

ABSTRACT

HALBUR, JONATHAN CHANDLER. Co-Presence of Durable Flame Retardant and Repellent Nano-Finishes. (Under the direction of committee Dr. Xiangwu Zhang).

Due to the costs associated with processing and materials, and the inherent difficulties of applying durable flame retardant and/or repellent finishes, alternatives to conventional finishing methodologies are of large interest in the textile industry. Surface modification of textile substrates using mixed silanes and ceramic nanoparticles have become of interest as a means of functionalizing textiles.

Blended 50/50 polyester/cotton fabrics were treated with a combination of ceramic nanoparticles, hydrophobic silanes (such as hexadecyltriethoxysilane), silane crosslink enhancers [such as 1,3 bis(triethoxysilyl)ethane], and flame retardants [such as tetrakis(hydroxymethyl)phosphonium chloride (THPC) and urea]. These fabrics were treated using conventional pad-dry-cure laboratory scale processing. Following finishing, fabrics were evaluated for flame resistant performance using a vertical flame chamber. Fabrics were also evaluated for repellency through the use of a goniometer. After initial testing, all fabrics were laundered, dried, and re-tested to evaluate the durability of both flame resistance and repellency.

Results of this work show that the use of organofunctional silane crosslink enhancers, hydrophobic silanes, ceramic nanoparticles, and THPC/Urea flame retardants was successful in creating fabrics with durable flame resistant and water repellent properties. When ceramic nanoparticles were added to the finish, the flame resistance and repellency of the finished fabrics both increased, even at concentrations as low as 0.1% by weight, and the char length, afterflame time, and water contact angle were all enhanced as the concentration of ceramic

nanoparticles increased. When the titania concentration was 1-3%, the use of THPC/Urea was much lower than the recommended level for commercial THPC based FR's. It was also found that titania treated fabrics had better flame resistance than did fabrics treated with silica, but no apparent difference was seen between titania or silica nanoparticles with respect to repellency. In addition, the use of traditional silane crosslink enhancers (such as tetraethoxysilane and 1,3 bis(triethoxysilyl)ethane) were successful in creating finishes that maintain repellency after laundering, but the durability of flame resistance of treated fabrics needed improvement.

In order to improve the durability of flame resistance, organofunctional silane crosslink enhancer 3-isocyanatopropyltriethoxysilane was used. It was found that treated fabrics were durable to laundering and maintained flame retardance even at concentrations as low as 30%, which is 10% lower than the recommended concentration for THPC based flame retardants. For example, prior to laundering, fabrics treated with 5% 3-isocyanatopropyltriethoxysilane, 2% hexadecyltriethoxysilane, 1% titania, and 30% THPC/Urea had average char lengths of 3.2 inches and average contact angles of 141°; after laundering, average char length was 3.4 inches and average contact angle was 135°. The retention of both flame resistance and repellency after laundering shows much promise for the use of multifunctional silanes, ceramic nanoparticles, and phosphorus based FR's in finishing fabrics to create dual functionality.

It is suggested that future work should focus on further increasing the durability of the finish to laundering, as well as incorporating the finish on different types of fibers. Additional organofunctional silanes, flame retardants, and curing processes should be investigated also.

Co-Presence of Durable Flame Retardant and Repellent Nano-Finishes

by
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Biography

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1 Introduction

The purpose of this research is to use commercially available ceramic nanoparticles (TiO_2 and SiO_2), tetrakis hydroxyphosphium chloride (THPC) flame retardants, and multifunctional silanes to produce durable flame retardant and repellent fabric finishes. Due to the emphasis of the research on ceramic nanoparticles and multifunctional silanes, the literature review will describe the principles behind repellency and flame retardance, mechanisms for fabric functionalization, and the properties of ceramic nanoparticles.

Due to the fact that synergistic effects between the repellent and flame retardant finishes are desired, it is important to understand surface energy and its relation to repellency, as well as the combustion process and the mechanisms for flame retardancy. Fabrics used for this research are 50/50 polyester/cotton blends, which were chosen due to their widespread use in industry. Furthermore, 50/50 polyester/cotton blends are of great interest for this research because of the difficulty in achieving durable flame retardant properties on synthetic/natural blends. Durable flame retardant properties are difficult to achieve on blended synthetic/natural blended fabrics due to the inability of many flame retardants to bond to both synthetic and natural fibers at the same time, and what is known as the “wicking” effect, where charred cellulosic fibers trap synthetic fibers within the yarn structure and prevents the polymer from melting or dripping.

