ABSTRACT

HUNT, LAUREN ANN. Ultraviolet Curable Process Chemistry for a Biofilm Resistant Finish on Textiles. (Under the direction of Peter Hauser and Ahmed El-Shafei).

A biofilm is a group of microorganisms in which cells stick to each other on a surface. They can grow virtually anywhere there is moisture, nutrients, and a surface; therefore, they affect many natural and industrial environments. One example of a biofilm is bacterial growth on apparel and footwear. These biofilms not only causes unpleasant odors, but they can also lead to serious medical issues. Preventing the formation of these biofilms on textile fibers offers a significant improvement in the odor and safety of the final textile product. This study aims to develop UV-cure process chemistry for coatings that impart biofilm resistant properties to textiles. New technologies within the textile industry are needed to improve efficiency and economic feasibility; as well as, reduce the environmental impacts associated with production. Ultraviolet curing technology provides a customizable, rapid commercial process with reduced energy consumption to impart value-added functional finishes to textile substrates when compared to traditional textile finishing processes.

In previous research, wide arrays of acrylate and methacrylate monomers were analyzed to determine their ability to support or hinder cell growth. This research project examines five acrylate and methacrylate polymers, which were selected because they most effectively inhibited cell propagation. Homopolymer/copolymer formulations and necessary curing parameters were optimized to achieve the most efficient UV induced polymerization, and ideal biofilm resistant properties. Performance evaluation of each when applied to polyester film and then polyester fabric was conducted via Fourier Transform Infrared Spectroscopy (FTIR), contact angle testing, wicking and wetting time testing, and antibacterial activity assessment.

The antimicrobial properties of the final samples were determined qualitatively using ASTM E1428-99, Standard Test Method for Evaluating the Performance of Antimicrobials in or on Polymeric Solids Against Staining by *Streptoverticillium reticulum* (A Pink Stain Organism). The AATCC 147 test method, Antibacterial Activity of Textile Materials: Parallel Streak Method, was also used with *Streptoverticillium reticulum* to assess which test method worked best for the given application. The AATCC 100 test method, Assessment of Antibacterial Finishes on Textile Materials, was used to evaluate the antimicrobial activity of the samples quantitatively using *S. aureus,* and *K. pneumoniae*. To assess the lowest percent solid add-on limit, a range of reduced add-on samples were created with each monomer. To determine if the final finishes had appropriate durability for use in commercial textile products, standard wash tests were performed up to 20 washes. Antimicrobial analysis was repeated after these launderings to confirm durability and lowest necessary percent solid add-on for an effective product.

The treated samples created with readily commercially available, UV curable, acrylate monomers show excellent durability and antimicrobial properties without significantly affecting the final hand of the fabric.

Ultraviolet Curable Process Chemistry for a Biofilm Resistant Finish on Textiles

by
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BIOGRAPHY

Lauren Ann Hunt was born on April 10, 1991 in Raleigh, NC to Dawn R. Hunt and Louis D. Hunt Jr. She graduated from Needham Broughton High School in 2009. Shortly thereafter she began her Bachelor of Science in Textile Technology with a minor in Materials Science Engineering at North Carolina State University. After finishing her degree in 2013 she was accepted to the Master of Science in Textile Chemistry Program and NC State. She worked under the instruction of Dr. Peter Hauser and Dr. Ahmed El-Shafei and concentrated on the study of biofilm resistant finishing of textile fabrics applied through the use of ultraviolet curing.

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1. INTRODUCTION

Antimicrobial textiles offer a number of benefits for a broad spectrum of different applications and markets. These range from staving off disease when used in the healthcare industry, to preventing unwanted odor when used on exercise apparel, to extending the life of marine textiles by hampering biofouling.

Textiles are often subject to microbial growth. Efforts to reduce this growth can greatly improve the functionality and safety of the final product. To create a useful functional finish, it must have a particular efficacy and durability. The purpose of this research is to develop a textile finish based on radical UV-curing of acrylate monomers on polyester fabrics to bestow biofilm resistant properties to the substrate.

This literature review will discuss the state of the art of antimicrobial finishes, including the technology and mechanisms. It will also discuss ultraviolet curing technology, its benefits, and current uses.

2. LITERATURE REVIEW

The purpose of this review of literature is to establish the current state of the art as it pertains to antimicrobial finishing, biofilm resistance, and the use of ultraviolet curing technology. A thorough explanation of the spectrum of materials that have been engineered for different degrees of cell attachment will be provided. Using the available literature on biofilm resistance, as related to textile applications and the available processing techniques, this review will strive to demonstrate the necessity and novelty of the research it precedes.

The necessity of antimicrobial technology, as well as the available methods to impart these properties to textile substrates will be outlined. While this research aims to establish a durable biofilm resistant finish, it is important to understand the difference between antimicrobials and biofilm resistance. UV-curing technology, including its history, mechanism, equipment, advantages and disadvantages are discussed.

2.1 Functionalization of Textiles

Textile fabrics are used in a wide array of industries for a range of end uses. For this reason, textiles must often be imparted with some type of functionalization to improve their appearance and/or performance properties for their intended use. These finishes are one of the last steps of production following fabric preparation and dyeing. Examples of this functionalization are flame-retardants, water repellents, soil repellents, durable press finishes and antimicrobial finishes, among others. This paper will focus on antimicrobial functionality, its purpose, mechanism, and other ways to achieve a similar end result, such as, inherent resistance to bacterial growth.

When engineering a chemical finish there are a number of variables that must be considered. These include the type of fabric, the durability required, other auxiliaries being applied to the fabric, and the cost of applying the chemistry. While these finishes are most often applied to the fabric, some can also be applied to the yarn before fabric construction. Textile finishes can be separated into two categories: durable and nondurable. In some cases, the properties a finish provides are only needed temporarily, or they are applied to a material that will not be washed, in which case, a nondurable finish is sufficient. More commonly, however, the finish will have to withstand numerous washes without losing its efficacy. In this instance, a durable finish is required. Textile finishes can also be classified as mechanical or chemical finishes[1].

There are different approaches that can be used to provide a textile fabric with the desired properties. One of the common ways this is done is by coating the substrate. An additive can also be added to the polymer melt in the case of extrudable fibers, or a functional fiber can be woven into the yarn/fabric itself. The chemical can also be directly grafted to the fiber with a linker and a curing process. While the typical textile finish is thermally cured, more novel curing processes, such as ultraviolet curing, are becoming increasingly popular due to their positive attributes.

2.2 Microorganisms and Bacteria

2.2.1 Overview

A microorganism is a microscopic living organism. They can be single celled or multicellular and make up the majority of the biomass present on earth. Bacteria are the simplest form of microorganisms. There are thousands of different types of bacteria and they

can be classified in a number of different ways. One of the more common ways of organizing bacteria types is by their shape. The three main shapes bacteria take are rod (bacillus), sphere (coccus), and spiral (spirillus). These are show in Figure 1[2].

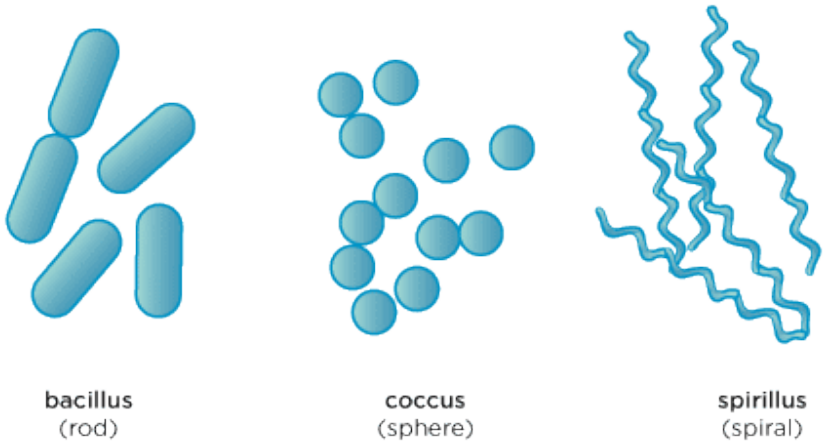

Figure 1. Bacterial Shapes

The mechanism through which bacteria break down organic matter can also be used as a form of classification. They can use aerobic respiration, which is done in the presence of oxygen, or anaerobic respiration, which occurs in environments that lack oxygen. Anaerobic respiration is often referred to as fermentation[3]. Bacteria can also be classified as gram positive or gram negative, which is based on their staining and their shape. Differential staining is used to determine and visualize whether a certain type of bacteria is gram-negative or gram-positive. The bacteria are first stained with a violet dye, a mordant is applied and the bacteria are washed. The bacteria are then dyed with red dye (Figure 2). The gram-positive bacteria maintain the violet dye in their thicker cell walls and therefore cannot be dyed red. The violet dye is washed out of the gram-negative bacteria's thin cell walls and they adopt

the red color[4]. *Staphylococcus aureus* and *Escherichia coli* are common examples of gram-positive and gram-negative bacteria, respectively.

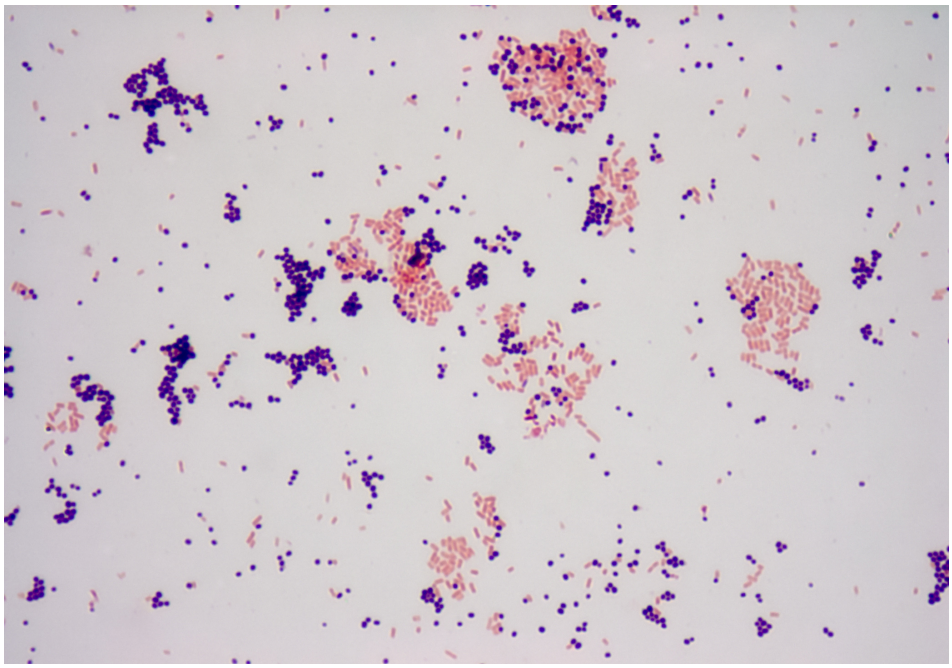

Figure 2. Gram Positive and Gram Negative Staining[5]

While there are a number of beneficial bacteria, many strains cause disease and odor and it is often desirable to limit or eliminate their growth. For microorganisms to survive and propagate, they require energy in order to create new biological material, grow, and reproduce. This process is known as the active metabolic rate.

The energy per unit time available to an organism (Rorg) can be compared to the minimum metabolic rate (Imin), the maintenance metabolic rate (Imaint), and the growth/active metabolic rate (Igrow) in order to determine how suitable a particular environment is for microorganism proliferation. For an environment to harbor life, the Rorg

must be greater than or equal to the Igrow. An environment with Rorg close to Igrow or Imin/Imaint is going to be less hospitable to growth. Therefore, the incompatibility between an organism and an environment could be due to a low Rorg of the environment or a high Igrow of the organism[6].

2.2.2 Streptoverticillium reticulum

The *Streptomyces* genus has over 500 species. The *Streptomyces* genus is one of the most commonly used bacteria type to produce antibacterial, antifungal, and anti-parasitic drugs. *Streptoverticillium reticulum* (Figure 3), a member of the *Streptomyces* genus, is a gram-positive bacterium and is a pink stain organism that is often used to evaluate the antimicrobial properties of textiles.

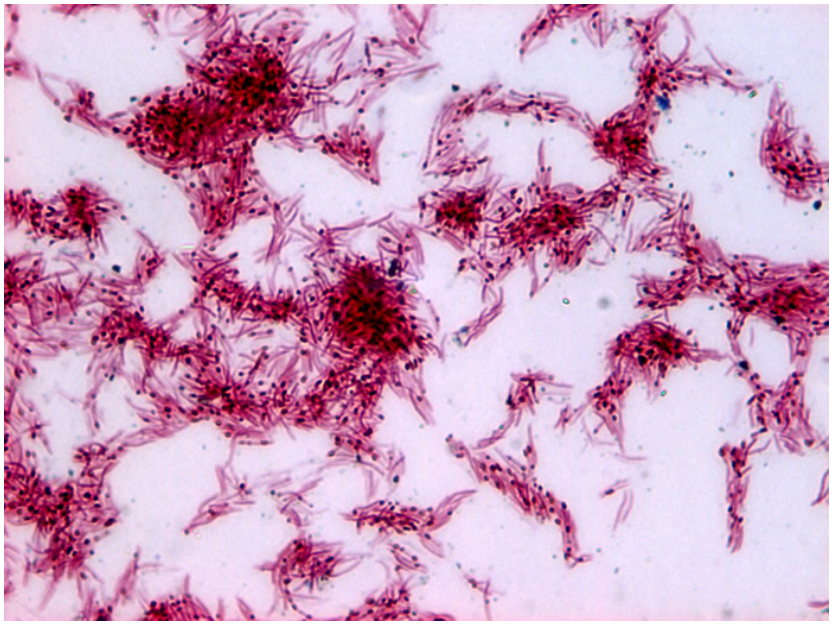

Figure 3. *Streptoverticillium reticulum*[7]

2.2.3 Klebsiella pneumonia

Klebsiella pneumoniae (Figure 4) is a rod shaped, gram-negative bacteria. It is naturally found in the human gastrointestinal tract; however, it can also cause disease, for example, pneumonia. It is fairly easy to disinfect and is used in some antimicrobial test methods[8].

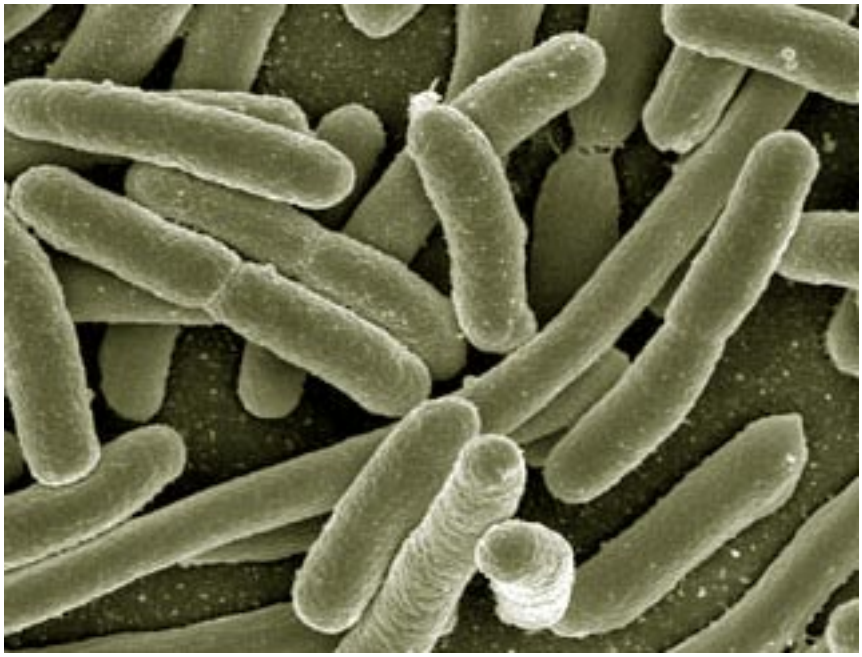

Figure 4. *Klebsiella pneumoniae*[9]

2.2.4 Staphylococcus aureus

Staphylococcus aureus (Figure 5) is a spherical shaped, gram-positive bacteria that is often associated with infection. It is relatively difficult to disinfect and is used in a number of antimicrobial evaluation test methods[8].

