SIEBER, MICHAEL DAVID. Influence of Surface Structure on Hydrophobicity of Electrospun Nylon 6 Coated Fabric and Improvement of Durability using Atmospheric Pressure Plasma. (Under the direction of Dr. Xiangwu Zhang and Dr. Marian G. McCord).

The purpose of this work is to utilize atmospheric pressure plasma to increase the adhesion between an electrospun nanofiber layer and a textile substrate. Woven fabric is pretreated in audio frequency glow discharge plasma and mounted on a rotating collector prior to deposition of the electrospun fibers. Both atmospheric pressure plasma and electrospinning can be scaled up to an industrial, continuous process, and promise cost and energy savings relative to many traditional and current textile finishing methods.

In this study, surface structure is shown to significantly affect static Water Contact Angle (WCA) independent of surface chemistry or the use of low surface energy chemical treatments. Repellency is controlled by choice of solution and processing parameters. Nylon 6 (WCA 62.6°) was chosen in this study due to its ease of electrospinning and well-characterized properties. To show the role of structure in surface hydrophobicity, beaded-nanofiber nonwoven webs were electrospun atop a woven Nylon 6,6/cotton military fabric to have static WCA as high as 140.85 ± 2.15°. Repellent coating surfaces such as these could be applied for use as protective fabric coatings or filtration barriers against aerosols and other contaminants.

Interfacial adhesion between nanofibers and substrate pretreated plasma prior to electrospinning was evaluated using both direct and indirect characterization techniques. Modifications to Martindale Textile Abrasion and 90° Interfacial Peeling Tests were performed to take into account nanofiber/fabric interactions. Results indicate increased adhesion resulting from plasma effects on the substrate fabric. Both the number of
Martindale rubbing cycles and peeling toughness increased as polymer concentration, flow rate and substrate treatment time increased. This indicated increased interfacial strength between nanofibers and fabric. Substrate effects to plasma treatment were also verified by increased surface wettability using WCA and exhaust dyeing intensity.

A quick, simple and durable hydrophobic finishing process for woven military Nylon 6,6/cotton fabric is demonstrated, maintaining similar bulk garment characteristics like moisture vapor transmission to promote necessary dissipation of heat. The promotion of necessary heat transfer while providing protection against chemical and thermal hazards using a multilayered garment approach has become important for many textile applications including military and industrial uses for Chemical-Biological (CB) hazard protection, as well as medical and activewear textiles. Incorporation of a nanofibrous coating with a fabric imparts composite multifunctional properties, while demonstrating the potential for greatly decreased processing time and uses less water, energy, and hazardous chemicals than traditional finishing techniques.
Influence of Surface Structure on Hydrophobicity of Electrospun Nylon 6 Coated Fabric and Improvement of Durability using Atmospheric Pressure Plasma

by
Michael David Sieber

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

Textile Engineering
Raleigh, North Carolina
2011

APPROVED BY:

_______________________________  ______________________________
Dr. Xiangwu Zhang          Dr. Marian G. McCord
Co-chair of Advisory Committee          Co-chair of Advisory Committee

_______________________________  ______________________________
Dr. Mohamed A. Bourham          Dr. Henry Boyter, Jr.
Minor Representative          ITT Committee Member
DEDICATION

I dedicate this thesis to my parents: Dr. Ronald David Sieber, and the late Nancy Beth Sieber. I have learned much from you both and thank you for your support and guidance throughout my life.
BIOGRAPHY

Michael David Sieber was born and grew up in Durham, North Carolina. He graduated from North Carolina State University’s College of Textiles with a B.S. in Textile Engineering. After graduation, he enrolled in the Graduate School to obtain his Master of Science in Textile Engineering, as a research fellow for the Institute of Textile Technology. After graduation he hopes to enter industry relevant to performance and technical textiles.
ACKNOWLEDGEMENTS

I would like to thank and express gratitude towards my Advisory Committee members:

- Dr. Xiangwu Zhang, whose encouraging words while motivating me during my graduate studies;
- Dr. Marian G. McCord, whose support and advice helped me much in my research;
- Dr. Mohamed A. Bourham, whose technical opinion and expertise inspires me to work harder;
- Dr. Henry Boyter, Jr, whose technical expertise helped me with the organization of research writing.

I also would like to thank many on staff at the College of Textiles, including but not limited to:

- Jeff Krauss, NCSU COT Pilot Plant, for his help with fabrics and dyeing in the Pilot Plant;
- Judy Elson, TECS Laboratory, for guidance with sputter-coating and SEM;
- Dr. Julie Willoughby, for the use of her contact angle instrumentation;
- Teresa White, Physical Testing Laboratory, for her help with abrasion testing;
- Dr. Russell Gorga, for the use of his Instron test apparatus;
- Angie Brantley, TECS office, for her advice with registration and enrollment issues;
- Patrice Hill, ITT, for much help involving paperwork, internships, and guidance through the many confusing yet necessary steps graduate school seemed to present.

Lastly, I would like to express many thanks to the Institute of Textile Technology, for funding and support of my graduate research and fellowship.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>List of Figures</td>
<td>x</td>
</tr>
<tr>
<td><strong>Chapter 1: Introduction</strong></td>
<td></td>
</tr>
<tr>
<td>1.1 Significance of Study</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Problem Statement</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Research Objectives</td>
<td>3</td>
</tr>
<tr>
<td><strong>Chapter 2: Literature Review</strong></td>
<td>5</td>
</tr>
<tr>
<td>2.1 Introduction, Related Topics</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Repellent Surfaces: Does Nature have the Answers?</td>
<td>5</td>
</tr>
<tr>
<td>2.2.1 Different Natural Superhydrophobic Surfaces</td>
<td>5</td>
</tr>
<tr>
<td>2.3 Repellent Surfaces: What are the Governing Factors?</td>
<td>12</td>
</tr>
<tr>
<td>2.3.1 Surface Tension and Contact Angle</td>
<td>12</td>
</tr>
<tr>
<td>2.4 Roughened Surface Wetting</td>
<td>14</td>
</tr>
<tr>
<td>2.4.1 Recent Progress with Roughened Surfaces</td>
<td>17</td>
</tr>
<tr>
<td>2.5 Application of Textile-Based Repellent Finishes</td>
<td>18</td>
</tr>
<tr>
<td>2.5.1 Textile Wet Finishing</td>
<td>18</td>
</tr>
<tr>
<td>2.5.2 Repellent Textile Chemistry</td>
<td>19</td>
</tr>
<tr>
<td>2.5.3 Non-Traditional Repellent Finishes</td>
<td>24</td>
</tr>
<tr>
<td>2.6 Polymer Finishes using Electrospinning</td>
<td>24</td>
</tr>
<tr>
<td>2.6.1 Electrospinning of Polymer Nanofibers</td>
<td>25</td>
</tr>
<tr>
<td>2.6.2 Nanofibers in Filtration</td>
<td>26</td>
</tr>
<tr>
<td>2.6.3 Superhydrophobic Electrospun Nanofibers</td>
<td>27</td>
</tr>
</tbody>
</table>
2.6.4 Challenges with Nanofiber Processing ................................................................. 29
2.7 Atmospheric Plasma Finishing of Textiles ................................................................. 30
  2.7.1 Polymer, Textile Surface Needs in Application ...................................................... 30
  2.7.2 Atmospheric Plasma Surface Modification ............................................................ 30
  2.7.3 Benefits to Using Atmospheric Plasma with Textile Treatments ......................... 33
2.8 Summary, Prelude to Experimental Work ................................................................. 35

Chapter 3: Development of a Repellent Electrospun Deposition onto Woven Nylon6,6/cotton Fabric ................................................................. 36
  3.1 Background ............................................................................................................ 36
  3.2 Experimental ........................................................................................................ 36
    3.2.1 Materials ......................................................................................................... 36
      3.2.1.1 Substrate Preparation .................................................................................. 37
      3.2.1.2 Electrospinning Solution Preparation ......................................................... 38
    3.2.2 Electrospinning Procedure ............................................................................... 38
  3.3 Characterization ...................................................................................................... 39
    3.3.1 Observed Static Water Contact Angle ............................................................. 39
    3.3.2 Fiber Characterization ..................................................................................... 40
  3.4 Results and Discussion ........................................................................................... 41
    3.4.1 WCA Effects .................................................................................................. 43
      3.4.1.1 Effect of Concentration on WCA ................................................................. 46
      3.4.1.2 Effect of Voltage, Flow Rate on WCA ......................................................... 46
      3.4.1.3 Areal Density Effect on WCA .................................................................. 48
    3.4.2 Discussion on Nanofiber Characteristics and WCA ......................................... 49
      3.4.2.1 Surface Morphology ............................................................................... 49
      3.4.2.2 Fiber and Bead Diameter ....................................................................... 53
3.4.2.3 Web Porosity, Expected WCA with Cassie-Baxter Model ........................................... 56
3.5 Summary, Future Research ............................................................................................. 63

Chapter 4: Plasma Effects on Development of a Durable Repellent Electrospun Textile Surface ........................................................................................................................................... 66

4.1 Background ...................................................................................................................... 66
4.2 Experimental .................................................................................................................... 67
4.2.1 Materials ...................................................................................................................... 67
4.2.1.1 Substrate Selection ................................................................................................. 67
4.2.1.2 Electrospinning Solution ....................................................................................... 67
4.2.2 Atmospheric Pressure Plasma System ....................................................................... 68
4.3 Methods .......................................................................................................................... 68
4.3.1 Substrate Preparation ................................................................................................. 68
4.3.2 Plasma Treatment Prior to Electrospinning ............................................................... 69
4.3.3 Electrospinning Procedure ......................................................................................... 69
4.4 Characterization of Nanofiber/Substrate Interactions .................................................... 69
4.4.1 Martindale Abrasion ................................................................................................. 70
4.4.2 Interfacial Peel Testing .............................................................................................. 72
4.5 Verification of Evidence of Plasma using Substrate ......................................................... 76
4.5.1 Contact Angle of Treated Nylon 6,6 Film ................................................................. 76
4.5.2 Exhaust Dyeing of Fabrics ......................................................................................... 77
4.5.2.1 Nylon 6,6 Fabric Exhaust Dyeing Procedure ....................................................... 78
4.5.2.2 Cotton Fabric Exhaust Dyeing Procedure ............................................................ 78
4.5.3 Experimental Design ................................................................................................. 78
4.6 Results and Discussion ................................................................................................. 79
4.6.1 Effects of Interfacial Mechanical Testing .................................................................. 79
LIST OF TABLES

Table 2-1: Force balance between adhesive and cohesive forces............................................. 13

Table 3-1: Experimental settings for Nylon 6 coated nanofiber fabrics, varied in order to find factors and levels which maximize observed WCA. Observed average WCA at different experimental settings can be seen within table cells............................................................... 51

Table 3-2: SEM images of nanofiber surface coatings, shown to demonstrate transition of bead-dominated to nanofiber-dominated morphology as concentration increases................. 52

Table 3-3: Average nanofiber diameters of electrospun nanofiber surface coatings, showing nanofiber diameter increasing with polymer concentration increasing from 6-15%............. 55

Table 3-4: Nylon 6 solid area fraction (or $f_{\text{Solid}}$) used for calculation of expected WCA, compared to actual WCA observed for experimental factors and levels (shown below). Electrospinning parameters: Polymer concentration (6-15%), applied voltage (15, 17 kV), and flow rate (0.5, 1, 2 mL/hr). Difference (%) of observed-expected WCA is also shown . 57

Table 3-5: Selected morphology of electrospun nanofiber surface coatings prepared by varying experimental parameters: Polymer concentration (7, 15% shown), flow rate (0.5, 1, 2 mL/hr), and applied voltage (15, 17 kV) ............................................................................. 60

Table 4-1: Experimental parameters used for evaluation of Martindale abrasion: concentrations used were 11-15%, flow rates used were 0.5, 1, and 2 mL/hr respectively... 80

Table 4-2: Experimental settings used during Peel test: concentrations used were 11-15%, Flow rates used were 1, and 2 mL/hr respectively. Control substrates were coated and tested for load required to remove web................................................................. 81

Table 4-3: Static WCA comparison for Nylon 6,6 film treated in Helium and Helium-Oxygen atmospheric plasma................................................................. 95

Table A-1 Polymer Surface Tensions and WCA ................................................................. 118

Table A-2: Dimensions and other Constants related to Martindale Abrasion testing ....... 120

Table A-3: List of Dimensions and other constants related to Peel Testing....................... 122
LIST OF FIGURES

Figure 2-1: Lotus leaves on a pond, and water droplets atop a lotus leaf (A, B). SEM images of lotus leaves with different magnifications showing micropapillae and epicuticular wax crystals (C, D). The inset of (D) is of a water droplet on a lotus leaf, having WCA = 161.28° with sliding angle of 3°. ................................................................. 7

Figure 2-2: (A) Water droplet on roughened surface having WCA below 90° and high contact angle hysteresis. This displays greater hindrance to rolling and contaminant removal when moving during time (t = 1→3). (B) Water droplet on roughened surface having WCA > 90° with low contact angle hysteresis ................................................................. 8

Figure 2-3: Anisotropic surface features of rice leaf (A, B). Water droplets floating on rice leaf. SEM images of rice leaf at different magnification (C, D). Inset of (D) shows WCA profile on a rice leaf to be ~ 157°. ............................................................................................ 9

Figure 2-4: Examples of Petal Effect: (A, B) SEM images of rose petal surface, showing hierarchical morphology consisting of micropapillae and nanofolds. (C) Shape of water droplet on rose petal, indicating superhydrophobicity (WCA ~152°). (D) Adhesion of droplet to rose surface when rotated 180°. (E, F) SEM images of surface of Chinese Kafir lily petal showing a periodic array of closely-packed hexagons and helices in two scales. (G, H) SEM images display sunflower morphology being composed of two scales, seen with helical indentions forming a larger parallel array ............................................................................... 10

Figure 2-5: A water strider’s legs support itself when atop a body water ......................... 11

Figure 2-6: Model of static liquid droplet on a flat, ideal surface. Equilibrium, or Young’s WCA as denoted by θ in the figure, is related to force balance of interfacial tensions (γX-Y) between solid, liquid, and vapor phases ........................................................................................................................ 13

Figure 2-7: Example of stearic acid melamine derivative applied as repellent finish ........ 21

Figure 2-8: Components of silicone water repellents, which react to form a cross-linked repellent layer for textiles. Hydrogen bonds between siloxane backbone and fabric provide good durability ................................................................................................................... 22

Figure 2-9: Perfluoro-containing acrylic polymer, an example of a fluorocarbon-based repellent finish as applied to fiber surfaces .......................................................................................................................... 22

Figure 2-10: Simple electrospinning schematic: Shown are (A) high-voltage power supply connected to a syringe (B), and (C) respective streaming and whipping jet regions of polymer
solution traveling across electric potential. The polymer jet deposits fibers onto (D) a collection apparatus, which can be either grounded or oppositely-charged. .......................... 26

Figure 2-11: SEM images of as-spun PHBV electrospun beaded-nanofiber morphology at different magnifications: (A) 1 kX magnification; (B) 10 kX magnification................................. 28

Figure 2-12: SEM images of as-spun PMMA electrospun fibers with (A) and without (B) surface pore structures ............................................................................................................ 29

Figure 2-13: Schematic of atmospheric pressure glow discharge plasma system designed and developed at NCSU. .............................................................................................................. 34

Figure 3-1: Rendering of experimental setup used for electrospinning; shown are charged syringe (A) which displaces polymer solution (B) across electric potential to oppositely-charged or grounded collection apparatus (C). ................................................................. 39

Figure 3-2: OCA20 Contact Angle Analyzer for observing surface wettability.................. 40

Figure 3-3: Example images of electrospun Nylon 6 nanofiber coating surface profiles with 5 µL droplet; average WCAs included: (A) 6% concentration, 17 kV applied voltage, 2 mL/hr flow rate. (B) 7%, 17 kV, 2 mL/hr. (C) 15%, 0.5 mL/hr, 17 kV. (D) 15%, 17 kV, 1 mL/hr.................................................................................................................................... 43

Figure 3-4: Oneway ANOVA and Student’s paired t-estimates used to compare how experimental factors have effect on observed WCA: polymer concentration (6-15%) (top); flow rate (0.5, 1, 2 mL/hr) (bottom left); and applied voltage (15, 17 kV) (bottom right)..... 45

Figure 3-5: Observed WCA versus concentration (6-15%) for nanofiber surface coatings. Shown are WCA for concentrations having 15 kV applied voltage (left) and 17 kV (right). Electrospinning when having flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green) also shown, respectively ................................................................................................................. 47

Figure 3-6: Observed WCA versus areal density (g/m²) for nanofiber surface coatings, shown when electrospinning using flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green), respectively................................................................................................................ 49

Figure 3-7: Areal density (g/m²) versus polymer concentration (6-15%) for nanofiber surface coatings, electrospun when varying flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green), respectively ................................................................................................................ 50

Figure 3-8: Fiber diameter versus polymer concentration (6-15%) for nanofiber surface coatings spun using applied voltage of 15 kV (left) and 17 kV (right); electrospinning flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green) also shown, respectively................. 54
**Figure 3-9:** Solid area fraction versus concentration (6-15%) for nanofiber surface coatings when having electrospinning applied voltage of 15 kV (left) and 17 kV (right); flow rate of 0.5 (purple), 1 (orange), and 2 mL/hr (green) shown, respectively. ................................................................. 59

**Figure 3-10:** Observed WCA versus polymer concentration (top). Expected WCA was calculated from nanofiber surface porosity using image analysis (bottom). Differences between expected and observed show need for revised model to accurately predict observed WCA. ...................................................................................................................................... 63

**Figure 4-1:** Martindale abrasion testing apparatus located in NCSU COT, showing mounted samples which oscillate against standard worsted wool fabric abradant ......................... 71

**Figure 4-2:** Sample preparation of electrospun webs for Martindale abrasion testing. These samples are mounted upside-down and oscillate against a standard woolen fabric abradant, with the mounted sample having a minimum pressure of 1.7 kPa, oriented downward. .... 73

**Figure 4-3:** Example of modified Martindale abrasion failure, which was used as a qualitative classification of nanofiber web durability. This results after oscillatory rubbing motions against standard abradant Martindale; the average number of rubs until failure were recorded as metrics for analysis. Holes in the nanofiber layer are highlighted with orange circles. ..................................................................................................................................... 73

**Figure 4-4:** Peeling test sample setup in Instron using modified (ASTM D 6862-04) method. This modified test is intended to maintain 90° peel between nanofibers and fabric using the standard tongue tearing method ......................................................................................................................... 74

**Figure 4-5:** Example of peeling test output. Vertical axis (load applied to peel layer from substrate) is expressed in kgf, while horizontal axis (extension) is indicated in mm ............ 75

**Figure 4-6:** Apparatus used for WCA acquisition in NCSU College of Textiles ................. 77

**Figure 4-7:** Average Martindale rubs versus areal density for coated fabrics electrospun using 11 (cyan), 13 (magenta), and 15% polymer solution concentrations (gold) ............... 82

**Figure 4 - 8:** Average Martindale rubs versus nanofiber areal density for coated fabrics electrospun using 0.5 (purple), 1 (orange), and 2 mL/hr (green) flow rates, respectively. .... 83

**Figure 4-9:** Average peeling toughness versus nanofiber areal density for coated fabrics electrospun using 1 (orange), and 2 mL/hr (green) flow rates, respectively ..................... 84

**Figure 4-10:** Average peeling toughness versus nanofiber areal density for coated fabrics electrospun using 11 (cyan), 13 (magenta), and 15% polymer solution concentration (gold). ......................................................................................................................................... 85
**Figure 4-11:** Average Martindale number of rubs until failure versus substrate treatment type for nanofiber coated fabrics: comparing untreated (control) coated fabrics with those treated in Helium and Helium-Oxygen plasmas (applied for 2, 5 min.). Also shown are flow rates of 0.5 (left), 1 (middle), and 2 mL/hr (right), and polymer solutions of 11 (cyan), 13 (magenta), and 15% concentration (gold) varied during electrospinning................................................. 86

**Figure 4-12:** Average peeling toughness versus substrate treatment type for nanofiber coated fabrics: comparing untreated (control) coated fabrics with those treated in Helium and Helium-Oxygen plasmas (applied for 2, 5 min.). Also shown are flow rates of 1 (left), and 2 mL/hr (right), and polymer solutions of 11 (cyan), 13 (magenta), and 15% concentration (gold) varied during electrospinning....................................................................................... 90

**Figure 4-13:** Comparison of plasma intensity using exhaust dyeing on 100% Nylon 6,6 fabrics: Shown is K/S intensity spectrum at visible wavelengths comparing control to treated fabric. ...................................................................................................................................... 91

**Figure 4-14:** Comparison of K/S intensity peaks shown in Figure 4-13 for plasma-treated versus non-treated 100% Nylon 6,6 fabric. ................................................................................................................................. 92

**Figure 4-15:** Comparison of plasma intensity using exhaust dyeing on 100% cotton fabric: Shown is K/S intensity spectrum at visible wavelengths comparing control to treated fabrics. ................................................................................................................................................. 93

**Figure 4-16:** Comparison of K/S intensity peaks shown in Figure 4-15 for plasma-treated versus non-treated 100% cotton fabric. ................................................................................................................................. 93

**Figure 4-17:** Comparison of static WCA on control and plasma-treated Nylon 6,6 films. (A) Nylon 6,6 untreated film. WCA average = 66.56°. (B) Nylon 6,6 treated with Helium plasma, 5 minutes. WCA average = 40.71°. (C) Nylon 6,6 film, treated in Helium-Oxygen plasma, 5 minutes. WCA average = 42.53°. ............................................................................................................................................... 95

**Figure A-1:** WCA versus critical surface tension for various polymers................................. 119

**Figure A-2:** Additional view of Martindale testing apparatus................................................. 120

**Figure A-3:** Depiction of how nanofiber layer-fabric are peeled apart at 90° using modified peeling test ........................................................................................................................................ 121
Chapter 1: Introduction

1.1 Significance of Study

Development of chemical biological (CB) weapons has become an increasing threat to soldiers, whose personal protective equipment (PPE) includes short-term protective apparel and ocular and respiratory protection. Often are dispersed as aerosols CB agents create the need for liquid and particulate protection incorporated into military uniforms. Current CB protective clothing provides adequate protection yet offer limited breathability.\textsuperscript{1} Electrospun nanofiber webs layered within a clothing ensemble have been shown to maintain breathability while providing protection from liquid and vapor contaminants.\textsuperscript{2,3} In addition to military garments these webs can be applied to industrial and civilian clothing for protection against other Toxic Industrial Materials (TIM) and contaminants.

