

## ABSTRACT

DAVIS, RACHEL LEE-TUCK. Durable Nanolayer Graft Polymerization of Textile Finishes: Waterproof and Antimicrobial Breathable Fabrics Via Plasma Treatment for Single Sided Treatments. (Under the direction of Dr. Ahmed El-Shafei and Dr. Peter Hauser).

Traditionally, chemical finishes are applied to textiles through a wet process which involved solvents, drying, and curing. One way that energy costs can be reduced while increasing quality of the product is through the use of plasma treatments to impart textile chemical finishes to fabrics. The purpose of this research was to use a nonthermal, atmospheric plasma treatment to impart a textile finish to a fabric surface that is both water repellent and antimicrobial. The water repellent treatment was single sided, so that the fabric is hydrophobic on the exterior of the garment while hydrophilic against the wearer's skin, allowing the fabric to be breathable and more comfortable. The results of this research will benefit the textile industry by demonstrating a process that enables the production of high quality products at a lower cost of energy using a more environmentally friendly process.

In this work, cotton/polyester blend fabric was treated with a water repellent treatment through activating the surface with plasma, depositing a vaporized fluorocarbon based monomer, (TG-10, Unidyne<sup>TM</sup>), then curing the finish with a second plasma exposure. The purpose of the first plasma exposure is to generate active free radicals on the surface which can react with the monomer, initiating free radical polymerization. The polymerization is completed through a second pass through the plasma, which allows the monomer to continue reacting to form a crosslinked network polymer nanolayer that is

covalently bonded (grafted) to the fabric surface. The treated fabric samples were then evaluated for water repellency and durability to laundering.

Once parameters were optimized to maximize the water repellent properties of the fabric, samples that showed the most effective water repellent treatment system were further treated with an antimicrobial agent. The antimicrobial treatment consisted of padding the fabric with a solution of diallyldimethylammonium chloride (DADMAC), a quaternary ammonium salt. Samples were padded with baths of different concentrations of DADMAC. The samples were then dried in an oven at low temperature (50°C), to prevent thermal curing, and then treated with a second plasma exposure of 10 or 20 seconds. The plasma treatment induced free radical polymerization of the DADMAC, causing a polymerized network to form on the fabric that should provide durable antimicrobial properties to the fabric. These antimicrobial properties were tested on *K. pneumoniae* and *S. aureus*.

The results found that the water repellent treatment via plasma induced graft polymerization was successful in lowering the surface energy so that the fabric is more hydrophobic. Medium levels of monomer flow and plasma exposure time resulted in the most repellent samples. The treatment was durable to laundering, although some functionality of the water repellent was lost. This may be due to surface abrasion or the fluorocarbon chains re-orienting themselves on the surface of the fabric during laundering. The durability of the finish may be increased through a plasma pre-activation treatment, thereby generating free radicals on the fabric surface so that the monomers can react with

the surface more efficiently.

The results of the antimicrobial tests has shown that the treated fabric reduced the activity of both gram positive and gram negative bacteria by more than 99.994%, demonstrating that the antimicrobial agent can function effectively in combination with the water repellent.

Future studies are suggested to include applying the antimicrobial agent before the water repellent finish, or dual applications with a single polymerization step. These procedural changes may increase the durability of the finishes, and may also increase the effectiveness of the water repellent on the antimicrobial treated fabric. In addition, crosslinking agents may be added to increase durability of the fluorocarbon finish.

Durable Nanolayer Graft Polymerization of Textile Finishes: Waterproof and Antibacterial  
Breathable Fabrics via Plasma Treatment for Single Sided Treatments

by  
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## **DEDICATION**

I dedicate this work to my husband, Michael, who supported me through everything. Also,  
to my daughter, Alaina, for giving me the hope to work toward our future.

## **BIOGRAPHY**

The author, Rachel Lee Tuck Davis, was born on July 21, 1985. Raised in Cary, NC with her parents and older brother Phillip, she graduated from Athens Drive High School in 2003 and attended college at North Carolina State University. In 2005 she married Michael Davis, and the couple welcomed their first child, Alaina Marie Davis, in 2009. In 2008 Rachel graduated with a degree in Polymer and Color Chemistry and became an Institute of Textile Technology fellow, pursuing a Master's Degree in Textile Chemistry. Upon completion of her Master's Degree, Rachel will continue her education at North Carolina State University by pursuing a PhD in Polymer and Fiber Science, continuing in the research field of atmospheric plasma treatments on textiles.

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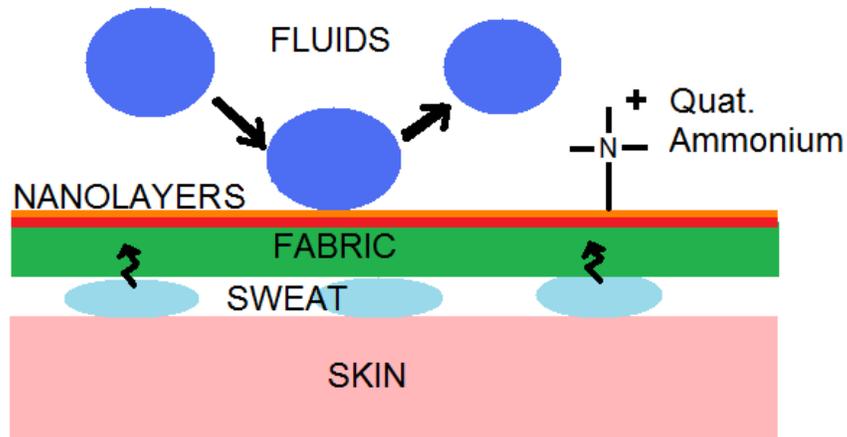
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## **Chapter 1 Introduction**

The purpose of this research project is to use non-thermal high-density plasma to induce free radical, graft polymerization on the surface of a fabric to produce a nanolayer of a functional finish. In this research project, there will be two layers, the first being a fluid repellent layer and the second being an antimicrobial/antiviral layer. The first layer will be graft polymerized and covalently bonded to the fabric while the second layer will be covalently bonded to the polymer of the first layer. Because of the covalent bonds, these layers will be durable and their functionality will be tested before and after simulated home launderings using standard American Association of Textile Chemists and Colorists (AATCC) tests.

End uses for this research include surgical gowns, as well as fleet uniforms. In professions that would require such attire, liquids and body fluids are likely to come in contact with the wearer, and thus both fluid repellency and antimicrobial activity are important. In addition, such professions often require long shifts, so the clothing would have to be comfortable. By applying the finish only to the outside layer, the inside layer is still hydrophilic and would absorb sweat, increasing the comfort of the garment. A schematic diagram showing a modified fabric against the skin is shown in Figure 1-1.



**Figure 1-1: Diagram of modified fabric layer against skin**

The first layer will be a C8 based fluorocarbon water repellent, and the second will be a quaternary ammonium antimicrobial agent. The fabric will be a 50:50 intimate blend of woven polyester:cotton fabric. A cotton/polyester blend was chosen due to the current interest in the industry of using cotton/synthetic blends for garments. Due to the mass production of such products, blending with more cost effective synthetic fiber is desirable.

Traditional textile wet finishing has the inherent problem of wastewater treatment/disposal, at an added cost to the processing. Utilizing plasma technology for textile finishing overcomes this problem, as there is no wastewater produced and no monomer is wasted. There is also the added benefit of reduced energy cost, as the fabric typically does not need a drying or curing step. These advantages of plasma finishing will benefit the textile industry by enabling the production of high quality products at a lower

cost of energy using a more environmentally friendly process. Also, the process can be used to produce fabric with unique properties, such as a hydrophobic face and a hydrophilic backing.

A nonthermal, atmospheric pressure glow discharge plasma will be used in this research. Thermal plasma is not suitable for textiles because the high temperatures damage the fabric, and low pressure and vacuum plasma is difficult to adapt to open-width continuous textile processing. The plasma will be applied to the fabric to generate free radical on the surface while maintaining the bulk properties of the fabric intact. Next, then the water/oil repellent monomer will be vapor deposited. A second plasma exposure will bring the free radical polymerization to a completion, causing the monomer to graft to the surface and self-crosslink, forming a functional polymer nanolayer. Then, a second nanolayer of a different monomer with antimicrobial properties will be applied by pad bath application. The antimicrobial agent used, diallyldimethylammonium chloride, is available in water solution and thus cannot be vapor deposited. Once the samples have dried, the layer will then be polymerized through plasma exposure.

This research will investigate the parameters of monomer flow rate (mL/min), plasma exposure time (seconds), and the effect of the plasma pre-activation treatment (seconds). The ultimate goal of this research is to develop a process for treating a fabric with both a durable water repellent finish and a functional antimicrobial agent.

## Chapter 2 Literature Review

There is a need for fabrics that are both water repellent and antimicrobial, while being comfortable against the skin. An important aspect of comfort is the ability of the fabric to transfer moisture through wicking or allowing the passage of water vapor. The human body regulates its temperature through a balance of heating and cooling. Passive heating is provided by metabolism, where calories are “burned” in an exothermic process which releases heat into the surrounding tissue. The body may also warm itself by shivering, in extreme cold conditions. Passive cooling is provided through the endothermic process of sweating. Moisture is moved from the body out onto the surface of the skin, where it evaporates. Evaporation, being an endothermic process, pulls heat from its surroundings. Thus, as the sweat evaporates, heat is pulled from the body, and the body temperature is lowered.<sup>1</sup>

The body’s ability to cool itself can be hindered if the sweat is not allowed to come in contact with air, where it may evaporate to fulfill its primary function. This may occur if the skin is covered with something, such as a clothing item. This can be compounded if the textile is coated or laminated to protect the wearer from exterior liquid contamination.<sup>2</sup> In order for the body to remain comfortable, the surface moisture must be transferred away from the skin. With textiles, water can be transferred from a surface in one of three ways. It can be absorbed into the fiber, diffused into the space between yarns, or moved through

capillary action along the fiber bundles.<sup>3</sup> Coating a fabric with a waterproof finish can obstruct this transfer, by sealing the yarn bundles and preventing the direct contact between fluid and fiber that is required for absorption to occur. This will lead to a buildup of sweat on the skin's surface and interfere with the body's natural cooling mechanism.

In order to produce a water repellent fabric which is also breathable, the repellent finish must be on a single side of the fabric. This layer of water repellency must also be thin enough to allow water vapor from the underside of the fabric to escape.

A fabric which is water repellent can be achieved through post-fabric formation finishing, which was traditionally carried out through textile wet processing. However, the rising costs associated with wet processing, as well as an increase in interest over environmental concerns, have led to research into alternative textile processing. Utilizing plasma technology to finish textiles is one way that the industry may overcome the shortcomings of traditional wet processing.

While the polyester content in a fabric blend give the yarns some hydrophobicity (water repellency), the overall fabric generally needs a surface finish in order to prevent water from entering the fabric structure through inter-yarn penetration. In addition, polyester is not oil-repelling, but there are some textile finishes that can impart both hydrophobicity and oleophobicity (oil repellency). The application of a second layer comprised of a quaternary ammonium compound will provide the antimicrobial properties

required of the finished product.

## **2.1 Textile Finishing**

Textile finishing is the treatment of a fabric with a chemical or mechanical finish to impart a desirable property or characteristic. Mechanical finishing uses a physical action, such as brushing, to change the property of the fabric. Chemical finishing uses the application of chemicals to bring about new properties, or improve upon existing characteristics of the fabric. It is typically carried out after the fabric has been prepared (desizing, scouring, and bleaching, as required), and dyed. Thus it is referred to as “finishing” because it is usually the last step in processing the fabric. Some textile finishes are done to improve dyeability of the fabric and thus are performed before the coloring step. Others, such as a permanent crease finish, are applied after the fabric is in a garment form.

Typical Chemical Finishes:

- Wrinkle resistant/ durable press
- Soil release
- Repellents (liquid, stain)
- Antimicrobials
- Fire retardants
- Softeners
- Hydrophilic treatment
- Hand building

- Antistatic
- Slip repellents
- UV protection
- Insect repellent

A chemical finish is chosen based on its suitability. This is determined by what properties the final product must have, what the starting fiber and fabric composition are and the ratio of cost to benefit of the finish.<sup>4</sup> A higher quality finish typically has higher costs associated with it. A lower quality finish may not have adequate properties and may have undesirable side effects. Cost includes factors like the availability of machinery, the floorspace required by the machinery in the processing plant, the operating and energy costs, as well as the cost of the chemicals, additives, and disposal of any waste. Newer technology may allow for lower operating costs, less floor space, and waste. However, the cost of the machinery may be higher, and the operators may need a higher skill level which would require higher salaries. Overall a balance must be made.

Undesired side effects of some finishes may be color change or degradation of the fabric. Some finishes use chemicals which may be harmful, either during processing and/or in the final product. If multiple finishes are being used, certain chemicals may not be compatible. Improving one property of a fabric may come at the cost of a decrease in another property, such as a wrinkle resistant finish that may decrease the fabric's strength. There may be environmental concerns surrounding a specific chemical used. Continued research is necessary to improve upon these textile finishes and to minimize the drawbacks.

### 2.1.1 Conventional Wet Processing

A conventional wet process follows the general scheme of padding on the necessary chemicals, drying, and if necessary, a curing step where the fabric is brought to high temperature to initiate a reaction. An optional step of washing and drying to remove any unreacted chemical may be included. The chemicals are typically in a water solution or suspension when they are padded on. The water is then removed during the drying step. One setup of a continuous wet finishing line consisting of a pad, dry, and cure step is shown in Figure 2-1.

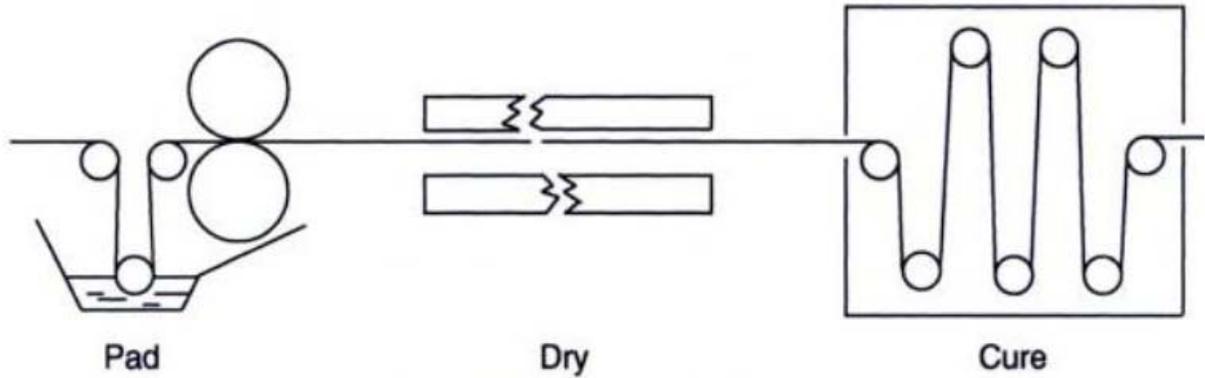


Figure 2-1: Schematic of a conventional finish application <sup>5</sup>

In Figure 2-1, the open-width fabric runs through rotating rolls which dip it into the

finishing bath and then pass the fabric through squeeze rolls which remove excess solution. It then passes through an oven which heats the fabric to evenly dry it. In the curing step, the fabric passes into a second oven, where it is brought to an even higher temperature to allow the reaction to take place. High temperature curing is required for many finish chemical reactions to take place, and the fabric must be thoroughly dry first or else the surface temperature of the fabric will not be able to rise above 100°C, the boiling temperature of the water in the fabric. If the fabric is not evenly dry before entering the curing step, then the finish will not be even as portions of the fabric react before others. Thus the drying step and curing step are often done in separate ovens. Because these large ovens require a high output of energy, technology that by-passes these steps would allow for a great savings, both monetarily and environmentally.

The advantages behind textile wet processing are that it uses relatively inexpensive equipment that is widely available to a textile processing plant. Use of existing equipment is cost effective, as a new piece of equipment does not have to be purchased, and workers do not require additional training to operate the equipment. Textile wet processing is a widely used and accepted method for applying finishes to fabric.

However, there are disadvantages associated with textile wet processing. The first disadvantage is the use of water or organic solvents. Water requires a cost, not only from the purchase of providing the water, but also in the removal of the water from the fabric

(drying) and the disposal of wastewater. Water prices are rising around the world because wastewater treatment prices are increasing significantly. One study found that between 1989 and 1997, the cost of wastewater disposal in the UK increased 100%.<sup>6</sup> Wastewater is expensive because it often contains chemicals which must be removed or neutralized before being released into the environment. Salts, surfactants, dispersants, emulsifiers, and other chemicals commonly found in textile wet processing wastewater have a high aquatic toxicity and thus are limited in the amount that can be released from a processing plant.<sup>7</sup> If organic solvents are used, they are often expensive and can pose a health hazard to the workers, as well as environmental concerns with the waste disposal. Many organic solvents used in textile wet processing have limitations placed on them.

Another disadvantage of textile wet processing is the potential for waste. Solutions used in finishing often contain auxiliaries such as dispersing agents to aid in the application of the finish. Many dry application methods use the pure chemical, which in the case of fluorocarbon water repellents, would be the fluorocarbon monomer. There is also a waste of the monomer itself. Monomer would be wasted when the leftover finishing bath is drained and the basin washed. Many dry application methods, such as plasma treatments, cause little to no monomer waste.

One study conducted by D&K Consulting in 1993 estimated a savings of approximately 65% of production costs if traditional wet processing was replaced with

plasma technology.<sup>8</sup> This study was done on pre-treatment of textiles; the desizing, scouring, and bleaching which can be done using a plasma treatment. The study estimated that the savings would equate to a pay-back period of three years on the cost of the plasma machine.

## **2.2 Plasma**

In the 1980's, low pressure plasmas were beginning to be used for surface treatments of polymer-based compounds. Shortly thereafter, the technology was applied to textiles as research groups picked up the cause and commercial manufacturers began manufacturing low pressure plasma systems for the purpose of textile surface treatment. Initial results showed promising benefits behind using this relatively new technology. Despite this, plasma treatments have been slow to catch on with the mainstream textile processing industry. One possible reason is that there are significant gaps in research knowledge on how to apply plasma treatments to overcoming the shortfalls of conventional textile processing.<sup>9</sup>

### **2.2.1 Plasma Basics**

If all matter is divided into four states, on an increasing scale of energy, then plasma would be considered the fourth state of matter. Solid, liquid, and gas would precede plasma, in order of increasing energy or temperature. Plasma is a state of highly energized

ionized gas, where the electrons have become separated from the atoms or molecules of a gas, leaving negatively charged electrons, positively charged atoms or molecules, and neutral species. Because stars, like our sun, are made of plasma, it is estimated that 99% of our universe is comprised of a matter in the plasma state.<sup>10</sup> Because of the charge carriers, it is electrically conductive. Although individual particles are charged, the overall charge of the system is zero, and thus plasma can be called a “quasi-neutral system.”<sup>11</sup> An everyday example of plasma is a flame from a very high temperature fire, where the gases in the fire have begun to ionize.

A plasma medium is generated when energy is applied to a volume of gas. The applied energy may be thermal, electromagnetic, or a high electric current. This energy causes the species of the gas to collide with one another, and if the energy is high enough, these collisions cause the atoms to break apart. The gas atoms or molecules break apart into ions, electrons, neutral species, free radicals, and other excited species, which make up the plasma medium. The excited state species are generally very short lived, and drop back down to the ground state by emitting a photon, causing a visible light.

Plasmas use electron collisions to generate a high density of free radicals. These species have the ability to activate the surface of a fabric substrate without affecting its bulk properties. With higher densities of plasma, there are more free radicals, and thus more of the surface is functionalized. Thus, high density plasma is desirable. Figure 2-2 shows how

different plasma technologies produce plasma with different densities. Knowledge of this is important when selecting a technology for a specific application.

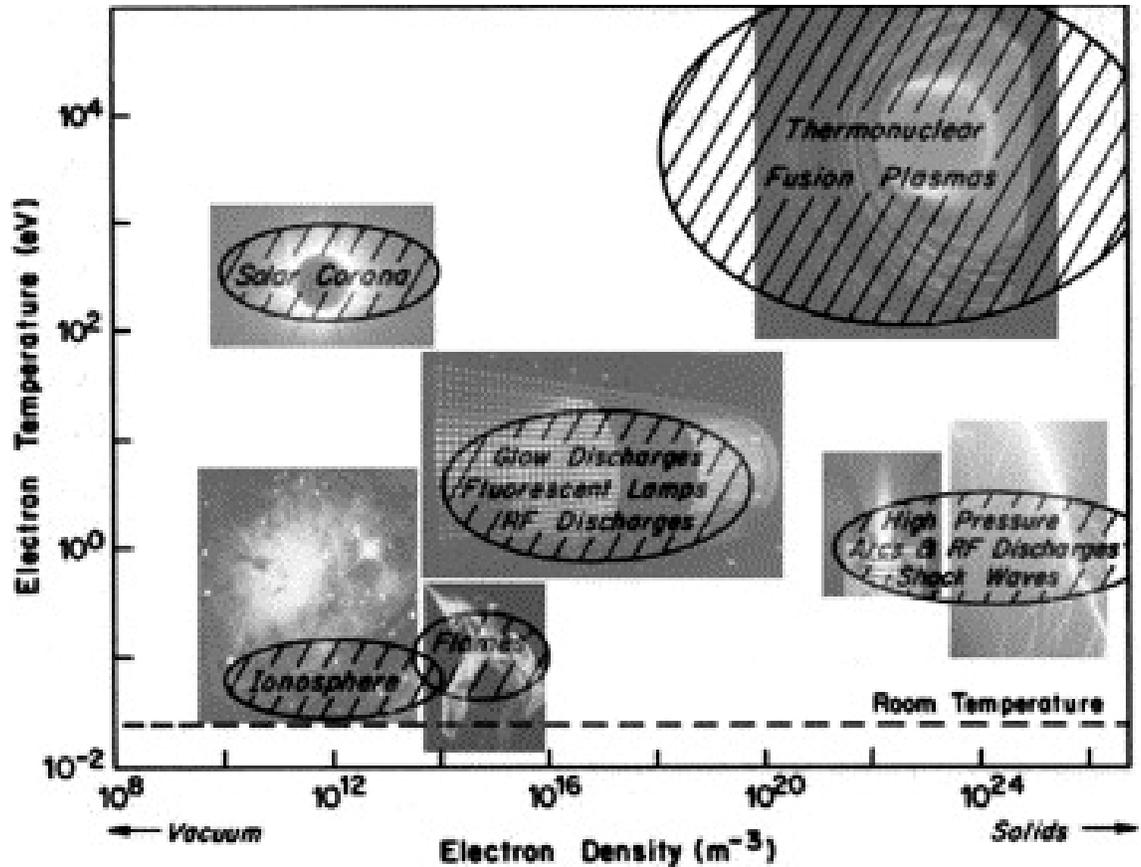


Figure 2-2: Different plasma classifications in relation to the electron temperature and electron density<sup>12</sup>

Plasma can be classified by temperature, pressure, ion density, or by the technology used to create it. Thermal plasmas are generated at high temperature, and are useful in

chemistry applications such as inductively coupled plasma (ICP), which can be used to identify metals present in a substance. The temperature used for analytical ICP is very high, in the range of 600 to 8,000 K.<sup>13</sup> By contrast, nonthermal plasmas can be conducted at room temperature. With nonthermal plasma, this can be conducted at room temperature because although the electrons are very “hot”, the air itself remains at ambient temperature. This is due to the plasma’s ability to exist far from thermodynamic equilibrium. Hence, thermal plasma is referred to as local thermodynamic equilibrium (LTE) plasmas, and non-thermal plasma is referred to as non-local thermodynamic equilibrium (non-LTE) plasmas.

As can be seen in Table 2-1, LTE plasma heavy particle temperature ( $T_h$ ) is the same temperature as the electron temperature ( $T_e$ ). The majority of the mass is made up by the heavy particles, and so the temperature of the bulk is governed by the temperature of the heavy particles. Highly excited electrons in the plasma state are very high temperature, and this causes the bulk of the plasma in LTE plasmas to also be at very high temperature. By contrast, non-LTE plasma does not follow thermodynamic equilibrium and the heavy particle temperature is much lower than the electron temperature. This has the benefit of allowing the bulk to be at a lower temperature than the electrons. The bulk of the plasma can be as low as room temperature (300 K). The downside is that the electron density tends to be lower with non-LTE plasmas.

