Abstract

PEREZ RIVERA, BELEN M. Plasma-Aided Antimicrobial and Insect Repellant Finishing of Cotton. (Under the direction of Marian G. McCord and Mohamed A. Bourham.)

This research aimed to impart antimicrobial and insect repelling finishes to cotton fabrics using atmospheric pressure plasma-aided graft copolymerization of active monomers. The process consists of multiple steps; first, surface activation of fabric samples via atmospheric pressure plasma, followed by polymerization reaction of glycidyl methacrylate (GMA). Following GMA grafting, antimicrobial agents (β-cyclodextrin or quaternary ammonium chitosan derivative, HTCC) are reacted with grafted GMA epoxide groups to produce cotton/GMA/antimicrobial agent. Samples grafted with β-cyclodextrin are reacted with insect repelling agents (such as extracts of citronella, sweet basil, jasmine) as inclusion into the cavities of β-cyclodextrin.

Samples were exposed to plasma, which has 99% helium and 1% oxygen, for times up to 2 minutes with incremental exposure times to determine the optimal exposure to plasma. Samples were conditioned in an environmental chamber prior to plasma exposure. Weight changes were recorded to determine the percent add-on in each step. Samples were analyzed post plasma exposure and inclusion of the active agents using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Standard washing test was conducted to determine the effectiveness of grafting after washing. Analysis is repeated after storing the samples for several weeks to determine any aging effects.

Antimicrobial and insect repellency assays were conducted on treated samples and compared to control. Treated samples have shown excellent antimicrobial and insect repelling efficiency.
BIOGRAPHY

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1. Introduction

Antimicrobial finishes for textiles may be an effective means of prevention of disease transmission with applications in the consumer, military, and healthcare markets. A growing domestic threat is the transmission of diseases by insects. Worldwide statistics show that malaria is responsible for over 1 million deaths per year.

Fabrics that provide both insect repelling/insecticidal and antimicrobial properties can be used for apparel, upholstery, tenting, and insect netting. Treatments with halamines may damage the fabric, leading to poor mechanical properties. Current antimicrobial and insect repellent/insecticidal finishing techniques are effective but lose potency after repeated washings or field use [20 & 24].

The objective of this research was to produce insect repelling/antimicrobial cotton to repel flying and crawling insects, and to permanently kill or inhibit the growth of microorganisms such as bacteria, molds, and fungi. The mechanism utilized plasma graft copolymerization of bioactive monomers in combination with addition and fixation of insecticidal and antimicrobial agents to create fabrics that provide enhanced protection.
2. Literature Review

Literature of plasma-aided treatments of textiles, graft copolymerization, and antimicrobial agents has shown several attempts on biocidal finishes. Cellulosic fabrics, specifically cotton, were investigated as cotton is the main focus of this study. Atmospheric plasma treatments were also reviewed in comparison to other techniques and to determine the different mechanism by which each technique works. Graft copolymerization of GMA, as a linking agent, was reviewed to further understand the mechanism of graft copolymerization, as well as the properties that make GMA an attractive linking agent for graft copolymerization. Several antimicrobial agents were also reviewed to understand the properties of each agent and to compare to quaternized ammonium chitosan as the agent used for this research (HTCC). Finally, the properties and some uses of β-cyclodextrin, as an antimicrobial agent and inclusion of guest insect repelling extracts into the cavities were also reviewed.

2.1. Cellulosic Fabrics

Cellulose is a natural long chain polymer made up of repeating units of D-glucose, a simple sugar. It is the basic building block for many textiles and for paper [19]. In the cellulose chain, the glucose units are joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring (six-membered rings of glucose units) and the C-4 of the next ring. The most important chemical group on the cellulose polymer is the hydroxyl group [19]. In cellulose, all functional groups are in the equatorial positions, or the β configuration. This configuration causes the molecular chain of cellulose to extend in a straight line, making it a good fiber-forming polymer. Because of the equatorial positions of
the hydroxyls on the cellulose chain, they protrude laterally along the extended molecule, making them readily available for hydrogen bonding.

![Figure 1. Structure of Cellulose](image)

These hydrogen bonds cause the chains to group in highly ordered, semi-crystalline structures (about 65% to 70% of cotton is crystalline) [19]. Because the chains are longer than the crystalline regions, they are thought to pass through several different crystalline regions, with areas of disorder in between. The inter-chain hydrogen bonds in the crystalline regions are strong, giving the resulting fibers good strength and insolubility in most solvents. They also give cellulose non-thermoplastic properties (prevent cellulose from melting). In the less ordered regions, the chains are further apart and more available for hydrogen bonding to other molecules.

### 2.1.1. Cotton

Cotton is the purest natural form of cellulose. The cellulose polymers are laid down in layers in the cotton fiber, forming a primary cell wall, a winding layer, and a 20-30-layer secondary cell wall. The polymers spiral around the fiber instead of being oriented to the fiber axis.
Cotton is a hydrophilic fiber. The high degree of moisture content is partially due to water being attracted to the numerous hydroxyl groups. It is also due to the drawing up of water between the various layers and the absorption of water between the many fibrils on the
fiber surface. Because the interpolymer spaces in the crystalline regions are too small, water molecules enter the polymer system in its amorphous regions only.

Cotton fiber provides a set of properties that leads to acceptable fabric performance in over 100 different textile end uses [19]. The properties that make cotton unique are hydrophilicity; medium tenacity, stiffness, and modulus; and low elongation and elastic recovery. Because cotton makes up more than half of all fiber used in the manufacture of apparel fabrics, it is considered the most used apparel fiber. About one fourth of the fiber used in household and institutional textiles is cotton.

2.2. Plasma Treatments

Plasma has been defined as an ionized gas with mixture of charged particles, excited atoms or molecules, neutral particles (including free radicals), and photons, produced by discharges at atmospheric pressure or low pressure [5]. Everyday examples of plasmas are the solar corona, “neon” signs, and bolts of lightning [3]. Plasmas are generated by high electric fields and can interact with solids to provide unique surface properties. Plasma treatments have been used to induce both surface modifications and bulky property enhancements of textile materials, resulting in improvements to textile products ranging from conventional fabrics to advanced composites. These treatments have been shown to enhance dyeing rates of polymers, improve color fastness and wash resistance, increase adhesion of coatings, and modify wettability of fibers and fabrics. Recently, plasma treatments have produced increased moisture absorption in fibers, altered degradation rates of biomedical materials (such as sutures), and deposition of low friction coatings [1].
The general reactions to be achieved by plasma treatment are the oxidation of the surface of a material, the generation of radicals, and the edging of the surface; when using special gases a plasma-induced deposition polymerization may occur. Both the surface chemistry and topography may be influenced to result in improved adhesion or repellency properties as well as in the confinement of functional groups to the surface. Plasma treatment has been used to achieve shrink resistance on wool, hydrophobization of cotton, and increased adhesion strength and hydrophilicity of synthetic fibers [2].

Plasma treatment may be performed at either low pressure (vacuum) or atmospheric pressures. Low-pressure systems require a continuous flow of gas be fed into the plasma chamber and operation at sub-atmospheric pressure, typically in the milli Torr ranges [3]. The fact that vacuum conditions are necessary for low-pressure plasma treatments makes this process impractical to use in industries requiring high rates of throughput, e.g. textile industry. Atmospheric plasma treatment, on the other hand, is well suited for continuous processing, but the technology is relatively new [2].

The effectiveness of a particular plasma treatment is determined by the composition of the gas used and the type of textile, the pressure within the plasma chamber, the frequency and power of the electrical supply, and the temperature and duration of the treatment [2]. In general, three main effects can be identified, depending on the plasma treatment applied: etching or cleaning, surface chemical modification, and plasma polymerization.