Electrospinning is a simple method employed to produce nonwoven mats or webs composed of micro- and nano-scale diameter fibers. Many polymers have been shown to be capable of electrospinning from solution into nanofiber webs and have extremely high surface area-volume ratios. Nanofiber webs can have high porosity with small individual pore diameters, enabling them to offer good protective barriers against liquids or aerosols. A challenge for nanofiber webs, limiting their integration into textile materials, is the ability to withstand mechanical stresses that are repeatedly incurred during such use.\textsuperscript{4-6}

The use of atmospheric pressure plasma has become a popular technique for surface modification using organic materials, including textile surfaces. Plasmas can be applied continuously or in batch processes, depending on desired finishing effects, and allow for production requirements of textile products.\textsuperscript{7} Plasma-based finishes provide similar
functionality yet can eliminate much of the aqueous application and subsequent thermal curing processes required with many traditional pad-dry-cure finishes. Surface energy and physical features can be modified without changing bulk properties to influence wetting or dyeability as well as other properties like adhesion to other surfaces.

1.2 Problem Statement

Repellency of contaminants such as water, oils and solids is important to common acceptance of commercial textile garments, and a matter of significant importance in CB protective clothing. A majority of repellent finishes rely on chemical repellency through low surface energy molecules yet are known to produce harmful environmental effects such as large quantities of wastewater and chemical effluent. In recent years, research on surface wetting has focused on maximizing hydrophobicity through control and modification of submicron-scale physical structure. This concept was first realized through observation of highly-roughened physical features found on many natural surfaces which create repellent or self-cleaning exteriors, preventing these from interaction with potential liquid and solid contaminants. If enough roughness is present, a hydrophobic solid surface can be created even if using hydrophilic materials.

A garment with a repellent exterior surface and the ability to transfer perspiration away from the body is critical for those in contact with hazardous chemicals or in high-temperature environments. Electrospinning or plasma finishing has been used to create fabrics that possess both repellent and moisture-wicking characteristics by using multilayer or composite fabrics, with coatings utilizing chemical vapor deposition, cross-linking, or grafting. Electrospinning onto fabrics can enable surface repellency without
sacrificing breathability,\textsuperscript{2,34-39} however, a challenge to nanofiber development and production is mechanical durability, resulting in shortened functional lifetime and hindering application. Chemical interactions like covalent bonding between nanofibers and substrate could be made using plasma treatment, enabling better attachment of nanofibers to fabric. Treatment of fabric in plasma before electrospinning deposition could promote interaction when electrospinning onto this surface through addition of polar groups, functionalizing or increasing surface free energy of the fabric.

1.3 Research Objectives

Development of a hydrophobic Nylon 6 nanofiber surface coating to fabric is described in Chapter 3. Here, a polymer nanofiber coating was applied by electrospinning onto military Nylon 6,6/cotton (NyCo) woven fabric. In Chapter 4, atmospheric pressure glow discharge plasmas (APGD) using 100\% Helium and 99\% Helium with 1\% Oxygen were applied to fabrics prior to electrospinning. Coated fabrics were then characterized for effect of increased adhesion or durability of the layer to fabric. The overall project outcome is summarized in Chapter 5 where efforts to combine this highly-porous yet hydrophobic fabric coating with increased interfacial adhesion are reviewed and evaluated.

APGD surface treatment followed by electrospinning of polymer nanofiber coating layers when combined in series are intended to simulate that, if scaled up to production levels, how a quick and simple finishing technique could repel liquid contaminants while maintaining fabric breathability. Plasma treatment to fabric prior to electrospinning deposition will increase adhesion between nanofibers and substrate while maintaining fabric
bulk mechanical properties and comfort. In Chapter 5, further research is also proposed with intentions to develop better, more efficient treatments to fabric in continuous process.
Chapter 2: Literature Review

2.1 Introduction, Related Topics

Research surrounding surface wetting and citing many examples of non-wetting surfaces found in the natural world are first discussed in this chapter. Traditional and current water repellent application technologies are reviewed to highlight methods and materials used. Electrospinning and plasma processing will be discussed in detail describing examples of novel or nature-inspired (biomimetic) surface science related to these concepts.

Background regarding traditional and progressive textile finishes verifies the need for continued research using these methods and materials. Many water repellent treatments to fabric surfaces historically have been inefficient and chemical-intensive processes, which produce excess effluent and create environmental concerns. Recent improvements in the application of novel textile finishes could lessen the long-term costs and environmental impact for the producer as well as the consumer.

2.2 Repellent Surfaces: Does Nature have the Answers?

2.2.1 Different Natural Superhydrophobic Surfaces

Most water repellent finishes can be applied to fabric surfaces through application of low surface energy chemicals, though many of these processes use vast amounts of water use in padding application of these chemicals. The use of improved finishing techniques which result in lower water usage and minimizes resulting chemical effluent should be explored for implementation. Many examples of plant and animal exterior surfaces provide us with illustrations of how physical composition combined with chemistry can display self-cleaning
surface attributes resulting from *superhydrophobicity*. On superhydrophobic surfaces, drops of water will have static water contact angle (WCA) of at least 150° and remain almost spherical.\(^{41,42}\) Some of these surfaces allow easy roll-off and removal of spores, dirt, or dust particles in their path.\(^{43-47}\) Different physico-chemical surface composition creates a range of superhydrophobic surfaces found on leaves. Different morphological phenomena affect wetting properties of leaves found on *Alchemilla vulgaris* (lady’s mantle),\(^{26,34}\) *Senecio cineraria* (silver ragwort),\(^{34}\) *Nelumbo mucifera* (lotus),\(^{48}\) *Oryza sativa* (rice),\(^{49}\) and *Rosea rehd* (rose).\(^{50}\)

Superhydrophobic plant surfaces exhibit two defined microroughness scales which in combination enhance roughness, lower wettability and thus prevent adsorption from foreign contaminants. Different morphological features like concave or convex protrusions with arrays of *epicuticular* wax crystals are seen in **Figure 2-1** with the lotus plant and numerous other leaves. When compiling and documenting surface roughness of many plants, Neinhuis and Barthlott in 1997 defined the *Lotus Effect*, which classifies highly-roughened surfaces characteristic of many plants that allow easy sliding and removal of liquids, solids, and other contaminants.\(^{51}\) These self-cleaning surfaces have low contact angle hysteresis, measured as the difference of advancing (\(\theta_A\)) and receding (\(\theta_R\)) WCAs. **Figure 2-2** shows how \(\theta_A\) and \(\theta_R\) relate to sliding angle or dynamic wetting properties of a surface.\(^{45-47}\)
Figure 2-1: Lotus leaves on a pond, and water droplets atop a lotus leaf (A, B). SEM images of lotus leaves with different magnifications showing micropapillae and epicuticular wax crystals (C, D). The inset of (D) is of a water droplet on a lotus leaf, having WCA = 161.28° with sliding angle of 3°.\textsuperscript{48}

Leaves of plants, i.e., rice, demonstrate an anisotropic version of the Lotus Effect. Figure 2-3 shows alignment of rice leaf surfaces, where aligned papillae atop parallel fibers create anisotropic roughness and direct fluid flow along their length.\textsuperscript{49} Figure 2-4 shows the Petal Effect of red rose petals as well as \textit{Clivia miniata} (Chinese kafir lily), and \textit{Helianthus annuus} (sunflower), recently discovered by Feng et al.\textsuperscript{50,52,53} The Petal Effect defines surfaces having similar static wetting as the Lotus Effect, but with different dynamic wetting due to strong adhesive force that develops between surface and droplet. Surprisingly, lady’s mantle leaves are superhydrophobic macroscopically resulting from very hairy, rough
surfaces. Contact angle measurements of single hairs show hydrophilic wetting properties individually (WCA < 90°). The hairy surfaces of lady’s mantle illustrate how a hydrophilic surface found in nature can have superhydrophobic properties through roughness-induced wetting.25,26

![Figure 2-2: (A) Water droplet on roughened surface having WCA below 90° and high contact angle hysteresis. This displays greater hindrance to rolling and contaminant removal when moving during time (t = 1→3). (B) Water droplet on roughened surface having WCA > 90° with low contact angle hysteresis. Low sliding angle displays self-cleaning properties characteristic of Lotus Effect. Water droplets on these surfaces slide easily during time (t = 1→3).](image)

The animal kingdom also provides many examples of superhydrophobic surfaces. The feet of a gecko display patterned, nanostructured roughness which provide superhydrophobic properties with high interfacial tension, much similar to a rose petal. One species of gecko (Coleodactylus amazonicus, or pygmy gecko) is even capable of locomotion atop water.48,54,55 Many insect surfaces are non-wetting and can prevent from drowning or
assist with locomotion. A single hind leg of *Gerris remigis* (water strider), the insect shown in Figure 2-5 can support over 15 times its own mass, while a common mosquito leg (*Culicidae* family) can support over 23 times its mass and has a static WCA over 153°.\textsuperscript{56,57}

![Figure 2-3: Anisotropic surface features of rice leaf (A, B). Water droplets floating on rice leaf. SEM images of rice leaf at different magnification (C, D). Inset of (D) shows WCA profile on a rice leaf to be \(\sim 157^\circ\).\textsuperscript{49}](image)

Magnification of many insect exoskeleton surfaces show needle-shaped hairs or *microsetae*, having fine nanometer-scale grooves patterning each seta. These grooves create a plastron layer (surrounding layer of air) if immersed and prevent interaction with contacting water.\textsuperscript{41,58}
Figure 2-4: Examples of Petal Effect: (A, B) SEM images of rose petal surface, showing hierarchical morphology consisting of micropapillae and nanofolds. (C) Shape of water droplet on rose petal, indicating superhydrophobicity (WCA ~152°). (D) Adhesion of droplet to rose surface when rotated 180°. (E, F) SEM images of surface of Chinese Kafir lily petal showing a periodic array of closely-packed hexagons and helices in two scales. Different features of micro- and nanoroughness at low and high magnification. (G, H) SEM images display sunflower morphology being composed of two scales, seen with helical indentions forming a larger parallel array.
This plastron layer exists indefinitely and eventually reaches equilibrium after immersion. Zimmerman and co-workers suggested that repellent textile surfaces with capability to create a plastron layer could lower frictional drag and provide repellency even after full immersion.\textsuperscript{59} The wings of various types of butterflies also exhibit self-cleaning, superhydrophobic properties and are actually multifunctional. Patterned nanoscale ridges on butterfly wings provide repellency from rain and solids and create a polychromatic interference pattern of light scattering and diffraction. These patterns provide the colorful appearances for which butterflies are synonymous.\textsuperscript{60,61} Many of these previously-mentioned examples show how both physical and chemical composition are factors in the ability of a natural surface to repel water.

\textbf{Figure 2-5:} A water strider’s legs support itself when atop a body water. The very rough surface features of the legs form a plastron layer, a thin layer of air that develops at the leg-water interface, minimizing interaction with the water.\textsuperscript{56}
2.3 Repellent Surfaces: What are the Governing Factors?

2.3.1 Surface Tension and Contact Angle

As mentioned, a water repellent or hydrophobic solid surface is one that can resist wetting by a mass of water (when a water droplet has static WCA greater than 90° water contact angle (θ), is associated with the surface energy or force balance related to liquid-, solid-, and vapor-phase contact lines. Figure 2-6 and Table 2-1 show relationships between surface tensions and contact angle. Thomas Young\textsuperscript{62} first defined the relationship between surface tension and contact angle while investigating capillary phenomena. Young’s equation relates wetting of an ideal or perfectly flat, homogenous solid surface to solid, liquid, and gas phase component surface energy or surface tension (expressed in dyne/cm or N/m). Dependent upon molecular species the equation presents a unique contact line resulting where all three phases meet. Interaction between cohesive and adhesive forces determines extent of wetting (how a liquid will spread over a surface) showing WCA as a function of total system energy. Later revised, the Young-Dupré equation explains surface tension through the balance of surface energy components\textsuperscript{62} as seen in Figure 2-6 and Table 2-1.

Surface energy for textile (and polymer) materials, in general, is most commonly measured using a contact angle goniometer, an instrument which displaces a small amount of liquid onto a flat viewing stage. Typically, these instruments can calculate contact angle for evaluation of both static and dynamic wetting properties, and many current contact angle goniometers incorporate computer-assisted optical and software systems for specific measurement and device calibration.
Figure 2-6: Model of static liquid droplet on a flat, ideal surface. Equilibrium, or Young’s WCA as denoted by $\theta$ in the figure, is related to force balance of interfacial tensions ($\gamma_{X-Y}$) between solid, liquid, and vapor phases.

Table 2-1: Force balance between adhesive and cohesive forces. As interactions increase between solid and liquid phases, contact angle decreases. Decreasing contact angles indicate increased surface wetting ability.

<table>
<thead>
<tr>
<th>Contact Angle, $\theta$</th>
<th>Wettability</th>
<th>Solid/Liquid Interaction</th>
<th>Liquid/Liquid Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta = 0^\circ$</td>
<td>Perfect Wetting</td>
<td>Greatest</td>
<td>Weak</td>
</tr>
<tr>
<td>$0 &lt; \theta &lt; 90^\circ$</td>
<td>High Wettability</td>
<td>Strong</td>
<td>Weak-Medium</td>
</tr>
<tr>
<td>$90 &lt; \theta &lt; 180^\circ$</td>
<td>Low Wettability</td>
<td>Weak-Medium</td>
<td>Strong</td>
</tr>
<tr>
<td>$\theta = 180^\circ$</td>
<td>Nonwetting</td>
<td>Weak</td>
<td>Greatest</td>
</tr>
</tbody>
</table>

If a surface is hydrophobic, then the WCA of a droplet will be greater than $90^\circ$, while smaller contact angles and higher surface energy are characteristic of hydrophilic materials. Water has inherently high surface energy; it is polar and forms Hydrogen bonds. The following equation provides the relationship for Young’s contact angle, or equilibrium contact angle ($\theta_{\text{Equil}}$):
\[
\cos \theta_{Equil} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]

where \(\gamma_{SL}, \gamma_{LV},\) and \(\gamma_{SV}\) are three interfacial tension components existing between solid and liquid, liquid-vapor, and solid-vapor, respectively. The revised Young-Dupré equation states that neither \(\gamma_{SV}\) nor \(\gamma_{SL}\) can individually be larger than the sum of the other two respective surface energies. Since \(\gamma_{SV} = \gamma_{SL} + \cos \theta \cdot \gamma_{LV}\),

If \(\gamma_{SV} > \gamma_{SL} + \gamma_{LV}\), complete wetting will occur \((\cos \theta = 0^\circ)\). And, if \(\gamma_{SL} > \gamma_{SV} + \gamma_{LV}\), zero wetting will occur \((\cos \theta = 180^\circ)\).

The Young equations for equilibrium or microscopic WCA assume a perfectly flat surface; in many real-life cases, imperfect surfaces exhibit surface roughness or other impurities which skew this assumption. In order to more accurately characterize the surface of a textile or other rough surface, a more complex model is necessary.\(^{63,64}\)

### 2.4 Roughened Surface Wetting

Other than the chemistry related to surface free energy and interfacial tension, physical hierarchical roughness scales create the superhydrophobic properties seen with many plant and animal species. A common feature in the world among naturally-repellent solid surfaces is having a high degree of surface roughness. Highly-roughened surfaces have a large amount of three-dimensional (or actual) area contacting a fluid droplet in proportion to the two-dimensional area that the droplet is seen to cover. Historically, these physical
characteristics found in nature have been divided into two primary wetting models for these roughened or non-ideal surfaces. The first method identified and quantified general roughness-induced wetting, proposed by Wenzel in 1936.\textsuperscript{65} In 1945, Cassie and Baxter observed that a layer of air can form between a liquid droplet atop a highly-roughened solid surface when in their experiments using many repellent textile and naturally-found surfaces. A Cassie-Baxter composite or heterogeneous wetting surface is one in which the total area contacting a liquid is composed of both solid and air (vapor) components.\textsuperscript{66} These surfaces differ from Wenzel or homogeneous wetting surfaces in which the solid area underneath a droplet is completely wetted. Recent discoveries utilizing these models have led to the development of superhydrophobic surfaces created out of inherently-hydrophilic molecules while possessing necessary physical characteristics.\textsuperscript{21,23-26,67}

Many polymeric material assemblies, i.e., a fabric, would be inaccurately modeled if using the Young equation for equilibrium or intrinsic contact angle. The Wenzel model describes a homogeneous roughened surface, where a liquid completely wets or fills the grooves of a roughened surface.\textsuperscript{63,64,68,69} Wenzel showed that the intensity of surface free energy was proportional to the respective surface area in contact with a liquid. He quantitatively defined surface roughness as \( r \), the ratio of \( \text{true area wetted} \) over \( \text{apparent area wetted} \). For a hypothetical roughened surface, \( r > 1 \). With fabrics this roughness can occur from a surface exhibiting a structural network which increases surface area in contact with the droplet. The Wenzel apparent contact angle, \( \theta_W \), results from this ratio:

\[
\cos \theta_W = r \times \cos \theta_{\text{Eql}},
\]
where $\theta_{\text{Equil}}$ is denoted as the Young’s, equilibrium, microscopic, or inherent WCA for a given molecule composing the fiber surface. Apparent surface roughness is measured using profilometry to quantify surface areas that compose $r$. The Wenzel equation proposed that as $r$ increases, apparent contact angle increases proportionally, showing that surface area contributes significantly to apparent contact angle. Within the geometric features of the roughened surface, individual menisci form between solid and liquid which have a microscopic contact angle dependent on molecular structure. If roughened patterns are small enough $\gamma_{\text{Solid-Liquid}}$ (solid-liquid surface tension) will be minimized, resulting in a high fractional area of air in contact with the liquid body preventing liquid from penetrating or completely wetting a surface. This development of air pockets defines features created by a heterogeneous wetting surface. The critical contact angle ($\theta_{\text{Critical}}$) at which air pockets develop and resist wetting or impregnation of surface features, is shown by:

$$\cos \theta_{\text{Critical}} = \frac{f_{\text{solid}} - 1}{r - f_{\text{solid}}}$$

The fraction of solid touching the liquid at the interface is denoted $f_{\text{solid}}$. The apparent WCA at or above $\theta_{\text{Critical}}$ for a given molecular $\gamma_{\text{Solid-Liquid}}$ is the transition from homogeneous to heterogeneous wetting. The contact angle of a heterogeneous surface can be modeled using the Cassie-Baxter apparent WCA, ($\theta_{\text{CB}}$):

$$\cos \theta_{\text{CB}} = f_{\text{solid}} \cdot \cos \theta_{\text{Equil}} - f_{\text{Air}}$$

or, if rearranging:
\[ \cos \theta_{CB} = f_{\text{Solid}} (\cos \theta_{\text{Equil}} + 1) - 1. \]

In this model, \( f_{\text{Air}} \) is the fraction of the total surface area of the liquid that is in contact with air, where \( f_{\text{Solid}} + f_{\text{Air}} = 1 \). The Cassie-Baxter model proves that surface heterogeneity contributes to a material’s apparent contact angle and, in maximizing, this can effectively create superhydrophobic surfaces even from such hydrophilic materials.