**Table 2-1: Characteristics of LTE and non-LTE plasmas**

	LTE plasmas	Non-LTE plasmas
Current name	Thermal plasmas	Cold plasmas
Properties	$T_e = T_h$ High electron density: $10^{21} - 10^{26} \text{ m}^{-3}$ Inelastic collisions between electrons and heavy particles create the plasma reactive species whereas elastic collisions heat the heavy particles (the electrons energy is thus consumed)	$T_e \gg T_h$ Lower electron density: $< 10^{19} \text{ m}^{-3}$ Inelastic collisions between electrons and heavy particles induce the plasma chemistry. Heavy particles are slightly heated by a few elastic collisions (that is why the electrons energy remains very high)
Examples	Arc plasma (core) $T_e = T_h \approx 10,000 \text{ K}$	Glow discharges $T_e \approx 10,000 - 100,000 \text{ K}$ $T_h \approx 300 - 1000 \text{ K}$

Textiles are temperature sensitive materials which melt or degrade at high temperature. For this reason, LTE plasmas are not appropriate for use in textile applications. Non-thermal plasma prevents degradation of the fabric which occurs at the high temperatures required of thermal plasmas. The intended textile finish can be applied in vapor or aerosol form and then passed through non-thermal plasma for a curing step.<sup>14</sup>

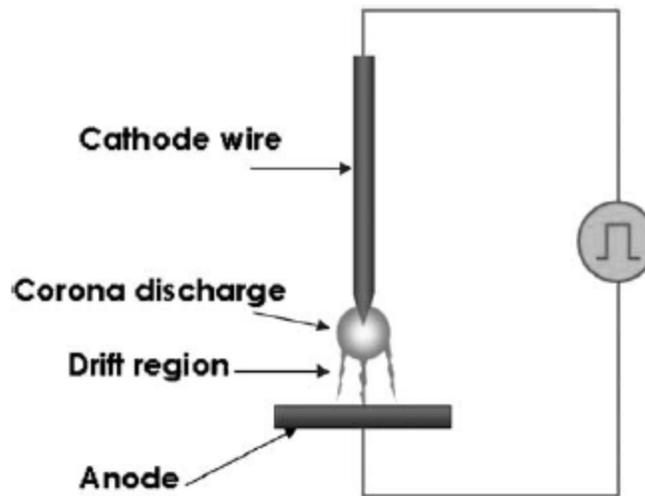
Plasma can be classified by the pressure under which it is generated. There is low pressure plasma, which is conducted in vacuum, atmospheric pressure plasma, and high pressure plasma. Because low and high pressure plasmas must be conducted in a pressurized chamber, they are typically not suitable for continuous processes or for large surface area treatments.

Plasma is sometimes classified by the resulting electron density. High density plasma produces a high density of free radicals, while low density plasma produces fewer active species per volume. Because the active species initiate reactions, high density plasma reacts faster and with greater yield than low density plasma.

### **2.2.2 Atmospheric Plasma Categories**

Finally, plasma can be further categorized by the specific technology used to create it. There are three main kinds of non-LTE plasma used at atmospheric pressure: corona plasma, dielectric barrier discharge (DBD) plasma, and glow discharge plasma.

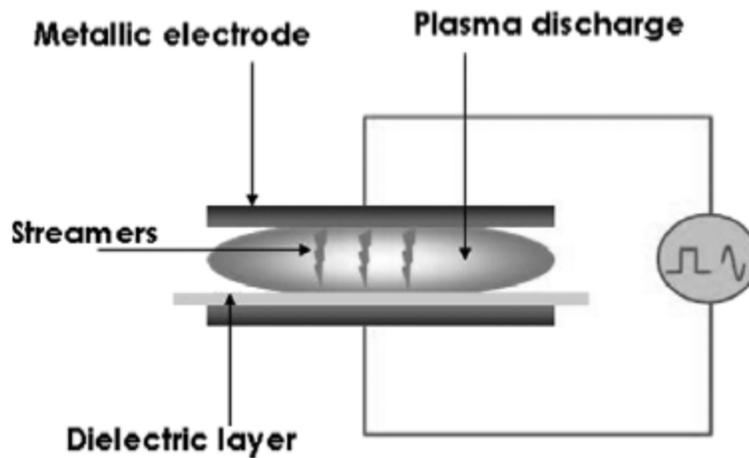
Corona plasma is characterized as occurring at a localized area around a sharp tip (cathode wire) in a highly nonuniform electric field.<sup>15</sup> As it can be seen in Figure 2-3, the discharge is present only at the tip of the wire, and drifts down onto the substrate, which would be on the anode.



**Figure 2-3: Scheme of corona discharge**

Corona plasma is well established and is a relatively simple process in that it is conducted at atmospheric conditions, usually with air as the reagent. However, it lacks the strength to penetrate deeply into textile substrates and requires narrow electrode gaps. Due to this, corona plasma is only suitable for thin, loose materials. Due to the narrow discharge and drift region, the treatments tend to lack uniformity.

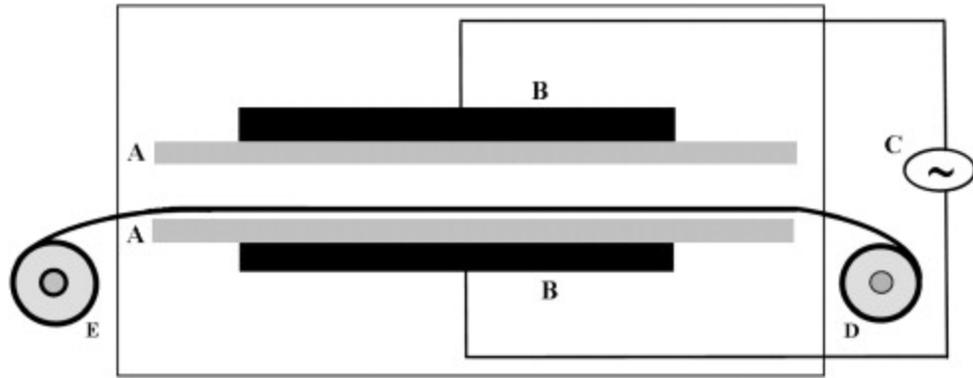
DBD plasma uses an insulating dielectric barrier between the electrodes.<sup>16</sup> The gap between the two electrodes is relatively narrow, and the plasma gas flows in the space in between. A scheme for this is shown in Figure 2-4.



**Figure 2-4: Scheme for dielectric barrier discharge**

Electrons from high voltage build up on the dielectric surface. The discharge then occurs as a glow or as filament in the form of mini-discharges, aided by randomly distributed streamers. These streamers are fine stainless steel wires arranged as a brush, which directs the discharge. Numerous, random arcs formed by DEB plasma can cause uneven treatment on textile surfaces.

The most promising form of plasma used for applying textile finishes is glow discharge plasma. Also known as atmospheric pressure glow discharge (APGD), it has the benefits of uniform treatment usually associated with vacuum plasma, but is conducted at atmospheric pressure.



**Figure 2-5: Scheme of Atmospheric Pressure Glow Discharge<sup>17</sup>**

As can be seen in Figure 2-5, APGD typically consists of two parallel plates (A and A), two electrodes (B and B), a power source (C), and a means of feeding the substrate through, such as feed and take up rollers (E and D). Parts A and B may be combined into a single electrode plate with many technologies. APGD is the type of plasma that is used to conduct the research outlined in this thesis.

### **2.2.3 Plasma Treatment on Textiles**

Plasma treatment on textiles provides the advantages over wet processing of lower cost, less energy consumption, less labor, speed of production, and less pollution. Moreover, it offers the potential for higher quality results. Because plasma treatment only affects the surface of the substrate, it can impart a functional finish without changing the substrate's bulk properties.<sup>18</sup> Instead, a nanolayer of a finish can be applied to only the substrate surface. The properties of this nanolayer can be altered by the chemistry

selected, and the thickness of the nanolayer can be carefully tailored by controlling the variables of the plasma treatment and the monomer flow rate (mL/min). Nanolayer thickness can be controlled through process parameters such as the plasma power, the precursor flow rate, and the speed at which the substrate moves through the plasma system.<sup>19 20</sup>

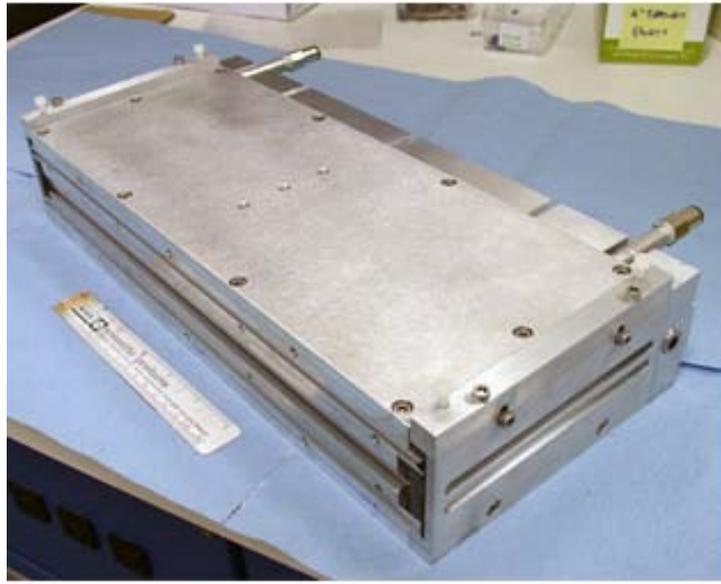
Plasma has been studied for use in pretreating textiles by removing size, scouring, and even bleaching.<sup>21, 22</sup> Etching of fabrics with functional groups from a gas based plasma treatment can impart functionality, such as grafting polar surface groups to impart hydrophilicity on a hydrophobic fiber surface.<sup>23 24</sup> There have even been studies conducted on greige fabric treated with plasma. The intent of the research was to allow greige fabric to be dyed without the requirement of fabric preparation (desizing, scouring, and bleaching). The research found that exposing a greige fabric to plasma altered the surface so that it became hydrophilic. The increased hydrophilicity was explained through the formation of polar groups on the fabric surface during plasma treatment, as confirmed by Fourier Transform Infra-Red (FTIR). This change allowed the surface to become more dyeable.<sup>25</sup>

#### **2.2.4 APJeT® Inc. Atmospheric Pressure Plasma Jet (APPJ)**

The source of plasma used in this research is an APPJ, also known as atmospheric pressure plasma reactor (APPR) from APJeT® Inc. This piece of technology was developed at

Los Alamos National Laboratories in collaboration with the University of California, Los Angeles. The current device used in this research is located at North Carolina State University Centennial Campus. The technology is unique in that it uses radio frequency (RF) electric fields to generate a non-thermal, atmospheric pressure glow discharge which is homogenous, stable, and up to 1,000 times more efficient with generating active species than traditional atmospheric plasma methods like corona or DBD.<sup>26</sup>

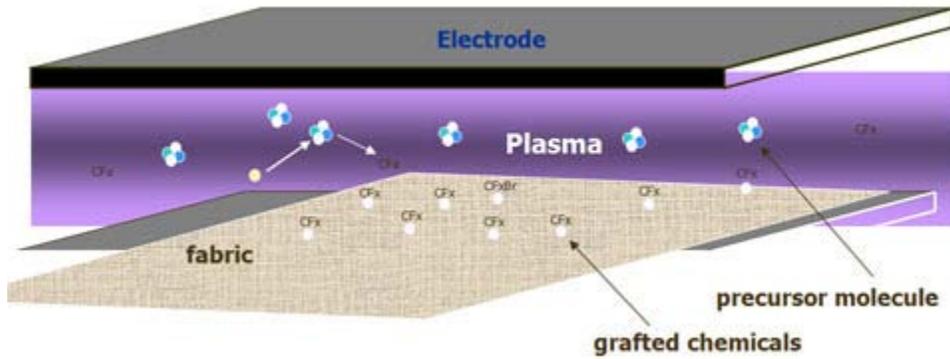
The basic design of the instrument is a capacitatively coupled device with two coaxial electrodes. By using two parallel flat plates, a large surface area may be treated, as seen in Figure 2-6. Gas, which may be helium (He), nitrogen (N), or argon (Ar) flows between the electrode and is activated by the plasma. The electrodes are powered by RF power, creating a electromagnetic field in the gap between them. This field causes the gas to break down, ionizing, and create a stable glow plasma. These active species then react with the surface of the substrate, or with chemical species on that surface, initiating the desired chemical reactions.



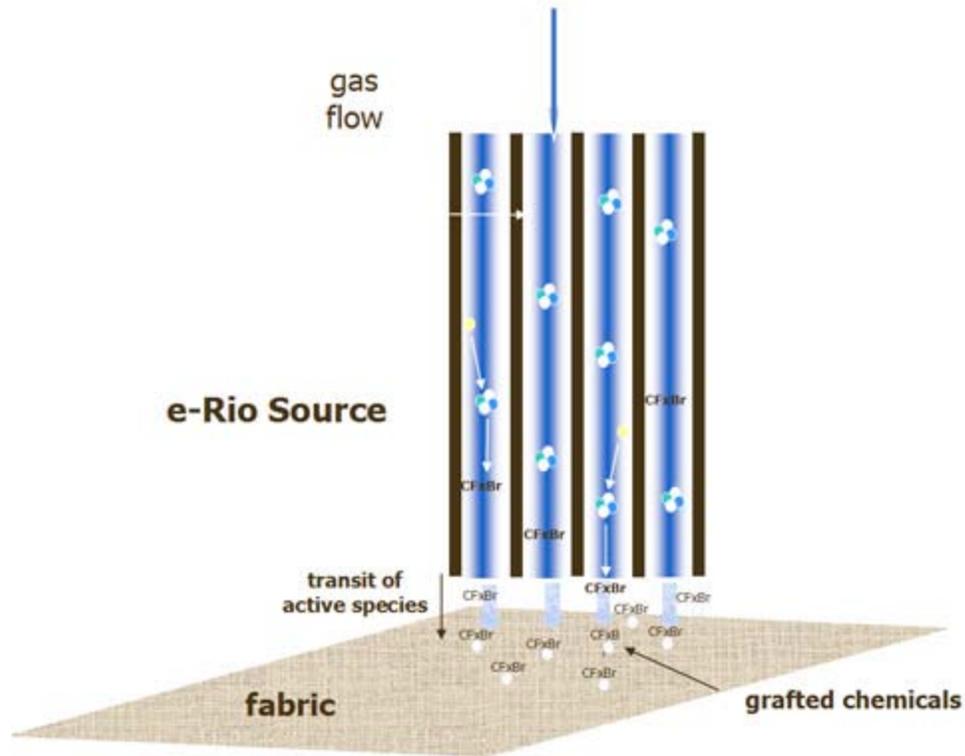
**Figure 2-6: Flat Jet with Parallel Plate Geometry**

This process can be either in situ or downstream. With the in situ, the substrate is adhered to the bottom electrode, and the plasma is generated within the same field as the fabric, as can be seen in Figure 2-7. However, this can have problems with impurities in the plasma field causing arcing. Arcing exists when the atmosphere in the plasma chamber ignites, and is highly thermal. This can cause damage not only to the substrate, but also to the equipment of the AAPR. Thus, every measure is taken to avoid arcing. One such measure was the upgrading of the AAPR at North Carolina State University to a new downstream model. In the downstream model, the plasma is generated in a chamber above the stage, then pushed down onto the fabric using the feed gas flow, as can be seen in Figure 2-8. This image shows the patented e-Rio source which was developed by APJeT

Inc. The potential drawback is that the active species of the feed gas are short lived, and this might reduce the amount of active species that reach the fabric surface. For this reason, a gas with a longer active life, such as ammonia, may be added into the feed gas in small amounts (1-3%).



**Figure 2-7: In-Situ process method**



**Figure 2-8: Downstream Process Method with e-Rio Source developed by APJeT Inc.**

The standard method of treating a textile with a plasma finish is to first pass the fabric under the plasma with only the feed gas mixture on. This is to activate the surface of the substrate with active free radical sites. Then the monomer is deposited on the fabric. The fabric is mounted on a stage equipped with a chiller, which continuously cools the surface so that the buildup of heat does not cause arcing in the plasma chamber, and to aid in the deposit of monomer. Monomer is typically deposited in a vapor form, where the pure monomer enters an evaporation chamber, where it is heated above the boil. The

monomer vapor is then pushed down onto the fabric using an inert gas such as argon. Because the fabric has been cooled on the stage, the monomer condenses on the surface. This is then passed through the plasma a second time for the curing step. During this curing step, free radical species generated by the plasma initiate free radical polymerization of the monomer.

## **2.3 Water Repellents**

Water repellency is by definition the ability of a surface to resist wetting by applied liquid water. This is usually different from a waterproof coating, where the surface is completely covered with a coating which is impermeable to water, water vapor, and air. However, water repellent fabrics are often limited in applications because they may not perform well under hydrostatic pressure, such as the forces that a textile would experience during a rain shower.

### **2.3.1 Wetting of Textile Substrates**

Wetting of a textile involves the processes of immersion, capillary sorption, adhesion, and spreading.<sup>27</sup> Wetting is a thermodynamic process and thus governed by the laws of free energy. When wetting occurs, the solid-air interface is replaced with a solid-liquid interface, and the air space in between the surfaces is removed. This process can be

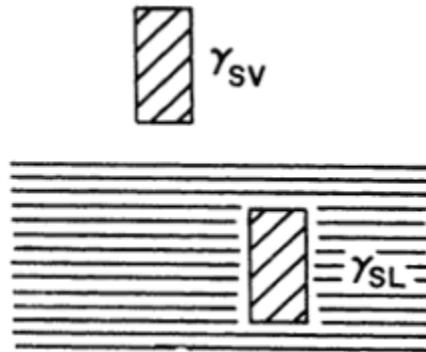
described in thermodynamic terms as shown in Equation 1, where  $\gamma$  is the surface tension, and  $A$  is the surface area.  $F$ , the sum of interfacial energies, can then be defined as:

$$F = A_S \gamma_{SV} + A_L \gamma_{LV} + A_{SL} \gamma_{SL} = \Sigma A \gamma \quad \text{Equation 1}$$

If the change in  $F$  during the process of applying water to the surface is negative, then wetting will occur spontaneously, as demonstrated by Equation 2.

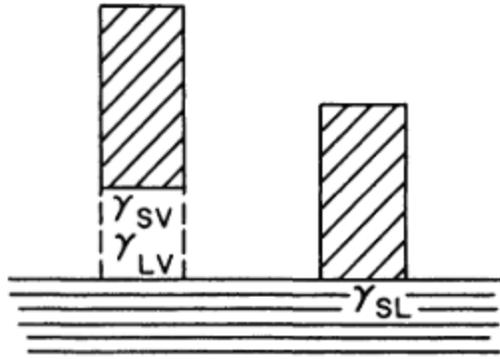
$$\Delta F = F_2 - F_1 = \Sigma(A \gamma)_2 - \Sigma(A \gamma)_1 \quad \text{Equation 2}$$

There are primary three processes involved when a textile surface is wetted with water. They are immersion, adhesion, and spreading.<sup>28</sup> The process of replacing the solid-air interface with a solid-liquid interface occurs during immersion, as shown in Figure 2-9.



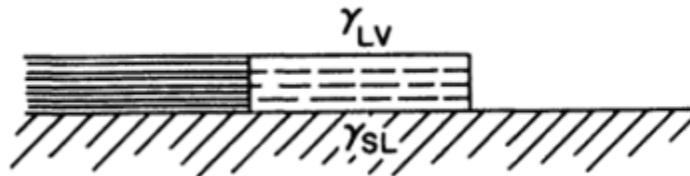
**Figure 2-9: Immersion of the Solid Textile in Water**

The second step is adhesion where the liquid and solid come into full molecular contact. This is shown in Figure 2-10.



**Figure 2-10: Adhesion between Solid Textile and Water**

If the liquid then flows across the surface of the textile, then spreading has occurred. The area of the solid-liquid and liquid-air interfaces increases.



**Figure 2-11: Spreading of Water on a Textile Surface**

Spreading force,  $\vec{S}$ , can be defined as shown in Equation 3:

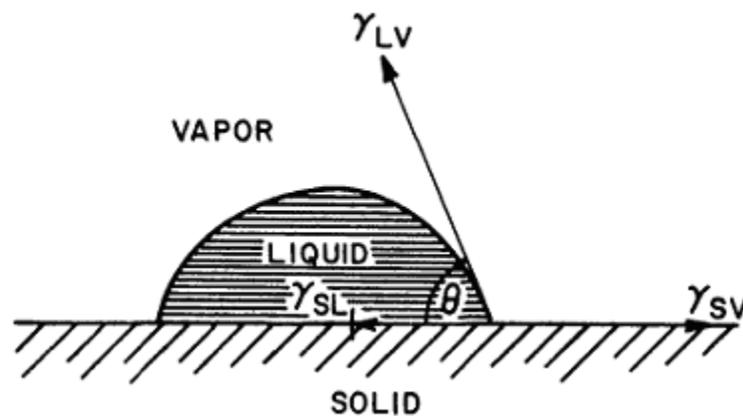
$$\vec{S} = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos \theta \quad \text{Equation 3}$$

Where S represents the solid, V represents the vapor, and L represents the liquid phases. At equilibrium, Equation 3 is written as Equation 4:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

**Equation 4**

If spreading does not occur when a drop of liquid is placed on the fabric surface, then a contact angle can be observed. If the drop maintains a relatively constant shape and size, then the angle,  $\theta$ , can be measured. Figure 2-12 shows this relationship, where the inside angle is the contact angle  $\theta$ .



**Figure 2-12: Contact angle between Liquid and Textile Surface**

This is known as the contact angle or equilibrium contact angle, and is a property of the surface tensions. This relationship was first quantified by Thomas Young in 1805.<sup>29</sup> His theory can be summarized by Equation 5:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

**Equation 5**

This relationship only holds true for perfect surfaces, which are smooth, non-

deformable, and are impermeable without capillary spacing's. A good repellent is one that lowers surface energy, so that the equilibrium contact angle increases.

For a surface to be considered hydrophobic, the contact angle must be at minimum 90°. For the surface to be considered superhydrophobic, the contact angle must be at least 150°. Some surfaces are so hydrophobic so that water does not adhere to the surface at all, and is able to freely roll on the surface, similar to a rain droplet rolling on the surface of a leaf. This effect is called the lotus effect, and is often associated with self-cleaning surfaces which are highly texturized to be superhydrophobic, such as a leaf from a lotus plant.<sup>30</sup> This effect is found in nature, but can be recreated on textile surfaces using water repellent finishes. One such article focused on the use of silicone based water repellent finishes to alter the surface of a polyester fabric so that it was superior in hydrophobicity than the lotus leaf.<sup>31</sup>

### **2.3.1 Chemistry of Water Repellents**

A water repellent for textiles is anything that lowers the surface energy of the textile so that water will not wet it. It must be something that can be applied to either the surface of the textile for a single sided treatment, or used as a bulk finish, where the entire depth of the fabric would receive the treatment. The finish may or may not be durable.

The chemical nature of a finish can be predicted using the concepts of surface energy and contact angle measurements. According to the concepts laid out by Zisman,<sup>32</sup>

water repellency requires the repellent to have a lower surface tension than water. Water's surface tension ( $\gamma_{LV}$ ) at standard room temperature is 72.0 dyne/cm. If a fabric's critical surface energy ( $\gamma_C$ ) is near or higher than the surface tension of an applied liquid, then there will be spreading of the liquid. The average surface energy for cotton fabric, by contrast, is about 200 dyne/cm. Thus water will readily wet out untreated cotton fabric. To be effective at repelling water, a hydrocarbon based water repellent needs to have a surface energy less than 30 dyne/cm or 24 dyne/cm for a polysiloxane finish. A fluorocarbon based repellent finish with a surface tension of 15 dyne/cm or less will adequately repel both water and hydrocarbon oils.

A water repellent finish may impart water repellency to a fabric surface through lowering the surface energy, by creating an impermeable barrier, or by providing an outward facing surface that is hydrophobic and will repel water. For example, a repellent finish which can orient itself on the fabric so that hydrophobic hydrocarbons are facing up will provide the fabric with a water repellent surface.

A fabric's ability to repel liquids depends on its surface roughness, chemical composition, and critical surface tension. In order to be liquid repellent, a fabric must have: a tight fabric construction comprised of fine yarns, be free of impurities, especially residual surfactants, and have a uniformly applied chemical finish which lowers the critical surface tension to below the critical surface tension of the intended liquid.<sup>33</sup>

### 2.3.2 Classifications of Water Repellent Finishes

Historically, water repellent textiles were produced by applying a hydrocarbon material, commonly a soft wax such as paraffin, to the surface of the fabric. They were applied by heating the wax and applying it in the molten state, or by emulsifying the wax in organic solvents to be used for application. This would give the fabric an outer layer of hydrophobicity. However, this basic formulation had poor durability, so various crosslinkers and additives were used to attempt to increase durability of the finish.

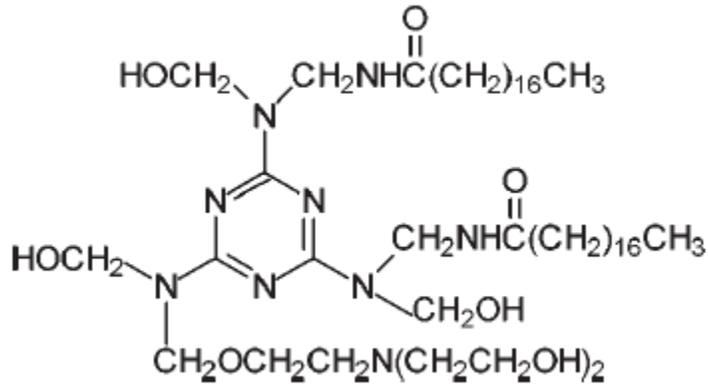
In the 1880's, water repellent finishes were used on cotton canvas using a metal salt bath. The fabric was soaked in an aluminum acetate solution for a long dwell time, typically 24-48 hours. An alternative to aluminum acetate was aluminum formate. Aluminum formate did not discolor fabric, which was a problem with aluminum acetate finishes.

Solvent applied rubbers are another category of solution based water repellent finishes used historically. There were several problems associated with this technology. Applied rubbers tended to get stiff and crack in the cold wintertime. In addition, the rubber coating would be pierced by the needle as the garment was being sewn together, leaving holes for rainwater to enter. Then in the warm summertime, the garment would be stuffy and uncomfortable to wear. However, the solvent rubber applied raingear was popular enough that in some parts of the world, rain jackets are still known as "Macs" named after the inventor of the applied solvent rubber, Charles Macintosh.