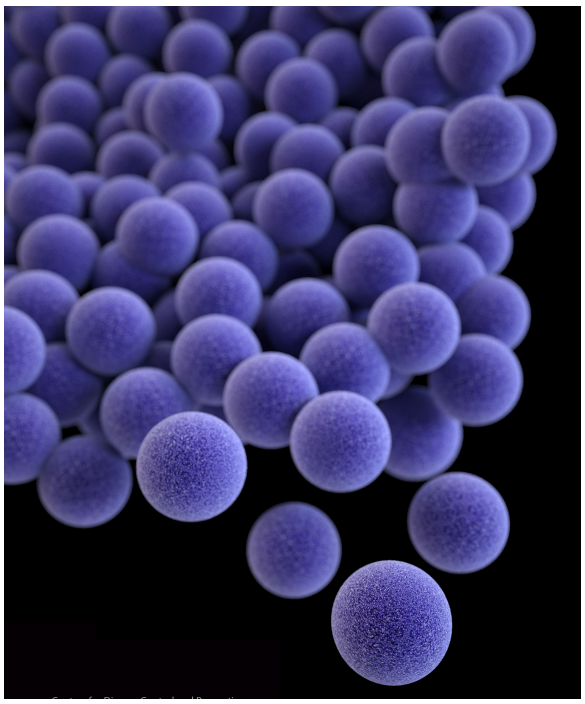

Figure 5. *Staphylococcus aureus*[10]

2.3 Biofilms

2.3.1 Planktonic Cells vs. Films

A body of microorganisms adhered to a surface is considered a biofilm (sessile)[11]. Antonie van Leeuwenhoek, a Dutch microscopist in the 17th century, was the first to discover the existence of biofilms. He built high-end microscopes for the time and first noticed colonies of bacteria forming as dental plaque[12]. Biofilms are communities of bacteria that are often large enough to be seen by the naked eye; and, they have been shown to have unique properties as compared to their planktonic counterparts. When biofilms are formed, planktonic cells form a monolayer, which then proliferates into a microcolony, and

eventually a mature biofilm on a surface. As much as 99% of bacteria on earth exist in the form of a biofilm[13].

Biofilms have proven useful in a number of situations. For example, the organisms that make them up can be used to purify wastewater, or to clean up an oil spill. However, their presence is often undesirable. Biofilms can grow virtually anywhere, and therefore affect many natural and industrial environments (Figure 6). Their effects are widespread and affect many industries, including food, maritime, water systems, sporting and paper industries, as well as, residential environments[13]. They are found on inert and living surfaces[14]. One of the industries affected most significantly is the medical industry, and the results are often quite detrimental. Biofilms can form on medical implants, and because they are frequently resistant to antibiotic therapies, sometimes the only viable treatment is complete removal of the device. Biofilms are also present in a large number of chronic infections[11,14]. This not only increases patient trauma, but also medical costs. Because of these issues, it is highly desirable to study biofilms and their mechanisms in order to create materials that can inhibit their growth.

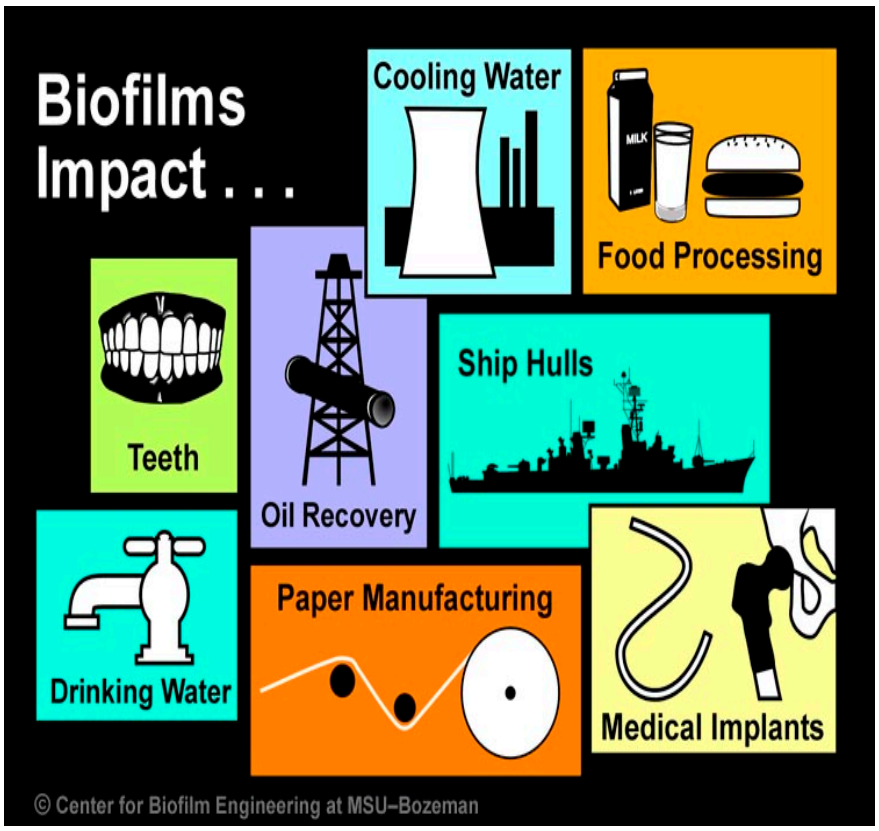

Figure 6. The Scope of the Impact of Biofilms[15]

Studies have shown that biofilms pose a higher threat of resistance to antimicrobials and biocides[14]. Advantages to the bacteria of growing as a biofilm include, protection from antibiotics, disinfectants, and harsh environments, and an increased ability to survive in conditions devoid of nutrients[13]. Biofilms can be homogeneous or heterogeneous in nature. Often the number of species of bacteria present in a biofilm can exceed 500[11]. When bacteria grown as a biofilm are compared to those grown as singular cells, their resistance to antimicrobials can increase up to 1000 times, making the removal of biofilms difficult[16,17,18,19].

This increased resistance to antimicrobials is not fully understood. It has been shown that while the type of bacteria, as well as the type of drug being applied, has an effect on the exact mechanism of resistance, there are some commonalities between all biofilms. Biofilms allow survival in a hostile environment because they provide a protected form of growth[14].

Biofilms have been shown to form complex internal structures, such as channels, which can be used for the transport of nutrients[14,20]. Biofilms produce a matrix of exopolysaccharide or glycocalyx. This matrix could play a large role in preventing antimicrobials from penetrating the biofilm, and protecting the body of the film from drug contact. In some cases, the drug binds with components of the biofilm, but this is not always the case, and other mechanisms must also be considered.

The thickness of the biofilms present also plays a role in the effectiveness of the antimicrobials. While even thin films are more resistant than planktonic cells, they are not as resistant as thicker films. This is because one of the main mechanisms of antimicrobial resistance is the ability of a biofilm to prevent the antimicrobial agent from diffusing throughout the entire depth of the film. The structure of the biofilm significantly retards the diffusion rate. Another possibility of the reduced efficacy of antibiotics against biofilms is the reduced metabolic rate of some bacteria within the biofilm, which means those cells are growing more slowly and are less affected by antibiotics[14].

2.3.2 Bacteria Attachment to Surface Mechanisms

There are multiple mechanisms to consider when classifying bacterial attachment to a particular surface. Van der Waals forces, surface energy, roughness, and other factors have been studied to evaluate their effect on the surface attachment of bacteria. The process of

bacterial adhesion to a surface begins with a physicochemical interaction, followed by a molecular and cellular interaction. It is based on the physical properties of the bacteria, the characteristics of the substrate, and the surrounding environment. There are a few different methods that can be used to evaluate these interactions[21]. If the initial bacteria-surface interaction does not promote attachment to the surface, harmful biofilms can be avoided.

Bacteria attachment can be broken down into phases, shown in Figure 7. "Phase one" consists of the initial attraction between the surface and the bacteria, followed by adsorption, and attachment. It is initiated by hydrophobic interactions, electrostatic charge, or van der Waals forces, for example, which attract the bacteria from the liquid to the available surface. A firmer adhesion of the bacteria to the surface occurs in "phase two". In this phase, physical bonding though the use of pili, fimbrae, slime, or capsules begins (Figure 8). A mature biofilm takes on a mushroom like shape. The final step of the biofilm growth cycle is the detachment of cell clusters from the body of the biofilm. In this step, the rate of cell regeneration is equal to that of cell death. Once available nutrients have been depleted, the biofilm itself creates enzymes that breakdown the colony allowing regrowth on another more suitable surface[13].

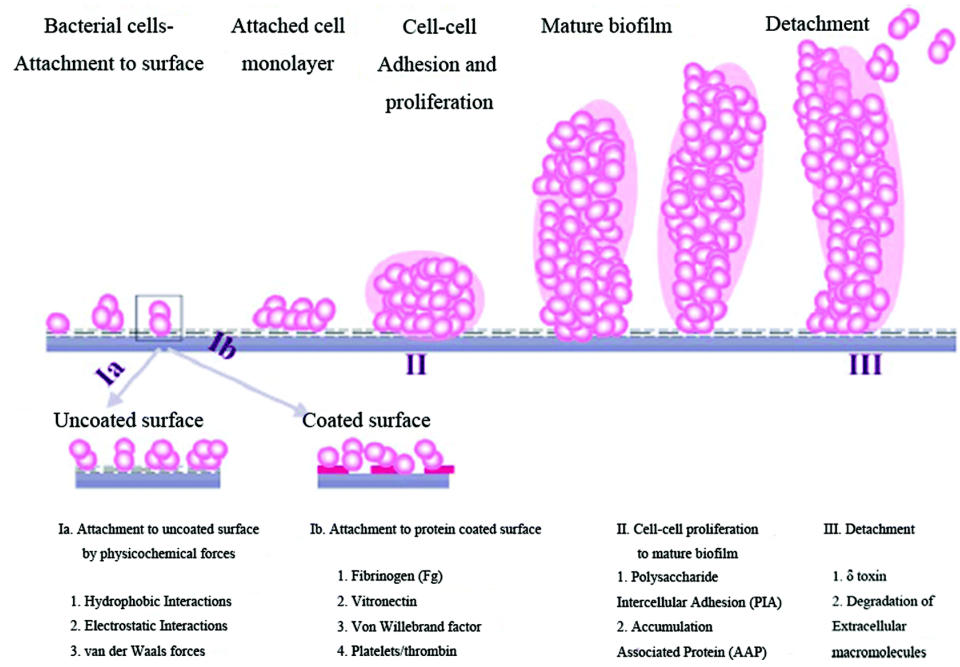

Figure 7. Phases of Biofilm Maturation[21]

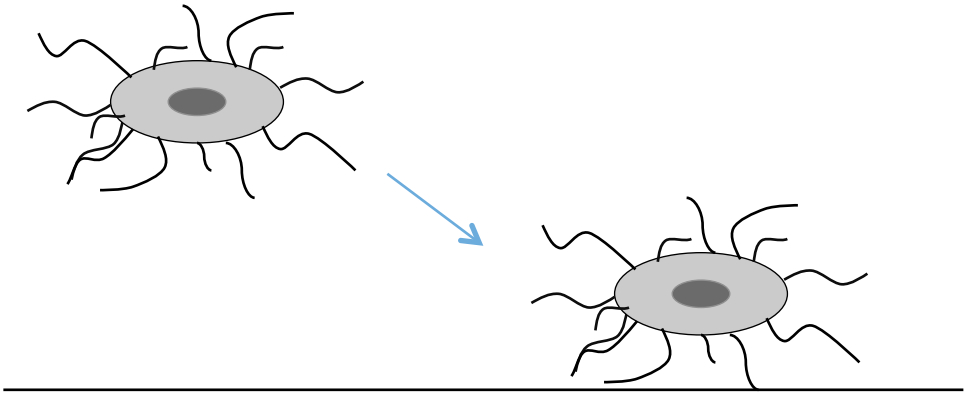

Figure 8. "Phase Two" of Biofilm Attachment: Physical Bonding

Various factors can influence the level of adhesion bacteria have to a surface. The surrounding environment including the temperature, the flow conditions, the presence of antibiotics, and the exposure time play a significant role. The surface chemistry of the

material, such as the hydrophobicity and charge, the surface roughness, and the surface configuration are also important[22]. For example, rough surfaces favor bacterial adhesion and biofilm deposition, while smooth surfaces do not. Porous surfaces are also more susceptible to bacterial bonding than non-permeable surfaces[21]. The pH of the surrounding environment also plays a role in the success or failure of a biofilm. For example, if the pH is gradually made more acidic, bacteria have the ability to alter their pH in response to that of the environment. However, when a rapid change in pH occurs, the bacteria are not able to adapt and the rate of cell survival is much lower[13].

The type of bacteria also has an effect on surface adhesion. Like attracts like, and hydrophobic bacteria tend to be more attracted to hydrophobic surfaces, and vice versa with hydrophilic bacteria and materials. The surface charge of the bacteria, which is typically negative in a planktonic suspension, may also play a role.

2.3.3 Evaluation of Bacterial Adhesion

Techniques used to evaluate the factors influencing adhesion must be developed to gain a more through understanding of the mechanisms. These techniques can be used to quantitatively evaluate the likelihood of a particular interaction between bacteria and material.

Static assays are a simple way to evaluate cell adhesion. Cells are laid on a surface, and after a period of time, the surface is rinsed, and the cells that did not adhere or only weakly adhered are washed away. This method can also be used to measure the strength of adhesion, if a centrifuge is used in the methodology. The test results for the amount of adhered bacteria are, however, only qualitative.

Flow adhesion assays can also be employed to evaluate adhesion. In a parallel-plate flow chamber, as used in rheological studies, water passes through one end and exits through the other. This technique can be used to measure the shear stress at the wall and is shown in Figure 9. Because the bacteria are attached to the wall, it can be assumed that the shear stress at the wall is the same shear stress on the bacteria. A radial flow chamber, also often used in rheology studies, can be used as well (Figure 10). In a radial flow chamber, there is an incline in shear stress toward the center of the discs.

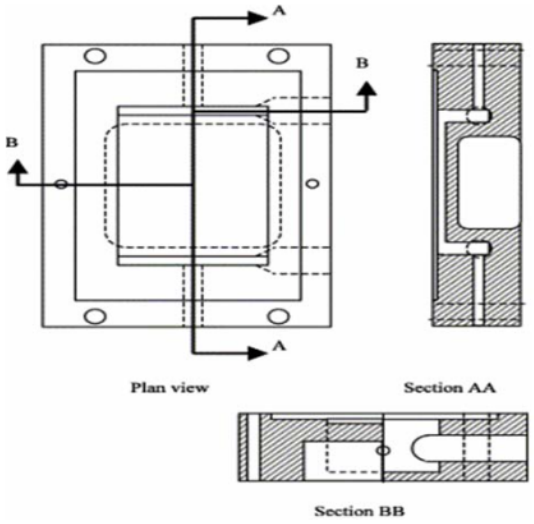

Figure 9. Parallel Plate Flow Chamber[21]

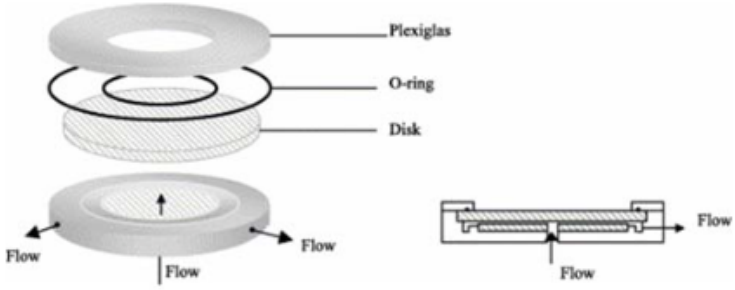

Figure 10. Radial Flow Chamber[21]

Atomic force microscopy (AFM) can be used to assess the cell-material interaction. These include the van der Waals forces and electrostatic forces. Standard methods using AFM can only measure the interactive forces between the cells and the substrate. They cannot measure the detachment forces necessary. To use AFM to quantify the detachment forces, a modification to the device must be implemented. This is done by measuring the deflection of a cantilever attached to the tip of the AFM**,** as seen in Figure 11.