### 2.4.1 Recent Progress with Roughened Surfaces

Historically, all superhydrophobic surfaces were thought to have resulted from hydrophobic substrates and respective surface structures. However, recent studies show that roughness can also lead to a superhydrophobic contact angle even from a hydrophilic substrate.\(^4\) Since its introduction, this concept has been found to be similar to findings regarding Wenzel and Cassie-Baxter wetting models. The Lotus and Petal Effects model superhydrophobic surfaces which have low and high contact angle hysteresis, respectively. Their surface features create different Laplace pressure (internal-external differential air pressure) gradients and have similar static wetting but dramatically different dynamic wetting properties, resulting from different patterns of surface roughness.

Throughout most of the published literature, many researchers have applied only hydrophobic materials when creating superhydrophobic surfaces. Such studies have often described this equation only for molecules composing surfaces that exhibited a WCA > 90°. Many studies show that superhydrophobicity is not limited to surfaces with microscopic WCA > 90°. Park et al\(^{22} \) focused on modeling the slope of indentations or bumps using several non-ideal hydrophilic surfaces ranging from natural leaves to silicon wafers.
decorated in Gold nanoparticles (Gold WCA ~ 70°). Studies published by Nosonovsky,\textsuperscript{64} Patankar,\textsuperscript{23,24} and Liu\textsuperscript{49} have shown that the degree of wall steepness of a cavity or abscess directly relates to the internal-external differential or Laplace air pressure that is created to support a droplet for heterogeneous wetting. Also, contributing factors are height, spacing, and diameter of the elevated surface features fabricated. Otten and Herminghaus\textsuperscript{25,26} studied the roughness of the lady’s mantle leaf, creating a superhydrophobic surface using a roughened hydrophilic material structure. They also fabricated molds of these profiles using wax for contact angle modeling. Material surfaces composed of molecules having $\theta_{\text{Equil}} < 90^\circ$ have been found to require re-entrant structures or some extent of overhang to create a Cassie-Baxter heterogeneous wetting surface area composed of both solid and air beneath a droplet. The suggestion has been made by Ma et al\textsuperscript{28,34-36} that a nanofiber web-based nonwoven structure is ideal from which to create such a network of cavities and could be easily fabricated or transformed from a hydrophilic material into a superhydrophobic surface.

2.5 Application of Textile-Based Repellent Finishes

2.5.1 Textile Wet Finishing

Advantages with textile wet processing are that it uses relatively inexpensive equipment currently readily available to a textile processing facility. Using existing equipment is cost effective as new equipment does not have to be purchased and no additional training is required for workers.\textsuperscript{11,40} However, several important disadvantages are associated with textile wet processing. Using water or organic solvents is incorporated into many textile processes. The need for water requires upfront costs as well as funds to pay for the removal of water from fabric (drying) and expenses for wastewater, whether disposed,
treated, or recycled. Globally, as water prices continue to rise, wastewater treatment prices are rising in proportion.\textsuperscript{71} Wastewater is expensive since it often produces chemical effluent which must be removed or neutralized before being released into the environment. Textile finishing chemicals like salts, surfactants, dispersants, emulsifiers, or other chemicals commonly found in textile processing wastewater, often have high aquatic toxicity. These chemical effluents are restricted in the way in which they are released from a processing plant.\textsuperscript{72} If organic solvents are used they are expensive and can require certain types of personal protective equipment (PPE) due to the risk of health hazards to workers, and also environmental concerns related to waste disposal. Many organic solvents used in textile wet processing have restrictions pertaining to their use. Another significant disadvantage of textile wet processing is the potential and volume of waste produced. Solutions used in finishing often can contain chemical auxiliaries, like dispersing agents, to aid in the finishing applications.\textsuperscript{71} Many chemicals are wasted when remaining finishing baths are drained, whereas, many dry application methods, like plasma treatments, cause little to no chemical or water-related waste.

2.5.2 Repellent Textile Chemistry

Molecules having low surface free energy are commonly used as water repellent finishes. A water repellent finish may impart water repellency to a fabric surface by lowering the surface free energy, creating an impermeable barrier, or providing an outward-facing hydrophobic surface. A repellent finish which can orient itself on the fabric so that hydrophobic hydrocarbons are facing “upwards” will provide water repellency to the surface.
At standard room temperature and humidity, water has \textit{wetting tension} of 32 dyne/cm. To effectively repel, the wetting tension or surface free energy of a fabric finish must be below this amount.\textsuperscript{73}

Historically, water repellent textiles were produced with the use of heat, by which a molten hydrocarbon, like soft paraffin wax, was applied to the surface of a fabric. In Appendices 1 and 2, \textbf{Table A-1} and \textbf{Figure A-1} list many polymer contact angles and surface energy, showing the WCA for paraffin to be around 109°, resulting from its hydrocarbon backbone. This also enables them to bond to many textile surfaces, providing hydrophobicity yet hindering fabric breathability.\textsuperscript{33} Improved types of these finishes emulsified paraffin wax in water with stearic acid salts. Once emulsified, the waxy portion of the molecules would be hydrophobic and repel water, with fatty acid portions attracted to the fabric surface. Stearic acid-applied paraffin wax finishes had poor durability, created several toxic reaction products, and required the longest treatment time of any repellent treatment. In an attempt to overcome the disadvantages of waxes emulsified with stearic acid, melamine-based water repellents were developed. These repellents are formed by reacting stearic acid and formaldehyde with melamine. An example of these types of finishes is shown in \textbf{Figure 2-7}.

Silicone water repellents have a \textit{-Si-O-Si-O-} backbone, as shown in \textbf{Figure 2-8}. This figure shows components used to create silicone repellents such as poly(dimethylsiloxane) (PDMS). Creating PDMS finishes usually requires a silanol, a silane, and a catalyst such as tin octoate. The metal catalyst enables condensation polymerization conditions and promotes orientation of the silicone film on fiber surface. Outward-oriented methyl groups provide
water repellency, while silanol and silane components react during drying processes to form a cross-linked network, increasing the finish durability. Silicone water repellents require minimal application (< 1 % owf) and provide good garment properties such as soft texture and appearance. Disadvantages to silicone repellents include decreased fabric mechanical properties and toxicity of wastewater.

Fluorocarbon repellent finishes are formed by modifying an acrylic or urethane monomer with a perfluoro alkyl group. These perfluoro alkyl chains are extremely hydrophobic and provide excellent repellency. An example of a fluorocarbon repellent is shown in Figure 2-9. During ring polymerization, cross-linking extenders form, create a durable network of the coating attached to the fiber surface. In some cases the monomer may even react with a polymer surface. Fluorocarbon-based chemical finishes like poly(tetrafluoroethylene) (PTFE) are often used, and are impermeable to a range of chemicals. Fluorocarbons provide fiber surfaces with –CF₃ groups, giving the lowest surface
Figure 2-8: Components of silicone water repellents, which react to form a cross-linked repellent layer for textiles. Hydrogen bonds between siloxane backbone and fabric provide good durability.\textsuperscript{11}

Figure 2-9: Perfluoro-containing acrylic polymer, an example of a fluorocarbon-based repellent finish as applied to fiber surfaces.\textsuperscript{11}

energies of all common repellent finishes in use.\textsuperscript{71,75} These finishes are popular because low surface energies enable repellency to a variety of oils and soiling. Fluorocarbon repellent treatments provide very high repellency at relatively low percent add-on (usually less than
1% owf), and require low drying time for treated fabrics; however, they are expensive and cause environmental concern due to production of carcinogenic fluorocarbon derivatives. Exhaust air of the drying and curing processes with fluorocarbon finishes account for high amounts of volatile organic compounds dispersed by facilities as aerosols. Certain fluorocarbon finishes degrade to form perfluorooctanoic acid (PFOA), which is of great environmental concern due to its low degradation rate and its potential for bioaccumulation; hence, the U.S. Environmental Protection Agency (EPA) has taken measures to limit emission of PFOA aerosols.\textsuperscript{72}

Effluent created from applying most repellent finishes bioaccumulates in water and is toxic to marine life because it bonds with Oxygen molecules present in water. Many garment repellent treatments result in decreased garment breathability, i.e., sweat cannot escape from the body, creating a burden to the user.\textsuperscript{76} A number of new finishing surface modification methods have been produced over time, including plasma-based processes. Over time, improved finishing techniques like those using plasma have evolved and now help modify textile surfaces while maintaining breathability, minimizing water usage, and producing less hazardous products during processing.

The general trend in many fields of recent scientific research has been to create less waste during manufacturing. Repellent finishing for textiles is but one contributor to the environmental waste stream of the textile industry. Recent progress to create more environmentally-friendly surface finishes has led to the creation of many surfaces that utilize less harmful chemicals and processes. By introducing dry finishing processes such as plasma
or other surface modification techniques, net process energy, time, and water could potentially be reduced.

2.5.3 Non-Traditional Repellent Finishes

2.6 Polymer Finishes using Electrospinning

Two general methods have been identified to create superhydrophobic surfaces where surface modification can occur through the use of (1) low surface energy chemicals, and by (2) highly-roughened surfaces.\textsuperscript{63,77} Many examples of both of these techniques have been applied using natural and synthetic textile materials, with many involving electrospinning of various polymer fibers. The novel approaches related to electrospinning seem to provide many possible products utilizing biomimicry. Products such as polymeric membranes or other barrier materials, chemical and biological protective materials, and biomaterial implants or drug delivery devices are potentially applicable if applying biomimicry to electrospinning. Water repellency with electrospun fibers using many different polymers could be fabricated through control of solution or processing parameters. When using a polymer of known solid-liquid interfacial tension ($\gamma_{\text{Solid-Liquid}}$), nanofiber surfaces can decrease the impact molecular surface energy has on repellent characteristics from their extremely high surface area. Due to the extreme surface area/volume ratios that nanofibers possess, these surfaces can be exploited to produce a variety of different properties not otherwise possible.
2.6.1 Electrospinning of Polymer Nanofibers

Electrospinning utilizes a high electric field that can create fibers with nanometer diameters, if desired, making it an increasingly popular method capable of producing continuous fibers and imparting many different properties depending on the desired product. With a typical electrospinning setup, a polymer of high molecular weight in solution with solvent is subjected to a high voltage. The charged polymer solution is propelled in a jet out from a capillary across the electric field created by the voltage potential, resulting in significant decrease of jet diameter through whipping instability. The whipping action can decrease the diameter of the jet by over $10^3$ times from its initial diameter at the capillary tip.\textsuperscript{78,79}

Figure 2-10 shows a typical experimental electrospinning setup, which can be arranged either vertically, or horizontally. Gravitational force is negligible in comparison to electric field forces generated from the power supply. With many electrospinning setups, the positive electrode is often connected to the capillary containing polymer solution, having a collecting surface that is either grounded or of opposite-induced polarity. The applied electric field propels the polymer across the voltage potential from one electrode to the collection surface. Several types of electrospinning collection methods can exist, which result in different nanofiber and processing characteristics. The simplest collection method is a stationary, grounded collection plate. The rotating collector shown in Figure 2-10 provides a more ideal collection system to apply within a production setting, and is the collection method used during this research. Most electrospun systems deposit fiber in an asymmetrical
arrangement, creating a nonwoven web or mat. Electrospinning is considered a form of nonwoven spinning though alignment of fibers is possible with specific experimental setups.

Figure 2-10: Simple electrospinning schematic: Shown are (A) high-voltage power supply connected to a syringe (B), and (C) respective streaming and whipping jet regions of polymer solution traveling across electric potential. The polymer jet deposits fibers onto (D) a collection apparatus, which can be either grounded or oppositely-charged.

2.6.2 Nanofibers in Filtration

Nanofibers can exhibit a range of useful properties when compared to other, conventional nonwoven fabric constructions. For electrospun nanofiber mats, characteristics such as low density, large surface area, high pore volume, and small pore size make these appropriate for a wide range of filtration applications. Nanofibers have significant potential for use in ultrafine filters compared with many other nonwoven constructions since
nanofibers have substantially greater surface areas and have smaller micropores. High porosity and large surface area make nanofibers ideal for filter applications such as blocking hazardous aerosols or other submicron particles. If combined with other fabric products, nanofibers could be used as aerosol filters, facemasks, and protective clothing. Developmental industrial and military fabrics have been enhanced using nanofibers as a functional layer within a multilayered composite fabric designed to protect against Chemical-Biological (CB) and thermal hazards.\textsuperscript{1,3,27,80,81}

### 2.6.3 Superhydrophobic Electrospun Nanofibers

Electrospun fibers are seen throughout related literature to exhibit significantly useful properties in a variety of applications due to their high surface area. Likewise, surface area/volume ratio of nonwoven electrospun nanofiber webs can enable polymer surfaces to have highly-hydrophobic properties, which is not limited to electrospinning of hydrophobic surfaces using hydrophilic polymers, currently being reported in several studies. Zhu et al\textsuperscript{21} electrospun superhydrophobic surfaces having a porous, beaded nanofiber morphology with smaller pores present on individual fibers and beads, as seen in Figure 2-11. This experiment was performed using the polymer poly(hydroxyl butyrate co-valerate) (PHBV, WCA \(\sim 70^\circ\)) in solution with chloroform. WCAs as high as 158.1\(^\circ\) with a sliding angle of 7\(^\circ\) were reported.

A research group at MIT, led by Gregory Rutledge, found that electrospinning beaded nanofibers of poly(methyl methacrylate) (PMMA, \(\theta_{\text{Equil}} = 70^\circ\)), with chloroform as solvent, also created a hierarchical structure of a nonwoven mat having a highly-porous nanofiber structure with each fiber containing individual pores (average \(\sim 80\) nm) creating an apparent
average WCA ~ 147°.35 These PMMA porous nanofibers are seen in Figure 2-12. Other studies displaying overhanging or re-entrant structures can be seen which create similar contact angles using hydrophilic materials.

![SEM images of as-spun PHBV electrospun beaded-nanofiber morphology at different magnifications: (A) 1 kX magnification; (B) 10 kX magnification.](image)

When creating high surface areas, many natural materials repel water and effectively maintain self-cleaning properties, proving that surface chemical composition corresponding to $\gamma_{Solid-Liquid}$ is not the most critical factor. Natural and prepared surfaces mentioned in this review demonstrate dual-scale hierarchal structure consisting of microspheres and nanofibers which display heterogeneous wetting behavior, essential for attaining high WCA.82 Several examples of polymer nanofibers electrospun with beaded nanofiber, nonwoven features have been found to exhibit similar qualities found in self-cleaning plant and animal surfaces throughout the natural world.52,83 These micro- and nano-scale structural features can be quickly fabricated using a simple technique. Beaded nanofiber morphology can be electrospun onto fabrics to provide a repellent surface coating while mitigating subsequent
process steps. If newer water repellent techniques using biomimicry were applied, they could be utilized to repel water and maintain clean surfaces to prevent interaction with foreign matter like soil contaminants, CB aerosols, or other TIMs.\textsuperscript{1,2,55}

![Figure 2-12: SEM images of as-spun PMMA electrospun fibers with (A) and without (B) surface pore structures. Note that scale bars in larger images are 1 µm while inset images have 10 µm scale bars.\textsuperscript{35}](image)

\textbf{2.6.4 Challenges with Nanofiber Processing}

Compared to conventional fibers manufacturing techniques, the process of making nanofibers is quite expensive due to the low production rate and high capital cost of updating for improved industrial application. In addition, evaporated solvent vapors resulting from the electrospinning process require recovery or proper disposal of chemicals, posing potential environmental hazards. Mechanical properties are naturally low for nanofibrous materials due to their small dimensions, and many result in easy damage or effective failure. Many electrospun nanofibers perform well in laboratory settings but fail to provide applicability for real-world use. Because of the exceptional qualities electrospun nanofibers provide, there is
tradespace between factors related to nanofiber production capabilities, environmental impacts, and mechanical properties limiting applicability. Even though these factors all are the focus of related nanofiber literature, all are currently limiting factors which inhibit viability in usable application and implementation by industry currently.

2.7 Atmospheric Plasma Finishing of Textiles

2.7.1 Polymer, Textile Surface Needs in Application

The use of plasma has become a well-established, versatile technology for modifying polymer surfaces for which less water and production time are required than traditional pad-based finishing. Material surface characteristics can be tailored to meet specific requirements when appropriate choice of plasma composition and process conditions are incorporated. Such processes are able to be performed using dry conditions without high consumption of energy, raw materials, or pollutant creation.\textsuperscript{8,9,84} The cost of new environmental laws has motivated researchers to improve or even replace some textile finishing steps. One type of finishing process now popular with textile materials applies nonthermal plasma at atmospheric pressure to modify these surfaces without using wet chemistry.

2.7.2 Atmospheric Plasma Surface Modification

Atmospheric plasma treatments to textile substrates have recently been expanded to continuous processing, which has enabled the treatment of textiles as well as many other commodity products. Until this process was available, plasma treatments were limited to high-value products, as plasmas required vacuum conditions and batch processing subsequently. Enhancements in textile processing, i.e., desizing,\textsuperscript{16,85} dyeing,\textsuperscript{17} printing,\textsuperscript{15} and
other related surface energy increases, can result from using atmospheric plasma.\textsuperscript{86-89}

Atmospheric plasma systems require less capital than earlier plasma technologies requiring ultralow pressure conditions, which this suits the application needs of the textile industry, since these systems have become a viable option for finishing use.

Organic material surfaces are best suited for processing using weak plasmas (lower temperatures) characteristic of atmospheric pressure than those at requiring a vacuum, which create higher plasma intensities. Organic materials suffer from excessive degradation if exposed to excessive energy or vacuum plasma. Organic materials are better suited for modification using low temperature plasmas due to their amorphous and crystalline nature which requires less energy to modify. Highly-organized, rigid inorganic surfaces require a higher plasma intensity to be rendered reactive. Inorganic material surfaces, therefore, are more commonly treated using stronger plasmas operating at lower pressure, like that in a vacuum. For both vacuum and atmospheric pressure plasmas, these treatments modify the top layer of both inorganic and organic surfaces in the angstrom (Å) to nanometer (nm) range, or $10^{-10}$ - $10^{-9}$ m.

Corona discharge, dielectric barrier discharge (DBD), and atmospheric pressure glow discharge (APGD) are three types of atmospheric plasma.\textsuperscript{7,90} Corona treatments are one example of these capacitively-coupled systems. With corona discharge plasma, a low-temperature discharge is generated by high voltage in contact with an array of electrodes having either linear or asymmetric fashion. Voltage buildup on thin electrodes ionizes gas species present in the space separating the electrode and the substrate, creating corona
plasma. Gas molecules become excited and reconfigure into a variety of free radicals. These radicals bombard the surface and increase its polarity through distributing available bonding sites. When treating with the aim of gaining large increases in surface energy, defects to the substrate, such as surface degradation and accelerated treatment decay, sometimes can occur with corona discharges resulting from nonuniform discharge. Another disadvantage is that corona treatment decays rapidly with handling and age, especially when in humid environments. Deionization during processing may be needed as well, resulting from static buildup.