Another solution-based water repellent was paraffin wax emulsion. The paraffin wax is emulsified in water with stearic acid salts. Once emulsified, the waxy portion of the molecules would be hydrophobic and repel water while the fatty acid portions would be attracted to the fabric surface. However, the stearic acid applied paraffin wax had very poor durability. In addition, many of the by-products of the application process were toxic. Overall this process fell out of favor for use in garment finishing.

A semi-durable water repellent finish has been achieved through organo-metallic complexes utilizing chromium or aluminum chemistry. The most popular of these products was Quilon<sup>®</sup>, a marketed solution from Du Pont. Quilon<sup>®</sup> was a chromium-based compound which imparted a high initial water repellency without sacrificing the hand of the fabric. However, it caused a green-blue discoloration of the fabric which greatly limited its use. It is commonly used in tents, awnings, and outdoor covers. In these applications, water durability is required, but durability to laundering is not required as the products do not typically require laundering. In addition, the green-blue discoloration is not a problem in such applications, as a wide range of colors is rarely requested.

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. The structure is shown in Figure 2-13.

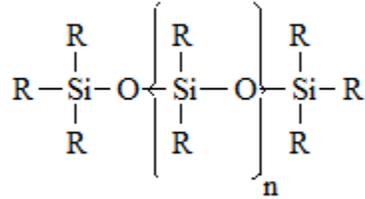


**Figure 2-13: Melamine Formaldehyde + Stearic acid Water Repellent**

The resulting compound contains the hydrophobic stearic acid portions, while the remaining methylol groups are free to react with cellulose (cotton), or react with other compounds to form a crosslinked network. This gives the finish added durability. Their ability to crosslink has allowed melamine based repellents to be used as extenders for fluorocarbon repellents. However, a disadvantage of this class of water repellents is the potential to release formaldehyde, which is a suspected human carcinogen. Formaldehyde may be released both during processing and when the product is being used by the consumer. Due to increased public awareness and concern over this potential hazard, increased regulations are restricting the use of these types of finishes.

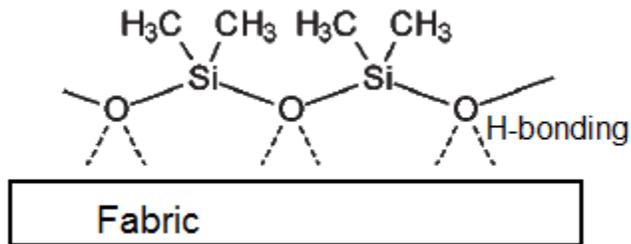
Silicone based water repellents have been made based off of polysiloxanes. The backbone is  $\text{-O-Si-O-Si-}$  with a basic structure shown in Figure 2-14. Here, the R groups may

by hydroxyl, alkoxy, alkyl, or simply hydrogen atoms.



**Figure 2-14: Polysiloxane Basic Structure**

Commercially available silicone- based water repellents are generally block copolymers comprised of monomers with different R groups, but still following the same basic structure with the same backbone. A common repellent is polydimethylsiloxane, which would be the structure shown above with both R groups being methyl groups.



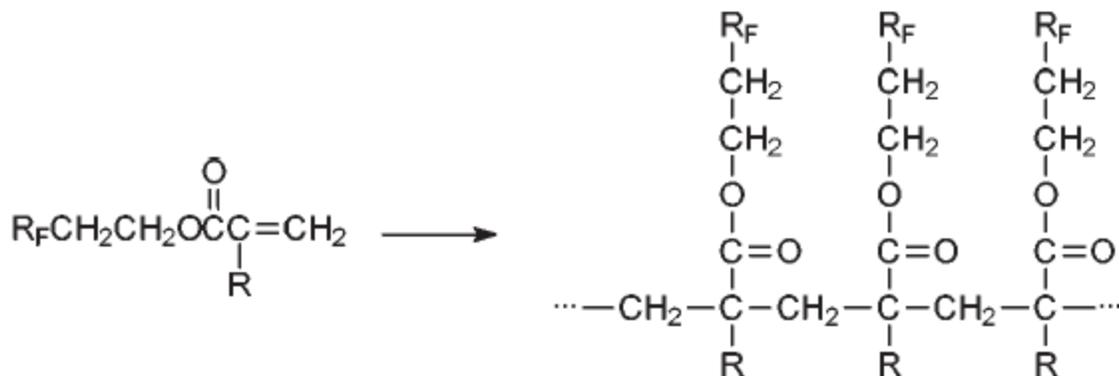
**Figure 2-15: Polydimethylsiloxane Hydrogen Bonding with Fabric Surface**

As can be seen in Figure 2-15, hydrogen bonding occurs between the ether groups on the polydimethylsiloxane and the fabric surface, giving it some durability. The methyl groups are thus oriented up, providing a hydrophobic surface facing outward. This orientation is usually aided through the use of a metal catalyst.

Silicone based water repellent finishes are more durable than waxes or melamines, but the price is higher. However, it requires a relatively small add-on, so less chemical is used. In addition, silicone based treatments give fabric a soft hand and improves the sewing performance of the fabric. Along with the higher price, another disadvantage of silicone based water repellents is the poor abrasion resistance.

Silicone based repellents are highly effective at reducing the surface energy of a textile, but another class of repellents is even more effective. Fluorocarbon based repellents have the lowest surface energy of all current textile finishes. The resulting surface energy is low enough to repel oil as well as water.

Fluorocarbon repellent finishes are formed by modifying an acrylic or urethane type monomer with a perfluoro alkyl group. The monomer can then react either with itself to polymerize, or with crosslinking extenders to form a polymer network. In some cases the monomer may even react with a polymer surface.



**Figure 2-16: Polymerization of a Fluorocarbon Repellent**

The polymerization of a fluorocarbon repellent is shown in Figure 2-16. The perfluoro alkyl chains, which range in length from 6 to 12 carbons, are extremely hydrophobic and oleophobic, and provide repellency. Traditionally, a fluorocarbon finish is applied to the textile through a pad, dry, cure process where the finish is applied in emulsified polymer form. The heat step causes the polymer film to become oriented so that the CF chains are crystallized in such a way as to maximize repellency. However, this orientation can be disrupted by laundering, and a new heat treatment must be applied to re-establish the high repellency. However, a typical consumer laundering regime that includes either tumble drying or ironing will fulfill this requirement. In addition, there are new fluorocarbon repellent treatments that do not require a repeating heat step after laundering, and are called laundry-air-dry, or LAD fluorocarbon treatments.<sup>34</sup>

Fluorocarbon based repellents have been shown in past research to be compatible with other textile finishes. In one paper, a fluorocarbon based water repellent was modified with a multi-epoxy to produce a fabric that was both water repellent and durable press. The results found that the fabric was both durable press and superior with oil repellency, making it suitable for stain repellent products.<sup>35</sup> This treatment consisted of a single compound being applied rather than two separate treatments for dual functionality.

Fluorocarbon repellent treatments have the advantage of very high repellency at relatively low percent add-on (usually less than 1% owf). However, they are high cost and there is a potential environmental concern about fluorocarbon derivatives. Certain fluorocarbon finishes, especially those consisting of 8 carbons in the perfluoro alkyl chain, can degrade to form perfluorooctanoic acid (PFOA). PFOA is of environmental concern because it bioaccumulates.<sup>36</sup> The EPA has taken measures to limit the use of PFOA's and PFOA precursors in the industry.<sup>37</sup> Thus, there has also been research into the potentially harmful effects of such compounds, which found that mice have adverse neurobehavioral responses to exposure.<sup>38</sup> Research is currently being conducted to find an alternative, such as a fluorocarbon with only 6 carbons in the perfluoro alkyl chain, which has similar water repellent characteristics.<sup>39</sup>

### **2.3.3 Plasma Water Repellents**

Using plasma to impart water repellent treatment in textiles has several key

advantages over traditional methods. In addition to the advantages previously listed for plasma treatments, such as energy savings and lack of waste water concerns, there is the advantage that plasma treatments furnish thin layer finishes. These layers are usually in the range of angstroms to nanometers ( $10^{-10}$ - $10^{-9}$ m) in thickness. In addition, it opens the field to garment processing so that not only the fabric could be made waterproof, but also the seams and fasteners. This would increase the ability of the garment to protect the wearer from rain or other water exposure.

A challenge facing the prospect of using plasma for water repellent treatments is potential for the plasma to degrade, as well as polymerize. Long, often complex chains are required function as a water or oil repellent, and these chains could be disrupted by the plasma ionization. Refined processing techniques have to be tailored to the specific chemical in order to achieve a cured finish without damaging the functional groups. Another challenge is the cost of the machinery and the potentially slower line speeds that are required for plasma treatments. With consumer textiles, lower price is generally more important than fabric functionalism when assessing value.

One study conducted on using plasma to apply water repellents used a fluorocarbon based repellent. In this instance, the intention of the plasma treatment was to increase durability of the finish rather than replace the application method. Untreated acrylic fabric samples were exposed to a plasma treatment using an atmospheric pressure plasma system

provided by APJeT. He gas was used in conjunction with a small portion of O<sub>2</sub> gas to increase functionality. The samples were then treated with a perfluoroalkyl acrylate copolymer emulsion with added methoxymethyl melamine resin as cross-linking agent, which was applied to using a traditional pad-dry-cure method. The results showed that plasma pretreatment of the fabric increased the long term laundering durability of the water repellent finish.<sup>40</sup>

A different study attempted to use plasma to introduce a water repellent finish to a polyester textile substrate by injecting a fluoropolymer directly into the plasma as it was being generated in DBD plasma. The study employed the use of nebulizers which injected an aerosol of fluoropolymer directly into the discharge, where it was ionized and atomized. The intention was that the plasma would activate the polymer so that it would readily react with the surface of the fabric. The paper found that while the fluoropolymer was activated and grafted to the surface enough to provide the surface with some hydrophobicity, it was not sufficient to create a truly water repellent surface. The assumption is that the aerosol atomization treated the surface with too small amount of fluoropolymer to create good functionalities.<sup>41</sup>

Another water repellent plasma treatment study similarly used fluorochemical directly in the feed for the plasma, but used CF<sub>4</sub> rather than a fluoropolymer. The intention of this study was to roughen the surface of a polystyrene surface by etching it with the

fluorocarbon. Samples etched in this manner were then evaluated alone and evaluated as a pretreatment for substrates which were then treated with a fluoropolymer based water repellent. The study found that the plasma treatment increased the hydrophobicity of the surfaces and, as a pretreatment to a fluoropolymer water repellent treatment, it increased the superhydrophobicity of the substrate.<sup>42</sup>

Surface water repellency is affected by both the chemical nature of the surface and the texture of the surface. With this in mind, one study sought to use plasma to deposit a thin polymeric film in a texturized manner, so that the surface topography was controlled as well as the chemical properties. Using plasma etching, the roughness of the surface was controlled to impart either a superhydrophobic or a superhydrophilic finish. This treatment was applied to both smooth surfaces and relatively rough surfaces, using silicone substrates. The results show that the treatment functionality was independent of the underlying topography, which shows promise for treating a wide range of substrates.<sup>43</sup>

Plasma treatment has also been studied as a way of imparting both water repellent and a secondary functional finish. In one study, a water repellent was combined with a flame retardant, which was then applied to a fabric substrate using glow discharge plasma. In this study, two monomers, one for a flame retardant and a fluorocarbon for water repellency, were mixed and applied in a bath before using plasma to cure the finishes simultaneously, which resulted in fabric that was both water repellent and flame

retardant.<sup>44</sup> However, plasma has not been previously researched to the author's knowledge as a means to apply two separate layers for a bifunctional finish on a textile surface.

## **2.4 Antimicrobials**

Antimicrobial finishes are a section of textile finishing that is growing in interest and importance. Not only can they limit the growth and prevent transmission of disease-causing pathogens and infectious bacteria, but they can reduce odor-causing bacteria as well. For instance, a pair of socks treated with an antimicrobial finish will not promote the growth of bacteria which will cause foot and shoe odor. In addition, antimicrobials can reduce the growth of discoloring mildew on textile substrates which may come in contact with moisture on a regular basis, such as shower curtains or patio cushions. This mildew is not only aesthetically unpleasant, but it can also damage and weaken the fibers, degrading them over time and causing strength loss.<sup>45</sup>

In garment textiles, there exists a space between the skin and the textile, where it is warm and humid. This is a perfect environment for microorganisms to grow and flourish, given the moisture from sweat and the growing medium of the textile substrate. The textile often harbors food for the microbes in the form of dirt and processing chemicals. Starch warp size especially encourages microbe growth, and thus any greige good which was sized with a starch based size must be treated with an antimicrobial finish if it is going to be

transported or stored in relatively high humidity, high temperature conditions. There are three primary microorganisms of concern with textiles: bacteria, fungi, and viruses.

Viruses are mostly a concern with textile due to health reasons. Some disease causing viruses can survive on a textile substrate, and when that textile comes in contact with an uninfected person, the virus can infect them. The severity of the resulting illness can be as simple as the common cold, or as devastating as hepatitis or HIV.

Fungi attack textile in the form of mold. Mold can grow on a textile substrate, damaging the fibers and posing health concerns with the resulting spores. Mildew, a type of mold, can also attack a textile, causing discoloration and fiber damage.

Bacteria are the most common concern with textiles because of its ability to colonize rapidly in a textile substrate. This leads to concerns such as foul odor and health hazards. Even a bacterium which is harmless in small amounts may become dangerous once it has colonized sufficiently. For instance, a dish cloth can be used to clean a kitchen counter, but because it is frequently damp, it is a prime substrate for growing microorganisms such as bacteria. These bacteria not only cause an unpleasant odor, but they can be re-spread on kitchen counters and eating utensils, potentially spreading disease.

Bacteria are generally categorized as being either gram positive or gram negative. This is differentiated by the ability of a bacterium to be stained by Gram staining, which

results in a violet color. This is due to high amounts of peptidoglycan in their cell walls of gram positive bacteria. They also lack an outer cell membrane, which is present in gram negative bacteria and prevents the absorption of the dye.<sup>46</sup> Most bacteria which are pathogenic to humans are gram positive, but there are exceptions.

Antimicrobials fall into two main categories: biocides and biostats. A biocide kills microorganisms, and thus has to be registered with the EPA as a pesticide. All products advertised as having this ability must be labeled with a public health claim which must be tested and approved as useful. A biostat merely inhibits the growth of microorganisms, and thus does not need to be registered or require special labeling.

#### **2.4.1 Chemistry of Antimicrobials**

Antimicrobial finishes for textiles operate through one of two different mechanisms. Leaching type antimicrobial finishes leach a substance from the surface to the microbes. This type of controlled release mechanism is highly effective against microbes on the fabric surface as well as in the surrounding environment. However, the reservoir of chemical is not endless and eventually the finish will lose its antimicrobial properties. There is also a concern about releasing an antimicrobial agent into the environment where it may interfere with necessary microbiology.

A bound antimicrobial finish has strong ionic or covalent bonds with the fiber

surface, and does not leach away, but rather remains attached to the surface. It can only control microbes on the surface of the fabric and is not effective against microbes existing in the environment. Bound type antimicrobial finishes also face the challenge of being worn off mechanically through normal wear.

Antimicrobial finishes work against microbes through several possible mechanisms. Antimicrobials can control microbe growth through blocking their enzymes, preventing the cells from dividing and thus stopping reproduction. Some antimicrobials work by reacting with the cell membrane in such a way as to destroy the cell wall. Cationically charged antimicrobial agents, for example, are thought to interact with the phospholipids in the cell wall, although the exact mechanism is not known.

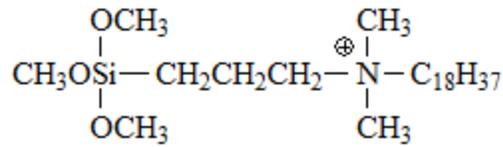
#### **2.4.2 Classifications of Antimicrobials**

Many of the historically used classes of antimicrobials have been discontinued. They were potentially toxic or had other environmental concerns that prevented them from meeting current EPA requirements. Some of these were organo-mercury compounds, which were extremely hazardous. Other types of antimicrobial finishes were copper naphthenate, tributyl tin oxide, dichlorophene, and 3-iodopropynylbutyl carbonate. These compounds are highly effective as antimicrobial agents, but have obstacles such as durability and concerns with application.

An antimicrobial agent which is currently approved for use is a chlorophenyl ether known as “triclosan”. This is commonly used in antibacterial hand soaps and deodorants. Triclosan is a leaching type antimicrobial finish, which can be depleted over time. Although it is used in textiles, it can be difficult to apply. Triclosan’s low water solubility requires dispersing agents and binders to be used as a textile finish. In addition, triclosan is highly effective against bacteria, but lacking in effectiveness against fungi.

A large class of antimicrobial agents is based on silver chemistry. organo-silver compounds, silver zeolites, and silver chloride nanoparticles are all possible antimicrobial textile finishes.

While the previously mentioned antimicrobials were leaching types, there are several alternatives which are bound types. For example, silicone quaternaries, which are shown in Figure 2-17 can exhaust to the fabric surface. During a curing step it self-reacts to form a coating, and can be used on a wide range of fibers. Being ionic, it can act as a multifunctional finish, imparting both antistatic and hydrophilic properties while providing antimicrobial activity.



**Figure 2-17: Silicone Quaternary Antimicrobial Agent**

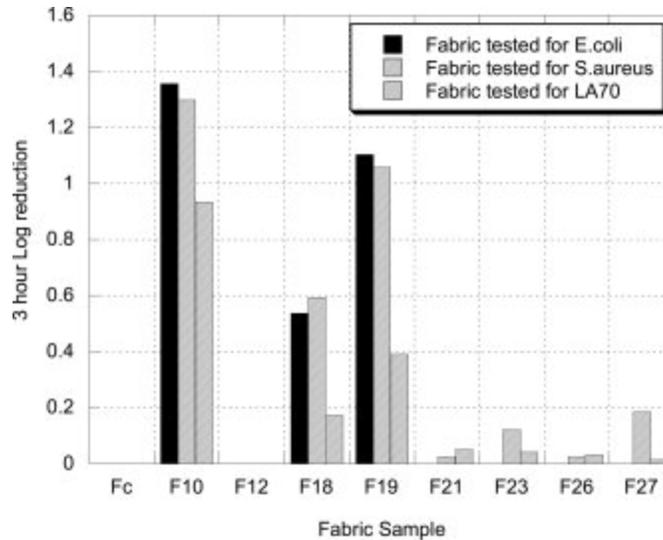
Polymers can also be used as antimicrobial finishing agents. For example, polyhexamethylene bioguanide is a polymer which is durable on cotton. It can be exhausted or pad applied, without the requirement of a curing step, and yet still has good bound antimicrobial activity. It is durable on cotton through strong hydrogen bonding between the amine groups and the cellulose structures.

Some antimicrobial agents have been developed to have activity that is regenerated during laundering. The main one that exhibits this characteristic is methylol-5,5 dimethyldyantoin. This binds to the cotton fibers, and when the cotton is washed with hypochlorite bleach, it reacts with the antimicrobial compound to form chloramide on the fibers. After interacting with bacteria, the structure returns to its original chemical formula, which can then be activated again with another wash in hypochlorite bleach. This antimicrobial finish is continuously reusable, but has the problem of yellowing and tendering of the fibers by the released chlorine.

### 2.4.3 Antimicrobial Plasma Treatments

Identifying an antimicrobial treatment which will be compatible with the water repellent finish is one of the goals of this research. Previous studies done have failed to find a combination of repellent and antimicrobial treatments that do not hinder the effectiveness of each other.<sup>47</sup>

One research paper used plasma treatments on nonwoven polypropylene (PP) to graft polymerize glycidyl methacrylate (GMA)<sup>48</sup>. The authors then reacted the grafted epoxide group with modified cyclodextrin, monochlorotriazynyl  $\beta$ -cyclodextrin (MCT), or a tertiary ammonium chitosan derivative, N-(2 hydroxy propyl) 3-trimethylammonium chitosan chloride. Biocidal agents were then complexed within the cyclodextrin cavity. The percentage of GMA add on was explored with regards to plasma exposure time, GMA concentration, and grafting time. However, the percentage of GMA was determined by weighting the fabric, which is a fairly inaccurate method when dealing with such thin polymer layers. The resulting characterization of biocidal activity, seen in Figure 2-18, showed a decrease of microbial activity up to log 1.3.<sup>49</sup>



**Figure 2-18: Log reduction in Wafa paper**

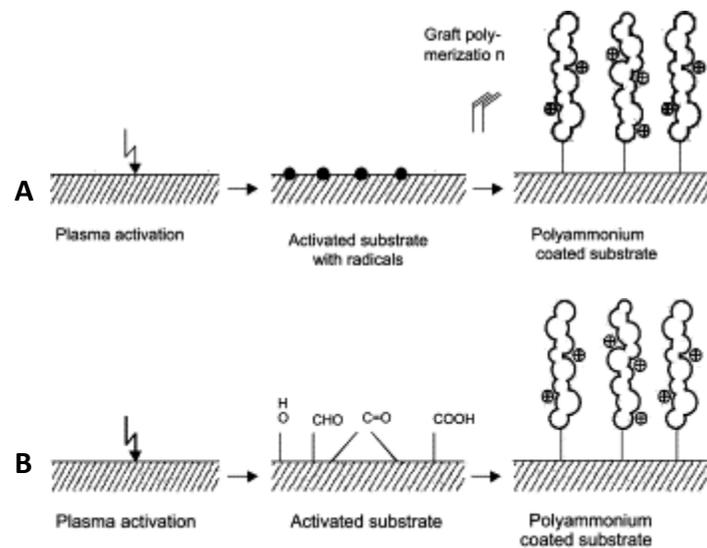
Although this is a decrease, it is not considered significant by current standards, which typically aim for a minimum decrease of log 3.

Similarly, studies have been conducted on using atmospheric pressure plasma to graft GMA on nylon fabric surfaces for the purpose of treating the GMA with functional finishes. In one such paper, the GMA was reacted with triethylene amine or a quaternary ammonium chitosan derivative for the purpose of imparting antimicrobial properties to the fabric. The study found that the grafting was successful, and while both antimicrobial agents provided decreased microbial activity on the fabric, the triethylene amine treated fabric was superior to the quaternary ammonium chitosan derivative treated fabric.<sup>50</sup>

Another research paper used radio frequency air plasma to prepare a cotton surface

to be modified with neem leaf extract for the purpose of imparting a durable antimicrobial treatment.<sup>51</sup> The plasma treatment in this paper was used to increase the hydrophilicity as a pre-treatment so that the applied neem leaf extract would bond to the fabric more readily. The results showed a reduction in antimicrobial activity for the samples first treated with plasma versus the samples which were only treated with the neem leaf extract. This research also found that the antimicrobial activity of the surface was sustained after repeated home launderings.

One research paper focused on using diallyldimethylammonium chloride (DADMAC) to treat a polyethylene film with a nanolayer finish for antimicrobial properties. The paper investigated using DADMAC monomer on surfaces which had been activated with low pressure plasma. The intent is that the active species on the surface of the polyethylene films would induce free radical polymerization of the DADMAC, leading to an ultrathin polymer network coating (scheme A from Figure 2-19). The experiment was then modified so that the polyethylene surface was plasma etched with oxygen functionalities, then treated with various DADMAC copolymers (scheme B from Figure 2-19). The samples were then tested for antimicrobial functionality through inoculation with both gram positive and gram negative bacteria.<sup>52</sup>



**Figure 2-19: Scheme A and B for applying DADMAC using Plasma Activation**

The results of this research found that the coatings were extremely thin, at 1-2 nm in thickness, as measured by XPS. The thickness was calculated by assuming that the coating was uniform and that all nitrogen present on the surface came from the polymer coating. The antimicrobial tests confirmed strong antimicrobial properties, with a reduction in microbe activity ranging from log 5 to log 6 on the pure DADMAC coating samples.

