter was measured from SEM images using the ImageJ software. It was observed that the average diameter of fibers was 0.689µm, 1.305µm and 2.221µm in fibers electrospun using 18, 20 and 25 wt. % PS solutions respectively. Fibers with smaller
diameters were difficult to obtain from dilute polymer solutions without obtaining beads. The formation of beads is as a result of air borne ions that are produced by corona discharges during electrospinning.\textsuperscript{[101]} Beads are by-products of the polymer\textsuperscript{[102]} and because they increase the roughness of fibers, they are disadvantageous in the context of this project. The reason is that the consequent additional increase in roughness limits the attempt to observe how other variables of concern such as voltage and fiber deposition time affect wetting behavior.

Attempts were made to limit occurrence of beads and avoid confusion in monitoring the effects of key variables. Another set of fibers was electrospun on Thunder\textsuperscript{®} unimorph substrates. For this set, infusion rate for the spinning of 18% PS fibers was changed from 2.5µl/min used for the previous set to (0.5-1µl/min) which resulted in a change in morphology of the fibers by limiting the occurrence of beads. Scanning electron micrographs of this set were also taken and are shown in figure 4.1 below.

![Figure 4.1: Polystyrene fibers on a nylon substrate at (a) 18% (b) 20% (c) 25% concentration by weight](image-url)
Figure 4.2: Plot showing fiber diameter with respect to solution concentration of PS fibers electrospun on nylon meshes

![Graph showing fiber diameter with respect to solution concentration of PS fibers electrospun on nylon meshes.](image)

Figure 4.3: SEM images of (a) 18% PS, (b) 20% PS and (c) 25% PS fibers electrospun for on Thunder® unimorphs

![SEM images of (a) 18% PS, (b) 20% PS and (c) 25% PS fibers electrospun for on Thunder® unimorphs](image)
Figure 4.4: Plot showing fiber diameter with respect to solution concentration of PS fibers electrospun on Thunder® unimorph substrates

The error bars in the fiber diameter versus concentration plots (figure 4.2 and 4.4) above were calculated using “t distribution”\textsuperscript{[103]} at a 90\% confidence interval. A combination of the results from both sets shows that the average fiber diameters of 25, 20 and 18\% PS fibers are $2.097 \pm 0.079$, $1.376 \pm 0.099$, $0.583 \pm 0.077$ microns respectively at 90\% confidence.

4.3 Fiber spacing

The experiment to determine the influence of fiber spacing was carried out by varying the deposition time of electrospinning. This indirectly varies fiber spacing as increased deposition time produces fibers that are more tightly packed. Fibers were spun from 25 wt. % polystyrene solutions at 2, 4, 6, 8 and 10-minute durations. Unimorph substrates holding fibers for each deposition time were placed on the stage of the contact angle goniometer. A 6μl water droplet was placed on a spot in the mid section of the
unimorph and a picture was taken after focusing the live image of the drop.

An electric field was gently applied to the unimorph using a high voltage power supply (Test Driver™, TD-2) with the droplet still sitting on the coating and another picture was taken. Measurements of capacitance and voltage were made using a Tektronix DMM914 digital multimeter. This process was repeated for a total of six drops on each unimorph. Measurement of contact angles was achieved using Screen Protractor. Tangential lines drawn on both sides of the images of individual droplets were used to determine the left and right angles using the protractor. The average of the angles on both sides was taken as the contact angle of each droplet. Scanning electron microscopy was used to determine morphological details. The focus of results discussed in this section is only on individual droplets before the application of electric field, other results are addressed in chapter 5 (section 5.2).

After obtaining results from the experiment described above, the same procedure was repeated for fiber coatings electrospun for higher deposition times ranging from 15 to 40 minutes in 5-minute increments. SEM analysis showed that changing the deposition time varied the spacing between electrospun fibers as depicted in Figure 4.5 below. At higher deposition times, the inter-fiber spacing decreased, as fibers appeared much closer from the SEM images.
The outcome of the contact angle measurements for the fiber coatings representative of each deposition time is shown in figure 4.6 (a) and (b) below.
Figure 4.6: Plots showing the average water contact angles with respect to fiber deposition time for 25%PS fibers, (a) for 2-10 minutes with 2-minute increments, (b) for 2 to 40 minutes with 5-minute increments beyond 10 minutes.

