ABSTRACT

HOIT, SARAH. Liquid Droplet Behavior on Yarns: Modeling of Filament Level Interaction. (Under the direction of Dr. Hoonjoo Lee).

Liquid repellency and wetting resistance, both of water and oils, shows promise of application in many fields, often as a means of protection against fouling of a surface. The interaction between a liquid and the surface it is in contact with is governed by two major components, the chemical interactions between the two materials and the mechanical structure of the surface. Optimization of both elements will result in highly desirable customizable liquid repellency.

Textile surfaces are uniquely positioned to provide a substrate with customization and surface modification specifically designed for optimal liquid repellency. Current mathematical models concerning wetting of textile surfaces function based on yarns being expressed as extensible cylinders. This research tested the models by constructing monofilament structures that matched the physical assumptions of the models, and had enough geometrical simplicity make for ease and accuracy of measurement.

Utilizing direct measurement, the predictive quality of the Cassie-Baxter and Wenzel equations were tested on monofilament structures. Experimental results showed good agreement with predicted contact angles. Roll-off angles of both water and dodecane were also tested, the relationship between multiple types of liquid-solid contact area measurements were assessed for their predictive qualities.
Liquid Droplet Behavior on Yarns: Modeling of Filament Level Interaction

by
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A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Master of Science

Textiles

Raleigh, North Carolina
2011

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DEDICATION

I would like to dedicate this work to my parents and Graham Friedman.
BIOGRAPHY

Sarah Hoit was born in Gainesville, Florida in 1986. She studied set and costume design at New York University, receiving her Bachelors of Fine Arts in 2008. After graduation she worked as a freelance designer in New York, designing for a variety of productions. While working at Mood Fabrics she realized the breadth of the textile industry, and also learned about the existence of another company that shaped her path. Spending five months as an intern at the New York branch of the Material ConneXion library fully cemented her love for materials and the science behind them. In 2010 she entered the Masters of Science program at the College of Textiles. Upon graduation she hopes to work in industry, focusing on innovation and functionality in product development.
ACKNOWLEDGEMENTS

Specific gratitude to my advisor Dr. Hoon Joo Lee is more than due, for taking a chance on me. Her expectations for me, and faith that I could achieve them, made it possible for me to do so. Thanks to Dr. Stephen Michielsen for his support and perspective. I would also like to thank my committee, Dr. William Oxenham and Professor Nancy Powell, for their insight and advice throughout this process. Also, to my lab mates for generosity with their time and brains, Jinmei Du, Priscilla Tan, Yongxin Wang, Archana Mohan, Rahul Saraf, Jinlin Zang, Xiaohang Sun, and Jihye Lim.

Cacophonous thanks to my parents for their support as well as their sarcasm. I also appreciate the support of my friends both on campus and off.

This work has been generously supported by the Air Force Research Laboratory (AFRL) [grant number FA8650-07-1-5903]; and The Defense Threat Reduction Agency-Joint Science and Technology Office for Chemical and Biological Defense [grant number HDTRA1-08-1-0049]. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon.
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1. Introduction

Superhydrophobic and self-cleaning surfaces are seen throughout nature, displaying the benefits of passive cleaning and liquid repellency.\textsuperscript{2,3,4} The lotus leaf and duck’s feather are only two of many examples of the possible advantages of biomimetic structures. The macro and micro scale textures on each encourage water droplets to minimize contact with the surface rather than spreading or wetting. This behavior encourages the droplets to roll-off the surface, taking debris with them on their path. Self-cleaning is often referred to as the lotus effect, though other natural structures exhibit the same behavioral qualities.

Hydrophobic (water fearing) and oleophobic (oil fearing) textile surfaces are indicated by a liquid contact angle of greater than 90°.\textsuperscript{5} Contact angle is defined as the angle with an origin at the point of contact between the liquid and the solid, and tangent to the droplet edge.\textsuperscript{6} In order to be defined as superhydrophobic or super oleophobic, the apparent contact angle of a liquid droplet on the surface must meet or exceed 150°. Super-phobicity is achieved by two means, chemical grafting resulting in low surface energy, and surface roughening. Achieving oleophobicity is a different challenge than hydrophobicity; oils have a surface tension of around half that of water, and require both mechanical and chemical means to reach a superoleophobic state, while water can be repelled by structural means alone. Optimization of both elements will result in highly desirable customizable liquid repellency. Textile
surfaces are uniquely positioned to provide a substrate with customization and surface modification specifically designed for liquid repellency.

Extensive investigation into increased liquid repellency has been occurring across many fields since the early 20th century.7-8 Great advances in chemical modification and optimization of surface topography have been made. Significant developments in understanding the mechanical behaviors of liquids have provided predictive modeling for many different physical situations. Surfaces with superhydrophobicity and high levels of oleophobicity have been produced with great success. The scalability of production of many of these samples is a significant challenge for future developments.

The structural complexity of textile surfaces has been a challenge to the modeling of its performance in all aspects and properties. Physical simulation of mechanical attributes is difficult, due to the non-orthogonal properties of fabrics. For the purposes of modeling the multiple scales of textile surfaces increases complexity as well. Textile components can exist on the macro, micro, and nano scales.9 Surface structure is also varied on these same levels, creating highly complex levels of roughness scales. Current modeling techniques investigate textiles as a version of rough and porous solid surfaces. Assumptions made about the physical geometry of the textile structure and surface result in simplification and lack of precision. Many forms of mathematical modeling base their calculations on the presupposition that yarns can accurately be described as flexible, extensible cylinders. Not only does this simplify the surface roughness of the yarn itself, as it can be comprised of
multiple filaments and staple fibers that lend it texture and variability to its shape; it is also true that incorporation of a yarn into a textile product modifies the shape of the yarn as well.

The spaces present between components within a multifilament construction are consistently clear in a variety of images. This micro-scale roughness, as well as increased area of air inclusion, is vital to the performance of the textile surface in response to liquid. The geometric simplifications of previous models fail to include the detailed and variant structures that comprise yarn. The smallest part of a textile structure is a yarn and needs to be studied and understood as an individual surface, in order to understand its role as a unit within the textile surface whole.

Though significant work has been done in the study of rough surface optimization, the variability of textiles’ many structural attributes continue to pose problems. For this reason the investigation of textile roughness is undertaken from its compositional element, yarn. Monofilament fibers are used to simulate the yarn components in a variety of structures. Since monofilament is the closest empirical model to an extensible cylinder, it is a logical place to work from. This research starts with single nylon monofilaments, of three different diameters, treated with a chemical grafting of 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (FS) for hydro and oleophobic properties. The filaments will be used in a variety of assemblages, with varying diameter fibers and inter-fiber spacing. In this way more accurate modeling of the contribution of yarn structure to surface roughness can be achieved with the goal of improved predictive modeling for hydro and oleophobic behavior of textiles.
The objectives of this research are to study the impact of filament spacing on liquid interactions; extend the understanding of multifilament structure/shape on liquid interaction; and develop improved mechanical modeling of simple filament structure as pertaining to liquid interaction.
2. Literature Review

Literature is reviewed concerning the behavior of liquid droplets, due to chemical and mechanical means. The basics of wetting behavior and quantification are outlined, including hydrophobicity as well as oleophobicity. Natural occurrences of water repellency and the means by which it is achieved are discussed. The chemical and mechanical impacts on wetting are reviewed. The history of wetting observation, calculation and modification are examined. Mathematical modeling for prediction by a variety of scientists is included. An assessment of both static and dynamic contact angles of water and oil is provided, as pertaining to liquid repellency. Discussion of the geometric variance between textile structures and mathematical models is included.

2.1 Wetting

Liquid behavior is applicable to many different fields and studies, its quantification and understanding continues to develop in depth and specificity. The interaction between a liquid and the surface it is in contact with is governed by two major components, the chemical interactions between the two materials and the mechanical structure of the surface.

2.1.1 Biomimicry for Liquid Repellency

The hydrophobic properties of natural structures have been observed and noted since 400 B.C., by the Gautam Buddha. Buddhism finds personal symbolism in the self-cleaning
properties of the lotus. “The spirit of the best of men is spotless, like the lotus in the muddy water which does not adhere to it.” More recently the mechanical means by which these behaviors are accomplished were recognized and modeled. Fogg reported the hydrophobic properties of a variety of flora. Fogg’s observation was used by Cassie-Baxter as further fortification of their assertion that mechanical means independent of chemicals and coatings are responsible for the repellant properties seen in nature.

Figure 2.1 Examples of water repellant structures in nature, lotus leaf and duck feather.

As per their example, it is not the chemical composition of the cuticle of a duck’s feather but rather the intricate and optimized spacing of the barbs that allow for droplets to roll-off the duck’s back. Here the distinction between that of apparent and intrinsic contact angles
becomes crystallized, Figure 2.2. The intrinsic contact angle is based solely on the interaction between the surface energies of the two materials, while the apparent contact angle includes the input of the surface structure to the liquid behavior. This exemplifies the two components of liquid repellant surfaces; low surface tension and proper topography are needed.