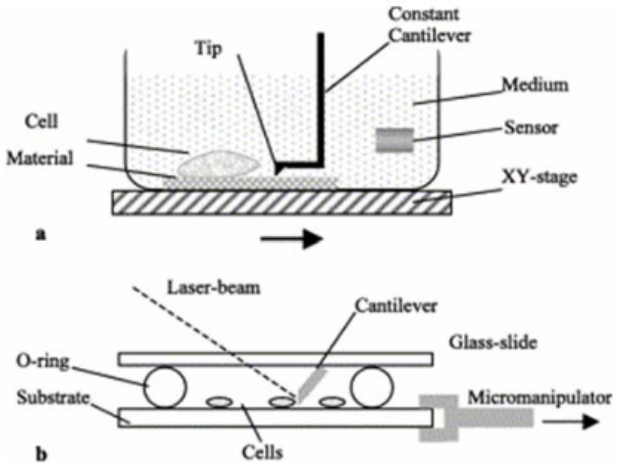

Figure 11. AFM with Cantilever Attached[21]

2.4 Antimicrobial Textiles

Many textiles offer ideal growth conditions for a range of microbes. This growth can lead to a variety of problems, including fiber degradation, odor, discoloration and health issues. Microorganisms can destroy textile fibers by consuming the fiber itself, or any finishes or coatings present on the fabric. To combat these issues a large amount of research has been conducted to make textiles less conducive to the growth of these microbes. Merely washing the affected textile does not remove the microbe and therefore it is necessary to treat the susceptible fabrics with an antimicrobial finish. Antimicrobial finishes can provide hygienic benefits to the user, improve the durability of the textile, and prevent possible staining.

There are many applications that require or would benefit from microbial resistance. These include but are not limited to, protective clothes used in medical settings, textiles used in schools, hotels, and crowded public areas, or textiles that are exposed to weather, such as, awnings, tents, and boat fabrics, as well as exercise garments, which are often soiled with sweat to prevent unpleasant odors[1].

Because of the rapid rate of growth seen in most bacteria, antimicrobial finishes must not only stop the growth of the microbes, but they must also do it quickly while being durable and consumer safe.

2.4.1 Antimicrobial Mechanisms

Different antimicrobials use different mechanisms to kill or block the bacteria that is present. They can inhibit the synthesis of the cell wall, proteins, or nucleic acid. They can also alter the cell membrane or the metabolic pathways, all of which are vital to the bacteria's

survival[23]. Antimicrobials can also be used to block the enzymes necessary for the bacteria to break the fiber down into digestible parts, effectively starving the bacteria. Another technique is applying a physical protective barrier to the substrate as a coating, efficiently blocking bacterial growth. These coatings can be used on nearly any type of fabric and display good durability. However, they do have some negative qualities such as increased stiffness and color change.

The fiber itself can also be altered to impart antimicrobial properties. This can be done through surface treatments such as grafting, copolymerization, or chemical modification. These methods are usually used to confer charged functional groups, either cations or anions, to the fiber. Along with effectively inhibiting the growth of microbes, antimicrobial finishes must have the following properties in order to be considered a viable textile finishing option:

- Ease of application
- Low cost
- No toxic effects to the consumer
- No toxic effects to the environment
- Durable to laundering and dry cleaning (the necessary durability is dependent on the end use of the product)
- No adverse effects when applied with other finishing agents
- Minimal negative effects on the final hand of the product
- No negative effects on the final properties of the fabric, such as, tensile strength.

Different types of antimicrobial finishes can also be separated into the categories of biocides and biostats. It is important to understand the difference between biocides and biostats. Biostats only control the growth of the microbes. Biocides kill the bacteria and are subject to more government regulations than biostats. In textiles, leaching and bound are the two main mechanisms of antimicrobial finishes.

2.4.2 Controlled Release Antimicrobials

Controlled release antimicrobials employ leaching agents that "leach off" of the textile. Leaching agents prohibit the growth of microorganisms on and around the substrate. This area around the substrate is called the area of inhibition. However, because they do gradually leach off, their efficacy tapers and they are eventually rendered ineffective. Also, because the antimicrobial agent is leaking into the surroundings it can have an adverse effect on the environment. For this reason many effective controlled release antimicrobial finishes for textiles have been banned. Some examples of controlled release antimicrobials are[1]:

- Tributyltin oxide
- Dichlorophene
- Triclosan
- Triclocarban
- 3-Iodopropynylbutyl carbamate
- Organo-silver compounds

Some controlled release mechanism products can regenerate themselves when exposed to bleaching agents during laundering, or when exposed to ultraviolet light. Because the antibacterial agent is regenerated, there is an endless reserve making it a durable finish[24].

2.4.2.1 Tributyltin Oxide

Tributyltin oxide (Figure 12) was once used as an antibiofouling agent and is effective against bacteria, fungus, and mulluscs. However, because of its toxicity and persistence in the environment, it has been banned in many countries[24].

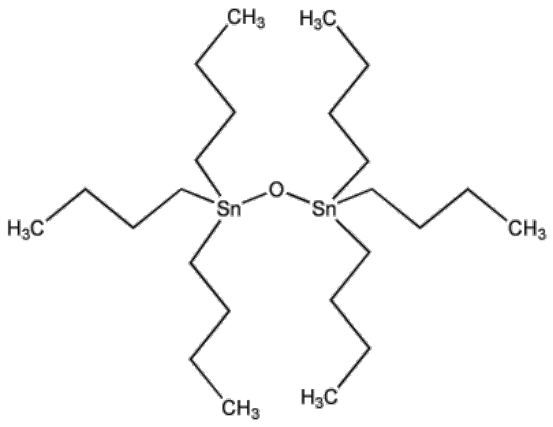

Figure 12. Structure of Tributyltin Oxide

2.4.2.2 Triclosan

Triclosan, or 2,4,4'-trichloro-2'-hydroxydiphenyl ether (Figure 13), is found in many consumer products including toothpaste, soaps, and detergents. It is one of the most common antimicrobial agents because thus far it has not been found to have any adverse side effects either to the consumer, manufacturer, or to the environment. It is also used in the medical

field in soaps and surgical scrubs. Patients with methicillin-resistant *Staphylococcus aureus* (MRSA) are often prescribed to bathe in a triclosan solution. Triclosan is an example of an antimicrobial agent that blocks the production of enzymes. In this case, it blocks the fundamental enzyme needed for synthesis of fatty acids called the protein reductase enzyme (ENR)[25].

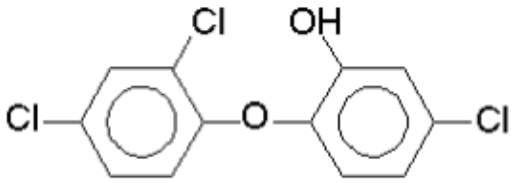

Figure 13. Structure of Triclosan

Triclosan is applied to textiles through a pad-dry-cure process and diffuses into the fiber. It is not water-soluble and is bound within the fiber, similar to the application of disperse dyes, making it durable to washing[26].

Triclocarban (Figure 14) has a very similar antimicrobial mechanism as triclosan, and is used in many similar applications, such as lotions, soaps, toothpaste, and medical applications. It is most effective against gram-positive bacteria such as *Staphylococcus aureus.*

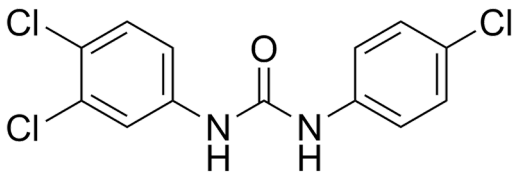

Figure 14. Structure of Triclocarban

2.4.3 Bound Antimicrobials

Bound finishes are chemically attached to the fiber and only prohibit the growth of microorganisms directly in contact with the material. Because the molecules are chemically bonded to the fiber, they are considered durable finishes[1]. Examples of bound antimicrobials are:

- Octadecylaminodimethyltrimethoxysilylpropylammonium chloride
- Polyhexamethylene biguanide or polyhexanide (PHMB)
- Chitosan

2.4.3.1 Octadecylaminodimethyltrimethoxysilylpropylammonium chloride

Octadecylaminodimethyltrimethoxysilylpropylammonium chloride (Figure 15) is a common antimicrobial used on textiles. The quaternary nitrogen provides the antimicrobial properties. A continuous or exhaust method followed by a curing step forms a siloxane polymer coating on the fiber, resulting in a durable finish[1].

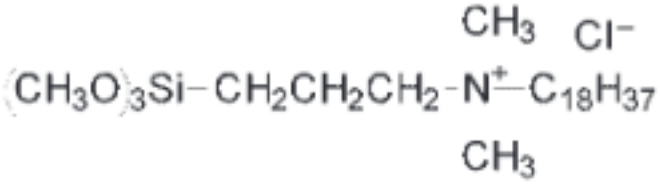

Figure 15. Structure of Octadecylaminodimethyltrimethoxysilylpropylammonium chloride

2.4.3.2 Polyhexamethylene biguanide

Polyhexamethylene biguanide or Polyhexanide (Figure 16) is currently used as a disinfectant and antiseptic. It is often found in wound dressings and is effective against gram-positive and gram-negative bacteria[27]. Many of the bacteria types it is effective against are commonly found in biofilms including *Klebsiella pneumoniae, E coli, and S epidermidis*[28]. PHMB works by binding with the cell DNA and destroying the cell membrane causing the cell to leak necessary ions. It can be applied as a solution, gel, or by being chemically bonded to a textile substrate[29].

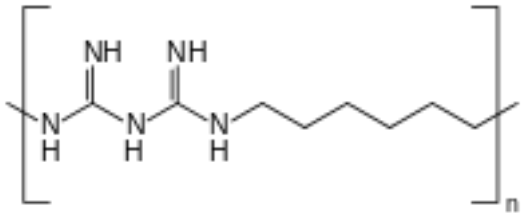

Figure 16. Structure of Polyhexamethylene biguanide

2.4.3.3 Antimicrobial Chitosan Finish

Chitosan (Figure 17) is made from natural waste products and is therefore inexpensive. Chitin found in crustacean shells, such as those from crab or shrimp, is turned

into chitosan through an alkali treatment shown in Figure 18[30]. Chitosan is a cationic polymer that can be crosslinked and covalently bonded to cotton fibers.

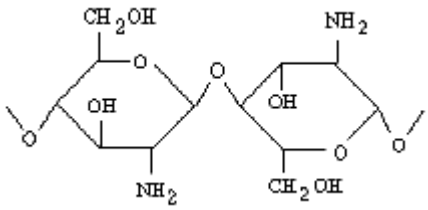

Figure 17. Structure of Chitosan

Chitosan provides a number of positive attributes when used as an antimicrobial agent. It is non-allergenic, non-toxic, and biodegradable. It also has high-absorbency and moisture control. Not only does chitosan act as an antimicrobial agent, but it has been shown to increase the rate of skin regeneration when applied to wounds and burns. It also acts as a hemostat and naturally blocks nerve ending, effectively reducing pain[31]. These properties make it ideal for use in wound care products[32]. Chitosan has also been used successfully when used as a scaffold for three-dimensional tissue growth, as it triggers cell generation. It is easy to manipulate chitosan into a number of different forms, such as, nanofibers membranes, sponges, and hydrogels, which makes it ideal for use in many different applications[31].

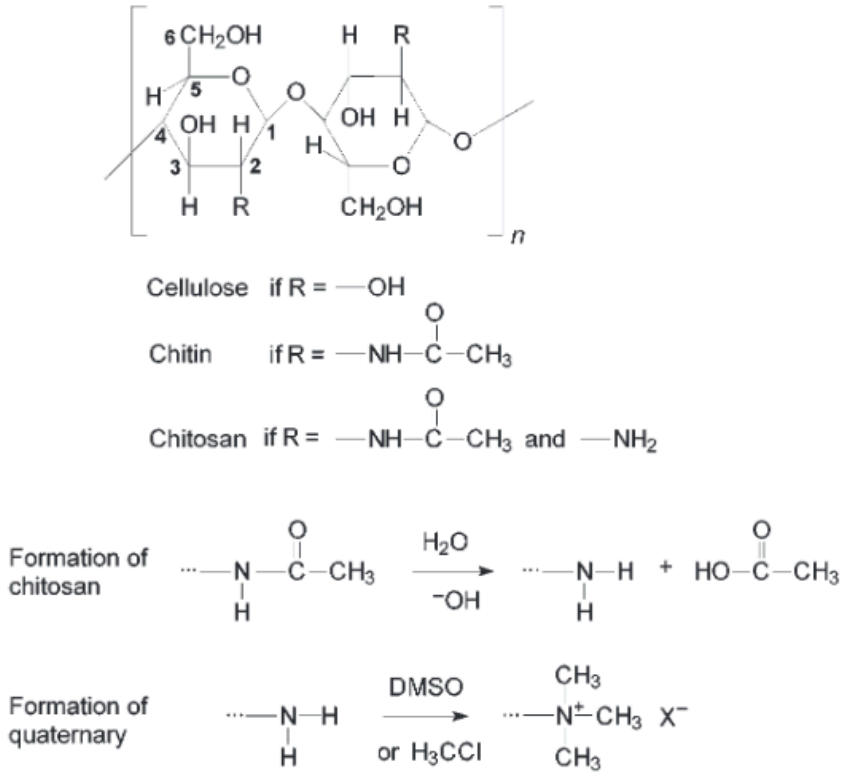

Figure 18. Chitosan from Chitin[1]

Research to improve the use of chitosan as an antimicrobial agent is being done. Although already used in the textile industry for dyeing and finishing, the use of chitosan as an antimicrobial agent has shown so issues. These include a reduction in efficacy under alkaline conditions and a lack of sufficient bonding to the textile resulting in poor durability.

2.4.3.4 Metals and Metal Salts

Metals and metal salts have been shown to have antimicrobial properties. These include mercury, silver, and copper, which have been shown to be effective on natural and synthetic fibers. Today quaternary ammonium salts and silver ions are commonly used as

antimicrobials. The most common metal used as an antimicrobial agent for textile products is silver. Silver is effective against gram positive and gram negative bacteria, however, it is not effective against fungi, mold, or mildew[33].

2.5 Antimicrobial Test Methods

There are a number of standard test methods used to evaluate antimicrobial finishes. Most of these test methods involve evaluating the zone of inhibition in an agar, or counting the number of bacteria remaining on the sample after a predetermined period of time. Many antimicrobial finishes are only potent against certain strains, so it is important to understand which strains a particular finish is effective against. Often it is necessary to combine different components into one finish to give the substrate more effective antibacterial properties. Although these standards give some idea of the efficacy of an antimicrobial finish, they often do not correlate directly to results seen in the field. Poor reproducibility is a common problem.

2.5.1 ASTM E1428-99

ASTM E1428-99, or The Standard Test Method for Evaluating the Performance of Antimicrobials in or on Polymeric Solids Against Staining by *Streptoverticillium reticulum* (A Pink Stain Organism), is a common test method used to evaluate antimicrobial finishes.

This test method uses *Streptoverticillium reticulum* to qualitatively analyze bacterial attachment in or on synthetic polymeric solids. *Streptoverticillium reticulum* is an indicator organism that stains the test material pink. The *Streptoverticillium reticulum* cells are first harvested from the culture plate with 3mL of phosphate buffered saline, and then the cell-

laden swab is used to streak the agar in a manner that ensures total coverage the plate. Once the agar surface is inoculated with *Streptoverticillium reticulum*, a control sample and a treated sample are immediately placed on the agar surface ensuring good contact. The agar is then incubated for 14 days at 29° C. After incubation, sample ratings are assigned based on the percentage of sample area that is stained. Each agar holds a control sample and a treated sample.