As shown above in Figure 4.6 (a) representing WCA measurements of fiber coatings spun for 2-10 minutes, hydrophobicity appears to increase with deposition time.
However, after a deposition time of 10 minutes, measured contact angles start to decrease. In order to better understand the results, the Cassie-Baxter equation was used to calculate the fraction of solid in contact with the liquid (see section 2.1) representative of the various deposition times after which the values were plotted. The plot below (figure 4.7) contains the observed trend.

![Figure 4.7: Plots showing the fraction of solid in contact with the liquid (f parameter) with respect to fiber deposition time for 25%PS](image)

The fraction of solid in contact with the liquid ($f$) is found to decrease with increasing deposition but after 10 minutes, an increase is observed (from ~0.21 at 10 min to 0.38 at 40 minutes). The trend observed appears to be the opposite of the behavior of the average WCA relative to deposition time, which is expected based on the Cassie-Baxter equation.
4.4 Discussion

The increase in contact angles at higher deposition times (up to 10 minutes) is likely due to the fact that fibers are more closely packed at higher spinning periods thereby enhancing roughness. This consequent increase in roughness causes water droplets to bead up atop fibers and show a higher contact angle. However, a threshold is reached where this trend does not hold. A decrease occurs likely because the spacing between fibers starts to become so small that the behavior of the surface approaches that of a flat piece of polystyrene (WCA of 90° to 95° [16, 62]).

The fact that the \( f \) versus deposition time (figure 4.7) and WCA versus deposition time (figure 4.6) plots shows an inverse relationship is expected. As the spacing between fibers decreases due to an increase in deposition time, more fibers are in contact with the droplet. This increase in fiber contact implies an increase in the area fraction of the solid in contact with the liquid, \( f \). From the Cassie-Baxter equation, \( f \) and \( \cos(\theta^*) \) are directly proportional. Mathematically, a higher cosine implies a smaller angle consequently; the measured contact angle decreases with an increase in the area fraction, \( f \). Note that Figure 4.7 shows no units for \( f \) because it is a dimensionless value.
CHAPTER 5 Experimental Section II: Tuning of Wetting Behavior

The wetting behavior of generated polystyrene fibers was tuned by the application of an electric field to the unimorph substrate on which the fibers were spun. The influence of parameters including fiber diameter and fiber deposition time was also investigated under applied voltage. Figure 5.1 below shows the approach used to manipulate the hydrophobicity of fibers. The left of the cartoon represents a piezoelectric unimorph in its initial state. After exposure to an electric field, the unimorph flattens to some extent and an assumption is made that inter-fiber spacing is consequently reduced. This then influences the shape of the droplet and its WCA is decreased. It is important to note that the unimorph does not completely flatten as depicted by the blue line on the right side of Figure 5.1 below. The image is an exaggerated cartoon of what actually takes place.

![Figure 5.1: Cartoon illustrating change in droplet WCA with voltage](image)

The pictures (Figure 5.2 - Note that scale bars represent ~2 mm) below show images of a droplet on an 18 % wt. PS fiber coated unimorph before and after 400V DC
was applied. Images show bending of the unimorph indicated by the droplet in (b) slightly below that in (a). Also, there is a decrease in contact angle shown by the droplet on the right being slightly more spread out than the one on the left. In the above image contact angle of the water droplet decreases from 146.9° to 130.7° (16.2° decrease). These values confirmed a decrease in contact angles with the application of positive voltage.

![Images showing water droplets](image)

(a) (b)

Figure 5.2: Goniometer image showing a water droplet on 18 wt. % PS (a. without voltage (b. after application of 400V

The target of the first step of experiments described in this section was to observe how electric field applied to the piezoelectric substrate affects hydrophobicity. The goniometer was used to capture images of water droplets on unimorphs coated with aligned polystyrene fibers both initially and after applying a positive DC voltage. An attempt was subsequently made to observe how different fiber diameters respond to applied voltage by analyzing fibers electrospun from 18 and 25 wt. % polystyrene solutions, how fiber spacing plays a role by analyzing fibers spun for various durations and how much change is observable at specific voltages.
5.1 Electric Field Effects on Hydrophobicity

An experiment was done to determine the effect of electric field, which involved electrospinning of 25% PS fibers on a thunder unimorph at an infusion rate of 2.5µl/min and a needle to drum distance of 7.5-8.5cm. The samples were placed on the contact angle goniometer stage and the unimorphs were connected to a voltage amplifier as well as a multimeter. Electrodes were connected across the thickness of the unimorph in a direction orthogonal to fiber orientation (see figure 5.3). The positive electrode was connected to the top layer of the unimorph made of aluminum while the negative electrode was connected to the stainless steel bottom layer.