### Chapter 3 Experimental and Methodology

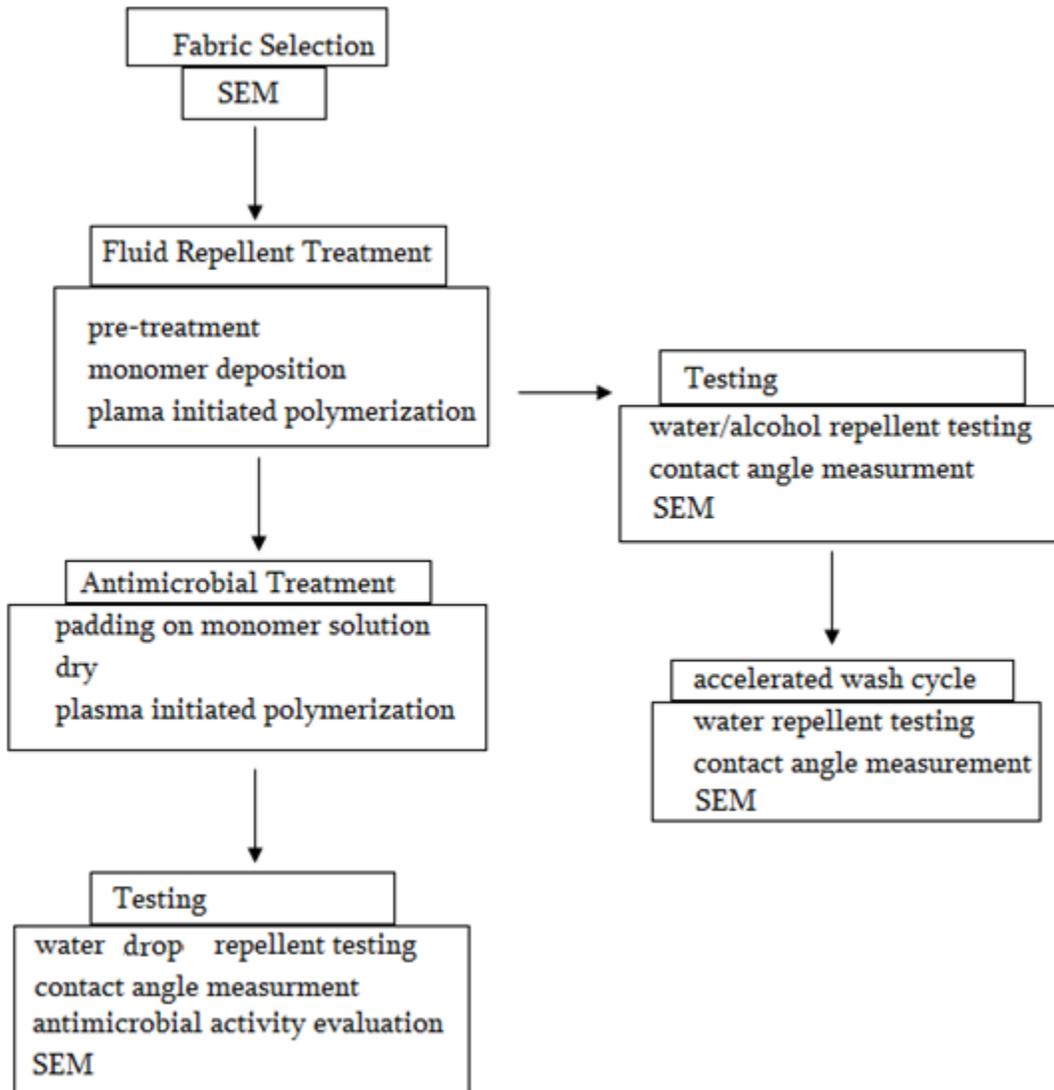


Figure 3-1: Experimental Design

### 3.1 Introduction

The intent of this research was to treat a cotton/polyester blend woven fabric substrate with a single-sided treatment of water repellency, followed by an antimicrobial treatment. The objective was for this finish to be durable to home laundering, and polymerized using atmospheric plasma.

The methodology began with selection of an appropriate fabric. The fabric chosen was 50/50 % cotton, polyester blend, woven fabric. This was chosen because cotton, polyester blends are the most commonly used in the industry for apparel applications. The polyester is typically blended into the cotton to reduce costs, but the cotton is kept in significant proportions due to its desirable properties, such as high strength and water absorbency.

Figure 3.1 shows the flow of the experiments conducted and resulting characterization tests performed on the samples. The first experiment was conducted to determine the water repellency properties of fabric treated with fluorocarbon monomer deposition and a plasma treatment. The parameters of plasma exposure time and carrier gas flow rate were investigated. It should be noted that plasma exposure time was tied to the amount of monomer deposited on the fabric. This was due to the moving stage, which moves the fabric through the plasma field and consecutively beneath the monomer applicator. If the plasma exposure time is shortened, then the exposure to the applicator is

also shortened, and less monomer is deposited on the fabric.

The results from experiment 1 were expanded to experiment 2, which was conducted to determine the effect of the pre-deposition plasma treatment, the flow rate of the monomer, and the plasma exposure time. These samples were tested for durability of the water repellency after home laundering.

Experiment 3 built upon the results from experiment 2 by reproducing a water repellent finish, and treating it with an antimicrobial monomer finish. The monomer was padded onto the fabric that had been treated and cured with the water repellent finish. The antimicrobial finish was then polymerized through plasma exposure, and the water repellency and antimicrobial properties were investigated.

## **3.2 Fabric Selection and Preparation**

### **3.2.1 Materials**

Approximately five yards of plain weave greige cotton/polyester blend (intimate blend) of 50:50 composition.

### **3.2.2 Chemicals**

Desizing bath:

- 2% owf  $\alpha$ -amylase enzyme (Hipozyme<sup>®</sup> 2000)
- 0.5 g/L surfactant (Pentex<sup>®</sup> OS-NF)

Scour/Bleach bath:

- 0.5 g/L surfactant (Pentex<sup>®</sup> OS-NF)
- 3 g/L NaOH (sodium hydroxide 50%)
- 6 g/L H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide 35%)

### **3.2.3 Methodology**

Fabric preparation was carried out in the pilot plant located at the College of Textiles in Raleigh, NC. Fabric was weighed, cut into four equally sized pieces, and all edges were serged. All baths were carried out in a TexColour NC6DM washer. Warp size was

determined to be starch based through iodine solutions drop test<sup>53</sup> (See Appendix A). An enzyme desize bath was selected, and all four pieces of fabric were desized in the same bath. Fabric was placed in bath, and water, enzyme, and surfactant were added. The bath was heated to 100°C for 15 minutes with agitation, followed by a 15 minute hot rinse.

Fabric was then scoured and bleached in a combination bath containing surfactant, sodium hydroxide, and hydrogen peroxide. The bath heated to 100°C for 30 minutes with agitation, followed by two 15 minute hot rinses. The fabric was then put through a neutralizing rinse containing a small amount (0.25 g/L) of acetic acid. Fabric was then dried, allowed to condition in the pilot plant overnight, and weighed. Iodine drop test repeated to determine effect of desizing bath.

### **3.3 Fabric Evaluation**

#### **3.3.1 Materials**

Plain weave cotton/polyester blend of 50:50 composition that has been desized, scoured and bleached

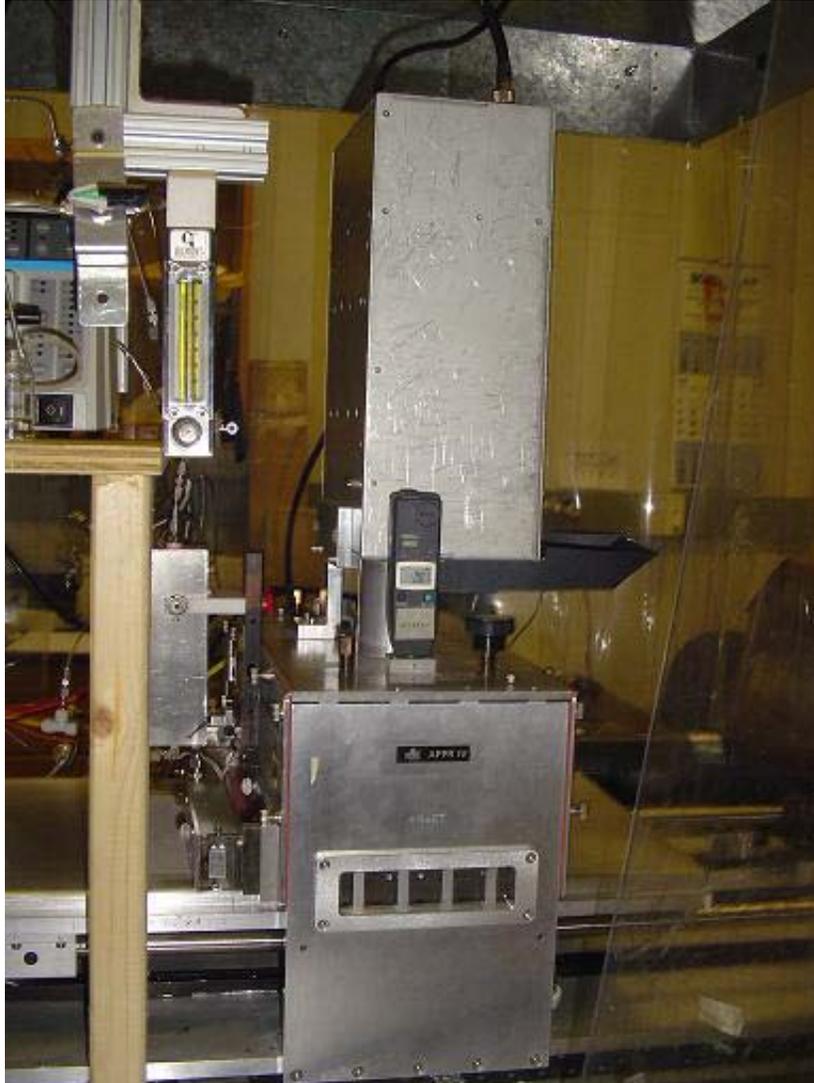
#### **3.3.2 Methodology**

Surface cleanliness was determined qualitatively using scanning electron microscopy (SEM). Four samples were taken from different areas of the fabric, mounted, and sputter

coated with a nanolayer of gold palladium under vacuum. The samples were then observed under SEM, and viewed at different magnifications.

### **3.4 Plasma Lab Set-Up**

The atmospheric plasma lab at North Carolina State University's Centennial Campus was equipped with a plasma generator, as can be seen in Figure 3-2, an electrode power supply (Figure 3-3, B), an evaporator/applicator as can be seen in Figure 3-4, and a moving stage (Figure 3-4, C). The stage was cooled using a chiller, and the applicator supplied the monomer vapor. The monomer was first pumped into the evaporator, which operates at a temperature greater than the boiling point of the monomer, and pushed with the aid of Ar gas in the vapor form into the applicator. The fabric moves on the stage beneath the plasma electrodes, where the gas flow pushes the activated plasma species down onto the fabric, as shown in Figure 3-5. The stage then passes under the applicator, which deposits the vaporized monomer. The stage then reverses direction and passes back beneath the plasma for the curing step.



**Figure 3-2: Atmospheric Pressure Plasma Jet (APPJ)**

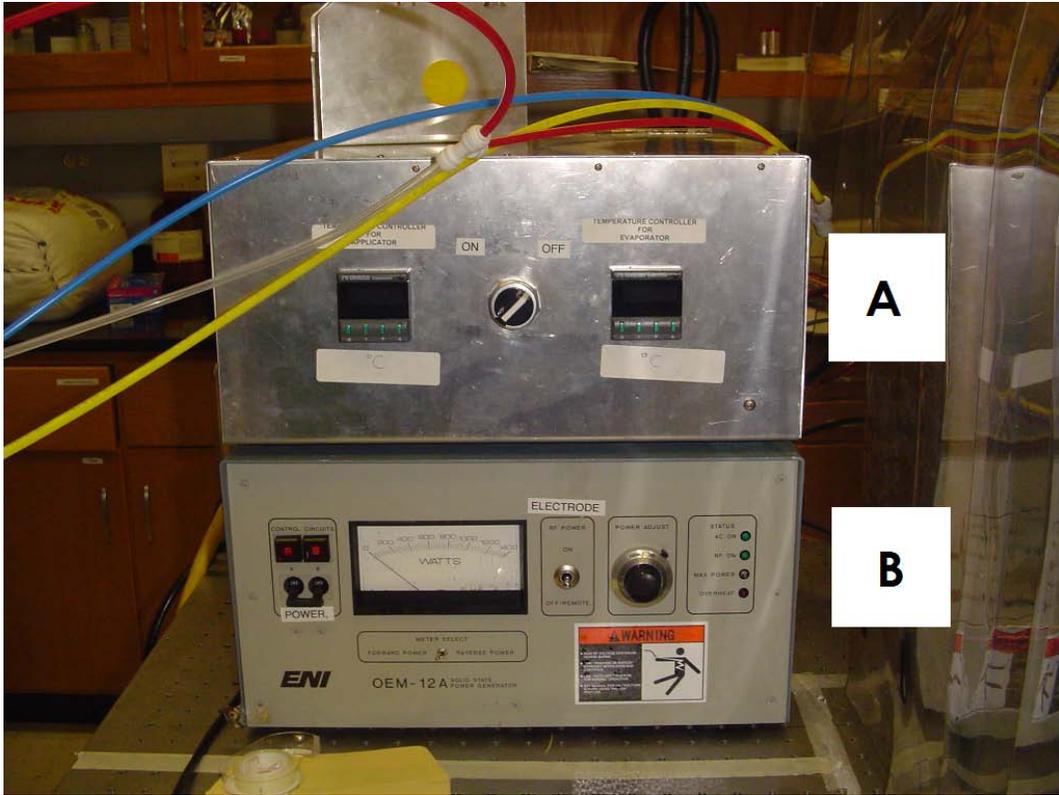
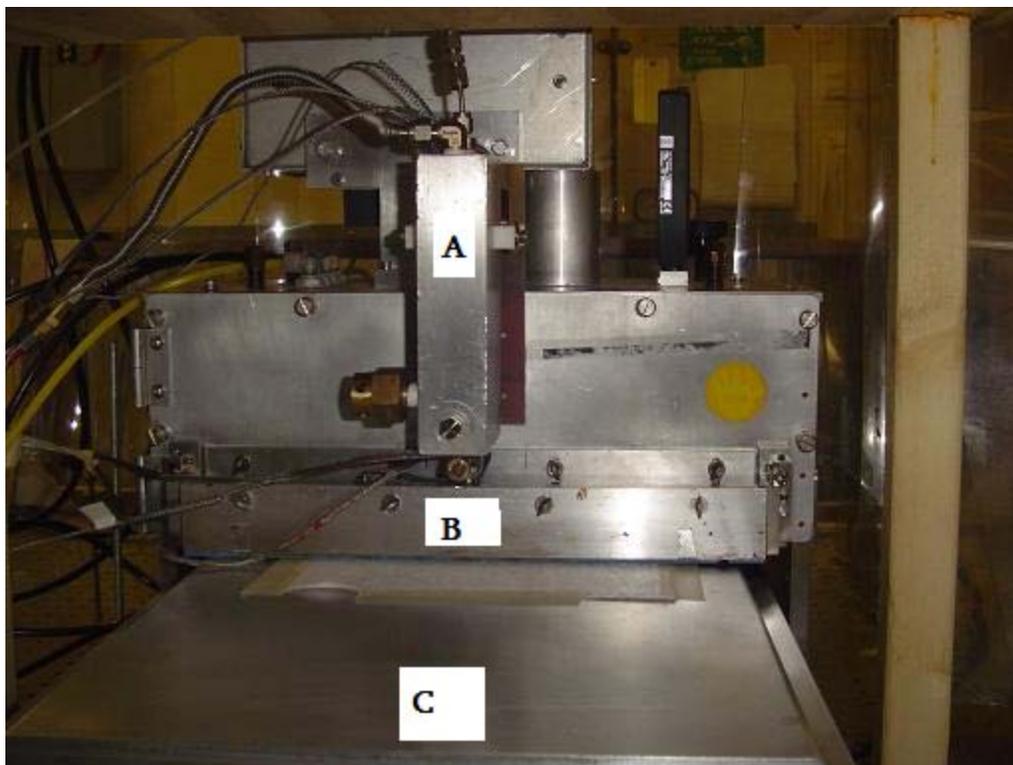
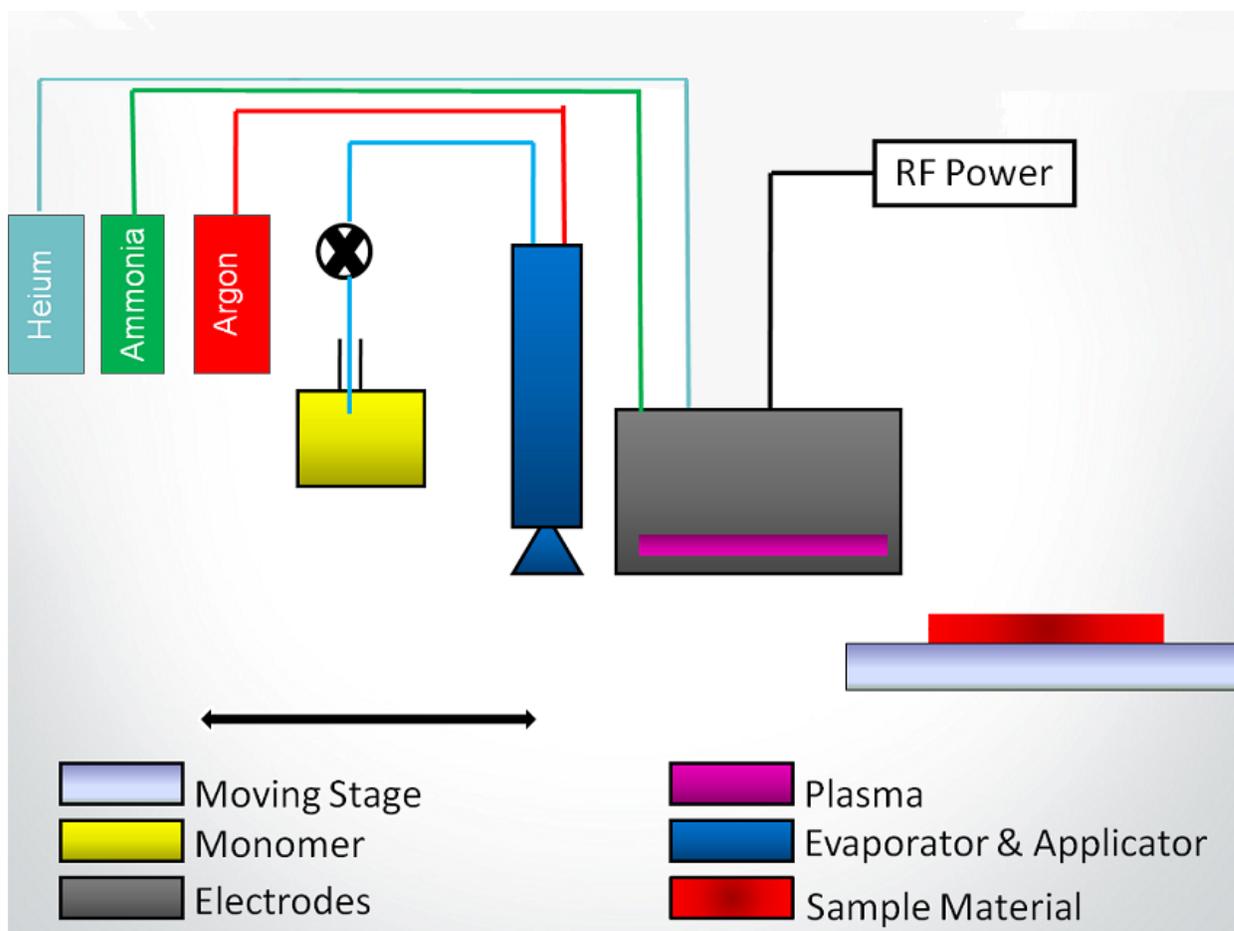


Figure 3-3: Evaporator Heater (A) and Electrode Power Supply (B)



**Figure 3-4: Lab Designed Evaporator (A), Applicator (B), and Cooled Stage (C)**



**Figure 3-5: Scheme of Plasma Treatment**

### 3.4.1 Equipment

Prototype downstream APJeT Atmospheric Pressure Plasma Reactor (APPR) IV (serial number 0007m), equipped with a controlled stage (Lesson Speedmaster™ motor control), and a solid state power generator (Power Systems 2-phase, model number ENI OEM-12A-21041-51). The stage was cooled using a chiller (Neslab CFT-75 refrigerated recirculator,

using R134-A refrigerant and a PD-2 pump). The monomer was pumped through a MasterFlex® LIS by Cole-Parmer Instrument Company, model 77200-50, equipped with MasterFlex® 96400-13 tubing. The monomer was pumped into a lab-designed heated evaporator/applicator.

### **3.4.2 Settings**

Standard settings for application of TG-10 to flat fabric for hydrophobic treatment:

Evaporator temp - 170°C

Applicator temp - 180°C

Applicator height – 3.0mm

Stage height – 4.0 mm (gap between ground electrode and stage)

He gas flow – 40-50 standard liter per minute (SLPM)

Ar gas flow – 0.3-1 SLPM

NH<sub>3</sub> gas flow – 0.17-0.21 SLPM

Radio Frequency (RF) power – 600-750 watts

Monomer flow rate – 0.6-1.0 ml/min

Exposure time – 5-30 seconds (controlled by stage speed)

Environmental conditions:

The lab was kept at an average room temperature of 21°C and 50-55% humidity

### **3.5 Initial Water Repellency Treatment (Experiment 1)**

In experiment 1, the ability to use nonthermal atmospheric pressure plasma to

impart a water repellent finish was investigated. The laboratory setup described in section 3.4 and the fabric prepared in section 3.2 were used. The fabric was activated with the plasma before a fluorocarbon monomer was deposited onto fabric samples in the vapor form. This was then polymerized via a second plasma exposure and tested for water repellency.

### 3.5.1 Materials

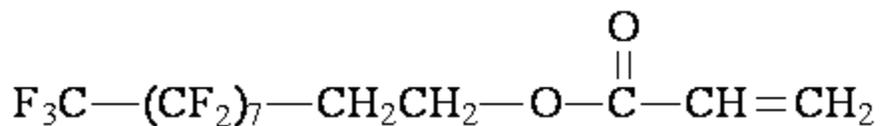
Fabric Samples (cotton/polyester blend, prepared in section 3.2)

TG-10 (filtered) 100% UNIDYNE™ (Daikin Industries, Ltd.)

TG-10 is a perfluoroacrylate derivative mixture from UNIDYNE™ (Daikin Industries, Ltd.). It contains two components, shown in Figure 3-6 and Figure 3-7.

70-90% 1,1,2,2-tetrahydroperfluorodecyl acrylate (Figure 3-6)

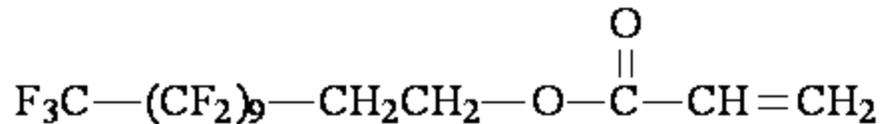
Molecular Formula: C<sub>13</sub>H<sub>7</sub>F<sub>17</sub>O<sub>2</sub>      Molecular Weight: 501 g/mol



**Figure 3-6: Component A of TG-10**

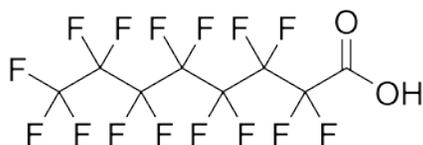
10-30% 1,1,2,2-tetrahydroperfluorododecyl acrylate (Figure 3-7)

Molecular Formula: C<sub>15</sub>H<sub>7</sub>F<sub>21</sub>O<sub>2</sub>      Molecular Weight: 597 g/mol



**Figure 3-7: Component B of TG-10**

It is worth noting that Component A: 1,1,2,2-tetrahydroperfluorodecyl acrylate is a so-called “C8 Fluorocarbon” and is a suspected precursory chemical to perfluorooctanoic acid, which is of environmental concern. The structure for perfluorooctanoic acid is shown in Figure 3-8, and it can be seen how similar the structures are. For this reason the industry is currently moving away from fluorocarbons containing 8 carbon atoms in the fluorocarbon chain portion of the compound, and toward the use of new “C10” fluorocarbons, such as the 1,1,2,2-tetrahydroperfluorododecyl acrylate contained in TG-10, or “C6” fluorocarbons. TG-10 was chosen for these experiments due to the dependability of consistent water repellent results. Future research can be conducted to adapt these procedures to the new fluorocarbon water repellents.



**Figure 3-8: Perfluorooctanoic acid (PFOA)**

### 3.5.2 Parameters and Variables

The RF power (watts), monomer flow rate (mL/min), and exposure time (sec) were all variables which were investigated in this experiment. Variations in plasma gas flow were adjusted to avoid arcing in the plasma reactor. He gas was used at 40 SLPM and ammonia was used at 0.17 SLPM, with a stage height of 3.0 mm.

**Table 3-1: Planned Variables for Experiment 1**

	RF Power	Monomer Flow	Exposure Time
High	750 W	0.6 mL/min	20 seconds
Medium	700 W	0.8 mL/min	10 Seconds
Low	600 W	1.0 mL/min	5 Seconds

### 3.5.3 Methodology

Fabric was cut into 6" by 6" square samples. The samples were ironed to reduce wrinkling and give an even surface height for treatment. Samples were then mounted on the stage using double sided sticky tape. Sample surface was made as smooth as possible, and loose yarns were removed or taped down.

Once stable plasma was generated, stage was turned on to move sample into the plasma field for the desired exposure time for the pre-deposition surface activation

treatment. As the sample passed out of the plasma field, it passed beneath the applicator, which deposited the monomer to condense and graft to activated species on the fabric surface. Monomer flow was then turned off.

Stage direction was reversed, and the sample passed through the plasma field a second time to induce free radical polymerization of the monomer on the fabric surface. Fabric sample was then removed from the stage, and the treatment side was labeled.

**3.5.4 Samples**

Three samples were successfully treated with the fluorocarbon plasma treatment. The parameters which they were treated with are displayed in Table 3-2:

**Table 3-2: Sample Variables for Experiment 1**

Sample ID	Plasma RF Power (watts)	Plasma Exposure (sec)	Monomer Flow (mL/min)	Monomer Carrier Gas (Ar) Flow (SLPM)
Sample 1	600	20	0.6	0.5
Sample 1A	600	10	0.6	0.5
Sample 1B	600	10	0.6	0.3

Samples at higher RF power levels and higher monomer flow rates had difficulty in creating and maintaining stable plasma. This is due to the prototype nature of the technology and is not expected to be a long term hindrance. To overcome this problem, the

standard settings for the experiment were re-evaluated. Lower power levels, wider gaps between the stage and electrode, and higher gas flows were implemented. When increased hydrophobicity was observed on the underside of the fabric, an attempt was made to reduce this effect by lowering the rate of the monomer carrier gas from 0.5 to 0.3 SLPM. The hydrophobicity observed on the non-treated side was due to the monomer being pushed through the thickness of the fabric and polymerizing. Reducing Ar flow rate should decrease the depth of monomer penetration.