Etching is associated with changes in surface texture and wetting properties (i.e. changes in surface roughness). Surface chemical modification involves the introduction of particular chemical functional groups, depending on the nature of the gas plasma. These groups may improve wettability, biocompatibility, and adhesion of the textile. Plasma polymerization of
plasma enhanced vapor deposition (PECVD) enables the deposition of very thin films of polymers that possess highly cross-linked structures onto textile surfaces.

Examples of different gases commonly applied and their effects follow:

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<td>Argon</td>
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<td>Oxygen</td>
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<tr>
<td></td>
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<tr>
<td>Fluorocarbons</td>
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<td></td>
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<td>Ammonia, Carbon Dioxide</td>
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Plasma treatments offer several commercial advantages. One of these advantages is that this process doesn’t require the use of water or an organic solvent as a medium, which are required in many wet chemistry conventional coating processes [3-5]. Plasma treatment, therefore, can be considered a dry, clean technology, operating in a closed system. Also, the versatility of plasma treatments can lead to textile surface properties unobtainable by most conventional techniques [3]. Other advantages include reduced degradation of surface morphology and elimination of pin-holing and backside treatments [4]. A unique feature of plasma modification is that the surface structure of the polymer can be selectively modified for a specific application without affecting the bulk properties of the polymer [11].

The challenge with plasma surface treatment is that the choices and capabilities are expansive [10]. The surface specificity of plasma modification makes it difficult to explain the nature of the chemical changes with conventional techniques [11]. Also, the complexity of the plasma itself makes it difficult to unravel the mechanisms responsible for the surface modification [3, 10, &11]. However, careful measurements of plasma parameters in
conjunction with surface kinetics and plasma-surface interaction phenomena can lead to definitive mechanisms by which surface functionalization could be induced.

2.2.1. Atmospheric Plasma Treatments

Atmospheric plasma treatment of textiles is an environmentally friendly, sustainable manufacturing process that holds enormous, untapped potential for the textile industry worldwide [1-5]. Atmospheric plasma treatment is a useful technique to modify polymer surfaces and leads to polymerization, grafting, and crosslinking of chemical inclusion [11]. Atmospheric plasma treatment of textile materials is being investigated as an alternative to or for enhancement of conventional processing technologies. A wide variety of plasma processing effects on textile substrates have been demonstrated [1-5]. The applications are widespread and encompass enhancement of flame retardancy, water and soil resistance, resin adhesion, and barrier properties, among others [6-10].

The three types of atmospheric pressure plasmas are: corona discharge, silent discharge (SD), and atmospheric pressure glow discharge (APGD). Corona discharges are characterized as bright filaments extending from a sharp high voltage electrode towards the substrate. These discharges produce active species non-uniformly and the production rates for the active species are too low for many applications [5]. Corona treatment uses a high voltage, high frequency electrical discharge to ionize air to increase the surface tension of non-porous substrates [4]. Silent discharges are formed in a parallel plate dielectric barrier configuration, and have been recently used for polymer treatments. However, the SD is of short duration that interrupts the sequence of chemical reactions required to produce reactive species. Its filaments are not uniform and have potential to cause uneven treatments such as
pitting or pinholes. Glow discharge generated at atmospheric pressure (APGD) has the advantage of being a uniform and stable discharge [5].

APGD is usually generated in helium or argon because these gases have low dielectric breakdown voltages [5]. APGD is an alternative homogeneous “cold” plasma source, which has many benefits of vacuum, cold plasma methods while operating at atmospheric pressure [8 & 9]. “Cold” plasmas are non-equilibrium plasmas where the electrons and not the ions carry the kinetic energy [9]. When free electrons of a low-pressure gas or gaseous mixture are accelerated by electric or electromagnetic fields to a kinetic energy level at which ionization, excitation, and molecular fragmentation processes are generated by an electromagnetic radiation, electric energy-initiated cold plasmas are formed [11]. Active molecular fragments such as free radicals are generated when the chemical bonds are cleaved by the 0-5eV energy spectrum of cold plasmas [11 & 20]. If the free radicals formed are unstable, they will quickly go through recombination. Stable radicals, though, will remain in the polymer as living radicals. These radical sites can then “catalyze” the next steps for further chemical processing such as initiation of grafting, cross-linking, or functional group attachment [11 & 20]. Atmospheric pressure non-equilibrium plasmas can be used to produce large area, uniform surface modification of materials under continuous process conditions [8 & 9].

Polymer surface modifications that use various plasma methods have received significant attention [11]. The chief advantage of modifying polymer surfaces with plasma is the ability to alter the surface (altering the reactivity of the surface) without changing the structure and polymer’s bulk properties [8, 9, & 11]. Currently, studies in which polymer surfaces are being chemically modified so they bond with water-based dyes instead of the less
environmentally friendly solvent-based dyes are being conducted [11]. Extension of atmospheric plasma application to graft copolymerization is a novel technique that provides permanent covalent fixation of polymers onto fabrics.

2.3. Graft Copolymerization

Plasma grafting is grafting molecules on the material surface after plasma activation. The effects of the plasma do not penetrate more than 100Å from the surface. Graft copolymerization of bioactive monomers into the fabric is traditionally initiated by chemical means (wet process), or irradiation techniques such as high-energy electron beams and gamma rays. Plasma-aided grafting is a dry technique as plasma is formed by ionized gaseous species. Furthermore, atmospheric plasma can be embedded on-line into the textile production line without changing the flow process [20 & 24]. Atmospheric plasma provides the means by which efficient graft copolymerization can be achieved.

Plasma grafting, often referred to as plasma graft-copolymerization, can occur through either of the following two mechanisms [20 & 21]:

(1) The creation of active species on the polymer surface, followed by contact with the monomer:

```
\[ \text{inert-gas plasma} \rightarrow \text{activated polymer chain} \rightarrow \text{Graft-copolymers} \]
```

In this mechanism, free radicals are formed on the polymer surface as a result of inert gas plasma treatment. These radicals can either directly initiate grafting or be converted into peroxide or hydroperoxides by the inclusion of an oxidative gas. These activated peroxides will also initiate grafting in the presence of the monomer species [20, 22, & 13].
(2) Direct grafting of the polymer with common or unconventional monomers under “monomer”-plasma conditions:

\[
\text{Polymer} \xrightarrow{\text{“monomer”-plasma}} \text{Graft-copolymers}
\]

Unlike the previous method, this involves a combined plasma and monomer exposure in one step by the use of gaseous monomers in the working gas mixture [20 & 21]. Both of these techniques have shown great advantages over conventional grafting by offering a large range of chemical compounds to be used as monomers, varying thickness of monomer layers, and limited destruction [20 & 23].

In similar studies conducted by Simionescu and Sun, the plasma grafting of cotton, polyester, and wool fibers was examined. It was shown that after plasma treatment and grafting there was altered surface roughness, increased compatibility between natural and synthetic materials, improved surface properties by removal of the outer fiber shell, water absorption and rejection properties, adhesive properties, reduced shrinkage, and improved dyeing and printing properties [20, 23, & 12]. Graft copolymerization allows for the reaction of agents with copolymerized layer to permanently add new effects.

### 2.3.1. Graft Copolymerization of Cellulose

For many years, the method used to graft monomers on cellulosic fabric was based on the use of catalysts as initiators of the copolymerization between cellulose and the monomer. The main disadvantage of these methods is the generation of highly toxic wastes. Several studies have been conducted using radiofrequency plasma process to modify textile substrates [32]. With this technology, active radicals are introduced within the cellulose
chain and used as initiators for subsequent copolymerization with other monomers. In a study by Abidi and Hequet, water repellent cotton fabric was created by activating and grafting using microwave plasma. They found that the exposure of cotton fabrics to the plasma for 240s with a microwave power of 500 W was sufficient to create active carbonyl groups [32]. They also discovered that Ar-plasma generated more active groups than N₂- and O₂-plasmas.

