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A study of antimicrobial properties of fabric treated with silane and N-halamine complex

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A STUDY OF ANTIMICROBIAL PROPERTIES OF FABRIC TREATED WITH SILANE
AND N-HALAMINE COMPLEX

by

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DEDICATION

With God's blessing, I would like to pay gratitude to my mother, Mrs. Urmil Yadav, for her unconditional love and faith in my strengths. She is my role model who inspires me to pursue my dreams and fly high on the wings of my ambition.

ACKNOWLEDGEMENTS

ABSTRACT

The Dimethyl hydantoin (DMH) – Isocyanatopropyltriethoxysilane adduct was prepared and applied onto the fabric using pad – dry – pad – dry – cure method. The treated fabric is then chlorinated using NaOCl (6% and 10%) to impart the antimicrobial properties. The treated fabric surface and the chlorine percentage present at the surface of the fabric are evaluated using SEM- EDX and peak of NCO was determined using FTIR analysis. The fabrics were tested for antimicrobial properties using ATCC 2695 gram positive bacteria *Staphylococcus aureus* and ATCC 8739 gram negative bacteria *Escherichia coli.* The treated samples provided very good antimicrobial properties even after three vigorous soap washings. The fabric durability properties such as tensile strength, abrasion resistance, and stiffness and comfort properties such as thermal resistance and evaporative resistance were also measured.

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CHAPTER 1: INTRODUCTION

Textile products particularly made from natural fibers have a serious problem of microorganism growth because of their surface area and ability to retain moisture (Aly et al., 2007). The use of antimicrobial agents for textiles has also become indispensible to avoid cross-infection by pathogenic microorganisms, to control the infestation by microbes, and arrest metabolism in microbes in order to reduce odor formation. Antimicrobial treated fabric protects garments from staining, discoloration, and quality deterioration (Vigo, 1994).

The increasing demand for comfortable, aesthetic, durable, functional, and safe textile products dictates the development of new and contemporary techniques of processing and designing textiles (Tomsic et al., 2008; Heywood, 2003). Therefore, it is becoming important day by day to include the superior functionality in daily wear which is durable and demanding. As far as antimicrobial property is concerned, numerous antimicrobial agents are known and have already been tested in combination with many hydrocarbon and fluorochemical (Lee et al., 1999), and sol-gel based finishes (Mahltig et al., 2003; Mahltig et al., 2004; Mahltig et al., 2005) have also been investigated by researchers and proved to have variable success. The present study is based on improving the antimicrobial property of the textiles using a unique combination of *N*-halamine and isocyanatopropyltriethoxysilane (CPTES). The isocyanate group of silane reacts with one NH site of Dimethyl hydantoin (DMH) and other NH site of DMH compound forms bond with Chlorine (from NaOCl treatment) to provide the active N-Cl group which acts a powerful antimicrobial agent. This provides rechargeable and durable antimicrobial properties to the fabric, which is not known to have any health hazards.

Problem Statement

Antimicrobial treatment is widely popular among areas of medical, household, and hygiene products to prevent biocontamination. A lot of research has been conducted to explore the areas of antimicrobial property of the product.

A comparison of effectiveness of the various antimicrobial agents reveals that the antimicrobial agent that can be cross-linked to the textile substrate will be desirable with regard to antimicrobial efficacy, washing durability, and long term behavior.

For practical applications, a high biocidal effect and also a long-term stability of the coatings against leaching are required.

Research Question

What is the antimicrobial efficacy of the silane and N – halamines based antimicrobial agent on the textile? What are the effects of the antimicrobial treatment on the textile properties?

Purpose of Study

The goal of this study is to develop a process for rendering antimicrobial treatment to the textile materials, which involves the crosslinking between the compound and the textile substrate. Also, the study aims to determine the effect of the crosslinking of antimicrobial agent to the textile substrate on the antimicrobial efficacy, washing durability, and comfort properties. The antimicrobial treatment involves three steps. The first step is to form isocyanatopropyl-trithoxysilane (CPTES) and Dimethyl Hydantoin (DMH) adduct in presence of triethylamine. The second step is to apply on 50/50 nylon/cotton fabric using

modified pad – dry – cure method. The final step is the chlorination of the treated substrate resulting in antimicrobial property.

Specific Objective

1. Develop synthetic procedure for the reaction between the isocyanatopropyltriethoxy silane and Dimethyl hydantoin in presence of triethylamine.

2. Apply antimicrobial agent on the 50/50 nylon/cotton blend fabric using pad – dry – cure method.

3. Determine the antimicrobial efficacy, washing durability of the treated fabrics, and its effect on chlorine content.

4. Determine the effect of antimicrobial coating on the textile properties such as thermal and moisture resistance, stiffness, tensile resistance, and abrasion resistance property.

CHAPTER 2: REVIEW OF LITERATURE

Introduction to Sol-Gel Chemistry

Sol-gel chemistry has been a demanding and interesting area of research that opened wide possibilities for the material scientist and chemists. The synthesis of materials whose properties can be controlled and altered at the atomic level is a challenging task. Thus, organosilicon chemistry has a great future because of its property to form ideal links between molecular and solid-state chemistry. It has been found that silicon – carbon bonds are stable, silicon containing moieties can be included in number of sites in organic molecules and can start the formation of varied polymers. It can further lead to the formation of solid materials such as silicides, oxides, and thermomechanical ceramics (Corriu et al., 1996). While Sol-Gel technology became a source of attraction as early as mid 1980s with Ebelman and Graham's studies on silica gels (Hench et al., 1990); its potentials were explored recently in order to use the organo-silicon compounds as potential metal organic precursors.

There are numerous areas where sol-gel chemistry can provide unique capabilities and novel materials such as chemicals, optical materials, antireflection coatings, smart materials, biosensors (Kunzelmann et al., 1997), easy-to-clean coatings, corrosion resistant coatings and so on (Uhlmann and Teowee, 1998). Figure 2.1 shows diverse areas of application of Sol – Gel processes (Reuter, 1991).
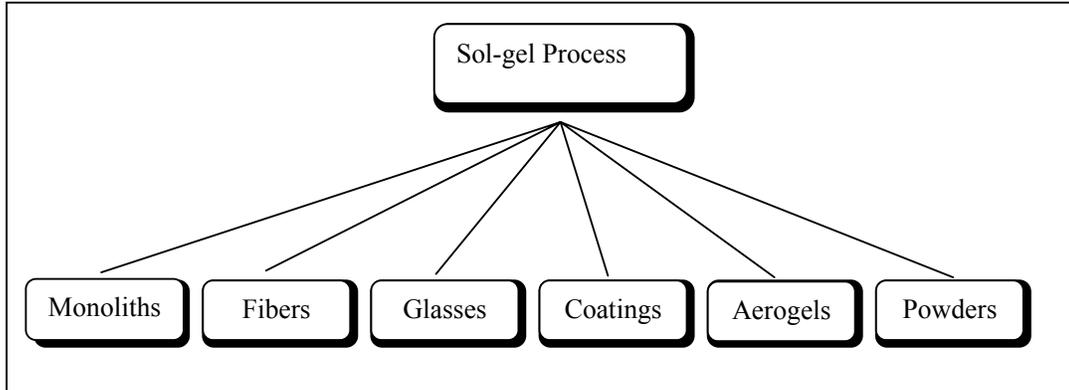
Figure 2.1. Areas of application of Sol-Gel processes (Reuter, 1991)