### **3.5.5 Sample Testing- Water Drop Tests**

The samples were tested using water drop test on both sides of the fabric. This was done by dropping a droplet of water on the fabric in 5 different places around the sample. It was then timed for how long it took the fabric to absorb the drop of water. Fabric samples that did not absorb were then evaluated using American Association of Textile Chemists and Colorists test method (AATCC TM) 193-2004 (water/alcohol solution resistance). In this test, solutions are made of water and isopropyl alcohol in the proportions shown in Table 3-3, with each solution corresponding to a grade.

Table 3-3: Composition Parameters for AATCC TM 193-2004

Grade	Composition of solutions
0	None
1	98:2 water:isopropyl alcohol
2	95:5 water:isopropyl alcohol
3	90:10 water:isopropyl alcohol
4	80:20 water:isopropyl alcohol
5	70:30 water:isopropyl alcohol
6	60:40 water:isopropyl alcohol
7	50:50 water:isopropyl alcohol
8	40:60 water:isopropyl alcohol

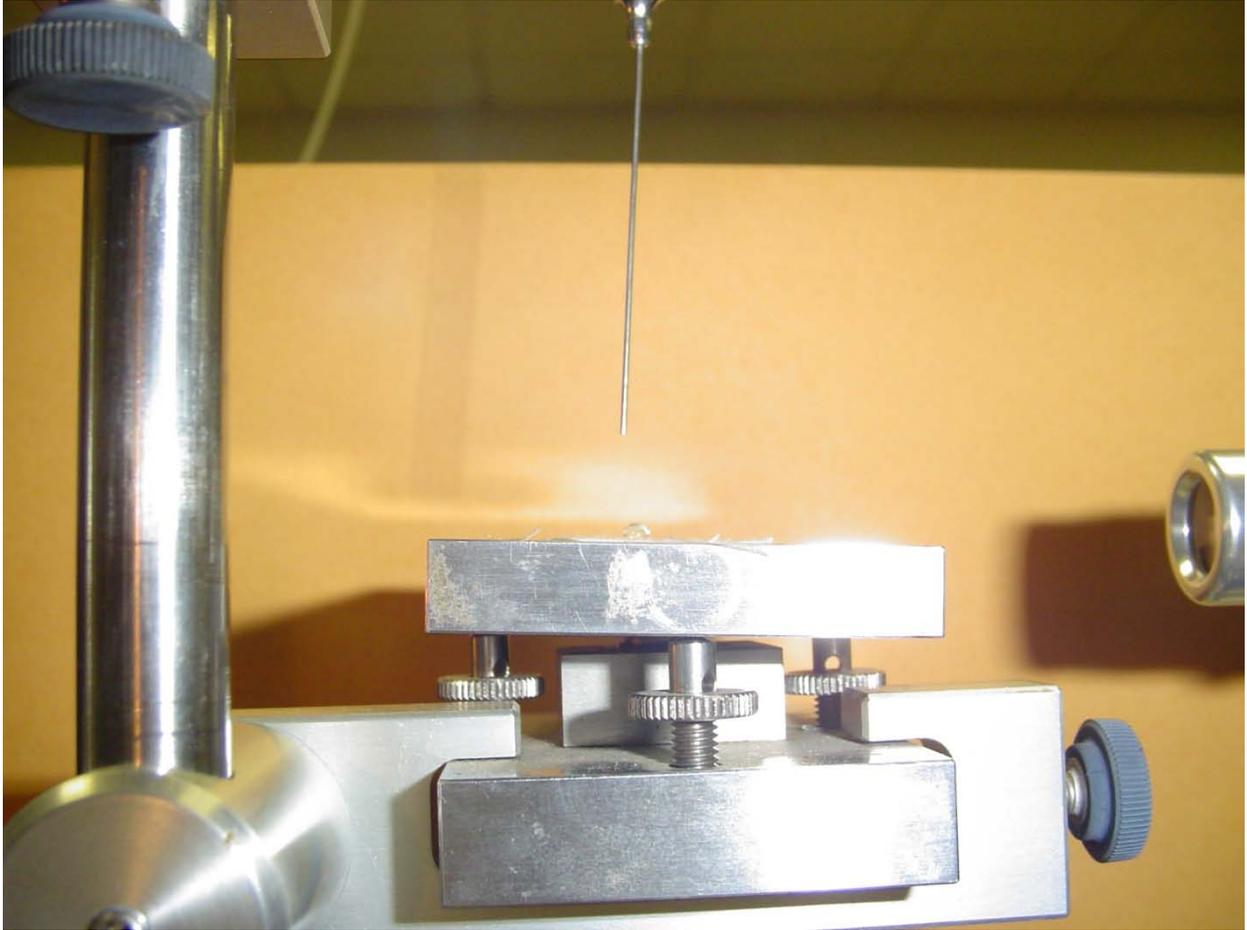
A single drop of each solution is placed on the treated side of the fabric surface. The drop is then observed for a time period of 10 seconds. If the drop maintains its shape and does not absorb into the fabric, then it is considered a pass for that grade. If the drop begins to lose its shape but does not absorb, then it is considered a partial pass. If it begins to absorb, then it fails that grade. The lowest grade which did not absorb is given to the fabric. For example, if solution 3 did not absorb but solution 4 did, then the fabric would be given a grade of 3. If solution 3 did not absorb and solution 4 did not absorb but lost its shape and partially passed, then it would be given a grade of 3.5.

### 3.5.6 Sample Testing- Contact Angle Measurements

Contact angles were estimated using a laboratory designed goniometer, as seen in Figure 3-9.



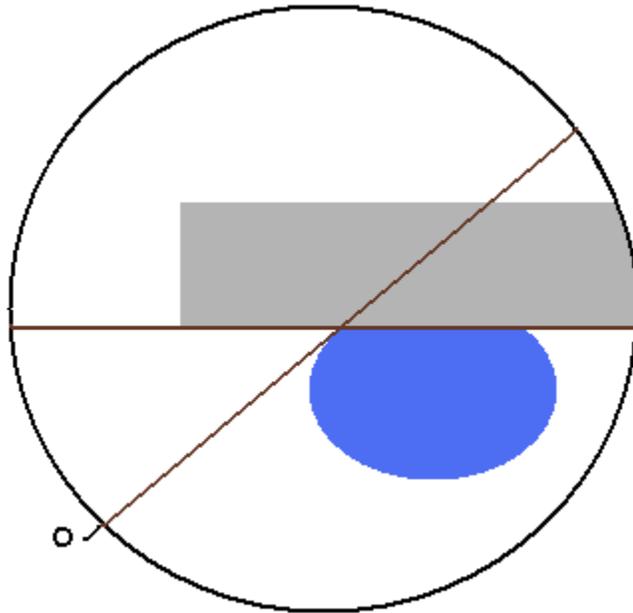
**Figure 3-9: Laboratory Designed Goniometer Consisting of viewing lens (A), Water-filled Syringe (B), Platform (C), and Light Source (D).**



**Figure 3-10: Water Droplet on Goniometer Stage**

Contact angles were measured by adhering a small fabric (approximately 2 cm<sup>2</sup>), sample to a stage using tape on the outer edges. A syringe was then loaded with 50μL of deionized water, which was used to form a drop of water on the fabric surface. The sample was then viewed through a magnifying lens, and the angle measured using a goniometer scale. Lines on the lens are lined up with the contact of the water droplet and fabric, and a

second line is lined up with the angle of contact, as shown in Figure 3-11.



**Figure 3-11: View of Goniometer**

Note that the image view is flipped due to the reflection of the magnifying lens. An angle measurement is then read from the scale around the outside of the viewing circle. Due to the subjective nature of this method, there is an expected margin of error due to the user's interpretation of the angles.

### **3.6 Secondary Water Repellency Treatment (Experiment 2)**

The results from experiment 1 showed that the application of fluorocarbon monomer to the fabric, followed by a plasma polymerization step, did increase the contact

angle with water, showing water repellency. To build off of this, the parameters of monomer flow rate and inclusion of a pre-deposition surface activation through plasma treatment step were investigated. The resulting samples were tested for water repellency through contact angle measurements before and after an accelerated wash cycle.

### **3.6.1 Materials**

Fabric Samples (cotton/polyester blend, prepared in section 3.2)  
TG-10 (filtered) 100% UNIDYNE™ (Daikin Industries, Ltd.)

### **3.6.2 Parameters and Variables**

The stage height was lowered so that a 4.0 mm gap existed between the ground electrode and the fabric sample. This was done to prevent arcing. In addition, the He and ammonia gas flows were increased to 50 SLPM and 0.21 SLPM, respectively, to prevent arcing. The flow rate for Ar gas (carrier gas for the monomer vapor) was increased to 1 SLPM. This change was made to compensate for poor performance from the monomer liquid pump.

**Table 3-4: Samples for Experiment 2**

	Variables		
	Monomer flow (ml/min)	Pre-deposition plasma exposure (sec)	Post-deposition plasma exposure (sec)
R1	0.6	0	10
R1B	0.6	10	10
R2	0.8	0	10
R3	0.8	0	5

\*RF power was set to 600 W for all samples

### 3.6.3 Methodology

The samples were treated with nonthermal atmospheric plasma using the same method described in section 3.5.3 with the exception that samples R1, R2, and R3 did not include a pre-deposition plasma surface activation step. This change was meant to investigate how well fabric could be finished using nonthermal plasma in a textile plant which had only one atmospheric plasma unity and therefore could not easily run consecutive plasma treatments.

### 3.6.4 Testing

The samples were tested using a lab-designed goniometer made from parts supplied by Ramé-Hart™. Due to the proprietary nature of this setup, photographs and specific details were not possible for illustration. In general, the setup consisted of a stage on which a glass specimen slide could be placed. A light source was provided by a separate

attachment, and attached to the stage was a magnifying lens. A high resolution camera was attached to the lens so that it could take photographs of the sample at high magnification.

Small fabric samples of approximately  $1 \text{ cm}^2$  were adhered to a glass specimen slide using double-sided sticky tape. The slide was then mounted on the stage so that it could be viewed through the lens. A syringe was used to deposit a  $10 \text{ }\mu\text{L}$  droplet of deionized water onto the edge of the fabric surface. A photograph was then taken of the water droplet on the fabric sample.

These photographs were then uploaded to Adobe® Photoshop® CS4 version 11.0 software. Lines were drawn along the surface of the fabric and extending from the point of contact with the water droplet. The measuring tool was then used to measure the contact angle.

For samples with high levels of water repellency, a drop of water applied to the surface can roll across the surface without sticking. In these cases, the rolling contact angle can be measured. This was conducted by mounting small fabric samples of approximately  $1 \text{ cm}^2$  onto a glass specimen slide using double-sided sticky tape. The slide was then mounted on a movable stage, which could tilt at gradual angles. A high resolution camera was set up on a tripod with the settings set to capture successive pictures of the water drop on the sample as the stage rotated.

A syringe was used to deposit a 100  $\mu\text{L}$  drop onto the fabric surface. The stage was then turned on so that it began rotating slowly. The measured angle increased from zero, with zero being the position parallel to the floor. The stage was stopped as soon as the water droplet began to roll. The more hydrophobic the surface, the sooner the droplet would roll. Therefore smaller rolling contact angles correspond to more hydrophobic surfaces.

The untreated fabric sample was not hydrophobic enough to cause a water drop to roll, so this test was conducted only on the treated samples.

### **3.7 Durability Testing**

#### **3.7.1 Methodology**

All samples from experiment 2 were washed using an accelerated wash cycle to determine the laundering durability of the water repellent finish. This wash cycle was from AATCC TM 61-2007. Test number 2A was used, which corresponds to 5 standard wash cycles.

The samples were put into separate canisters to prevent fluorocarbon polymer transfer. The canisters contained 150 mL of solution which contained 0.15% standard AATCC test detergent and 50 stainless steel balls of 6mm diameter. The canisters were then clamped shut and loaded into an Atlas LEF Launder-ometer®. The launderometer

rotated the canisters for 45 minutes at a temperature of 49°C. The samples were then unloaded, given two cold water rinses, and dried.

### **3.7.2 Testing**

Dried samples were allowed to condition in the lab for 24 hours before testing. All washed samples were ironed on the untreated side before testing. This is to remove surface wrinkles which may negatively impact the water repellency as well as to reorient the fluorocarbon chains through heat. The samples were ironed on their untreated side to prevent transfer of the fluorocarbon finish between samples.

Contact angles were then measured using the procedure outlined in 3.6.4. Static contact angles only were measured, as the washed fabric samples did not repel water droplets enough to allow rolling.

## **3.8 Application of Antimicrobial Treatment (Experiment 3)**

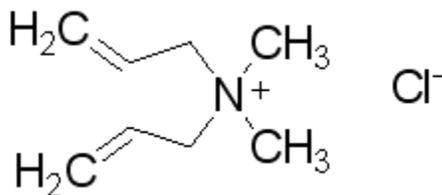
### **3.8.1 Materials and Chemicals**

50/50% cotton/polyester blend woven fabric

TG-10 fluorocarbon water repellent monomer

65% diallyldimethylammonium chloride (DADMAC)

The structure for DADMAC is shown in Figure 3-12. It is an antimicrobial agent which is a quaternary ammonium salt. These are believed to have antimicrobial properties through interfering with the cell wall of a bacterium, causing it to die. The structure is able to react and polymerize through the double bonds on the end of the hydrocarbon chains. This double bond is open to attack by a free radical, which is provided by the plasma treatment. Because there are two such chains containing a double bond per molecule, DADMAC is bifunctional and able to crosslink with itself, forming polymer networks.



**Figure 3-12: Diallyldimethylammonium chloride (DADMAC)**

### 3.8.2 Parameters and Settings

Based on the results of experiments 1 and 2, the best water repellent treatment was one with a pre-deposition plasma treatment, medium monomer flow rate, and medium plasma exposure time. Thus, the parameters were chosen to be the following:

- 20 seconds pre-deposition plasma exposure
- 0.8 mL/min monomer flow

- 10 seconds plasma exposure
- 600 Watts RF power
- 50 SLPM He, 0.21 SLPM NH<sub>3</sub>, and 1 SLPM Ar

**Table 3-5: Sample Variables for Antimicrobial Treatment**

Sample	DADMAC (g/L)	Plasma Exposure (sec)
A1	4	10
B1	8	10
C1	12	10
D1	16	10
E1	20	10
F1	24	10
A2	4	20
B2	8	20
C2	12	20
D2	16	20
E2	20	20
F2	24	20

### 3.8.3 Methodology

Fabric samples were cut from untreated fabric to measurements of 8" x 12". The samples were then treated with the fluorocarbon plasma treatment, using the above parameters and the method outlined in 3.5.

The fabric samples, after being treated with the water repellent, were cut into 12

equal pieces of 4" x 4". Solutions of diallyldimethylammonium chloride (DADMAC), shown in Figure 3-12, were made by diluting a stock solution of DADMAC 65% to the following concentrations: 4 g/L, 8 g/L, 12 g/L, 16 g/L, 20 g/L, and 24 g/L. Stock solutions were measured with volumetric pipettes and diluted in volumetric flasks.

The antimicrobial agent DADMAC was padded on using a Mathis AG CH-8155 at 1 bar of pressure with a speed of 1 mL/minutes. Three passes were required per sample to wet the hydrophobic surface, but this could be aided in future work through the use of a wetting agent or surfactant added to the pad bath. The first sample was weighed before and after padding to determine the wet pick up (wpu) of the treatment bath:

Dry weight: 1.54g    Wet weight: 2.94g

$$\% \text{ wet pick up} = \frac{2.94g - 1.54g}{1.54g} * 100 \approx 90\% \text{ wpu}$$

The samples were then dried in a Yamoto mechanical convection oven at 50°C for 20 minutes. Due to DADMAC's ability to thermally cure, the temperature was carefully regulated to not go above 60°C.

Once dried, the samples were cured using nonthermal atmospheric plasma, as outlined in the curing step of experiment 1. The following parameters were selected: 600 watts RF power, 10 or 20 second exposure time, with 50 SLPM He flow and 0.21 SLPM NH<sub>3</sub> flow. The samples were mounted onto the cooled stage and passed through the plasma.

### 3.8.4 Testing

The samples were tested for both antimicrobial and water repellent properties. The samples were sent to Antimicrobial Test Laboratories in Round Rock, Texas for antimicrobial testing. The test selected was AATCC 100-2004. The following parameters were used for the test:

Sample size - 2 stacked small (~1/2 inch) squares

Test Microbes - *S. aureus* and *K. pneumoniae*

Contact time - 24 hours at 36C

Surfactant - 1% Triton X-100

Diluent for Culture - Phosphate-buffered Saline (PBS) rather than full strength broth

Target colony forming units (CFU)/sample stack -  $1 \times 10^5$

This test uses two species of bacteria: a gram positive bacteria, *Staphylococcus aureus*, which is the bacteria which causes staph infections, and a gram negative bacteria, *Klebsiella pneumoniae*, the bacteria responsible for pneumonia. The surfactant was added to fully wet out the samples. Both untreated fabric and fabric treated with only the water repellent were used as test controls. In addition, the laboratory provided an alternate control which was sterile cotton fabric. The AATCC standard test calls for the samples to be soaked in full strength broth, but a buffered saline solution was selected for more precise results.

The samples were inoculated and held at 36°C for 24 hours. Before and after the incubation period the samples were examined for the presence of colony forming units of bacteria. Any less than 5 units were considered zero microbial activity.

The samples were also tested for water repellency. This was conducted by placing a drop of water on the surface and timing how long before the drop was fully absorbed by the fabric. Each sample was tested twice, and the averages taken.

## **Chapter 4 Results and Discussion**

### **4.1 Results from Fabric Selection and Preparation**

The fabric was tested for residual size using drops of iodine solution. It was visually confirmed (through lack of color change) that the size had been removed from the fabric.

Fabric before desizing: 0.64 kg

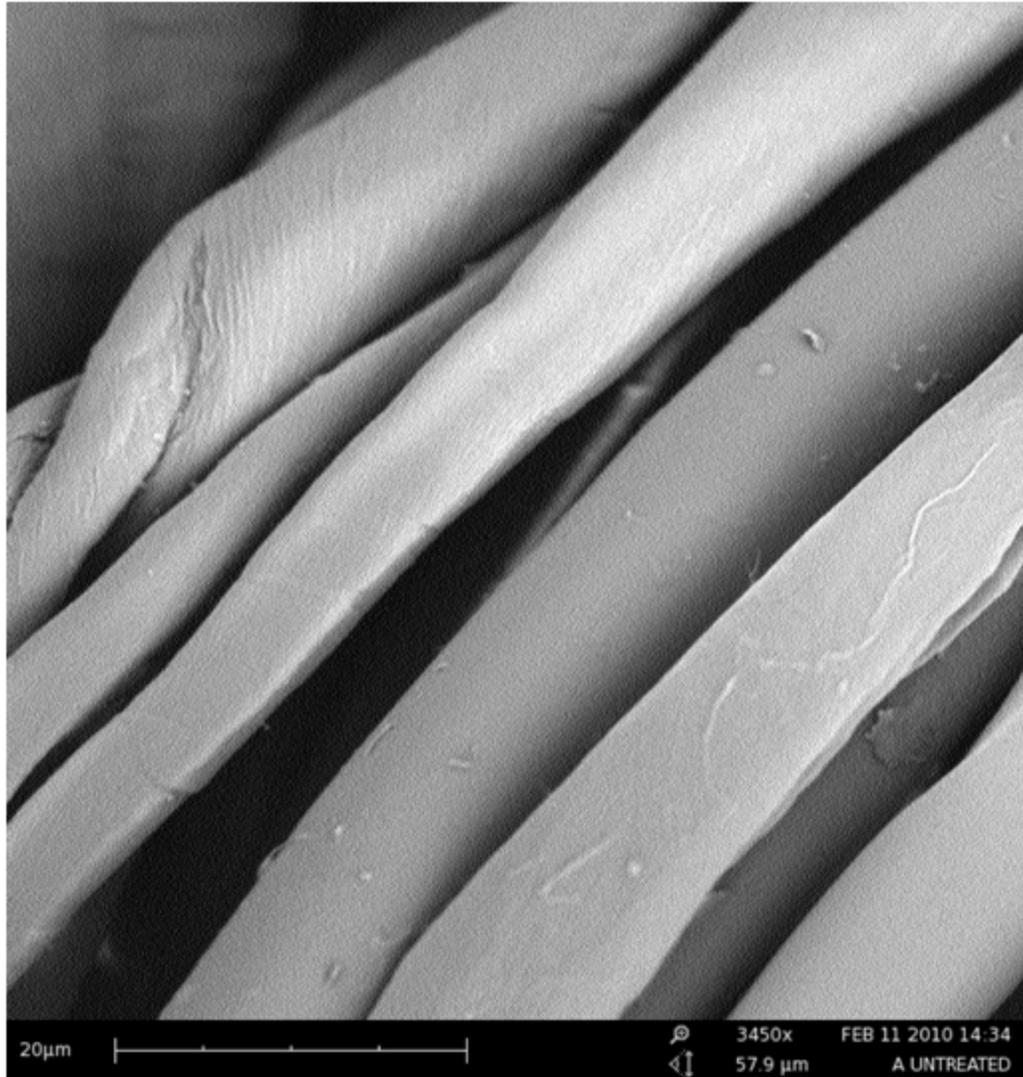
Fabric after desizing: 0.58 kg

% warp size add-on:  $(0.64 \text{ kg} - 0.58 \text{ kg}) / (0.58 \text{ kg}) * 100 = 10.34\%$

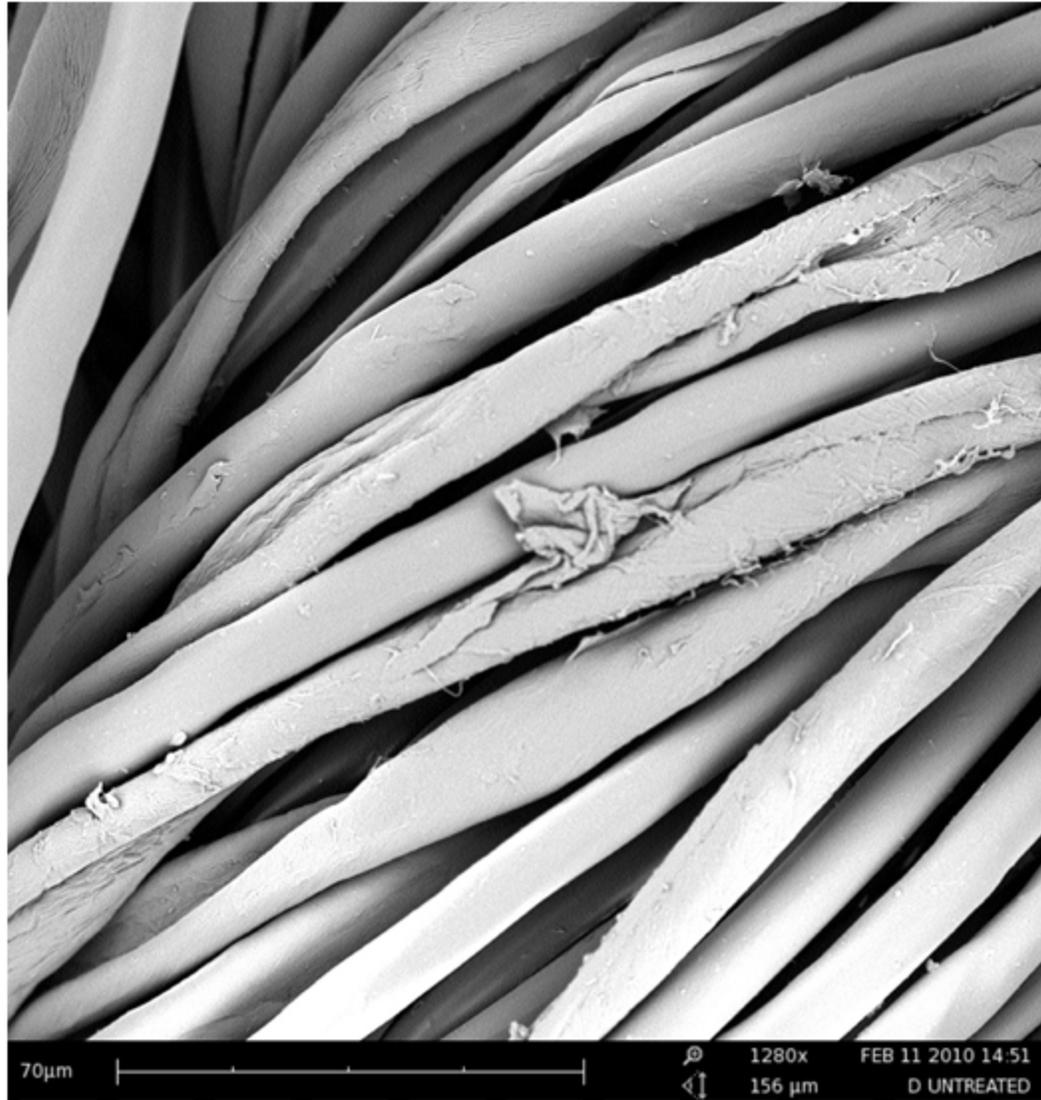
### **4.2 Results from Fabric Characterization**

The fabric was characterized using SEM after being desized, scoured, and bleached. Two images representing the observation of the fabric samples are shown below.