![Diagram of contact angles](image)

**Figure 2.2** Indication of location and difference between intrinsic and apparent contact angle measurements. $\theta_e$ indicates the intrinsic contact angles, $\theta_r$ indicates apparent contact angle.

Extremely rough surfaces can generate apparent contact angles potentially significantly higher than the $\theta_e$ contact angle, due to structure. This goes against the assumption made by Wenzel and Adams that apparent contact angle was a direct function of $\theta_e$ contact angle; that is to say that surface roughness would increase the inherent quality of the surface.³ The exceptional repellency witnessed by Fogg clearly counters this conclusion.⁴ Behavior modeling, techniques, and physics are discussed in greater detail in the following sections.
2.1.2 Hydrophobicity

Hydrophobicity is the ability of a surface to repel liquid, indicated by an apparent contact angle of greater the 90°. Contact angle is used to quantify the liquid repellency of a surface. In order for a surface to be considered superhydrophobic a water droplet on the surface must exhibit a contact angle of 150° or greater. The droplet shape, or contact angle, can be thought of as a scale from fully wet to fully dry (0° to 180°) as depicted in Figure 2.3. Increasing contact angle indicates a more sphere like droplet and decreased area of contact between a liquid and a solid surface.

![Figure 2.3 Scale of the relationship between wettability and contact angle. Second droplet from right shows a contact angle of 150°, indicating super-phobicity.](image)

<table>
<thead>
<tr>
<th>θ_e</th>
<th>0°</th>
<th>90°</th>
<th>180°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Complete wetting</td>
<td>Equilibrium</td>
<td>No wetting</td>
</tr>
</tbody>
</table>

Apparent contact angle is a useful form of assessment due to its ability to be observed and measured directly. Intrinsic contact angle, referred to as θ_e, is a measure of the shape of a droplet in relation to the surface it rests on, this is separated into three measurements of interaction, solid (surface) liquid (water or oil) and vapor (air), depicted in Figure 2.4. Apparent contact angle is describing the phobicity of a surface based on the observed angle between γ_{SL}, solid liquid interaction, and γ_{LV}, liquid vapor interaction. The measurable angle
that expresses the contact angle is that tangent to the liquid with an origin at the edge of the liquid solid interface.

![Diagram of contact angle](image)

Figure 2.4 Apparent contact angle as defined by the interactions of solid, liquid, and vapor.

Due to the difficulty of directly measuring surface energy, apparent contact angle is used as a proxy to calculate it. Young’s equation (equation 2.1) is used for this calculation, gathering the inputs by measuring the apparent contact angle between the solid, liquid and gas phase components.

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

(2.1)

Equation 2.1 can be simplified by removing the vapor interaction in the calculation; this exclusion is justified by the assumption that the vapor has minimal impact on the droplet’s behavior, when the droplet exhibits a contact angle of over 20°. The limited impact of vapor interaction is due to the small size of the droplet and the supposition that the vapor is air, subsequently having limited effect on the liquid. It should be noted that Young’s equation works under the assumption of a flat smooth surface.
The contact interaction between two surfaces is governed by their interface on a molecular level. The quantification of this interaction can be described in many ways. Young’s equation (2.1) describes the interactions between each of the phase states in relation to the intrinsic contact angle of the droplet on a smooth surface. The interaction can also be described as the work of adhesion by the Dupre equation.\(^\text{(12)}\)

\[W_{SL}^a = \gamma_{SV}^a + \gamma_{LV}^a + \gamma_{SL}^a\] \hspace{1cm} (2.2)

As free energy is the negative of the work of adhesion thermodynamically, this equation (2.3) also serves to provide the free energy of adhesion in the system.

\[\Delta G_{SL}^A = \gamma_{SL}^a - \gamma_{SV}^a - \gamma_{LV}^a\] \hspace{1cm} (2.3)

Equation (2.1) and equation (2.2) are combined to form the Dupre-Young equation.

\[W_{SL}^a = \gamma_{SV}^a + \gamma_{LV}^a - \gamma_{SL}^a = \gamma_{LV}^a (1 + \cos \theta_e)\] \hspace{1cm} (2.4)

This equation can also be used to quantify the Lifshitz-van der Waals (LW) solid-liquid interaction energy. Which is another means of describing adhesion between materials.

\[W_{SL}^{LW} = (\gamma_{SV}^{LW} - \gamma_{SL}^{LW}) + \gamma_{SL}^a = -\Delta G_{SL}^{LW} = \gamma_{LV}^{LW} (1 + \cos \theta_e)\] \hspace{1cm} (2.5)

The surface liquid interaction can be quantified by a series of expansions to the Dupre-Young equation (2.4). The interfacial tension between the liquid and solid, in the case of dispersion interactions, are explained by Fowkes in the following equation.\(^\text{(14)}\)

\[\gamma_{SL}^{LW} = \left(\sqrt{\gamma_{SV}^{LW}} - \sqrt{\gamma_{LV}^{LW}}\right)^2\] \hspace{1cm} (2.6)

Taking the geometric mean will then be utilized to calculate the LW components of the solid liquid interaction.
Inclusion of this component into the modified Dupre-Young for LW gives a new equation for interfacial energy quantification.

\[ \gamma_{SL}^{LW} = \gamma_{LV}^{LW} + \gamma_{SV}^{LW} - 2\sqrt{\gamma_{LV}^{LW} \gamma_{SV}^{LW}} = \gamma_{LV}^{LW} + \Delta G_{SL}^{LW} \]  

(2.8)

The surface tension of an interface is the combination of multiple inputs that govern the intermolecular interactions.

\[ \gamma = \gamma^d + \gamma^p + \gamma^H + \gamma^{ind} + \gamma^m \ldots \]  

(2.9)

In this instance each of the super scripts are representative of a given molecular interaction in contribution to the total work of adhesion of the interface. The super scripts are representative of London dispersion forces, \(d\); permanent dipoles, \(p\); hydrogen bonds, \(H\); induced dipoles, \(ind\); and metallic interactions, \(m\). This summation can be applied separately to the liquid and solid components to garner \(\gamma_{SV}\) and \(\gamma_{LV}\); expanding understanding by investigating the components separately. The first three components have the most impact on the surface tension of the majority of materials; hence simplification is prudent, resulting in the following.

\[ \gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p + \gamma_{LV}^H \]  

(2.10)

\[ \gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p + \gamma_{LV}^H \]  

(2.11)

Equation (2.12) expresses the summation of molecular forces that create the work of adhesion at the liquid solid interface, and the resultant intrinsic contact angle. The components of the surface liquid interaction are shown to be the driving factors that create
the equilibrium contact angle on a flat surface; this is a manifestation of molecular interaction between the two materials.

\[ \gamma_{LV} \left(1 + \cos \theta_e \right) = 2 \left( \sqrt{\gamma_{SV}^d \cdot \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \cdot \gamma_{LV}^p} + \sqrt{\gamma_{SV}^H \cdot \gamma_{LV}^H} \right) \]  

(2.12)

With the predictive possibility based on the molecular interactions as defined by equation (2.8) it is possible to use it to predict the contact of a given liquid and solid based on known quantities of intermolecular forces. These forces, specifically London dispersion forces, permanent dipoles, and hydrogen bonds, are well quantified and accepted in the literature. Using the information in a table such as below, Table 2.1, can account for the behavior of multiple parings of phased materials for the contact angle they will exhibit on a surface with no roughness.
Polymer films, though the closest facsimile to a smooth surface, have micro levels of texture. In the case of textile surfaces it is abundantly clear that the surface is far from smooth, and requires more detailed modeling than Young’s equation provides. The intrinsic contact angle based solely on surface energy is vital to the subsequent models developed in defining the intrinsic state of chemical interaction and the physics of the droplet. This forms the basis of complex models by providing the comparison for understanding the responses in liquid behavior to variant physical structures.

<table>
<thead>
<tr>
<th>Material</th>
<th>London dispersion forces</th>
<th>Permanent dipoles</th>
<th>Hydrogen-bonds</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>21.8</td>
<td>1.4</td>
<td>49.6</td>
<td>72.8</td>
</tr>
<tr>
<td>Decane</td>
<td>23.9</td>
<td>-</td>
<td>-</td>
<td>23.9</td>
</tr>
<tr>
<td>Dodecane</td>
<td>25.4</td>
<td>-</td>
<td>-</td>
<td>25.4</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>27.6</td>
<td>-</td>
<td>-</td>
<td>27.6</td>
</tr>
<tr>
<td>Poly(ethylene)</td>
<td>31 ~ 31.5</td>
<td>-</td>
<td>-</td>
<td>31 ~ 31.5</td>
</tr>
<tr>
<td>Poly(propylene)</td>
<td>29.6</td>
<td>-</td>
<td>-</td>
<td>29.6</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>30 ~ 36</td>
<td>-</td>
<td>-</td>
<td>30 ~ 36</td>
</tr>
<tr>
<td>Poly(hexafluoropropylene)</td>
<td>16.2 ~ 17.1</td>
<td>-</td>
<td>-</td>
<td>16.2 ~ 17.1</td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>18.5</td>
<td>-</td>
<td>-</td>
<td>18.5</td>
</tr>
<tr>
<td>Nylon</td>
<td>40.8</td>
<td>-</td>
<td>6.2</td>
<td>47.0</td>
</tr>
</tbody>
</table>

Table 2.1 Surface tensions of various substances
2.1.3 Oleophobicity

When dealing with low surface tension liquids, such as oil, multiple behaviors must be accounted for. Theoretically, oleophobic surfaces may be created through both appropriate surface topography as well as chemically modified surface for low surface energy with a $\theta_e$ of greater than 90°. It is possible to achieve contact angles with oils of 150° and greater with variations in surface roughness. Oils resist roll-off, even when high apparent contact angles are present. However if the Young’s contact angle, on a smooth surface, is $>90^\circ$ roll-off is achievable. Interestingly the physical state does not simply match the Cassie-Baxter model as seen with water, but creates a new state, meta-stable Cassie-Baxter. The meta-stable state describes the transition of the droplet over time from initial Cassie-Baxter state to an eventual Wenzel wetting state, as the air is displaced and liquid moves into the structure.