This processing methodology has enabled fabrication of inorganic and hybrid materials with carefully controlled features at the nano-scales (McGraw Hill Encyclopedia of Science and Technology, 693-696). Basically, Sol-gel process is a technique of creating solid materials from chemical suspension or colloidal particles (sol) to produce an integrated network (gel) with diverse characteristics, through a series of hydrolysis and condensation polymerization reactions (Gollakota et al., 2008). The schematic of the steps involved in the sol-gel process are shown in the Figure 2.2.

```
┌─────────────────────────────────────┐
│                                       │
│        Si (OR)₄ + H₂O/ROH             │
│                                       │
│               │  1                    │
│               ▼                       │
│        Colloidal solution             │
│                                       │
│               │  2                    │
│               ▼                       │
│              Gel                      │
│                                       │
│               │  3                    │
│               ▼                       │
│            Xerogel                    │
│                                       │
│               │  4                    │
│               ▼                       │
│        Glasses, Ceramics              │
│                                       │
└─────────────────────────────────────┘
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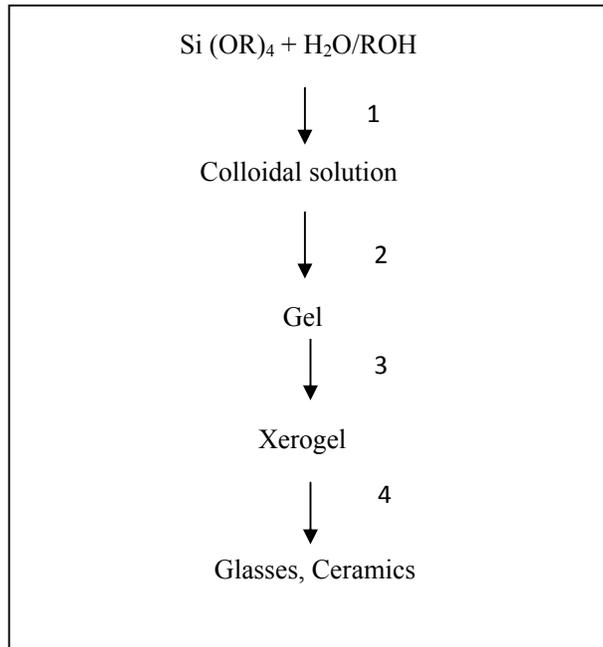
Legends – 1. Hydrolysis/ Condensation 2. Sol-Gel Transition 3. Drying 4. Densification

Figure 2.2. Schematic of Sol-gel process (Gollakota et al., 2008)

There are two main methods to produce sol-gels. In one method alkoxide solutions are used as a precursor for the gel, and in the other method colloidal sols are used as a precursor. Because colloidal sols dry more quickly than sols made from alkoxides, they provide a time advantage (Gollakota et al., 2008).

Typical starting compounds, generally known as sol-gel precursors, are usually metal salts, metal alkoxides, or organo-metal alkoxides. The most widely used precursors are silicon compounds, especially compounds of metals such as Ti, Zr, Al, Sn. Some commonly used sol-gel precursors are listed in Table 2.1, and their chemical structures are shown in Figure 2.3 (Wang et al., 2009).

Table 2.1

Chemical names and abbreviations of some commonly used sol-gel precursors (Wang et al.,

2008)

Chemical name	Abbreviation
Tetraethoxy orthosilicate	TEOS
Tetramethoxy orthosilicate	TMOS
Titanium tetraisopropoxide	-
Zirconium tetraisopropoxide	-
Aluminum tri-sec-butoxide	-
Methyl triethoxysilane	MTES
Methyl trimethoxysilane	MTMS
Vinyl trimethoxysilane	VTMS
Phenyl trimethoxysilane	PTMS
3-Aminopropyltrimethoxysilane	APTMS
3-Glycidoxypropyltrimethoxysilane	GPTMS
Methacryloxypropyltrimethoxysilane	MAPTS
Mercaptopropyltrimethoxysilane	MPTMS
Bis-[3-(triethoxysilyl)-propyl]tetrasulfide	BTSTS
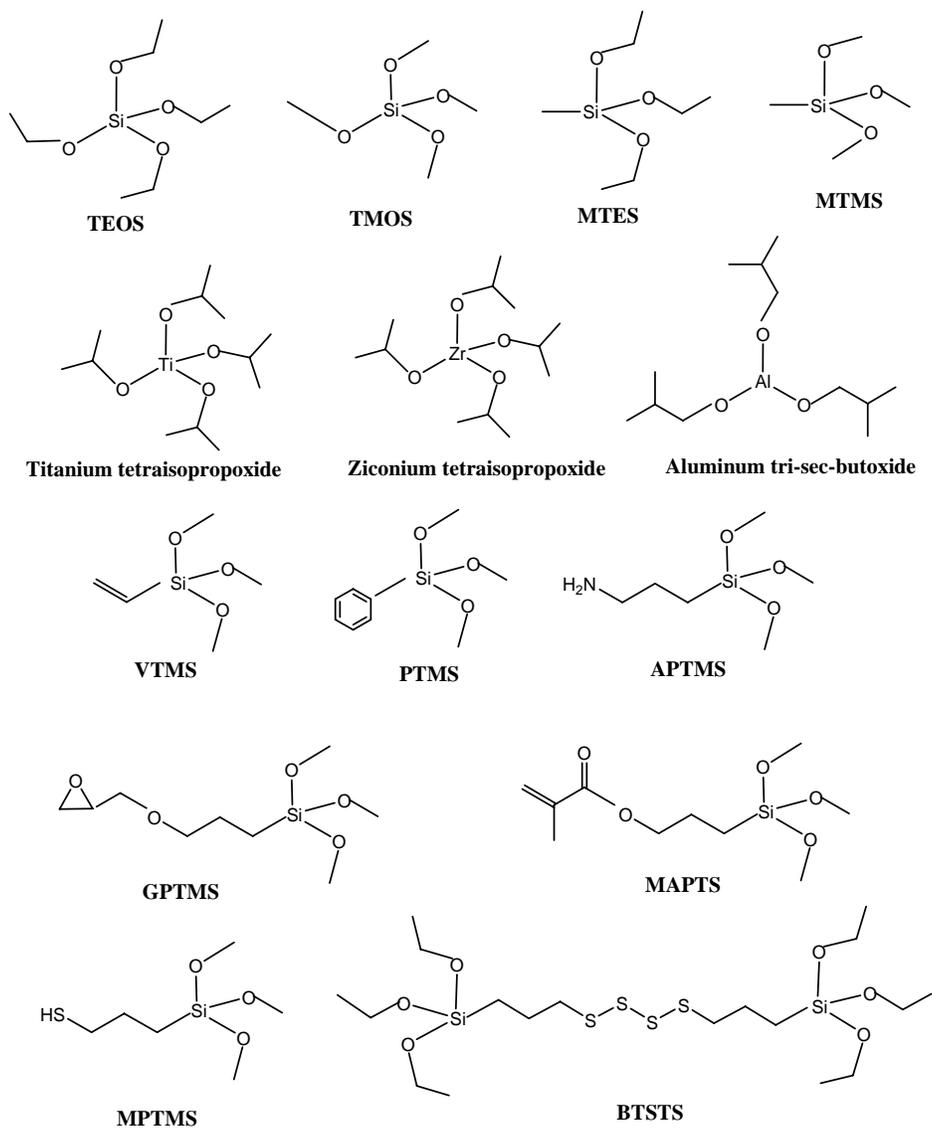
Figure 2.3. Chemical structures of some commonly used sol-gel precursors (Wang et al.,

2008)

Table 2.2

Products obtained according to the relative rates of hydrolysis and condensation of sol-gel

process (Livage et al., 1988).

Hydrolysis Rate	Condensation Rate	Result
Slow	Slow	Colloids/Sols
Fast	Slow	Polymeric Gels
Fast	Fast	Colloidal Gel or Gelatinous Precipitate
Slow	Fast	Controlled Precipitation

A good rule of thumb for the sol-gel chemist is reported in Table 2.2. It suggests that, depending on the relative hydrolysis and condensation rates, different products can be obtained (Livage et al., 1988).

In general, the processes of hydrolysis and condensation polymerization are difficult to separate. Condensation reactions begin before all alkoxide groups of a precursor are completely hydrolyzed. This result into complex set of reactions that take place simultaneously at different rates.

Hydrolysis
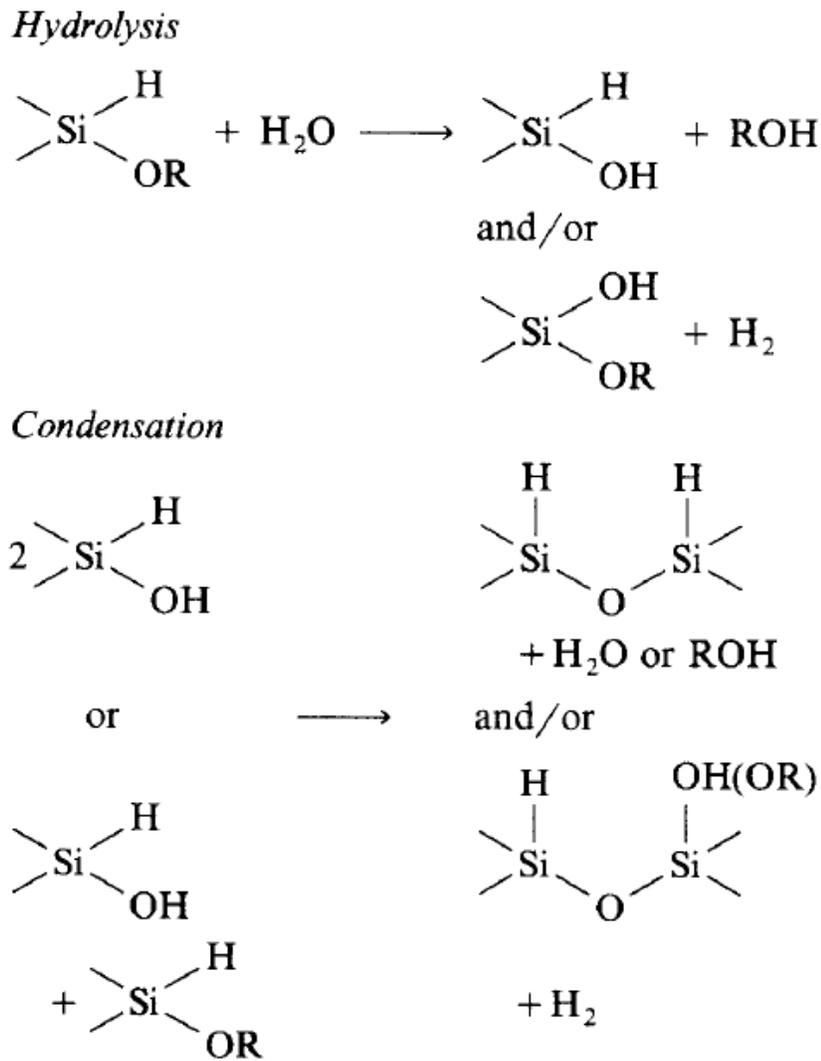
Condensation

Figure 2.4. Hydrolysis and condensation reactions involved in sol-gel process of silicon based precursor (Pauthe et al., 1989)

Several parameters have been shown to influence these reactions, including temperature, pH of solutions, and type of precursors, solvents, and relative concentration of each constituent. Both acids and bases can catalyze hydrolysis and condensation reactions (Brinker et al., 1990). It is important to note that the rate of these competing reactions and

their reaction mechanisms are very different for acid and base catalyzed systems. This results into final materials with significantly different morphology and properties. Therefore, the important aspect in deriving useful sol-gel materials requires careful selection of type and relative proportions of precursors, solvents catalysts, and processing parameters.

Among the most successful applications of sol-gel materials is their use as thin film coating onto a variety of substrates such as glasses, metals, plastics, composites, and textiles. One distinguishing characteristic of such films is their ability to form covalent bonding with the substrate, enhancing their adhesion and durability (McGraw Hill Encyclopedia of Science and Technology, 693-696). Sol-gel coatings with controlled morphology and chemical structure provide fabric coatings, resulting in many interesting bulk and surface properties.

However, the future of the sol-gel technology still depends on whether it will be able to make better and cheaper materials or even completely new material**.** Therefore, scientific knowledge and technological expertise are essential for process development. A major advantage of the sol-gel process is to create tailor-made materials from the molecular precursor (Livage et al., 1988).

General Application of Sol-Gel for Textile Use

Recently, investigations have been conducted to improve properties of textile fabrics by embedding various finishes in sol-gel coating to enhance fabric performance. The following section will focus on different sol-gel applications that create new functional properties in textile fabrics. Textiles coated with sol-gel are reported to impart many important properties, as shown in Figure 2.5.
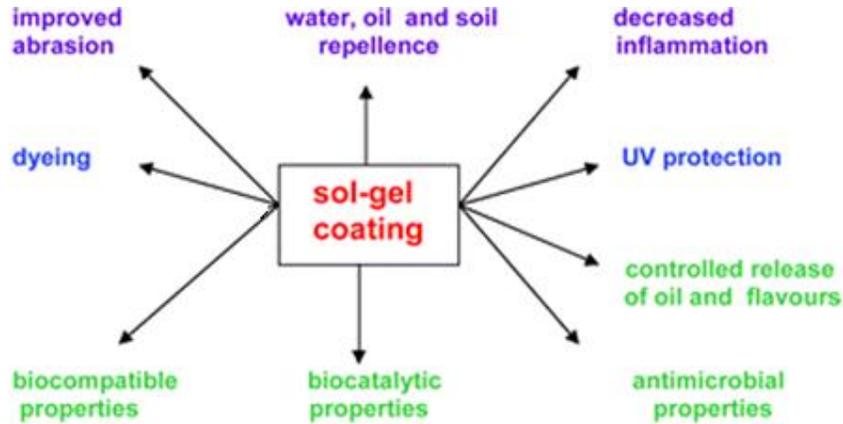
Figure 2.5 Different applications of sol-gel coating on textiles (Mahltig, 2003)

Durable Press Finish on Cotton Fabric with Sol-Gel

Schramm et al. (2004) investigated durable press finishing of cotton fabric using 1, 2, 3, 4-Butanetetracarboxylic acid (BTCA) and TEOS (tetraethoxysilane). The investigators used a two-step process for the application. Cotton fabric was first treated with BTCA, and sodium hypophosphite (SHP) was used as a catalyst. In the second bath the fabric was treated with TEOS and glycidoxypropyltrimethoxysilane (GPTMS) to enhance anti-wrinkle property of the fabric. The wrinkling occurs on the fabric because of distortions imposed on the fiber assembly by external forces. If these forces cause irreversible distortions, the material will remain in the deformed configuration. The weak hydrogen bonds between the adjacent cellulose chains flex and bend to yield to the deforming stresses applied to the fabric. As more stresses are applied to the fabric, bonds break, slide over one another, and form new hydrogen bonds. As a consequence of breaking and reforming of the bonds, the distortion becomes permanent. A durable press resin, dimethyloldihydroxyethyleneurea (DMDHEU), is the most commonly used for wrinkle-free property that can form covalent link with two cellulose molecules. The strong bonds between the cellulose chains through crosslinking

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increase the crease resistance of the resin-treated fabric by replacing the weak H-bonds with stronger covalent bonds. When this structure is stressed, the relatively strong covalent bonds tend to bend rather than rupture, thereby creating a more elastic structure (Ghosh et al., 1990).

DMDHEU is an effective resin for wrinkle-free treatment and also relatively inexpensive. It is known that DMDHEU releases formaldehyde although it is not yet classified as a carcinogen. There is an awareness of toxicity for DMDHEU that might be caused by this resin. BTCA has been used as a substitute for DMDHEU, which is a formaldehyde-free system but more expensive for industrial applications.

The fabric samples treated with TEOS/GPTMS solution only did not show any improvement in wrinkle recovery of the fabric, which was evaluated by a Dry crease recovery angle (DCRA) method using ISO 2312 procedure. No improvement in crease recovery angle probably indicated that no crosslinking reaction took place between the sol-gel network and the cellulose chains; hence no durable performance was imparted to the cotton fabric. When BTCA-finished cotton fabric was treated with TEOS/GPTMS solutions there was a significant improvement in DCRA values. Since DCRA values of the fabric increased after the BTCA finish was applied even without sol-gel network, it was concluded that sol-gel has little or no contribution to the crease recovery property of fabrics.

However, it was noted that fabric's abrasion resistance was reduced as a result of BTCA finish treatment. Another important finding in this study (Schramm et al., 2004) was that abrasion resistance of the fabric improved significantly when the fabric was treated with TEOS/GPTMS. During this application the epoxide ring of GPTMS probably opened and reacted with the hydroxyl groups in the cellulose, resulting in better fixation of the silicone network on the fabric surface. Abrasion resistance was measured using a Martindale tester

following a DIN EN ISO 12947-3 procedure. Combined application of BTCA and sol-gel

provides wrinkle recovery and high abrasion resistance.

Improving Dyeing Fastness Using Sol-Gel

Mahltig et al. (2006) investigated the role of sol-gel coating in improving the fastness

properties of dyes on textiles. Inorganic sol-gel coating is one of the useful ways for

embedding the organic dyes and applying it to different type of substrates like glass, paper, or

textile. Sol-gel method is very popular for optical pH sensors, UV and IR protective coatings,

and embedded dyes for drug delivery systems. The investigators intended to find whether

application of sol-gel and dye need to be carried out in two different steps or in a single

process application of sol-gel and dye solutions together. A single-step application has

industrial application advantage. Addition of sol gel in separate step can be desirable if

fastness property of the colored fabrics can be improved significantly. Figure 2.6 shows the

illustration of different schemes for coating sol-gel on the dyed fabric.
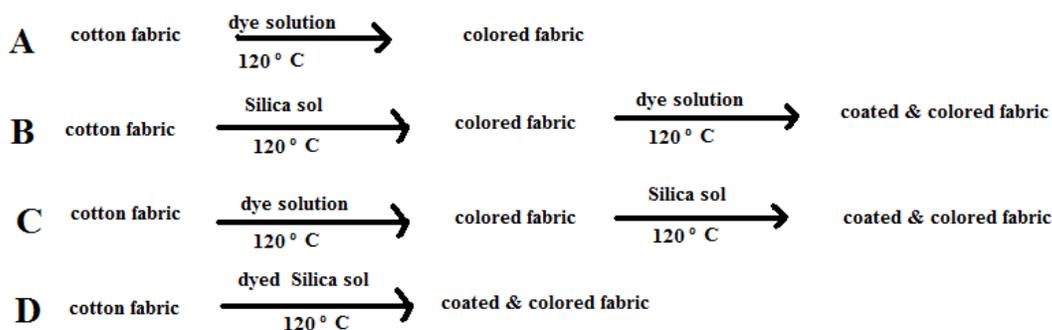
Figure 2.6. Different schemes of sol-gel coating on dyed fabric (Mahltig et al., 2006)

Triphenylmethane dyes such as Malachite Green MG and Guinea Green GG were

applied on the plain weave cotton fabric (102 g/m^2) using four different procedures as

schematically shown in Figure 2.6. Cotton substrate was used in the study because silica sols

can be uniformly spread and distribute on cotton as compared to other textile substrate such as polyester and nylon that might need plasma pretreatment. The fabrics were dip-coated at speed 30 cm/min and dried at room temperature and cured for 1 hour at 120^{o}C. Silica sol containing 10% of an epoxysilane additive was used in all the experiments to improve the fastness properties compared to pure silica sols.

Leaching and bleaching tests were used to investigate the durability of application on dyed samples. The study showed that color fastness and dye uptake were influenced by the type of application methods used in the research. Method A (without Sol component) resulted in highest uptake and retention of color whereas Method B and C exhibited lower color retention. Method D provided the lowest color intensity because both dye and sol-gel were applied in one step and both components had to be taken up by textile substrate simultaneously. The samples showed a small increase in leaching even when washing temperature was kept at $60\,^{o}$C. This investigation essentially showed that color fastness can be improved by application of modified silica-sols. The pretreatment with silica-sols before dyeing does not improve color fastness. The investigator demonstrated that treatment of dyed fabric with sol-gel followed by simultaneous application of dye and sol-gel improves colorfastness.

Aksit et al. (2008) studied the wash fastness, light fastness, rubbing fastness and dyeing yield, leaching property, and so on of the direct, basic, and reactive dyes applied using sol-gel process and exhausting method. They embedded the dyes into the sol-gel coating and deposited on textile materials. For this, silica particles were prepared by hydrolyzing tetraethyl orthosilicate (TEOS) with water and ethanol, and then sodium acetate trihydrate, 3-glycidoxypropyl trimethoxysilane (GPTMS) and dyes were added. pH of the solution after addition of each chemical was recorded. Transparent solution resulted due to the vigorous

mixing of solutions using magnetic stirrer for 10 min at room temperature. The detailed

flowchart of dyeing with a) sol-gel process b) exhausting process is shown in Figure 7a-b.

Adding TEOS + Ethanol + water

↓

Adding water +dye+ sodium sulphate +sodium hydroxide (if req.)

Adding sodium acetate trihydrate (if req.)

↓

↓

Adding GPTS

Heating dye bath to 80^{o}C

↓

↓

Adding dye

Adding fabric and exhausting at 80^{o}C for 15minutes

↓

↓

Vigorously stirring for 10 minutes at magnetic mixer

Adding sodium carbonate (if req.)