Dielectric barrier discharge systems employ an AC audio frequency from 1-100 kHz, with high voltage usually less than 20 kV applied across parallel metal electrodes coated in a capacitive shroud. Helium is required as a component of the working atmosphere usually, in order to prevent arcing with DBD plasma systems. Other source gases like Argon, Oxygen, Nitrogen, or fluorinated gases can be added to the working atmosphere to generate enhanced surface reactions, like etching effects or surface repellency. Monomer application, prior to the use of plasma, can promote graft and cross-linking which occur from induced polymerization, enhancing durability and fixation of surface finishes.

Atmospheric plasma glow discharge plasmas can be produced if electron density is adequate; APGD systems have the highest power density of all atmospheric plasmas. An example of an APGD system can be seen in Figure 2-13 and was used during the following experimental study. These plasmas require a radio frequency of 13.56 MHz or higher, while using a lower voltage of ~ 200 V across metal electrodes. These types of units are produced on commercial scale and provide the fastest production speeds because lower exposure times
are required. By employing these techniques, plasma equipment has been shown to produce finishes which rival properties produced using traditional pad-dry-cure finishing processes.

### 2.7.3 Benefits to Using Atmospheric Plasma with Textile Treatments

After the plasma is applied, the surface is modified with many active radical species produced on the surface. Three processes can occur when free radicals bombard the surface of polymer substrates:

1. **Etching/Ablation**: Surface cleansing caused by removal of the outer molecular layer of substrate.
2. **Cross-linking**: Induced chemical bonding and joining of long-chain molecules, creating a more interconnected, network-type structure.
3. **Activation**: Changes in molecular surface energy or functionality can be caused by the impartation of reactive molecules from the ambient atmosphere.

Polar groups, like carbonyls and hydroxyls on the surface, increase in number during plasma treatments, due to the presence of Oxygen in ambient atmosphere. Surface tension is composed of polar and dispersive components. The polar component is modified most significantly which lowers $\gamma_{\text{Solid-Liquid}}$ of textile and polymer surfaces after exposure to plasma.\(^{15}\) Surfaces of many textile materials often need to be able to be wetted to adsorb various chemicals during processing, and transmit moisture and vapor during their functional lifetimes. Examples of subsequent processes that can have enhanced effects if applied following atmospheric pressure plasma include mercerization, desizing, dyeability, and
adhesion. Molecular species used as dyes, inks, coatings, adhesives, or other specific functions are able to flow better and adhere more uniformly than prior to plasma treatment. Free radicals formed on the surface provide sites for adhesion of the desired molecule to the surface.

Figure 2-13: Schematic of atmospheric pressure glow discharge plasma system designed and developed at NCSU. The capacitively-coupled discharge consists of two parallel copper electrodes embedded within a polycarbonate insulator. Specimens are placed between the electrodes and exposed to plasma while in ambient atmosphere.

Plasma surface modification to polymer sand textiles is one of several techniques that can alter surface properties without altering bulk property needs for application. High throughput and lower process waste are two advantages that result from the application of these techniques, which compare favorably to other novel textile finishing techniques. Though more recent and less established than traditional techniques, atmospheric pressure
plasma-based finishing processes cause environmental concerns due to decreased water consumption and waste. Conventional techniques used for textile finishing require chemical padding, evaporation of water applied, and thermal curing. The employment of recent plasma processes in industry has initiated a decline in the cost of necessary capital for production facilities. Combined with cost savings from a decrease in waste production and use of resources, plasma processes may result in long-term efficiencies for producers, consumers, and the environment.

Plasma treatment is powerful, provides the ability for specific and predictable surface functionalization, and can meet demanding or specialized requirements. Plasma treatment will continue to be a primary topic of polymer surface treatment technologies and methods.

2.8 Summary, Prelude to Experimental Work

The experimental work has been carried out in two phases, to be explained in Chapters 3 and 4. Chapter 3 investigates maximizing WCA for a Nylon 6 nanofiber deposition onto a woven fabric. Following analysis and conclusions made in this chapter, Chapter 4 will focus on characterization of the durability of selected experimental factors and levels. Chapter 5 will summarize Chapters 3 and 4 and recommended future experimental focuses. Additional information related to details of Chapters 3 and 4 can be found in the attached Appendices.
Chapter 3: Development of a Repellent Electrospun Deposition onto Woven Nylon6,6/cotton Fabric

3.1 Background

Electrospun nanofibers have been found to provide extreme properties for a variety of applications by utilizing their high surface area/volume ratios. Repellent garment surfaces have long been a popular concept; such surfaces, traditionally, have resulted from using low surface energy chemical treatments, applied using wet processing techniques. Historically, these treatments have been shown to use large amounts of water, energy, chemistry, and/or time. The goal of this study was to use a quick and simple process that yielded effective water repellent coatings on a woven fabric.

The first intent of this project was to examine the effect of nanofiber properties on apparent WCA. Keeping substrate and deposited polymer constant, the goal was to maximize WCA by variation of material and process variables. Discussion starting in Section 3.4 incorporates related roughened surface wetting research in an attempt to explain possible surface phenomena creating high apparent WCA nonwoven surface coatings.

3.2 Experimental

3.2.1 Materials

Materials were chosen based on intended application, background of materials used, and simplicity of technique. Here, a commonly-used electrospun polymer and fabric are mated, and relationships of electrospinning solution and process variables with resultant WCA studied. Polymer and fabric were chosen to prove conceptual feasibility, though
similar concepts should be applied to other nanofiber fabric coatings in later research. Depending on desired application, many potential polymers and substrate combinations could be studied.

The commonly used polymer Nylon 6 has been electrospun in many studies.\textsuperscript{2,5,93-100} Known for processing ease, Nylon 6 can produce very small fiber diameters using melt extrusion and solution spinning techniques, the chemistry of which allows it to be tailored for specific purposes, resulting in a good platform material for many functional electrospun surfaces. By using Nylon 6, several solution and process parameters are varied in order to obtain different surface morphologies. The U.S. Army Combat Uniform (ACU) ripstop woven Nylon 6,6/Cotton (NyCo) fabric was used as the experimental substrate to demonstrate its use with a current, commonly-fielded military garment lacking protection from liquid and aerosol contaminants.\textsuperscript{1,3,27,80}

### 3.2.1.1 Substrate Preparation

Greige ACU NyCo fabric was acquired from North Carolina State University (NCSU) College of Textiles (COT) supply stock. The fabric consists of an intimate blend of cotton and Nylon 6,6 fiber woven into a ripstop fabric construction (56 ends/inch, 56 picks/inch). The fabric was washed prior to experiments in order to remove any warp sizing and other impurities, for which desizing and scouring were necessary. After washing, fabrics were hung to dry, and left to condition for at least 48 hours prior to experimentation. Prior to deposition of electrospun nanofibers, fabric areal density was determined to by weight to be 288.46 g/m\textsuperscript{2}, or around 8.5 oz/yd\textsuperscript{2}. 

37


3.2.1.2 Electrospinning Solution Preparation

Nylon 6 pellets and 2,2,2-Trifluoroethanol (TFE) which was used as solvent were acquired from Sigma-Aldrich and used without further modification. Solutions with concentrations made ranging from 3 to 15% (wt/vol) of Nylon 6/TFE were made, and left to stir overnight before electrospinning onto fabric.

3.2.2 Electrospinning Procedure

The substrate NyCo fabric was cut into sizes of 15 X 8 cm and adhered onto aluminum foil, which was then attached to a grounded cylindrical rotating collector, which was powered by a miniature DC gearmotor. A rotating collector allows for more uniform deposition throughout the respective sample width compared to a stationary collector electrospinning setup. Figure 3-1 depicts the actual experimental setup. Electrospinning was performed using a syringe displacement pump, a standard 10 mL syringe with a stainless steel capillary (22 gauge, 90° blunt-tip needle). Separate DC high-voltage power supplies were connected to capillary tip and collector motor, respectively. The distance from the capillary tip to the collector was kept constant at 15 cm. Electrospinning deposition time was kept constant at 20 minutes, after which samples were removed from the collector and dried at room temperature for at least 48 hours before characterization in order to allow for residual solvent to evaporate. Experimental design employed three main factors, each having at least two levels: (1) concentrations between 3 and 15%; (2) applied voltage of 15 and 17 kV; and (3) flow rate (or extrusion rate) of 1 and 2 mL/hr. Using this range of factors and levels, different nanofiber surface features were to be electrospun and evaluated for physical properties intended to maximize WCA.
Figure 3-1: Rendering of experimental setup used for electrospinning; shown are charged syringe (A) which displaces polymer solution (B) across electric potential to oppositely-charged or grounded collection apparatus (C).

### 3.3 Characterization

#### 3.3.1 Observed Static Water Contact Angle

Using static contact angle, WCA is found in this study using the American Society for Testing and Materials (ASTM) D 5946-09 sessile drop method. Using a 5 µL water droplet, contact angle was measured after being in contact with the surface for 30 seconds. Averages were created for each specimen from eight measurements using a model OCA20 Contact Angle System Goniometer (FDSC), which can be seen in Figure 3-2.
3.3.2 Fiber Characterization

Nanofiber mats were weighed to acquire areal mass density (g/m²) deposited onto the fabric surface. Observed areal density was used for comparison with theoretical areal density for each experimental parameter, which assumes 100% nanofiber deposition onto the fabric. Six 3 X 3 cm measurements were recorded in different locations chosen randomly for each experimental sample.

Samples were first coated on a S67620 miniature sputter coater (Quorom Technologies), with Gold-Palladium at a thickness of 100 Å to produce a conductive surface. Then, a Phenom Scanning Electron Microscope (SEM) (FEI), operating at 5 kV, was used to acquire images of nanofiber webs. Micrographs were then analyzed using ImageJ analysis software (NIH) to determine nanofiber and bead diameter. Fifty (50) individual
measurements were made with each sample to determine the mean nanofiber diameter and standard deviation. If beads were present, they were measured for diameter; yet, standard deviations were not taken into account since every specimen could not yield 50 measurements.

Porosity characteristics were also calculated using ImageJ. Porosity was measured by converting SEM images into grayscale, where the fibrous area was differentiated from the void area. Porosity values were determined as a percentage of the void area with respect to the total area of the mat. The layer of visible fibrous mat was considered as the total solid area in contact with a water droplet. According to Wenzel homogeneous wetting behavior, a droplet is assumed to contact the total area apparent. Porous nanofiber mats were calculated to have solid area fraction \( f_{\text{Solid}} \), and assumed as a theoretical percentage of solid surface in contact with a droplet. Solid area fraction was used in calculating expected heterogeneous or Cassie-Baxter apparent contact angle due to the porous nature of nanofiber surfaces. Calculation of solid area fraction was performed using ImageJ using three samples were acquired at each experimental specimen to find average expected \( WCA \) using Cassie-Baxter's formula. Expected WCA was used to compare against observed WCA for each specimen. Using the two wetting models these assumptions were used to help explain wetting properties of experimental Nylon 6 nanofiber webs, in order to explain the observation of apparent WCAs observed.

### 3.4 Results and Discussion

Initial trials were conducted to determine appropriate experimental parameters used during subsequent trials. Having no preceding data on wettability of the nanofiber coatings,
revisions of experimental settings were to be made as necessary. For example, insufficient polymer deposition resulted when electrospinning time of deposition was less than 20 minutes, e.g., when contacting a water droplet, surfaces immediately allowed penetration and wetting to the fabric below. Electrospinning time of 20 minutes became standard for trials that followed. As mentioned in Section 3.2.2, initial polymer solutions were made with concentrations ranging from 3 to 15% and having flow rates of 1 and 2 mL/hr, and applied voltage of 15 and 17 kV. Electrospun surfaces using a lower flow rate (1 mL/hr) and higher voltage (17 kV) provided better WCA results; therefore, a third flow rate (0.5 mL/hr) was added to experimental trials using only the higher voltage level. These experimental parameters are seen in the following data tables and figures. Importantly, electrospun coatings resulting from 3 and 5% concentration exhibited interesting morphology yet had insufficient deposition to exhibit hydrophobic properties. This led to full surface characterization that would be performed only for successful, hydrophobic coating surfaces, or for those between 6 and 15%. Figure 3-3 shows several examples of different experimental parameters which successfully created repellent nanofiber coatings, from which measurements were compiled into averages for each experimental combination. Experimental parameters which created surfaces displayed wetting behavior were noted for surface morphology, yet were not included in detailed characterization results.
Figure 3-3: Example images of electrospun Nylon 6 nanofiber coating surface profiles with 5 µL droplet; average WCAs included: (A) 6% concentration, 17 kV applied voltage, 2 mL/hr flow rate. (B) 7%, 17 kV, 2 mL/hr. (C) 15%, 0.5 mL/hr, 17 kV. (D) 15%, 17 kV, 1 mL/hr.

3.4.1 WCA Effects

Independent of flow rate and voltage factors, initially it was found that lower concentrations seemed to provide higher observed contact angles, as seen in Figure 3-4; here, analysis of variance (ANOVA) and paired Student’s t-estimates are used to compare
mean WCA for each concentration between 6-15%. In this figure, concentration can provide statistically-different mean WCAs for the nanofiber layers, determined from having a paired Student’s t-estimate of 1.9687. Also included in this figure are ANOVA and paired Student’s t-estimates for flow rate and applied voltage. These paired mean estimates also exhibited statistically different means, having respective t-estimates of 1.9686 (flow rate) and 1.99685 (applied voltage) when using 95% confidence.

The intention of the paired t-test is to compare samples that are subjected to different conditions, provided the samples in each pair are identical otherwise. In this scenario, the paired t-test has some statistical power yet cannot explain the interdependence of factors inherent to any electrospinning process. This leads to evident quantitative relationships that explain WCA related to the factors of electrospinning voltage, flow rate, and polymer concentration which are seen with positive paired t-estimates. Electrospinning is a very difficult process to model and accurately predict due to the complex interplay of factors affected on the molecular level. Therefore, no single factor here should independently be used to explain physical nanofiber mat properties such as WCA when conducting proper analysis during an electrospinning study.\textsuperscript{78,79} In this research, nanofiber surface WCA will be compared and evaluated through the coupling of both solution and process factors and levels for accurate interpretation and analysis of results.
Figure 3-4: Oneway ANOVA and Student’s paired t-estimates used to compare how experimental factors have effect on observed WCA: polymer concentration (6-15%) (top); flow rate (0.5, 1, 2 mL/hr) (bottom left); and applied voltage (15, 17 kV) (bottom right). Student’s t-estimates for comparisons of sample population means are shown to the right of each graph; these estimates depict factor levels’ differentials between each population’s mean if assuming equal variance and normal sample distribution, and are used to reduce confounding effects within large sample populations. With each figure isolating individual factors, it can be seen with each figure that Student’s paired t-estimates show difference in mean WCAs between levels for each factor. Statistical differences are expressed as positive t-estimates, and can be found in Section 3.4.1.
3.4.1.1 Effect of Concentration on WCA

A table of average WCA values for electrospun surfaces is included and can be seen in Table 3-1. Average surface coating WCAs displayed maximum values between 6 and 8% for 15 and 17 kV depending on applied voltage and flow rate. Nanofiber WCA data is plotted visually in Figure 3-5. Nanofiber surface WCAs were observed with maximum values which displayed a limiting factor, a critical concentration where WCA reached maximum level and below which WCA would decrease until surfaces displayed wetting behavior. Concentrations where the highest WCAs were exhibited were between 6 and 8% dependent on flow rate and voltage; thus, no definite conclusions were made regarding critical concentration. More research is needed to accurately predict this critical concentration when considering the factors of flow rate and voltage. Figure 3-5 shows the trend in which below a certain concentration and lower, contact angles for webs decreased until hydrophilicity resulted. Hydrophilic coating webs were evaluated at 3 and 5% concentration, from which a droplet could not be supported and which allowed penetration to the fabric below.

3.4.1.2 Effect of Voltage, Flow Rate on WCA

Coatings electrospun at 17 kV provided only slightly higher WCA than those at 15 kV, though Figure 3-4 shows voltage statistically different when kept independent of other factors. In electrospinning literature, the effect of applied voltage is well documented; yet, in the current study, minimal difference in WCA was noticed when considering concentration and flow rate for the nanofiber surfaces. In future research, a greater range of applied voltage levels should be used to determine its effect on nanofiber surface WCA.
In terms of flow rate, samples displayed slightly higher WCA with 1 mL/hr than with 2 mL/hr. To better determine the effect of flow rate, 0.5 mL/hr was electrospun using only 17 kV. Different mean WCAs were found to be statistically different when comparing using paired Student’s t-estimates in Figure 3-4. Figure 3-5 and Table 3-1 show average nanofiber WCAs observed at 0.5 mL/hr having a different trend from those electrospun using 1 and 2 mL/hr. When using flow rates of 1 and 2 mL/hr during electrospinning, increasing polymer concentration decreased surface WCA. This is observed at both 15 and 17 kV. For surfaces electrospun using 0.5 mL/hr, there was less dependence of WCA on polymer concentration—Figure 3-4 and Table 3-1 show that for surfaces electrospun between 6 and 15% there was

Figure 3-5: Observed WCA versus concentration (6-15%) for nanofiber surface coatings. Shown are WCA for concentrations having 15 kV applied voltage (left) and 17 kV (right). Electrospinning when having flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green) also shown, respectively. Constant time of deposition (20 minutes), capillary tip-collector distance (15 cm).
only a slight change in average WCA. With surfaces electrospun using 0.5 mL/hr flow rate, increasing concentration slightly increased average WCA (6% averaged 137.91 ± 4.25°, 15% averaged 139.49 ± 2.45°). For webs electrospun using different flow rate, surface WCA measurements show dependence (slight, however) on flow rates used; the same can be said for applied voltage.

When coupling the factors of flow rate, voltage and concentration, concentration and flow rate together appear to provide the greatest effect on nanofiber webs’ WCA measurements. Lower concentrations and lower flow rates, in general, led to higher nanofiber surface coating WCAs, though with the lowest extrusion rate (0.5 mL/hr), there was little dependence on concentration. More testing regarding dependence on WCA with respect to flow rate and voltage at different concentrations should be performed to confirm or revise these findings.

3.4.1.3 Areal Density Effect on WCA

The range of concentrations used, coupled with three extrusion levels (rate of volume displaced), provided different areal densities of mass deposited onto fabric, measured in g/m². Areal densities were measured for nanofiber surface coatings which had applied voltage of 17 kV only, in order to take into account three levels of flow rate (0.5, 1, 2 mL/hr). It is worth noting that no measurable effect of applied voltage was found with respect to areal density. Figure 3-6 shows areal density when compared to observed WCA of nanofiber surfaces, and Figure 3-7 shows nanofiber areal density versus concentration. Both of these figures show nanofiber surface WCA decreases as areal density increases. However, apparent in both figures is less evidence of this trend when spun using a flow rate of 0.5 mL/hr than
Figure 3-6: Observed WCA versus areal density (g/m²) for nanofiber surface coatings, shown when electrospinning using flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green), respectively. Constant applied voltage (17 kV), deposition time (20 minutes), capillary tip-collector distance (15 cm).

with 1 and 2 mL/hr. This is due to the smaller range of observed WCAs at the lowest level of flow rate, discussed in Section 3.4.1.2. When analyzing both mentioned figures together, higher WCAs were observed at lower areal densities, where both concentration and flow rate provided interactive effects on nanofiber surface WCA. The general effects of areal density on nanofiber surfaces were important and will be discussed more in Chapter 4.