2.2 Rough Wetting

The molecular work of adhesion outlined in the previous section is only half of the attributes governing liquid behavior on a surface. The mechanical structure of the surface can impact the wetting by contributing to its intrinsic behavior or even counteracting it. The importance of structure is most clearly exemplified by the great success of natural surfaces in achieving water repellency based solely on their physical structure. The mathematical models of these behaviors are outlined in greater depth in the following section.
2.2.1 Surface Topography

There are two primary methods of creating a highly hydrophobic and oleophobic surface; the first being mechanical surface modification resulting in increased roughness, the second being lowering the surface energy of a solid through chemical modification. Recognizing and quantifying the variation in physical structure elevates modeling beyond the surface energy interactions outlines defined by Young. Surface roughness is an important component in the potential for super hydrophobic properties in textiles. The physical structure of a surface is a key component in the determination of wetting behavior. Textiles provide both an interesting challenge and opportunity to the production of hydro and oleophobic properties. Their uniquely irregular surface qualities provide innumerable variables with which to alter and control the physical and aesthetic properties of the textile. The two primary models for wetting behavior are the Wenzel and Cassie-Baxter models. Each defines a different degree of wetting, or non-wetting, due to surface roughness and the surface energy interactions outlined by Young. Figure 2.5 exemplifies the interaction between droplet and substrate according to the two models. Wonderfully torrid
2.2.2 Wenzel

The Wenzel model (equation 2.13) shows that surface roughness is a significant contributing factor to the behavior of the liquid.\(^7\) The addition of roughness, \(r\), to the equation is the inclusion of structural surface variation as a ratio with the projected area, adding roughness in combination with surface energy.

\[
\cos \theta_r^W = r \cos \theta_e
\]  

(2.13)

Wenzel’s model Figure 2.5 (a) of droplet surface interaction states that increased roughness increases the inherent state of the surface in regards to water interaction. A hydrophobic surface with increased roughness will become more hydrophobic, while a hydrophilic surface with increased roughness will become more hydrophilic. Greater surface area of the phobic or philic surface will be exposed causing an increase to the level of inherent behavior. Wenzel denotes two options for droplet surface interaction. The first state being that of

Figure 2.5 Wenzel (a) state of homogeneous wetting, and Cassie-Baxter (b) state of heterogeneous wetting.
hydrophilicy, with a contact angle of less than $90^\circ$, in this instance the liquid is understood to fill the gaps and spaces of the rough surface. With an inherent contact angle greater than $90^\circ$ the liquid can remain in contact with only the top most portion of the surface topography and remain above the texture depths, producing a phobic surface. This is also based on the presupposition that no air has been trapped in the surface, which is untrue for porous textile surfaces.\(^7\)

### 2.2.3 Cassie-Baxter

The Cassie-Baxter model Figure 2.5 (b) expands upon Wenzel’s model through the inclusion porous surfaces.\(^{16}\) Establishing that the liquid may not fully penetrate into the textured surface, resting partially on the peaks of the substrate and partially the gas (usually air) filling the interstices. This describes the heterogeneous, or composite, surface that defines the difference between the Wenzel and Cassie-Baxter models.\(^{16}\)

$$\cos \theta_{CB}^r = f_1 \cos \theta_e - f_2 \tag{2.14}$$

$$f_1 = \frac{\text{area in contact with the solid}}{\text{projected area}}$$

$$f_2 = \frac{\text{area in contact with air}}{\text{projected area}}$$

Since textile surfaces are well known to be rough and porous surfaces, both macro and microscopically, the Cassie-Baxter equation is more apt in its description of potential behaviors. Not only does the Cassie-Baxter model better predict the contact angle of a droplet on a heterogeneous surface but also it can be utilized to calculate optimal surface roughness to impart a desired contact angle. Without the air content of the composite the
equation defaults to the Wenzel model. The manifestation of either the homogeneous surface interaction of Wenzel or the heterogeneous surface of Cassie-Baxter state is due to a variety of factors, including the inherent contact angle $\theta_c$, as well as the minimization of Gibbs free energy.\(^{18}\) The Cassie-Baxter state will occur when the free energy of the system is minimized and the droplet motion is stopped by Laplace pressure optimization, before the liquid is able to reach the base or substrate of the surface. Laplace pressure is the combination of internal (liquid) and external (vapor) pressures that define the shape of a liquid droplet; further discussion of its impact follows. If this does not occur the droplet will continue downward, replacing the gaseous portion of the heterogenous wetting and shifting into the homogeneous wetting state of the Wenzel model.\(^{18}\)

There are multiple versions of the Cassie-Baxter model, having been simplified, as well as expanded for the specifics of various situations. The original equation (2.14) is suitable for the majority of applications. The other two most commonly used versions of the equation are specifically applicable for surfaces with flat protrusions, and for those comprised of heterogeneous composite surfaces. This is applicable if the surface texture is comprised of flat protrusions, like pillars seen in flocked fabrics, etched surfaces, or nanotube arrays.\(^{17,19,20}\)

It is clear in the work of both Marmur and Tuteja et al. that the roughness of a surface is not necessarily equal to unity.\(^{18,19}\) There is the possibility to have a textured surface that has occluded surfaces, which increases the area available for surface or air interaction with the
liquid without increasing the projected area. This is distinctly applicable to textile surfaces the majority of which are comprised of yarns, fibers, and filaments that form a roughly cylindrical profile. These structures are aligned primarily in the x and y directions along the width and length of the fabric; rather than vertically through the thickness of the assembly. The alignment of a plain weave is demonstrated in Figure 2.6.

![Plain weave structure](image)

**Figure 2.6 Plain weave structure.**

For this reason it is logical to model the cross section as a circle, which in turn creates occluded surfaces in the structure, below the midpoint of the structure, seen in Figure 2.7.
Figure 2.7 Occluded areas of cylindrical fibers in cross sectional view of textile model.

Acknowledging the occluded area is vital to proper modeling. Greater agreement in the predicted contact angle of the Cassie-Baxter equation and empirical testing were achieved by a change to the modeling of the shape of the air liquid interaction. In Figure 2.8 the role of occluded surfaces in creating roughness within the Wenzel model is depicted. The dashed horizontal line depicts a cross-sectional projection of the surface area, while the dotted line indicates the full surface roughness of the cylinder profile. As used in the predicted models for apparent contact angle and in creating the ratio of fiber spacing, \( R \) is the radius of the fiber, and \( D \) represents one half of the air space (or distance) between the solid components.
Figure 2.8 Wenzel roughness applied to cylindrical fibers.

The profile of the surface roughness is critical to the behavior of a droplet. By empirically observing the interaction between horizontal cylindrical filaments and a droplet it is possible to compare with the current modeling, and apply it to smaller scale interactions of individual filaments within multifilament yarns. The Cassie-Baxter model of a textile surface uses a horizontal array of cylinders to represent individual yarns, showing the droplet resting on the composite air/solid surface, in a heterogeneous interaction with the liquid.

2.2.4 Roll-off Properties

Super hydro and oleophobicity are not only defined by contact angles of over 150°, droplet roll-off at low angles is also required. Low roll-off angles are the defining feature of self-cleaning surfaces, and the means for their functionality. A surface requiring <5° of incline to induce full droplet roll-off is considered to be super-phobic. A large portion of droplet roll-off is directly attributed to droplet volume and mass. A droplet on a horizontal surface at
equilibrium should demonstrate equivalent apparent contact angles at each side of the droplet; but on an inclined surface the shape of the droplet will change due to gravitational acceleration.

Figure 2.9 Droplet shift with substrate incline $\alpha$, inherent contact angles $\theta_e$, become advancing $\theta_A$, and receding angles $\theta_R$.

Seen in Figure 2.10 roll-off is affected by many factors, indicated in the image are the liquid vapor interaction/ surface tension of the liquid $\gamma_{LV}$, the gravitational force, $g$, as impacted by the mass of the droplet, $m$, and inclination of the substrate, $\alpha$, resulting in the advancing $\theta_A$, and receding $\theta_R$ contact angles.
Figure 2.10 Forces at work impacting roll-off properties; advancing $\theta_A$, and receding contact angles $\theta_R$, are indicated.