↓

↓

Transparent solution

Exhausting at 80 ^{o}C for 15 min

↓

↓

Exhausting at 80 ^{o}C for 10 min

Drying fabric on air

↓

(b)

Drying 120 ^{o}C for 20 min

(a)

Figure 2.7. Flow charts of dyeing with (a) sol-gel process, (b) exhausting process (Aksit et

al., 2008)

Results showed the significant difference between dyeing yields which were measured using Kubelka Munk equation to calculate K/S values of dyed fabric using different process. K is the absorption of light and S is the scattering of light. Dyeing yield of sol-gel process with addition of sodium acetate trihydrate was 5.93 as compared with 0.95 obtained with direct dyes using exhausting process. It may be due to dye removal at washing. Also, dyeing time and temperature were reduced as compared to conventional dyeing conditions to 80 ^{o}C and 30 min dyeing time. It was also proved that higher dye yield was obtained because of partial immobilizing into silica oxide and sodium acetate act as an electrolyte, which was helpful in neutralizing negative charge of cotton fibers that would otherwise repel direct or reactive dye anion.

Improving Water Repellence with Sol-Gel Coating

Mahltig et al. (2003) evaluated water repellent property of textiles with different modified silica sol. In this study, pure and 3-glycidoxypropyl triethoxysilane co-condensed silica sols were modified by three types of additives such as alkyltrialkoxysilanes, polysiloxane derivatives, and a fluorine-containing silane. The coated fabric was evaluated for a contact angle measurement and water repellency using common rain test and water uptake test. The pure silica sol was prepared through acidic hydrolysis of tetraethoxysilane (TEOS) dissolved in a mixture of ethanol and water at ambient temperature. The modified silica-sol was produced in a mixture of TEOS, HCL and 3-glycidyloxypropyltriethoxysilane (GPTES) at room temperature. The mixtures of silica sol and hydrophobic additives were mixed for 30 minutes or more before dip-coating was performed on the substrates. Glass, nylon, and polyester/cotton fabric were coated with additive containing silica sols. Samples were dried at room temperature followed by curing at 120^{o}C for an hour.

Results showed that hydrophobic properties of coatings were obtained via addition of hydrophobic polysiloxane or fluorine containing silicon compounds to commercial available silica sols while the alkyl silane additives also provide good water repellent properties via addition of hexadecyltrimethoxysilane. It was shown that silica sols containing fluorine compounds and hexadecylsilane additives give high washing durability. Wash fastness of these coatings is very important for the success of industrial applications.

Controlled Fragrance Release Using Sol-Gel Coating:

Wang et al. (2006) modified cotton fabric surface by anchoring the β-cyclodextrins using a sol-gel process for controlled fragrance release. In this study, β-cyclodextrins (CD) was mixed in a solution of ethanol and distilled water and emulsified in a high-speed mixture for 15 min. TEOS and GPTMS were added into emulsified solution under stirring. The mixture was allowed to shake for 8 hours at 40 ^{o}C. The cotton fabric was immersed in diluted β-cyclodextrins-sol-gel solution for 10 min at room temperature. The padded fabric was dried at 80^{o}C for 5 min. Padding, immersing, and spraying techniques were used to load the fragrance on the fabric. The fragrance substance (1g) was dissolved in water or ethanol (1000ml) using a high speed mixture. The cotton fabric anchored with β-cyclodextrins (CD) was immersed in fragrance solution for 24 h, sprayed with a sprayer, or padded twice to achieve 100% wet pick up. After the fabric was treated with sol-gel and the β-cyclodextrins was anchored, the fabric can form the inclusion complexes with other guest components (like fragrance in this case). The fragrance depositing amount on the fabric depends on the amount of CD on the fabric. The greater the amount of CD anchored on fabric, the more chances of fragrance molecules to diffuse into the cavities of CD molecules and forms inclusions. The lower rate of perfume release and detection threshold determines that the fabric smell well for long time. A panel of 10 subjects was asked to smell the fabrics every five days to feel the

perfume scents. The test results exhibited that treated fabric can release fragrance over 30 days and the durability of cyclodextrin can last for 20 laundering cycles.

Sol-Gel Encapsulated UV Absorber to Provide Sun Screening

Lapidot et al. (2003) published a method of sol-gel microencapsulation technology that utilizes an interfacial polycondensation sol-gel process to encapsulate UV absorber. There is a progressively increased use of sunscreen active ingredient to decrease the effect of phototoxic and photoallergic reaction of UV rays from sun. Investigators developed a sol-gel microencapsulation technology that uses an interfacial polymerization process that allows forming transparent silica glass microcapsule at sizes varying from 0.3- 3 microns. These capsules form a core-shell structure where nearly 80% of the product consists of UV absorber core enclosed by a silica shell.

In this process different sunscreen active ingredients were encapsulated alone and also as a mixture of several ingredients. In their (Lapidot et al., 2003) procedure, the oil phase consisted of a sunscreen/TEOS mixture that was added to water containing a surfactant and a catalyst. Several tests were conducted that include particle size determination, leaching test, protection factor, in vitro skin penetration test to determine the effectiveness of the product. The investigators demonstrated that encapsulate sunscreen ingredient using sol-gel process showed high SPF values. Furthermore, this product reduces the contact between the active ingredient and human tissue, hence eliminating prolonged exposure to these chemicals.

Encapsulation of Organic Pigment Particles with Silica via Sol-Gel Process

Yuan et al. (2005) reported a novel preparation method of silica coated organic pigment. First, surfaces of the organic pigment were orderly modified by poly (sodium 4-styrenesulfonate) (PSS) and poly (diallyldimethylammonium chloride) (PDADMAC), and then coated by silica via sol-gel process of tetraethylorthosilicate (TEOS). The resulting silica coated organic pigment showed improved UV scattering property and therefore improved the weather durability of organic pigment. The morphology of the silica coated organic pigments was analyzed using Transmission Electron Microscope – TEM and Scanning Electron Microscope – SEM. It was believed that because the surface of organic pigment is inert, silica particles could not be coated evenly on organic pigment particles that were verified with the TEM images. In order to have enough affinity of organic pigment particles with silica, organic pigment was treated with PSS and PDADMAC, so that surface of the organic pigment becomes positively charged. Since silica is negatively charged, they can be successfully coated on the surface of the positively charged organic pigment.

It was observed that at a pH of 8.5 to 11.3, homogeneous coating of silica on the surface of organic pigment was possible due to slow hydrolysis and condensation of TEOS at lower pH. In this study, investigators successfully prepared organic pigments encapsulated with silica using sol-gel process of TEOS after modified by two types of polyelectrolyte such as PSS and PDADMAC.

Flame Retardancy Cotton Fabric with Sol-Gel Coating

Cireli et al. (2007) developed a flame retardant cotton fabric doped with phosphorous and undoped SiO_2 thin films. Sol-gel method using metal-based precursors was used to coat the fabrics with doped phosphorous and undoped SiO_2 thin films. Sol-gel solution was

prepared with TEOS as precursor, and ethanol and water as solvent. Phosphoric acid or ethyldichloro phosphate was used to impart flame retardant property. In their study, transparent sol was prepared by mixing TEOS with ethanol and water, and then HCl was added for the acid hydrolysis and the solution was stirred for 60 minutes at room temperature. To this solution, phosphoric acid or ethyldichloro phosphate was added drop by drop at room temperature, and the solutions were stirred for 30 minutes at 25^{o}C. Cotton fabric was dipped into these solutions and treated for 30 minutes at 80^{o}C and then they were squeezed.

The coated cotton fabrics were evaluated for their flame retardant property using the test method TS 5569 EN ISO 6941. Flame spread time for the coated fabrics along warp direction was carried out before and after 10 washing cycles.

The untreated and fabrics coated with only SiO_2 start to ignite after flame-exposing time of 5s. But with P-doped SiO_2 based on phosphoric acid, the coated fabric is completely nonflammable even after flame exposing time of 15s. After the fabrics were subjected to 10 washing cycles, flame spread time was found out to be 8s, which is higher than that observed for the untreated fabric. Thus cotton fabrics coated with P-doped SiO_2 coating using sol-gel method show significant flame retardant property. Moreover, the concentration of phosphoric acid used for this study was 83g/L, which is much less than the conventional flame retardant finishing process. Thus, sol-gel method of imparting flame retardant property to the cotton fabric is cost effective and it also imparts durability.

Studies on Antimicrobial Properties of Textile Fabrics

Lee et al. (2003) studied the antibacterial effect produced with the help of nanosized silver colloidal particles. In their study, the nanoscaled silver particles were dispersed on cotton, polyester, and their blends; then their antibacterial effect and its durability were evaluated. Undyed and dyed cotton and polyester fabrics were padded through 25 ppm and

50ppm silver colloidal particles. The antibacterial properties were evaluated according to KS K 0905-1996 test against Staphylococcus aureus, a Gram-positive bacterium and Klebsiela pneumonia, a Gram negative bacterium. The laundering durability was also evaluated for the treated fabrics after 5, 10, and 20 washing cycles.

The bacterial reductions of all samples were excellent against both the bacteria. Also the bacterial reduction was more effective for dyed samples than undyed samples. The fabrics padded with 50ppm silver colloidal solutions shows a better bacteriostasis than the samples treated with 25ppm solution. The bacterial reduction % for cotton fabrics varies from 99.7 to 99.9%, and for polyester samples, it ranges from 99.5 to 99.9%. All samples showed strong bacteriostasis even after 20 washing cycles against Staphylococcus aureus. Cotton dyed fabric had 90.8% and polyester had 84.3% bacterial reduction after 20 washing cycles. But the bacterial reduction against Klebsiela pneumonia was significant for cotton till 10 washing cycles; after that it reduces to very low value of around 30%. For polyester, even after 5 washing cycles, bacterial reduction is only around 36% against Klebsiela pneumonia. Thus the authors obtained a good antibacterial efficacy and laundering durability on textile fabrics using nanosilver colloidal solution by padding.

Lee et al. (2004) also studied the antibacterial effect on polyester nonwoven fabrics with the help of silver colloidal particles. Polyester nonwoven fabrics were treated with colloidal silver solution through padding method. The concentrations of colloidal silver were varied at 200, 50, 30, 20, and 10 ppm. Also the effect of two different silver particle sizes of 11.6 and 2-5 nm was analyzed. Antibacterial properties were evaluated against Staphylococcus aureus, a gram positive bacterium, according to test method FC-TM-19-2001 and Klebsiela pneumonia, a gram negative bacterium, according to test method KS K 0693-2001.

The results showed a bacterial reduction of over 99.98%, against both the bacterial types for the concentration of 50ppm and above, for 11.6 nm particle size silver coating. But for the nanosilver coating, which contains 2-5nm particle sized silver, bacterial reduction of 99.99% was achieved even with a low concentration of 10ppm. SEM results showed a proper dispersion of nanosized silver particles on fibers in polyester nonwovens.

Ye et al. (2006) obtained durable antibacterial effect on cotton fabrics with the help of Chitosan. They showed that antibacterial activity of chitosan against various bacteria and fungi is due to its polycationic nature.

In their study, two core shell particles, one with poly (n-butyl acrylate) soft core and another with cross linked poly (N-isopropylamide) hard core, were synthesized and applied to the cotton fabric by a conventional pad-dry-cure process. The antibacterial activity against Staphylococcus aureus evaluated quantitatively using a shaking flask method developed by Dow Corning Corp shows bacterial reduction of over 99% for both the types of coatings, whereas untreated cotton fabrics has a bacterial reduction of less than 10%. The laundering durability of the treated fabrics was evaluated based on AATCC test method 61-1996. The results showed that even after 50 washing cycles, the washed samples maintained high bacterial reduction of around 90%. This shows the good durability of the applied coating. SEM analysis shows smooth fiber appearances for both treated and untreated cotton samples, which shows proper dispersion of chitosan particles in the cotton fabric.