Initially, a 6µl droplet of water was gently placed on the aligned fiber coating of the unimorph at the highest point of its curvature located in the midsection while the voltage amplifier was off. A picture of this drop was taken after which the voltage amplifier was turned on and gently used to apply a bias voltage of 400-500V (this corresponds to electric field of 5.89-7.36kV/cm for the Thunder® LI-1 unimorph). Afterwards, another image of the drop was taken using the goniometer software, and saved. Contact angles of all the droplets were measured and recorded in a table. The average values were obtained as well as the associated error for each set.

Figure 5.3: Diagram illustrating direction of fiber alignment, droplet location and contact points for application of electric field (note that image is not drawn to scale)
Table 5.1: Table showing average change in WCA due to applied electric field in 25% PS fibers spun for 2 and 5 minutes

<table>
<thead>
<tr>
<th>25% PS DEPOSITION</th>
<th>INITIAL WCA (°)</th>
<th>AFTER 400-500V BIAS</th>
<th>CHANGE IN WCA (°)</th>
<th>ERROR (+/-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2MIN</td>
<td>127</td>
<td>124</td>
<td>3.5</td>
<td>1.37</td>
</tr>
<tr>
<td>5MIN</td>
<td>142</td>
<td>135</td>
<td>7.7</td>
<td>1.37</td>
</tr>
</tbody>
</table>

The table above (Table 5.1) shows the results. An average decrease in contact angle of 7.7° (± 1.37° at 90% confidence) due to voltage applied was observed in 25%PS coatings spun for 5 minutes while a 3.5° (± 1.37° at 90% confidence) change in WCA was observed in samples spun for 2 minutes. This shows a decrease in contact angles with applied positive bias however; the amount of decrease depends on the deposition time of the electrospun coating. It appears that lower deposition time results in smaller changes in WCA with respect to voltage.

In this set of data, the maximum WCA observed before voltage was applied to the unimorph, after bias voltage applied as well as change in WCA due to tuning were 153°, 149°, 19° respectively. Even though on average the observed WCA values and changes in WCA seem small, there are a few occurrences of much higher values not only in this particular set but also in the data sets of other sections.

5.2 Fiber spacing and tuning of hydrophobicity

This section is the second facet of the experiment described in section 4.3. In addition to seeing how contact angles change with deposition time, which has been established to correlate with fiber spacing there is also a variation in changes in WCA due
to electric field observed for each deposition time. The figure below (figure 5.4) shows average WCA of droplets representative of various deposition times of electrospun 25% PS fibers. The average changes in WCA with applied electric field are also displayed. For this set of data 12 drops are represented for deposition times between 2 and 10 minutes and 6 drops for 15-40 minute data.

Figure 5.4: Plot showing average WCA before and after voltage for various deposition times of 25% PS electrospun fibers
In each of the plots above (Figure 5.4), there is a decrease in WCA once bias has been applied. However, the decrease is not very significant for data representing the coatings spun for the four deposition times except for 25 minutes for which there is approximately a 5-degree decrease in WCA observed.

![Figure 5.5: Plot showing the change in WCA before and after electric field applied to 25% PS fibers with respect to deposition time](image)

The plot above shows no significant changes in WCA due to tuning between 2 and 10-minute depositions but after 10 minutes, the values increased. After 25 minutes, change in WCA values drop once again to form another cluster of fluctuating values. The changes in contact angle due to electric field ranged from as low as 1.2° to about 5°.