The advancing angle at the moment of roll-off is often considered to be 180° due to the shift into a spherical droplet. The receding angle is an indicator of the level of adhesion the surface and the droplet are exhibiting. Contact angle hysteresis, provided by $\theta_A - \theta_R$, is the metric applied to indicate the ease of complete roll-off, the lower the hysteresis the more complete the roll-off. The term hysteresis is used with consideration to droplet deformation quantification.

To understand the function of surface structure on contact angle hysteresis and droplet roll-off angle the following equation is used. The gravitational acceleration of the droplet due to its mass and the degree of incline is countered by the surface tension of the liquid and the work of adhesion with the surface below.
\[ mg \sin \alpha = -d \gamma_{LV} (\cos \theta_A - \cos \theta_R) \]  

(2.15)

The inputs noted in Figure 2.10 are also seen here, mass, \( m \), gravitational force, \( g \), liquid surface tension, \( \gamma_{LV} \), advancing, \( \theta_A \), and receding, \( \theta_R \) contact angles, as well as \( \alpha \), the incline of the surface at the point of droplet roll-off. The addition to the equation is \( d \), the diameter of wetting contact between the liquid droplet and the surface. This is garnered through either calculation based on droplet volume and contact angle for diameter of the base, or by direct measurement of an image. In this way \( d \) can be understood in its impact on the success of droplet roll-off and in the design of a self-cleaning superphobic surface.

### 2.2.5 Robustness

In understanding the mechanics of wetting there is an additional element of behavior that impacts the droplets interaction with the substrate. Droplet sag is a functional measure of the potential of shift between Cassie-Baxter and Wenzel states as well as a method of categorizing wetting behavior in response to the specified physical geometry of the substrate.

In the case of fibrous constructions we can clearly see the heterogeneous nature of the substrate, as outlined by Cassie-Baxter, but it is important to note that unlike the undeformed liquid bottoms that they posited in their original assumptions, the liquid sags in the air interstices. This “droplet sag” is governed by the chemistry and morphology of the solid liquid interaction. Tuteja et al. discuss the calculation and prediction of droplet sag in relation to wetting as well as robustness pressure. Robustness pressure is the ability of the substrate to resist wetting in response to force being applied to the droplet, towards inclusion into the
system and wetting. This small-scale interaction, applied over the projected area of liquid solid interaction has great impact on apparent contact angle and resistance to wetting.

Figure 2.11 Quantification of droplet sag; distance of sag $h_H$, maximum sag height before wetting $h_2$.

In the Figure 2.11 Tuteja et al.’s detailed modeling incorporates the variety of inputs to each fiber that Cassie-Baxter applies to the entirety of the system. The specificity garnered by this manner of analysis allows for the optimization of fiber spacing in response to desired attributes. The requirements of robustness pressure and apparent contact angle at maximum efficiency are contrary. Greater solid surface area will increase the amount of force required to include liquid into the substrate and wet the surface, conversely a high ratio of air interstices increases the apparent contact angle of the surface. In order to design a surface
with optimized spacing robustness pressure will limit the maximum value of $2D$ while apparent contact angle will govern the minimum value of $2D$. Decisions about the intended functionality of the final product must be taken into account when the discussion about fiber spacing optimization is made.

2.2.6 Rough Surface Optimization

Utilizing the models provided by Cassie-Baxter and Wenzel along with the understanding of surface energy and tension, it is possible to calculate optimal roughness, based on desired results. It is also important to know the inherent contact angle of the surface, to understand the surface energy component of the droplet behavior. Utilizing morphology calculation and optimization allows for greater understanding of desired structural qualities, which in turn lends itself to surface customization and design for functionality. The Cassie-Baxter model’s accuracy is beholden to the system being studied conforming to assumptions and constraints; specifically that a droplet is in contact with upwards of ten fibers within the space of its projected area. This is untrue for the assemblies undergoing investigation in this study, so a more localized model must be utilized to create the greatest specificity in optimized spacing. Modeling posited by Tuteja et al. allows for the assessment of droplet behavior on a single interstice between two fibers. Working backwards from desired contact angle, robustness pressure, and fiber geometry it is possible to calculate a range of optimized fiber spacing.

The Cassie-Baxter model provides the most opportunity for inputs and therefore provides a successful base for the apparent contact angle predictions for optimized fiber spacing. The
work done by Manmur and Tuteja et al. allows for the \( f_1 \) and \( f_2 \) to be governed by fiber radius and inter-fiber spacing inputs, providing a calculated base geometry with which to describe the air-liquid and liquid-solid portions of the interactions of the droplet on a solid surface. Utilizing this geometric understanding along with the \( \theta_e \) for the inherent chemical behavior allows for an apparent contact angle prediction, with variables for behavior optimization through geometrical contortions. The modeling also clearly explains the impossibility of a droplet on a solid surface having a contact angle of 180°. This outcome would only be possible in a state of no liquid surface interaction and liquid being in contact with air only, the only opportunity for this would be in a vacuum.

Inter-fiber spacing, \( 2D \), is a variable geometrical facet the optimization of which is dependant on the chemical interacting and lowered surface energy provided by the chemical grafting introduced in the grafting of fluorochemicals. As Cassie-Baxter first proffered in equation (2.14), the decreased interaction at the solid-liquid interface will increase the apparent contact angle of the droplet on the surface. The increased detail work in the equations of Tujeta et al. goes forward in expanding the understanding of liquid-solid contact minimization. The air/liquid interface provides the lowest possible surface energy, hence the highest apparent contact angle. At some point the increase of fiber spacing will fail to support the droplet and lead to complete wetting.

In understanding the appropriate model for the structural implications, it is understood that droplet behavior must also be governed by the chemical interactions, surface tension, and
energy of the liquid. In following examples the inter-fiber spacing and cylindrical shape will be input into the Cassie-Baxter and Wenzel equations for apparent contact angle based on surface roughness. Due to the hydrophobic nature of the treated nylon filaments the Cassie-Baxter equation is the most appropriate, while the fluorochemical treatment increases the inherent contact angle of the dodecane on the nylon film it fails to reach 90° and oleophobicity, making the Wenzel model appropriate for subsequent modeling. With this equation modification and combination it is possible to understand spacing optimization as a form of roughness.

Tuteja et al. provide the equation (2.16) to predict apparent contact angle as a function of ratio of fiber size and spacing.  

\[
\cos\theta^c_B = \frac{R}{(R + D)} \left[ \sin\theta_e + (\pi - \theta_e) \cos\theta_e \right] - 1
\]

(2.16)

This equation is a combination of geometrical and trigonometric measurements adapted to the Cassie-Baxter equation. Since the dodecane exhibits a Wenzel wetting state a new equation is needed, incorporating the inputs of the Wenzel equation with experimental measurements to garner a predictive model.

The Wenzel equation (2.13) defines apparent contact angle as a function of surface roughness and inherent contact angle based on the surface energy interactions outlined by Young. The inherent contact angle is garnered directly from measurement of the treated film. It is the roughness factor, \( r \), which must be varied to predict the impact of filament spacing on the apparent contact angle.
\[ r = \frac{\text{actual surface}}{\text{projected surface}} \] (2.17)

Wenzel defines the geometric surface as the planar projection of the surface area, having only two dimensions. The actual surface is the real area of the topography of the surface, having z direction as well.

\[
\cos \theta_r^* = \left[ \frac{\pi R^2 + (R + D)}{(R + D)} \right] \cos \theta_c
\] (2.18)

In this instance the model is using roughness, as defined by inter-fiber spacing ratio, as the variable to predict the apparent contact angle for dodecane. This model is specifically adapted for the filament assemblies utilized in this investigation.

The source of the geometries can clearly be seen in Figure 2.8, where the dashed arrow indicates the geometric surface, and the dotted arrows indicate the actual surface. In equation (2.18) these areas are quantified in terms of \( R \), radius of filament, and \( D \), one half of the inter-fiber spacing.

### 2.3 Textile Based Structures

Textile based structures are of specific interest due to their ability to be produced on a mass scale and with specified surface topography. The highly complex and multi-scale structure of yarn-based textile structures warrant closer investigation for improved modeling and optimization. Multi-filament and monofilament structures are discussed. As can be clearly
seen in Figure 2.12 and Figure 2.13 not only are yarns not cylindrical, especially upon inclusion in a system, but they are also not solid.