This test method is meant to suggest how an antimicrobial finish will perform in real life conditions. This test method should not be used to evaluate dark samples, as they will mask the pink staining. The degree of staining is then evaluated (Table 1). A zone of inhibition surrounding the treated sample indicated that the antimicrobial finish is leaching from the specimen[34].

Table 1. Stain Rating

Observed Stain on Specimens	Rating
No Stain	0
Trace of Stain (less than 10% coverage)	1
Slight Stain (10 to 30% coverage)	2
Moderate Stain (30 to 50% coverage)	3
Heavy Stain (50% to complete coverage)	4

2.5.2 AATCC 147

The AATCC 147 test method, Antibacterial Activity of Textile Materials: Parallel Streak Method (Figure 19), uses a gram-positive and a gram-negative bacteria in inoculated agars. Streaks of the bacteria are made and a rectangular sample is placed over the streaks. The results are assessed visually after incubation. The bacteria growth is evaluated based on the zone of inhibition around the treated sample and the level of attachment to the substrate[35].

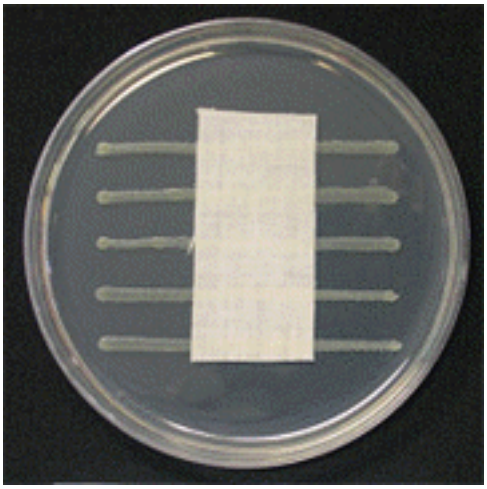

Figure 19. AATCC 147 Parallel Streak Method

2.5.3 AATCC 100

This test method is used to determine the performance of antimicrobial finishes. It evaluates antimicrobial finishes quantitatively using a gram-positive and a gram-negative bacteria inoculum broth, although the test method can be altered for use with bacterial, fungal, and/or viral species. The treated substrate is imbued with 1 mL of inoculum and incubated for a specific contact time. This contact time can range from 10 minutes to 24 hours. The number of colony-forming units (CFU's) is measured at time zero and after the

determined contact time. This is done through sequential dilutions, which are then used to incubate a sterile agar. An untreated sample is used as a control and the microbial reduction is calculated for each sample. This test method can be used to assess nearly any porous material, including textiles[36].

2.6 Biofilm Resistant Technology/Bioengineered Finishes and Materials

Polymers themselves have been shown to have varying degrees of bacterial attachment. Identification of these materials, and developing an understanding of the underlying mechanism affecting the level of cell attachment, would be useful in engineering biocompatible or biofilm resistant finishes. Understanding of the interaction between cells and substrates is important in the creation of biomaterials. For example, to effectively use stem cells, the cell activity and growth must be highly controlled. Roughness, hydrophobicity, and other surface properties can affect the cell growth on the surface of the material. If the relationship between the cell growth and the surface characteristics of the material are determined, the level of cell activity needed for a specific application can be specifically engineered. For the medical industry, it is important to understand these mechanisms to both inhibit undesirable cell growth, and initiate and control desired cell growth.

2.6.1 Biofilm Resistant Acrylates

Acrylates have previously been used for a number of medical uses such as surgical glues and they are commercially available, making them very suitable for the study of cell-surface interaction[22].

Analyzing microarrays of acrylate derivatives to find those that promote the growth of human embryonic stem cells, led to the study of acrylates meant to inhibit cell growth. Through the use of microarrays, hundreds of materials can be analyzed in a short period of time. Studies have shown that ester groups and cyclic hydrocarbons moieties significantly reduce bacteria attachment. These were shown to be substantially more effective when compared to commercial silver coatings and were proven effective when tested in vitro and in vivo[37].

Other materials have been shown to be innately restrictive to bacterial attachment and growth. These include polyethylene glycol brushes or zwitterionic polymers. It may be more effective to use these materials than it is to use biocides.

2.6.2 Polyethylene Glycol Brushes

Polymer brush coatings have been shown to prevent biofilm adhesion to a surface. They do this by preventing the initial attachment of the bacteria to the surface of the material. The bacteria are physically blocked from attaching to the surface of the substrate by the brush layer[38].

2.7 Acrylate Polymers/Copolymers

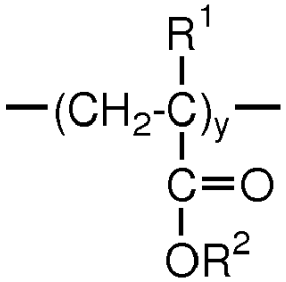

Figure 20. Acrylate Monomers

Acrylates are derivatives of acrylic acid. They are versatile and their properties can be easily modified in order to achieve different properties based on the desired end use. A range of final polymer characteristics can be manipulated, such as, Tg, tackiness, tensile strength, elongation, and hardness. This is often done by altering the R^1 and R^2 groups, shown in Figure 20, or by combining different acrylates into alternating or block copolymers. Variations in their characteristics make acrylates useful for many different applications, and provide endless opportunities for research and experimentation.

For example, by copolymerizing Ethyl Acrylate (EA) (Figure 21) and Methylmethacrylate (MMA) (Figure 22), and altering the ratio of each, the Tg can range from -23°C to 105°C, and the hardness can be significantly increased or decreased. EA, MMA, and butyl acrylate (BA) can be copolymerized with Anisylmaleimide (AMI) (Figure 23) to improve thermal stability[39].

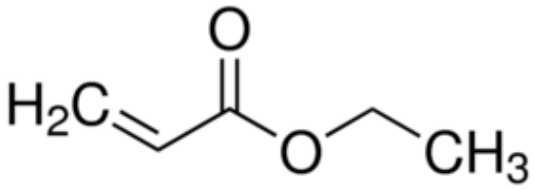

Figure 21. Structure of Ethyl Acrylate

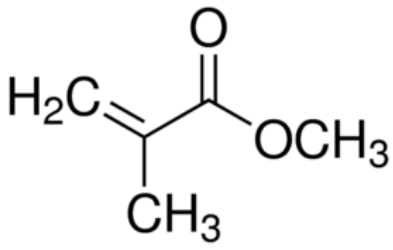

Figure 22. Structure of Methylmethacrylate

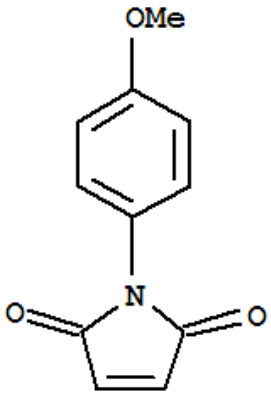

Figure 23. Structure of Anisylmaleimide

Acrylates can take on a variety of different properties and are therefore found in many different applications, including soil release finishes, warp sizes, and biomaterials. Acrylate monomers are UV-curable making them useful for implementation and optimization in increasingly popular UV-cure technology. Acrylates span many different fields and research topics due to their ability to be easily modified.

The versatility of acrylates explains their rise in demand and current production, and the proliferation of related research. There are abundant journal references about acrylates, which span many different disciplines. These range from soil release[40], warp

sizes[41], and biomaterials[22]. Many of the authors referenced here deal with manipulation of acrylate characteristics to enhance specific applications, though some authors examine production related aspects of acrylates, such as UV-curing or industrial scale up[42].

2.8 Ultraviolet Curing Technology

2.8.1 History

The use of ultraviolet light has been used for centuries to cure polymers. The oldest form of UV curing was through the use of the sun. For example, the ancient Egyptians used the UV light of the sun to cure the resins that they used to preserve their dead. Today, there are a number of different ultraviolet lamps that can be used. These include, mercury vapor lamps with iron or gallium additives, fluorescent lamps, or LED lamps. UV curing spans multiple industries and applications[43].

2.8.2 Benefits

Ultraviolet light can be used to cure or set many different chemistries. It is used in a number of different industries, and on a variety of substrates, including plastics, paper, film, foil, wood, metal, glass, fiber, and composite[44]. It can be used to create a range of end products, such as coatings, electronic materials, adhesives, and inks. UV-curing is not only highly customizable, but it also offers many additional benefits over traditional thermal curing methods, such as increased processing speed, low solvent emission, low temperature, and reduced energy consumption. UV curing is becoming increasingly popular due to these benefits.

2.8.3 Applications

Ultraviolet curing is used as the curing mechanism in many industries, and for a wide variety of products. These industries include the automotive, electronics, telecommunications, printing, plastics, glass, and graphic arts.

2.8.4 Mechanism

The process of UV curing uses ultraviolet light to initiate chain-addition polymerization, ultimately converting the initial liquid solution to a polymeric solid. The addition of a photoinitiator to the solution in small quantities generates the polymerization. The photoinitiator absorbs the UV light causing a reaction. This process is represented in Figure 24.

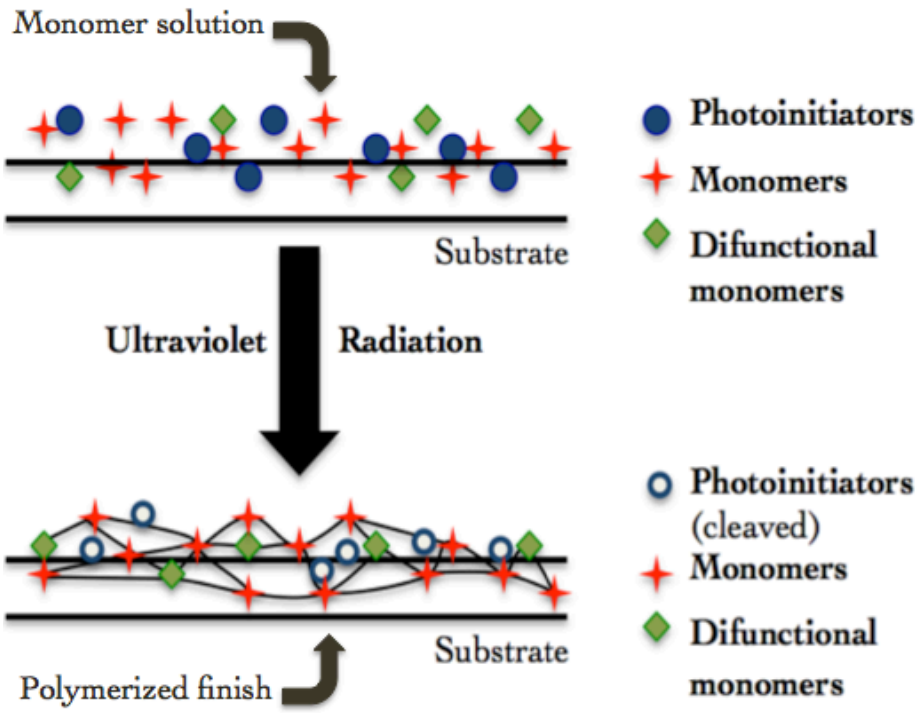

Figure 24. Ultraviolet Curing Mechanism

2.8.5 Issues

One issue that must be considered when using UV-curable systems is oxygen inhibition. This occurs when oxygen in the atmosphere interferes with the cure on the surface of the film or finish. This is due to oxygen's high reactivity to radical species[45]. The oxygen reacts with the available free radicals creating low activity peroxide radicals. Oxygen inhibition presents itself as tackiness on the surface of the film, leading to a reduction in many of the desired properties such as hardness and impact resistance[46]. There are a number of factors to consider when looking to eliminate the effects of oxygen inhibition. These include the finish formulation, curing time, distance from the lamp, and the heat and intensity

of the UV spectrum generated by the curing system. Using a nitrogen or carbon dioxide atmosphere is also an option.

It has been shown that samples cured in a nitrogen atmosphere cure immediately. In an air atmosphere there is a period of time until an exothermic reaction begins. This period of time increases as the intensity of the light source decreases. The rate of polymerization also decreases as the intensity decreases. As the oxygen concentration increases, the molecular weight and crosslinking is significantly reduced.

3. RESEARCH OBJECTIVES

The objectives of this research are to:

1. Create a durable finish to impart biofilm resistant properties to polyester fabric
2. Polymerize said finish using UV radiation

This research expands upon previous work completed in the article "Combinatorial discovery of polymers resistant to bacterial attachment"(Hook) which was presented in section 2.6.1. The authors studied an array of UV-curable acrylate monomers and evaluated the level of biofilm resistance each provided when polymerized on a glass slide. The research presented here will result in the development and characterization of a durable biofilm resistant finish on polyester fabric. The finish will be UV curable resulting in reduced environmental impact and an increase in production speed.

4. EXPERIMENTAL

4.1 Fabric Selection

White, knit, 100% polyester fabric was chosen for this research because of its relevance and use as the desired final application. Nike, Inc. supplied all fabric. The fabric was initially used as received and later scoured prior to treatment to remove any left over processing chemicals.

4.2 Finishing Variables

The variables considered for manipulation were as follows:

- Monomer/chain extender combination
- Amount of chain extender
- Curing time
- Type of photoinitiator
- Amount of photoinitator
- Distance from light source
- Percentage power of the light source

4.3 Ultraviolet Curable Finishing on Polyester

Experimental designs were based on coating chemical composition, coating viscosity, add-on weight, and surface energies of coating and substrate. The resultant polymerized coating properties were measured as a function of UV intensity and irradiation. The level of biofilm resistance on coated substrates was identified via bacterial assays and additional trials

were conducted to maximize the efficacy of the final finish. A general process flow diagram is shown in Figure 25.

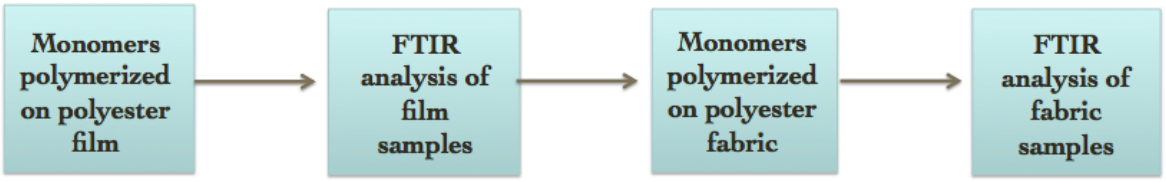

Figure 25. Process Flow Diagram

4.3.1 Chemicals

Five monomers were chosen based on published research, as shown in Figure 26. They will henceforth be referred to as monomers A, B, C, 1, and 2. Photoinitiator selection was based on compatibility with the light source. Sigma Aldrich supplied these chemicals.