3.4.2 Discussion on Nanofiber Characteristics and WCA

3.4.2.1 Surface Morphology

Depending on process parameters, fiber-dominated, beaded-nanofiber or even bead-dominated morphologies were exhibited. Scanning Electron Microscopy (SEM) images show
Figure 3-7: Areal density (g/m²) versus polymer concentration (6-15%) for nanofiber surface coatings, electrospun when varying flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green), respectively. Constant deposition time (20 min), and applied voltage (17 kV).

beaded nanofiber morphology most evident at lower concentrations and higher flow rates. Appendix 5 contains SEM micrographs for each experimental specimen at multiple magnifications (1, 5, 10 kX magnification). Table 3-2 shows nanofiber morphology to transition from a bead-dominated to a beaded nanofiber structure for surfaces electrospun using 6% concentration. Transition from this to a nanofiber-dominated structure occurs around 11-13% concentration. Table 3-2 only shows morphology of nanofibers electrospun using 15 kV applied voltage and 1 mL/hr extrusion rate; similar trends are seen with additional SEM micrographs in Appendix 5, which shows all experimental parameters used.
Table 3-1: Experimental settings for Nylon 6 coated nanofiber fabrics, varied in order to find factors and levels which maximize observed WCA. Observed average WCA at different experimental settings can be seen within table cells. WCA was measured after varying the following electrospinning parameters: Polymer concentration (6-15%), flow rate (0.5, 1, 2 mL/hr) and applied voltage (15, 17 kV).

<table>
<thead>
<tr>
<th>Concentration, % wt/vol</th>
<th>Applied Voltage, kV</th>
<th>Flow Rate, mL/hr</th>
<th>1</th>
<th>2</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>6</td>
<td>134.59 ± 3.62</td>
<td>130.91 ± 3.38</td>
<td>137.91 ± 4.25</td>
<td>140.85 ± 2.15</td>
<td>137.17 ± 3.36</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>138.05 ± 2.69</td>
<td>132.49 ± 2.54</td>
<td>138.71 ± 3.38</td>
<td>138.45 ± 1.88</td>
<td>139.60 ± 2.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>138.89 ± 2.85</td>
<td>134.73 ± 3.69</td>
<td>139.19 ± 3.88</td>
<td>138.32 ± 3.54</td>
<td>137.04 ± 3.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>136.01 ± 4.35</td>
<td>133.40 ± 3.02</td>
<td>139.39 ± 3.21</td>
<td>138.23 ± 3.31</td>
<td>133.24 ± 4.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>134.84 ± 2.99</td>
<td>130.38 ± 1.85</td>
<td>138.53 ± 3.18</td>
<td>136.88 ± 3.09</td>
<td>134.26 ± 3.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>136.00 ± 2.62</td>
<td>131.69 ± 3.58</td>
<td>138.44 ± 2.76</td>
<td>136.81 ± 3.42</td>
<td>132.25 ± 6.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>131.34 ± 3.85</td>
<td>129.62 ± 1.49</td>
<td>139.49 ± 2.45</td>
<td>133.23 ± 4.04</td>
<td>128.89 ± 1.68</td>
<td></td>
</tr>
</tbody>
</table>
Table 3-2: SEM images of nanofiber surface coatings, shown to demonstrate transition of bead-dominated to nanofiber-dominated morphology as concentration increases. Parameters shown: 15 kV, 1 mL/hr, 3-15% concentration (5 kX Magnification).

| Morphology Transition with Increasing Concentration; Shown for 15kV, 1mL |
|---------------------------------|-----------------|-----------------|
| 3%                              | 15              | 11              |
| 5                               | 13              | 15              |
| 6                               | 15              | 15              |
| 7                               | 15              | 15              |
| 8                               | 15              | 15              |
At lower concentrations, bead presence was more prominent. The presence of beads is attributed to dilute polymer solutions having insufficient molecular entanglement to overcome surface tensional forces when exposed to an applied electric potential. The majority of surface charge lies on the surface of the electrospinning jet as it leaves the capillary. A lack of molecular entanglements and lower surface charge density lead to unstable electrospinning jets which are not able to form continuous fibers and result in a beaded-nanofiber structure after depositing onto the collector. In terms of mechanical properties, beads are known as defects and undesirable; in terms of apparent WCA, however, bead presence seems to increase this metric to some extent. In related literature, beaded nanofiber morphology has been found to increase surface roughness, resembling highly-roughened structures found in the natural world.\textsuperscript{34,52,102} Quantitative characterization of nanofiber mat properties is included in following sections to better understand related repellency theories.

3.4.2.2 Fiber and Bead Diameters

Fiber diameter was observed to increase primarily as concentration increased, producing a noticeable relationship within each flow rate and applied voltage used. Table 3-3 and Figure 3-8 display diameters calculated from SEM micrographs. The smallest average nanofiber diameters were found when electrospinning using 7% concentration, 17 kV, and 1 mL/hr. These nanofibers averaged 68.78 ± 19.20 nm. Nanofiber diameters were found to be the smallest when using lower concentration and flow rate. These smaller diameter samples also provided structures containing microbeads. Microbead averages were not have a consistent size, or exhibit any trend in terms of size. Also, only surfaces electrospun using
Figure 3-8: Fiber diameter versus polymer concentration (6-15%) for nanofiber surface coatings spun using applied voltage of 15 kV (left) and 17 kV (right); electrospinning flow rates of 0.5 (purple), 1 (orange), and 2 mL/hr (green) also shown, respectively.

Polymer concentration under 11% displayed enough beads to count for appropriate statistics. Microbead diameters averaged around 1.5 µm, seen in Table 3-3. Applied voltage and flow rate affected diameter less than concentration. Slightly larger fiber diameters were observed for similar samples at 15 kV than at 17 kV, other factors being equal. Increasing flow rate did not show evidence of increasing diameter when including all three experimental levels.
Table 3-3: Average nanofiber diameters of electrospun nanofiber surface coatings, showing nanofiber diameter increasing with polymer concentration increasing from 6-15 %. There was less evidence of nanofiber diameter increasing as electrospinning flow rate (0.5, 1, 2 mL/hr) or applied voltage (15, 17 kV) increased. If present, average bead diameters are included in the table. As concentration increased, bead presence decreased; beads were not evident enough to be counted for nanofiber coatings electrospun above 11% concentration.

<table>
<thead>
<tr>
<th>Voltage, kV</th>
<th>Flow, mL/hr</th>
<th>Diameter, nm</th>
<th>Concentration, % wt/vol</th>
<th>NFs</th>
<th>Beads</th>
<th>NFs</th>
<th>Beads</th>
<th>NFs</th>
<th>Beads</th>
<th>NFs</th>
<th>Beads</th>
<th>NFs</th>
<th>Beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1</td>
<td>153.18</td>
<td>1365.21</td>
<td>98.80</td>
<td>1433.23</td>
<td>109.71</td>
<td>1334.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>138.27</td>
<td>1495.57</td>
<td>126.97</td>
<td>585.98</td>
<td>86.90</td>
<td>1759.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>59.12</td>
<td>759.09</td>
<td>86.90</td>
<td>1759.09</td>
<td>144.00</td>
<td>1249.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
More difference was observed with increasing flow rate from 1 to 2 mL/hr; yet, fiber diameters spun when using 0.5 mL/hr provided conflict with this trend. A greater range of applied voltage and flow rates should be evaluated during future research work in order to illustrate a greater effect on fiber diameter.

3.4.2.3 Web Porosity, Expected WCA with Cassie-Baxter Model

Figure 3-9 shows solid area fraction versus concentration of nanofiber coatings. This figure shows nanofiber mat porosity decreasing with concentration increasing. Fractional solid area or $f_{\text{Solid}}$ shows almost no effect when increasing applied voltage from 15 to 17 kV. Table 3-4 shows calculated porosity and expected WCA at every experimental parameter, and also compares this to observed WCA. Concentration was found to have the most dependence on resulting mat porosity. Increasing flow rate from 0.5 to 2 mL/hr shows little effect on $f_{\text{Solid}}$ as well. Slight trends with extrusion rate and voltage are seen yet are statistically insignificant. Table 3-5 shows SEM images and porosity values for specimen electrospun 7 and 15% with each flow rate and applied voltage. From this table of SEM micrographs and corresponding values, nanofiber web porosity is seen most dependent on concentration. Less porosity dependence is seen with flow rate and increasing applied voltage. Further evaluation should be performed with greater ranges of such factors to better characterize porosity effects for more accurate expected WCAs to be determined.

The microscopic contact angle or $\theta_{\text{Equil}}$ of a 100% Nylon 6 surface that is in contact with a droplet is 62.6°; even so, macroscopic apparent contact angle can vary greatly depending on the actual surface features present. Modeling of surface roughness parameters
Table 3-4: Nylon 6 solid area fraction (or $f_{\text{Solid}}$) used for calculation of expected WCA, compared to actual WCA observed for experimental factors and levels (shown below). Electrospinning parameters: Polymer concentration (6-15%), applied voltage (15, 17 kV), and flow rate (0.5, 1, 2 mL/hr). Difference (%) of observed-expected WCA is also shown. For each flow rate and applied voltage used, as polymer concentration increased, $f_{\text{Solid}}$ increased; this porosity dependence used to calculate expected WCA was compared to observed WCA, and shown using percent difference.

<table>
<thead>
<tr>
<th>Applied Voltage, kV</th>
<th>Flow Rate, mL/hr</th>
<th>Concentration, % wt/vol</th>
<th>Solid Area Fraction, %</th>
<th>Expected WCA, Degrees</th>
<th>Observed WCA, Degrees</th>
<th>WCA Difference, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>±</td>
<td>37.23</td>
<td>117.24</td>
<td>134.59 ± 3.62</td>
<td>14.80</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>±</td>
<td>41.58</td>
<td>113.28</td>
<td>138.05 ± 2.69</td>
<td>21.87</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>±</td>
<td>42.84</td>
<td>112.09</td>
<td>138.89 ± 2.85</td>
<td>23.91</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>±</td>
<td>42.90</td>
<td>112.03</td>
<td>136.01 ± 4.35</td>
<td>21.41</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>±</td>
<td>48.30</td>
<td>107.24</td>
<td>134.84 ± 2.99</td>
<td>25.74</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>±</td>
<td>46.13</td>
<td>109.14</td>
<td>136.00 ± 2.62</td>
<td>24.61</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>±</td>
<td>48.78</td>
<td>106.82</td>
<td>131.34 ± 3.85</td>
<td>22.96</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>±</td>
<td>40.94</td>
<td>113.83</td>
<td>130.91 ± 3.38</td>
<td>15.01</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>±</td>
<td>42.55</td>
<td>112.35</td>
<td>132.49 ± 2.54</td>
<td>17.93</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>±</td>
<td>43.95</td>
<td>111.10</td>
<td>134.73 ± 3.69</td>
<td>21.27</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>±</td>
<td>43.18</td>
<td>111.78</td>
<td>133.40 ± 3.02</td>
<td>19.35</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>±</td>
<td>46.28</td>
<td>109.02</td>
<td>130.38 ± 1.85</td>
<td>19.60</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>±</td>
<td>46.80</td>
<td>108.55</td>
<td>131.69 ± 3.58</td>
<td>21.32</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>±</td>
<td>48.85</td>
<td>106.75</td>
<td>129.62 ± 1.49</td>
<td>21.42</td>
<td></td>
</tr>
</tbody>
</table>
Table 3-4 Continued:

<table>
<thead>
<tr>
<th>Applied Voltage, kV</th>
<th>Flow Rate, mL/hr</th>
<th>Concentration, % wt/vol</th>
<th>Solid Area Fraction, %</th>
<th>Expected WCA, Degrees</th>
<th>Observed WCA, Degrees</th>
<th>WCA Difference %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>±</td>
<td>40.55</td>
<td>114.17</td>
<td>137.91</td>
<td>20.79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>44.00</td>
<td>111.04</td>
<td>138.71</td>
<td>24.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>44.23</td>
<td>110.83</td>
<td>139.19</td>
<td>25.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>45.23</td>
<td>109.94</td>
<td>139.39</td>
<td>26.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>46.15</td>
<td>109.13</td>
<td>138.53</td>
<td>26.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>46.12</td>
<td>109.15</td>
<td>138.44</td>
<td>26.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>47.93</td>
<td>107.56</td>
<td>139.49</td>
<td>29.68</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>±</td>
<td>39.48</td>
<td>115.15</td>
<td>140.85</td>
<td>22.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>41.38</td>
<td>113.40</td>
<td>138.45</td>
<td>22.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>46.42</td>
<td>108.89</td>
<td>138.32</td>
<td>27.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>46.77</td>
<td>108.58</td>
<td>138.23</td>
<td>27.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>47.08</td>
<td>108.31</td>
<td>136.88</td>
<td>26.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>47.56</td>
<td>107.90</td>
<td>136.81</td>
<td>26.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>47.75</td>
<td>107.72</td>
<td>133.23</td>
<td>23.69</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>±</td>
<td>41.25</td>
<td>113.51</td>
<td>137.17</td>
<td>20.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>44.92</td>
<td>110.21</td>
<td>139.60</td>
<td>26.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>46.28</td>
<td>109.01</td>
<td>137.04</td>
<td>25.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>46.50</td>
<td>108.81</td>
<td>133.24</td>
<td>22.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>48.06</td>
<td>107.44</td>
<td>134.26</td>
<td>24.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>49.30</td>
<td>106.36</td>
<td>132.25</td>
<td>24.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>48.73</td>
<td>106.86</td>
<td>128.89</td>
<td>20.61</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-9: Solid area fraction versus concentration (6-15%) for nanofiber surface coatings when having electrospinning applied voltage of 15 kV (left) and 17 kV (right); flow rate of 0.5 (purple), 1 (orange), and 2 mL/hr (green) shown, respectively.

is necessary to fully understand the wetting behavior of highly roughened surfaces, particularly those with $\theta_{\text{Equil}} < 90^\circ$. Using the $f_{\text{Solid}}$ calculated to be in contact with a droplet, expected WCAs were calculated for each specimen using the Cassie-Baxter model of a heterogeneous wetting surface. In this equation, solid surface fraction and void area fraction were assumed as $f_{\text{Solid}}$ and $f_{\text{Air}}$, respectively, for calculating a Nylon 6 surface with such features. Expected apparent WCAs were compared with observed apparent WCAs. Literature suggests that hydrophilic surfaces display non-wetting properties if enough roughness exists that air is trapped when in contact with a fluid. Recall from Chapter 2 that Wenzel's law $^{65}$

59
Table 3-5: Selected morphology of electrospun nanofiber surface coatings prepared by varying experimental parameters: Polymer concentration (7, 15% shown), flow rate (0.5, 1, 2 mL/hr), and applied voltage (15, 17 kV). SEM images show morphology change from increasing concentration, resulting in increased nanofiber diameter and decreased porosity (indicated by increased solid area fraction or $f_{\text{solid}}$).

<table>
<thead>
<tr>
<th>Voltage, kV</th>
<th>Rate, mL/hr</th>
<th>7% wt/vol</th>
<th>15% wt/vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1</td>
<td><img src="image1.png" alt="SEM image" /></td>
<td><img src="image2.png" alt="SEM image" /></td>
</tr>
<tr>
<td></td>
<td>Solid %</td>
<td>41.6%</td>
<td>48.8%</td>
</tr>
<tr>
<td></td>
<td>Dia., nm</td>
<td>89.76 ± 21.14</td>
<td>219.45 ± 78.01</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="SEM image" /></td>
<td><img src="image4.png" alt="SEM image" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solid %</td>
<td>42.6%</td>
<td>48.9%</td>
</tr>
<tr>
<td></td>
<td>Dia., nm</td>
<td>133.17 ± 36.49</td>
<td>257.63 ± 102.37</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td><img src="image5.png" alt="SEM image" /></td>
<td><img src="image6.png" alt="SEM image" /></td>
</tr>
<tr>
<td></td>
<td>Solid %</td>
<td>44.0%</td>
<td>47.9%</td>
</tr>
<tr>
<td></td>
<td>Dia., nm</td>
<td>98.11 ± 37.82</td>
<td>226.24 ± 113.05</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td><img src="image7.png" alt="SEM image" /></td>
<td><img src="image8.png" alt="SEM image" /></td>
</tr>
<tr>
<td></td>
<td>Solid %</td>
<td>41.4%</td>
<td>47.8%</td>
</tr>
<tr>
<td></td>
<td>Dia., nm</td>
<td>68.78 ± 19.20</td>
<td>221.41 ± 109.93</td>
</tr>
<tr>
<td>2</td>
<td><img src="image9.png" alt="SEM image" /></td>
<td><img src="image10.png" alt="SEM image" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solid %</td>
<td>44.9%</td>
<td>48.7%</td>
</tr>
<tr>
<td></td>
<td>Dia., nm</td>
<td>137.73 ± 59.61</td>
<td>236.03 ± 115.75</td>
</tr>
</tbody>
</table>
states that molecular $\theta_{\text{Equil}}$ for an ideal surface is amplified when roughened: $\cos \theta_W = r \times \cos \theta_{\text{Equil}}$. According to Wenzel’s law of homogenous wetting, a surface composed of a molecule like polypropylene ($\theta_{\text{Equil}} \sim 102^\circ$) should become more hydrophobic if roughened; likewise, a surface like Nylon 6 ($\theta_{\text{Equil}} = 62.6^\circ$) should become more hydrophilic. Note that $r$ is the roughness factor and is measured using profilometry.

Cassie and Baxter$^{66}$ proved apparent WCA of highly-roughened surfaces could result from air beneath a droplet: $\cos \theta_{\text{CB}} = f_{\text{Solid}} \cos \theta_{\text{Equil}} - (1 - f_{\text{Solid}}) \cos \theta_{\text{Air}}$; or, when simplified, $\cos \theta_{\text{CB}} = f_{\text{Solid}} (\cos \theta_{\text{Equil}} + 1) - 1$. In order to determine whether a surface exists in the Wenzel or Cassie-Baxter state, there is an inequality that must be satisfied in which a critical contact angle ($\theta_{\text{Critical}}$) is found. This inequality appears as follows:

$$\cos \theta_{\text{Critical}} > \frac{f_{\text{Solid}} - 1}{r - f_{\text{Solid}}}$$

In this research, $\theta_W$ and $\theta_{\text{Critical}}$ for a Nylon 6 surface composed of nanofibers were not found, as $r$ was not found using profilometry. Assumptions were made in order to help explain large WCAs experienced using Nylon 6 as coating material. Porosimetry was not used to calculate web porosity; however, when examining these surfaces using SEM images, it was apparent that these surfaces were indeed very porous, characteristic of many nonwoven and more specifically, nanofiber webs. Perhaps, porosity helped increase apparent or observed WCA. Porosity was calculated using image analysis and with the assumption that the entire portion of solid was wet by the liquid droplet. Under this assumption, complete
wetting for a solid surface with $\theta_{\text{Equl}} < 90^\circ$ present was satisfied while, at the same time, observed web porosity was taken into consideration.

Observed apparent contact angles were compared to these calculated or expected WCAs, using corresponding interstitial porosities. For example, if a sample was found to be 50% solid, then 50% was $f_{\text{Solid}}$ used in the Cassie-Baxter formula; this provided an expected WCA for the nanofiber surfaces. Calculation of solid and air fractions were performed using ImageJ using three samples which were acquired from each experimental specimen to find the average expected WCA angle using Cassie-Baxter's formula.

**Figure 3-10** and **Table 3-4** show expected (or predicted) apparent WCAs compared to observed (or recorded) apparent WCAs. These show significant differences between predicted apparent WCAs found using the simple Cassie-Baxter model, and observed apparent WCAs recorded during trials. More air was present at a solid/liquid interface than predicted using the simple image analysis technique and Cassie-Baxter equation—these $f_{\text{Solid}}$ values substituted into the equation predicted lower a WCA for each analyzed micrograph. These results show that the surface physical phenomena present contribute greatly to the observed WCAs recorded, suggesting further research to be conducted on this topic. With future work, a revised image analysis technique should be found which takes into account a more accurate solid surface fraction contacting the water droplet. Further research must also be conducted in order to validate or revise the traditional Cassie-Baxter equation when using complex nanofiber surfaces. Expanding upon this research will result in more accurate modeling of the interplay between surface area, porosity, and repellency for electrospun nanofiber surfaces, including those fabricated from hydrophilic materials such as Nylon 6.
Figure 3-10: Observed WCA versus polymer concentration (top). Expected WCA was calculated from nanofiber surface porosity using image analysis (bottom). Differences between expected and observed show need for revised model to accurately predict observed WCA. If substituting calculated porosity into the Cassie-Baxter equation for a roughened Nylon 6 surface it can be seen that this porosity has less effect on WCA than the Cassie-Baxter model predicts. The need for a revised porosity/surface roughness measurement should be conducted in future research, in order to better predict observed WCA when creating a repellent surface using inherently-hydrophilic molecules such as Nylon 6.