Figure 2.12 SEM of woven textile cross section.\textsuperscript{17}

The profile of the yarn is varied by its multiple components, but also by the pressures of the surrounding yarns, resulting in circular elliptical and “lens” shaped cross sections.\textsuperscript{21,22,23} Micro-scale texture imparted by the incorporation of multiple fibers or filaments into to a yarn plays an important part in creating roughness as well as a heterogeneous surface with air inclusions. This secondary scale of topography creates a multi-scale surface. \textsuperscript{24}

\subsection*{2.3.1 Yarn Structures}

The structure of a yarn is complex and highly variable. Current mechanical modeling techniques pertaining to liquid behavior utilize geometric simplifications of the yarns, and textile structures, to facilitate calculations. The modeling techniques outlined in the previous sections are very useful and accurate; their effectiveness is not undermined by the
assumptions applied. Current models function with yarns being expressed as extensible cylinders. It is abundantly clear that multifilament structures have multiple surface variations and air interstices within the general structure of a single yarn.\textsuperscript{25,21}

![Figure 2.13 Heavy twisted filament yarn exemplifying surface detail.\textsuperscript{25}](image)

Current modeling of textile roughness based on yarns within the structure is limited by the intense complexity of yarn structures. The modeling of extensible cylinders is applicable to individual filaments and fibers, successfully representing the structure of Nonwoven assemblies, which are formed directly from fibers, by-passing the sliver and yarn formation process.
Understanding the micro-structure that occurs within the macro-structure of a given textile surface is key to increasing specificity in the modeling of droplet behavior. With this perspective it is vital to understand the intricacies of filament behavior within a multifilament yarn.

2.3.2 Fiber Structures

Droplet behaviors on single fibers are controlled not only by the surface liquid interaction but by Laplace pressure as well. “Laplace pressure ΔP of a liquid on a cylinder is determined by the liquid surface tension, the radius of the cylinder and the liquid volume.”

Laplace pressure defines the geometric shape and general
behavior of a droplet. Defined by the internal liquid pressures and external vapor pressures a given droplet will form the shape that minimizes the Gibbs free energy of the system.

The original Laplace equation (2.19) quantifies the pressure differences between a liquid, and vapor as determined by the dimensions of the droplet, defined by the two principle curvatures of the internal radii: $R_1$ and $R_2$; and surface tension of the liquid, $\gamma_{lv}$. The uniformity of the system is indicated by the constant, $K$, which is equal to $\frac{\Delta p}{\gamma_{lv}}$.

\[ \Delta p = \frac{2\gamma_{lv}}{R_0} \]  

(2.19)

In the instance of a liquid droplet on a flat solid surface, in which it will form a roughly spherical shape, $R_1$ and $R_2$ can be simplified and unified into $R_0$ as the single radius can serve to define the spherical drop. With this change the equation (2.19) can be simplified into equation (2.20).

\[ \Delta p = \frac{2\gamma_{lv}}{R_0} \]  

(2.20)

In order to apply the Laplace equation (2.19) to a cylindrically shaped solid, rather than a flat solid equation (2.20) is expanded to include more inputs that describe the solid dimensions and interactions of the increasingly complex solid structure.
In equation (2.20) the $R_f$ is the radius of the fiber, and $n = \frac{h}{R_f}$, where $h$ is the maximum height of the droplet. The maximum height of the droplet is defined by two components the fiber radius, $R_f$ and the droplet volume, $V_0$. The Laplace pressure of the system is defined by the interaction between the radial dimension of the cylinder, surface tension of the liquid, and the liquid volume.$^6,^6$

![Figure 2.15 Laplace pressure creating shape of a droplet on a cylinder.](image)

As defined by Carroll the predictability of the droplet shape is contingent on the symmetry of the droplet about the center longitudinal axis of the cylinder.$^6$ Symmetry in droplet shape is largely contingent on the $\theta_e$ of the solid liquid interaction as defined by Young. When the inherent contact angle of the two materials is less than $60^\circ$ the droplet will form a
symmetrical “barrel” shape, encircling the fiber, Figure 2.15. The “barrel” shape is defined by greater spread along the length of the fiber and even circumference of the fiber. When a $\theta_c$ of greater than 60° occurs the droplet can trend toward a “clamshell” shape, minimizing its contact with the surface of the solid with a significant portion of the droplet distending below the fiber. Rather than an equation to solve for the physical parameters of the clamshell shape and its Laplace pressure, a series of computational equations are run in simulation to garner the shape with lowest free energy. The droplet is not symmetrical, which makes direct calculation of its shape in one step impossible.

Figure 2.16 clamshell and barrel shaped droplets on fibers.

Methods of measuring contact angle on cylindrical fibers have been developed and adapted
since the 1940’s. One of the challenges in accurate contact angle measurement on a fiber is the inflection point, at which the droplet surface dramatically changes angles. The inflection point is due to the abutting of the two radii, internal (convex) and external (concave), that define the shape of the droplet around the fiber.

2.4 Chemical Modification

Chemical modification for hydrophobic behavior has long been investigated and executed. A variety of coating, padding and curing techniques have been applied to produce textiles with large apparent contact angles and low angles of hysteresis. The development of oleophobic chemical treatments that move beyond the biomimetics of previous work has been accomplished by a variety of means, since the 1940’s. 29,29,20

Originally hydrophobicity was thought to be a manifestation of solely the chemical interaction of the surface, leading to the addition of chemical alterations such as coatings to surfaces in an attempt to increase water repellency, from simple coatings of paraffin wax to in-situ formation of polymers in the early half of the 20th century. Cassie-Baxter discussed the importance of structure over that of chemical surface, as seen in a variety of biological manifestations of superhydrophobic surfaces on both plants and animals, formed to create appropriate air interstices, which produced the proper ratio for a heterogeneous surface, leading to the realization of the heterogeneous surface of the Cassie-Baxter state, hydrophobicity, and droplet roll-off.
In combination with surface topography chemical structure is vital to surface energy interactions that govern droplet behavior, especially for oils. Though hydrophobicity is seen in nature through multiple mechanical means, oil repellency or oleophobicity requires proper structure as well as lower surface energy of the substrate to prevent wetting. This is necessitated by the low surface tension of oils. While water displays tension of 72.8 dynes/cm, a common oil such as Sunflower oil is as low as 33.0 dynes/cm. The surface energy of the solid must be lower than that of the liquid to prevent liquid spread.

Chemical treatments change the surface molecules of the substrate but also can be utilized in forming micro-structure on the surface of a material, adding to phobic behavior through proper surface shape creation, as well as the chemical structure.

The addition of silicon based chemicals for the creation of hydrophobic surface began as early as 1942, utilizing a variety of manners of application, from vapor phase application, to solution treatments. A review of the literature mentions 332 patents through 1947. In 1946 Barry developed a treatment process involving the use of silanes in a variety of compounds. These were put into solution with dry-cleaning fluid and textiles were immersed in the solution. Curing with a hot iron set the chemical reaction and creates durable water repellant textiles.

Fluorochemicals can be used for surface modification, and is particularly notable for its ability to impart the properties of oleophobicity, while still delivering the levels of
hydrophobicity seen with other chemical grafts. Most methods of chemical surface modification with silanes are based on the processing technique outlined by Stoeber and Hoefnagels.  

Grafting FS using both deionized water and ammonium hydroxide as catalysts Lee and Owens created highly hydro and oleophobic textiles.  

This grafting technique was adapted from that of Hoefnagels and Stoeber, The process consists of soaking the substrates in a solution, of substance, solute, and catalyst; and has been adapted to include the use of a microwave for radiation and curing. Microwave radiation increases the speed of processing and improves the reaction rate of bonding between the material and silanes. The most improved results were seen with use of ammonium hydroxide as a catalyst, increasing attachment between the material and the silane as well as creating a multi-scale structure with the FS.  

8, 8
3. Experimental

3.1 Materials

Nylon monofilament fishing line comprised of a Nylon 6 and Nylon 6,6 blend in 0.5 mm diameter (Omniflex 30 lb. test, Shakespere, Pure Fishing, Columbia, SC), 0.3 mm diameter (High Impact 20 lb. test, Stren, Spirit Lake, IA), and 0.1 mm diameter (Trilene Big Game 10 Lb. test, Berkley, Pure Fishing, Columbia, SC) were used to simulate extensible cylinders. These were adhered with latex adhesive (Rubber Cement, Elmer’s Products Inc., Westerville, OH), to rigid transparent sheets of polystyrene (C₈H₈, Shrinky Dinks, K&B Innovations, Inc., North Lake, WI). Nylon 6,6 film (Du Pont, Canada) was used for garnering inherent contact angles on a flat surface. For chemical grafting 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (C₈F₁₇CH₂CH₂Si(OCH₃)₃, Gelest, Morrisville, PA), ammonium hydroxide (NH₄OH, Aldrich, St. Louis, Mo), and isopropyl alcohol (CH₃CHOHCH₃, BDH®, VWR, Radnor, Pennsylvania) were used. Testing was completed with droplets of deionized water (NCSU), and dodecane (C₁₂H₂₆, Aldrich, St. Louis, MO, USA).

3.2 Chemical Modification

Chemical modification of the nylon surface is required for investigation of both philic and phobic chemical interaction, and the impact structure can have on droplet behavior, in conversation with the inherent behavior.
3.2.1 FS Grafting on Nylon Film

A solution, 11.046 g, was prepared using Isopropyl alcohol, 10.725 g; FS, 0.214 g; and ammonium hydroxide, 0.107 g. A 5×5 piece of nylon 6,6 film was rinsed with isopropyl alcohol to clean the surface and wet the film; the film was then immersed in the solution for two hours, to fully include the FS onto the entire surface area. After removal from the solution the nylon 6,6 film was padded to remove excess liquid, and cured at in an oven at 100 to 170°C for one to ten minutes to graft the FS, dependant on the materials. After being
allowed to return to room temperature the nylon film was then rinsed in methanol twice to remove any un-grafted FS. After rinsing the film was again cured and dried in the oven for complete setting and drying.