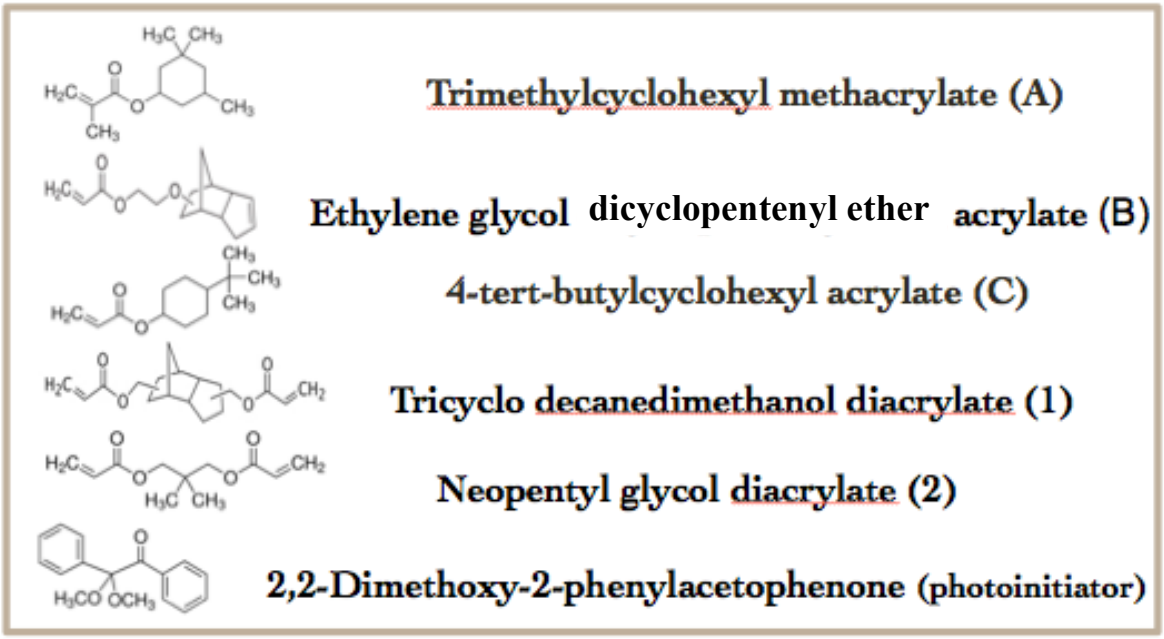

Figure 26. Monomers and Photoinitiator Evaluated

4.3.2 Padding Equipment

A Meyer rod was used to apply the chemistry to the selected fabric. A Meyer rod is a stainless steel rod with a thread on the surface created from grooves or wrapped wire (Figure 27). These grooves can vary in area depending on the type of finish being applied and the substrate. The fabric was saturated with the chemistry and the excess was removed with the Meyer rod to simulate an industrial padding process, but on a smaller scale.

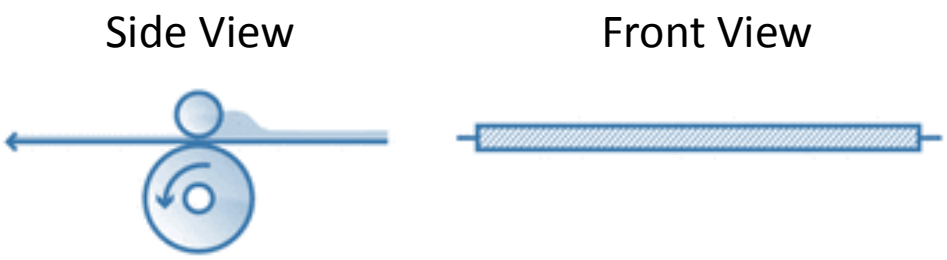

Figure 27. Schematic of a Meyer Rod

4.3.3 Curing Equipment

Ultraviolet light curing was used, rather than the heat curing method traditionally used in most textile manufacturing processes. The UV-curing equipment used was an IntelliRay 600 from Uvitron International (Figure 28), located on the Centennial Campus of North Carolina State University. The light source is a standard IntelliRay UVA enhanced 600-Watt Metal Halide arc lamp. The typical peak irradiance is 150-180 mW/cm2 UVA. This unit contains an adjustable shelf to control the distance of the fabric from the light. It is also easily adjusted to control the exposure time and the lamp intensity.

Figure 28. Uvitron International IntelliRay 600

The absorption spectrum of the selected photoinitiator was compared to the spectral distribution of the UV-light source. The light source used was a standard IntelliRay UVA enhanced 600-Watt Metal Halide arc lamp with a typical peak irradiance of 150-180 mW/cm2 UVA. The spectral distribution of this light source is shown in Figure 29. It is important that the photoinitiator used is compatible with the light source to ensure maximum curing efficiency and minimum fabric damage. A filter can be applied to the light source to reduce the unnecessary wavelengths. Based on the spectra shown in Figure 30, 2,2-Dimethoxy-2-phenylacetophenone was chosen as a suitable photoinitiator.

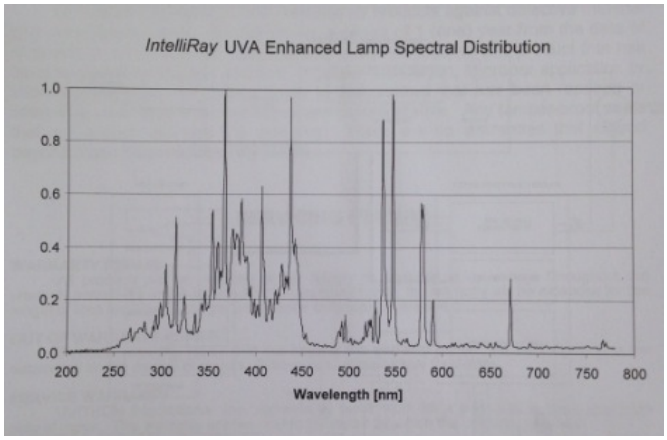

Figure 29. Spectral Distribution of Light Source

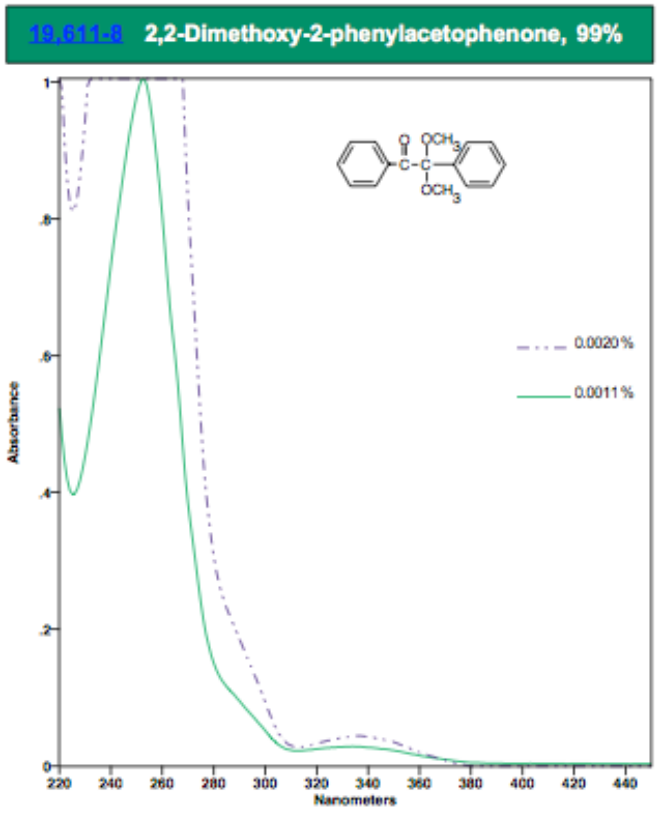

Figure 30. 2,2-Dimethoxy-2-phenylacetophenone Spectra

4.3.4 Application of Monomers to Polyester Film

Prior to testing on the polyester fabric and for ease of analysis, monomers were initially applied to polyester film to determine the approximate necessary curing parameters of each monomer.

The initial batch of monomers was applied using 1% photoinitiator and a 75/25 monomer/solvent ratio applied to the polyester film. The initial solvent used was Dimethylformamide (DMF). For comparison, each of the monomers was also applied with the two difunctional monomers (Tricyclo [5.2.1.0] decanedimethanol diacrylate and Neopentyl glycol diacrylate), separately at 5% and 20% wt. at two different curing times (10 sec and 30 sec). Regardless of cure time, or the amount of bifunctional monomer, the film remained tacky. This was most likely due to the presence of the DMF which, with a boiling point of 153°C, was not fully evaporated in the short cure time. Because the monomers used are not exceedingly viscous, the amount of solvent was reduced and acetone, with a boiling point of 56°C, was used as it would be more apt to evaporate and would provide more desirable results. Removing the DMF further improved the curing of the film; however, full curing was not achieved due to oxygen inhibition. Trimethylolpropane tris(3-mercaptopropionate) (thiol), which is commonly used to reduce the effects of oxygen inhibition was added to address this issue (Figure 31).

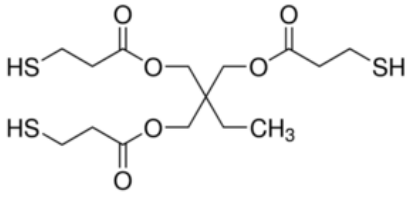

Figure 31. Structure of Trimethylolpropane tris(3-mercaptopropionate)

Monomers A, B, and C were each polymerized with 1, 3, 5% photoinitiator at a range of times from 10s-300s. Monomer samples were also created with 1, 3, 5, 7 mol% thiol. Copolymers of monomers A, B, and C each with 0%, 10%, 50%, and 90% crosslinker monomers (1) and (2) were prepared. Acetone was added at 1 wt% to dissolve the photoinitiator.

Each of the polymer films and its affinity for the polyester film was evaluated, to assess its affinity for the polyester fabric. FTIR analysis was used to determine the amount of uncured monomer remaining on the sample.

4.3.5 Application of Monomers to Polyester Fabric

Each of the monomers (A, B, C, 1, 2) were prepared with 1, 3, and 5% photoinitiator. Samples of these solutions were cured at 50, 150, and 300s. The necessary curing parameters for each of the monomers on polyester fabric were determined using previous knowledge from curing on polyester film. FTIR analysis was used to determine the C=C conversion ratio.

After the series of initial tests, it was determined that samples would be kept at 6 inches from the light source, that the lamp would remain at 100% power, and that the chemistry would contain 5% photoinitiator would be used. To improve the cost effectiveness of the

processing chemistry for potential use on an industrial scale, it was decided that with 5% photoinitator, a sufficient cure could be achieved without the use of thiol.

4.4 Evaluation of Treated Samples

4.4.1 Percent Solid Add-on

The percent solid add-on was measured for each of the treated samples. The initial percent solid add-on was initially too high, and would not be suitable for commercial implementation; therefore, samples with reduced add-on were created. In this step, acetone was added to the chemistry before application, and allowed to evaporate before curing was induced. Acetone was added to each of the monomer solutions at 10, 30, 50, 70 and 90 wt% to produce samples with lower add-on.

4.4.2 FTIR Analysis

FTIR analysis was completed using a Nicolet Nexus 470 FT-IR with a Ge crystal. Thermo Scientific™ OMNIC™ Series Software was used to determine the C=C bond conversion ratio. The FTIR spectra were evaluated at the 810 cm^{-1} peak for the acrylate C=C-H out of plane bend and 1640 cm^{-1} peak for the C=C-H bending. Each of the chosen monomers was polymerized with varying amounts of photoinitiator and exposure time, as explained in Section 4.3.4. This was used to determine the necessary curing time based on the amount of photoinitator.

4.4.3 Qualitative Bacteria Test Methods

Two methods were used to qualitatively assess the antibacterial properties of the samples.

The first was, ASTM E1428-99, Standard Test Method for Evaluating the Performance of Antimicrobials in or on Polymeric Solids Against Staining by *Streptoverticillium reticulum* (A Pink Stain Organism). In this procedure, yeast malt extract agars were created and streaked with an inoculated cotton swab in a manner that ensured total coverage. Test samples and controls were placed on the agar surface and incubated for 14 days at 29°C (Figure 32). The samples were then rated on the amount of staining seen on the sample when lifted from the agar. These ratings are shown in Table 2.

The second method used was, AATCC 147, Antibacterial Activity Assessment of Textile Materials: Parallel Streak Method. In this procedure the agar plate was streaked with an inoculating loop. The test sample was placed across the inoculum streaks, ensuring intimate contact to agar surface and incubated for 5 days at 29°C. This method is shown in Figure 33.

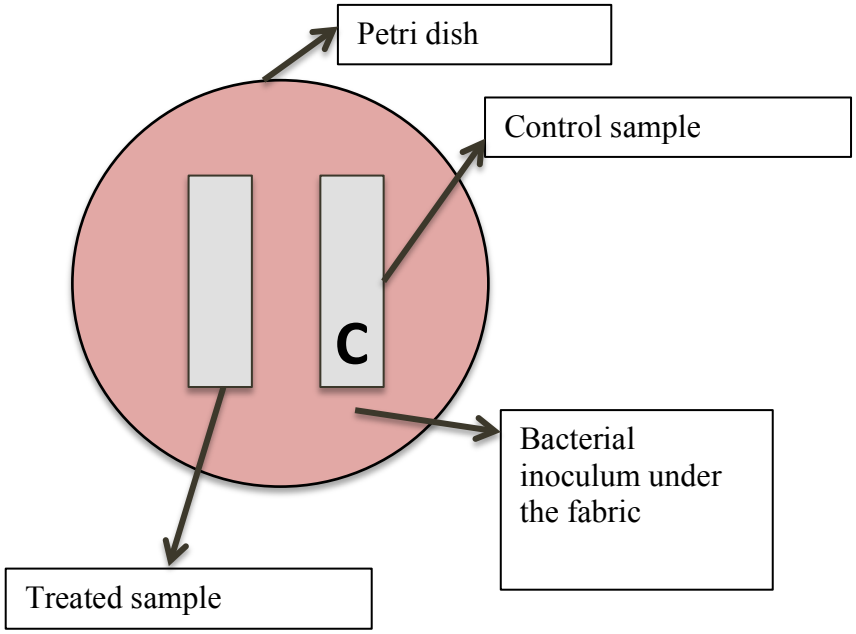

Figure 32. ASTM E1428-99 Test Method

Table 2. Stain Rating for Treated Samples

Monomer	Rating
Monomer A	0
Monomer B	0
Monomer C	0
Monomer 1	1

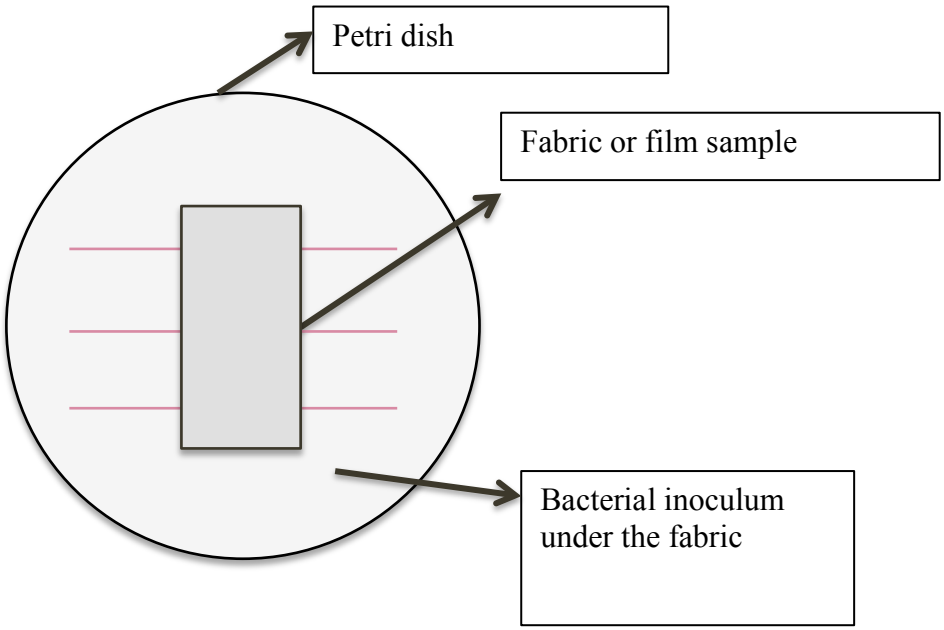

Figure 33. AATCC 147 Test Method

4.4.4 Quantitative Antimicrobial Testing

AATCC's quantitative test method for evaluating the antimicrobial properties of textiles is AATCC 100, "Assessment of Antibacterial Finishes on Textile Materials." For this standard, samples are inoculated with 1 mL of the selected inoculum and allowed a contact time of 24 hours. *S. aureus* 6538 and *K. pneumoniae* 4352 were the test organisms used. After the allotted contact time, the samples are placed in the neutralizing solution to remove the bacteria present on the swatches. The bacteria present in the liquid are counted and a Percent Reduction is calculated. The equation to calculate the Percent Reduction is:

Equation 1. Percent Reduction

$$\text{Percent Reduction} = \left(\frac{B-A}{B}\right) \times 100$$

Where:

- R= % reduction
- A= the number of bacteria recovered from the inoculated treated test specimen swatches after the contact period
- B= the number of bacteria recovered from the inoculated treated test specimen swatches immediately after inoculation (contact time=0)

A Log_{10} Reduction is also calculated using the equation:

Equation 2. Log_{10} Reduction

$$\text{Log}_{10}\text{Reduction} = \text{Log}\left(\frac{B}{A}\right)$$

Where:

- A= the number of bacteria recovered from the inoculated treated test specimen swatches after the contact period
- B= the number of bacteria recovered from the inoculated treated test specimen swatches immediately after inoculation (contact time=0)

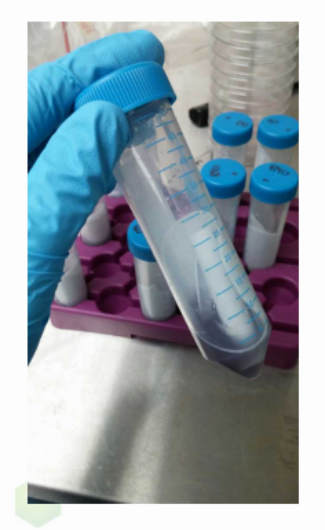

Figure 34. Quantitative Testing Sample Inoculation

After the contact time (Figure 34), carriers were harvested into a neutralization bath. The AATCC 100 test method does not specify a result that classifies a sample as "passing". It is decided by the testing party. However other similar test methods such as ISO 20743 suggest a 99% reduction (2-Log_{10}) while the Environmental Protection Agency (EPA) suggests a 99.9% reduction (3- Log_{10}).