### 5.3 Fiber Diameter and Tuning of Hydrophobicity

Electrospinning was used to generate fibers from 18% and 25% polystyrene solutions on unimorph substrates. Fibers were spun from 18% PS for 10 minutes with a needle-to-drum distance of 9-10cm and an infusion rate of 0.5-1µl/min. The same process
was repeated for a 25% PS solution at 2.5\textmu l/min however the deposition time for 25%PS was calculated using the equation below:

\[ \text{deposition time of 25\% PS} = 10\text{min} \times \left( \frac{\text{ratio of concentration}}{\text{ratio of infusion rates}} \right) \] (4)

![Figure 5.6: Figure showing (a) 18\% PS spun for 10 minutes and (b) 25\%PS spun for 2 minutes](image)

This calculation was done to ensure a balanced amount of deposition derived from both solutions as much as possible. During spinning the infusion rate for 18\% PS was slightly varied between 0.5 and 1\textmu l/min in this experiment. Based on calculation, the spinning time for 25\% PS coatings ranged from 1 min and 26 seconds to 2 minutes and 53 seconds. A compromise value of 2 minutes was therefore used for spinning of the 25\%PS samples consistently in this experiment. The solvent proportion used in this experiment was the same as stated in the experimental apparatus section and this ratio was consistent throughout all experiments. As previously described (section 5.1), water contact angles were measured for each set of coatings before and after exposure to an electric field and average values for the contact angles were obtained and recorded in a table.
Table 5.2: Table showing average changes in water contact angle ($\Delta$WCA) of 18 and 25% PS fibers

<table>
<thead>
<tr>
<th>Deposition Time (min)</th>
<th>PS concentration (wt. %)</th>
<th>Average $\Delta$WCA</th>
<th>Error (+/-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>18</td>
<td>2.5</td>
<td>0.82</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>3.5</td>
<td>1.37</td>
</tr>
</tbody>
</table>

From the tabulated results above (Table 5.2), 25% PS was shown to experience a higher change in WCA with applied electric field when amount of deposition is equivalent as accounted for by the calculated deposition time however, it is difficult to tell exactly which coating is more hydrophobic based on the confidence interval. Figure 5.7 below also shows a clustered bar graph of both sets before and after voltage applied. The average WCA with applied voltage of 18% fibers electrospun for 10 minutes is higher than the set for 25% PS spun for 2 minutes as shown in the graph although the latter result only differs by one degree in WCA from the former.

![Figure 5.7: Plot showing WCA versus solution concentration with and without 400V bias](image-url)
5.4 Changes in Hydrophobicity with Specific Voltages

In order to investigate how voltage changes affect hydrophobicity of fiber coatings, WCAs of a droplet on 18% PS fibers (electrospinning and imaging processes remain the same as described previously - see chapter 5 opening and section 5.3) were measured at -200V, -100V and at higher voltages subsequently in 50V increments till a maximum voltage of 500V DC. The droplet was placed at the center of the unimorph, as this is the region where maximum deflection is experienced.

Figure 5.8: Plot showing WCA versus voltage for 18%PS fibers

Figure 5.8 above shows the effect of applied voltage on a single droplet of water on 18% PS fibers as voltage is applied. The starting point, which was before any voltage was applied, is indicated as 0V on the plot. Afterwards, positive voltages were applied and the plot shows a decrease in WCA with increase in voltage. Then voltage was increased in the
negative direction. The result showed that the more negative the voltage, the smaller the contact angle observed.

When consideration was given to the nature of the piezoelectric substrate, the trends on this plot were not as expected. The substrate “domes”, on the application of negative voltage and the more negative the voltage applied, the more defined the dome configuration should become. This should then lead to a consequent increase in contact angles. On the other hand the unimorph should flatten increasingly with positive voltage. As a result a water droplet should spread out more over the fiber coating on its surface and contact angles should decrease. The decrease in contact angles with positive voltage is observable in the plot but there might be more to this result, which will be discussed later.

In order to better understand these trends, three other tests were done. The same unimorph was cleaned up and coated with a new set of fibers with similar dimensions as the previous ones. This was then used for the three sets of data collected. Initially one drop was observed at negative voltages ranging from 0 to -500V then the same test was repeated from 0 to 450V for a different drop. Finally a third drop was observed over time without any voltage.
The plot (figure 5.9) above shows the results for a water droplet observed over increasingly negative voltages. The plot shows a positive slope which indicates that the less negative the voltage, the higher the contact angle observed, in other words as the voltage applied is more negative, the contact angle decreases. This trend is similar to that observed previously in Figure 5.8.
The plot (Figure 5.10) above shows the response of a water droplet observed at increasingly positive voltages. The trendline shows a general decrease in contact angles with voltage. This is also similar to previously observed results. An interesting part of this result is that the first data point representing the contact angle before voltage was applied appears much higher than subsequent values. This will be discussed further in the discussion section. However, the difference in WCA measured at 10V and 500V is 9.4°.