### 3.2.2 FS Grafting on Nylon Fibers

A solution, 65.66 g; was prepared using isopropyl alcohol, 63.75 g; FS, 1.275 g; and ammonium hydroxide, 0.637 g. Sixty pieces of fifteen-inch long nylon monofilament were rinsed with isopropyl alcohol to clean the surface and wet the filaments, then squeegee-ed twice to remove excess liquid. The filaments were then immersed in the solution for two hours, to fully include the FS onto the entire surface area. After removal from the solution the nylon 6,6 film was squeegee-ed to remove excess liquid, and cured at in an oven at 100 to 170˚C for one to ten minutes to graft the FS, dependant on the materials. After being allowed to return to room temperature the nylon filaments were rinsed in methanol twice to remove any un-grafted FS. After rinsing the filaments were again cured and dried in the oven for complete setting and drying.

Nylon filaments were grafted with a fluorochemical treatment to lower the surface energy of the solid and allow for phobicity. Utilizing this grafting treatment renders the nylon filament hydrophobic and oleophilic. The Young’s or inherent contact angle of water on FS grafted nylon film is 113˚, and 70˚ for dodecane on the same surface. The only factor with which to increase apparent contact angle will be the geometry of the filaments. In this way both phobic and philic liquid behaviors can be observed, and in doing so highlight structure and spacing as the variable.
3.3 Testing

3.3.1 Testing of Filament Assemblies for Apparent Contact Angle

Assemblies were mounted to glass microscope slides and positioned in the center of the viewer. Droplets of 10 µL were deposited onto the fibers from a syringe positioned slightly above the filaments, and centered over the assembly. Once deposited the droplet was allowed to rest for three seconds before being photographed. Due to the short focal length of the microscope two images were taken for each test, one with the tips of the filaments in full focus and the other with the liquid droplet in full focus. The combination of the two images provides a complete perspective on droplet filament interaction.

For further testing the stage was then rotated 180 degrees, in most cases this removed the droplet, any residual liquid was removed with Kimwipe®, and the assembly was left to dry for one minute. The droplet deposition and photograph process was then repeated. Testing both "sides" of the assembly aided in accounting for slight filament distortion by providing multiple tests on a single sample. This process was repeated with both water and dodecane.

3.3.2 Testing of Filament Assemblies for Roll-off Angle

Assemblies were mounted on a glass slide and positioned at the center of a rotation stage (Newport, 495, Irvine, CA, USA), which was used to incline the filament assembly and observe droplet roll-off. Droplets of 50 µL of water and dodecane were placed at the center of the filament assembly and the stage was inclined, the angle at which the droplet began to roll-off was recorded. The process was recorded on a video camera, from which still images
were taken to measure the diameter of the wetting area, advancing and receding contact angles.

3.4 Characterization

3.4.1 SEM

Scanning electron microscope JSM-6400F (JEOL, Tokyo, JPN) was used to determine the surface variations and success of chemical grafting. 5K volts were used at magnifications ranging from 1000 × to 50K×.

3.4.2 Apparent Contact Angles

A goniometer was used to measure contact angles on flat substrates. The nylon films used for garnering apparent contact angle and verifying grating success were observed in this manner. For the purposes of imaging the behavior of the droplet on arrangements of individual filaments a Lab-phot optical microscope (Nikon, Japan) was used in combination with a digital single lens refraction camera (Cannon EOS EF-S-18-55IS) and MM-SLR adapter (Martin Microscope, Easley, SC) the connect the two. Since a cross sectional view was desired the microscope was positioned in a lying down position, with the “spine” of the machine being held by a wood support system. Making it possible to simultaneously see the top and bottom of the droplet, through the eyepieces and camera. In this position the camera was at table level, allowing it to be used directly as the focus viewer.
In order to view the cross sections of the filaments with a droplet on top a series of filament assemblies were created, as seen in Figure 3.3. Short sections of filament were adhered to squares of clear plastic. Filaments were also used to provide the inter-fiber spacing, by positioning them perpendicularly between the filaments for testing, and parallel to the plastic base. Glue was applied to the plastic squares in the desired location of the filament bases. Positioning was stabilized with a hemostat on the un-glued ends of the filament. The fibers were held vertically for drying by hanging them, bases placed on aluminum blocks with unglued fiber ends pointed downwards, holding the filaments straight and flush in the appropriate spacing. Once the assembly was completed, filament ends were trimmed to be of equal length.
The truncated depth of field of the microscope negates the potential issue of the glue and base plastic disrupting the image; their optical clarity is only necessary to allow for the transmission of light that come from under, or with horizontal orientation, behind the stage. Images were loaded into Photoshop, utilizing rulers to determine actual filament spacing as well as to measure apparent and intrinsic contact angles.

Filaments were tested in various assemblages, beginning with investigation of droplet behavior on a single filament. Subsequently sets of four filaments of the same diameter were aligned at various spacing, $0.2R, 0.3R, 0.6R, R, 1.2R, 1.67R, 2R, 2.66R, 3R, 3.33R, 5R, 10R$, droplet behavior and contact angle were observed.
3.4.3 Roll-off Angles

Roll-off angles were recorded from the rotational stage’s display (figure 3.4) upon complete roll-off of the droplet. The entire duration of platform inclination until roll-off was recorded on a video camera. (Canon, EOS EF-S-18-55IS)

![Schematic of rotational stage set up for droplet roll-off angle measurement.](image)

Due to the need for an extended length of fibers a secondary set of filaments was constructed for testing. These were build to rest on a flat sage by gluing the filament tips along a slide,
leaving 50% of the length overhanging the edge, to allow for fibers with no substrate, as seen in figure 3.5.

![Diagram of filament assemblies](image)

Figure 3.5 Multiple views of filament assemblies for roll-off testing.

These videos were uploaded to a computer, and played using video editing software (Image Mixer 3, SE Version 5). At the moment directly before the droplet released from the fibers and rolled-off the video was paused and a screen shot of the still image was taken. This image was then placed into Photoshop. The ruler tool was used to measure contact area and advancing and receding contact angles from the image.
4. Results and Discussion

In investigation of the optimization of fiber spacing and specification of multi-scale yarn structures, testing samples of monofilament were created to mimic the assumptions of current modeling techniques. A full understanding of droplet behavior warranted testing with both phobic and philic liquids, to achieve this the nylon monofilament was chemically grafted to lower its surface energy, and water and dodecane were used as test liquids. In this way the structure can be observed in potentially all response iterations, increase phobicity, decrease phobicity, increase philicity, decrease philicity, move from phobic to philic, or move from philic to phobic. By monitoring behavior of liquid solid interaction with \( \theta \), both above and below 90° it is possible to indentify the contribution of structure to rough surface wetting behavior.

4.1 Chemical Modification

In order to investigate the behavior of multiple liquid behaviors on cylindrical monofilament it was necessary to chemically graft the filaments to create a hydrophobic surface, and decrease the oleophilicity of the surface. Verifying the success of the chemical grafting process as outlined in the experimental section was the first step.

Due to the expression of all three major forms of intermolecular adhesion water has a high level of surface tension, 72.8 dynes/cm. While dodecane has only London Dispersion forces at work, having a much lower surface tension at 25.4 dynes/cm. Using the Dupre-Young
equation (2.4) to calculate the contact angle due to the work of intermolecular adhesion the results garnered are cohesive with those expected, Table 4.1.

**Table 4.1** Verification of grafting success through comparison of predicted and observed contact angle values.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface</th>
<th>Predicted</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Nylon</td>
<td>73°</td>
<td>72°± 2</td>
</tr>
<tr>
<td></td>
<td>FS grafted</td>
<td>119°</td>
<td>117°±6</td>
</tr>
<tr>
<td>Dodecane</td>
<td>Nylon</td>
<td>0°</td>
<td>&lt; 5°</td>
</tr>
<tr>
<td></td>
<td>FS grafted</td>
<td>52°</td>
<td>70°± 8</td>
</tr>
</tbody>
</table>

When placed on a flat nylon solid water would be expected to show an inherent contact angle of around 73°. This is similar to the experimental results garnered of 67.8°. Placed on the same nylon surface dodecane should show an inherent contact angle of around 0°, or complete wetting. In experiment the droplet fully wet the surface, garnering a contact angle of ~ 0°. With FS grafting the surface energy of the solid is significantly lowered, completely removing the interactions of permanent dipole as well as hydrogen bonds. For the purposes of predictive calculations of the adhesion contributions of FS, the quantification of molecular interactions of poly(hexafluoropropylene) are used to represent the properties of FS due to the ready availability of this information from the literature, and the chemical similarity between
the two. With poly(hexafluoropropylene) as a model, a droplet of water on a FS-grafted nylon surface should exhibit a contact angle of approximately 119°, in experimental results water on a grafted surface resulted in an inherent contact angle of 113°. The predicted contact angle of dodecane on the FS-grafted nylon is 52°; the inherent contact angle resulting from experimentation was similar at 56°.