Gorensek et al. (2007) evaluated antibacterial effect of nanosilver on cotton fabrics. In their study, 20mg/L of nanosilver was applied to the cotton fabrics. The size of the nanosilver used in this study was 80nm. Antibacterial effectiveness was analyzed using ASTM E 2149-01 against five different bacteria: Staphylococcus aureus, Escherichia Coli, Streptococcus faecalis, Pseudomonas aeruginosa, and methicillin resistant Staphylococcus aureus. The

results show significant bacterial reduction for bacteria types Streptococcus faecalis, Staphylococcus aureus. The reduction percentage for both these type of bacteria is about 98%. The laundering durability of the treated fabrics was evaluated according to ISO 105 C03 standard. The results showed bacterial reduction of 86% and 95%, respectively, against bacteria types Streptococcus faecalis and Staphylococcus aureus, even after 10 washing cycles.

<center>Use of Sol-gel to Impart Antimicrobial Properties</center>

Numerous antimicrobial agents are known and have already been tested in combination with many hydrocarbon and fluorochemical (Lee et al., 1999), and sol-gel based finishes (Mahltig et al., 2004, 2005), all have been applied with variable success. Some of those techniques are discussed in this text.

Antimicrobial finishing of cotton textile based on water glass by sol-gel method was investigated by Xing et al. (2007). They prepared the silica sol by acidifying water glass solution with 0.05M H_2SO_4 solution to pH 11. Antimicrobial treatment was performed by impregnating cotton textile in silica sols and then treated with silver nitrate solution. The antimicrobial activity of the treated cotton fabrics was determined according to AATCC Test method 100-1999. The anti-microbial activity is evaluated by determining the percentage reduction of bacteria count on the sample after exposing the treated fabric to the bacteria. This result was compared to an untreated control sample by exposing to a bacterial lawn. This antibacterial activity was measured by washing the samples several times after sol-gel treatment. Mahltig et al.,'s (2005) results exhibited that antimicrobial durability of the treated samples increased with increase in water glass content. For the samples without water glass, bacterial reduction % was zero only after 10 washing cycles. But with a water glass content of 2% and 5%, higher silver ions were retained that resulted in more than 99% bacterial

reduction even after 20 and 50 cycles of washing. The bacterial reduction % also increases with increase in silver content as well.

Haufe et al. (2008) made an effort to impart the antibacterial activity by immobilizing the bioactive liquids and investigated the controlled release of the same via a modified silica coating method. Primrose and perilla oil were used for the antimicrobial applications. In their method, first silica sol was synthesized by acid hydrolysis of tetraethoxysilane with acetone. Then silica sol was mixed with the bioactive liquids primrose oil and perilla oil in various ratios. The solution is then coated on cotton fabric and air-dried. The treated fabrics were tested for the antimicrobial activity against Escherichia coli (gram negative bacteria) and Staphylococcus aureus (gram positive bacteria). The antimicrobial activity was determined by counting number of colony-forming units (CFU) before and after coating. The results show that the antimicrobial activity against gram positive bacteria was high even after 5 ECE washing cycles. But the effect against gram negative bacteria decreased with increasing washing cycles. Therefore the coating is more effective against gram positive bacteria than gram negative bacteria.

Mahltig et al. (2004) investigated antibacterial effect by embedding the biocides in silica coatings. Biocides used in this study were silver nitrate, colloidal Ag, (cetyltrimethylammoniumbromide) CTAB, and octenidine. Silica sol solution was prepared from tetraethoxysilane (TEOS) and 3-glycidyloxypropyltriethoxysilane (GOPTS). Properties such as antibacterial efficacy wash-out and long-term behavior were analyzed. Their results showed biocidal additives Octenidine and CTAB exhibit high inhibition rate of more than 90% against the fungi Aspergillus niger after 4hr of leaching, whereas colloidal Ag treated samples without sol-gel have the lowest inhibition.

Daoud et al. (2004, 2005) coated the cellulosic fibers with titanium oxide nanoparticles, which were obtained from aqueous titania sol. Titanium isopropoxide was hydrolysed and condensed in water to obtain the titania sol coating at low temperature. The stability of titania coating and the antibacterial activity of the coating was analyzed. Treatment with sodium carbonates solutions showed less leaching behavior, which indicated that titania sols were strongly bonded with the cellulosic substrate. They confirmed the same with the help of FESEM images, which shows uniform distribution of the titania sols. The treated fabrics exhibited good antibacterial activity because of the formation of TiO_2 surface on the cellulose substrate which prevented the formation of a protective biofilm of adsorbed bacteria.

Adibi et al. (2007) studied the antibacterial activity of the cotton fabric by treatment with dodecanethiol-capped silver nanoparticles-doped sol solution. In order to impart the ultraviolet radiation protection, the cotton fabrics were then padded with titania nanosol solution. The treated fabrics showed good antibacterial activity against Escherichia coli. Titania nanosol increased the Ultraviolet Protection Factor of the treated fabric by 91.8%. Thus, excellent antibacterial and UV protection properties with the help of dodecanethiol-capped silver nanoparticles and Titania nanosols were achieved.

Sun & Sun (2001) imparted antimicrobial property on the textile fabrics using N-Halamines. Novel cyclic-amine-containing vinyl monomers could be synthesized in good yields by reacting allyl halides (Br, Cl, etc.) with corresponding 5,5- disubstitued hydantoin in alkaline solutions. The hydantoin units in the copolymers could be easily transformed into N-halamine structures upon exposure to a chlorine bleach solution. N-Halamine derivatives of the corresponding copolymers exhibited powerful, durable, regenerable antibacterial properties against *Escherichia coli.*

Summary and Comments

The goal of sol-gel processing is to control the structure of a material on a nanometer scale from the earliest stages of processing. The potential of improved properties due to ultra structural processing, control of higher purity, and greater homogeneity has been realized. Other engineering advantages of the lower temperature chemically based sol-gel processing such as net-shape casting, fiber pulling, and film coating have also reached economic potential (Hench et al., 1990).

CHAPTER 3: RESEARCH DESIGN AND METHODOLOGY

The research design is quantitative and the research method is experimental.

Materials and Chemicals

Substrate – desized, scoured and dyed, 6.72 oz/yd^2 50/50 Nylon/ Cotton blend fabric was used as received from the manufacturer. 5, 5 - Dimethyl Hydantoin, 97 % (M.P 174^{o}C) was obtained from Aldrich Chemical Co. Ltd. (used as obtained). Bromophenol Blue A.C.S. reagent, Sodium hypochlorite, available chlorine 10-13% (B.P 111^{o}C) (reagent grade), Tetrahydrofuran, minimum 99% (B.P 65-67 ^{o}C, M.P -108 ^{o}C), Dimethyl sulfoxide anhydrous 99.9+ % (B.P 189 ^{o}C), Triethylamine, Acetone are obtained from Sigma Aldrich Inc. and used without further purification. Silquest A-Link 25 γ –Isocyanatopropyltriethoxysilane (B.P 238 °C) was obtained from Momentive and used without further purification.

Experimental Methods

Reaction between DMH and CPTES

1. Weighing of chemicals: DMH and CPTES are reacted in the mole ratio of 1: 1/2. Solution of DMH was prepared in Acetone and DMSO. 10% solution of Triethylamine in THF was used as a catalyst. Then CPTES was added to the above reaction mixture.

2. The above prepared reaction mixture was added to the reactor.

3. Connections of the reactor with condenser, nitrogen cylinder, and temperature controller were made.

4. Temperature controller was set at 65 ^{o}C, which is the boiling point of acetone.

5. The stirrer was started and the reaction was allowed to run for 8 hours.

Determination of % NCO Content of Isocyanate Component:

Objective: To determine % NCO content of isocyanate component.

Reagents:

- 0.1N n-dibutyl amine solution in dry toluene

- 0.1 N Hydrochloric acid solution in Isopropyl alcohol

- Bromophenol blue indicator

Procedure:

1. 0.1 g sample was weighed into a conical flask.

2. Weigh 20 ml of 0.1 N n- dibutylamine solutions and added to the conical flask.

3. Sample was warmed at 60 -70 ^{o}C for 5 min.

4. The sample was cooled and 4-5 drops of bromophenol blue indicator was added.

5. This is titrated against 0.1 N HCL solutions until yellow end point was reached.

6. Blank titration was carried out by following the same procedure without the sample.

7. Calculate % NCO using equation (2)

$$\% \text{ NCO } = \frac{(B\text{-}S) \times N \times 4.202}{W} \quad \text{……………………………………. (2)}$$

B = Blank burette Reading in ml

S = Sample Burette Reading in ml

N = Normality of HCL Solution = 0.1 N

W = Weight of Sample (g)

Application of DMH – CPTES Adduct On 50/50 Nylon/Cotton Substrate

50/50 Nylon/ Cotton Blend fabric was finished using the pad – dry – pad – dry – cure approach and padding mangle was used to pad the samples.

1. Two fabric specimens of dimension 10" x 10" were used for application.

2. 250 ml of concentrated DMH-CPTES adduct solution prepared in step A was poured in the padding mangle trough.

3. Samples were immersed in the solution for 2 hours and then padded on the Laboratory Padder LP (LAB –PRO GmbH, CH- 4806 Wikon) at a padding pressure of 0.12 MPa. The fabric was passed between the rollers at 0.12 MPa padding pressure in order to remove the excess chemical from surface.

4. The treated samples were dried at 80 ^{o}C for 1 hour and then immersed in the solution for 2 hours and padded again.

5. Finally the sample was dried overnight and cured at 130 ^{o}C for 25 minutes.

Chlorination of Treated Fabrics:

DMH-CPTES adduct finished nylon/cotton blend fabric was treated with sodium hypochlorite, to impart the antimicrobial property to the fabric.

1. DMH-CPTES adduct treated samples were saturated with sodium hypochlorite solution containing 13 % available chlorine for 15 min at 80 ^{o}C and then 15 min at room temperature.

2. The samples were dried at 60 ^{o}C overnight.

3. The cloth was rinsed in hot deionized water and then washed three times with soapy water at 55-60 ^{o}C for 30 minutes.

4. The cloth was rinsed in hot deionized water.

5. Finally, the cloth was dried at room temperature for 4 hours.

Characterization of Chlorinated Fabrics

The following test methods were used to characterize the fabrics:

FTIR Technique to Determine the Extent of Reaction:

Infrared spectroscopy is used to identify and quantitatively analyze chemical compounds, mixtures, extent of reaction, and molecular structure. Different chemical compounds absorb infrared radiation at frequencies corresponding to their own molecular vibrational frequencies (Sibila and et al., 1988).

Fourier Transform Infrared Spectra (FTIR) of unreacted and reacted chemical solution containing DMH-CPTES adduct, Tertiary ethyl amine, Acetone, Dimethylsulfoxide was observed using Bruker FTIR spectrometer (model Tensor 27) in order to identify the NCOpeaks to determine the extent of reaction. One drop of liquid sample is placed between two plates of sodium chloride (salt) where it forms a thin film between the plates. Salt is used because it is transparent to the infrared light; and is frequently used for polymer identification (Fourier Transform Infrared Spectroscopy, WCAS, Bodycote testing group).

Scanning Electron Microscopy

S-3400 N (Scanning Electron Microscope) Hitachi was used to capture SEM micrograph by placing the sample on the sample holder and at magnification of approx 1.2 k at 12 kV and 30 probes current.

Elemental Analysis

Elemental analysis of the fabric was examined using EDS 2006 (IXRF systems, Inc. 500 digital processor). For the EDX analysis, a good image was captured at 30 ampere probe current and 12 kV, and then voltage was increased to 20 kV and probe current was raised to

74 ampere in order to get an intensity to near 1000c/s to set a good condition for EDX analysis.

Antimicrobial Testing

The treated fabrics were checked for antimicrobial activity using AATCC test method 147 using gram positive bacteria at Accugen Laboratories, Inc. (Parallel Streak Method, Test Method 147-1993, 1996).

The test objective was to determine the antibacterial activity of diffusible antimicrobial agents on treated textile fabric. In this method, the agar surface is inoculated by making a parallel streak, and the sample is pressed on the plate inoculated. After incubation, antibacterial activity is estimated by observing the decrease in growth of organism from one end of each streak to the other end and from one streak to the next streak. The size of the zone of inhibition and the narrowing of the streaks caused by the presence of the antibacterial agent permit an estimate of the residual antibacterial activity.

One loopful of the diluted inoculum was streaked to an agar plate. The test specimen (25 x 50 mm) is gently pressed transversely across the agar surface, which is incubated at 37 ± 2°C for18-24 hours. Incubated plate was examined for the interruption of growth along the streaks of inoculum beneath the specimen and for a clear zone of inhibition beyond its edge. The average width of a zone of inhibition along a streak on either side of the test specimen is calculated using the following equation:

$W = (T - D)/2$

Where:

W = width of clear zone of inhibition in mm

T = total diameter of test specimen and clear zone in mm

D = diameter of the test specimen in mm

There cannot be any bacterial colonies directly under the sample in the contact area in order to be considered acceptable antibacterial activity. The test bacteria were *Staphylococcus aureus* AATCC 6538, Gram positive organism and E. coli AATCC 8739.

Textile Testing Methods

Textile materials used in different application areas are regularly subjected to stretching, twisting, bending, shearing, and compression, and thus it is important to know that the fabric will have the expected minimum level of fabric strength.

The fabrics were evaluated for the tensile strength, abrasion resistance, stiffness, fabric coating thickness, fabric density, moisture vapor resistance, and thermal resistance properties at Eastern Michigan University textile lab.

Durability Tests

Tensile strength of the fabrics ASTM D 5034

Fabric tensile strength was evaluated using Grab test according to ASTM D 5034 on Galdabini material testing machine, Quasar 250 (Serial # V9AL). It works on the principle of CRE (Constant Rate of Extension). Five specimens per sample were cut into dimensions of 1" x 9" samples. The fabric was placed in between the clamps, which were set 6 inches apart. A weight was used to insure that the same amount of tension was put on each of the samples while securing the clamps. The testing machine was set to run 2 inches per minute. Peak load and breaking elongation of the fabric samples were measured. Average and standard deviation of fabric tensile strength data are reported.

Abrasion resistance (Martindale Abrasion Tester Method)

The resistance of textile materials to abrasion as measured on a testing machine is one of the factor contributing to wear performance durability as experienced in the actual use of the material.

Abrasion is the wearing away of any part of a material by rubbing against another surface. It is stated in terms of number of cycles on a specified degree or amount of abrasion. Standard test method ASTM D4966 -98 was used to determine the abrasion resistance of textile fabrics using Martindale Abrasion tester (Model GT –7012 –M). In this test method, abrasion resistance was measured by subjecting the sample to rubbing motion in the form of a geometric figure under known conditions of pressure and abrasive action. Specimen face was placed down into the specimen holder and polyurethane foam was placed between the specimen and the metal insert. The assembled holder was put on the machine above the fabric/ felt piece and pressed by a weight of 1.31 ± 0.03 psi (9 ± 0.2 kPa). After this, counter was set at 2000 cycles to record the desired movements and abrasion machine was started. Difference between the weight of the fabric before and after abrasion was used to evaluate the abrasion resistance of the fabrics. The weight loss was calculated as follows.

$$((A-B)/A) \times 100$$

where:

A = sample weight before abrasion cycle

B = sample weight after abrasion cycle

Average and standard deviation of abrasion resistance data of five samples are reported.

Stiffness (Taber type tester)

Test specimen of 1.50 ± 0.01" x 2.75 ± 0.01" dimension was bent through a 15^{o} angle in right and left hand side on the Teledyne Taber stiffness tester (model 150- B). The resulting bending moment was recorded from the instrument scale.

The instrument is motor driven and consists of pendulum. The conditioned test specimen was placed in the vise with its end approximately level with its top edge and the other end between the rollers. The specimen should be aligned with clamping screws of the vise with the center line of the pendulum. The pressure of the clamping screws may impact test results, and clamping pressure should be firm enough to hold specimen. The motor was switched on to rotate the loading disk to the left and thus reflect the specimen until the engraved mark on the pendulum is aligned with 15^{o} mark on the loading disk. The motor was stopped, the scale reading on the fixed annular disk was recorded, and the loading disk was returned to zero position. Similar reading was taken by deflecting the specimen to the right.

Taber stiffness unit – bending moment of 1/5 of a gram applied to a 1 1/5 inch wide specimen at a 5 cm test length, flexing it to an angle of 15^{o}.

Stiffness values in millinewton.meters = Taber unit x 0.098066.

Comfort Testing

Thermal and Evaporative Resistance of clothing materials was measured using a MTNW inc. made Sweating Hot Plate (Serial # 223-21) inside the TPS Lunaire Climatic Chamber (Model # CEO 910 -4) according to ASTM F 1868 -02.

Thermal resistance of the fabric was measured by first measuring the bare plate thermal resistance using the test plate software. For the bare plate test, humidity and temperature of the chamber was maintained at 65% and 21 ^{o}C. The humidity sensor and wind

sensor should be connected correctly to the controller. Wind sensor should be adjusted at height of 7 mm using a black lock of height 7 mm on the plenum and according to fabric thickness, plenum can be raised or lowered in order to maintain that gap. The Rcbp ASTM F 1868-02 test was started from the test program. After the test reach the steady state and temperature and heat flux are in tolerance for 30 minutes; then the test is saved and exited. The average of the thermal values was used to calculate the thermal resistance of fabric. Rct (ASTM F 1868-02) test used measures the resistance of bare plate plus the resistance of fabric in the similar way as Rcbp was measured by placing the fabric sample (10" x10") on the test plate and taping it on all the edges.

Bare plate moisture resistance was calculated according to ASTM F1868-2 as Rebp. The deionized water was filled in the resource tank and then the water tube connecting to sight glass is connected to test plate and water is pushed using a pump by placing thumb on the sight glass. Water should be pumped such that the test plate is completely wet and water is coming from all the holes on the test plate. Extra water was removed using a sponge. Cellophane film was used because when it is wet, it resembles the skin and moisture can pass through this but not the water. Cellophane was completely wet on one side and then placed on the test plate. Cellophane was trimmed from the side and then scotch blue painter's tape was used to hold it on all four sides. The height of the wind sensor on the top of the test plate was adjusted using a black metal block. Then Rebp test was run on the software and continued till the temperature and heat flux remained in steady state and in tolerance for 30 minutes. After this, Moisture resistance of the fabric plus the bare plate (Ret) was evaluated by placing the fabric on cellophane.

Finally, moisture resistance of fabric was calculated by subtracting the Rebp from Ret. Similarly, thermal resistance of the fabric was calculated by subtracting Rcbp from Rct.

Thickness of Textile Materials ASTMD1777-96(02)

Thickness of the fabric was measured using Elektro Physik precision standard 526 µm ± 1% on the Minitest 600B coating thickness gauge. This coating thickness gauge is battery powered and equipped with 1 m probe cable. It works on the magnetic induction principle and should be used for measuring non-magnetic coatings such as aluminium, chrome, copper, paint, rubber and so on on iron or steel substrates (ElektroPhysik Minitest 600, Operating Instructions Manual, 2007). Average and standard deviation of coating thickness are reported.

Data Analysis: Variance statistics

A statistical analysis of the test results was evaluated with 95% confidence interval. One-way Analysis of Variance (ANOVA) using SAS (Statistical analysis software) program was carried out for the comparison of properties of untreated and treated samples. The SAS program created is provided in the Appendix C.

CHAPTER 4: RESULTS AND DISCUSSION

Introduction

The ultimate goal of this research is to create a fabric that will kill microbes but maintain all necessary textile properties including durability and comfort properties. A set of strategic objectives were developed to achieve this goal. Experiments were designed to support these objectives.

This chapter reports the test results and discussion of process and several tests performed on the formed solution and treated fabrics that include N- CO content, FTIR, SEM, EDX, fabric tensile, fabric abrasion resistance, fabric stiffness, fabric thermal and evaporative moisture resistance. This chapter also presents the experimental results and discusses the implication of the results on the objective as stated in Chapter 1. Results are presented in different sections as shown below.

Formation of DMH – CPTES Adduct

Dimethyl hydantoin (DMH) and γ - Isocyanatopropyl triethoxy silane (CPTES) were allowed to react at 65 $^{\circ}$C for 8 hours by first dissolving DMH in acetone and dimethylsulfoxide and then mixing the solution with CPTES in presence of catalyst, Tertiary ethyl amine. The reaction was carried out in a reactor that has a capacity of 250 ml. The reactor was assembled and proper connections were made. Nitrogen was supplied to create an inert environment. The detailed scheme is provided in the Methods section.

Dimethyl hydantoin (DMH)

γ - Isocyanatopropyl triethoxy silane (CPTES)

Tertiary ethyl amine   65°C, 8 hrs

γ –Isocyanatopropyltriethoxysilane - Dimethyl hydantoin adduct
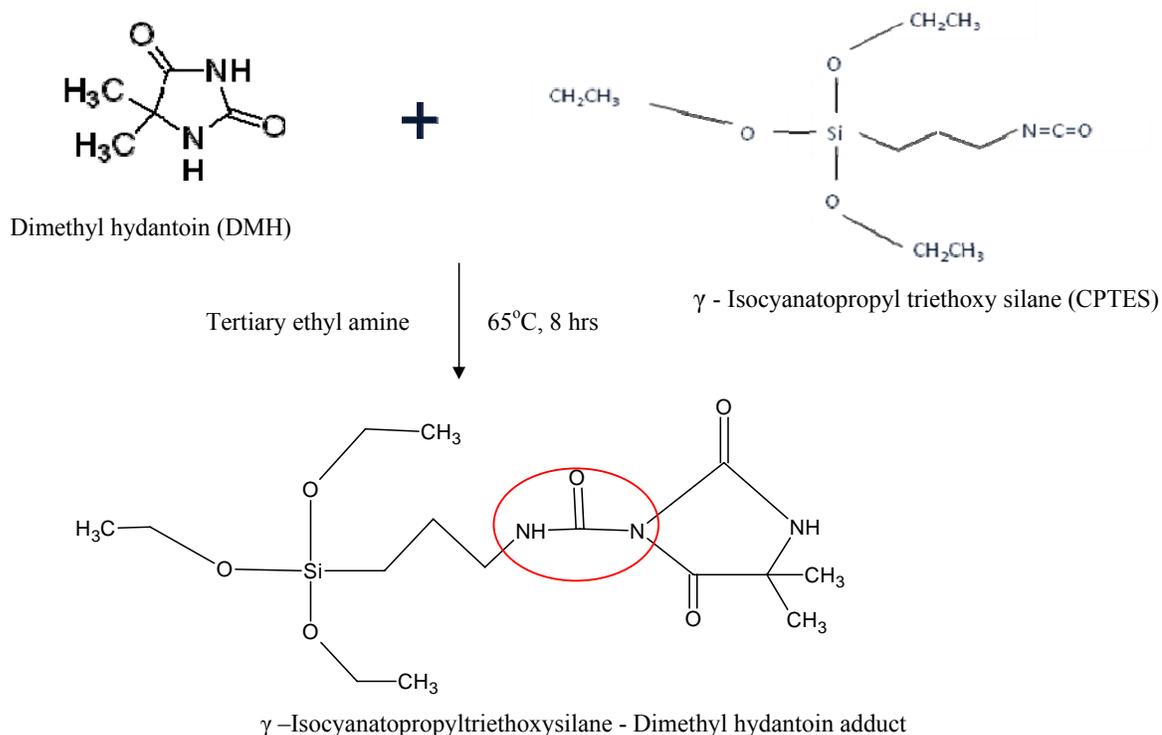
Schematic 4.1. Synthesis of γ –Isocyanatopropyltriethoxysilane and Dimethyl hydantoin adduct

Scheme 4.1 shows the basic reaction principle between DMH and CPTES in which isocyanate (NCO) group of CPTES form bond with NH site of DMH. This results in the formation of isocyanatopropyltriethoxysilane –dimethyl hydantoin adducts.

Results of NCO%

NCO is a significant bond representing CPTES, and this is the active bond site which reacts with NH site of hydantoin ring. Our aim was to react one NH site with NCO of CPTES, while the remaining NH group on the DMH would be allowed to react with chlorine. The important test to determine the degree of reaction is to find the NCO content before and after the reaction by using the titration method illustrated in method section. Isocyanate component of the DMH-CPTES adduct was calculated using following equation (1):

$$\% \text{ NCO} = \frac{(B\text{-}S) \times N \times 4.202}{W} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(1)$$

Where B = Blank reading

S = burette reading with sample

N= normality of the HCL

W = weight of the sample

% NCO of the treated and untreated sample is shown in Table 4.1

Table 4.1

% NCO content in treated and untreated sample

Sample	% NCO
Untreated sample	13.0
Treated sample	2.63

From Table 4.1, we can notice that there is a drastic reduction in the % NCO content in the treated sample. This proves the formation of DMH-CPTES adduct between CPTES and DMH. The degree of reaction is calculated to be 80%. Following this it can be concluded that 80% reaction was completed and % NCO has reduced after reaction because of the complex formation between CPTES and DMH.

DMH – CPTES Analysis by FTIR

Infrared spectroscopy technique is an important technique to identity the chemical group in a material. Different chemical compounds absorb infrared radiation at frequencies corresponding to their own molecular vibrational frequencies. Using this technique, presence/absence of NCO group in the treated fabric can be easily identified. Fourier Transform Infrared Spectra (FTIR) of unreacted and reacted chemical solution containing DMH, CPTES was compared using Bruker FTIR spectrometer (model Tensor 27) in order to

determine the presence of NCO peaks and relative intensity. The FTIR spectra of DMH-

CPTES solution before and after adduct formation, respectively, are shown in Figure 4.1 and

Figure 4.2. Before the reaction, samples show a band at 2271 cm^{-1}, attributed to the stretching

of the NCO group present in the unreacted solution. This refers to the NCO group present in

CPTES compound. The FTIR spectra of the solution after 8 hours reaction show the

disappearance of band at 2271 cm^{-1} as shown in Figure 4.2. Thus it is clear that NH site of

DMH has reacted with NCO groups of silane (CPTES) and as a consequence reaction took

place resulting into the formation of urea linkage between hydantoin and silane.
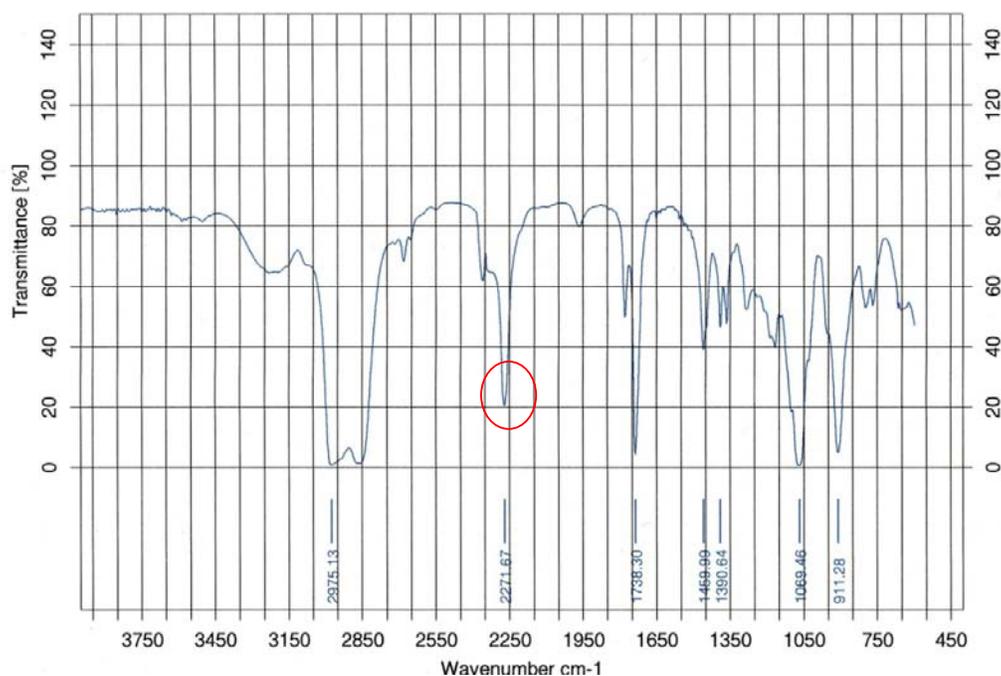
Figure 4.1. FTIR spectra of the unreacted DMH-CPTES solution showing presence of NCO peak at 2271 cm^{-1}
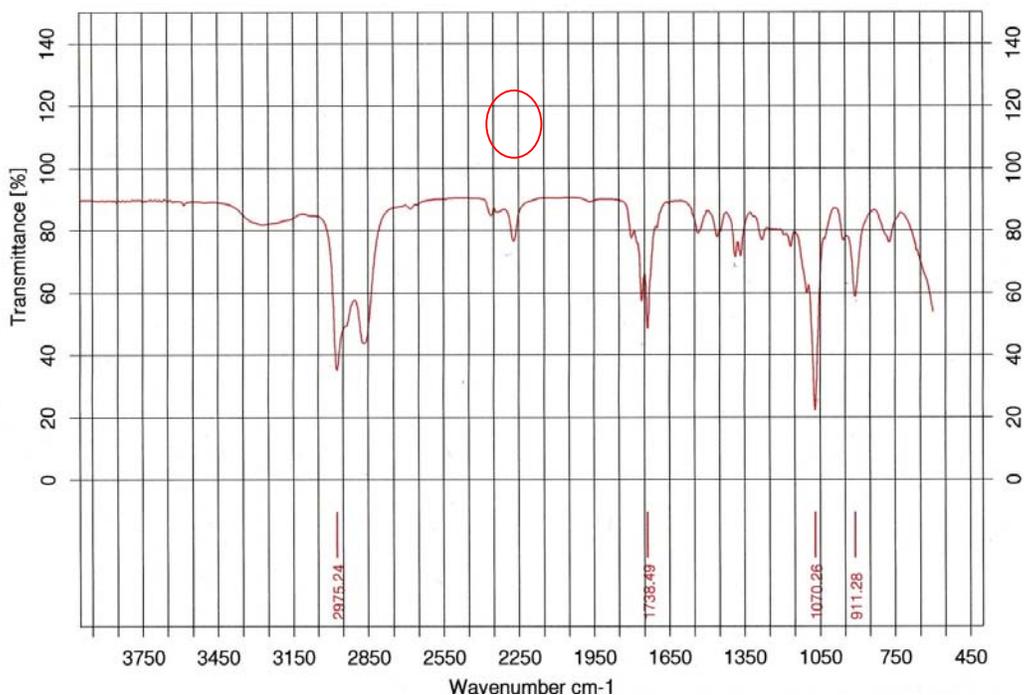
Figure 4.2. FTIR spectra of the reacted DMH-CPTES solution showing absence of NCO peak at 2271 cm^{-1}

NCO peak cannot be seen in the spectra for the reacted product (DMH-CPTES Adduct) indicating the formation of complex between DMH and CPTES.

Application of DMH-CPTES Adduct on Fabric

The substrate used in the study is 50/50 Nylon/Cotton blend fabric and cotton contains 95% natural cellulose. It is believed that DMH–CPTES adduct form an ether linkage with the cotton cellulose. This covalent bond between cellulose and Adduct provides a durable linkage that withstands vigorous washing. Scheme 4.2 shows the application of DMH-CPTES adduct on the fabric.

Cellulose

γ –Isocyanatopropyltriethoxysilane - Dimethyl hydantoin adduct
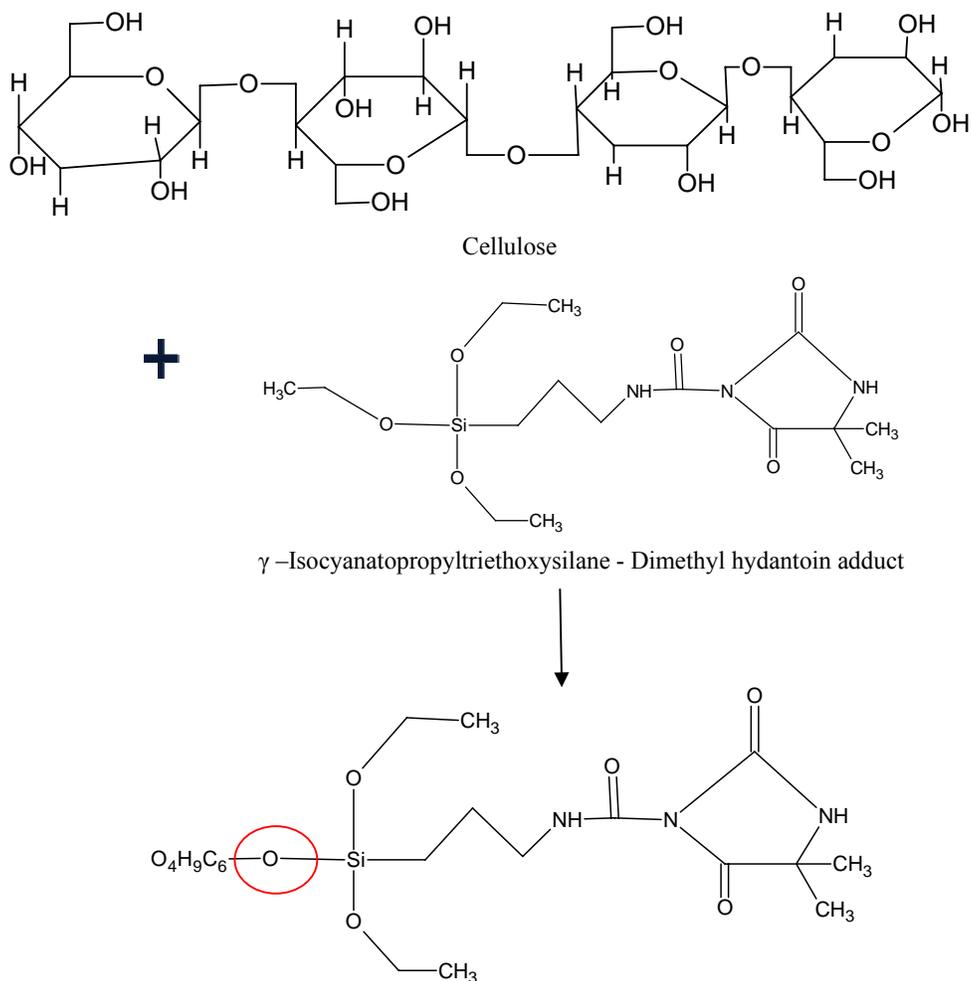
Schematic 4.2. Application of DMH –CPTES on Nylon/Cotton Fabric

The application of DMH-CPTES adduct to the fabric was performed according to the pad-dry- pad -dry-cure method (Schematic 4.2). The process is explained fully in the method section.