2.4. Glycidyl Methacrylate

Glycidyl methacrylate (GMA) is a high purity, dual functionality monomer used for coatings and resins. GMA contains both acrylic and epoxy groups. GMA is considered one of the more important vinyl monomers because of the presence of the epoxy groups which have the ability to undergo consecutive modification leading to the introduction of basic or acidic groups to the fibers; which in turn leads to the formation of cationic, anionic, or amphoteric ion-exchange fibers [32 & 33]. The dual functionality of GMA combines the chemical resistance of an epoxy with the weatherability of an acrylic. Acrylic and epoxy functionality means that GMA can react with a wide variety of monomers and functionalized molecules.

![Figure 4. Structure of Glycidyl Methacrylate](image)

The acrylic/vinyl functionality allows for copolymerization with a variety of other vinyl monomers. The resulting polymers show a unique combination of epoxy functionality with
an acrylic backbone. The epoxy functionality allows crosslinking reactions with amines, carboxylic acids, anhydrides, and hydroxyl-containing polymers. It also allows structural modification of the polymer backbone that can result in differentiated properties and higher performance.

Recent studies by Zou, Kang, and Neoh have shown that the adhesion strength can be enhanced through surface modification of the polymer substrate via UV or thermally induced graft copolymerization of GMA. The epoxide functional group in the grafted GMA chain can serve as an effective adhesion promoter through chemical bonding and charge transfer interaction at the interface [18].

In studies conducted by Shukla and Athalye, GMA was graft-copolymerized onto cotton using photo-initiation and chemical initiation techniques, using different initiators. They were successful in grafting GMA onto cotton cellulose and getting high percent add-ons. Shukla and Athalye found the optimal temperature and GMA concentration for each initiation system. They found that the graft add-on level greatly depends on the nature of the initiator used [14]. Shukla and Athalye found that grafting of hydrophobic monomer GMA decreased both the breaking load and the thermal stability of cotton significantly [14 & 23].

### 2.5. Antimicrobial Finishes

An antimicrobial, by definition, inhibits the growth of or kills microorganisms. It has long been recognized that microorganisms can thrive on textile substrates. These microorganisms can cause fiber degradation by feeding on unreacted monomers and/or chemicals found in the fibers such as oils, dyes, finishes, and coatings. Natural fibers such as cotton are more susceptible than synthetics because their porous hydrophilic structures retain
water, oxygen, and nutrients, which provide a perfect environment for growth of microorganisms [6].

Microbial infestation has unpleasant consequences such as foul odors, mold and mildew stains, discoloration and loss of functional properties (e.g. tensile strength and elasticity). Microbes can disrupt manufacturing processes, textile dyeing, printing and finishing operations through the reduction of viscosity, fermentation, and mold formation [6]. Microbial infestation cannot be removed by the most frequent washing, with the exception of washing at boiling temperature, which is not suitable for textiles [6]. Currently, there are four modes of action to prevent fiber degradation:

1. Kill the organism
2. Block enzyme production necessary for food consumption
3. Barrier insertion (i.e. coating)
4. Modify fiber (surface or whole)

The first approach is achieved through the use of a biocide, which has two kill mechanisms. By causing a chemical reaction with the cell membrane, the metabolic process of the organism is stopped, prohibiting its life processes. The biocide can also penetrate the cell wall and poison the cell from within.

The second mode of action requires blocking the enzymes elucidated by the microorganisms. This prevents them from breaking down the fibers into digestible components, thereby eliminating their food source.

Another approach involves coating the fiber/fabric with a protective barrier. This process gives direct surface contact activity against microbial growth. Physical barrier or blocking action is achieved by using inert films or coatings for physically blocking bacteria, or by films and coatings having direct surface contact activity against bacterial growth. Coatings can be universally applied to all fiber types and other surfaces to produce activity against a
broad range of microorganisms and be durable to normal washings [6]. The coating, however may cause undesirable aesthetic and physical changes to the finished good, such as stiffness. One method of coating involves an organo-silicon polymer that contains quaternary ammonium groups. The chemical process involves a condensation reaction and needs available hydroxyl groups for permanent bond formation.

One final antimicrobial process is the modification of the fiber itself. This can be either a surface or a bulk treatment. Multifunctional property fabrics are produced by grafting polymers, homopolymers, and/or copolymerization onto the fiber or by chemical modification of the fiber by formation of covalent bonds [6]. Graft, homo-, and/or copolymers are usually attached to fabrics to create a positively or negatively charged functional group on the fiber, which is then immersed in counterions [6].

The majority of antibacterial finishes function by controlled-release mechanism. A chemical finish produces an active germicidal species continually regenerated by the addition of a bleach agent during laundering, or exposure to UV light, which would break some strategic covalent bonds in the chemically modified fiber during regeneration. Therefore, theoretically, the model has an unlimited reservoir of antibacterial agent. The micro-encapsulation technique is similar to this model, but its reservoir of antibacterial agent is not unlimited [6].

Micro-encapsulation is a physicochemical technique where a substrate reservoir of antimicrobial compound is held between two layers of protective plastic. As the active compound is used up, it is replaced by additional amounts from the reservoir by a controlled release mechanism.
Chemical methods involve insolubalization of chemical reagents in or on the fiber. Insolubalization is achieved by incorporation of agents into spinning baths for synthetic or regenerated fibers, or by padding natural or synthetic fabrics with solutions that when evaporated by curing or other methods, deposit a water-insoluble agent onto the fiber [6]. Various nitro compounds have been used to impart antimicrobial activity on a broad spectrum of fabrics [6, 7].

In general, antimicrobial properties of textile materials can be achieved by chemically or physically incorporating functional agents onto fibers or fabrics [26]. The durability of antimicrobial properties can be grouped into two categories: temporary or durable functional fabrics [26]. Temporary antimicrobial properties of textiles are easy to achieve, but are easily washed off. Durable biocidal properties are generally achieved by the slow-release method, in which the treated fabrics slowly release the antimicrobial agent to inactivate bacteria. The problem is that the biocidal agent will completely vanish if impregnated in the fabric without forming covalent bonds. In a study by Sun and Xu, durable and regenerable antimicrobial properties were achieved on cotton and cotton blend fabrics. The authors used halamine chemistry to form biocidal agents. In their method, the N-halamines hold onto chlorine atoms that then kill any microorganisms the fabric contacts.

A variety of antimicrobial finishes have now been developed for application to textiles. In addition to the effective control of bacteria, molds, and fungi, such finishes must also exhibit the following requirements [6, 43]:

- Durability to laundering, dry cleaning, or leaching
- Selective activity towards undesirable microorganisms
- Acceptable moisture transport properties
- Compatibility with other finishing agents
- Absence of toxic effects for both manufacturer and consumer
- Ease of application
• Applicable with no adverse effect on the fabric
• Environmental safety
• Cost-effectiveness

2.5.1. Metals and Metal Salts

This group of biocides uses heavy metals, either alone or in compounds, including mercury, silver, and copper. These agents act as antimicrobial agents by combining with cellular proteins and inactivating them. In addition, high concentrations of heavy metal salts will coagulate cytoplasmic proteins, resulting in cell damage or death [38]. These have been successfully used on a variety of natural and synthetic fibers. The most common metal salt used is silver based, but it is not effective against fungi, mold, or mildew [39].