![Figure 4.1 10 µL droplet on a nylon surface, (a) water, contact angle is 75°. (b) dodecane, contact angle is ~ 0°.](image)

Chemically grafting the FS onto the nylon surface decreases the surface energy of the solid and increases the contact angles observed with both water and dodecane. Water contact angle is increased enough to render the surface hydrophobic, while the increase in contact angle of dodecane is not great enough to achieve oleophobicity, but serves to decrease philicity.
Figure 4.2 10 µL droplet on a FS grafted nylon surface, (a) water, contact angle is 117° (b) dodecane, contact angle is 70°.

In further confirmation of the grafting success, SEM images of the nylon 6,6 films were taken to observe the structure and distribution of the grafting on the surface. A control image of the untreated nylon was used as a basis for comparison.

Figure 4.3 SEM of (a) untreated nylon filament. ×20K magnification, 5KV (b) FS treated nylon film ×50K magnification.
This image, Figure 4.3 (a), displays the slight topographical variation that is inherent to all surfaces, and Figure 4.3 (b) the increased roughness and layers of texture, due to FS grafting onto the nylon film. With this image it can be observed that the surface of the solid has been modified structurally as well as chemically by the FS grafting process.

4.2. Rough Surface Formation

Structure is of great importance in creating a surface with phobicity. A variety of filament arrays were constructed utilizing different diameter filaments and varied spacing, Table 4.2; providing a means to observe the simplest manifestation of the current modeling techniques. As depicted in Figure 4.4 the filament assemblies were constructed to provide a cross sectional view of the droplet interaction with the structure of the filaments. This was achieved by gluing one end of short lengths of the nylon monofilament to a polystyrene substrate.
Table 4.2 Assembly Constructions

<table>
<thead>
<tr>
<th>Filament Diameter (2R)</th>
<th>Inter-fiber spacing (2D)</th>
<th>Spacing ratio (D/R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mm</td>
<td>0.1 mm</td>
<td>0.2</td>
</tr>
<tr>
<td>0.3 mm</td>
<td>0.1 mm</td>
<td>0.3</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>0.3 mm</td>
<td>0.6</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>0.5 mm</td>
<td>1</td>
</tr>
<tr>
<td>0.3 mm</td>
<td>0.3 mm</td>
<td>1</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>0.6 mm</td>
<td>1.2</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>0.8 mm</td>
<td>1.6</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>1.0 mm</td>
<td>2</td>
</tr>
<tr>
<td>0.3 mm</td>
<td>0.6 mm</td>
<td>2</td>
</tr>
<tr>
<td>0.3 mm</td>
<td>0.8 mm</td>
<td>2.6</td>
</tr>
<tr>
<td>0.3 mm</td>
<td>1.0 mm</td>
<td>3.3</td>
</tr>
<tr>
<td>0.1 mm</td>
<td>0.5 mm</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 4.4 A filament assembly constructed for testing, with the flat tips of the monofilament in full focus. Horizontal lines on the tips are slight marks from cutting.

The liquid used in testing determined the equation appropriate for prediction. Since the monofilament assembly is simultaneously hydrophobic and oleophilic both the Wenzel (equation 2.13) and Cassie-Baxter models (equation 2.17) are applicable.

As depicted in Figure 2.5 (a) the Wenzel model assumes full wetting in the case of philic interactions. According to Wenzel increased surface area increases the inherent behavior of the intermolecular forces that occur on a flat substrate, as proffered by Young. Extrapolating the Wenzel model to the filament structure results in the relation of geometric and actual area as depicted in Figure 2.8.

With this model the increasing actual area in relation to the geometric area creates an increased roughness factor $r$. Increasing roughness decreases the apparent contact angle predicted by the Wenzel model as the substrate is oleophilic.
Conversely the apparent contact angle of water is seen to increase with the increased amount of inter-fiber spacing in the instance of water on the hydrophobic filaments, which exhibit the Cassie Baxter model of behavior. This model is adapted to cylindrical surfaces by Tuteja et al. in equation (2.16). The Cassie Baxter model assumes a heterogeneous wetting state with the liquid droplet resting on a composite surface of the solid and air interstices. The 2D indicated in Figure 2.11 represents the air interstices that will have a positive effect on the level of phobicity. With this assumption, decreased proportion of the solid surface, in this case the FS grafted nylon monofilament, will respond with higher apparent contact angle. This is due to the fact that the air will have less adhesion with the liquid than the solid surface and hence increase the phobicity of the system. This is reflected in Figure 4.6,
depicting the degree of apparent contact angle in relation to the fiber spacing ratio of the filaments.

Figure 4.6 Graphical depiction of the relationship between inter-fiber spacing and apparent contact angle as governed by the Cassie Baxter equation.

To further the comparison of the two models Figure 4.7 shows the apparent contact angles predicted by both models at the same fiber spacing ratio. The increased spacing of the filaments serves to increase roughness in the Wenzel model decreasing the contact with the increased surface area exhibiting the inherently philic behavior. Simultaneously the Cassie-Baxter equation displays increased apparent contact angle with the increasing spacing between filaments; as based on air having a lower work of adhesion and increasing the
phobicity of the surface through a favorable balance of surfaces comprising the heterogeneous surface of wetting.

Figure 4.7 Here the predictive slope of apparent contact angle as a function of fiber spacing ratio highlights the difference between the Cassie-Baxter model as compared to the Wenzel model.

The Cassie-Baxter model functions on the presumption that increased air ratio in the heterogeneous wetting surface will increase contact angle, and hence increased spacing will have a positive effect on phobicity. The Wenzel model interprets larger spacing of the fibers as increased roughness, which effects an enhancement of the inherent behavior of the solid liquid interaction, decreasing the predicted contact angle.
Figure 4.8 Comparison of predicted and observed apparent contact angle as a function of fiber spacing ratio for dodecane using the Wenzel model.

The apparent contact angle exhibited by the dodecane was measured from the image of the assembly. This process was repeated multiple times and an average was taken. The observed contact angle taken from the image was then compared to the predicted contact angle calculated from the Wenzel equation, based on spacing ratio. Direct measurement from images was used for increased accuracy in understanding the size of 2D that should be input in to the equation. The measured $R$ and $D$ from the image analysis were highly variant due to degree of zoom and image focus. In order to compensate for this discrepancy $D$ was measured in terms of $R$, since the radius of the filament in each image was fixed and known.
In comparison to the calculated apparent contact angle provided by the predictive version of the Wenzel equation the observed contact angles are slightly lower than expected. Also, due to high levels of variance between observed angle for the same spacing two averages were provided for each spacing ratio of the values, one, one and a half, and three. This meta-stable response is exemplified in Figure 4.9 in which the same fiber spacing ratio is exhibiting both oleophobic and oleophilic wetting behaviors.

![Figure 4.9](image)

**Figure 4.9** Fiber assembly $R = .25$ mm $D = .3$ mm, with 10 µL of dodecane, exhibiting two different types of wetting behavior, apparent contact angle in left image is 21° and in right image 130°.
Figure 4.10 Comparison of predicted and observed apparent contact angle as a function of the fiber spacing ratio for water using the Cassie Baxter model.

The apparent contact angle exhibited by water was measured from the image of the assembly. This process was repeated multiple times and an average was taken. The observed contact angle taken from the image was then compared to the predicted contact angle calculated from the Cassie Baxter equation, based on spacing ratio. Direct measurement from images was used for increased accuracy in understanding the size of $2D$ that should be input into the equation. The variation between the images in terms of measuring $R$ and $D$ as explained previously for the Wenzel model with dodecane were negated for water due to a ratio of $R$ and $D$ being used as the spacing input within the Cassie Baxter model. The observed apparent contact angles group close to the predicted apparent contact angles.
calculated. At spacing ratios greater than three the observed contact angle decreases significantly as can be seen in Figure 4.10, deviating from the predicted model.

Figure 4.11 10 µL water droplets exhibiting superhydrophobicity on filament assemblies. (a) \( R = 0.25 \) mm \( D = 0.68 \) mm apparent contact angle is 143°; (b) \( R = 0.15 \) mm; \( D = 0.27 \) mm \( D/R = 1.8; \theta^C_B = 150° \)

Figure 4.12 10 µL water droplet on fiber assembly. \( R = 0.5 \) mm \( D = 1.3 \) mm apparent contact angle is 26.1°.
4.3 Roll-off Angle

Due to the complexity of textile surfaces the simplification of solid liquid structural interaction has been utilized in the calculation of predicted roll of angle, based on the diameter of the interaction area (equation 2.15) using a cross sectional planar projection to garner the length of the droplet. An example of this cross sectional view can be seen in Figure 4.13. When using filament structures as the substrate more specific areas of interaction can be observed and quantified. With this in mind it is prudent to consider the possible options for the input of $d$, depicted in Figure 4.13. Defined as $d_p$, the original projected area being the diameter of the interaction area, $d_d$, the diameter of the filaments in contact with the drop, and $d_a$, measuring the actual circumference of the fiber in contact with the droplet.