The percentage weight increase of the fabric was observed to be 52.3% after the application of DMH-CPTES adduct and drying and curing. After chlorination and washing, the weight of the fabric decreased and the final percent weight increase was 7.14%, which is the final add on (%) of chemicals on fabric. The fabric thickness of untreated and treated fabric was measured using Elektro Physik (Mini Test 600 BF) as explained in the method section. The average and standard deviation of fabric thickness are reported in Table 4.2.

Table 4.2

Fabric thickness data of the treated and untreated fabric

	Untreated fabric	Treated fabric 6% Cl
Average thickness	405.25	448.375
Standard deviation	5.18	5.63

Chlorination

The chlorination of the sample was done using sodium hypochlorite solution, which introduces chlorine as an antimicrobial agent onto the fabric as shown in Schematic 4.3. The chlorination of DMH-CPTES adduct treated fabric samples were conducted at two concentrations (6%) NaOCl and (10%) NaOCl. NaOCl solution was made in water and then fabric samples were immersed in the solution for 15 min at 80°C and then 15 min at room temperature. The fabric was then dried at 60 °C for 4 hour and then rinsed and washed. Chlorine forms bond with DMH in adduct and the *N*-Halamine (N-Cl) structure was created.
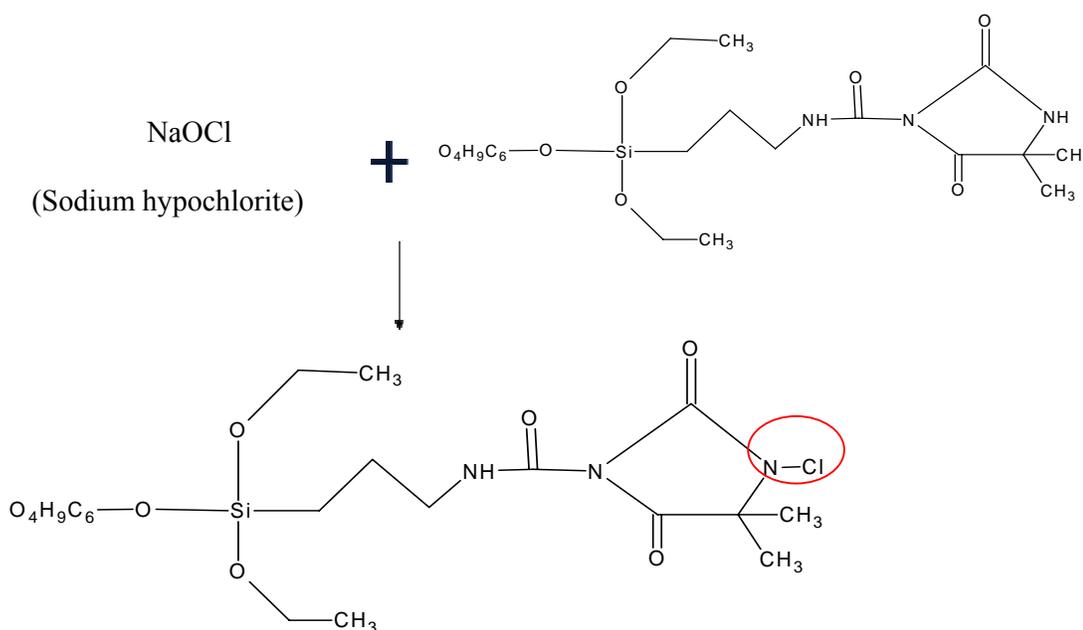
Schematic 4.3. Chlorination of the DMH-CPTES adduct treated fabric

A number of literature emphasize on the role of halogenated polymers on the antibacterial properties. Literature demonstrates that *N*-Halamine structures exhibit not only strong antimicrobial properties but also provided durable and regenerable biocidal properties (Sun & Sun, 2001).

Gottardi and Nagl (2005) explained the role of chlorine as an important disinfectant in their article. It is shown that use of chlorine as antimicrobial agent became important following the reduction of puerperal fever using chlorine bleach. Later on, active chlorine compounds such as O- Cl and N-Cl gained attention as strong disinfectant. The action of active chlorine compounds on the microbes was divided in two sections: a) nonlethal – reversible chlorination of the bacterial surface, and b) penetration through the cell covers combined with irreversible alterations. The chlorine cover on the bacteria remains for a very short time, and it involves three types of mechanism by which chlorine covers degrade (Gottardi and Nagl, 2005).

i) Reaction with reducing substances:

ii) Transhalogenation:

iii) Intra-molecular redox reactions (elimination of HCl):

The *N* – Halamine compounds have a broad spectrum of antimicrobial activities that have been used in water treatment. Their antimicrobial activity is a consequence of the high oxidative attributes of the halamine bond (N-Cl). In deactivating microorganism the *N* – Halamine bond is reversibly reacted with N-H. This inactive material, however, can be recharged with a chlorine bleaching solution during laundering (Gao and Cranston, 2008).

N-Halamine treatment may result in a substantial amount of absorbed chlorine remaining on the fabric surface if is not covalently bonded to *N* –Halamines, and this may

discolor fabrics or produce odor unless the amount of chlorine treatment is optimized and the fabric is properly washed after chlorination.

SEM Analysis

SEM micrograph was used to evaluate the surface morphology of both the untreated and silane and N-halamine treated fabric. Figures 4.3 – 4.6 show the SEM micrograph of untreated Nylon/Cotton fabrics, unwashed silane –DMH adduct treated Nylon/Cotton fabrics with 6% NaOCl and 10% NaOCl, respectively. It was noticed that the surface of the treated textile was coarser than that of untreated textile because of the silicon matrix on fibers.
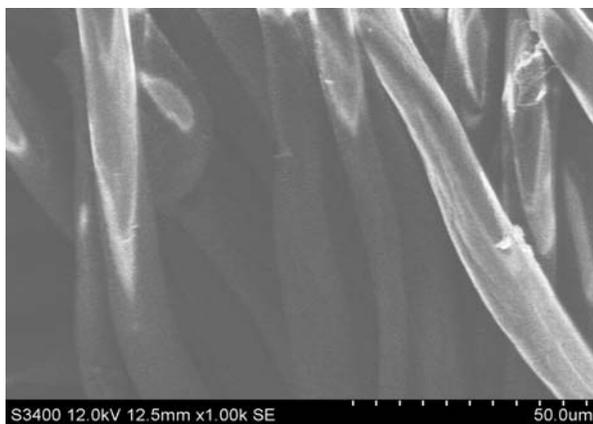
Figure 4.3. SEM micrograph of untreated Cotton/Nylon fabric
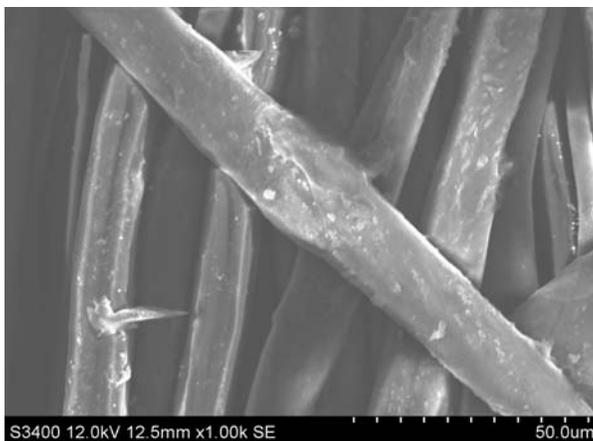
Figure 4.4. SEM micrograph of Silane and *N*-Halamine treated unwashed
Nylon/Cotton Fabric with 6% NaOCl
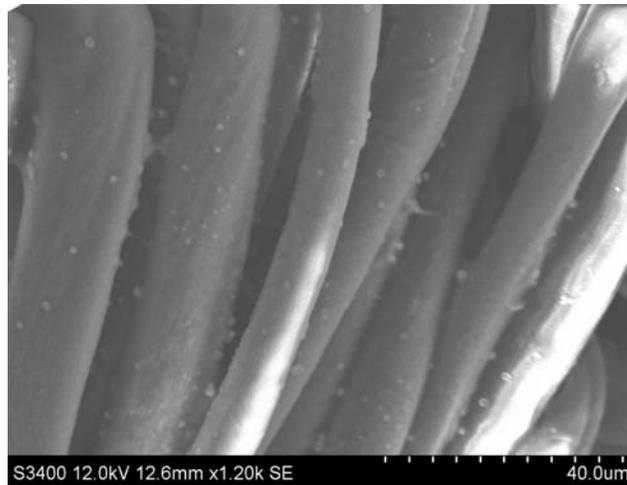
Figure 4.5. SEM micrograph of Silane and *N*-Halamine treated unwashed Nylon/Cotton Fabric with 10% NaOCl
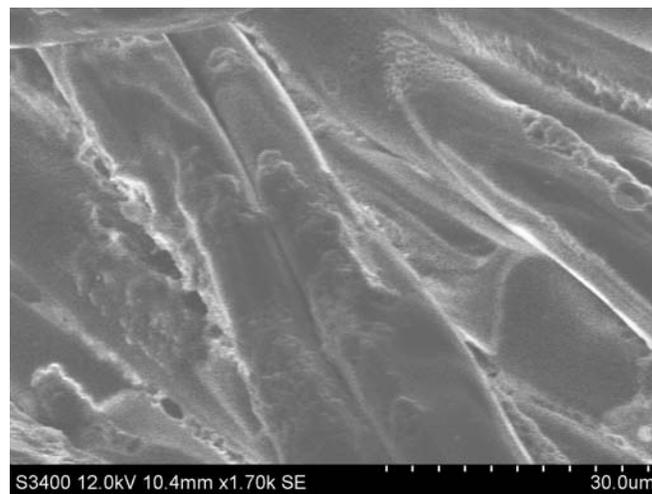
Figure 4.6. SEM micrograph of Silane and *N*-Halamine treated unwashed Nylon/Cotton Fabric (with 10% NaOCl) at higher magnification

Figures 4.5 and 4.6 show the morphological changes due to the coating of *N*-Halamine and Silane on Nylon/Cotton fabric containing 6% NaOCl and 10% NaOCl, respectively. These figures show concentrated particles at some locations on the fabric and also the modification in the fiber surface at a magnification near 1.2 k at Scanning Electron Microscopy (Model 3400 N). It appears in SEM image of the fabric treated with 10% chlorine that some modification of the fiber surface occurred and at that high level of chlorine treatment, oxycellulose may have formed.

The SEM micrographs of the washed samples were also collected to examine the washing effects of the treatment. Figures 4.7 and 4.8 show the SEM micrograph of the *N*-Halamine and Silane treated and washed fabric.
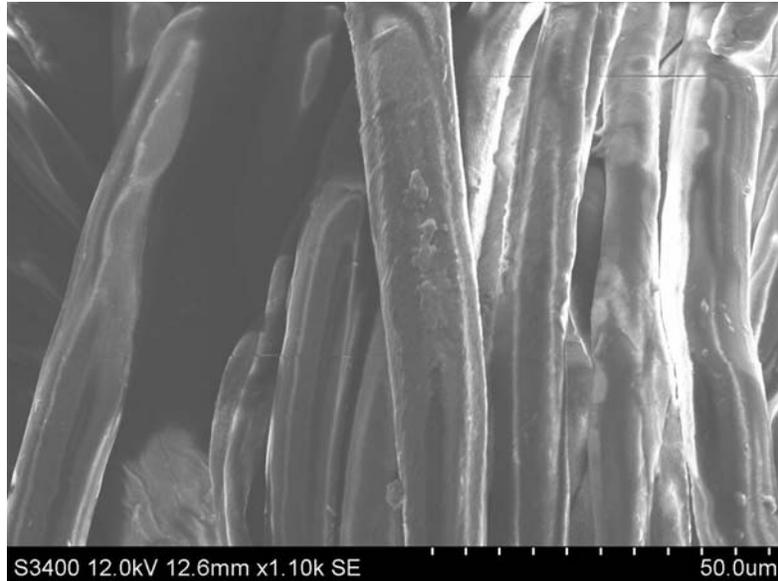
Figure 4.7. SEM image of Silane and *N*-Halamine treated washed Nylon/Cotton Fabric (6 % chlorine)
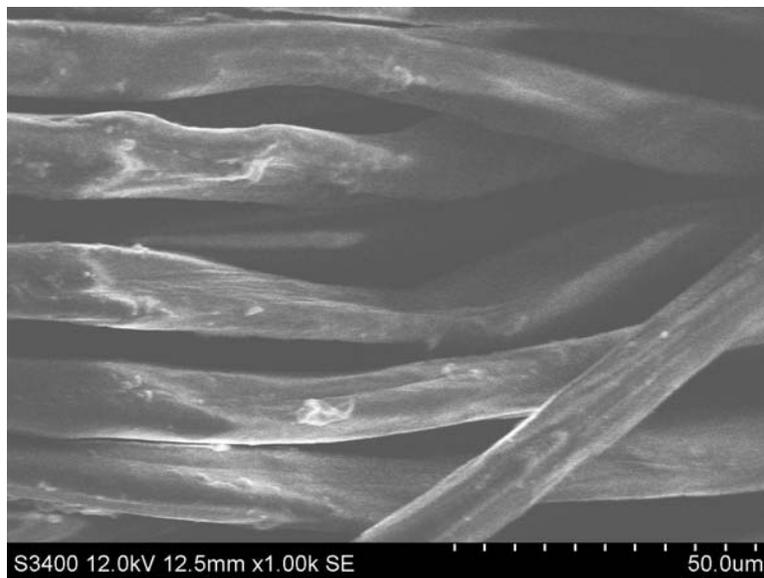
Figure 4.8. SEM image of Silane and *N*-Halamine treated washed Nylon/Cotton Fabric (10 % chlorine)

Energy Dispersive X-ray Spectrometry

Energy dispersive x-ray (EDX) analysis of the untreated and treated fabric was carried out to identify different elements present on the fabric surface due to prior treatments or processing.   EDX was examined using EDS 2006 (IXRF systems, Inc. 500 digital processor). For the EDX analysis, a good image was captured at 30 ampere probe current and 12 kV and then voltage was increased to 20 kV and probe current was raised to 74 ampere. Counts near to 1000 c/s indicate a good condition for EDX analysis. It is shown that a slight amount of Na, Cl, Si, Mg, and others are present in trace amounts on untreated fabric. Figures 4.9 – 4.13 show the EDX spectra of untreated Nylon/Cotton fabrics, unwashed and washed Nylon/Cotton fabrics treated with 6% NaOCl and 10% NaOCl CPTES-DMH adduct.

Figure 4.9. EDX spectra of untreated Nylon/Cotton Fabric
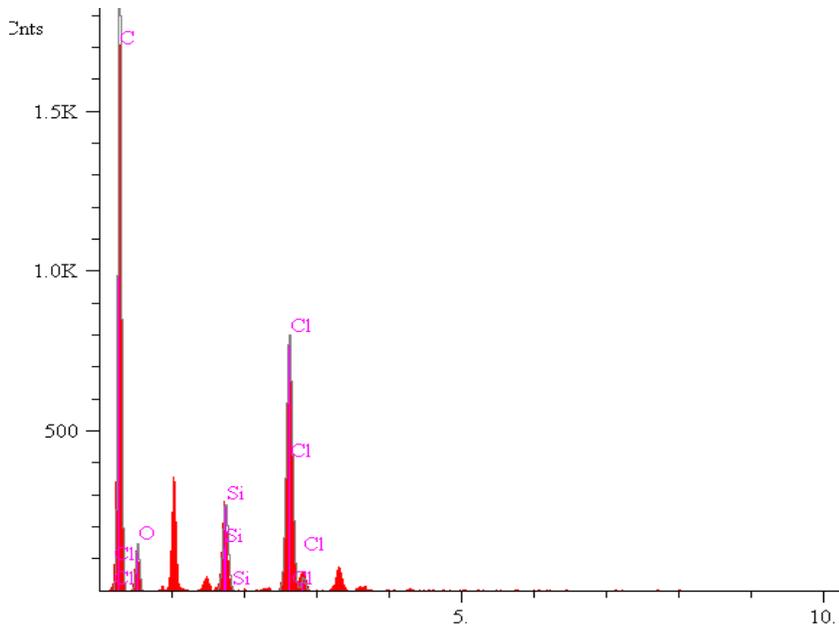
Figure 4.10. EDX spectra of treated unwashed Nylon/Cotton Fabric with 6% NaOCl
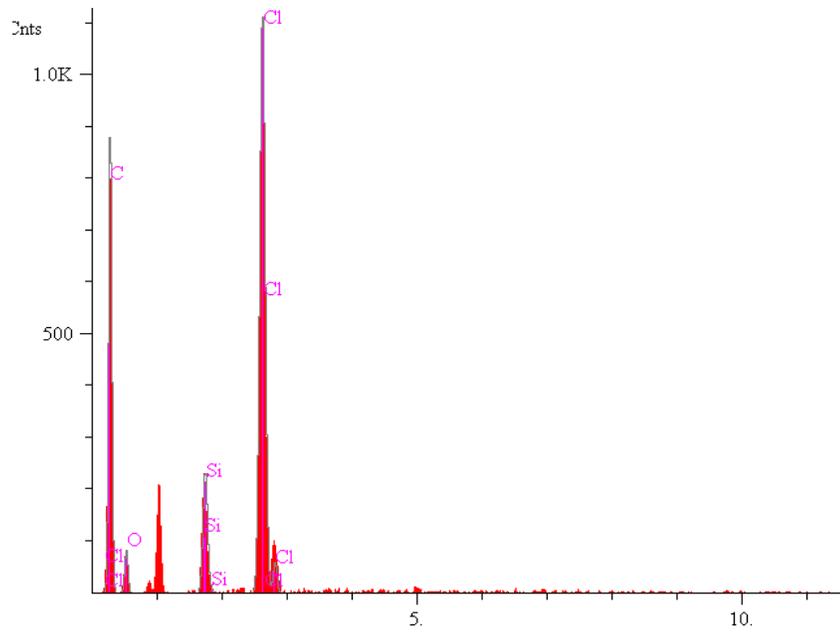
Figure 4.11. EDX spectra of treated unwashed Nylon/Cotton Fabric with 10% NaOCl
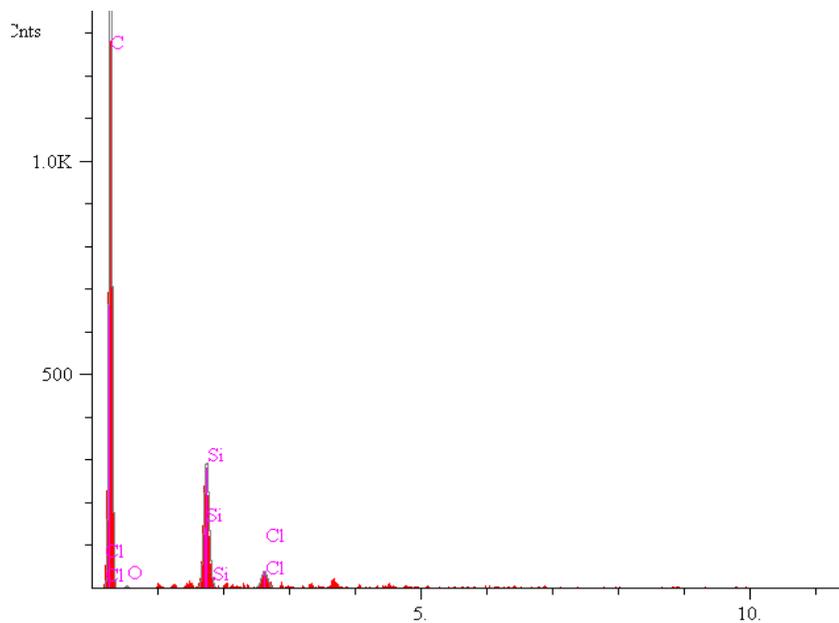
Figure 4.12. EDX spectra of Silane and *N*-Halamine treated washed
Nylon/Cotton Fabric (6% chlorine)
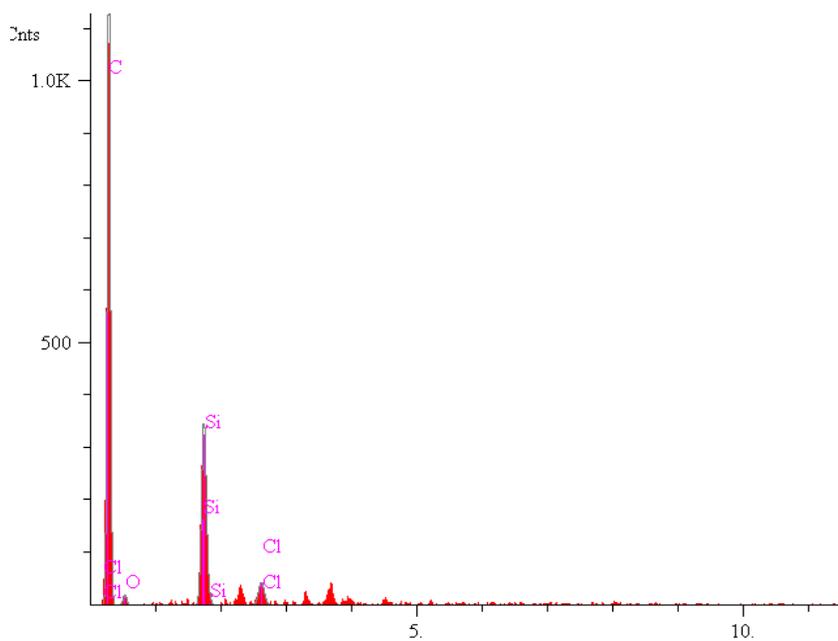
Figure 4.13. EDX spectra of Silane and *N*-Halamine treated washed
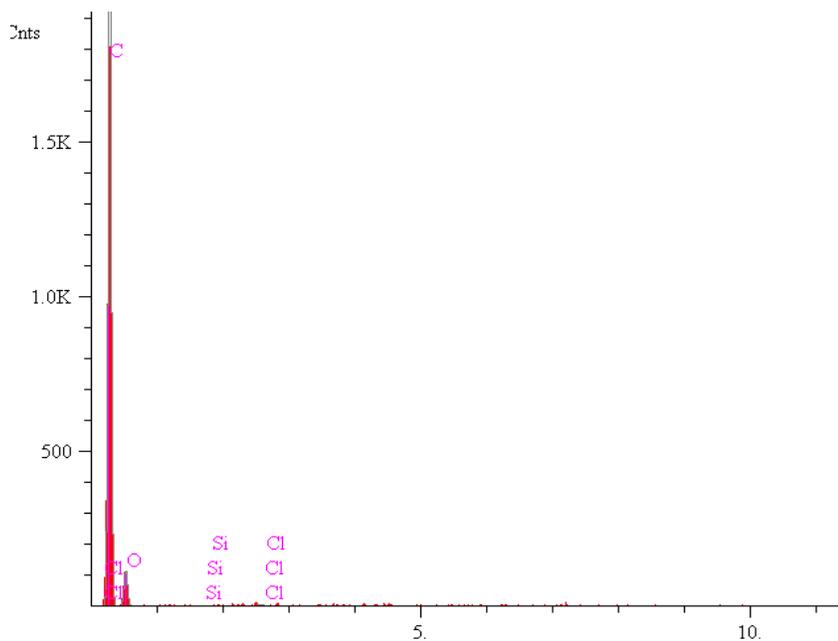Nylon/Cotton Fabric (10% chlorine)

EDX spectrum of the untreated fabric was compared with that of treated fabric and it
was noted that peaks of Chlorine and Silicon are missing in the untreated fabric (Figure 4.9).

The EDX spectrum of the surface of the fabric containing Silane and *N*-Halamine complex is illustrated in Figure 4.10 and Figure 4.11 shows the presence of Chlorine and Silicon along with Carbon and Oxygen. The % concentration of the elements is provided in Table 4.3 for untreated Nylon/Cotton fabrics and unwashed and washed Nylon/Cotton fabrics treated with 6% NaOCl and 10% NaOCl CPTES-DMH adduct.

Table 4.3

Concentration of different elements using EDX analysis of untreated and treated

Nylon/Cotton Fabric

Element	Untreated sample (wt. %)	6% NaOCl Treated fabric (wt. %)		10% NaOCl Treated fabric (wt. %)	
		Unwashed	Washed	Unwashed	Washed
C	82.53	80.39	91.79	77.72	88.62
O	17.23	9.23	0.89	8.12	4.18
Si	0.009	1.97	5.93	1.81	6.02
Cl	0.024	8.42	1.4	12.35	1.19

From the table it can be noticed that concentration of Cl is 8.42% and 12.35%, respectively, for the Nylon/Cotton fabrics treated with 6% and 10 % NaOCl. It further confirms the presence of chlorine particles on the specimen surface depending upon the chlorine concentration added which acts as the antibacterial agent. Presence of higher % of Carbon shows the higher cellulosic content, and presence of Si element proves the silane presence and we can also see some percentage of chlorine. The absence of Nitrogen may be because of presence of DMH inside the coating and not in the detectable range of EDX spectra. It may be also due to overlapping by the broad peaks of Carbon.

Figure 4.12 and Figure 4.13 show the EDX spectra of the *N*-Halamine and Silane treated and washed fabric. Table 4.3 contains the concentration of the elements present after washing. The fabrics thus treated with 10% NaOCl results in 12.4% chlorine, and after soap

washing three times it was seen that chlorine was leached out rapidly during 3 washing cycles and still remained 1.19 % after washing. This is the reason that fabric samples treated with DMH-CPTES adduct and chlorinated using NaOCl still had good antimicrobial activity after 3 soap washings and also implied that even only a small quantity of chlorine existing on fabrics would offer a good inhibition to *Staphylococcus aureus* and *Escherichia coli*. It suggests that the loss of chlorine might be associated with the unattached chlorine that is absorbed by the fabric and mechanically retained.

Antibacterial Efficacy

The antimicrobial property of the specimens was tested using an AATCC method147-2004. The test objective was to determine the antibacterial activity of diffusible antimicrobial agents on treated textile fabric. In this method, the size of the zone of inhibition and the narrowing of the streaks caused by the presence of the antibacterial agent permit an estimate of the residual antibacterial activity.   The average width of a zone of inhibition along a streak on either side of the test specimen is calculated using the following equation:

$$W = (T - D)/2$$

Where:

W = width of clear zone of inhibition in mm

T = total diameter of test specimen and clear zone in mm

D = diameter of the test specimen in mm

There cannot be any bacterial colonies directly under the sample in the contact area in order to be considered acceptable antibacterial activity. The test bacteria were *Staphylococcus aureus* ATCC 6538, Gram positive organism and *Escherichia coli* ATCC 8352, Gram negative organism.

N-Halamine and Silane treated fabrics were soap washed three times for ½ hour at 55 ^oC – 60 ^oC and then rinsed using distilled water, and after wash, the antibacterial properties were tested with results shown in Table 4.4. This Table shows excellent laundering durability of bacteriostasis of *N*-Halamine and Silane treated fabric.

Table 4.4

Antimicrobial Test Data of washed treated and untreated fabric samples against

Staphylococcus aureus and Escherichia coli

Type of Microbial Agent Added	*Staphylococcus aureus*		*Escherichia coli*	
	Growth under the Sample	Zone of Inhibition (mm)	Growth under the Sample	Zone of Inhibition (mm)
N- Halamines and Silane coated 50/50, Nylon/cotton fabric (6% NaOCl)	No	1.75	No	0
N- Halamines and Silane coated 50/50, Nylon/cotton fabric (10% NaOCl)	No	6.05	No	3.45
Untreated Fabric	Yes	0	Yes	0

DMH-CPTES treated fabric specimens with different amount of chlorine to create antibacterial agents exhibited significant biocidal activities with varying degrees of zones of inhibitions depending on the Sodium hypochlorite concentration, while the untreated fabric specimen did not show any antimicrobial activities. It can be seen that the *N*-Halamine and Silane treated Nylon/Cotton fabric when treated with 10 % NaOCl demonstrate a total kill against *Staphylococcus aureus* (gram positive bacteria) with a zone of inhibition of 6.05 mm, while the *N*-Halamine and silane treated Nylon/Cotton fabric that are treated with 6% NaOCl exhibited no growth of bacteria and zone of inhibition of 1.75 mm. This indicates that for both chlorine concentrations no bacterial presence was observed which is considered acceptable antimicrobial activities of a treated fabric. It is to be noted that untreated fabric

exhibited full bacterial growth under the specimen after incubation. The results of the

antimicrobial efficacy against *Escherichia coli* (gram negative) organism can also be seen in

Table 4.4. It shows at 10% chlorination there was no growth under specimen with 3.45 mm

zone of inhibition. For 6% chlorination, there was also no growth but zero zone of inhibition.

The fabric exhibited acceptable antimicrobial activity according to the AATCC 147-2004 test

even at 6% chlorination.

It is to be noted that the tests were conducted on the sample after three vigorous

washings with soap at an elevated temperature. During washing some of the chlorine was

lost, particularly, which was absorbed by the fabric instead of covalently bonded to adduct.

These results confirmed that the fabric has antibacterial activities against both gram positive

(*Staphylococcus aureus*) and gram negative (*Escherichia coli)* organisms. These two

organisms were chosen for the biocidal activities because they are the most commonly used

organisms for testing purposes.

It is also possible that *N*-Halamine at the surface returned to their hydantoin

precursors but the one remained inside the coating layer acts as an active antibacterial agent.

Literature also shows that after rebleaching the sample, *N*-Halamine can be regenerated and

can kill bacteria again.

Testing of Fabric Properties

Durability

Tensile

Tensile strength of the fabric samples was measured on Galdabini Quasar 250 using

Grab test according to ASTM D 5034. Tensile strength results for treated and untreated fabric