5.5 Influence of Time - Control

In order to observe changes in water contact angles with respect to time on a used substrate, a droplet was observed over time with no voltage applied (as briefly mentioned in section 5.4 above). The droplet was imaged on a substrate with 18% PS fibers at 5s, 10s, 20s, 30s, 40s, 60s, 2min, 3min, 4min and 5min to observe the role of time in the results.
The plot (Figure 5.11) showed a general decrease in contact angles over time. This indicates that some surface wetting could be taking place. On the plot, there is an initial drop in the contact angle of the droplet most likely due to movement of the drop due to a slight wetting. Afterwards the droplet stabilized on the fibers and no significant changes were observable. However, relatively significant changes were observed after 50s.

![Plot showing WCA on 18% PS fibers with respect to time](image)

Figure 5.11: Plot showing WCA on 18% PS fibers with respect to time

Another thing to consider is that even though the voltage source was turned off at the end of each set of tests, the fact that the same unimorph has been used still creates a possibility of erratic results due to “depoling”. It is possible that the unimorph did not recover its original properties from the previous test. The same set of tests was repeated for 25%PS and the droplet was observed over 10 minutes.
The wetting rate was about the same for the 25% PS fibers in comparison to 18% PS fibers as shown from the plot (Figure 5.12).

5.6 Discussion

The droplets shown in figure 5.2 reflect one of 5 droplets analyzed in the set consisting of 18% PS fibers with a deposition time of 5 minutes. The average values of WCA for the 18% PS set were not compared with the values for 25% fibers spun for 5 min as the data points were from a preliminary set of data after which successful spinning of 18% PS proved difficult. More spinning was done later however, the higher change in contact angle may have been influenced by the presence of beads, as they were the first set before spinning under parameters found to be suitable were replicated.

In section 5.2 there is variation between average changes in WCA at 2-minute
deposition (2.1°) and that observed in a previous experiment discussed in section 5.1 with a change of 3.4°. This is likely due to the fact that the first set of fibers was electrospun with a needle-to-drum distance of 7.5cm while 9-10cm was used in the latter experiment. A shorter distance could result in formation of larger fibers, which could have improved hydrophobicity of the first set compared to the second as well as a better change in WCA with respect to electric field applied to the unimorph.

Even though 25 % PS fibers spun at higher deposition times showed a greater change in WCA (section 5.1), 18% PS electrospun fibers did not show this trend (section 5.3). This could be due to the fact that the data collected in the former experiment was also from fibers spun with a smaller distance from the tip of the needle to the drum. It is hard to determine at this point if in fact there is a direct correlation between deposition time of fibers and changes in WCA observed. This uncertainty is evident from figure 5.5 as it shows a fluctuation between values.

From figures 5.4 and 5.5 above, it is evident that there is a generally higher average of water contact angles on polystyrene fibers before voltage is applied to the unimorph substrates than after voltage (400-500V DC) has been applied. This indicates a general decrease in contact angles with positive voltage. This is expected with consideration to the fact that unimorphs tend to flatten on exposure to positive electric potential and this causes the substrate to be less hydrophobic as the droplet spreads out also.

As fiber diameter decreased due to increase in deposition time of electrospinning, contact angle was found to increase. The highest contact angle was observed for fibers from the 10-minute deposition process. After 10 minutes, contact angle no longer
increased but started to level off as no significant change was observed. This was likely due to the fact that fibers are so close together to the extent that there is hardly any spacing to manipulate.