Figure 4.13 Indication of various measurement options for $d$; $d_p$ projected interaction length, $d_d$, the diameter of the filaments, and $d_a$, measuring the actual circumference of the fiber.
4.3.1 Water Roll-off

Testing series were repeated by inclining a 50 µL water droplet resting on the filament array mounted on the rotating stage. When the droplet began to roll-off the stage was stopped and the angle was recorded.

![Image of water droplet rolling off filament array]

Figure 4.14 50 µL water droplet rolling off 0.05 mm/0.25 mm assembly, \( \alpha = 27.2^\circ, \theta_r = 70.9^\circ \).

Two spacing options of 0.5 mm diameter filaments were tested, at 0.5 mm spacing and 0.1 mm spacing. To keep consistency with the fiber spacing ratios presented previously in the paper they are referenced in terms of \( R \), fiber radius, and \( D \), which is one half of the inter-
fiber spacing. The testing series resulted in an average roll of angle for each spacing series. The 0.25/0.25 mm assembly achieved roll-off of a 50 µL droplet at 29.4°. The 0.05/0.25 mm assembly achieved roll-off of a 50 µL droplet at 32.8°. The advancing and receding contact angles were directly measured from still images taken from the video recording taken during testing. Average advancing contact angle for 50 µL of water placed on the 0.25/0.25 mm filament assembly was recorded at 146°, receding contact angle was recorded 63°. Average advancing contact angle for 50 µL of water placed on the 0.05/0.25 mm filament assembly was recorded at 154°, receding contact angle was recorded 73°. Table 4.3 below displays the predictions generated with various $d$ inputs.

Table 4.3 Predictions of roll-off angle for 50 µL water with variant $d$

<table>
<thead>
<tr>
<th>Types of $d$</th>
<th>Predicted Roll-off Angle $\alpha$</th>
<th>Fiber spacing ratio $D/R$</th>
<th>0.25/0.25 mm</th>
<th>0.05/0.25 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_a=180^\circ$</td>
<td>$\theta_a=146.6^\circ$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_p$</td>
<td>$\theta_r=63.05^\circ$</td>
<td>$\theta_r=63.05^\circ$</td>
<td>24.1°</td>
<td>32.8°</td>
</tr>
<tr>
<td>$d_d$</td>
<td>10.6°</td>
<td></td>
<td>25.6°</td>
<td>17.8°</td>
</tr>
<tr>
<td>$d_a$</td>
<td>13.9°</td>
<td></td>
<td>34.4°</td>
<td>24.7°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>65.1°</td>
<td>44.4°</td>
</tr>
</tbody>
</table>
The two most accurate predictions are provided by using $d_p$, the projected length of the droplet, and assuming the advancing contact angle is $180^\circ$, and $d_d$ when using the measured advancing and receding contact angles. The additional specificity of detailed liquid surface contact area does not provide increased accuracy of prediction when utilizing equation (2.15).

### 4.3.2 Dodecane Roll-off

Dodecane roll-off angles were recorded in the same manner as with the water testing series, again using a 50 µL droplet. Two spacing options of 0.5 mm diameter filaments were tested, at 0.5 mm spacing and 0.1 mm spacing.

![Image of dodecane droplet rolling off a filament assembly](image)

Figure 4.15 50 µL dodecane droplet rolling off 0.05 mm/0.25 mm assembly, $\alpha = 42.4^\circ$, $\theta_r = 47.7^\circ$. 
Since dodecane exhibits the Wenzel state the 0.25/0.25 mm assembly was not properly spaced to prevent wetting and hence was inappropriate for roll off testing. The 0.05/0.25 mm assembly did achieve roll-off of a 50 µL droplet, this is due to the close spacing of the fibers that generates a meta-stable Cassie-Baxter state, accomplishing roll-off at the proper incline, which was observed to be 42.9˚. The advancing and receding contact angles were directly measured from still images taken from the video recording taken during testing. Average advancing contact angle for 50 µL of dodecane placed on the 0.05/0.25 mm filament assembly was recorded at 122˚, receding contact angle was recorded 39˚. Table 4.4 below displays the predictions generated with various $d$ inputs. Note the N/A indicates that the equation predicted a roll-off angle greater than 180˚.

Table 4.4 Predictions of roll-off angle for 50 µL dodecane with variant $d$

<table>
<thead>
<tr>
<th>Types of $d$</th>
<th>Fiber spacing ratio $D/R$ 0.05/0.25 mm</th>
<th>Predicted Roll-off Angle $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_D$</td>
<td>$\theta_i=180^\circ$</td>
<td>$\theta_f=122^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\theta_i=39^\circ$</td>
<td>$\theta_f=39^\circ$</td>
</tr>
<tr>
<td>$d_d$</td>
<td>10.8˚</td>
<td>N/A</td>
</tr>
<tr>
<td>$d_a$</td>
<td>6.5˚</td>
<td>41.6˚</td>
</tr>
<tr>
<td></td>
<td>9.1˚</td>
<td>68.1˚</td>
</tr>
</tbody>
</table>
The only accurate prediction for dodecane roll off was provided by using $d_d$, the summation of the diameter of fibers in contact with the droplet, and measured advancing and receding contact angles. The additional specificity of detailed liquid surface contact area does not provide increased accuracy of prediction when utilizing equation (2.15). Though the dodecane droplet did roll-off the filament assembly it did not do so without leaving a residual trail. This incomplete roll-off is consistent with that seen in other roll-off testing of oils.
5. Conclusions

In order to observe the behavior of droplets on a simplified structure, nylon monofilaments were chemically grafted with FS to lower the surface energy. This grafting process made the filaments hydrophobic and decreased their oleophilicity. This allowed the structural aspect of liquid behavior to be observed with both philic and phobic interactions. The cross sectional images garnered by the observational method, were measured for apparent contact angle. Empirically observing the relationship between inter-fiber spacing and apparent contact angle is an addition to the specificity of mechanical modeling.

There is a reasonable level of agreement between predicted and observed contact angles based on inter-fiber spacing ratios; water as modeled by the Cassie-Baxter equation holds much more consistently to the expected values than dodecane as modeled by the Wenzel equation. There are notable outliers in both liquid tests, but these can reasonably be accounted for. The sudden collapse of apparent contact angle of the water droplets at large spacing can be accounted for by robustness pressure. A system with increasing air proportion should lead to increased contact angle, as air has the minimal amount of philicity possible. But, at some point the lack of physical structure will cause the droplet to enter the system, due solely to lack of support. This serves to provide an upper limit for inter-fiber spacing that creates a boundary within the accepted progression of increasing air space to increased apparent contact angle. The meta-stable Cassie-Baxter state exhibited by the dodecane on
filament assemblies with spacing ratios below three shows the promise of improving oleophobic properties by structural means.

Filament arrays were also utilized to test roll-off angle, by inclining the array on a rotational stage and recording the roll-off angle. Image analysis was also used to measure the amount of contact area between the droplet and the filament array. Roll-off angles calculated with different areas of liquid solid contact as the input were compared to experimentally garnered roll-off angles, to find the most accurate means of prediction. It was found that utilizing the summation of the diameter of the fibers in contact with the liquid produced the calculated roll-off angle most cohesive with those observed in experimentation. Interestingly the prediction for water roll-off was most accurate when advancing angle was assumed to be 180˚, while dodecane roll-off was best predicted when directly measured advancing and receding contact angles were used as inputs.

The assumptions of the models hold fairly true to the experimental outcomes. The predictive equations more accurately represent the responses of the textile surfaces they attempt to model than a structure created based on the physical assumptions. Due to the physical scale of the testing apparatus the distribution of fibers within a given ratio was limited. Textiles with very high permeability to air that are comprised of evenly distributed fine fibers, such as are seen in electrospinning, maybe able to provide enough support even at very high spacing ratios.
Liquid repellant surfaces have many possible applications in many fields. Challenges to scalability of superhydrophobic and superoleophobic surfaces would be well addressed by the utilization of textiles. Large-scale production capabilities, and the prevalence of applications currently seen are the clear draw. Further investigation into the complexity and detail of textile structures in relation to liquid repellency has the potential to provide great advancements.
6. Applications and Future Work

Liquid resistant structures hold many applications in preventing absorption and increasing dryness as well as protection from the natural elements. Such qualities could be applied to the automotive industry, outdoor wear, medical, and geotextiles. Also, hydrophobicity can create anti-freezing surfaces, which presents opportunities for the marine and aerospace industries. Of particular interest is the prevention of frozen ropes, which compromise physical performance. Oleophobicity, concerning repellency of oils and other low surface tension liquids, increases the amount and variety of applications even further. Self-cleaning fabrics could increase energy efficiency in home care of textiles, preventing stains and minimizing laundering. Protection from liquid hazards such as pesticides and other dangerous materials are valuable contributions to the safety of farm and factory workers as well as first responders. Benefits also include protection of military personnel through chemical and biological defense.

Increased investigation into methods of roughness and fiber ratio quantification would also serve to improve the understanding of liquid droplet behavior on textile substrates. Modeling of individual yarn structures with variable profiles would aid greatly in the specification of the muti-scale structure inherent to yarn based textiles.
REFERENCES