It can be seen in Figure 4-1 that the fibers, when viewed at high magnification, appear to have relatively smooth, clean surfaces. However, when the magnification is backed off as is shown in Figure 4-2, some of the fibers contain surface impurities, as well as particulates trapped between the fiber bundles. These impurities are most likely residual starch based warp sizing that were not fully removed during the desizing process. Starch residues, along with the tight weave and polyester content of the fabric, contribute to some initial repellency of the fabric.



**Figure 4-1: SEM of Fabric at 3450x Magnification**



**Figure 4-2: SEM of fabric at 1280x Magnification**

### **4.3 Results from Experiment 1**

#### **4.3.1 Calculation of percent add-on**

It is difficult to determine exactly what the percent add-on of monomer is because there is no data to support the theory that the rate of liquid monomer being pumped into the evaporator is equal to the amount of vapor monomer being released from the applicator. In addition, a large amount of vaporized monomer is lost due to ventilation rather than condensing on the fabric surface. This challenge is due to the prototype design of the laboratory set up and is being analyzed and reconstructed as needed to reduce the amount of monomer lost. Gravimetric analysis is not a suitable method for determining percent add-on because the layer of polymer on the surface is so thin that the difference in weight of the sample before and after treatment would be too small to accurately measure.

The percent add-on can be estimated quantitatively if large assumptions are made. First, it is assumed that the flow rate of monomer liquid into the evaporator is equal to the flow rate of monomer vapor out of the applicator. Second, it is assumed that no monomer vapor is lost due to ventilation (we know that this is not the reality due to visual assessment), and that all monomer released from the applicator condenses on the fabric surface and is subsequently polymerized. The amount of monomer deposited depends on both the flow rate of the monomer and the stage speed.

The calculation for the percent add-on is dependent on the parameters described in

Table 4-1.

**Table 4-1: Parameters Used to Determine Percent Add-on of Monomer Applied by Applicator**

Parameter (units)	Symbol used
Speed (in terms of exposure time, seconds)	s
Flow rate of monomer (mL/min)=	f
Sample length (inch)	l
Sample width (inch)	w
Sample weight (g)	wt
Monomer density ( g/mL)	$\rho$

The length of the plasma chamber is 8", so to calculate the speed in inches per minute:

$$\frac{8''}{s \text{ sec}} * \frac{60 \text{ sec}}{\text{min}} = \frac{480}{s}''/\text{min}$$

To calculate how many minutes the sample is exposed to the applicator, invert the formula and multiply by length of the sample:

$$\frac{s \text{ min}}{480 \text{ ''}} * l'' = \frac{ls}{480} \text{ min}$$

To determine the volume of monomer applied in milliliters, multiply by the flow rate and the percentage width (width of stage is 12") that the sample takes up:

$$\frac{ls}{480} \times f \text{ mL/min} \times \frac{w''}{12''} = \frac{lsfw}{5760} \text{ mL}$$

To determine the weight of the monomer applied, multiply by the density:

$$\frac{lsfw}{5760} mL \times \rho \frac{g}{mL} = \frac{lsfw\rho}{5760} g$$

Percent add on is determined by dividing the percent of monomer by the weight:

$$\% \text{ Add - On} = \frac{lsdwp}{5760 * wt} \times 100$$

For this calculation example, the parameters used are 0.8 mL/min flow rate of monomer with 10 second plasma exposure time. A typical fabric sample used in this research at 6 inches long by 12 inches wide would weigh approximately 6.0 grams. TG-10 has a specific gravity at 25°C of 1.7 g/mL. 0.1 mL of liquid would contain 0.17g of pure monomer. Thus:

$$\frac{lsfw\rho}{5760} g = \frac{6 \text{ inch} * 10 \text{ sec} * 0.8 \frac{mL}{min} * 12 \text{ inch} * 1.7 \text{ g/mL}}{5760 \text{ inch}^2 \text{ seconds/min}} = 0.17 \text{ g monomer}$$

$$\% \text{ Add - on} = \frac{0.17 \text{ g monomer}}{6.0 \text{ g substrate}} * 100 = 2.8\% \text{ add - on}$$

For this experiment, the percent add on is estimated to be 2.8%. The actual amount is realistically smaller due to the amount of vaporized monomer lost to ventilation. This is considerably less than a typical wet processing procedure, yet still yields a fabric with a functional finish.

### 4.3.2 Proposed Reaction Mechanism

Fluorocarbon acrylate based water repellents react through the C=C at the end of the chain. The  $\pi$  electrons involved in the carbon-double bond-carbon are open to attack by a free radical. These free radicals are supplied by the plasma treatment, and exist on the activated fabric surface and are deposited following the monomer deposition. Once opened, free radical polymerization ensues.

As seen in Figure 4-3, the graft polymerization occurs when the monomer reacts with a free radical of the surface of the fabric. The free radical attacks the double bond of the monomer, opening the bond and forming a new bond between the fabric and the monomer, through reaction 1. This leaves the free radical on the monomer, which may react in a variety of paths. Two such possible reactions are shown where the free radical begins on the second carbon atom of the fluorocarbon monomer. The reaction may continue through pathway A, in which the free radical attacks an unreacted monomer. This continues the free radical polymerization until the propagating species is terminated. Or it may terminate by reacting with a hydrogen atom, as seen in path B.

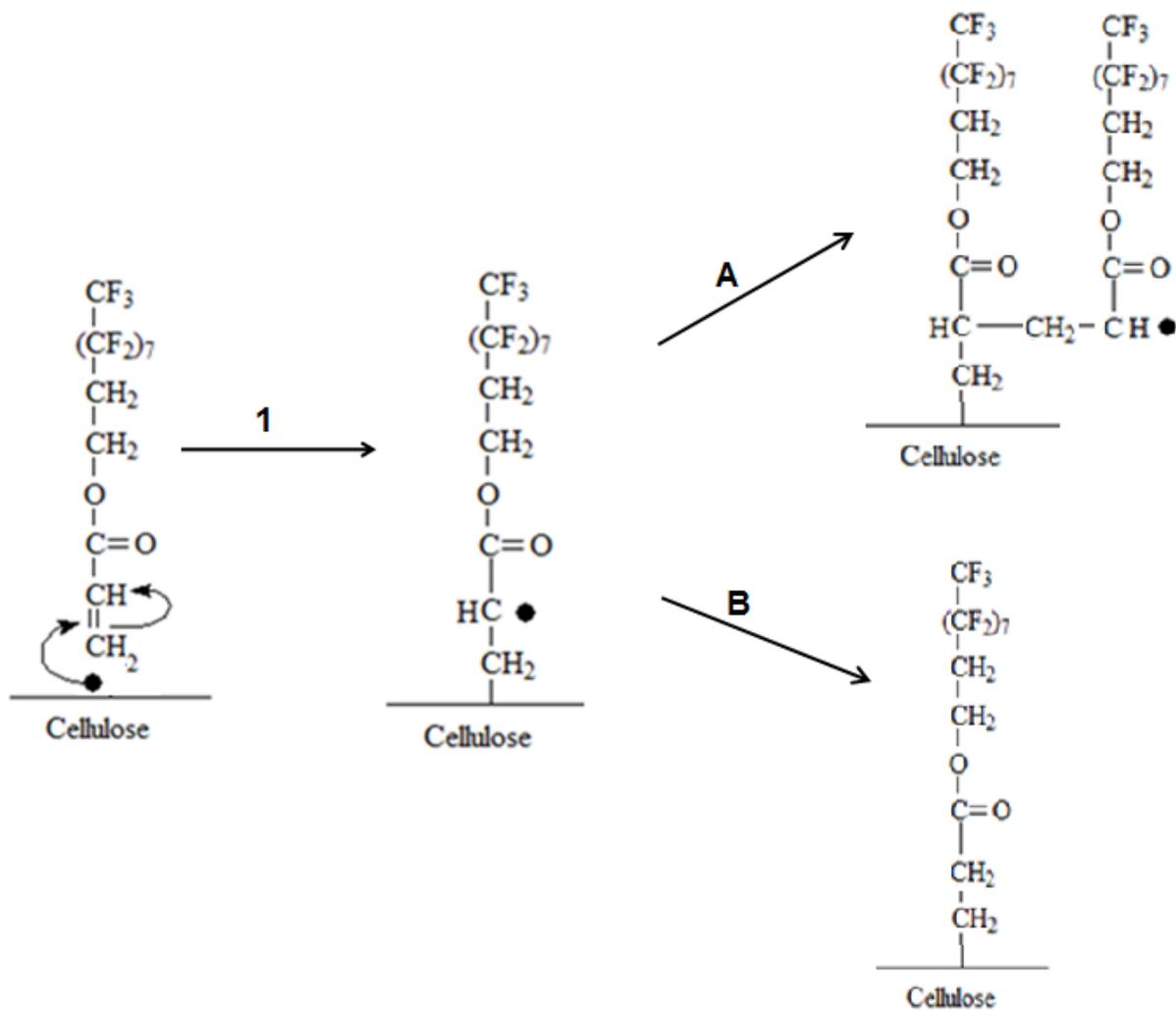


Figure 4-3: Graft Polymerization of 1,1,2,2-tetrahydroperfluorodecyl Acrylate on Cellulose

#### 4.3.3 Water Drop Test Results for Experiment 1

The fabric samples were tested by placing a drop of water at 5 locations on the sample. The fabric was then observed for any water absorption. If the drop did not absorb

after 1 minute, then it was considered water repellent. The sample was tested across the area of the fabric to determine if the treatment was consistently even.

As can be seen in Figure 4-4, there is high initial water repellency on the treated fabric, but after approximately 1 minute two of the five water drops absorbed into the fabric, as designated by the arrows. The remaining three water drops did not absorb into the fabric. This shows that the treatment was not successful in being completely water repellent, and that the treatment may have been unevenly applied by the applicator or unevenly cured by the plasma.

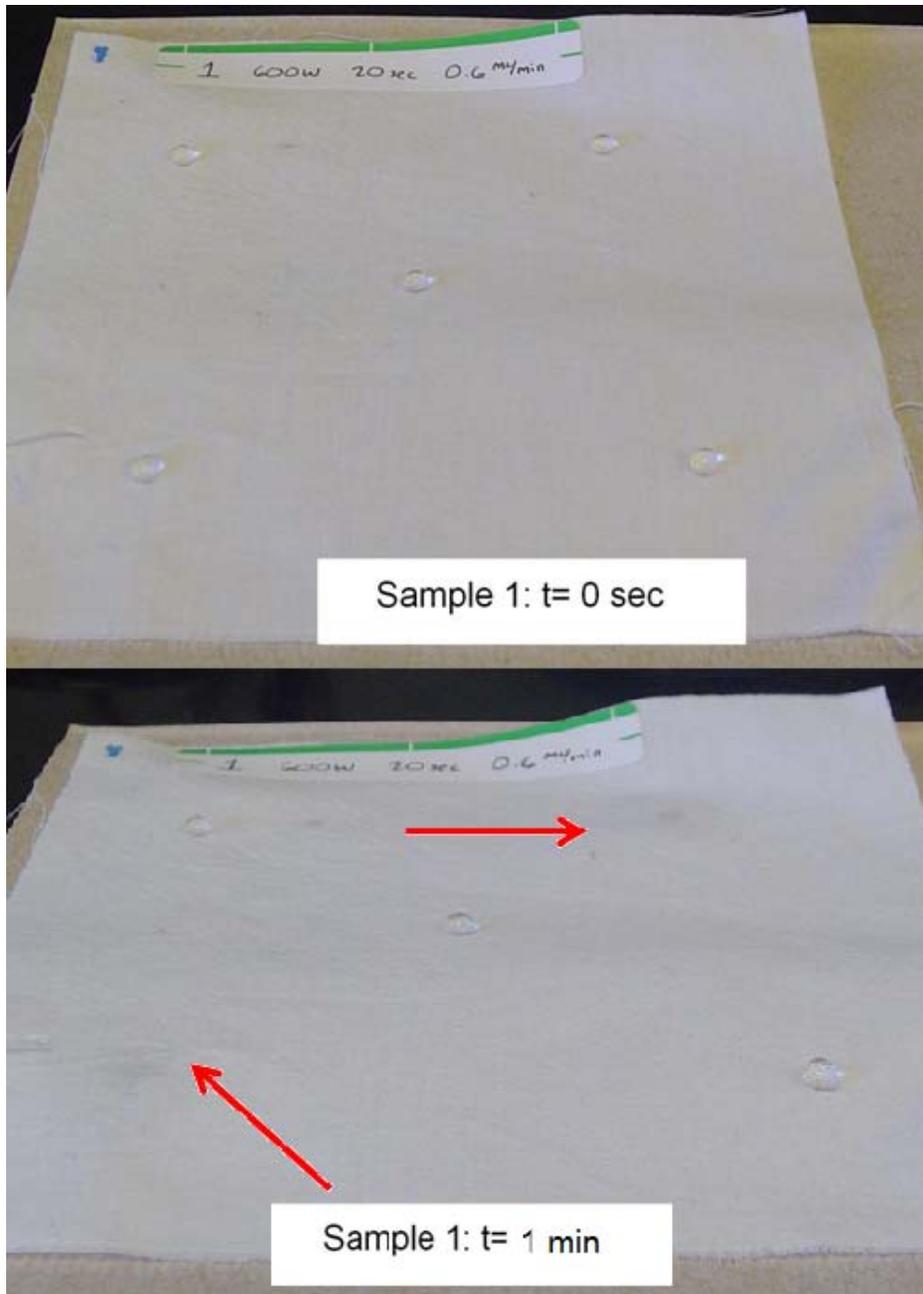


Figure 4-4: Water Drop Test for Experiment 1, with arrows showing where water was absorbed

It was determined, after the samples for experiment 1 were prepared, that the pump line supplying the liquid monomer to the evaporator was partially clogged. This may have contributed to the uneven finish. The tubing was replaced with new tubing, and the evaporator and applicator were cleaned before experiment 2 was run. In addition, the ground electrode was found to be warped, which may have caused an uneven plasma exposure, resulting in an uneven polymerization of the monomer, which would give an uneven finish. These problems are the product of the prototype nature of the system, which is being improved. These are not expected to be hindrances in a final production system.

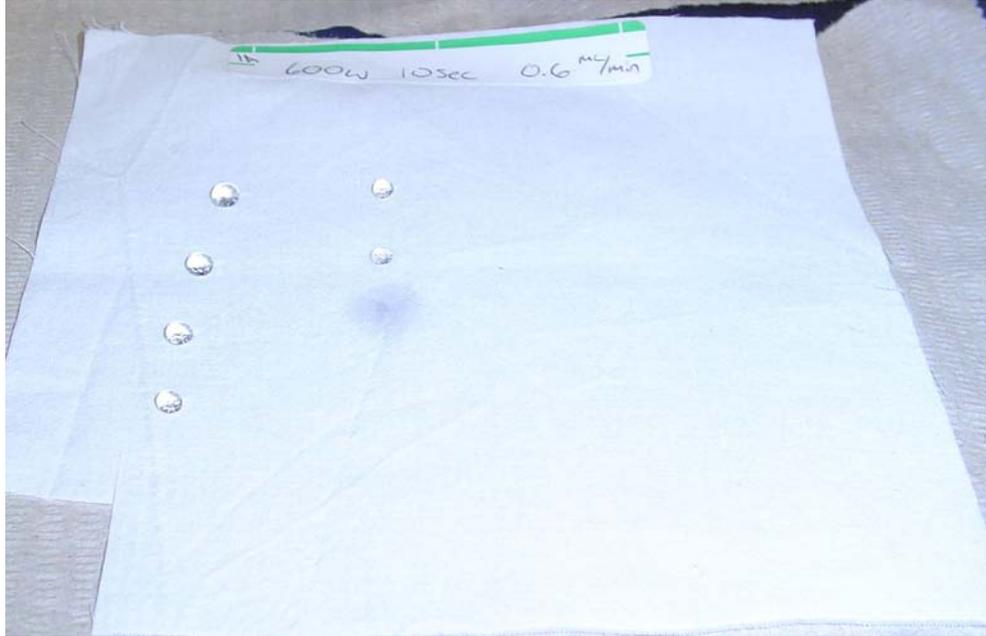
While Sample 1 did absorb some after one minute, samples 1A and 1B did not absorb any water droplets. Sample 1 had a longer plasma exposure time, at 20 seconds versus 10 seconds for sample 1A and 1B. The decrease in hydrophobicity could be due to the extended exposure to the plasma, which may have etched the water repellent polymer, causing it to decompose and lose functionality. In addition, the plasma may have grafted hydrophilic groups from the atmosphere onto the surface of the fabric, which would reduce its water repellency.

Samples 1A and 1B also did not absorb water drops on the untreated side. The difference in treatment for samples 1A and 1B is the flow of the carrier gas, Ar. Sample 1A was run with a flow rate of 0.5 SLPM Ar while sample 1B was run with a flow rate of 0.3

SLPM. The intention of lowering the flow rate of the Ar was to reduce the depth of penetration of the monomer, in order to prevent the underside of the fabric from becoming hydrophobic and thus not breathable. However, the water drop test did not find a difference between these two fabrics. A more sensitive test, such as measuring the contact angle of water on the fabric surface at high magnification, should be able to find any possible differences in the repellency of these two samples.

#### **4.3.2 Water/Alcohol Test Results for Experiment 1**

As it can be seen in Figure 4-5, sample 1A scored a grade of 6 on the water/alcohol solution resistance test (AATCC TM 193-2004). By referring to Table 4-2, it is seen that this grade means that the fabric sample did repel the solution drop with a composition of 60:40 water:isopropyl alcohol, but did absorb a solution drop with a composition of 50:50 water:isopropyl alcohol. Sample 1B also scored a grade of 6. Thus the water repellency of samples 1A and 1B are relatively similar.



**Figure 4-5: Water/Alcohol Test for Experiment 1 (Sample 1A)**

**Table 4-2: Results of Water/Alcohol Test for Sample 1A**

Grade	Passes Composition
0	None
1	98:2 water:isopropyl alcohol
2	95:5 water:isopropyl alcohol
3	90:10 water:isopropyl alcohol
4	80:20 water:isopropyl alcohol
5	70:30 water:isopropyl alcohol
<b>→6</b>	<b>60:40 water:isopropyl alcohol←</b>
7	50:50 water:isopropyl alcohol
8	40:60 water:isopropyl alcohol

#### **4.3.3 Contact Angle Measurements for Experiment 1**

The contact angles of the fabric were measured using a laboratory designed goniometer, with manual measurements being taken on a scale. Due to the subjective nature of this, there is an expected margin of error. The standard deviation was calculated for each sample and averaged over the samples using excel. The result found an average standard deviation of 4.24 degrees. However, this deviation would be much larger if more samples had been measured or if there had been multiple observers. Therefore the data is used to compare the relative repellencies within the sample set only.

**Table 4-3: Contact Angles for Experiment 1**

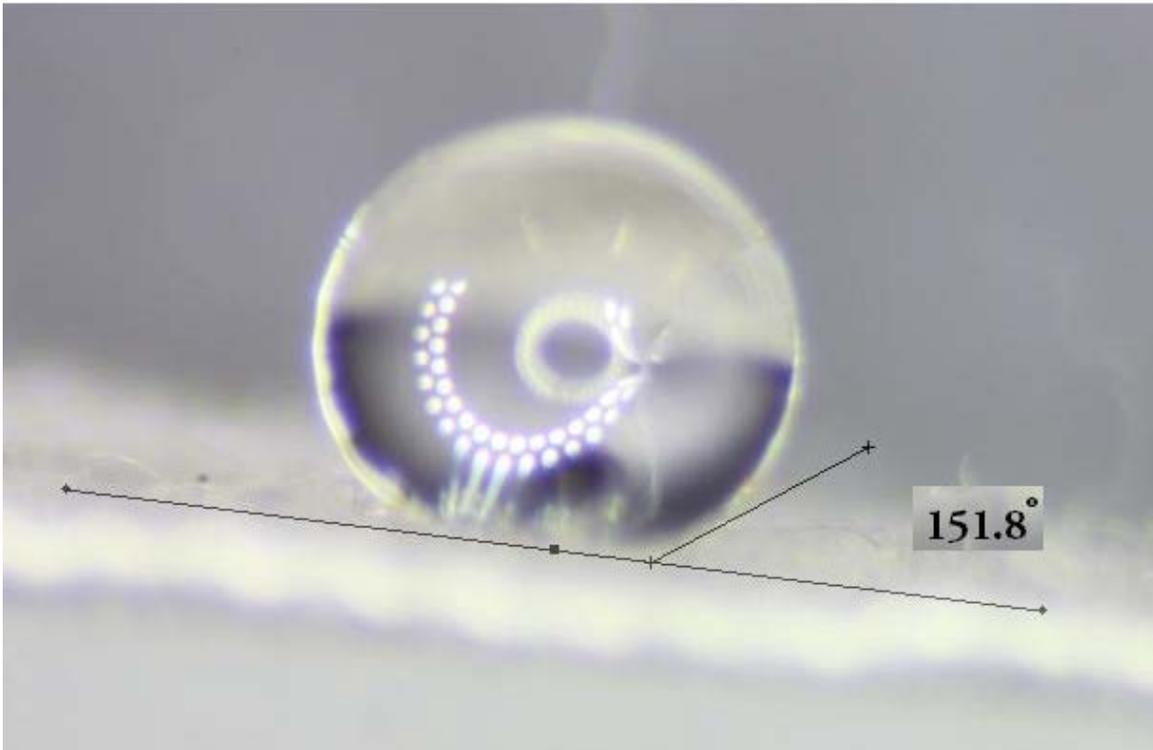
	Parameters		Right	Left	Average
Sample 1	20 sec plasma exposure, 0.5 SLPM Ar	Treated Side	74	79	76.5
		Untreated Side	76	74	75
Sample 1A	10 sec plasma exposure, 0.5 SLPM Ar	Treated Side	120	121	120.5
		Untreated Side	94	96	95
Sample 1B	10 sec plasma exposure, 0.3 SLPM Ar	Treated Side	117	116	116.5
		Untreated Side	85	91	88
Untreated	None	n/a	50	75	62.5

The results show that the treatment succeeded in imparting a water repellent finish. In addition, it confirmed that the longer plasma time caused a reduction in water repellency, as seen by the lower contact angle measured on sample 1. This is most likely due to degradation of the polymer finish by the prolonged plasma exposure.

The results of the contact angle measurements show that the higher flow rates of the monomer carrier gas, Ar, resulted in a more water repellent surface. The difference between the contact angles measured on the untreated sides of samples 1A vs. 1B are relatively small, especially when the margin of error is taken into consideration. Therefore the benefit of the higher carrier gas flow rate is greater than the potential of increasing the hydrophilicity of the untreated side.

#### 4.4 Results from Experiment 2

The samples prepared in experiment 2 were tested for water repellency using a goniometer which could take high resolution images of the water droplet on the surface of the fabric. These images were then uploaded to Photoshop Pro software, and the measuring tool was employed to measure the contact angle. This is shown in Figure 4-6.

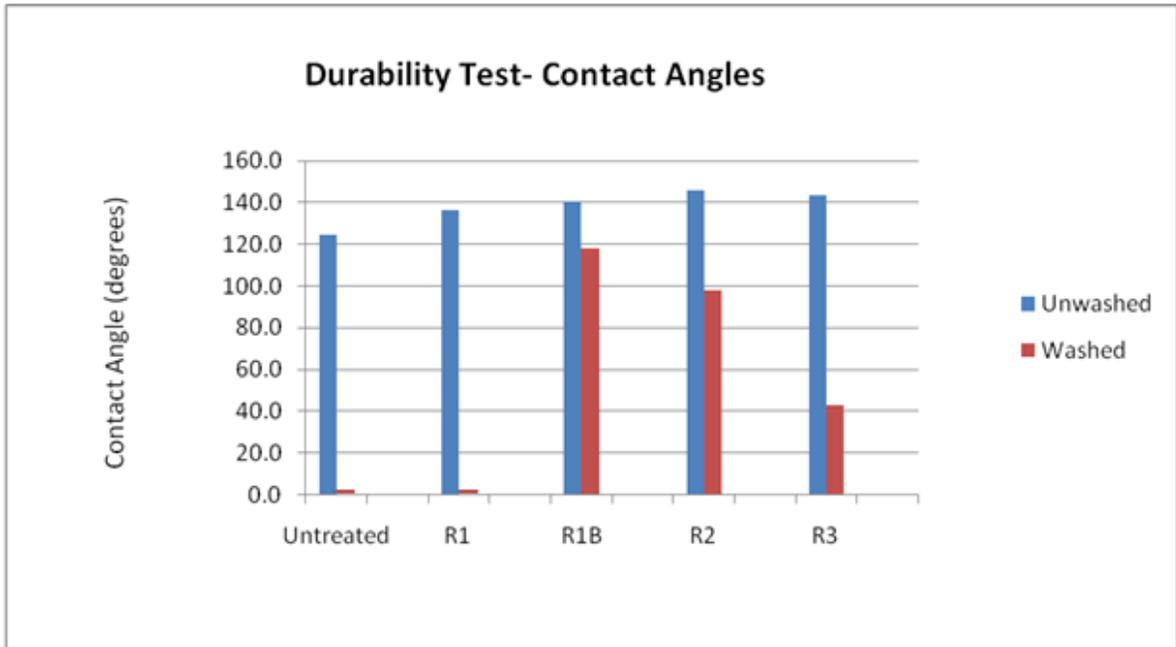


**Figure 4-6: Contact Angle Measured for Sample R2**

The image appears to be unlevel due to the angle of the camera lens, but the stage on which the sample is mounted is actually carefully parallel with the floor.