2.5.2. Dyes

Select dyes, such as azo disperse dyes; have been shown to selectively attack microorganisms. These have been successfully applied to nylon and wool fibers and have shown good biological activity against microorganisms [38].

2.5.3. Cationizing agents

Compounds in this class are typically ammonium salts. Quaternaries have been shown to have disinfectant and bacteriostatic properties, as well as fungicidal activity. Their antibacterial mechanism involves denaturation of proteins, interference with glycolysis, and cytoplasmic membrane damage. Two effective agents include (a) benzalkonium chloride and (b) cetyltrimethylammonium bromide [38].
Quaternary ammonium salts have recently been applied by using acid dyes as a bridge to link the antimicrobial agent to synthetic and natural fibers. This is accomplished through sulfonate groups found in the acid dyes which serve as bonding groups with the quaternary ammonium salts [40].

### 2.5.4. Chitosan

Chitosan is a very specialized product manufactured from a natural waste product (crustacean shells). It is a partially deacetylated polymer of acetyl glucosamine (2-acetamido-2-deoxy b-1,4-D-glucan). Essentially, chitosan is a natural, water-soluble derivative of cellulose with unique properties [15].
Protonated amine groups in chitosan inhibit the growth of microorganisms by holding negatively charged microorganism ions [41]. Oligomeric chitosan can also penetrate into the cell of the microorganism and prevent growth of the cells by preventing RNA transcription [38]. When applied to cellulose by crosslinking, chitosan gives both antimicrobial and moisture control properties [6]. It is well known that chitosan inhibits the growth of many bacteria, including gram-negative and gram-positive ones [7]. Chitosan itself is known to induce little skin reaction over a wide range of other antimicrobial compounds [7].

Several studies have shown high antimicrobial activity and durability of up to 80% after repeated laundering. In a paper by Shin, Yoo, and Min, water-soluble chitosan oligomer was prepared to apply by the pad-dry method as an antimicrobial finishing agent for polypropylene (PP) nonwoven fabric. The treated samples showed high antimicrobial activity against P. vulgaris at 0.01%, S. aureus and E. coli at 0.05% level showing above 90% reduction rate [7]. They found that chitosan oligomer was not effective against K. pneumoniae and P. aeruginosa below 1.0% treatment concentration [7].

Chitosan has also been attached to quaternary ammonium groups to form an improved antimicrobial finishing agent. This is achieved by a reaction (shown below) with glycidyltrimethyl ammonium chloride (GTMAC) with the amine groups on chitosan under neutral or alkaline conditions to form N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC) [36]. Even at low concentrations, this agent has shown excellent antimicrobial activity, indicated by an almost 100% reduction of bacteria, in comparison to chitosan alone, which produces only 30% reduction [41].
2.5.5. Magnesium Peroxides

Magnesium peroxides are obtained through the reaction of magnesium tetrahydrate and hydrogen peroxide, forming magnesium hydroperoxyacetate (MHPA) and magnesium dihydroperoxide (MDHP).

\[
\text{H}_3\text{C} = \text{C} + \text{O} \rightarrow \text{Mg} + \text{O} \rightarrow \text{O} \rightarrow \text{H}
\]

Figure 7. Synthesis of HTCC

Figure 8. Structure of MHPA
These agents are applied by a pad/cure process, and have shown to be most effective for cotton, polyester, and 50/50 blends [42]. Except for its stable oxygen releasing capability, magnesium peroxide has similar functions of other peroxides e.g. bleaching, disinfecting, deodorizing.

2.5.6. PHMB Based Agents

Polyhexamethylene biguainide (PHMB) is a broad-spectrum antimicrobial agent that is effective against gram positive and gram negative bacteria, as well as fungi and yeasts. It is a low toxic finish, with good durability [43].

\[
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \\
\text{\{CH}_2\text{\}_n\text{N-C-C-N-C-C\}_n\text{CH}_2\text{\}_n} \\
\text{NH} \quad \text{NH}
\end{array}
\]

\[n = 10-12\]

*Figure 10. Structure of polyhexamethylene biguainide (PHMB)*

2.5.7. Triclosan

Triclosan, or 2,4,4′-trichloro-2′-hydroxydiphenyl ether, is currently one of the most widely used antimicrobial agents. It is a broad-spectrum antimicrobial agent that can be found in toothpaste, soap, cosmetics, and many other consumer products.
Triclosan inhibits the growth of microorganisms by an electrochemical mode of action. The biocidal agent blocks the active site of the protein reductase enzyme (ENR), which is an essential enzyme for fatty acid synthesis in bacteria. By blocking this enzyme, the bacteria can’t synthesize fatty acid, which is necessary for building cell membranes and reproducing. Since humans do not have the ENR enzyme, it is considered harmless, and therefore accounts for its prevalent and wide usage [44].

This agent is applied through the pad process, and diffuses into fibers similarly to disperse dyes. During use, the active antimicrobial agent slowly migrates to the surface where it binds to the surface. There it acts as a barrier to microorganisms. Since this agent is not water-soluble, it does not leach out, and it continuously inhibits the growth of bacteria in contact with the surface [45].

2.5.8. MDMH

MDMH, or monomethyl-5,5-dimethyl hydantoin, is a bifunctional compound possessing one side for reacting with cellulose and another for reacting with active chlorine that is capable of forming a halamine bond.
This agent can be processed by standard pad methods, but must be activated prior to bacterial exposure. Activation can be achieved through a two-step chemical process involving:

(1) finishing under acidic conditions and

(2) rinsing with chlorine bleach.

The resulting finish is regenerable and durable to reversible oxidation reaction properties of the cyclic halamine structure [38].

2.5.9. Zeolites

Zeolites are natural or synthetic inorganic antimicrobial additives. Typical zeolites are mainly composed of an aluminosilicate framework of alkali or alkaline earth metal, with a three-dimensional skeletal structure consisting of tetrahedral linked SiO₄ and AlO₄ sharing oxygen bonds [38]. AgION Technologies developed one specific zeolite agent. This biocide has an aluminosilicate structure in which silver is incorporated into the mineral structure by means of an ion-exchange reaction. The added silver kills microbes by interacting with multiple binding sites on their surfaces.

Since the AgION compound is a ceramic, it can withstand high processing temperatures. As a result, it can be incorporated into fibers before melt extrusion. The silver
ions in the compound are released from the fiber at a steady controlled rate in response to humidity. As the ambient moisture level increases, more silver is released [45].

2.6. Cyclodextrin Inclusion Compounds

Cyclodextrins are considered to represent an important group of auxiliaries in the textile industry because of the growing requirement for biodegradability of the auxiliaries used [16]. Cyclodextrins are non-reducing cyclic linked oligosaccharides produced through the enzymatic degradation of starch [16 & 17]. Six, seven, or eight units bound into a ring are marked as cyclohexa-, cyclohepta-, or cycloocta-amyllose, which are known as α-, β-, or γ-cyclodextrin, respectively [16].

Figure 13. Structure of β-Cyclodextrin

Cyclodextrin derivatives are an interesting group of ligands because of their favorable toxicological and ecological properties. Cyclodextrin derivatives are cyclic sugar molecules with a toroidal shape in which the inner cavities of the molecules have hydrophobic character, which allows non-polar groups of organic compounds to be included. The molecules complexed by cyclodextrin derivatives could be perfume extracts, odorous...
components of sweat, or pharmaceutically active agents for slow chemical release.

Permanent fixation of cyclodextrin on the fabric surface adds new functionality to the fabric.