This portion of the antimicrobial testing was completed at the Antimicrobial Test Laboratories. The contact information for this laboratory is as follows:

http://www.AntimicrobialTestLabs.com

Diego Ugarte, Team Lead for Antimicrobial Surfaces & Textiles

1304 W. Industrial Blvd.

Round Rock, Texas 78681

Phone: 512-310-TEST

Email: Diego@antimicrobialtestlabs.com

4.4.5 Scouring of Fabric

To ensure that any processing chemicals that may remain on the fabric were not affecting the initial bacterial results, the fabric was scoured before treatment and the samples were tested again.

4.4.6 Rinsed Fabric

In some of the initial bacterial testing, areas of inhibition were observed in the agar surrounding the treated samples. To remove any uncured monomer remaining on the fabric the samples were rinsed. For the rinsing process, the samples were immersed in deionized water for 5 seconds and a mechanical action was applied. This step was repeated 3 times with new water for each sample.

4.4.7 Durability Testing

To determine the durability of the treated samples, each sample was washed 1, 5, 10, 15 and 20 times and bacteria testing was repeated. The laundering process followed the AATCC laundering method. To wash the fabrics, a GE home washing machine was used along with a GE home dryer. Tide detergent, original scent was used for each wash cycle. The washing machine was on normal settings with hot water and the dryer was set on the high heat, more dry setting. After each laundering set, the samples were run through the wash cycle again before drying to remove any leftover detergent from the sample as it could have an effect on the results of the bacterial testing.

4.4.8 Wetting Time

Wetting tests were used to determine the hydrophobicity of each of the treated fabrics when compared to the control untreated fabric. The wetting time is the amount of time it takes for a drop of deionized water to soak into the fabric. The test was repeated 5 times for each sample and the results were averaged.

4.4.9 Vertical Wicking

The AATCC 197 Standard Test Method for the Vertical Wicking of Textiles was used to evaluate the ability of the samples to transport liquid along their length. The distance the water wicked up the length of the fabric was measured at 2 and 10-minute intervals and was recorded in millimeters.

5. RESULTS AND DISCUSSION

5.1 Scoured Fabric

The first samples were created with fabric used "as received". However, it was not clear whether any processing chemicals would have an effect on the final results, so the fabric was scoured and the treatments were applied again. The results of this testing show that the bacterial results were improved slightly when the fabric was scoured before application of the chemical treatment. For the monomer A copolymers, all of the samples showed good results for biofilm resistance, though there is minimal attachment to the 50% sample that was not scoured. For the monomer B copolymers, there was moderate coverage on the 50% sample that was not scoured and no bacteria attachment on the scoured samples. The monomer C copolymer samples had slight attachment to the 50% sample that was not

scoured, and no attachment to the scoured samples, and the leaching of the monomer from the sample was reduced with the scoured fabric.

5.2 Rinsed Fabric

In the previous trial, Monomers A and C leached off of the fabric and into the agar. This is shown by the hindered bacteria growth in the monomer A and C agars. To improve this result, the samples were tested again after being rinsed to remove the remaining uncured monomer.

When monomers A and C were compared with and without rinsing there was an apparent decrease in the amount of monomer leaching off of the sample after rinsing. This is shown in Figure 35 and Figure 36 by the increase in bacteria growth on the agar plates containing the rinsed samples when compared to the agar plates containing the unrinsed samples.

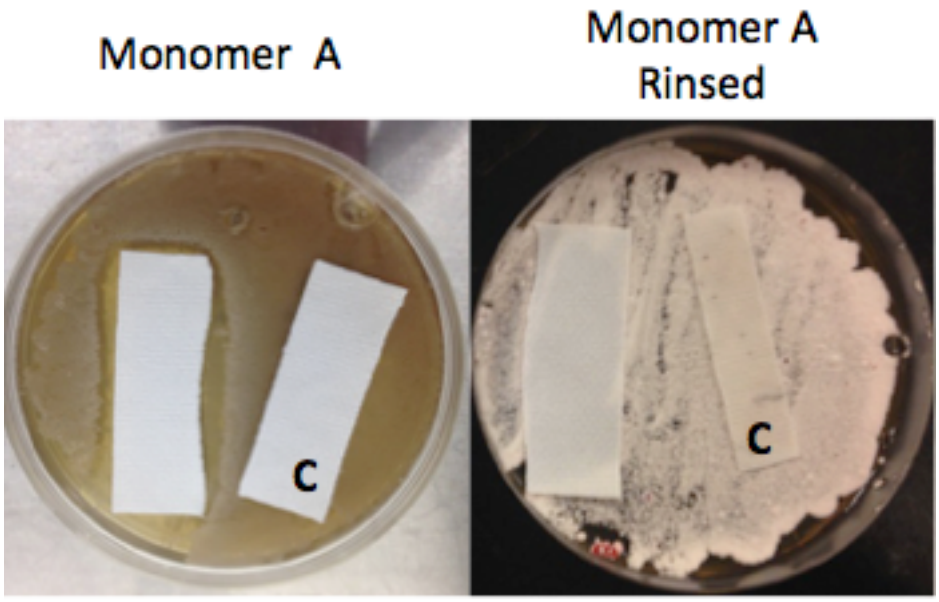

Figure 35. Monomer A Rinsed vs. Monomer A Unrinsed, C=Control

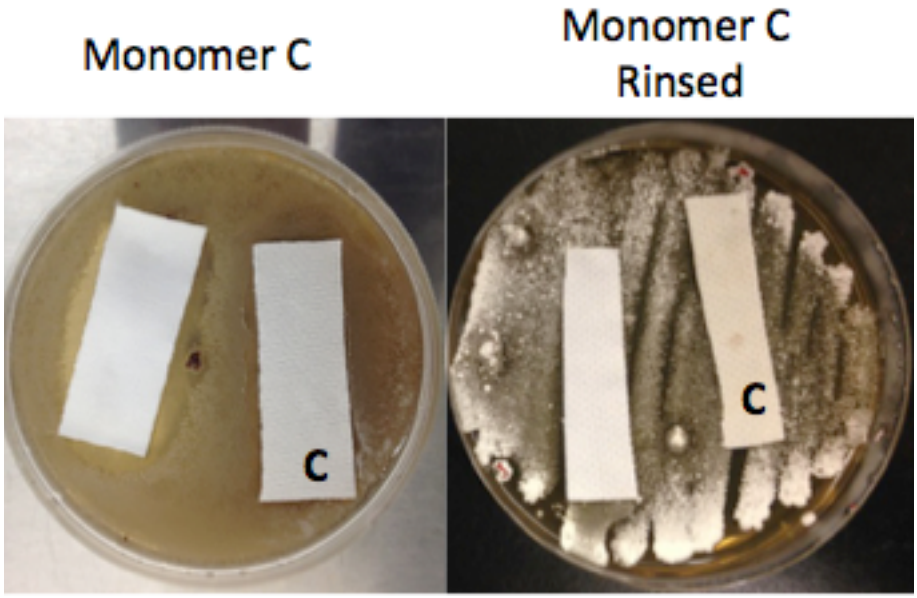

Figure 36. Monomer C Unrinsed vs. Monomer C Rinsed, C=Control

5.3 Copolymers

Copolymers of the chosen monofunctional monomers and the bifunctional monomer were created, as discussed in Section 4.3.4. Because monomer 1 is bifunctional, it improved the adhesion of each polymer to the fabric sample. This is shown in Figure 37 and Figure 38. As the percentage of monomer 1 is increased, the amount of leaching decreases. As the amount of leaching decreased, more bacteria was allowed to grow in the agar and therefore more bacteria was found on the control. The leaching of monomers A and C is greater than that of monomer B, because monomer B acts as a bifunctional monomer. The leaching of monomer C is greater than that of monomer A from the substrate. The addition of monomer 1 also improved the leaching and this can most likely be attributed to the bulky side group present on monomer.

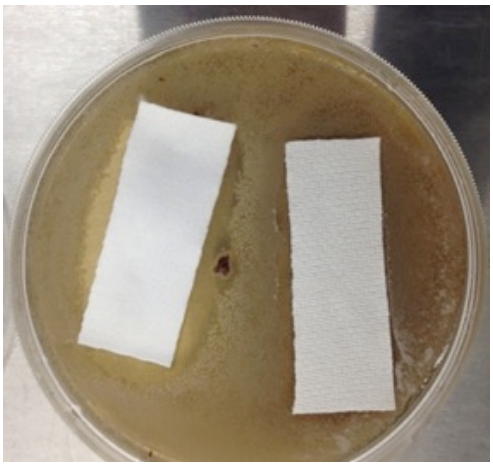

Figure 37. 100% Monomer C

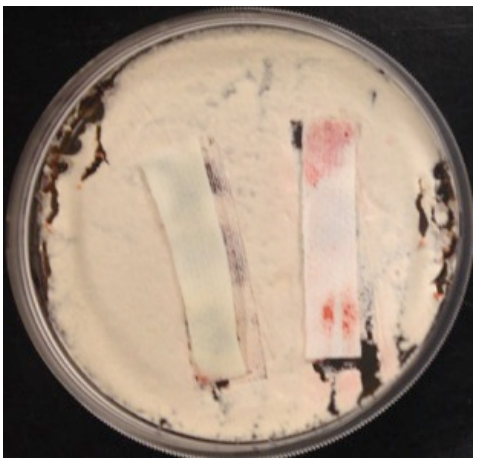

Figure 38. 10% Monomer C/90% Monomer 1 Copolymer

5.4 Reduced Percent Solid Add-on

The percent solid add-on was reduced by adding acetone to each of the monomer solutions at 10, 30, 50, 70 and 90 wt%. The resulting percent solid add-on is shown in Table 3.

Table 3. Reduced Percent Solid Add-on

% Acetone	Monomer A	Monomer B	Monomer C	Monomer 1
10	**9.34**	**106.25**	**99.51**	**167.67**
30	**9.98**	**90.68**	**84.69**	**126.37**
50	**7.85**	**65.81**	**52.13**	**71.01**
70	**4.79**	**39.13**	**28.12**	**41.61**
90	**0.63**	**13.35**	**14.78**	**12.93**

5.5 FTIR Analysis

In order to determine the necessary curing parameters FTIR analysis was used for the monomer cured on the polyester film as well as the monomer cured on the polyester fabric. The FTIR spectra were evaluated at the 810 cm^{-1} peak for the acrylate C=C-H out of plane bend and 1640 cm^{-1} peak for the C=C-H bending (Appendix A). A range of percent photoinitiator was evaluated to determine the optimal amount (Appendix B). A summary of the FTIR results when cured on the film are shown in Table 4. No amount of curing time or photoinitiator led to a peak reduction for monomer 2, possibly due to the inhibitor in the chemistry. Therefore, it was not used in the remainder of the trials.

The carbon-carbon double bond percent remaining of each monomer when applied with 5% photoinitiator on polyester fabric is shown in Table 5. Monomer B and Monomer 1 were the most reactive and show the most reduction in carbon-carbon double bonds.

Table 4. FTIR C=C Peak Reduction Results

	Monomer A	Monomer B	Monomer C	Monomer 1	Monomer 2
1% PI, 300s	C=C peak significantly reduced	No significant C=C peak reduction	C=C peak slightly reduced	150s: No significant C=C peak reduction	No significant C=C peak reduction
3% PI, 300s	Similar C=C peak as 1% PI	C=C peak significantly reduced	C=C peak significantly reduced	150s: C=C peak significant reduced	No significant C=C peak reduction
5% PI, 300s	Further reduced C=C peak	Similar C=C peak as 3% PI	Further reduced C=C peak	150s: Increased C=C peak compared with 3% PI	No significant C=C peak reduction

Table 5. Percent Carbon-Carbon Double Bond Percent Remaining at 5% Photoinitiator

Monomer	810 cm^{-1}	1640 cm^{-1}
A	2.44	9.17
B	0.99	2.15
C	5.53	13.98
1	0.94	3.31
2	No discernable peak change	No discernable peak change

5.6 Copolymer Durability Testing

The durability of the copolymer samples was assessed up to 20 washes using the ASTM E1428-99 test method. The Monomer A and Monomer B copolymer samples (Table 6 and Table 7, respectively) showed no bacteria attachment up to 20 washes. The Monomer C copolymer samples had no bacteria attachment up to 15 washes, shown in Table 8. The samples with 0% and 10% Monomer 1 had slight attachment after 20 washes showing the addition of bifunctional Monomer 1 improved the durability of the finish.

Table 6. Attachment Rating of Monomer A Copolymer

	0% Monomer 1	10% Monomer 1	50% Monomer 1	90% Monomer 1
1 wash	**0**	**0**	**0**	**0**
10 washes	**0**	**0**	**0**	**0**
20 washes	**0**	**0**	**0**	**0**

Table 7. Attachment Rating of Monomer B Copolymer

	0% Monomer 1	10% Monomer 1	50% Monomer 1	90% Monomer 1
1 wash	**0**	**0**	**0**	**0**
10 washes	**0**	**0**	**0**	**0**
20 washes	**0**	**0**	**0**	**0**

Table 8. Attachment Rating of Monomer C Copolymer

	0% Monomer 1	10% Monomer 1	50% Monomer 1	90% Monomer 1
1 wash	**0**	**0**	**0**	**0**
10 washes	**0**	**0**	**0**	**0**
20 washes	**2**	**1**	**0**	**0**

5.7 Reduced Add-on Durability Testing

The durability testing was repeated for the samples created with reduce percent solid add-on. The results of these tests are shown below. The durability results for Monomer A are shown in Table 9. The durability results for Monomer B are shown in Table 10. The Monomer C durability results are shown in Table 11 and the Monomer 1 durability results are shown in Table 12. Monomer B maintained the best stain rating, and therefore had the best washfastness.