3.5 Summary, Future Research

It can be seen that nanofiber surface features certainly relate to a surface’s static WCA. There are several factors to take into account when attempting to create a repellent
surface, especially when spinning with a material with reasonable surface free energy like Nylon 6. For a given voltage and flow rate, as concentration increased, nanofiber diameter increased. As concentration increased, porosity and WCA decreased. As flow rate increased, nanofiber diameter slightly increased, causing decreasing porosity; however, less effect on nanofiber surface WCA is seen with increasing flow rate than is seen with increasing concentration. Nanofiber diameter did not change considerably in relation to electrospinning voltage, and similar results were evident when comparing voltage levels with WCA. More variation in voltage or flow rate could have an effect on nanofiber surface WCA, as these results were found to be inconclusive.

Nylon 6 has surface tension of 43.9 dynes/cm; an ideal surface wets when exposed to a droplet, making a \( \theta_{\text{Equil}} \) of 62.6°. This chapter explains that nanofiber coating surfaces made of Nylon 6 can display static WCAs over 140.85 ± 2.15° with sufficient surface porosity. Nanofiber metrics such as fiber diameter, bead presence/diameter, and porosity characteristics were measured using ImageJ to help explain apparent WCAs observed. SEM images were used in order to simply model using assumptions from both Wenzel and Cassie-Baxter wetting. Using porosity, assumptions on expected Cassie-Baxter WCA were made and conducted without calculating surface roughness factor \( r \) (used in the Wenzel and Cassie Baxter equations). Along with actual surface roughness (\( r \)), porosity could be a focus of future research to better predict apparent static contact angles, which could be found using porosimetry, profilometry, or more in-depth image analysis techniques. These are recommended to better characterize the wettability of hydrophobic nanofiber surface coatings that have inherently hydrophilic wetting properties. Accurate surface roughness and porosity

64
data could better estimate which wetting model explains observed wetting behavior of such surfaces.

In future research, it would also be beneficial to perform more repellency characterization methods, such as American Association of Textile Chemists and Colorists (AATCC) Test Methods 22 (spray test), 118 (hydrocarbon repellency), 193 (water/alcohol solution resistance), and 61 (resistance to laundering). Contact angle measurements should be conducted after laundering in order to compare to initial WCA results. Though trends related to WCA were realized within this study, this analysis should be developed for other electrospinnable polymers and fabric combinations for future research. These nanofiber coatings to fabric should be further analyzed in order to help better describe repellency of roughened or porous hydrophilic coating surfaces. Such findings could aid with many fields not limited to material protection in civilian and military applications, as well as biomedical devices, and athletic apparel.
Chapter 4: Plasma Effects on Development of a Durable Repellent

Electrospun Textile Surface

4.1 Background

The previous chapter explored wetting properties of an electrospun Nylon 6 coating atop woven NyCo fabric. Chapter 4 evaluates adhesion of these surfaces to one another. A single fabric and polymer were used in Chapter 3 with similar experimental parameters. Factors that promoted interfacial adhesion were presented. Along with the best electrospinning settings, multiple plasma factors were included in experiments with the intent to maximize interfacial adhesion. Increased surface energy of the substrate resulting in more durable nanofiber depositions was seen using modifications of existing mechanical testing methods performed on textile and coated materials.

For these substrate and deposited materials in combination, there is a lack of data and methods used for characterization of interfacial adhesion. The goal of the study was to apply metrics to help characterize nanofiber adhesion for Nylon 6 nanofiber layers deposited onto the NyCo fabric. From related literature and in the present analysis, increases in related properties related to plasma were observed when pretreating fabric in plasma and also with an increase in plasma treatment time. These findings were characterized using modifications of standard testing methods for Martindale textile abrasion (ASTM D 4966-08) and 90° peel testing for coated materials (ASTM D 6862-04). Confirmation that plasma increased the surface free energy of NyCo fabric was affirmed using treatment to other substrates as well, seen with exhaust dyeing intensity of 100% cotton and 100% Nylon 6,6 fabrics, and with
static WCA measurement of a thin film of Nylon 6,6 treated with plasmas. The goals in this chapter were to investigate interfacial relationships using: (1) pretreatment time to substrate (prior to electrospinning); (2) gas species generating the plasmas; and (3) electrospinning factors.

4.2 Experimental

4.2.1 Materials

4.2.1.1 Substrate Selection

The NyCo blended ripstop woven fabric for the US Military ACU was used as mentioned in the previous chapter for treatment in atmospheric pressure plasma, followed by deposition of electrospun nanofibers. Included for the purpose of this analysis were two fabrics used to help show substrate effects prior to treatment. 100% cotton and Nylon 6,6 plainweave fabrics were each supplied by the Pilot Plant within the NCSU College of Textiles. A thin film (0.025 mm) of Nylon 6,6 (Goodfellow USA) was also used. These additional cotton and Nylon 6,6 film and fabrics were used to verify increased surface energy changes resulting from treatment in plasma.

4.2.1.2 Electrospinning Solution

Nylon 6 and TFE were the polymer and solvent combination chosen, with detailed description of solution materials and preparation found in Chapter 3. Identical solution concentrations were made during this chapter of research and developed from findings mentioned in Chapter 3.
4.2.2 Atmospheric Pressure Plasma System

The plasma treatments for fabrics and films were generated using an atmospheric plasma audio frequency glow discharge (APGD) system designed and developed at NCSU, a figure of which is shown in Figure 2-13. This capacitively-coupled system was composed of two parallel copper electrodes separated by a 5 cm gap, each embedded within a Lexan polycarbonate insulator. Operational frequency was 1.373 kHz, while source gas flow of 20 L/min was used for Helium and 0.3 L/min for Oxygen. Plasmas were generated using 100% Helium and with combination of 99% Helium-1% Oxygen species. Fabric samples were placed on polymer grid suspended in the middle of the test cell to enable complete and uniform plasma exposure from all sides.

4.3 Methods

4.3.1 Substrate Preparation

Greige woven NyCo fabric samples were desized and washed to remove warp size and residual contaminants. Details regarding this procedure can be found described earlier in Chapter 3. For unfinished 100% cotton and 100% Nylon 6,6 plainweave fabrics, similar procedures were conducted to remove finishes and contaminants. A Nylon 6,6 ultrasmooth film was used to show surface changes with this material resulting from plasma. The Nylon 6,6 films were thoroughly cleaned for contaminants in acetate, then washed and dried in a vacuum oven before plasma treatment.
4.3.2 Plasma Treatment Prior to Electrospinning

Control nanofiber/untreated fabric specimens were used for comparison with samples treated, using Helium and Helium-Oxygen (99% Helium, 1 % Oxygen) APGD plasma prior to electrospinning. Plasmas of both Helium and Helium-Oxygen were applied for 2- and 5-minute periods to see if increased treatment time displayed an increased effect on substrates. Plasma treatment was performed immediately before electrospinning to prevent decay of surface activation from loss of polar groups created during plasma cascade.

4.3.3 Electrospinning Procedure

The electrospinning procedure was similar to that mentioned in Chapter 3, except for time of deposition. For this chapter of the analysis, 40-minute deposition times were evaluated in order to gain sufficient nanofiber deposition for quantitative measurements. Nanofiber webs electrospun for 20 and 30 minutes were fabricated yet were not used in the analysis because they did not exhibit sufficient nanofiber/fabric interfacial properties for necessary characterization techniques.

4.4 Characterization of Nanofiber/Substrate Interactions

Properties, such as mat durability, nanofiber-fabric adhesion, and abrasion resistance, are important for practical application of nanofiber surface coatings onto fabric. Appropriate testing methods for characterizing these properties of nanofiber mats were established in this analysis. Modifications of techniques commonly performed in traditional fabric constructions were adapted for this analysis. Modifications from existing test methods had to be created using these surfaces because mechanical properties of nanofiber coatings are different from
those of regular nonwoven or traditional fabrics. Many current fabric characterization methods and standards exist for conventional fabrics and exceed requirements for characterizing fibers under 1 µm diameter for durability. Properties related to adhesion of the nanofiber web to fabric must be characterized mechanically to better portray effects of plasma in this system. Thus, in this chapter, two modifications on current mechanical characterization techniques for fabrics were performed after electrospinning, to help quantify nanofiber/substrate interfacial adhesion directly. These two modified techniques derived from the standard Martindale textile abrasion, and 90° interfacial peeling strength tests coated materials and fabrics.

4.4.1 Martindale Abrasion

Modification of the ASTM D 4966-10 standard test method for abrasion resistance of textile fabrics (Martindale abrasion tester method) was created for and performed on nanofiber-deposited fabrics. Testing was performed in the NCSU COT Physical Testing Laboratory using a standard Martindale tester (James H. Heal & Co.) for oscillatory abrasion of textiles. An image of the testing setup can be seen in Figure 4-1. Electrospun samples were cut using a 38-mm diameter dye in order to create necessary sample size for Martindale abrasion. Samples were mounted onto stubs that oscillated, rubbing a standard worsted woolen fabric while applying constant pressure of 1.7 kPa—corresponding to a load of approximately 0.2 kg on the nanofiber/fabric samples. A standard polyurethane foam layer was inserted between the nanofiber/fabric samples and the mounting piece. An image of how samples appear within the sample holder can be seen in Figure 4-2. Additional details about Martindale preparation can be found in Table A-2 within Appendix 3. Samples were
monitored during testing for abrasion by visual inspection, confirming when significant damage occurred to the nanofiber web. The number of rubbing oscillations until failure was recorded six times for each experimental parameter. A failure was classified as when solid or fluid matter below 1 mm in particle size could easily penetrate through nanofiber webs to the fabric below. This metric corresponds to that of the ASTM standard, which gauges failure of fabric specimen using visual inspection. An example of a failed nanofiber web specimen can be seen in Figure 4-3. The standard method utilizes visual inspection using normal, conventional fabrics. It evaluates for pilling and abrasion resistance indicated by fabric tearing, which both are different from the failure modes defined for the adapted test method using nanofibers attached to fabric. The number of

Figure 4-1: Martindale abrasion testing apparatus located in NCSU COT, showing mounted samples which oscillate against standard worsted wool fabric abradant.
rubbing motions before surfaces abraded to a level of failure were intended to develop trends that could be seen through changes in plasma species and treatment time and also for electrospinning factors such as flow rate, voltage, and concentration.

4.4.2 Interfacial Peel Testing

Modification to an interfacial peel testing technique was performed to further characterize effects of plasma on substrates. The total work needed to remove the nanofiber web from fabric quantifies the practical adhesion or toughness of a coating surface. A universal testing apparatus (Instron) was used to calculate work required to remove the nanofiber layer from fabric. Effectively, this test was a modified version of the standard test method for 90° peel resistance of adhesives, ASTM D 6862-04; more details on this can be seen in Table A-3 within Appendix 4. Tape was placed over nanofiber webs to prevent slippage. Tape was attached to the upper jaw (nanofiber layer) and lower jaw (fabric layer) of the testing apparatus. An image of a nanofiber-fabric sample during early stages of peel can be seen with Figure 4-4. Using constant extension, the upper jaw moved at a constant rate of 50 mm/min while peeling the nanofiber web from the fabric surface. Nanofiber web and fabric were at 90° (normal to one another) while peeling, in order to maintain a standardized extension used for measurement. A 5 N load cell was used to detect force required to remove nanofiber webs from the fabric surface. The load cell detected force required to peel a nanofiber mat from the fabric throughout the entire sample length. In order to calculate effective average load, interfacial toughness or work was calculated in units of
Figure 4-2: Sample preparation of electrospun webs for Martindale abrasion testing. These samples are mounted upside-down and oscillate against a standard woolen fabric abradant, with the mounted sample having a minimum pressure of 1.7 kPa, oriented downward.

Figure 4-3: Example of modified Martindale abrasion failure, which was used as a qualitative classification of nanofiber web durability. This results after oscillatory rubbing motions against standard abradant Martindale; the average number of rubs until failure were recorded as metrics for analysis. Holes in the nanofiber layer are highlighted with orange circles.
gf * cm and was provided in the form of load versus extension data. Each sample was peeled for 100 mm to calculate work required, found from integrating area under each load-extension output generated. **Figure 4-5** shows an example of this mechanical testing output, where measured load (gf) and extension (cm) data were used to calculate work or **toughness** (gf * cm) of nanofiber-fabric interfaces. Results used in analysis were averaged with at least four samples for each experimental parameter.

![Peeling test sample setup in Instron using a modified ASTM D 6862-04 test method. This modified test is intended to maintain 90° peel between nanofibers and fabric.](image)

**Figure 4-4:** Peeling test sample setup in Instron using a modified ASTM D 6862-04 test method. This modified test is intended to maintain 90° peel between nanofibers and fabric.
Figure 4-5: Example of peeling test output. Vertical axis (load applied to peel layer from substrate) is expressed in kgf, while horizontal axis (extension) is indicated in mm. The area under a curve was used to calculate total work to remove nanofiber layers from substrates, expressed in gf * cm.
4.5 Verification of Evidence of Plasma using Substrate

Two popular techniques for showing effects of plasma were used to indirectly characterize the change in surface energy on yarns composing NyCo fabric. First, 100% Nylon 6,6 and cotton fabrics were each treated and surface energy changes were characterized by measuring exhaust dye intensity. These fabrics were only used to help verify changes in surface energy to the fabric resulting from similar plasma exposure. The second method used to verify increasing surface energy was static contact angle using the sessile drop technique, described in Chapter 3. Plasma-treated Nylon 6,6 thin films were compared to untreated control films for this technique. Both dye uptake and measurement of contact angle correspond to changes in surface wetting properties resulting from increasing surface energy due to plasma exposure. Control films were compared with those treated in Helium plasma for 5 minutes and Helium-Oxygen plasma for 5 minutes.

Results of characterization of plasma interactions are well known for many polymers and textile materials. The increased presence of hydrophilic groups like –OH and –COOH are evident on the surface. These polar groups can be directly shown through elemental analysis, i.e., with X-Ray Photoelectron Spectroscopy (XPS). Simple and less-expensive techniques can show the effect of plasma through surface energy increases and are used in this analysis to indirectly characterize these effects. These two indirect techniques help verify the modified durability metrics used in order to help prove their validity.

4.5.1 Contact Angle of Treated Nylon 6,6 Film

Increases in surface energy can be shown through increasing contact angle measurement. Measurement of static WCA using the sessile drop technique
(ASTM D 5946-09) was performed on Nylon 6,6 films, used to model an ideal Nylon 6,6 surface. A picture of the setup used for these experiments at NCSU is shown in earlier in Figure 3-2 and below in Figure 4-6. Ten (10) measurements were recorded for each treatment type, and results were averaged.

4.5.2 Exhaust Dyeing of Fabrics

Measurements of difference in exhaust dye uptake were performed with Cotton and Nylon 6,6 woven fabrics to show evidence in increased surface energy resulting from plasma treatment. The woven NyCo fabric used throughout the study was not included due to its blended composition yielding confusing dye results. Differences in K/S intensity values were

Figure 4-6: Apparatus used for WCA acquisition in NCSU College of Textiles. This was used with evaluation of nanofiber webs in Chapter 3, and for Nylon 6,6 polymer film in Chapter 4.
determined using quantitative color analysis. A spectrophotometer was used to acquire $K/S$ intensities, where $K$ is the absorption coefficient and $S$ the scattering coefficient, respectively. This ratio is a common metric used in quantitative color analysis, and also a popular method to characterize surface energy changes resulting from plasma or related techniques.$^{15,17,106}$

4.5.2.1 Nylon 6,6 Fabric Exhaust Dyeing Procedure

A common acid dye (Telon Red 2BN-01) was used to dye the 100% Nylon 6,6 plainweave fabric. A 150 mL dye bath was composed of dye applied at 1 g/L. A 10% acetic acid solution was used to lower pH to approximately 4.5. Samples were dyed at a 20:1 liquor ratio using an Ahiba Nuance dye system, running at 100° C for 35 minutes.

4.5.2.2 Cotton Fabric Exhaust Dyeing Procedure

Plainweave 100% cotton fabric was dyed with a common reactive dye (Remozol Brilliant Red 3BS). In addition to dye components, sodium hydroxide and soda ash were added at 2.5 g/L and 5 g/L respectively. Resulting pH was measured at approximately 11. Samples were dyed at 1 g/L, using 200 mL baths at 20:1 liquor ratio, using an Ahiba Texomat dye machine, running at 75-80° C for 30 minutes.

4.5.3 Experimental Design

An appropriate experimental design was made for necessary factors and levels. Control NyCo substrates were electrospun upon and were compared to substrates treated using two different species combinations of plasma (Helium, Helium-Oxygen). Each plasma combination used two levels of treatment time (2 and 5 minutes) to further demonstrate effects. After plasma treatment, electrospinning deposition occurred for 40 minutes.
Electrospinning was performed at 17 kV applied voltage using concentrations of 11, 13, and 15% (wt/vol) and two electrospinning flow rate levels (1, 2 mL/hr). These specimen sets were made for both Peel and Martindale test methods. Initial results from modified peel testing seemed to provide less evident trends than Martindale results, and because of this, a third flow rate (0.5 mL/hr) was evaluated with the Martindale abrasion test in order to help characterize the effect of solution flow rate on durability to adhesion. Martindale experimental factors and levels can be seen in Table 4-1, while Peel test experimental factors and levels are seen in Table 4-2 with included results described in following sections.

4.6 Results and Discussion

During preliminary testing for interfacial peel strength and durability to rubbing abrasion, specimens at each concentration and treatment were tested. Not enough polymer was actually on the fabric to display any measurable effect when evaluating for coated fabrics having nanofibers spun at concentrations below 11%. Thus, for experimental designs during this analysis, only three polymer concentrations (11, 13, 15%) were compared, as described in the following sections.

4.6.1 Effects of Interfacial Mechanical Testing

Using Martindale abrasion testing, samples were characterized at 11, 13, and 15% concentration; nanofiber webs spun at or above 11% were the only specimens that displayed any measurable durability during trials. Nanofiber webs spun from concentrations below 11% apparently could not withstand the 1.7 kPa pressure with coupled oscillatory motion. From Chapter 3, application of 17 kV during electrospinning produced slightly higher WCAs than nanofiber webs spun using 15 kV; this was the only voltage used for Chapter 4 tests and
analysis. From rubbing data, two main parameters were seen to provide main effects: areal density and treatment type. In terms of peel testing, only 1 and 2 mL/hr specimens were used with the same parameters mentioned otherwise. Areal density and treatment type also were seen to have effects with peel testing, and are explained further in following sections.

Table 4-1: Experimental parameters used for evaluation of Martindale abrasion: concentrations used were 11-15%, flow rates used were 0.5, 1, and 2 mL/hr respectively. Control substrates were coated and tested for abrasion, comparing to substrates treated in Helium or Helium-Oxygen plasma prior to electrospinning for different durations (2, 5 minutes). Average results of number of Martindale rubbing motions until failure are included to compare to nanofiber and plasma experimental factors.