As the unimorph flattens due to bias voltage the expectation was that fiber spacing decreases. However; in this case the trend observed was not identical to that observed as deposition time decreases inter-fiber spacing. In order to understand this trend, it is important to revisit the wetting modes discussed earlier. There is a likelihood that a shift occurs from the Cassie-Baxter model to the Wenzel state in 18% PS solutions when electrospun for 5 to 10 minutes and 25% PS solutions spun for 2-5 minutes as they have much smaller fiber coverage in comparison to higher deposition times. This allows some seepage of water to take place and behavior observed agrees with the Wenzel model. In the Wenzel state a drop is in complete contact with the surface as no air pockets hold it above the surface projections. The equation that describes this behavior is:

$$
cos \theta^* = r (cos \theta)
$$  \hspace{1cm} (3)

Here, \( r \) represents the ratio of the actual area to the projected area. Since the projected area is smaller, \( r \) is usually a number greater than 1. Flattening of the unimorph increases the projected area, which in other words lessens the value of \( r \) hence; the measured contact angle is reduced. However, in the Cassie state, an air pocket beneath the droplet keeps it above surface projections and the relevant equation is:

$$
cos \theta^* = f (cos \theta) + 1 - 1
$$  \hspace{1cm} (2)

This can be rewritten as:
\[
f = \frac{(\cos \theta^*) + 1}{(\cos \theta) + 1}
\]  

(5)

In this state, when fibers are closer together as a result of increased deposition time, \( f \) which is the fraction of solid in contact with the liquid is increased which implies an increase in the measured contact angle, \( \theta^* \). This is a likely explanation of the difference in behavior with decrease in fiber spacing due to bias voltage versus increase deposition time.

Another aspect to consider is that 18% PS and 25% PS spun for the same deposition time (5 minutes) were tested for hydrophobicity. 25% PS has a higher density of fibers on the surface due to its higher concentration. It was observed that initial (before any bias voltage) average WCA (134°) is more than that in 18% PS (132°). However the change in WCA due to applied electric field is higher in 18% PS fibers. When voltage is applied after the droplet has been placed as described previously, the WCA measured differed from values measured from droplets placed after bias voltage has been applied to the unimorph. Sometimes it is greater than the value of the WCA of another droplet in close proximity imaged without bias voltage and sometimes it is less. This behavior shows a slight variation in the morphology of fibers across the substrate therefore observing the same droplet before and after bias was the approach used for collection of data to see the impact of bias on a drop.

The plot (figure 5.8) showing the behavior of one drop at different voltages shows the expected trend on application of voltage in the positive direction but not in the negative. As voltage is increased in the negative direction, the expectation is that WCA increases however; it was decreased. There is a possibility that the unimorph used gets “depoled” after application of voltage in the positive direction followed by negative


voltage. This could have resulted in a behavior that is not quite indicative of a regular unimorph. In the subsequent experimental results in which the positive and negative voltages were observed separately (Figures 5.9 and 5.10), the trends were the same as observed in Figure 5.8. The results could be due to initial conditions varying slightly from one substrate to the next. In addition, from one drop to the next even at the same voltage, a variation in WCA is observed as shown in the prior experiments.

In figure 5.11, the starting point shows a wide gap in WCA value in comparison to the second data point observed after 20 seconds. This observation is likely as a result of seepage taking place as the droplet partly wets the fibers. Once the droplet is stabilized contact angles continue to decrease with voltage but at a much smaller rate. During experiments that involved measurements taken before and after an electric field was applied, water droplets were allowed to stabilize (drop stabilizes in less than 10 seconds) during the cases in which seepage was observed. Therefore, recorded results were likely due to the influence of applied voltage rather than spontaneous change. As previously discussed, seepage of water through fibers could imply that the droplet is not suspended on an air pocket as described by the Cassie model.

It is also important to note that the density of electrospun fibers was slightly different with respect to location on the unimorph as evidenced by the SEM pictures. This accounts for variation in contact angles measured from one area to the next. This also accounts for slight variations in behavior. Some areas had more closely packed fibers than others. The droplets measured were concentrated in the center as much as possible. Initial conditions of imaging also could play a role in the different sets of experiments. The
results displayed in this thesis where droplets are imaged before and after an electric field is applied were pictures of the same droplet in each case. Therefore, the same unimorph while still seating on the coating is altered by the application of electric field.