Research is being conducted in using cyclodextrins in the textile industry in areas such as detergents, textile dyes, and of most interest to this thesis, textile finishing. A new finish was developed for easy removal of sweat degradation products from the textile by preventing their penetration into the fiber. Fabrics are being finished with cyclodextrin complexes to attain wash resistant, odor absorbing, antimicrobial, and insect resistant properties [29]. Researchers have used cyclodextrins as dual functional warp sizes for natural and synthetic fibers and a textile printing system [29].

2.7. Previous Research

The research for this thesis is based on extensive activity of an NC State University (NCSU) group since 1997 utilizing atmospheric plasma surface modifications of textile materials [20, 24, & 25]. Three atmospheric plasma devices were built at NCSU, two provide batch treatments, and one provides both batch and continuous on-line treatment.

Nonwoven polypropylene (PP) fabrics were prepared in the Nonwoven Cooperative Research Center at NCSU. This fabric was formed through hydroentanglement with a fiber linear density of 1.74 dtex and a fabric basis weight of ~46.7 g/m². Sample strips weighing approximately two grams were prepared by washing in acetone, and air-drying, prior to processing.

The nonwoven fabric strips were exposed to either oxygenated-helium plasma or helium-forming gas plasma for two and five minute intervals. Following plasma exposure, the samples were immediately graft copolymerized in a 50% aqueous methanolic solution of 10-
20% glycidyl methacrylate (GMA) at a liquor ratio of 1:30. The vial was placed in a shaking water bath at 70-80°C for 30-60 minutes. After grafting, the samples were thoroughly washed with warm distilled water, ethanol, and acetone, and then dried at 50°C.

Next, the PP/GMA fabrics were grafted with an antimicrobial agent. The agent used for this study was N-(2 hydroxy) propyl-3-trimethylammonium chitosan chloride (HTCC). The HTCC was used due to its superior antimicrobial activity compared to pure chitosan. This compound not only enhances the water solubility and antimicrobial activity of chitosan, but it can also be used as an antistatic finishing agent due to the presence of quaternary ammonium groups. The HTCC compound was synthesized using glycidyl trimethyl ammonium chloride (GTMAC) and chitosan.

3. Research Objectives

3.1. Plasma-Aided Finishing of Cotton

The specific objectives of this research are to:

1. Graft glycidyl methacrylate using plasma technology on cotton;
2. Develop antimicrobial finish on cotton;
3. Develop insect repellent finish on cotton.

The following research will result in the development and characterization of insect repellent biocidal textile surface chemistry. Biocidal fabrics represent a novel approach to preventing disease transmission. Insect repellent finishes have applications both in disease prevention and fabric preservation. The following study focuses on developing methodology for the production of insect repellent/antimicrobial fabrics by atmospheric plasma enhanced chemical finishing.
The focus is on finishing applications using plasma treatment, specifically plasma-aided graft copolymerization for antimicrobial/insect repelling finishing. In graft-copolymerization, the plasma initiates sites for grafting, followed by a set of chemical processes using bioactive monomers. Due to the ability of plasma to generate free radicals and –OH/-OOH sites, graft copolymerization can occur when exposed to the reacting medium. This process allows for biocidal finishing of textiles, which incorporates both antimicrobial and insect repelling finishes. Figure 14 illustrates the process of plasma-aided graft copolymerization to produce antimicrobial or antimicrobial/insect repellent finishes.

Figure 14. Illustration of Plasma Aided antimicrobial/insect repellent finishing process
4. Experimental

4.1. Atmospheric Plasma Apparatus

The atmospheric plasma chamber, located on NCSU’s Centennial Campus has an active exposure area of approximately 60 x 60 cm, a 5cm gap separation and is powered by a 4.8 kW audio frequency power supply operating in the frequency range of 5-10kHz. The device has an inner plasma chamber installed inside of an outer chamber, where the latter is equipped with a fabric rollers system. The working gas is fed to the chamber through a gas flow controller. Figure 15 shows a schematic drawing of the experimental unit. When helium or oxygenated helium flows into the plasma chamber, there will always be a slight amount of air due to the fact that the chamber is not pumped down and operates at atmospheric pressure. The apparatus is capable of batch treatment of textiles using a test cell, as well as continuous operation using the rollers feeding system. For the treatment of the cotton samples, oxygenated helium was used; power supply frequency was kept constant; exposure time was varied between 30 seconds and 2 minutes in 30 second intervals; power, voltage, plate distance, and flow rate were held constant.
Figure 15. Schematic of inner chamber of the atmospheric plasma facility

The device operates on the concept of dielectric-barrier discharge, which is a non-equilibrium discharge that generates low-temperature (1-2eV), low electron number density \(10^{14} - 10^{16} / \text{m}^3\) quasi-glow discharge plasma [35]. Such discharge generates electrons, ions, excited atoms and molecules, and induces UV radiation.

4.2. Materials

100% bleached and scoured cotton fabric was obtained from the Institute of Textile Technology for study. The samples were conditioned at 20°C and 65% RH for 24 hours in an Electro-Tech Systems, Inc (ets) environmental chamber prior to plasma exposure. Glycidyl methacrylate (GMA) containing 50ppm methyl hydroquinone was purchased from Aldrich Co. and was used without further purification. \(\beta\)-Cyclodextrin was purchased from Sigma-Aldrich, Inc. Chitosan (low molecular weight, Brookfield viscosity 20cps) was also purchased from Sigma-Aldrich, Inc. Glycidyl trimethylammonium chloride (GTMAC) was purchased from Sigma-Aldrich, Inc.
Plasma Graft Copolymerization Reaction

Following exposure of the cotton to plasma, the fabric was immediately graft copolymerized in a 250mL Erlenmeyer flask with screw cap containing a 50% aqueous methanol solution of 10-20% GMA, at a liquor ratio of 1:30 [14]. When cellulose is exposed to plasma, several possible radicals can form (Fig. 16). The flask was placed in a shaking water bath at 80°C for 30-60 minutes. After grafting, the fabric was thoroughly washed with warm distilled water, ethanol and acetone then dried at 50°C. Figure 17 illustrates the plasma graft copolymerization reaction scheme of cotton with glycidyl methacrylate (GMA) using one of the possible cotton radicals. The weight of the dried samples ($W_2$) were measured and compared to the original ($W_1$) to determine the percentage graft yield:

$$\%\ \text{add on} = \frac{W_2 - W_1}{W_1} \times 100$$

Structure of GMA

\[
\text{Structure of GMA}
\]

\[
\text{Structure of Cotton}
\]
Figure 16. Possible cotton radicals formed after plasma exposure
Reaction of Quaternary Ammonium Chitosan Derivative onto Cotton/GMA

The cotton/GMA graft was further reacted with the antimicrobial agent N-(2 hydroxy propyl) 3-trimethylammonium chitosan chloride (HTCC), which was synthesized according to known procedures [22, 24]. HTCC was used due to its superior antimicrobial activity compared to pure chitosan [23]. This compound not only enhances the water solubility and
antimicrobial activity of chitosan, but it can also be used as antistatic finishing agent due to the presence of quaternary ammonium groups. The HTCC compound was synthesized using glycidyl trimethyl ammonium chloride (GTMAC) and chitosan as illustrated in Figure 18 [24].

For this reaction, chitosan (1%, 4-20 cps) was dissolved in 1% acetic acid, followed by precipitation with 0.1N NaOH, then centrifuged at 0-4°C and air-dried. Chitosan (2%) and glycidyl trimethyl-ammonium chloride (8%, GTMAC) were dispersed in distilled water. The solution was stirred at 80°C for 24 hours [24]. After the reaction, the product was cooled and centrifuged, which separated the insoluble chitosan from the water-soluble chitosan fraction containing the quaternary ammonium chitosan. The soluble quaternary ammonium chitosan was then re-precipitated with a 50% ethanol/acetone mixture, and air-
dried under suction. Following the synthesis of HTCC, a cotton/GMA grafted fabric was allowed to react with 2g of HTCC in the presence of 1% NaOH; liquor ratio 1:30. The reaction was held at 80°C for the specified time to produce the grafted Cotton/GMA/HTCC fabric according to the reaction shown in Figure 19.