<table>
<thead>
<tr>
<th>Flow Rate, mL/hr</th>
<th>Substrate Treatment Type</th>
<th>Plasma Duration, minutes</th>
<th>11</th>
<th>13</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>Control</td>
<td></td>
<td>5.33 ± 1.63</td>
<td>25.67 ± 5.28</td>
<td>27.33 ± 4.13</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>2</td>
<td>13.00 ± 2.10</td>
<td>57.67 ± 9.07</td>
<td>46.33 ± 7.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>16.33 ± 1.97</td>
<td>103.00 ± 7.46</td>
<td>100.33 ± 17.36</td>
</tr>
<tr>
<td></td>
<td>Helium-Oxygen</td>
<td>2</td>
<td>13.33 ± 3.50</td>
<td>38.67 ± 4.32</td>
<td>45.33 ± 10.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>15.67 ± 2.34</td>
<td>63.66 ± 14.24</td>
<td>62.00 ± 7.48</td>
</tr>
<tr>
<td>1</td>
<td>Control</td>
<td></td>
<td>23.33 ± 7.31</td>
<td>165.67 ± 35.27</td>
<td>242.33 ± 55.60</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>2</td>
<td>37.67 ± 5.72</td>
<td>216.33 ± 70.49</td>
<td>304.67 ± 43.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>39.67 ± 13.83</td>
<td>334.33 ± 111.48</td>
<td>451.33 ± 192.71</td>
</tr>
<tr>
<td></td>
<td>Helium-Oxygen</td>
<td>2</td>
<td>30.33 ± 9.99</td>
<td>175.33 ± 40.69</td>
<td>300.00 ± 102.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>32.00 ± 7.80</td>
<td>275.33 ± 227.52</td>
<td>640.33 ± 310.09</td>
</tr>
<tr>
<td>2</td>
<td>Control</td>
<td></td>
<td>91.33 ± 12.56</td>
<td>584.00 ± 234.03</td>
<td>622.00 ± 154.97</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>2</td>
<td>133.67 ± 39.04</td>
<td>941.00 ± 144.51</td>
<td>814.33 ± 112.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>128.33 ± 32.56</td>
<td>1513.00 ± 601.92</td>
<td>1378.50 ± 581.29</td>
</tr>
<tr>
<td></td>
<td>Helium-Oxygen</td>
<td>2</td>
<td>163.33 ± 40.94</td>
<td>865.33 ± 101.50</td>
<td>707.00 ± 74.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>248.00 ± 103.04</td>
<td>1045.33 ± 139.36</td>
<td>956.50 ± 227.21</td>
</tr>
</tbody>
</table>
Table 4-2: Experimental settings used during Peel test: concentrations used were 11-15%, Flow rates used were 1, and 2 mL/hr respectively. Control substrates were coated and tested for load required to remove web. These were compared to substrates treated in Helium or Helium-Oxygen plasma for different durations (2, 5 minutes) prior to electrospinning. Average peeling toughness in gf * cm is included to compare nanofiber and plasma experimental factors.

<table>
<thead>
<tr>
<th>Flow Rate, mL/hr</th>
<th>Substrate Treatment Type</th>
<th>Plasma Duration, minutes</th>
<th>11</th>
<th>13</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td></td>
<td>24.03 ± 8.42</td>
<td>48.65 ± 7.55</td>
<td>40.43 ± 16.05</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>2</td>
<td>31.69 ± 14.63</td>
<td>88.02 ± 33.64</td>
<td>87.45 ± 47.79</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>5</td>
<td>46.87 ± 15.64</td>
<td>98.41 ± 48.52</td>
<td>146.20 ± 47.88</td>
</tr>
<tr>
<td></td>
<td>Helium-Oxygen</td>
<td>2</td>
<td>33.50 ± 25.18</td>
<td>82.34 ± 14.47</td>
<td>94.28 ± 34.99</td>
</tr>
<tr>
<td></td>
<td>Helium-Oxygen</td>
<td>5</td>
<td>39.41 ± 28.97</td>
<td>128.80 ± 59.10</td>
<td>117.67 ± 68.27</td>
</tr>
<tr>
<td>2</td>
<td>Control</td>
<td></td>
<td>35.38 ± 20.99</td>
<td>73.16 ± 16.01</td>
<td>90.70 ± 35.88</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>2</td>
<td>46.73 ± 21.08</td>
<td>87.40 ± 19.63</td>
<td>162.02 ± 78.97</td>
</tr>
<tr>
<td></td>
<td>Helium</td>
<td>5</td>
<td>66.32 ± 16.47</td>
<td>124.78 ± 68.63</td>
<td>119.79 ± 21.73</td>
</tr>
<tr>
<td></td>
<td>Helium-Oxygen</td>
<td>2</td>
<td>43.72 ± 12.82</td>
<td>101.21 ± 66.54</td>
<td>96.68 ± 23.35</td>
</tr>
<tr>
<td></td>
<td>Helium-Oxygen</td>
<td>5</td>
<td>55.69 ± 14.08</td>
<td>109.65 ± 42.59</td>
<td>134.49 ± 67.05</td>
</tr>
</tbody>
</table>

4.6.1.1 Effect of Areal Density with Martindale Abrasion and Peel tests

Areal density was calculated for control samples in the same manner depicted in Chapter 3. Both the polymer concentration deposited onto the fabric, as well as the flow rate used, seemed to both have an effect on the amount of rubs until failure occurred. In Figure 4-7, it can be seen that an increase in the average number of Martindale rubs results
Figure 4-7: Log(Average Martindale rubs) versus areal density for coated fabrics electrospun using 11 (cyan), 13 (magenta), and 15% polymer solution concentrations (gold). Constant 40-minute deposition, 17 kV applied voltage.

from increasing concentration. Figure 4-8 shows the average number of Martindale rubs increasing from increasing extrusion rate. Both figures depict similar trends in which an increase in nanofiber areal density provides increased Martindale rubbing durability. Figure 4-8 shows a stronger trend since more of a difference results from doubling flow rate (0.5 to 1, or 1 to 2 mL/hr) than with increasing polymer concentration by (11 to 13, 13 to 15%). Both figures infer that as more nanofiber mass is deposited, more Martindale rubs will increase before failure. These measurements, however, are treatment-independent. No difference in nanofiber deposition was found using different pretreatment to substrates after 40 minutes of electrospinning.
In terms of peel testing, areal density was a less evident factor in terms of interfacial strength measured in peeling toughness. In Figure 4-9, flow rate is used for grouping to compare peeling toughness versus areal density. In Figure 4-10 peeling toughness versus areal density are compared and grouped according to by concentration. There appears to be a correlation (though lesser) in terms of areal density and toughness of the nanofiber web.

Figure 4-8: Log(Average Martindale rubs) versus nanofiber areal density for coated fabrics electrospun using 0.5 (purple), 1 (orange), and 2 mL/hr (green) flow rates, respectively. Constant 40-minute deposition, 17 kV applied voltage.

Despite large sample deviations, peeling test data shows that as more mass is deposited onto fabric, toughness increases. Areal density increased when increasing either concentration or
extrusion rate, yielding increased peeling toughness, though less effective than with Martindale abrasion data. These peel test samples, which were evaluated for areal density, were untreated fabric (or control) samples. To evaluate effects of plasma treatment, other methods must be used to analyze treated and control samples.

4.6.1.2 Martindale Abrasion Results

In terms of treatment type applied to fabrics prior to electrospinning, substantial differences exist between control and plasma-treated specimen. Increasing treatment time from two to five minutes resulted in increased metrics, using both Martindale abrasion and Peel test methods. In terms of Martindale testing, Figure 4-11 and Table 4-1 depict average
Martindale rubs by treatment type, and also show differences of rubbing durability in terms of concentration, flow rate, and pretreatment. With Martindale abrasion figures, a logarithmic plot is best suited to depict average number of rubs using the experimental parameters.

Figure 4-11 shows that the presence of plasma treatment increases the average Martindale number of rubs when compared to control specimen at each concentration.

![Average Peeling Toughness vs. Nanofiber Areal Density for Coated Fabrics](image)

Figure 4-10: Average peeling toughness versus nanofiber areal density for coated fabrics electrospun using 11 (cyan), 13 (magenta), and 15% polymer solution concentration (gold). Constant 40-minute deposition, 17 kV applied voltage.

Fabrics electrospun upon using concentrations of 13 and 15% had the highest durability to Martindale abrasive rubbing. For both Helium and Helium-Oxygen plasma species, increase in time of treatment from two to five minutes shows an increased number of rubbing motions.

85
Figure 4-11: Log(Average Martindale number of rubs until failure) versus substrate treatment type for nanofiber coated fabrics: comparing untreated (control) coated fabrics with those treated in Helium and Helium-Oxygen plasmas (applied for 2, 5 min.). Also shown are flow rates of 0.5 (left), 1 (middle), and 2 mL/hr (right), and polymer solutions of 11 (cyan), 13 (magenta), and 15% concentration (gold) varied during electrospinning. Plasma treatment and duration, and increasing concentration provide an increase in average number of Martindale rubbing motions until failure.
until failure for 13 and 15% electrospun webs. Samples electrospun at 11%, and also samples electrospun using 0.5 mL/hr, did not exhibit adequate durability to rubbing motions until failure, which was thought to be due to the lack of sufficient polymer coating (areal density) by using either or both of these lowest factor levels; however, for webs spun using 13 and 15% concentrations there were significant increases in rubbing durability when compared to 11%. Also, for nanofiber webs spun using 13 and 15% concentrations, more of an effect can be seen with plasma treatment and with an increase in plasma treatment time.

Plasma treatment that displayed the greatest durability to rubbing was Helium applied for five minutes: here, webs spun using 13 and 15% concentrations exhibited similar amounts of average rubs. Helium-Oxygen treatment applied for five minutes to substrates also typically showed increased rubbing numbers compared with substrates treated with Helium-Oxygen for two minutes. Though Martindale rubbing averages for samples treated with Helium-Oxygen plasma generally were slightly lower than those treated with atmospheric Helium alone, a few individual samples using Helium-Oxygen plasma resulted in higher average number rubbing motions when compared to Helium for both 2- and 5-minute treatment times.

Within each concentration, as flow rate increased so did the number of Martindale rubs until failure. Although little difference in rubbing resulted when increasing concentration from 13 to 15%, concentrations electrospun using 11% yielded nanofiber coatings that exhibited much lower durability to rubbing. Table 4-1 shows large sample deviations for each experimental sample. Large deviations are commonly found using the standard ASTM Martindale textile abrasion method. These results are expected due to
humans evaluating abraded surfaces, and also due to the classification of a failure having a floating definition dependent on specific sample fabrics. The fact that a normal fabric test was modified to quantify nanofiber adhesion to a fabric should be taken into account and explored during future research to evaluate how to minimize any sample deviations or coating-fabric defects.

4.6.1.3 Peel Test Results

Figure 4-12 and Table 4-2 depict experimental average peeling toughness values. Similar trends were observed as with Martindale-tested samples. As concentration increased, so did nanofiber-fabric peeling toughness. More of an increase in peeling toughness resulted from increasing polymer concentration during electrospinning from 11 to 13% than exhibited when increasing concentration from 13 to 15%. This was similar to Martindale testing, where samples spun using 13% seemed to yield data almost as effective as those spun using 15% concentration. The presence of plasma treatment compared to control substrate resulted in increased peeling toughness at each concentration and flow rate evaluated. Increasing plasma treatment time also yielded greater nanofiber toughness. The highest peeling toughness values were recorded for samples (in ascending order) when using: 13% concentration, 1 mL/hr flow rate, Helium-Oxygen plasma treatment for five minutes (128.8 ± 59.10 gf * cm); 15%, 1 mL/hr, Helium plasma treatment for five minutes (146.20 ± 47.88 gf * cm); and 15%, 2mL/hr, Helium plasma treatment for two minutes (167.02 ± 78.97 gf * cm).

Though sample variances seen with these listed peak values are quite high, the nature of the nanofiber-deposited fabric samples provided inherent deviations sample-to-sample, which limited reproducibility. Also critical was sample handing, as samples were very easily
damaged when initiating layer peeling when applying tape prior to testing. This is noted by Lacombe\textsuperscript{105} in his text regarding evaluation of this peeling test method. Large sample deviations were anticipated to occur because of this test method and also for the nanofibers used as coating layer. Still, sample deviations were not desired were minimized when possible.

Though large sample deviations were made using the modified peel test along with modified Martindale abrasion, successful data was still acquired as there is no preceding information for samples having this type of construction and application methods. The deviations occurring within the peeling test are due to the nature of the technique used, yet were still an intrinsic measurement of samples. Lacombe\textsuperscript{105} notes in his adhesion measurement book that sample reproducibility is inherently low for peeling test methods and, therefore, toughness values should be evaluated for comparison and not evaluated for literal toughness. Toughness results in intrinsic properties for a sample and were not extrinsic measures, such as peak load recorded, which was important to note, along with this preliminary testing technique being used for characterization. Improvements in sample preparation and subsequent attachment to Instron jaws should lower deviation in future studies. Though less significant, these data still show trends similar to Martindale durability data.

With both test methods, the resulting significance in the amount of polymer deposited from concentration and extrusion factors provided corresponding interfacial differences, which were evaluated mechanically. The accompanying figures show concentration and flow rate have great influence on resultant mechanical testing. Plasma treatment also was shown to
Figure 4-12: Average peeling toughness versus substrate treatment type for nanofiber coated fabrics: comparing untreated (control) coated fabrics with those treated in Helium and Helium-Oxygen plasmas (applied for 2, 5 min.). Also shown are flow rates of 1 (left), and 2 mL/hr (right), and polymer solutions of 11 (cyan), 13 (magenta), and 15% concentration (gold) varied during electrospinning. Plasma treatment and duration, and increasing concentration increases average peeling toughness of nanofiber coated fabrics.
have a positive effect on the amount of rubs or the amount of toughness (respectively) that a
given nanofiber web could withstand and should be the focus of further research.

4.6.2 Evidence of Plasma Treatment to Substrate Effects

4.6.2.1 Effect of Plasma using Exhaust Dyeing

Using spectral measurements, differences in $K/S$ intensity resulting from plasma
treatment were seen for both 100% fabrics examined. Examination of Figure 4-13 shows $K/S$
dyeing intensity for Nylon 6,6 fabrics, while Figure 4-14 focuses in on these same spectral
peaks. Figure 4-15 shows $K/S$ intensity for cotton fabric, while Figure 4-16 shows the peak

![graph]

Figure 4-13: Comparison of plasma intensity using exhaust dyeing on 100% Nylon 6,6
fabrics: Shown is $K/S$ intensity spectrum at visible wavelengths comparing control to
treated fabric.
of cotton $K/S$ spectra. Helium-Oxygen plasma treatment (5-minute exposure time) appeared to provide a greater increase in surface energy to fabrics than did Helium plasma. This resulted in higher wettability illustrated by higher dyeing intensities of both Nylon 6,6 and cotton fabrics when separately exhaust dyeing the fabrics. For both fabrics, the intensities for

![Comparison of Exhaust Dyeing $K/S$ Intensity by Pretreatment Type for 100% Nylon 6,6 Fabric](image)

**Figure 4-14:** Comparison of $K/S$ intensity peaks shown in Figure 4-13 for plasma-treated versus non-treated 100% Nylon 6,6 fabric.

$K/S$ increased across the whole visible spectrum measured for Helium-Oxygen plasmas. With Helium-treated fabrics, only changes in $K/S$ intensity were observed, depending on the wavelength the figures show decreasing or increasing intensity with respect to control fabrics. Apparent from the figures, dependent on wavelength examined, Helium plasma was seen to provide increased, decreased, or similar $K/S$ intensity. A similar trend was seen with
Figure 4-15: Comparison of plasma intensity using exhaust dyeing on 100% cotton fabric: Shown is $K/S$ intensity spectrum at visible wavelengths comparing control to treated fabrics.

Figure 4-16: Comparison of $K/S$ intensity peaks shown in Figure 4-15 for plasma-treated versus non-treated 100% cotton fabric.
both Nylon 6,6 and cotton fabrics when comparing Helium-treated samples to control samples.

This evidence from $K/S$ intensity is used for qualitative purposes in this research. It is only used to verify increased surface energy resulting from plasma treatment to fabrics; however, the fact that Helium-Oxygen plasma significantly increased surface wettability for each fabric to respective dye may be explained by the etching effect of increased Oxygen species present in the plasma. Similar surface energy increases in the fabrics could have been obtained by each species; yet with an increased Oxygen presence, a greater etching effect could have allowed more surface area to be exposed to dye molecules. When applying the plasma treatment, the presence of Oxygen results in a lower density plasma discharge compared to an instance when only Helium is used as the plasma source gas; however, a larger amount of etchant molecular species will result if more Oxygen is present in the discharge. A greater number of polar groups may be obtained from Helium-Oxygen compared to Helium plasma due to the etching effect of the Oxygen, although, this was not confirmed in this research. Larger $K/S$ values were found using both Helium and Helium-Oxygen source gases for plasma treatment, observed by measuring dye intensity at the surface for both fabric types. This evidence is compared to that of static WCA in the following section.

4.6.2.2 Effect of Plasma using Static WCA

Static WCA images for Nylon 6,6 films can be seen in Figure 4-17, and results of WCA for control film and for treated films can be seen in Table 4-3. These images and corresponding table display average WCA data acquired after Helium and Helium-Oxygen
Table 4-3: Static WCA comparison for Nylon 6,6 film treated in Helium and Helium-Oxygen atmospheric plasma. Average WCAs were compiled using 10 individual measurements with each type of film treatment.

<table>
<thead>
<tr>
<th>Substrate Treatment</th>
<th>Control</th>
<th>Helium Plasma, 5 min.</th>
<th>Helium-Oxygen Plasma, 5 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average WCA (°)</td>
<td>66.56</td>
<td>40.71</td>
<td>42.53</td>
</tr>
<tr>
<td>±</td>
<td>4.01</td>
<td>7.23</td>
<td>3.95</td>
</tr>
</tbody>
</table>

Figure 4-17: Comparison of static WCA on control and plasma-treated Nylon 6,6 films. (A) Nylon 6,6 untreated film. WCA average = 66.56°. (B) Nylon 6,6 treated with Helium plasma, 5 minutes. WCA average = 40.71°. (C) Nylon 6,6 film, treated in Helium-Oxygen plasma, 5 minutes. WCA average = 42.53°.
plasma treatments were applied to the Nylon 6,6 film for five minutes. The measured control WCA is comparable to Nylon 6,6 having $\theta_{\text{Equil}}$ of 68.3° which is its true equilibrium contact angle. Viewing images of the treated films provides evidence that the contact angle has been significantly reduced. The reference images appear almost identical and correspond to similar contact angle values, which indicate that a similar increase in surface energy results to the film for both plasma species used. Contact angle data are easy to visualize and are often the most effective way to show evidence of surface energy modification. These effects from plasma treatment clearly show increased surface interaction with a droplet on the Nylon 6,6 “ideal” surfaces. Both plasma treatments seemed to provide similar contact angle information, with Helium plasma treatment providing a slightly lower average but with higher standard deviation than that of Helium-Oxygen plasma. Only one treatment time was used for simplicity, as it is well known that increased treatment time can result in increased properties related to surface energy.

Results of these two methods of characterization confirmed that plasma is indeed increasing the wettability of the NyCo fabric. Results using Nylon 6,6 film and with 100% Nylon 6,6 and cotton fabrics help explain these concepts indirectly, which are verified quantitatively using modified Martindale abrasion and 90° interfacial peeling tests.

4.6.3 Discussion of Results

A surface energy increase can indicate an increased presence of hydrophilic polar groups and possible surface etching effects, along with other chemical and physical changes resulting from plasma treatment. Both plasmas used in the study indicate changes to the chemical composition on the surface, as seen with a dramatic decrease of contact angle. The
decrease in contact angle mainly relates to an increase in polar groups on the fabric surface. Etching and roughness increases could occur with both plasma treatment types, as both incorporate ambient air which contains Oxygen. Chemical composition was not directly measured, although this should be performed to analyze which species are changing on the fabric during plasma exposure.

Surface roughness was not observed or measured directly. Likewise, chemical changes were not directly measured; however, evidence within this chapter indicates an increase of interfacial adhesive properties when plasma treatment is applied to the NyCo fabric. Increasing treatment time also increased interfacial properties for both plasma species of study using the Martindale and peel test methods. Large sample deviations with these methods were expected based upon results reported in the literature, and occur from low reproducibility between samples due to the nature of the mechanical forces applied to the nanofiber coatings.

Peeling toughness relates to the average load required over the course of extension measured during peeling of nanofiber layer from fabric. These data reflect true average force for the interfaces of study and are understood to be an intrinsic property of the fabric/web composite fabric. From peeling test data, results show that toughness (gf*cm ∝ average force required) of web and fabric significantly increased with the application of both Helium and Helium-Oxygen plasma treatments, and also from an increase in treatment time for both plasma species. Increasing polymer concentration from 11 to 15% led to increased toughness, with flow rate providing a less significant effect.
With Martindale abrasion testing, treated nanofiber-fabric samples took more oscillations to abrade than those that were not treated with plasmas. For most specimens tested, substantial increases in the number of Martindale rubs until failure resulted when comparing the untreated/control coated fabric specimens to those exposed to either plasma for five minutes. These results indicate increased durability resulting from the plasmas. In general, both species having 5-minute exposure to fabrics before electrospinning provided the largest increases in rubbing durability; no specific species provided higher durability to rubbing, indicating similar effects to substrates. Dramatic increases in durability to rubbing resulted with fabrics that encountered plasma exposure (both Helium and Helium-Oxygen), showing that plasma presence and duration was a primary factor in coating durability. Increased rubbing durability of plasma-treated fabrics was seen even while keeping independent the other primary effects contributing to durability. Increasing polymer concentration and flow rate increasing also led to increased nanofiber web durability. These show that increased areal density deposited atop the fabric increased durability using the modified Martindale abrasion (and modified Peel test) technique.