The full table of contact angle measurements can be found in Appendix B. The calculated standard deviation for the contact angle measurements is 7.04 degrees, averaged over the sample set.

All samples were measured in duplicate, with a measurement taken from each end of the fabric width-wise. The table of raw data can be found in Appendix B. From this it can be seen that the contact angles were relatively equivalent across the width of the fabric, which shows that the water repellent finish was consistent. The resulting average contact angles for each sample, before and after washing, are represented in Figure 4-7.



**Figure 4-7: Contact Angle for Durability Testing of Experiment 2 Samples**

For reference, sample R1 was treated with 0.6 ml/min monomer flow with 10

seconds of plasma polymerization exposure. Sample R1B was the same as R1 with the inclusion of the pre-deposition plasma surface activation step for 10 seconds. Sample R2 was treated with 0.8 mL/min monomer flow with 10 seconds of plasma polymerization exposure, and sample R3 was treated with 0.8 mL/min with 5 seconds of plasma polymerization exposure time. All samples were exposed to 600 watts of RF power.

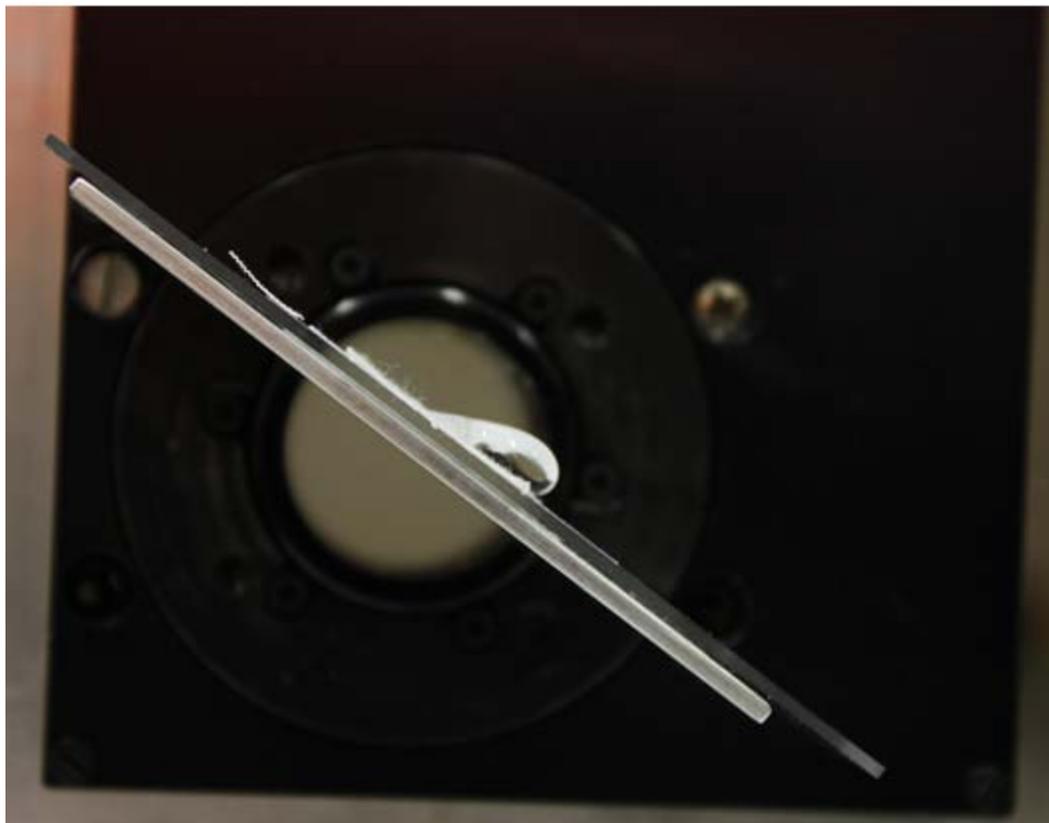
As can be seen in Figure 4-7, the water repellency is relatively equivalent for the treated samples. In addition, it is shown that some water repellency functionality is durable. Higher monomer flow rates can increase the durability of the treatment, but the inclusion of the pre-deposition plasma surface activation step has a greater impact on improving the durability. This is due to the surface activation of the fabric before the monomer is deposited, which allows the monomer to graft polymerize to the surface of the substrate. This covalent bond increases the durability of the finish.

It is notable that the water repellency of the untreated fabric before washing is greater than 90°. This means that the starting substrate was hydrophobic. This could be due to a variety of reasons. The high percentage of polyester in the intimate blend (50% PET) contributes to hydrophobicity. There may also be residual size and coning oils left over from processing, which were not fully removed during fabric preparation. The cause could also lay in the testing method. The samples are adhered to a glass specimen slide using double-sided sticky tape. Due to the thinness of the fabric, the water droplet placed on the

surface of the fabric may be interacting with both the fabric and the sticky tape below it, increasing the apparent water repellency. However, after the accelerated wash cycle, the untreated sample readily absorbed water. This may have been due to surface roughening of the fabric by the wash cycle.

For samples with high levels of water repellency, a drop of water applied to the surface can roll across the surface without sticking. In these cases, the rolling contact angle can be measured. The untreated and washed samples did not have sufficient water repellency to allow a water drop to roll, so the unwashed, treated samples were measured. The device consists of a stage which slowly rotates until the water drop begins to roll. At this point the rotation is halted and the angle of the stage is read.

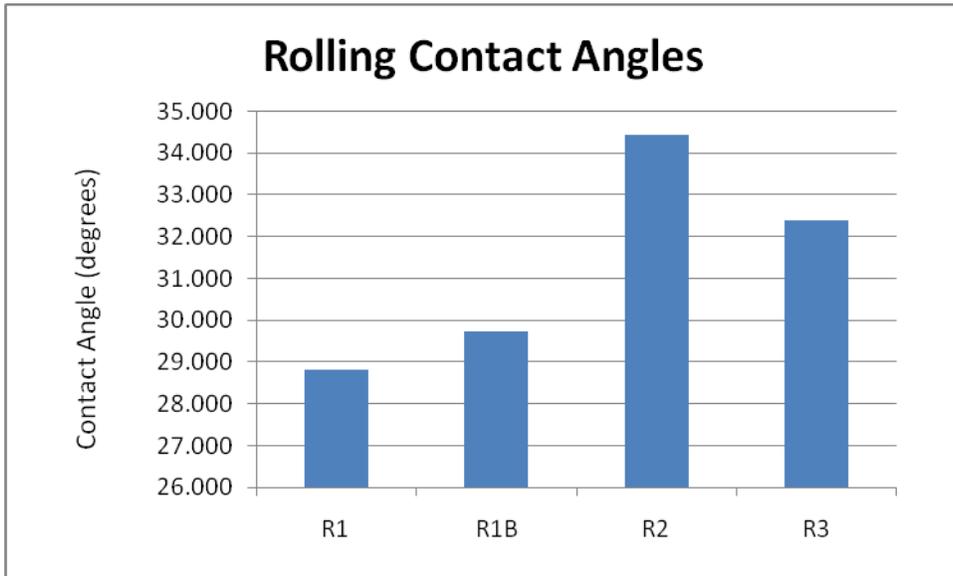
Figure 4-8 shows the stage's rotation just as the water droplet is about to roll when testing sample R2. Because the horizontal position is considered zero, the more the stage rotates, the higher the angle becomes. A drop of water will roll easier on a more hydrophobic surface than a less hydrophobic surface. Therefore, the higher the rolling contact angle, the less water repellent the surface.



**Figure 4-8: Sample R2 Preparing to Roll During Test**

Figure 4-9 represents the rolling contact angles. Here, the larger angles correspond to the samples with higher flow rates of the fluorocarbon monomer. Thus, the samples with more finish were less hydrophobic. This may be due to the increased thickness of the polymer layer interacting with the water drop in such a way as to cause the drop to stick to it. Or, what may have occurred is that an excess of monomer was applied to the fabric, and then the relatively low power and short exposure time which was used to polymerize it was not sufficient to fully polymerize all the monomer. Being volatile, the unreacted monomer

would vaporize before contact angle tests could be conducted.

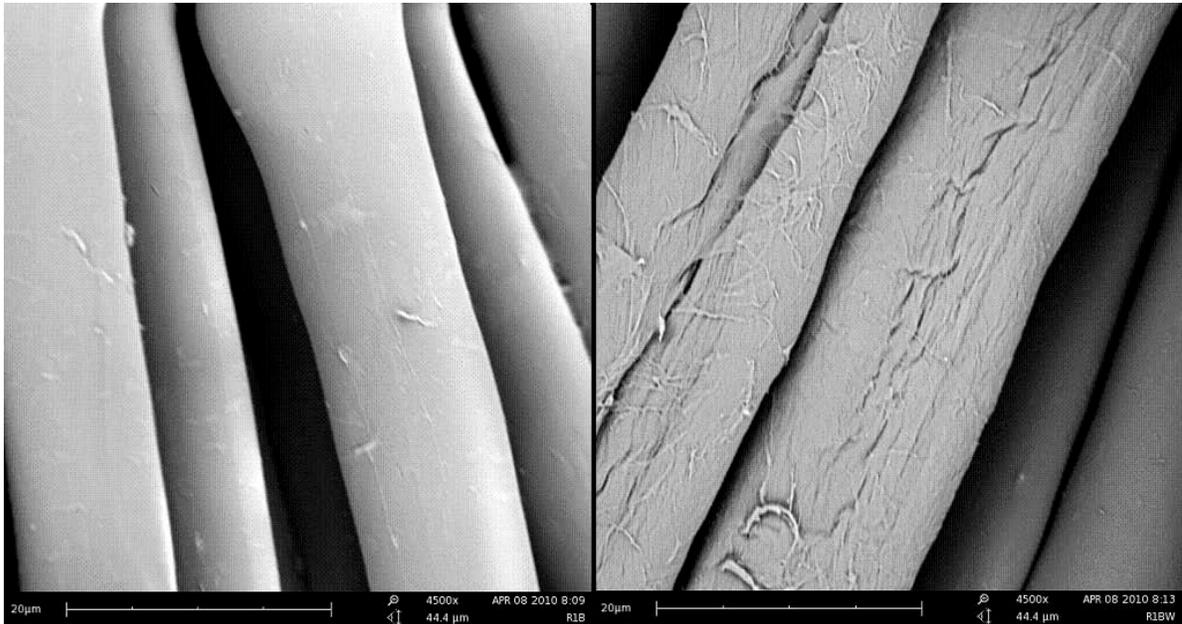


**Figure 4-9: Rolling Contact Angles for Experiment 2 Samples**

The significant decrease in contact angle following the accelerated wash cycle is of interest. All of the samples, following the wash cycle, were less water repellent than the unwashed, untreated fabric. Therefore there must be not only a loss of the function of the finish, but some change to the fabric itself. This was analyzed using SEM.

As can be seen by comparing the images in Figure 4-10, the surface of the fibers is greatly roughened by the accelerated wash cycle. This roughening of the surface could attribute to the loss in water repellency, rather than a lack of durability of the fluorocarbon finish. This may indicate that the accelerated wash cycle system outlined in AATCC TM 61-2007 is not the most suitable method for determining wash fastness with a surface finish.

AATCC TM 61 was developed to test colorfastness of dyes, which are not as sensitive to surface modifications. The mechanical action of the stainless steel balls may have roughened the surface of the fabric more than a typical home washer machine would have, even over five cycles.



**Figure 4-10: SEM at 4500x Magnification of Sample with Water Repellent Finish (left) and with Water Repellent Finish that has been through an Accelerated Wash Cycle (right).**

## 4.5 Results from Antimicrobial Application (Experiment 3)

### 4.5.1 Water Drop Test Results for Experiment 3

All samples, once treated with the antimicrobial agent, absorbed water. This is to be expected because the DADMAC antimicrobial agent is a charged compound, which is highly hydrophilic. The samples did not absorb the water readily, however, and thus the time for a water drop to be fully absorbed by the fabric could be measured. By examining the results of Table 4-4: Water Drop Test Results for Experiment 3, there does not seem to be a direct correlation between the concentration of DADMAC applied to the resulting water repellency properties nor does there seem to be a direct correlation between the duration of plasma curing exposure and the resulting water repellencies.

**Table 4-4: Water Drop Test Results for Experiment 3**

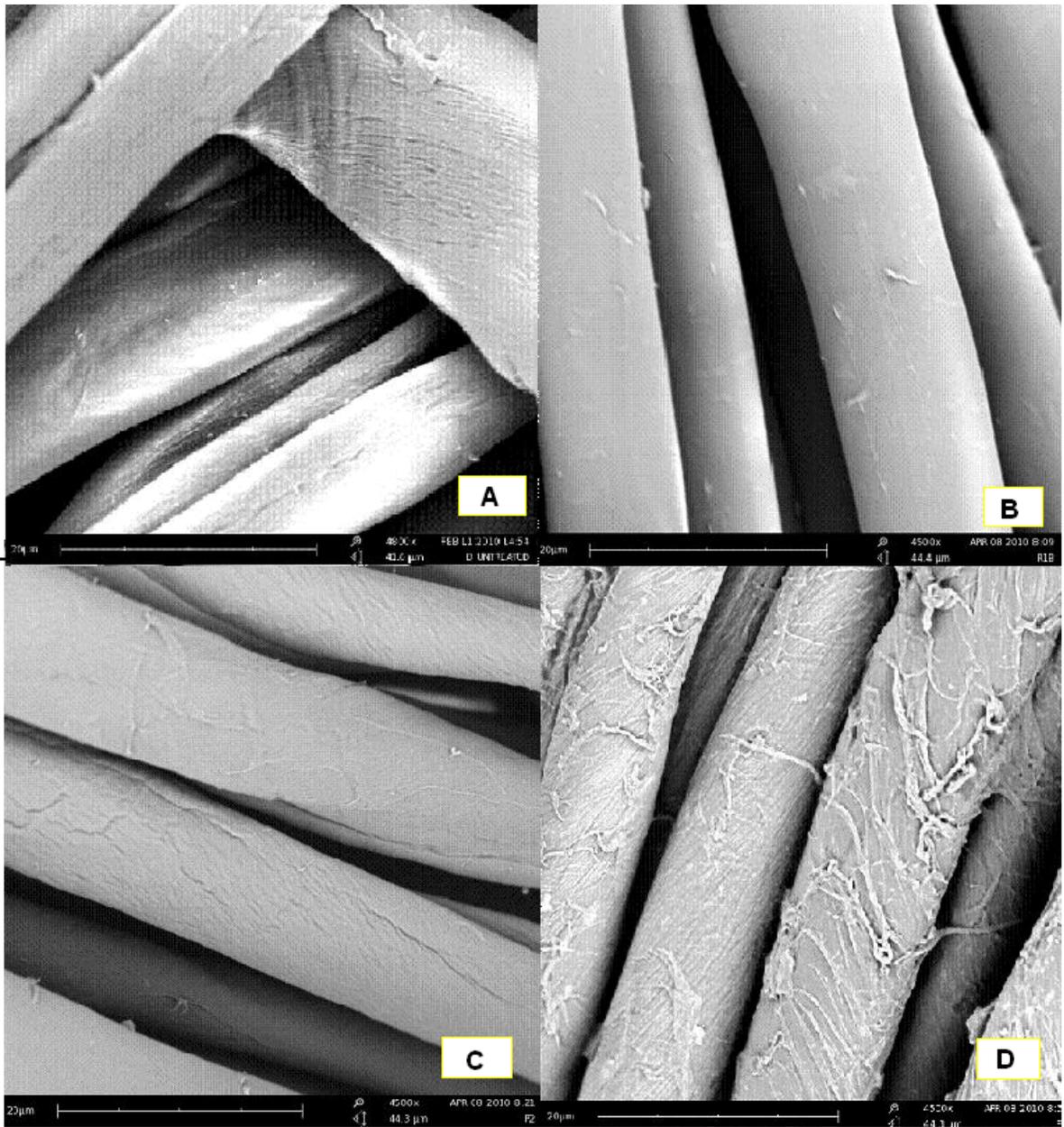
Sample	DADMAC (g/L)	Plasma Exposure (sec)	Time to fully absorb (sec)
A1	4	10	11
B1	8	10	10
C1	12	10	31
D1	16	10	8
E1	20	10	48
F1	24	10	8
A2	4	20	8
F2	24	20	10

This loss of water repellency is an obstacle that must be overcome in order for the fabric to be bifunctional as both a water repellent and an antimicrobial. With the water

repellent added to the fabric first, the hydrophilic antimicrobial layer is on the outermost layer, and thus the first to come in contact with applied water. Because the interactions of the water with the fabric are governed by the outermost layer, there may be some advantage to reversing the process and having the antimicrobial treatment applied first so that the outermost layer is the hydrophobic water repellent fluorocarbon treatment. Alternatively, these two treatments could be simultaneously applied.

#### **4.5.2 SEM Results from Experiment 3**

Figure 4-11 shows the fabric samples at each stage of the research, magnified at 4500x using SEM. The untreated fabric is shown as A, the water repellent treated fabric is shown as B, a fabric which was surface activated with plasma treatment without any chemical finish is shown in C, and the fabric which was treated with the water repellent followed by the antimicrobial finish is shown in D.



**Figure 4-11: SEM at 4500x Magnification of Untreated Fabric (A), Fabric Treated with Fluorocarbon (B), Fabric Treated with Plasma Exposure Only (C), and Fabric Treated with Water Repellent and Antimicrobial (D)**

Image B demonstrated how smooth the surface is after water repellent treatment. This was due to the very thin layer of fluorocarbon polymer that is applied for the water repellent finish, which smoothes over the fibers. C, by contrast, showed that the surface of the fibers become damaged during plasma surface activation without a chemical treatment. This is a factor in the increased hydrophilicity of the fabric following the plasma surface etching. D showed the antimicrobial treatment. The smooth rope-like structures of chemical finish is evidence that the finish polymerized, as DADMAC monomer on a fabric surface would appear as particulates and globules rather than smooth tendrils.

#### **4.5.3 Antimicrobial Activity Results for Experiment 3**

The fabric samples treated with both the TG-10 water repellent, plasma treatment followed by the DADMAC antimicrobial, plasma treatment were tested for their antimicrobial properties using AATCC TM 100-2004. This test uses two common species of bacteria: a gram positive bacteria, *Staphylococcus aureus*, which is the bacteria that causes staph infections, and a gram negative bacteria, *Klebsiella pneumoniae*, the bacteria responsible for pneumonia. Fabric swatches are soaked in solution, then inoculated with the bacteria. The samples are analyzed at time zero and again at 24 hours to determine how many colony forming units (CFU) are present. Less than 5 colony forming units is the baseline, and considered zero.

Table 4-5 and Table 4-6 compare the samples to an alternate control, which is plain, sterile cotton. According to this, there is some antimicrobial activity inherent in the untreated fabric. This may be due to the polyester content. Cellulose is a more porous material for bacteria to colonize in, and provides greater sustenance to the bacteria, encouraging more growth.

**Table 4-5: Results of AATCC TM 100 with *K. pneumoniae***

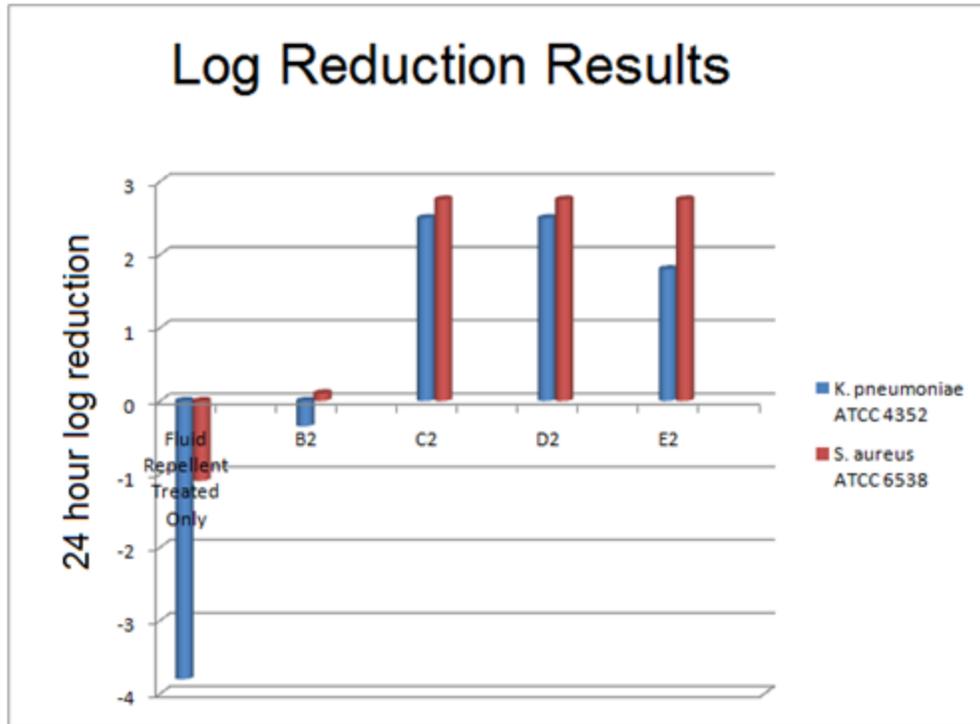
Microorganism	Sample	Sample Variables	Contact Time	CFU	% Reduction vs. Alternate Control
<i>K. pneumoniae</i> ATCC 4352	Control Sample	Untreated	Time Zero	1.66E+05	
			24 Hours	3.15E+02	99.96%
	Fluid Repellent Treated Only	Fluid Repellent only	Time Zero	1.66E+05	
			24 Hours	2.00E+06	None
	B2	8 g/L DADMAC	Time Zero	2.16E+05	
			24 Hours	7.00E+02	99.91%
	C2	12 g/L DADMAC	Time Zero	1.72E+05	
			24 Hours	<5	>99.9994%
	D2	16 g/L DADMAC	Time Zero	1.90E+05	
			24 Hours	<5	>99.9994%
	E2	20 g/L DADMAC	Time Zero	2.23E+05	
			24 Hours	5.00E+00	99.9994
	ATL Control	Plain cotton	Time Zero	1.58E+05	
			24 Hours	8.00E+05	N/A

**Table 4-6: Results of AATCC TM 100 with S. aureus**

Microorganism	Sample	Sample Variables	Contact Time	CFU	% Reduction vs. Alternate Control
S. aureus ATCC 6538	Control	Untreated	Time Zero	4.95E+04	
			24 Hours	5.65E+02	94.05%
	Fluid Repellent Treated Only	Fluid Repellent only	Time Zero	5.90E+04	
			24 Hours	7.00E+03	None
	B2	8 g/L DADMAC	Time Zero	5.30E+04	
			24 Hours	4.45E+02	95.32%
	C2	12 g/L DADMAC	Time Zero	6.10E+04	
			24 Hours	<5	>99.9473%
	D2	16 g/L DADMAC	Time Zero	8.05E+04	
			24 Hours	<5	>99.9473%
	E2	20 g/L DADMAC	Time Zero	6.95E+04	
			24 Hours	<5	>99.9473%
	ATL Control	Plain cotton	Time Zero	6.40E+04	
			24 Hours	9.50E+03	N/A

The results of this data are represented in charts which are found in Appendix C.

To determine the antimicrobial activity of the finishes, the samples are compared to the control which is untreated fabric used in this research. The log reduction was calculated in this comparison, and the results are represented in Figure 4-12.



**Figure 4-12: Log Reduction over 24 hours for both Bacterium Species**

It should be noted that the sample treated with water repellent, only, decreased the antimicrobial activity of the fabric. Although the reasons for this are unknown, it makes the difference with the samples that were treated with the DADMAC based antimicrobial finish more significant. These samples were antimicrobial enough to overcome the starting disadvantage caused by the water repellent and impart substantial antimicrobial functionality to the fabric.

From the log reduction graph, it is shown that samples C2 and D2 produced the

most antibacterial finishes. With *K. pneumoniae* and *S. Aureus* the log reductions were 2.5 and 2.8, respectively. These values were the largest possible within the restrictions of this test, and represent a complete reduction in colony forming units of bacteria. These values corresponded to samples prepared through a pad bath containing 12 g/L and 16 g/L of DADMAC, respectively. Lower concentrations had significantly reduced antimicrobial properties, as seen by the lower and even negative log reductions observed for sample B2, which was prepared using a pad bath which contained 8 g/L of DADMAC. Similarly, the antimicrobial functionality against gram negative bacteria was reduced at higher concentrations of DADMAC, as shown by the results for sample E2, which was prepared using 20 g/L of DADMAC in the pad bath.

## Chapter 5 Conclusions

It was found that the application of the fluorocarbon monomer, TG-10 by UNIDYNE™ (Daikin Industries, Ltd.), followed by a curing step using nonthermal atmospheric pressure plasma produced a water repellent finish that is durable to laundering. The textile is more hydrophobic on the treatment side than the non treated side, which gives the fabric dual functionality through water repellency on one side and hydrophilicity on the other side of the fabric. This allows a functional water resistant garment to be breathable and comfortable.

The fabric could also be treated with an antimicrobial monomer, which could be cured through a nonthermal atmospheric pressure plasma step. This antimicrobial finish is effective as a biocide against both *K. pneumoniae* and *S. Aureus* bacteria.