![Reaction Scheme](image)

**Figure 19. Scheme of reaction of cotton/GMA and HTCC**

**Reactions of Cyclodextrin onto Cotton/GMA**

A second set of cotton/GMA grafted fabrics was reacted with β-CD. The fabric was added to a solution containing 2% β-CD, 1M NaCl, and 1% NaOH [24]. The solution was stirred at 80°C for the desired time. The grafted fabric was washed with warm distilled water and acetone, then dried and weighed. The percent graft yield was calculated from the weight difference using the previous formula. The Cotton/GMA graft reaction with β-CD is illustrated in Figure 20.
Inclusion of Insecticidal Complexes into Cotton/GMA/CD Fabrics

Once the β-CD compound was grafted, additional insect repelling agents were incorporated inside the inclusion compound. One gram of the Cotton/GMA/β-CD fabric was immersed in a 25 ml mixture (90% distilled water and 10% ethanol) containing 1-2% of a guest molecule. These guest molecules included insect repelling oils such as citronella, jasmine, or sweet basil. The fabrics were soaked for 24 hours in this solution at room temperature to form the inclusion complexes. Samples were then washed several times with cold distilled water and ethanol. The rinsed fabrics were air-dried.
4.3. Characterization Techniques

4.3.1. Weight Changes

Each sample was weighed before (W₀) and after plasma treatment (W₁), and after grafting of GMA (W₂), HTCC (W₃), B-CD (W₄), and the inclusion compound (W₅) using an Explorer® microbalance with an accuracy of ±10 micrograms to determine weight changes, gain or loss. The percent weight change was then plotted versus the exposure time. The weight changes for the cotton fabric were correlated to percent graft yield, in which W₁ represented the weight of the fabric after grafting.

\[
\text{Weight add on (\%) = } \frac{W₁ - W₀}{W₀} \times 100
\]

4.3.2. Fourier Transform Infrared Spectroscopy (FTIR)

Cotton fabric samples were evaluated using a Nexus® 470 FTIR in conjunction with a Nicolet® Omnisampler.

4.3.3. Scanning Electron Microscopy (SEM)

Cotton fabric samples were evaluated using a Hitachi S-3200N Variable Pressure SEM. Photos were collected at ranges from 100X to 2000X.

4.3.4. Antimicrobial Assay

**Bacterial Strains and Growth Media**

*E.coli* K12 and *Staphylococcus aureus* were obtained from the U.S. Food Fermentation Laboratory Culture Collection (USDA-ARS, Raleigh, N.C.). Bacterial strains were grown overnight on cryptic soy broth or agar (Difco Laboratories, Detroit Mich.) for 14 hours. A modified form of AATCC (American Association of Textile Chemist and Colorist)
test Method 100 was adopted [25]. The reduction in numbers of bacteria was calculated using the following equation:

\[
\text{Reduction Rate (\%)} = \frac{(A-B)}{A} \times 100
\]

where \(A\) = the number of bacterial colonies from untreated fabrics and \(B\) = the number of bacterial colonies from treated fabrics. As explained by Table 2, a one-log reduction indicates that finished fabrics were able to kill about 90% of the bacteria, whereas a six-log reduction indicates that the treated fabrics killed 99.9999% of the population of bacteria.

**Table 2. Meaning of log reduction**

<table>
<thead>
<tr>
<th>Log Reduction</th>
<th>Percent Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 log reduction</td>
<td>90% bacteria kill</td>
</tr>
<tr>
<td>2 log reduction</td>
<td>99% bacteria kill</td>
</tr>
<tr>
<td>3 log reduction</td>
<td>99.9% bacterial kill</td>
</tr>
<tr>
<td>4 log reduction</td>
<td>99.99% bacteria kill</td>
</tr>
<tr>
<td>5 log reduction</td>
<td>99.999% bacteria kill</td>
</tr>
<tr>
<td>6 log reduction</td>
<td>99.9999% bacteria kill</td>
</tr>
</tbody>
</table>

**E. coli K12 and Staphylococcus aureus**

Two pieces of fabric (1x \(\frac{1}{2}\) inch) were transferred to sterilized plate. One piece of the fabric was transferred to a small (35x10 mm in diameter) Petri plate (Fisher brand), 100\(\mu\)L containing \(10^7\) CFU/ml of organism transferred onto the surface of fabric, and the fabric was covered by the second piece. The plate was covered and transferred to 100 x 15 mm in diameter Petri plate (Fisher), 1ml sterilized dH2O was added to the large plate outside the smaller Petri plate containing the fabric sample, to protect the fabric from dryness. Both plates were covered and incubated for 3 hrs at 37°C. After 3 hours the fabrics were transferred into stomacher bags (Spiral Biotech, Inc., Norwood, MA) with 10ml sterilized 8.5 g/liter Nail (Saline), which were treated for 1 minute on high in the stomacher (Model TR5T,
Tamar Co. Cincinnati, OH). The supernatant was diluted and plated on nutrient agar plates using a spiral platter (Model 4000, Spiral Biotech). After incubation for 24-48 hours at 30°C, the bacteria were counted by an automated spiral plate reader (QCount, Spiral Biotech).

4.3.5. Insect Repellency Tests

Housefly, Fruit fly, and Ant Assay

Housefly pupae, fruit flies, and Carolina black wood ants were purchased from Carolina Biological Co. All insects were lab-reared. The pupae were hatched in the tissue engineering lab on Centennial Campus at North Carolina State University.

An insect chamber, shown in Figure 21 and Figure 22 was designed and built in the plasma lab on Centennial Campus at North Carolina State University. The chamber consists of three compartments and it is intended for use in flying insect repellency tests, but can be modified to accommodate crawling insects.

To test flying insects, fabric samples were hung in each compartment and tested for insect repellency efficiency. For crawling insects, the fabric samples were laid on the floor of the chamber. The insect activity and behavior was observed for each sample and compared to the control, untreated sample for repellency efficiency.
Figure 21. Insect chamber front

Figure 22. Insect chamber top
**Tick Assay**

Brown ticks (*Rhipicephalus sanguineus*) were purchased from Professional Labs, Inc. A simple experimental setup consisting of a Petri dish with an untreated sample on one half and a treated one in the other, as shown in Figure 23, was used for tick repellency efficiency testing [25]. The ticks were placed in the middle of the Petri dish, as shown in the figure, and insect motion was monitored on time segments up to 3 hours. Ticks were counted to determine the number moving toward the control sample versus the number moving toward the treated sample.

![Figure 23. Schematic of experimental arrangement for tick repellency tests](image)

**4.3.6. Wash Fastness and Durability**

Fabric samples were washed in a Launder-Ometer, using AATCC Test Method 61 in order to assess the durability of the finishes. The samples were then evaluated for durability of the antimicrobial finish by using a colorimetric process.
4.3.6.1. Colorimetric Testing

Fabric samples were evaluated for HTCC finish using Dystar Telon Orange acid dye using a method in which the use of a unique dye staining process provides a rapid finish assessment [28]. In this method, they found that with the ionic interactions between the anionic sulfonate groups of the acid dye molecules and the cationic groups of the quaternary ammonium groups of the HTCC, a finished fabric containing quaternary ammonium compounds should be easily stained by contact with an acid dye [28]. Thus, immersing the fabric samples in acid dye solution for fifteen minutes and then rinsing and drying carried out colorimetric testing of the quaternary ammonium finish. The shade change and depth were visually assessed.