Results from mechanical testing modifications and from indirect evidence of substrate increasing surface energy show plasma pre-treatment of fabrics prior to electrospinning is effective in increasing adhesive force between electrospun nanofibers and substrate fabric. The increased adhesion is mainly due to the active species created by the plasma treatment. Plasma is an extremely chemically-active atmosphere. When the fabric and nanofibers are treated by plasma, the active species, i.e., radicals, ions, electrons and charged particles, will be generated on the surface. These active species possibly create more potential sites for
bonding and cross-linking affects at the interface. In the plasma treatment process, when the fabric is treated, the components of the fabric are bombarded leading to the formation of radicals, ion, and active charges on their surface and cause them to be firmly adhered to the substrate; however, this was not confirmed in this research and should be a focus of future related studies.

Along with plasma effects on interfacial properties, nanofiber factors also play a critical role in the issue of durability and peeling toughness, as well. Evidence from both Martindale and peel tests showed that nanofiber-dominated structures definitely had a role, as seen for abrasion testing, where durability to rubbing increased as bead presence decreased. Recall from Chapter 3 that as concentration increased, nanofiber surface morphology transitioned to nanofibrous surfaces from beaded nanofiber surfaces. Along with surface science which was described in Chapter 3, study results indicate that nanofiber structural integrity is governed primarily by concentration, and to a lesser extent, extrusion rate. These factors both affect areal density, which played a key role though was not a specified experimental factor; rather, areal density became a resulting factor.

4.7 Summary, Future Research

Free energy increases resulting from plasma treatment mainly occur from an increase of the surface tension polar component, which has been indicated in this analysis, using both direct and indirect testing methods. Increased surface energy after treatments can be attributed to an increased presence of plasma-created polar groups residing on the fabric surface. Indirect evidence of changes to substrate materials, resulting from atmospheric plasma treatment, were shown using measurement of dye uptake and contact angle
measurement. These measurements were applied to help verify the direct measurement techniques that were adapted to characterize the nature of these samples. Adhesion was seen to improve through increased interaction between nanofiber coatings and fabric. Plasma-created polar groups or surface roughness changes are thought to be responsible for increased bonding or contact points between the nanofiber electrospun layer and substrate.

Accurate data resulted from modifying textile characterization techniques in order to take into account a nanofiber layer coating a textile substrate. In future research using these characterization techniques, focus will be placed on improving sample preparation and handling to minimize deviations for a given sample set. Despite any improvements that could be made for sample preparation, the lack of sample reproducibility with statistical confidence was the inherent nature of both Martindale and peeling test methods. The Martindale abrasion test method is intended to characterize knitted, woven, or nonwoven fabrics and, though demonstrated here with nanofiber coatings adhered to fabrics, measured sample standard deviations likely result from the high repetitive shear forces acting on nanofiber layers. Peel test sample data provided even greater deviation within sample sets. The Instron device coupled with the sample size used for experiments, and type of tape applied to fabric and respective webs perhaps were not sensitive enough to measure with enough resolution to discriminate between materials. Though the method used for peeling allows precise control and simple test setup, Lacombe noted that a disadvantage is a relatively high strain rate when using flexible materials such as polymers, causing the test to reflect less than actual conditions and only providing comparable results relative to other samples within a set. Results within a sample set should, therefore, be compared relative to one another, not by
direct comparison. A primary difficulty stated in Lacombe’s book about adhesion tests was initiation of a peel strip when preparing samples—which was also experienced during this study. When removing nanofiber webs from fabrics, the slightest of sample-to-sample variation led to decreased sample reproducibility. Low reproducibility is known to be common with 90° peeling methods for a variety of coating and substrate combinations, simply due to the necessary initiation of a peel prior to the measured characterization. Especially with nanofibrous webs, low reproducibility presented concerns when trying to minimize sample error during testing. Nanofiber samples require delicate handling, and interfacial properties can easily be affected when preparing and mounting samples.

The fact that both of these fabric testing methods typically provide ample sample reproducibility led to numerous large sample errors during experimentation. In order to better predict trends and minimize error, more characterization should be necessary with peel test and Martindale abrasion methods, while exploring different nanofiber substrate combinations. Different sample preparation sizes and methods should be observed as well. Improving overall durability of the nanofiber webs is the main priority. In Chapter 3, hydrophobic surface properties were demonstrated for each concentration used in the study, and they proved easy and simple to attain. Many of these concepts have already been studied in related literature; however, there have been no reports of electrospun surfaces that exhibit sustainable and durable properties that can be used as wearable textile materials. Woven fabrics provide less interfacial adhesion than nonwovens and have less potential contact points for a given fabric area or mass.\textsuperscript{3,27,43-46} The surface of many nonwoven fabrics present
more potential surface area to interact with plasma species and also to contact nanofiber layers. Nonwoven substrates should be included in future research related to this topic.

Data and analysis in Chapter 4 shows that the effect of plasma on the fabric is evident with respect to concentration and flow rate of study. Duration of plasma treatment had a greater effect on interfacial properties, and it was the main factor independent of electrospinning factors and levels. There also was better web integrity for samples produced using higher concentrations and flow rates.
Chapter 5: Summary of Project Conclusions, Next Steps

5.1 Conclusions Related to Water Repellency of Electrospun Nanofiber Coatings

The role of nanofiber surface structure was shown to have great effect on static Water Contact Angle (WCA). Controlled hydrophobicity was shown through variation of both solution and processing parameters. The easily-electrospun and well-characterized polymer Nylon 6 ($\theta_{\text{Equil}} = 62.6^\circ$) was used in this study in order to show role of structure in surface hydrophobicity. Average nanofiber surface coating WCAs as high as $140.85 \pm 2.15^\circ$ were obtained atop the ACU NyCo fabric. These coating surfaces were also found to have high porosity with small individual pore size which would be beneficial if used as a barrier material for liquids and aerosols encountered as CB and other TIM hazards.

5.2 Conclusions Related to Improved Nanofiber-Fabric Durability Resulting from Plasma Treatment

Also shown was evidence of plasma increased interfacial adhesion between electrospun nanofibers and substrates treated in Helium and Helium-Oxygen APGD plasma prior to electrospinning was shown, using both direct and indirect characterization techniques. Direct techniques included modifications to Martindale standard textile abrasion and $90^\circ$ interfacial peeling tests. These test methods directly measured nanofiber/fabric interactions using qualitative metrics. Both the number of average Martindale rubbing motions and average peeling toughness increased as polymer concentration, flow rate and substrate plasma treatment time increased. This indicated increased interfacial strength.
between nanofibers and fabric as polymer areal density increased. This evidence is also indicated with the presence of and with increasing treatment time using both plasma species. Plasma effects on substrate surface were also verified by increased surface wettability using static WCA and exhaust dyeing intensity.

5.3 Potential Applications

Here a quick, simple finishing process using woven ACU NyCo fabric is demonstrated, and performed in order to maintain similar bulk garment characteristics like hydrophilicity to promote necessary metabolic heat and moisture vapor transmission. The promotion of necessary heat transfer while providing protection against chemical and thermal hazards using a multilayered garment approach has become important for many fields of industry. These include military and industrial uses for CB hazard protection, as well as medical and activewear textile products. This incorporation of a nanofibrous coating to a fabric has been shown to impart properties similar to that of a composite or multifunctional fabric. This research enabled initial stages for these types of material to be fabricated while demonstrating potential for greatly decreased processing time through using less water, energy, and hazardous chemicals applied using traditional finishing techniques. In a multilayer fabric design incorporating a nanofiber layer with properties like enhanced filtration or with the incorporation of functional additives to target specific agents, nanofibers would be best suited if their flexibility and durability could be maintained. In a surface or as a middle layer within a garment structure, nanofibers have been found to provide excellent properties for industrial and military CB textile materials.
5.4 Research Summary, Path Forward

This preliminary study should be succeeded by more research related to these topics, especially investigation of nanofiber/substrate adhesion through use of plasma. Surface treatment durability often is a critical (if not primary) issue when dealing with many textile, and even more so, nanoscale surfaces. Electrospun elastomeric polymer nanofibers seem a promising direction for exploration in future work. If combined in multilayer fashion with more conventional fabrics or coatings, elastomeric nanofibers could provide a microporous filtration layer with great flexibility and resiliency required for use as a garment while still providing enhanced functional properties deriving from extreme surface area.

The goal of this research was to characterize the wetting properties of a well-characterized nanofiber deposition atop a current fabric design. This was established using Nylon 6, where the surface energy of the molecular interactions were overcome by sheer surface area when spun into a nanofibrous web. Plasma treatment of Nylon 6,6/Cotton fabric was shown to increase nanofiber-substrate adhesion.

All of the testing results together help provide answers to the questions originally posed during earlier portions of this project: is there a way to create a durable fabric deposition using more environmentally friendly methods? Proper explanation would be that concepts were established using an arbitrary combination consisting of an easily-electrospinnable polymer and current military woven fabric. A naturally-wettable material (Nylon 6) was first made non-wetting by utilization of extreme porosity and surface area. With this, excellent filtration properties would be exhibited, aiding in related applications where this is a critical issue for wearable materials. This nonwoven nanofibrous mat was then
shown to have enhanced interfacial force with a fabric after it was treated by atmospheric pressure plasma. The principles of this composite fabric process should be applied to more types of polymers and fabrics in combination to better characterize these effects. Specifically, they should be intended to minimize use of energy and employment of hazardous chemistry. Electrospinning of Nylon 6 was performed using a solvent; the end goal would be to create a way to fabricate a superhydrophobic surface from aqueous electrospinning solution, or by using solvent that could be easily reclaimed and minimize potential hazards. Plasma treatment factors could be altered such that enhanced durability between interfacial layers is created while minimizing production inputs like time, energy, and chemistry.

The preceding material within these chapters first proposed a way to utilize the physical structure in attainment of a repellent electrospun surface, with great detail placed on resulting surface property science. After this, two methods were proposed to measure interfacial layer strength and durability. These incorporate traditional mechanical testing methods otherwise used with textile and flexible materials. Evidence from these and by verifying increased surface energy using simple methods show that plasma pretreatment to fabrics can help coat such surfaces with material that could enable entirely-different surface properties than are characteristic of the bulk. Future work should be performed to focus on durability, and also to even further increase water repellency with easily-spun nanofibers (even providing superhydrophobic characteristics). Different configurations of multilayered composite fabric design should also be explored, in order to promote greatest flexibility, durability, filtration efficiency, and liquid repellency. Findings from this analysis can be used to help revolutionize many textile finishing techniques as part of a larger, long-term study.
Chapter 6: References Cited


U.S. Environmental Protection Agency. 2010/2015 PFOA stewardship program, Washington, D.C.


LIST OF APPENDICES

Appendix 1: Common Polymer Surface Tensions and Resulting WCAs ......................... 118

Appendix 2: Figure of WCA for polymers listed in Appendix 1 ................................. 119

Appendix 3: Supplemental instructions for Modified Martindale Abrasion test ............ 120

Appendix 4: Supplemental Instructions for Modified 90° Peeling Test ........................ 121

Appendix 5: Supplemental SEM Images of Electrospun Nanofibers for each Experimental Parameter; Shown at Different Magnifications (1, 5, 10 kX Magnification) .............. 1213
## Appendix 1: Common Polymer Surface Tensions and Resulting WCAs

### Table A-1 Polymer Surface Tensions and WCA

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Solid-Liquid (dyne/cm)</th>
<th>Water Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile butadiene styrene (ABS)</td>
<td>38.5</td>
<td>80.9</td>
</tr>
<tr>
<td>Epoxies</td>
<td>44.5</td>
<td>76.3</td>
</tr>
<tr>
<td>Fluorinated ethylene propylene (FEP)</td>
<td>19.1</td>
<td>108.5</td>
</tr>
<tr>
<td>Hexatriacontane</td>
<td>20.6</td>
<td>108.5</td>
</tr>
<tr>
<td>Nylon 6 (polycaprolactum, aramid 6)</td>
<td>43.9</td>
<td>62.6</td>
</tr>
<tr>
<td>Nylon 6.6</td>
<td>42.2</td>
<td>68.3</td>
</tr>
<tr>
<td>Nylon 11</td>
<td>35.6</td>
<td>82</td>
</tr>
<tr>
<td>Nylon 12</td>
<td>37.1</td>
<td>72.4</td>
</tr>
<tr>
<td>Paraffin</td>
<td>24.8</td>
<td>108.9</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>29.3</td>
<td>96</td>
</tr>
<tr>
<td>Poly n-butyl methacrylate (PnBMA)</td>
<td>29.8</td>
<td>91</td>
</tr>
<tr>
<td>Poly t-butyl methacrylate (PtBMA)</td>
<td>18.1</td>
<td>108.1</td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td>44</td>
<td>82</td>
</tr>
<tr>
<td>Polychlorotrifluoroethylene (PCTFE)</td>
<td>30.8</td>
<td>99.3</td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS)</td>
<td>20.1</td>
<td>107.2</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>31.6</td>
<td>96</td>
</tr>
<tr>
<td>Polyethylene oxide (PEO, PEG, polyethylene glycol)</td>
<td>43</td>
<td>63</td>
</tr>
<tr>
<td>Polyethylene terephthalate (PET)</td>
<td>39</td>
<td>72.5</td>
</tr>
<tr>
<td>Poly(hexafluoropropylene)</td>
<td>16.9</td>
<td>112</td>
</tr>
<tr>
<td>Polysisobutylene (PIB, butyl rubber)</td>
<td>27</td>
<td>112.1</td>
</tr>
<tr>
<td>Polymethyl methacrylate (PMMA, plexiglass)</td>
<td>37.5</td>
<td>70.9</td>
</tr>
<tr>
<td>Polyoxymethylene (POM)</td>
<td>37</td>
<td>76.8</td>
</tr>
<tr>
<td>Polyphenylene sulfide (PPS)</td>
<td>38</td>
<td>80.3</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>30.5</td>
<td>102.1</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>34</td>
<td>87.4</td>
</tr>
<tr>
<td>Polysulfone (PSU)</td>
<td>42.1</td>
<td>70.5</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>19.4</td>
<td>109.2</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>26.5</td>
<td>92</td>
</tr>
<tr>
<td>Polyvinyl acetate (PVA)</td>
<td>35.3</td>
<td>60.6</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVOH)</td>
<td>37</td>
<td>51</td>
</tr>
<tr>
<td>Polyvinyl chloride (PVC)</td>
<td>37.9</td>
<td>85.6</td>
</tr>
<tr>
<td>Polyvinyl fluoride (PVF)</td>
<td>32.7</td>
<td>84.5</td>
</tr>
<tr>
<td>Polyvinylidene chloride (PVDC, Saran)</td>
<td>40.2</td>
<td>80</td>
</tr>
<tr>
<td>Polyvinylidene fluoride (PVDF)</td>
<td>31.6</td>
<td>89</td>
</tr>
</tbody>
</table>
Appendix 2: Figure of WCA for polymers listed in Appendix 1

Figure A-1: WCA versus critical surface tension for various polymers. This figure and Table A-1 were made using Diversified Enterprises’ company website, located at www.accudynetest.com. The figure plots many commonly-used polymer Solid-Liquid surface tensions (dyne/cm) versus WCA.
Appendix 3: Supplemental instructions for Modified Martindale Abrasion test (Modification of standard test method for Martindale textile abrasion, ASTM D 4966-08)

Figure A-2 shows another view of the Martindale test apparatus at NCSU. Up to six samples can be mounted at one time for oscillatory rubbing motion.

![Figure A-2: Additional view of Martindale testing apparatus.](image)

Table A-2 lists parameters kept constant using the testing method, including metrics related to sample holder, foam spacer, and standard wool abradant settings.

**Table A-2: Dimensions and other Constants related to Martindale Abrasion testing.**

<table>
<thead>
<tr>
<th>Martindale Abrasion Variables</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool abrasive fabric areal density, g/m²</td>
<td>195</td>
</tr>
<tr>
<td>Polyurethane foam thickness, mm</td>
<td>3 ± 0.01</td>
</tr>
<tr>
<td>Polyurethane foam density, g/m³</td>
<td>30 ± 1</td>
</tr>
<tr>
<td>Abradant mass, g</td>
<td>198.61</td>
</tr>
<tr>
<td>Abradant radius, mm</td>
<td>19</td>
</tr>
<tr>
<td>Abradant area, cm²</td>
<td>11.34</td>
</tr>
<tr>
<td>Abradant force, N</td>
<td>1.95</td>
</tr>
<tr>
<td>Net pressure on sample, kPa</td>
<td>1.72</td>
</tr>
</tbody>
</table>
Appendix 4: Supplemental Instructions for Modified 90° Peeling Test (Modification of ASTM D 6862-04 standard method for interfacial peeling strength for coated materials and fabrics)

Coated sample preparation steps: After removing coated nanofibers from electrospinning collection apparatus, place a 2” piece of adhesive laboratory tape (Kelly Scientific, Inc.) over top of nanofiber layer curl underneath edge of nanofiber layer to separate from fabric. Repeat this for fabric, placing piece of tape around it. Attach these extended “tongues” to the top and bottom jaws of the Instron device. Make sure while taping that there is adequate extra length of tape to be clamped onto by test jaws (at least 1”).

Figure A-3: Depiction of how nanofiber layer-fabric are peeled apart at 90° using modified peeling test. Lower fabric layer stays horizontal, and is attached to lower jaw in Instron test apparatus. In the figure the label $F$ denotes upward applied force, caused by moving jaw of test apparatus.
Table A-3: List of Dimensions and other constants related to Peel Testing.

<table>
<thead>
<tr>
<th>Peeling Test Constants Used</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric/nanofiber sample dimensions used for Instron tester:</td>
<td>8 X 2.54 cm</td>
</tr>
<tr>
<td>(Length X Width, cm)</td>
<td></td>
</tr>
<tr>
<td>Instron load cell resolution, N</td>
<td>± 5.00 N</td>
</tr>
<tr>
<td>Peeling (Extension) Rate, mm/min</td>
<td>50 mm/min</td>
</tr>
<tr>
<td>Length of Extension recorded for data, mm</td>
<td>&gt; 110 mm</td>
</tr>
<tr>
<td>Length of Extension, mm; this value was used for calculating peeling toughness (work, gf * cm);</td>
<td>100</td>
</tr>
<tr>
<td>**Note: start at x = 10mm extension, end at x = 110mm extension</td>
<td></td>
</tr>
</tbody>
</table>
Appendix 5: Supplemental SEM Images of Nanofibers

<table>
<thead>
<tr>
<th>Voltage, kV</th>
<th>15</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate, mL/hr</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>5%</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>6%</td>
<td><img src="image6" alt="Image" /></td>
<td><img src="image7" alt="Image" /></td>
</tr>
<tr>
<td>7%</td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
</tr>
<tr>
<td>8%</td>
<td><img src="image16" alt="Image" /></td>
<td><img src="image17" alt="Image" /></td>
</tr>
<tr>
<td>9%</td>
<td><img src="image21" alt="Image" /></td>
<td><img src="image22" alt="Image" /></td>
</tr>
<tr>
<td>11%</td>
<td><img src="image26" alt="Image" /></td>
<td><img src="image27" alt="Image" /></td>
</tr>
<tr>
<td>13%</td>
<td><img src="image31" alt="Image" /></td>
<td><img src="image32" alt="Image" /></td>
</tr>
<tr>
<td>15%</td>
<td><img src="image36" alt="Image" /></td>
<td><img src="image37" alt="Image" /></td>
</tr>
</tbody>
</table>