### 5.1 Conclusions from Fabric Evaluation

Not all impurities or warp size can be removed through textile wet preparation processing. These residual impurities may contain processing lubricants or oils. Coupled with some residual warp size, these contribute to the initial hydrophobicity observed with the untreated fabric samples.

## **5.2 Conclusions from Initial Water Repellency Treatment, (Experiment 1)**

The water drop test showed that the treatment is not consistent across the fabric, but that was due to machinery malfunction which was then corrected. Contact angle measurements showed that the water repellency is increased on the non treatment side as well as the treatment side. This was due to the monomer vapor penetrating the relatively thin fabric. Once monomer was inside the fabric structure and was exposed to plasma, the monomers formed a polymer network within the fabric which contributed to overall water repellency. However, the treatment side was still more hydrophobic than the untreated side.

Prolonged exposure to the plasma decreased the water repellency functionality of the fluorocarbon polymer nanolayer. In addition, reducing the flow of the monomer carrier gas did not affect the depth of penetration of the treatment on a thin fabric substrate.

## **5.2 Conclusions from Secondary Water Repellency Treatment, (Experiment 2) and Durability**

Contact angle measurements for these samples were equivalent on different parts of the fabric sample, thus the treatment was uniform. Rolling contact angle measurements show that the monomer-plasma treatment caused the surface to be highly hydrophobic,

but higher monomer flow rates contribute to the hydrophobicity of the fabric but does not allow water droplets to roll as easily as samples treated at lower flow rates.

Contact angle measurements show that faster processing times, which mean shorter plasma polymerization exposure time, can result in relatively equivalent initial water repellency. However, the shorter plasma exposure time also contributes to a decrease in durability of the finish.

The water repellent finish via plasma aided monomer deposition is durable to laundering. Increased durability was observed with higher percent add-ons and when a pre-deposition plasma surface activation step was included.

### **5.3 Conclusions from Experiment 3**

SEM images confirm that the antimicrobial monomer, DADMAC, is polymerized by exposure to nonthermal atmospheric pressure plasma.

Results of the antimicrobial assessment confirms that the DADMAC plasma treatment produces a fabric which is functionally antimicrobial and acts as a biocide against both gram positive and gram negative bacteria.

To increase the antibacterial functionality of the finish, higher concentrations of monomer may be padded on. However, very high concentrations of monomer also caused

a decrease in the antibacterial properties. Thus a pad bath that is between 12 g/L and 16 g/L DADMAC is ideal.

## **Chapter 6 Future Work**

Monomer deposition for plasma treatment is beginning to move from using Ar gas to push the monomer onto the fabric to using N gas. The reason behind this is that N is a less expensive gas than Ar. In addition, there are currently systems being developed to reclaim He gas used in plasma generations to reduce cost. Because there is some mixing of the plasma gas and the monomer flow gas, the monomer flow gas must be separated out from the He gas during reclaiming. N gas is much easier to separate from He than Ar gas. Replacing the Ar gas with N will aid in the use of the He reclamation systems, allowing for a decrease in cost of operating these plasma systems.

Poor durability of the water repellent was observed, in general, even using a pre-monomer deposition plasma treatment. Durability can be improved through the addition of crosslinkers. Crosslinking agents may be added to the pure monomer prior to deposition. In addition, the durability of the fabric may be more accurately determined by using standard wash cycles, repeated 5 times rather than the accelerated wash cycle, which might be altering the surface topography of the fibers.

The antimicrobial treatment displaced the functionality of the water repellent

treatment. This may be overcome by altering the relative thicknesses of the two polymer layers so that the antimicrobial's surface properties do not overwhelm the properties of the water repellent. In addition, the order of the layers could be explored. One proposed experiment is to pad on the antimicrobial agent, dry it, then polymerize it with a plasma treatment. The fabric could then have a second layer, which is water repellent, applied. In an alternate variation, the antimicrobial agent could be applied and dried but not cured. Then the water repellent monomer could be applied, and then undergo a polymerization step with plasma, leading to crosslinking and a single polymer network which is both water repellent and antimicrobial.

## Chapter 7 References

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- <sup>1</sup> Fiala, D., Lomas, K. J., & Stohrer, M. (1999). A computer model of human thermoregulation for a wide range of environmental conditions: The passive system. *Journal of Applied Physiology*, 87(5), 1957-1972.
- <sup>2</sup> Carr, C.M. (Ed.) (1995). *Chemistry of the textiles Industry*. London, UK: Chapman & Hall.
- <sup>3</sup> Sampath, M.B.; and Senthilkumar, M. (2009) Effect of moisture management finish on comfort characteristics of microdenier polyester knitted fabrics. *Journal of Industrial Textiles*, 39(2). 163-173.
- <sup>4</sup> Schindler, W. D., & Hauser, P. J. (2004). *Chemical finishing of textiles*. Cambridge, England: Woodhead Publishing Ltd.
- <sup>5</sup> *Cotton dyeing and finishing: a technical guide*. (1996) Cary, NC: Cotton Incorporated.
- <sup>6</sup> Skelly, K. J. (Ed.) (2003). *Water recycling in textile wet processing*. West Yorkshire, England: Society of Dyers and Colourists.
- <sup>7</sup> EPA Office of Compliance Sector Notebook Project (1997). *Profile of the Textile Industry*. U.S. Environmental Protection Agency. Washington, NC.
- <sup>8</sup> D&K Consulting. Plasma techniques versus wet pretreatments: a technical and economic assessment of potential savings. *Textile Month* March 1995. 17-24
- <sup>9</sup> Shishoo, R. (Ed.) (2007). *Plasma technologies for textiles*. Boca Raton, FL: CRC Press.
- <sup>10</sup> Tendero, C.; Tixier, C.; Tristant, p.; Desmaison, J.; and Leprince, P. (2006). Atmospheric

---

pressure plasmas: a review. *Spectrochimica Acta B*. 61. 2-30.

<sup>11</sup> Hippler, R.; Kersten, H.; & Schmidt, M.(ed.) (2008). *Low temperature plasmas: fundamentals, technologies, and techniques*. Weinheim, Germany: Wiley VCH.

<sup>12</sup> Boulos, M. I.; Fauchais, P; and Pfender, E. (1994). *Thermal plasmas: fundamental and applications*. Vol. 1. New York: Plenum Press.

<sup>13</sup> Manning, T. J.; and Grow, W. R. (1997). Inductively coupled plasma- atomic emission spectrometry. *The Chemical Educator*. 2(1). 1-19.

<sup>14</sup> O'Neill, L.; & O'Sullivan, C. (2009). Polymeric coatings deposited from an aerosol-assisted non-thermal plasma jet. *Chemical Vapor Deposition*, 15: 21-26.

<sup>15</sup> Schütze, A.; Jeong, J. K.; Babayan, S. E.; Park, J.; Selwyn, G. S.; and Hicks, R. F. (1998). The atmospheric-pressure plasma jet: a review and comparison to other plasma sources. *IEEE Transactions on Plasma Science*. 26(6). 1685-1694.

<sup>16</sup> (2005). *The Leader in Plasma Technology: The Technology Comparison*. Retrieved Mar. 15, 2010, from APJeT, Inc., Santa Fe, NM. Web site: <http://www.apjet.com/techcompare.html>.

<sup>17</sup> Samanta, K. K., Jassal, M., & Agrawal, A. K. (2009). Improvement in water and oil absorbency of textile substrate by atmospheric pressure cold plasma treatment. *Surface and Coatings Technology*, 203(10-11), 1336-1342.

<sup>18</sup> Poll, H. U., Schladitz, U., & Schreiter, S. (2001). Penetration of plasma effects into textile structures. *Surface and Coatings Technology*, 142-144, 489-493.

<sup>19</sup> Albaugh, J.; O'Sullivan, C.; & O'Neill, L. (2008). Controlling deposition rates in an

---

atmospheric pressure plasma system. *Surface and Coatings Technology*, 203: 844-847.

<sup>20</sup> Mittal, K. S. *Development of dual functional textile materials using atmospheric plasma treatments* (Masters Dissertation). 2009. North Carolina State University. Raleigh, NC.

<sup>21</sup> Bae, P.H.; Hwang, Y.J.; Jo, H.J. et al. (2006). Size removal on polyester fabrics by plasma source ion implantation device. *Chemosphere*, 63(6), 1041-1047.

<sup>22</sup> Cai, Z. & Qui, Y. (2006). The mechanism of air/oxygen/helium atmospheric plasma action on PVA. *Journal of Applied Polymer Science*, 99(5), 2233-2237.

<sup>23</sup> Wu, J.; Zeng, F.; Chen, B. (2008). The solubility of natural cellulose after DBD plasma treatment. *Plasma Science and Technology*, 10 (6), 743-747.

<sup>24</sup> Gawish, S. M.; Ramadan, A. M.; Matthews, S. R.; & Bourham, M. A. (2008). Modification of PA6,6 by atmospheric plasma and grafting 2-hydroxy ethyl methacrylate (HEMA) to improve fabric properties. *Polymer-Plastics Technology and Engineering*, 47: 473-478.

<sup>25</sup> Pandiyaraj, K. N.; & V. Selvarajan, V. (2008). Non-thermal plasma treatment for hydrophilicity improvement of grey cotton fabrics. *Journal of materials processing technology*, 199, 130-139.

<sup>26</sup> (2005). *Apjet, Inc.: The Leader in Plasma Technology*. Retrieved April 4, 2010 from APJeT, Inc., Santa Fe, NM. Web site: <http://apjet.com/technology.html>.

<sup>27</sup> Kissa, E. *Fluorinated surfactants and repellents: surfactant science series v. 97* (2<sup>nd</sup> ed.). (2001) New York: Marcel Dekker.

<sup>28</sup> Kissa, E. (1996). Wetting and Wicking. *Textile Research Journal*, 66(10), 660-668.

---

<sup>29</sup> Young, T. (1805) An Essay on the cohesion of fluids. *Philosophical Transactions of the Royal Society of London*, 95, 65-87

<sup>30</sup> Marmur, A. (2004). The lotus effect: superhydrophobicity and metastability. *Langmuir*, 20: 3517-3519.

<sup>31</sup> Gao, L.; & McCarthy, T. J. (2006). "Artificial lotus leaf" prepared using a 1945 patent and a commercial textile. *Langmuir*, 22: 5998-6000.

<sup>32</sup> W. A. Zisman. in "Contact angle, wettability, and adhesion," R. F. Good, ed., *Advances in chemistry series* Vol. 43, p. 1, American Chemical Society, Washington, DC (1964).

<sup>33</sup> Heywood, D. (Ed.) (2003). *Textile Finishing*. West Yorkshire, England: Society of Dyers and Colourists.

<sup>34</sup> Clariant. (2002). Fluorocarbon polymers- new generation water and stain repellents. *TexTalk*, vol 7.

<sup>35</sup> Shao, H.; Sun, J.Y.; & Meng, W.D. (2004). Water and oil repellent durable press finishes for cotton based on perfluoroalkyl-containing multi-epoxy compound with citric acid. *Textile Research Journal*, 74(10), 851-855.

<sup>36</sup> Armitage, J.M.; Macleod, m.; & Cousins, I.T. (2009). Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAsP and perfluorocarboxylates (PFCs) emitted from direct sources. *Environmental Science and Technology*, 43, 5830-5836.

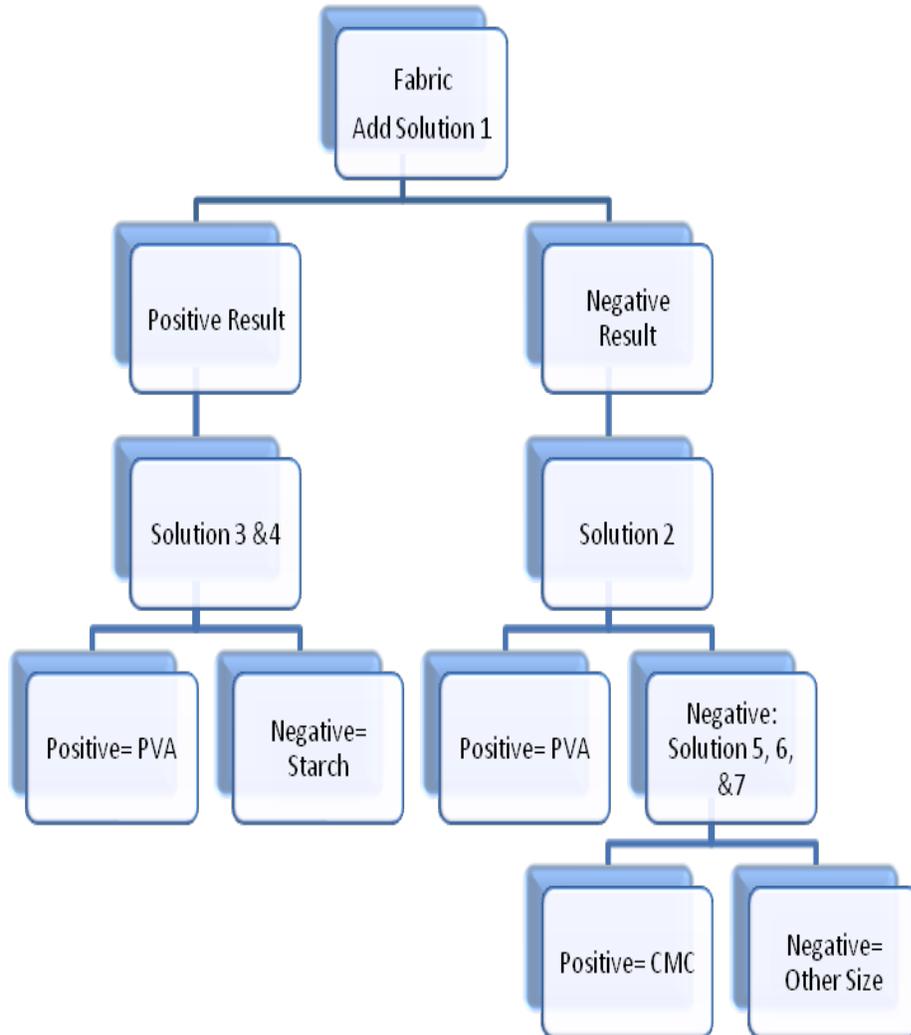
<sup>37</sup> U.S. Environmental Protection Agency. 2010/2015 PFOA Stewardship Program.

- 
- <sup>38</sup> Johansson, N.; Fredriksson, A.; & Eriksson, P. (2008). Neonatal exposure to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) causes neurobehavioural defects in adult mice. *Neurotoxicology*, 29(1), 160.
- <sup>39</sup> Eastern Color & Chemical Co. (2009). Stain Release without PFOS or PFOA. *AATCC Review*, 9(9), 22.
- <sup>40</sup> Ceria, A., & Hauser, P. (2010). Atmospheric plasma treatment to improve durability of a water and oil repellent finishing for acrylic fabrics. *Surface & Coatings Technology*, 204(9/10), 1535-1541.
- <sup>41</sup> Leroux, F., Campagne, C., Perwuelz, A., & Gengembre, L. (2008). Fluorocarbon nano-coating of polyester fabrics by atmospheric air plasma with aerosol. *Applied Surface Science*, 254(13), 3902-3908.
- <sup>42</sup> Di Mundo, R., De Benedictis, V., Palumbo, F., & d'Agostino, R. (2009). Fluorocarbon plasmas for nanotexturing of polymers: A route to water-repellent antireflective surfaces. *Applied Surface Science*, 255(10), 5461-5465.
- <sup>43</sup> Tsafack, M. J., & Levalois-Grützmacher, J. (2007). Towards multifunctional surfaces using the plasma-induced graft-polymerization (PIGP) process: Flame and waterproof cotton textiles. *Surface and Coatings Technology*, 201(12), 5789-5795
- <sup>44</sup> Tsafack, M. J., & Levalois-Grützmacher, J. (2007). Towards multifunctional surfaces using the plasma-induced graft-polymerization (PIGP) process: Flame and waterproof cotton textiles. *Surface and Coatings Technology*, 201(12), 5789-5795.
- <sup>45</sup> Rouette, H.K. (ed.) (2001) *Encyclopedia of textile finishing*. Woodhead Publishing

- 
- <sup>46</sup> Gregersen, T. (1977). Rapid method for distinction of gram-negative from gram positive bacteria. *Applied Microbiology and Biotechnology*, 5(2), 123-127
- <sup>47</sup> McLean, R.D. *Stain repellent – antimicrobial textiles via atmospheric plasma finishes* (Masters Dissertation). 2007. North Carolina State University. Raleigh, NC.
- <sup>48</sup> Gawish, S. M., Matthews, S. R., Wafa, D. M., Breidt, F., & Bourham, M. A. (2007). Atmospheric plasma-aided biocidal finishes for nonwoven polypropylene fabrics. I. synthesis and characterization. *Journal of Applied Polymer Science*, 103(4), 1900-1910.
- <sup>49</sup> Wafa, D. M., Breidt, F., Gawish, S. M., Matthews, S. R., Donohue, K. V., Roe, R. M., et al. (2006). Atmospheric plasma-aided biocidal finishes for nonwoven polypropylene fabrics. II: functionality of synthesized fabrics. *Journal of Applied Polymer Science*, 103, 1911.
- <sup>50</sup> Gawish, S. M.; Ramadan, A. M.; Cornelius, C. E., Courham, M. A.; et al. (2007) New functionalities of PA6,6 fabric modified by atmospheric pressure plasma and grafted glycidyl methacrylate derivatives. *Textile Research Journal*, 77(2), 92-104.
- <sup>51</sup> Vaideki, K., Jayakumar, S., Rajendran, R., & Thilagavathi, G. (2008). Investigation on the effect of RF air plasma and neem leaf extract treatment on the surface modification and antimicrobial activity of cotton fabric. *Applied Surface Science*, 254(8), 2472.
- <sup>52</sup> Thone, J.; Holländer, A.; Jaeger, W.; Trick, I.; & Oehr, C. (2003). Ultrathin antibacterial polyammonium coatings on polymer surfaces. *Surface and Coatings Technology*, 174-175: 584-587.
- <sup>53</sup> Livengood, C. D. Spot tests for identification of warp sizes on fabrics. *Textile Industries* September 1983.

## APPENDIX

## APPENDIX A: Warp Size Identification



SOLUTION NUMBER	CONTENT
1	2.4g potassium iodide; 1.3g Iodine dissolved in H <sub>2</sub> O
2	0.13g iodine; 2.6g potassium iodide; 4.0g boric acid (added in that order) diluted to 100mL
3	11.88g potassium dichromate; 25mL of concentrated sulfuric acid, diluted with 50mL H <sub>2</sub> O
4	30g sodium hydroxide in 70 mL H <sub>2</sub> O
5	0.012M ferric chloride
6	0.06M potassium thiocyanate
7	0.005M potassium ferrocyanide

Solution 1: Spot the fabric with one or two drops. The formation of a deep blue color indicates the fabric has been sized with starch or poly(vinyl alcohol), (PVA).

Solution 2: (use only if it is known that starch is not present). Spot fabric with one or two drops. The formation of a purple color indicates the fabric has been sized with PVA.

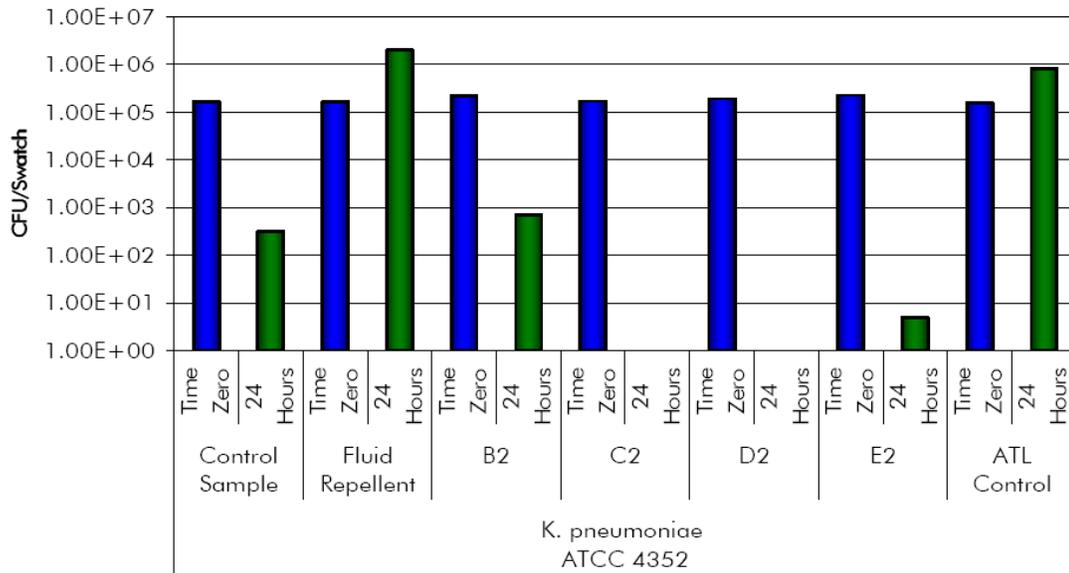
Solutions 3 & 4: Apply one drop of solution 3 and immediately neutralize it with three to four drops of solution 4. Wait five seconds, and then rub the mixture with a glass rod. Formation of a brown spot indicates the fabric has been sized with PVA.

Solutions 5, 6, & 7: Thoroughly mix five drops from solutions 5 & 6. Spot the fabric with one drop of this mixture and allow it stand for about three minutes. Rinse the fabric under running water for ten seconds and blot dry. Add one drop of solution 7 and allow it to stand for one minute. Rinse again under running water for five seconds and blot dry. A blue or green spot indicated the fabric has been sized with carboxymethyl cellulose, (CMC).

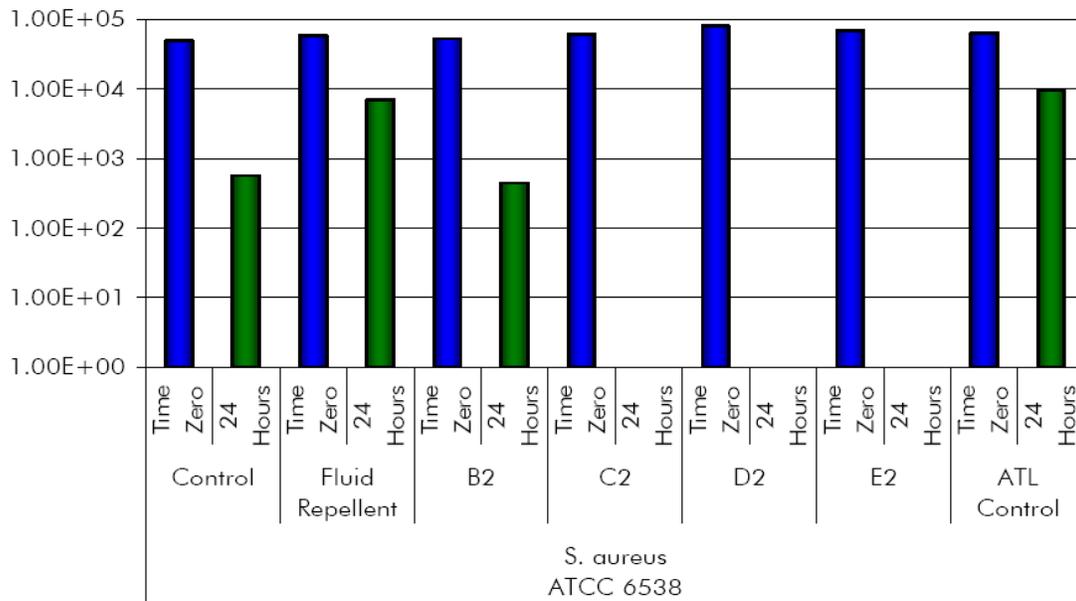
## APPENDIX B: Contact Angle Measurement for Experiment 2

Description	Sample ID	Contact Angles				Overall	
		Left	Right	Average			
Untreated	U	126.9	127.8	127.4	124.7		
	U (t=10 sec)	118.4	125.8	122.1			
600W; 0.6 ml/min; 10 sec	R1	132.4	131.0	131.7	136.2		
	R1	140.7	140.8	140.8			
Pre-plasma 600W; 0.6 ml/min; 10 sec	R1B	141.9	146.7	144.3	140.6		
	R1B	141.3	132.3	136.8			
600W; 0.8 ml/min; 10 sec	R2	154.2	151.8	153.0	145.5		
	R2	132.7	143.4	138.1			
600W; 0.8 ml/min; 5 sec	R3	136.8	142.0	139.4	143.5		
	R3	148.6	146.5	147.6			change
WASHED							
Untreated	U2	absorbed			0		
600W; 0.6 ml/min; 10 sec	Washed R1	absorbed			0.0	-136.2	
	Washed R1	absorbed					
Pre-plasma 600W; 0.6 ml/min; 10 sec	Washed R1B	113.3	119.8	116.6	118.0	-22.6	
	Washed R1B	102.1	136.7	119.4			
600W; 0.8 ml/min; 10 sec	Washed R2	99.0	107.4	103.2	97.7	-47.8	
	Washed R2	90.0	94.4	92.2			
600W; 0.8 ml/min; 5 sec	Washed R3	84.3	87.0	85.7	42.8	-100.7	
	Washed R3	Absorbed		0.0			

## Appendix C: Results of Antibacterial Tests



### Results of AATCC TM 100 with *K. pneumoniae*



### Results of AATCC TM 100 with *S. aureus*