5. Results and Discussion

5.1. Weight Changes and Graft Yield

Fabric weights were measured before plasma treatment and after exposure to GMA to determine the percent add-on. Based on the plasma exposure time, the GMA solution dwell time, and the concentration of the GMA solution, the add-on varied from 0.67% to 7.53%. Figure 24 illustrates the percent add-on dependence on plasma exposure time.
As seen in Figure 24, increasing the plasma exposure time increases the GMA graft yield. The best fit curve is an exponential curve with an exponent of 0.28, which means that the curve saturates with time, thus there is a limit to the amount of GMA add-on with respect to exposure time.

5.2. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of the plasma grafted cotton fabrics were obtained and are compared below in Figure 25. Additional spectra can be found in Appendix 1. The spectrum for Cotton/1.96% GMA (Sample 50) shows additional absorbance bands as compared to the cotton control. These bands can be attributed to the epoxide group of GMA found at 1260.6
cm$^{-1}$, with a shoulder and increase of the absorbance bands at 897.7 and 842.6 cm$^{-1}$ (Figure 26). The stretching and increased peak intensity at 1161.1 cm$^{-1}$ further confirms grafting with the formation of the –C-O-C- ether linkage of the grafted GMA. In contrast, the grafting of the quaternary chitosan in Sample 6 (6.55%GMA/23.8%HTCC) shows characteristic bands of the quaternary chitosan itself, but with lower absorbance, at 1558.6 cm$^{-1}$ (Figure 27) and 1033.5 cm$^{-1}$. The lower absorbance is probably due to its lower concentration. FTIR spectra were also useful in confirming the grafting of the cyclodextrin onto the Cotton/GMA fabric. This is illustrated by a significant decrease in the epoxide peak of Sample 72 (2.25%GMA/7.69%B-CD), and the absorbance bands at 1056.7 and 1032.4 cm$^{-1}$ in Figure 28, which are characteristic absorbance bands of the cyclodextrin itself.

Because cellulose, GMA, HTCC, and β-cyclodextrin have similar characteristic peaks, the subtracted FTIR spectra are shown in Figures 26-28. When the spectra are analyzed in the conventional way, it could be confusing because the peaks show up in similar regions. By using the subtractions, it can be shown that the different molecules were grafted. The fact that absorbance bands are still showing up after the subtractions, confirms grafting of each agent. In Figure 26 it is clearer to see the 1161 cm$^{-1}$ absorbance band of the ether linkage of the grafted GMA. In Figure 27, the characteristic absorbance bands of chitosan appear at 1652.7 cm$^{-1}$ (C-O stretch), 1558.6 cm$^{-1}$ (NH angular deformation), 3341.4 cm$^{-1}$ (OH group), and 1161-1033 cm$^{-1}$ (glycosidic linkage, C-O-C). In Figure 28, the absorbance band corresponding to the secondary alcohol groups of cyclodextrin show up at 3342 cm$^{-1}$. The bands from 1032-1652 cm$^{-1}$ are characteristic of the C-H and C-O vibrations of cyclodextrin.
Figure 25. Infrared Spectra of (top to bottom) control, cotton/1.96%GMA, cotton/6.55%GMA/23.8%HTCC,
Figure 26. Subtraction spectrum of Cotton/2.99%GMA
Figure 27. Subtraction infrared spectrum of Cotton/6.56%GMA/23.8%HTCC
Figure 28. Subtraction spectrum of Cotton/5.15%GMA/6.86%B-CD
5.3. Scanning Electron Microscopy (SEM)

SEM was conducted to view the extent of grafting on the cotton fabrics. Figure 29 shows the SEM micrograph of a sample of untreated cotton, where the surface is smooth and free from any additions. Figure 30 shows a sample of cotton grafted with GMA, in which it is clear that the surface has layer of addition and particulates on fibers. Figure 31 illustrates an SEM micrograph of a sample grafted with GMA and quaternary ammonium chitosan, in which surface morphology is different from that of GMA only; some flakes of HTCC are apparent on the surface. Figure 32 shows a sample with GMA and β-cyclodextrin, in which similar features to that of HTCC are seen on the surface.

Figure 29. SEM of untreated cotton control
Figure 30. SEM of Cotton/GMA sample

Figure 31. SEM image of Cotton/GMA/HTCC sample
The particulate and speckled matter on the cotton fibers in the resulting micrographs confirm the grafting of GMA and additional chitosan and β-cyclodextrin compounds.

**5.4. Antimicrobial Assay**

Following the plasma grafting study, additional testing was performed to determine the antimicrobial and insect repelling capabilities of the grafted fabrics. The control sample for S. aureus contained $1.84 \times 10^5$ cfu/ml while the control for the E. coli K12 contained $1.96 \times 10^6$ cfu/ml. Figure 33 shows 3-hour antimicrobial testing on the grafted cotton fabrics using *E. coli* K-12. The test indicates that all samples showed high antimicrobial activity, with a 6 Log reduction. The log reduction of 6.00 means 99.999% kill of the bacteria after the quantitative AATCC-100 modified test. Samples 67, 69, and 107 were grafted with HTCC at different concentrations, while samples 71 and 72 were grafted with β-cyclodextrin at
different concentrations (as seen in Table 3). An additional untreated cotton control was also tested. It is clear that chitosan HTCC has the highest effect followed by low-percentage β-cyclodextrin, which is consistent with previous results obtained on polypropylene [24,25]. Figure 34 shows the same 3-hour antimicrobial assay conducted on *S. aureus*. This test shows that the low concentration chitosan treated fabrics show the best antimicrobial activity, followed by the low-concentration β-cyclodextrin sample (sample 71). All antimicrobial testing confirms the viability of this process for antimicrobial finishing. It is clear from the antimicrobial assay test results that lower concentrations are more effective, which is consistent with previously obtained results using same methodology [25].

Table 3. Antimicrobial Assay Results

<table>
<thead>
<tr>
<th>Sample</th>
<th><em>E.coli K12</em></th>
<th><em>Staphylococcus aureus</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>No reduction</td>
<td>No reduction</td>
</tr>
<tr>
<td>4.85%GMA / 7.04%HTCC</td>
<td>6 log reduction</td>
<td>&gt;5 log reduction</td>
</tr>
<tr>
<td>(Sample 67)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.55%GMA / 6.18%HTCC</td>
<td>6 log reduction</td>
<td>&gt;5 log reduction</td>
</tr>
<tr>
<td>(Sample 69)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.83%GMA / 12.43%HTCC</td>
<td>6 log reduction</td>
<td>&gt;5 log reduction</td>
</tr>
<tr>
<td>(Sample 107)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.15%GMA / 6.86%β-CD</td>
<td>6 log reduction</td>
<td>2.5 log reduction</td>
</tr>
<tr>
<td>(Sample 71)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.25%GMA / 7.69%β-CD</td>
<td>6 log reduction</td>
<td>2.4 log reduction</td>
</tr>
<tr>
<td>(Sample 72)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 33. Graph of result of antimicrobial assay for E. coli K12

Figure 34. Graph of result of antimicrobial assay for S. aureus
5.5. Insect Repellency Assessment

All insect repellency tests were conducted on sample 87 (6.35%GMA / 3.28%B-CD / 2%Jasmine), sample 103 (5.31%GMA / 3.48%B-CD / 2%Citronella), and sample 115(4.63%GMA / 1.08%B-CD / 2%Sweet Basil) and compared to a control (untreated) cotton sample. The results of these simple tests are shown in Table 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Repellency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fruit Flies</td>
</tr>
<tr>
<td>Control</td>
<td>0</td>
</tr>
<tr>
<td>87 (6.35%GMA/3.28%B-CD/2%Jasmine)</td>
<td>66.67%</td>
</tr>
<tr>
<td>103 (5.31%GMA/3.48%B-CD/2%Citronella)</td>
<td>66.67%</td>
</tr>
<tr>
<td>115 (4.63%GMA/1.08%B-CD/2%Sweet Basil)</td>
<td>66.67%</td>
</tr>
</tbody>
</table>

Fruit Flies (Drosophila)

Because there were so many fruit flies and because they were so small, this test was more of a visual assessment. Immediately after released from the container, the fruit flies went toward the compartment with the untreated sample. After one hour there were approximately twice as many flies in the control chamber than there were in the compartment with the treated sample (for all three samples). After every hour, there were fewer flies in the treated sample chamber and more in the control chamber. After three hours, there were approximately three times as many fruit flies in the control side than in the side with the treated sample. After three hours and a half, the samples were placed on the floor of the
chamber. The fruit flies in the compartment with the control sample moved toward and even got on the sample, whereas they stayed away from the treated samples.