are given in Table 4.5. From the breaking load and % elongation at rupture values for

untreated and treated, it can be concluded that there is no significant decrease in fabric

strength values because of the *N*-Halamine and Silane coating. One-way ANOVA at 95% (α=0.05) confidence level was carried out to determine the significant difference in tensile property between untreated and treated fabric. The results of One-way ANOVA are given in Table 4.6-4.7.

Table 4.5

Tensile data of untreated and treated Nylon/Cotton fabric (Appendix B.1)

	Untreated Nylon/Cotton fabric		*N*-Halamine and Silane coated Nylon/Cotton fabric	
	Breaking load, lbf	Elongation at rupture, %	Breaking load, lbf	Elongation at rupture, %
Average	44.46	121.96	44.08	122.72
Standard deviation	5.11	2.73	3.86	2.99

Table 4.6

One-way ANOVA results for breaking load

Source	Degrees of freedom	Sum of Squares	Mean square	F-Value	p
Model	1	0.88	0.88	0.11	0.75
Error	8	65.43	8.18		
Corrected total	9	66.31			

Table 4.7

One-way ANOVA results for Elongation at rupture

Source	Degrees of freedom	Sum of Squares	Mean square	F-Value	p
Model	1	5.96	5.96	0.29	0.60
Error	8	164.02	20.50		
Corrected total	9	169.98			

From the table, p value (0.75) for breaking load > α (0.05), and p value for elongation at rupture 0.60 > 0.05. This shows that there is no significant difference in the breaking load and elongation at rupture values between untreated and treated fabric at 95% confidence level. Therefore it can be concluded that presence of *N*-Halamine and Silane in the treated fabric does not deteriorate the fabric tensile properties.

Abrasion

Abrasion resistance of the fabrics was determined using Martindale abrasion tester according test method ASTM D 4966 -98. The weight loss % for the untreated and treated Nylon/Cotton fabric is shown in Table 4.8. The weight loss for both untreated and treated fabrics is found to be less than 0.5%. This shows that fabric has very good abrasion resistance property. Table 4.8 demonstrates that abrasion resistance improved as compared to untreated fabric. This may be due to the coating layer which reduces the chances of pill formation and weight loss. But from the results of One-way ANOVA at 95% (α=0.05) confidence level, p-value is found to be 0.14 > 0.05 (Table 4.9). This shows that there is no significant difference between the abrasion resistance of untreated and treated fabrics at 95% confidence level.

Table 4.8

Abrasion resistance results of untreated and treated Nylon/Cotton fabric (Appendix B.2)

	Untreated Nylon/Cotton fabric	*N*-Halamine and Silane coated Nylon/Cotton fabric
	% Weight loss	% Weight loss
Average	0.28	0.14
Standard deviation	0.17	0.09

Table 4.9

One-way ANOVA results for % Weight loss

Source	Degrees of freedom	Sum of Squares	Mean square	F-Value	p
Model	1	0.05	0.05	2.61	0.14
Error	8	0.14	0.02		
Corrected total	9	0.19			

Stiffness

Stiffness test was conducted on taber stiffness equipment using ASTM D 5342-97 test method. Stiffness is a very important property of textile used for apparel construction. Average and standard deviation of stiffness data for untreated and treated fabrics are given in Table 4.10. One-way ANOVA at 95% (α=0.05) confidence level was carried out to determine the significant difference in the stiffness value between untreated and treated fabric. The results of One-way ANOVA are given in Table 4.11.

Table 4.10

Stiffness data of untreated and treated Nylon/Cotton fabric (Appendix B.3)

	Untreated Nylon/Cotton fabric Stiffness (milli-newton meters)	*N*-Halamine and Silane coated Nylon/Cotton fabric Stiffness(milli-newton meters)
Average	2.92	2.95
Standard deviation	0.06	0.07

Table 4.11

One-way ANOVA results for Stiffness data

Source	Degrees of freedom	Sum of Squares	Mean square	F-Value	p
Model	1	0.90	0.90	2.62	0.1443
Error	8	2.75	0.34		
Corrected total	9	3.65			

From the table, p value is $0.1443 > 0.05$. This shows that there is no significant difference between the stiffness value of untreated and treated fabrics. Thus it can be concluded that fabric stiffness property is unaltered with *N*-Halamine and Silane coating.

Comfort properties

Thermal and Evaporative resistance values are important factors in determining the fabric comfort properties. Thermal and Evaporative resistance of untreated and treated fabric was measured according to ASTM F 1868-02 to analyze the effect on *N*-Halamine and Silane coating on fabric comfort properties. The values of Thermal and Evaporative resistance for the fabrics are given in Table 4.12 and 4.13, respectively. No statistically significant changes in the comfort parameters were observed due to the fabric treatment.

Table 4.12

Dry Thermal resistance data of untreated and treated Nylon/Cotton fabric (Appendix B.4)

	Untreated Nylon/Cotton fabric	*N*-Halamine and Silane coated Nylon/Cotton fabric
	Dry Thermal resistance, Rct-Rcbp	Dry Thermal resistance, Rct-Rcbp
Average	$0.019 \text{ m}^2 \text{ }^{\circ}\text{C /W}$	$0.025 \text{ m}^2 \text{ }^{\circ}\text{C /W}$
Standard deviation	0.007	0.004

Table 4.13

Evaporative resistance data of untreated and treated Nylon/Cotton fabric (Appendix B.5)

	Untreated Nylon/Cotton fabric	*N*-Halamine and Silane coated Nylon/Cotton fabric
	Evaporative resistance, Rct-Rcbp	Evaporative resistance, Rct-Rcbp
Average	3.297 m^2 ^{o}C /W	4.830 m^2 ^{o}C /W
Standard deviation	1.763	0.893

Table 4.14

One-way ANOVA results for Dry Thermal Resistance data

Source	Degrees of freedom	Sum of Squares	Mean square	F-Value	p
Model	1	0.00011	0.00011	4.34	0.0708
Error	8	0.00019	0.00002		
Corrected total	9	0.00030			

Table 4.15

One-way ANOVA results for Evaporative Resistance data

Source	Degrees of freedom	Sum of Squares	Mean square	F-Value	p
Model	1	2.536	2.536	2.56	0.1484
Error	8	7.932	0.992		
Corrected total	9	10.468			

The results of One-way ANOVA at 95% (α=0.05) confidence level for thermal and evaporative resistance are given respectively in Table 4.14 and Table 4.15. For dry thermal resistance p value (0.07) is greater than α value (0.05). This shows that there is no significant

difference between the dry thermal resistance value of treated and untreated fabrics. Also, p value (0.1484) for evaporative resistance is greater than α value (0.05). This shows that there is no significant difference between the evaporative resistance value of treated and untreated fabrics.

Thickness

Thickness of the fabric coating was determined according to ASTM D1777-96(02). Table 4.16 shows the thickness value of the untreated and treated fabric. From the table it is clear that thickness of the treated fabric is higher than of untreated fabric because of *N*-Halamine and Silane coating. It was also observed in the SEM images (Figure 4.4 - 4.6) that some swelling took place due to the high level of chlorine treatment.

Table 4.16

Thickness data of untreated and treated Nylon/Cotton fabric (Appendix B.6)

	Untreated Nylon/Cotton fabric Thickness	*N*-Halamine and Silane coated Nylon/Cotton fabric Thickness
Average	405.25 µm	448.38 µm
Standard deviation	5.18	5.63

One-way ANOVA at 95% (α=0.05) confidence level was carried out to determine the significant difference in thickness value between untreated and treated fabric. The results of One-way ANOVA are given in Table 4.17.

Table 4.17

One-way ANOVA results for Thickness

Source	Degrees of freedom	Sum of Squares	Mean square	F-Value	p
Model	1	7439.06	7439.06	254.4	<0.0001
Error	14	409.38	29.24		
Corrected total	15	7848.44			

From the table, p value is <0.0001, which is less than α value of 0.05. This shows that there is a significant difference between the thickness value of untreated and treated fabrics. Thus it can be concluded that fabric thickness is changed with the application of *N*-Halamine and Silane coating; however, this change is so small that a textile use implication will be minimum.

CHAPTER 5: CONCLUSION

The study analyzes a method which probably is less costly, more convenient and provides durable antimicrobial property for everyday clothing, hygiene products, and military clothing.

The traditional method exigency in providing durable treatment leads to the development in this area. The further research in this area will contribute to an improved process, which, instead of coating the antimicrobial agent on the fabric, forms a chemical bond with the fabric. This research study will also be useful to different application areas.

The increased popularity of antimicrobial functional textiles in various application areas means that people are looking forward for a feasible, easy, and durable process that can be carried out in the textile processing plants, creating more durable property.

Objective 1: Develop the reaction between the isocyanatopropyltriethoxy silane and Dimethyl hydantoin in presence of triethylamine.

Conclusion 1: Isocyanatopropyltriethoxysilane and Dimethyl hydantoin adduct was formed successfully as supported by FTIR and NCO test results.

Objective 2: Apply antimicrobial agent on the 50/50 nylon/cotton blend fabric using pad – dry – cure method.

Conclusion 2: Chlorination of the treated samples was carried out successfully. A double pad – dry – cure method was used to apply the antimicrobial agent on the 50/50 nylon/cotton blend fabric as described in results and discussion section.

Objective 3: Determine the antimicrobial efficacy, washing durability of the treated fabrics, and its effect on chlorine content.

Conclusion 3: Antimicrobial efficacy against *staphylococcus aureus and Escherichia Coli* after soap washing was tested using parallel streak method and is proved that fabric provided effective antimicrobial activity against both gram positive and gram negative organisms.

Objective 4: Determine the effect of antimicrobial coating on the textile properties such as thermal and moisture resistance, stiffness, tensile resistance, and abrasion resistance property.

Conclusion 4: The effect of antimicrobial coating on the textile properties such as thermal and moisture resistance, stiffness resistance, tensile resistance, and abrasion property were also measured and results lie in the acceptable range without much alteration of the fabric properties as discussed in detail in the results and discussion section.

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Appendix A: Formulation of Chemicals used in the experiment

DMH – CPTES adduct formation	5,5 Dimethyl hydantoin - 13.16 g
	Acetone - 76.25 g
	Dimethyl sulfoxide – 5.7 g
	Tertiary ethyl amine – 0.1g
	Cyanatopropyltriethoxysilane – 23.2 g
Chlorination of fabric	
a) 6% NaOCl	NaOCl 6.03 g
	Water 94 g
b) 10 % NaOCl	NaOCl 10 g
	Water 90 g

Appendix B: Fabric Test Results

B.1 Tensile Strength Results

Grab test

Specimen dimensions - 1" x 9" with specimen length in between jaws = 6"

Specimen code	Elongation at Rupture	Load Max	Modulus
	%	(lbf)	(lbsf/inch^2)
Untreated 1	46.13	124.77	29760.06
Untreated 2	38.34	124.49	30157.42
Untreated 3	43.62	118.31	28852.64
Untreated 4	47.41	122.52	28112.27
Untreated 5	52.26	120.55	28945.77
Treated 1	42.42	127.02	24398.04
Treated 2	44.9	119.43	22270.49
Treated 3	43.75	121.68	21333.5
Treated 4	49.76	121.12	21338.61
Treated 5	39.21	124.36	30451.22

B.2 Abrasion Results

S. No.	Untreated fabric			N-Halamine and Silane coated Cotton/Nylon blend fabric		
	Initial Wt.	Final Wt.	% Wt loss	Initial Weight	Final weight	% Wt loss
1	0.3411	0.3406	0.1466	0.388	0.3874	0.1546
2	0.3428	0.3411	0.4959	0.3875	0.3875	0.0000
3	0.3399	0.3392	0.2059	0.381	0.3802	0.2100
4	0.3495	0.348	0.4292	0.3882	0.3873	0.2318
5	0.3415	0.341	0.1464	0.3879	0.3874	0.1289

B.3 Stiffness Results

	Taber Stiffness unit					
	Untreated fabric			N-Halamine and Silane coated Cotton/Nylon blend fabric		
S. No.	LHS	RHS.	Average	LHS	RHS	Average
1	27.5	31	29.25	28.5	31	29.75
2	28	31.5	29.75	27.5	31	29.25
3	27	31	29.00	28	34	31.00
4	27	32	29.5	28	33	30.5
5	27.5	33	30.25	27.5	33	30.25

B.4 Thermal Resistance Properties

Dry Thermal resistance results:

Test method ASTM F1868

Room Temperature = 25^{o}C   Relative Humidity = 65 %

Hot plate temperature =35^{o}C   Specimen dimensions = 10"x10"

S. No.	Sample	Dry Bare plate (Rcbp)	Dry thermal resistance (Rct)	Sample Dry thermal resistance (Rct-Rcbp)
1	Untreated Nylon/ cotton	0.055655	0.085043	0.029385
2	Untreated Nylon/ cotton	0.05426	0.071028	0.01676
3	Untreated Nylon/ cotton	0.050163	0.06593	0.015767
4	Untreated Nylon/ cotton	0.05077	0.065935	0.015165
5	Untreated Nylon/ cotton	0.05132	0.070832	0.019512
6	Sol-gel Treated Nylon/ cotton	0.048613	0.079344	0.030731
7	Sol-gel Treated Nylon/ cotton	0.05077	0.073667	0.022897
8	Sol –gel treated Nylon/Cotton	0.049679	0.073097	0.023418
9	Sol –gel treated Nylon/Cotton	0.050163	0.072429	0.022266
10	Sol-gel Treated Nylon/ cotton	0.054261	0.082206	0.027945

B.5 Evaporative Resistance Results

Test method ASTM F1868

Room Temperature = 25°C   Relative Humidity = 65 %

Hot plate temperature =35°C   Specimen dimensions = 10"x10"

S. No.	Sample	Wet Bare plate (Rebp)	Evaporative resistance (Ret)	Sample Evaporative resistance (Ret-Rebp)
1	Untreated Nylon/ cotton	4.1479	6.1982	2.0502
2	Untreated Nylon/ cotton	4.4342	8.9785	4.5443
3	Untreated Nylon/ cotton	4.35673	8.00263	3.6459
4	Untreated Nylon/ cotton	4.27894	7.24634	2.9674
5	Untreated Nylon/ cotton	4.01245	7.29715	3.2847
6	Sol-gel Treated Nylon/ cotton	4.1022	8.6303	4.5283
7	Sol-gel Treated Nylon/ cotton	4.4342	8.1487	3.7145
8	Sol –gel treated Nylon/Cotton	4.0075	9.3765	5.3690
9	Sol –gel treated Nylon/Cotton	4.0970	9.8046	5.7072
10	Sol-gel Treated Nylon/ cotton	4.3486	9.1734	4.8248

B.6 Fabric Thickness Results

Thickness in μm

S.NO	Untreated fabric	N-Halamine and Silane coated Cotton/Nylon blend fabric
1	404	444
2	404	444
3	409	449
4	414	454
5	404	459
6	409	444
7	399	444
8	399	449