Table 9. Bacteria Attachment Rating of Monomer A

	10% Acetone	30% Acetone	50% Acetone	70% Acetone	90% Acetone
1 wash	**0**	**0**	**0**	**2**	**2**
10 washes	**0**	**0**	**1**	**3**	**3**
20 washes	**0**	**1**	**2**	**4**	**4**

Table 10. Bacteria Attachment Rating of Monomer B

	10% Acetone	30% Acetone	50% Acetone	70% Acetone	90% Acetone
1 wash	**0**	**0**	**0**	**0**	**0**
10 washes	**0**	**0**	**0**	**0**	**1**
20 washes	**0**	**1**	**2**	**2**	**3**

Table 11. Bacteria Attachment Rating of Monomer C

	10% Acetone	30% Acetone	50% Acetone	70% Acetone	90% Acetone
1 wash	**0**	**0**	**0**	**2**	**2**
10 washes	**0**	**0**	**1**	**1**	**3**
20 washes	**1**	**1**	**2**	**3**	**4**

Table 12. Bacteria Attachment Rating of Monomer 1

	10% Acetone	30% Acetone	50% Acetone	70% Acetone	90% Acetone
1 wash	**0**	**0**	**1**	**1**	**1**
10 washes	**0**	**1**	**2**	**3**	**4**
20 washes	**1**	**1**	**3**	**4**	**4**

5.8 Wetting Time

The results of the wetting time test are shown in Table 13. The drop soaked into the untreated sample immediately. As the amount of monomer present on the sample was reduced the wetting time decreased. This shows that the chemistry applied to the fabric is hydrophobic.

Table 13. Treated Fabric Wetting Time

Monomer A	
% Acetone	Wetting Time
0	>10 min
10	>10 min
30	3:34
50	2:42
70	1:10
90	0:01

Monomer B	
% Acetone	Wetting Time
0	>10 min
10	0:26
30	0:23
50	0:16
70	0:03
90	0:02

Monomer C	
% Acetone	Wetting Time
0	3:31
10	0:23
30	2:43
50	3:12
70	2:50
90	0:03

Monomer 1	
% Acetone	Wetting Time
0	>10 min
10	4:52
30	2:23
50	1:56
70	0:36
90	0:17

5.9 Vertical Wicking (AATCC 197)

The Vertical Wicking Test results are shown in Table 14. The untreated fabric reached 112mm at 2min and reached the entire length of the fabric by 10min (150mm). As the amount of acetone increased, the wicking rate also increased. This is consistent with the wetting time results. Monomer A was the most hydrophobic, while monomer B was the least hydrophobic. All samples remained more hydrophobic than the untreated sample regardless of percent add-on.

Table 14. Vertical Wicking Results

% Acetone	0	10	30	50	70	90
Monomer A						
2 min	0mm	0mm	0mm	0mm	0mm	72mm
10 min	0mm	0mm	0mm	5mm	17mm	98mm
Monomer B						
2 min	0mm	7mm	22mm	32mm	38mm	47mm
10 min	0mm	12mm	32mm	53mm	77mm	89mm
Monomer C						
2 min	0mm	0mm	0mm	2mm	22mm	27mm
10 min	0mm	12mm	21mm	23mm	47mm	83mm
Monomer 1						
2 min	0mm	0mm	0mm	2mm	12mm	29mm
10 min	0mm	0mm	0mm	12mm	28mm	42mm

5.10 Quantitative Testing

Samples were chosen based on the qualitative testing performance results and durability. Ethylene glycol dicyclopentenyl ether acrylate (Monomer B) was rated the best and was therefore the only monomer chosen for quantitative testing. The samples tested are as follows: Monomer B, Monomer B after 20 washes, Monomer B applied with 90% acetone for reduced percent add-on (B90), Monomer B90 after 10 washes. The test bacteria used was *Staphylococcus aureus* (gram positive) and *Klebsiella pneumoniae* (gram negative). Circular

swatches 4.8 cm in diameter were created and saturated with 1.0 mL of inoculum. A total of three swatches were needed per sample to absorb the entirety of the 1.0 mL of inoculum. The inoculum concentration was 2.0 x 10^5 CFU/Carrier at an incubation temperature and contact temperature of 36^{o}C +/- 1 ^{o}C. After a 24-hour contact period serial dilutions were created and used to inoculate a sterile agar. The results are reported as the percent reduction and shown in Table 15 and Table 16. CFU= colony forming unit and the limit of detection for this assay is 5.00E+00 CFU/Carrier. Samples with no microbial recovery at the contact time are reported as <5.00E+00 CFU/Carrier. Figure 39 and Figure 40 visually present the results for the samples when tested with *Staphylococcus aureus* and *Klebsiella pneumoniae,* respectively. Minor sample contamination was observed. Morphology was distinguishable from target morphology and was not factored into results/reductions.

Table 15. AATCC 100 *Staphylococcus aureus* Test Results

Test Microorganism	Contact Time	Carrier Type	CFU/Carrier	Percent Reduction Compared to Control at Time Zero	Log10 Reduction Compared to Control at Time Zero
S. aureus 6538	Time Zero	ATL Control	6.90E+05	N/A	
	24 Hours	Control	1.55E+06		
		B	<5.00E+00	>99.9993%	>5.14
		B (20 Washes)	<5.00E+00	>99.9993%	>5.14
		B90	2.00E+01	99.997%	4.54
		B90 (10 Washes)	1.50E+01	99.998%	4.66

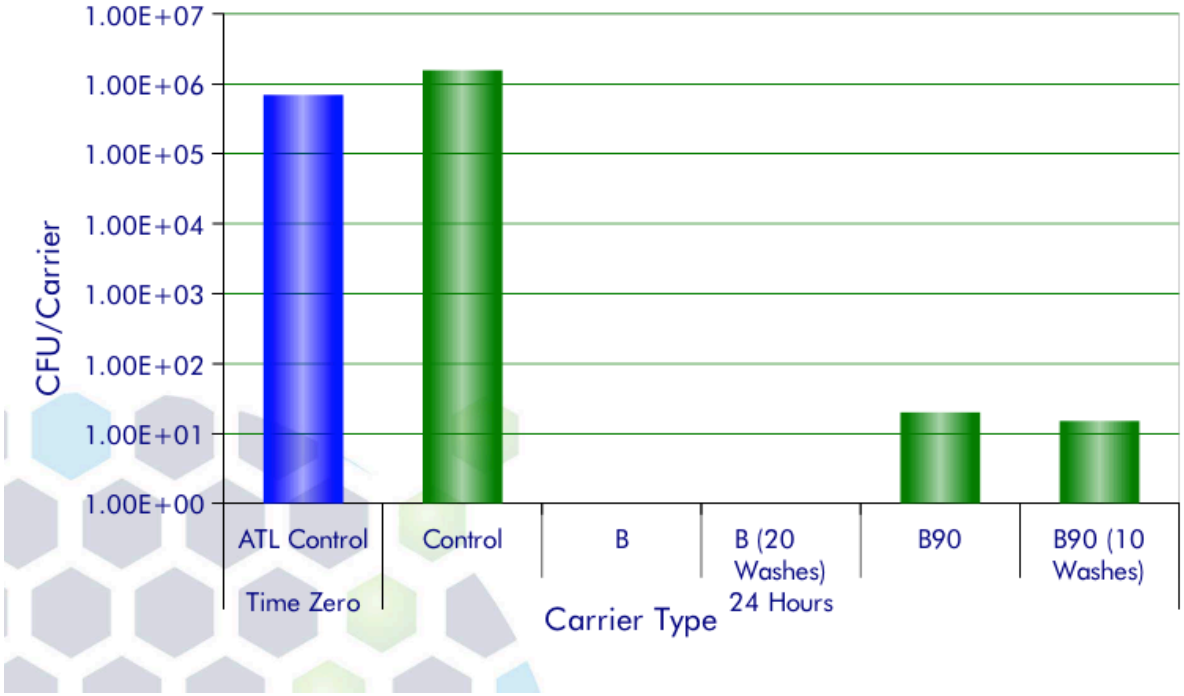

Figure 39. AATCC 100 *Staphylococcus aureus* Test Results

Table 16. AATCC 100 *Klebsiella pneumoniae* Test Results

Test Microorganism	Contact Time	Carrier Type	CFU/Carrier	Percent Reduction Compared to Control at Time Zero	Log10 Reduction Compared to Control at Time Zero
K. pneumoniae 4352	Time Zero	ATL Control	2.00E+05	N/A	
	24 Hours	Control	1.66E+07		
		B	<5.00E+00	>99.998%	>4.60
		B (20 Washes)	7.50E+02	99.63%	2.43
		B90	<5.00E+00	>99.998%	>4.60
		B90 (10 Washes)	<5.00E+00	>99.998%	>4.60

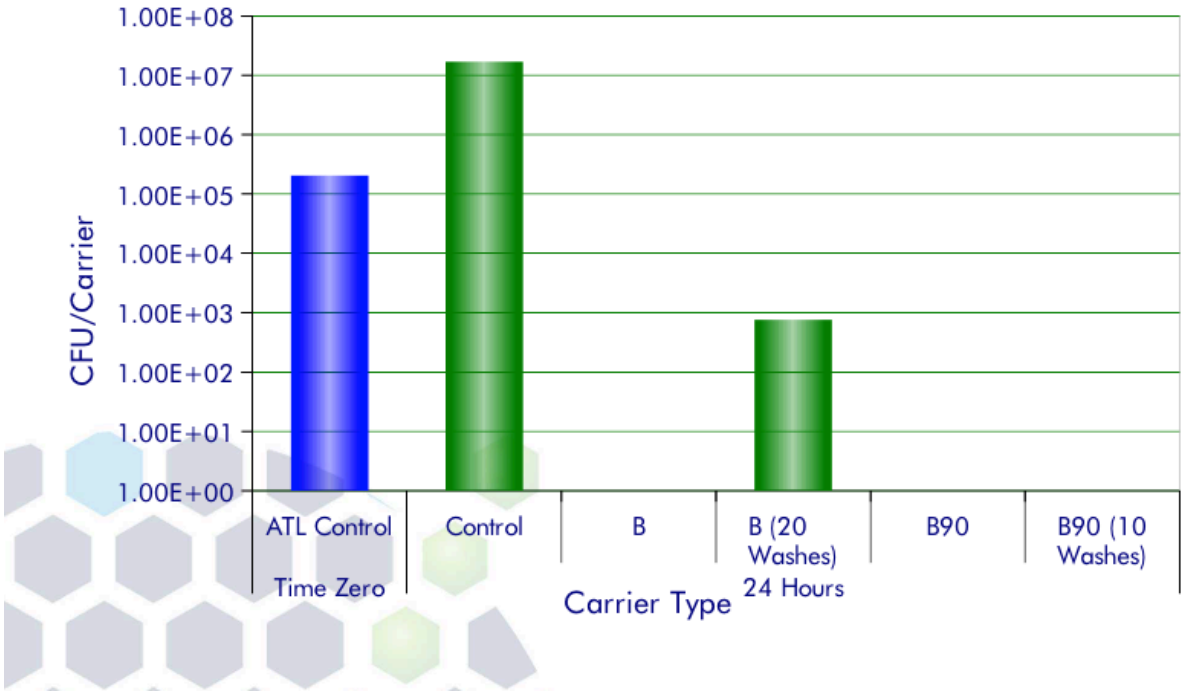

Figure 40. AATCC 100 *Klebsiella pneumoniae* Test Results

When tested against *S. aureus* samples "B" and "B after 20 washes" show no microbial recovery at the contact time while samples "B90" and "B90 after 10 washes" show only slight microbial recovery at the contact time. When tested against *K. pneumoniae* samples "B", "B90", and "B90 at 10 washes" show no microbial recovery at the contact time and "B after 20 washes" shows only slight microbial recovery at the contact time. All samples tested showed excellent biofilm resistance. The quantitative results shown here confirm the previous qualitative results.

6. CONCLUSIONS

The purpose of this research was to polymerize a biofilm resistant finish using ultraviolet radiation. It was shown that the monomers chosen could be polymerized using UV-light. It was also established that the resulting polymers showed resistance to the growth of bacteria when compared to the untreated fabric.

6.1 Ultraviolet Curing

The selected acrylate monomers could be successfully cured on polyester fabric. This was show through FTIR analysis and the reduced C=C peak. The durability was also shown as the efficacy remained even after 20 wash cycles.

6.2 Biofilm Resistance

The bacteria-material interaction is dependent on surface chemistry. Bacterial attachment is lower in monomers with cyclic carbon environments, tertiary butyl groups, and dimethyl hydrocarbon segments. The bifunctional monomers improved the adhesion of each polymer to the fabric and decreased the leaching of the finish from the sample. The ultraviolet curable process chemistry developed using ethylene glycol dicyclopentenyl ether acrylate provides a durable biofilm resistant finish on polyester fabric.

7. FUTURE WORK

There are many opportunities for future work in this area. The finishes applied in this research show great promise for providing a durable finish on textile fabrics used to impart biofilm resistance. Further work should be done to improve and further optimize the

processing steps. The finishes shown in this research can also be tested when applied to other fabric types to compare the efficacy and durability. The light source used should be studied along with the options of different photoinitiators to evaluate whether the curing time and/or the percent photoinitator can be reduced. A larger array of copolymers to further evaluate the washfastness as compared to the antimicrobial efficacy would also be valuable. Pilot scale up testing should also be done in a continuous online treatment.

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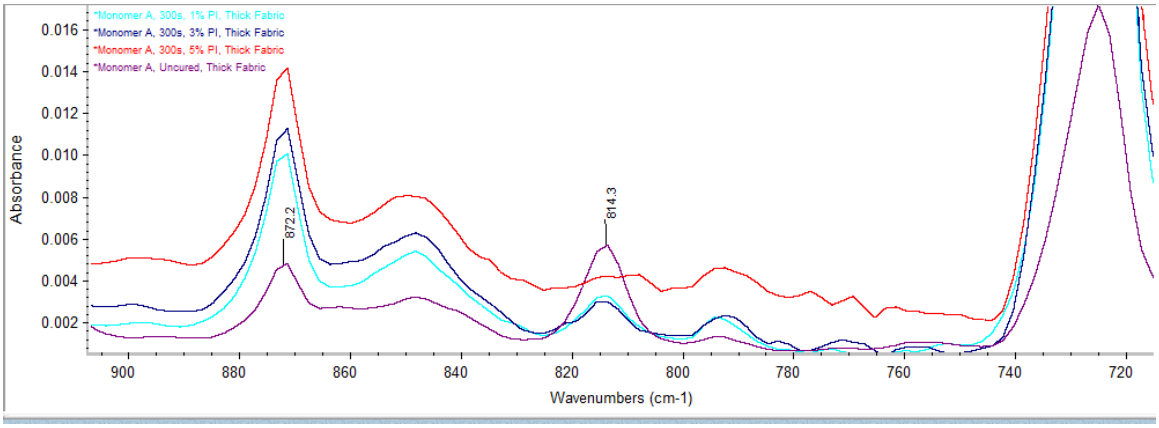
APPENDICES