**Figure 35. Chart of fruit fly repellency test results**

**House Flies (Musca domestica)**

After being released, the flies went in both compartments. The flies in the compartment with the treated sample remained as far away from it as they could get. The flies in the control side got on the fabric and stayed on for extended periods of time.

For sample 87 (6.35%GMA / 3.28%B-CD / 2%Jasmine), the flies that went on the fabric did not stay for long time periods. Only 1 fly remained on the fabric, compared to 11 on the control sample. This sample showed the best repellency, as compared to the other samples. Sample 103 (5.31%GMA / 3.48%B-CD / 2%Citronella) and sample 115 (4.63%GMA / 1.08%B-CD / 2%Sweet Basil) showed similar repellency. Sample 103 had 2 flies versus 10 on the control, and sample 115 had 3 versus 13 on the control.
House fly (*musca domestica*) repellency test result on sample 87 (6.35%GMA/3.28%B-CD/2%Jasmine)

![Chart of house fly repellency test on sample 87](image)

Figure 36. Chart of house fly repellency test on sample 87

House fly (*musca domestica*) repellency test result on sample 103 (5.31%GMA/3.48%B-CD/2%Citronella)

![Chart of house fly repellency test on sample 103](image)

Figure 37. Chart of house fly repellency test on sample 103
House fly (*musca domestica*) repellency test result on sample 115 (4.63%GMA/1.08%B-CD/2%Sweet basil)

**Figure 38. Chart of house fly repellency test on sample 115**

**Ants (Camponotus pennsylvanicus)**

At first, the ants would not approach the treated samples, but moved their food on top of and under the control sample. After half an hour, the ants that approached the treated samples were repelled and went away from them. Ten ants were isolated and all of them went straight to the untreated sample. After a few minutes, one ant wandered toward the treated sample, and when it got about a quarter of an inch from it, quickly turned around. All three treated samples repelled ants equally. Because no ants remained on the treated samples for a significant amount of time, the samples are almost 100% repellent toward ants.
Ant (*camponotus pennsylvanicus*) repellency test results

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Treated</th>
<th>Untreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>4</td>
</tr>
</tbody>
</table>

Figure 39. Chart of ant repellency results

**Ticks (*Rhipicephalus sanguineus*)**

Tick repellency testing showed initial evidence of repellency. Ten ticks were isolated in a Petri dish. They were placed in the middle of the Petri dish with the untreated (control) fabric on one side and the treated fabric on the other. The ticks were observed for a period of three hours. The results of this test are shown in Figures 40, 41 and 42. For each sample the ticks immediately went to the side with the untreated sample. Sample 103 (5.31%GMA / 3.48%β-CD / 2%Citronella) showed the best repellency of the three treated samples.
Tick (Rhipicephalus sanguineus) Repellency Test on Sample 103 (5.31% GMA + 3.48% B-CD + 2% Citronella)
Total number of test ticks=10

Figure 40. Chart of tick repellency result on sample 103

Repellency Test on Ticks (Rhipicephalus sanguineus) Sample 115 (4.63% GMA + 1.08% B-CD + 2% sweet basil)
Total number of test ticks=10

Figure 41. Chart of tick repellency test result for sample 115
5.6. Wash Fastness and Durability

Following the application of the antimicrobial and the insect repelling finishes, samples were washed according to AATCC Test Method 61. No weight measurements could be performed because the samples were highly frayed. Thus, the weight change would not have been a good indicator of durability of finish.

5.6.1. Colorimetric Testing

After washing, the samples were evaluated with the acid dye colorimetric test. For comparison, a control sample was stained, as well as an unwashed antimicrobial sample. The colorimetric test was used to evaluate whether the antimicrobial finish was durable or if it washed off with laundering.

There was a significant visual difference in color and shade depth (Figures 43 and 44) for the HTCC treated fabrics. All HTCC treated samples (washed and unwashed) showed...
clear and deep color stain, with a slightly deeper shade resulting for the 7.84%HTCC treated sample. The untreated cotton control showed little to no color change. Other fabric samples that contained no HTCC also showed indiscernible color change. The fact that the washed HTCC treated samples were stained by the acid dye shows that the finish is durable to laundering. The levelness of the stain also indicates a uniform finish application.

Figure 43. Comparison of stain test before (top left) and after washing

Figure 44. Comparison of shade depth between washed samples
6. Conclusions

From this study, it can be concluded that antimicrobial and insect repelling finishes can be successfully and efficiently applied to cotton fabric. The evidence of grafting lies in the graft yields, FTIR spectra, SEM images, colorimetric tests, and the antimicrobial and insect repelling assays. Although it may be difficult to see grafting in the FTIR spectra, the results from the antimicrobial and insect repellent testing are evidence of the grafting. The finishes are durable, as seen from the colorimetric testing after washing.

7. Future Work

Further research should be conducted in order to optimize the process used for this study. This study should be expanded to other textile materials. Different agents, exposure times, and gases should be investigated. The possibility of eliminating the use of a linking agent should be explored. Plasma exposure times should be optimized. The effect of increased input power to plasma should be studied in order to see if exposure times can be reduced. The effect of gas mixing ratio should be investigated to see if higher oxygen concentrations give better result. Finally, these experiments should be expanded to continuous (on-line) treatment. Future testing may include grafting fibers instead of fabric.
8. References


Appendices
9. Appendices

9.1. Appendix A

*Images of Cotton/GMA*

*Images of Cotton/GMA/HTCC*
Images of Cotton/GMA/β-CD
Images of Cotton/GMA/ β-CD/Citronella

Image of Cotton/GMA/ β-CD/Sweet basil
9.2. Appendix B

Subtraction spectrum of 2.25%GMA/7.69β-CD
Subtraction spectrum of 1.55%GMA/6.18%HTCC
Subtraction result of sample 72 (2.25%GMA/7.69%β-CD)
Subtraction result of 5.83%GMA/8.35%HTCC
Subtraction spectrum of sample 92 (3.47%GMA)
Subtraction spectrum of sample 94 (3.94\%GMA)
Subtraction spectrum of sample 76 (4.21%GMA/4.04%β-CD)
FTIR spectrum of sample 89 (4%GMA/4.27% β-CD/2%Citronella)
FTIR spectrum of sample 113 (4.96%GMA)
FTIR spectrum of sample 91 (4.15%GMA/5.93%HTCC)
FTIR spectrum of sample 61 (3.92\%GMA/5.66\%HTCC)
FTIR spectrum of sample 77 (4.08%GMA/2.94%β-CD/2%Sweet basil)
FTIR spectrum of sample 59 (2.99%GMA/4.35%β-CD)