```
data tensile;
input load elongation fabric$;
datalines;
124.77 46.13 untreated
124.49 38.34 untreated
118.31 43.62 untreated
122.52 47.41 untreated
120.55 52.26 untreated
127.02 42.42 treated
119.43 44.90 treated
121.68 43.75 treated
121.12 49.76 treated
124.36 39.21 treated
;
run;
proc glm data=tensile;
class fabric;
model load=fabric;
run;
proc glm data=tensile;
class fabric;
model elongation=fabric;
run;




data abrasion;
input wtloss fabric$;
datalines;
0.1466 untreated
0.4959 untreated
0.2059 untreated
0.4292 untreated
0.1464 untreated
0.1546 treated
0 treated
0.21 treated
0.2318 treated
0.1451 treated
;
run;
proc glm data=abrasion;
class fabric;
model wtloss=fabric;
run;
```

```
data stiffness;
input stiffness fabric$;
datalines;
29.25 untreated
29.75 untreated
29 untreated
29.5 untreated
30.25 untreated
29.75 treated
29.25 treated
31 treated
30.5 treated
30.25 treated
;
run;
proc glm data=stiffness;
class fabric;
model stiffness=fabric;
run;




data thermal;
input thermal fabric$;
datalines;
0.0294 untreated
0.0168 untreated
0.0156 untreated
0.0152 untreated
0.0195 untreated
0.0307 treated
0.0229 treated
0.0234 treated
0.0222 treated
0.0279 treated
;
run;
proc glm data=thermal;
class fabric;
model thermal=fabric;
run;


data evaporative;
input evaporative fabric$;
datalines;
2.0502 untreated
4.5443 untreated
3.6345 untreated
3.8546 untreated
3.7645 untreated
4.5283 treated
3.7145 treated
5.3690 treated
5.7072 treated
4.8248 treated
;
run;
```

```
proc glm data=evaporative;
class fabric;
model evaporative=fabric;
run;



data thickness;
input thickness fabric$;
datalines;
404 untreated
404 untreated
409 untreated
414 untreated
404 untreated
409 untreated
399 untreated
399 untreated
444 treated
444 treated
449 treated
454 treated
459 treated
444 treated
444 treated
449 treated
;
run;
proc glm data=thickness;
class fabric;
model thickness=fabric;
run;
```