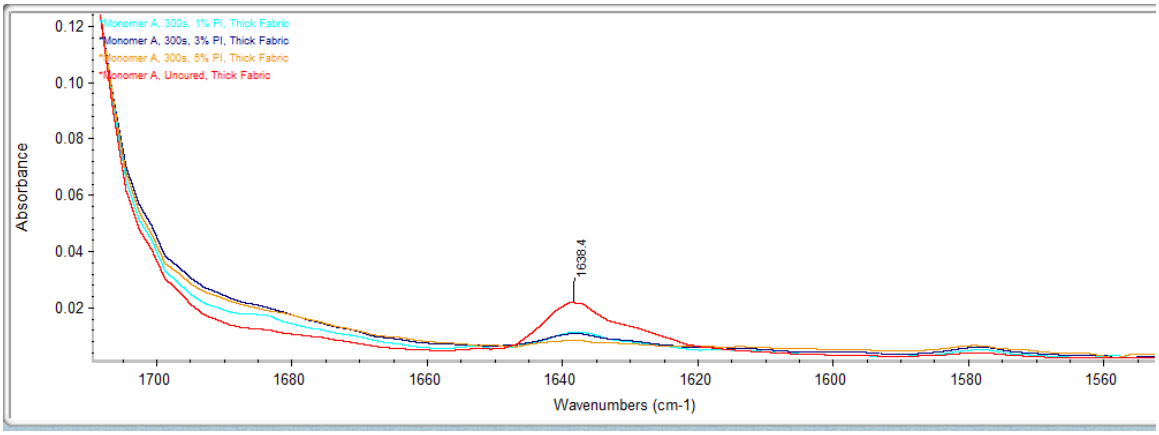
Appendix A

Monomer A FTIR

810 cm^{-1}

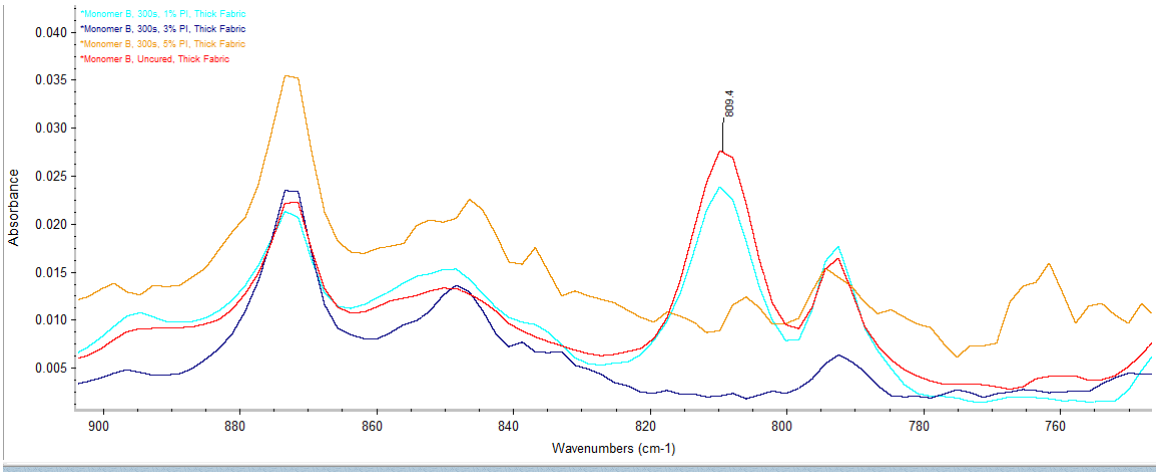


1640 cm^{-1}

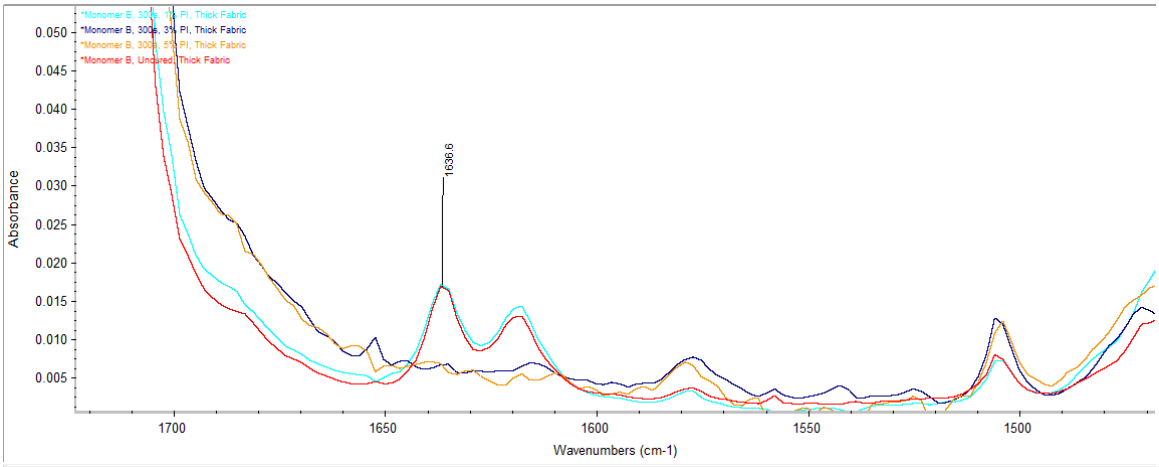


Monomer B FTIR

810 cm^{-1}

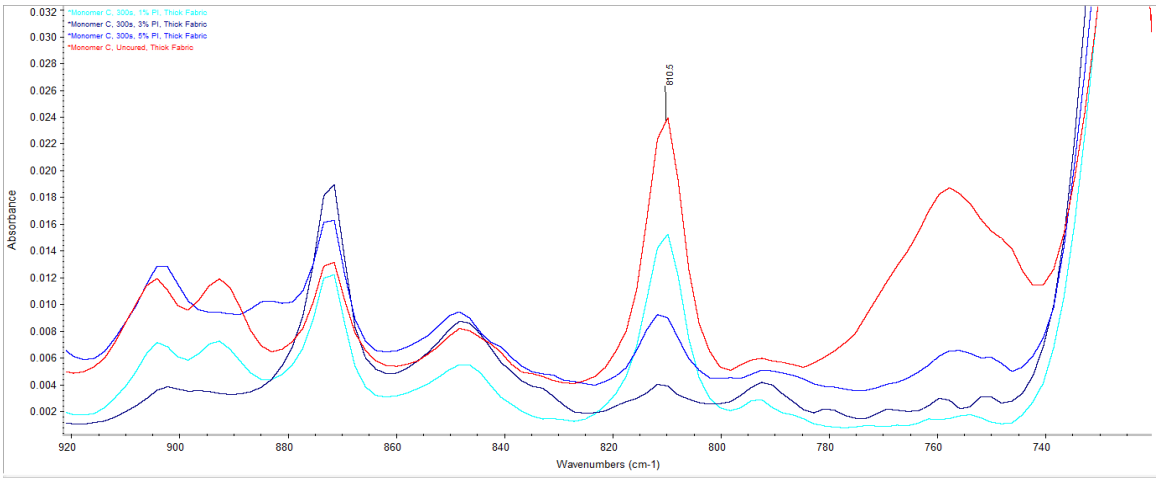


1640 cm^{-1}

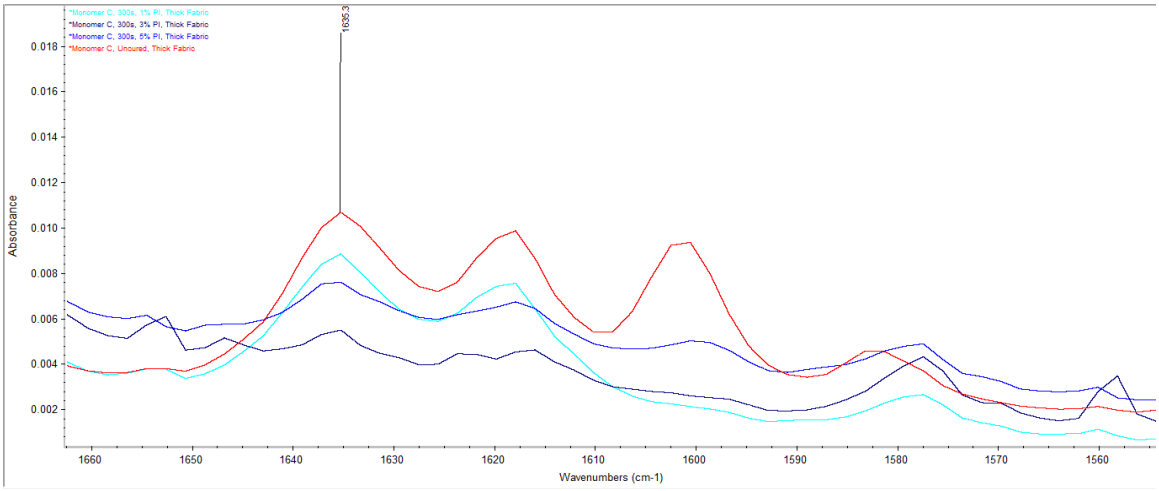


Monomer C FTIR

810 cm^{-1}

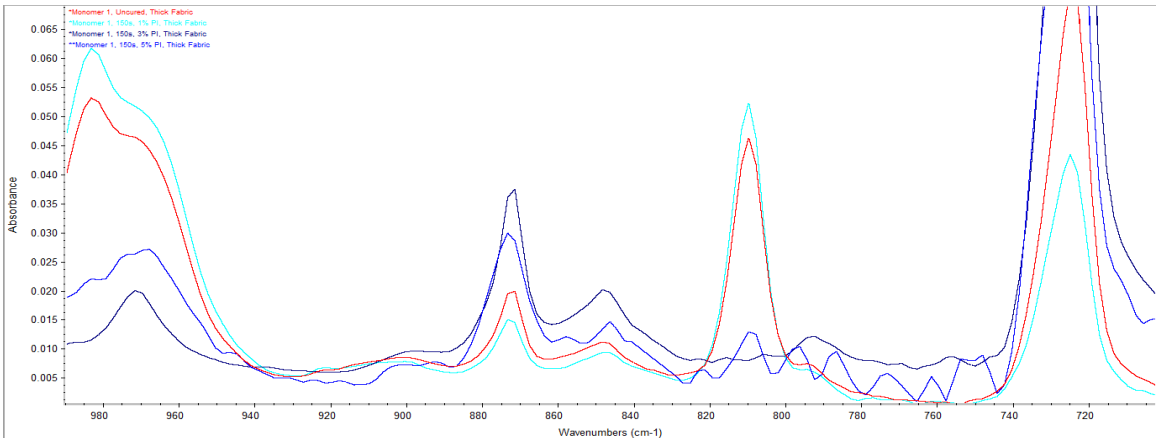


1640 cm^{-1}

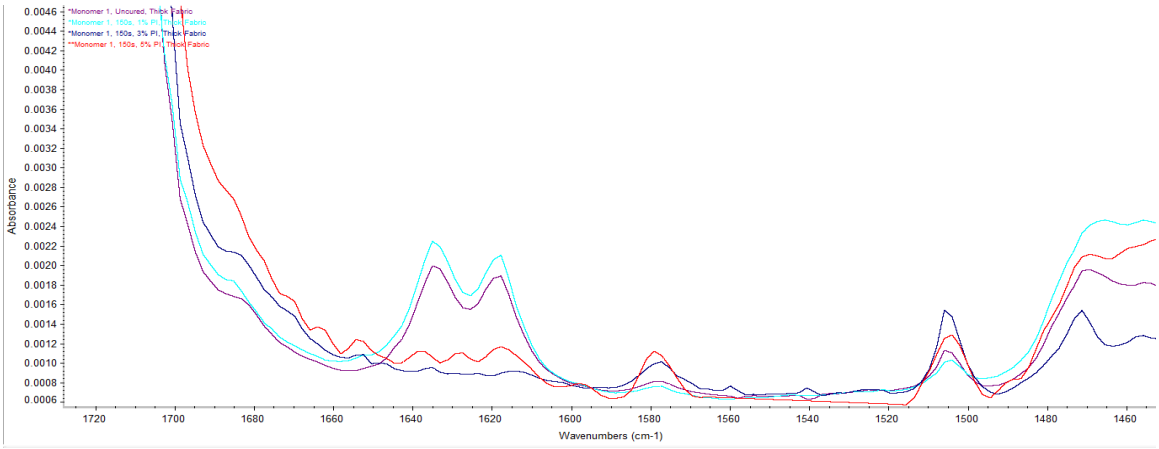


Monomer 1 FTIR

810 cm^{-1}

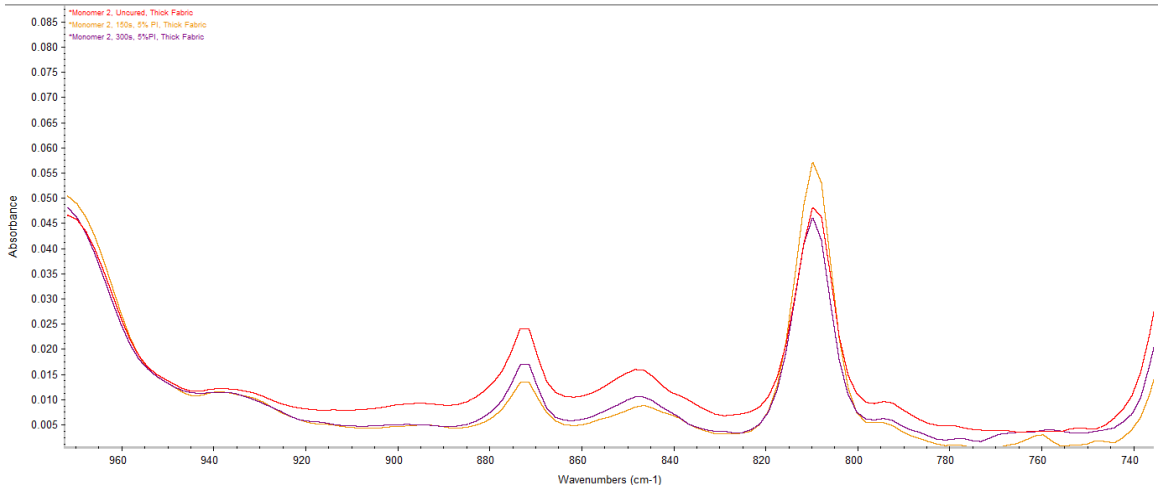


1640 cm^{-1}

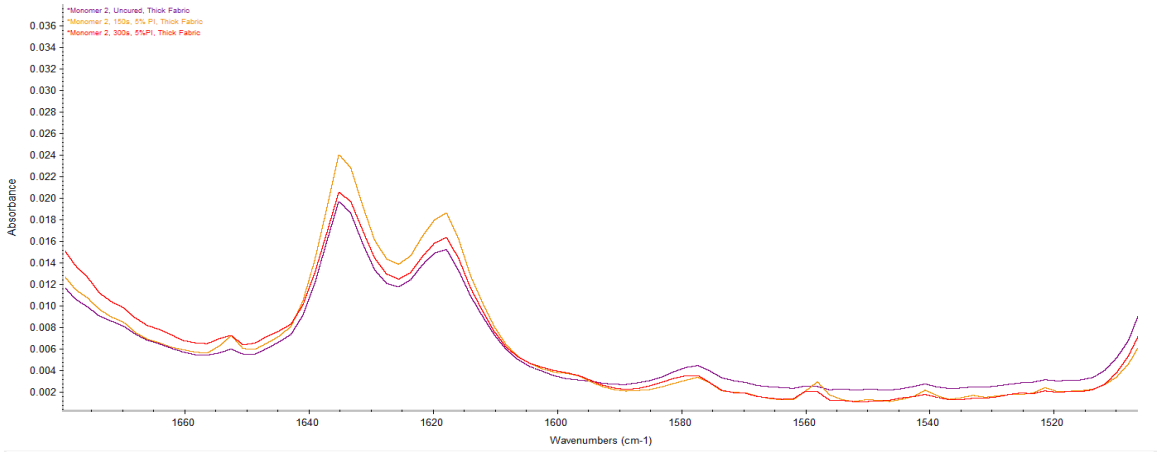


Monomer 2 FTIR

810 cm^{-1}



1640 cm^{-1}



Appendix B

Monomer A FTIR

810 cm^{-1}

C=C left @ 1% PI	18.76
C=C left @ 3% PI	11.21
C=C left @ 5% PI	2.44

1640 cm^{-1}

C=C left @ 1% PI	25.94
C=C left @ 3% PI	23.72
C=C left @ 5% PI	9.17

Monomer B FTIR

810 cm^{-1}

C=C left @ 1% PI	77.38
C=C left @ 3% PI	1.40
C=C left @ 5% PI	0.99

1640 cm^{-1}

C=C left @ 1% PI	124.08
C=C left @ 3% PI	2.65
C=C left @ 5% PI	2.15

Monomer C FTIR

810 cm^{-1}

C=C left @ 1% PI	63.10
C=C left @ 3% PI	20.98
C=C left @ 5% PI	5.53

1640 cm^{-1}

C=C left @ 1% PI	81.05
C=C left @ 3% PI	21.28
C=C left @ 5% PI	13.98

Monomer 1 FTIR

810 cm^{-1}

C=C left @ 1% PI	73.92
C=C left @ 3% PI	0.37
C=C left @ 5% PI	0.94

1640 cm^{-1}

C=C left @ 1% PI	76.93
C=C left @ 3% PI	0.59
C=C left @ 5% PI	3.31

Monomer 2 FTIR

810 cm^{-1}

No discernable peak area increase.

1640 cm^{-1}

No discernable peak area increase.