However, some experiments were done preliminarily where a different droplet in close proximity to the location of the droplet imaged initially is placed on the coating while the unimorph is still under the influence of the electric field. Majority of the contact angles measured in this way showed a decrease in comparison to the contact angle of the previous droplet before applying voltage. However, the WCA value was usually more than that of the previous drop placed on the unimorph after voltage was applied. On occasion, this value even exceeded the contact angle of the previous drop (before voltage) resulting in a negative change in WCA due to voltage. This implies that two factors could play a role. If the morphology of fibers were uniform in the mid region of the unimorph, all contact angles measured initially should be the same or at least very close considering calibration or experimental error. However, this is not the case so it is evident that the morphology is not completely uniform in the center and this is likely why the values for initial contact angles were different from one droplet to the next.

Another aspect to consider is that when voltage is applied, the fibers underneath the first droplet, which may have a slightly different morphology than the set underneath a subsequent drop placed near it, could have a contact angle that is lower due to this morphological variation. Consequently, once voltage is applied to the second droplet, the morphology of the fibers it sits on is changed in such a way that the measured contact
angle matches or even exceeds the contact angle of the first droplet if this set of fibers were more hydrophobic relative to those associated with the first drop.
CHAPTER 6 Conclusions and Recommendations

The results from experiments have shown that higher polystyrene solution concentration and voltage applied to the unimorph substrate enhance increase in water contact angles. However, water contact angles of an individual droplet decrease as voltage is increased. In the cases where droplets were observed over time without any influence of voltage, descent in contact angles was observed to take place over time however, changes are not as significant overall as those experienced due to influence of applied electric field.

With increase in deposition time of electrospun fibers, spacing between parallel fibers decrease. Water contact angles increase as the deposition time of spinning increases, however, a threshold is reached where values start to decrease. This is assumed to be a result of the coating tending towards a flat piece of polystyrene with no added roughness.

The changes in hydrophobicity with applied voltage observed are likely driven by the piezoelectric effect relevant to the substrate. In a piezoelectric material, applied electricity causes a change in dimensions conversely, a change in dimensions or applied stress produces an electric field. The change in dimensions of the substrate ultimately influences the spacing between aligned fibers and changes their hydrophobicity. Experimental results show relatively small changes in WCAs induced by voltage. However, we expect higher changes to occur through fine-tuning of the properties of fiber coating and the unimorph substrates.
Improvements in experimental and theoretical analysis are necessary for further study of the voltage induced tuning of wetting behavior. It is also necessary that future modifications incorporate geometry of substrate and coatings as a function of applied electric field for various polymers and fiber dimensions. In order to achieve better identification of factors responsible for observed changes, it would be helpful to monitor time, voltage and WCA simultaneously during experiments. This will especially help decouple the changes due to elapsed time and voltage induced changes in geometry and morphology. Some areas that could be explored further in this project include investigation of tuning effects on a hierarchical structure generated using both electrospinning and electrospraying and trying other kinds of polymers for the electrospun coatings.

In the introduction, it was stated that the aim of this project is to attempt to create a smart superhydrophobic material by manipulation of the wetting behavior of a hydrophobic coating through a voltage induced mechanical process. The results showed in fact that hydrophobicity can be changed through a voltage induced mechanical process of tuning microstructure of fiber coatings. The best results were found in 25% PS fibers electrospun for 5 minutes. It is important to note that only decrease in hydrophobicity was achieved by voltage induced tuning during experiments however, this has shown a potential for success in using a method such as this in influencing increase in hydrophobicity for the creation of a smart material with incorporation of aforementioned recommendations.
List of References


[29] www.wordlesstech.com


[100] http://www.ramehart.com


Adetoun Oludara Taiwo was born on July 8, 1988, in Ibadan, southwestern Nigeria. She completed her secondary education at United Missionary Comprehensive College, Ibadan, Nigeria in 2005. She received her Associates of Applied Sciences and Premedical Professions in Pre-medicine at Anne Arundel Community College; Arnold, Maryland in 2008 and later received her Bachelor of Science degree in Biomedical Engineering from Virginia Commonwealth University in 2011. She worked in the Hybrid Systems Laboratory from Fall 2011 to Fall 2012, when she transferred to the Nanoscale Materials Laboratory, both at the Virginia Commonwealth University Mechanical and Nuclear Engineering department. The latter laboratory is where this thesis work was done.