Currently, most durable flame retardants use either ammonia curing or bromine/antimony as a means of providing durability to laundering; however, the use of these materials presents potential environmental and health risks. Multifunctional silanes can serve to provide the hydrophobic properties of the finish as well as the durability to laundering for both the THPC based flame retardants and the ceramic nanoparticles. Current research presents numerous ways to apply nanosol coatings containing ceramic nanoparticles to achieve repellent or flame retardant surfaces, but little research has been done to apply nanosols to create a dual-functionalized repellent and flame retardant textile surfaces.

This research will focus on achieving a finish that is flame retardant, repellent, and durable to home and commercial laundering through the use of multifunctional silanes and ceramic nanoparticles.

2 Literature Review

2.1 Functional Textiles

Functional textiles can be described as any textile that provides extra functionality such as flame retardant, repellent, soil-release, antimicrobial, or antistatic properties in addition to maintaining basic textile properties such as hand, strength, comfort, and durability. Although the methods for achieving functional textiles could be very similar depending on fiber type and function, only flame retardant and repellent functionalities will be covered due to their relevance to the research.

Functional textiles can be created by three main methods: adding an additive to a polymer melt or solution prior to extrusion or spinning, chemical grafting of additives to fibers, and providing fibers with functional coatings.

Adding an additive (polymer, particle, or other chemical compound) to a polymer melt is a very simple way of achieving a functional textile, and has the benefit of very high durability due to the fact that the additive is directly processed with the polymer itself. However, this method is only viable when working with synthetic fibers, as natural fibers are not processed via extrusion.

Chemical grafting of additives to fibers is an excellent means of providing functionality to a textile; however, as fiber type changes, the chemistry necessary to provide reactivity changes. Thus, specific linkers must be developed in combination to provide reactive sites for grafting; the selection of linkers and their application become even more difficult when blended fabrics are used. Furthermore, typical chemicals for grafting only add a single functionality to the textile; when dual functionality is desired, it is difficult for chemical grafting to provide an adequate solution.

Coating textiles is a simple way to add functionality to a textile. Many functional coatings can provide functionality independent of fiber type. Depending on end use, chemical coatings can be either durable, where they are able to withstand repeated home or commercial laundering, or non-durable, where the textile is single use or not expected to be laundered. Application of chemical coatings to textile substrates can be achieved

continuously via padding or in batches. When applying coatings in a continuous environment, it is important to keep the speed, bath chemistry, and temperature constant in order to provide uniform application of the coating.

2.2 Flame Retardant Textile

Flame retardants for textiles can be generally categorized as any substance, which, when applied to a textile substrate, imparts or augments the substrate's resistance to ignition by flame. Although the definition of a flame retardant can be generalized for any textile, specific end uses, customer specifications, and government regulations can all affect the individual definition of flame retardance for a textile product. Traditionally, high concentrations of 40-50% on weight of bath are required to achieve flame retardance for textiles [38]. Due to the use of such high add-ons of chemicals, applying a flame retardant coating without negatively affecting the physical properties of a textile is very difficult. Some important properties of textiles that can be negatively affected by the addition of a flame retardant coating are luster, stiffness, hand, drape, soil-release, washability, tensile strength, elasticity, and pilling propensity [38]. Textiles finished with flame retardant finishes must generally meet the following specifications in order to be viable for commercial success [61]:

1. Finishing should have little or no adverse effects on the physical properties of the textile;

2. The textile should retain its aesthetic and physiological properties;
3. Application process should be simple and use conventional equipment;
4. The finished textile should be durable to repeated home launderings, dry-cleaning, and tumble drying

2.2.1 The Combustion Process

In order for a textile to combust, sufficient energy must be applied to the substrate to break the covalent bonds of the material. In general, dissociation energy of 200-400 KJ/mol is required to initiate the combustion of a textile [38]. However, the specific energy required to initiate combustion of a textile depends on fiber type, fabric construction, and chemical structure of flame retardant applied. Synthetic fibers have a propensity to melt and drip, whereas natural fibers, such as cotton, combust readily. As fabric construction goes from tight and heavy to loose and light, oxygen is able to penetrate the fabric more readily and provide necessary oxygen to the substrate for combustion. The availability of oxygen and fuel during the combustion process serves as a feedback mechanism to further combustion.

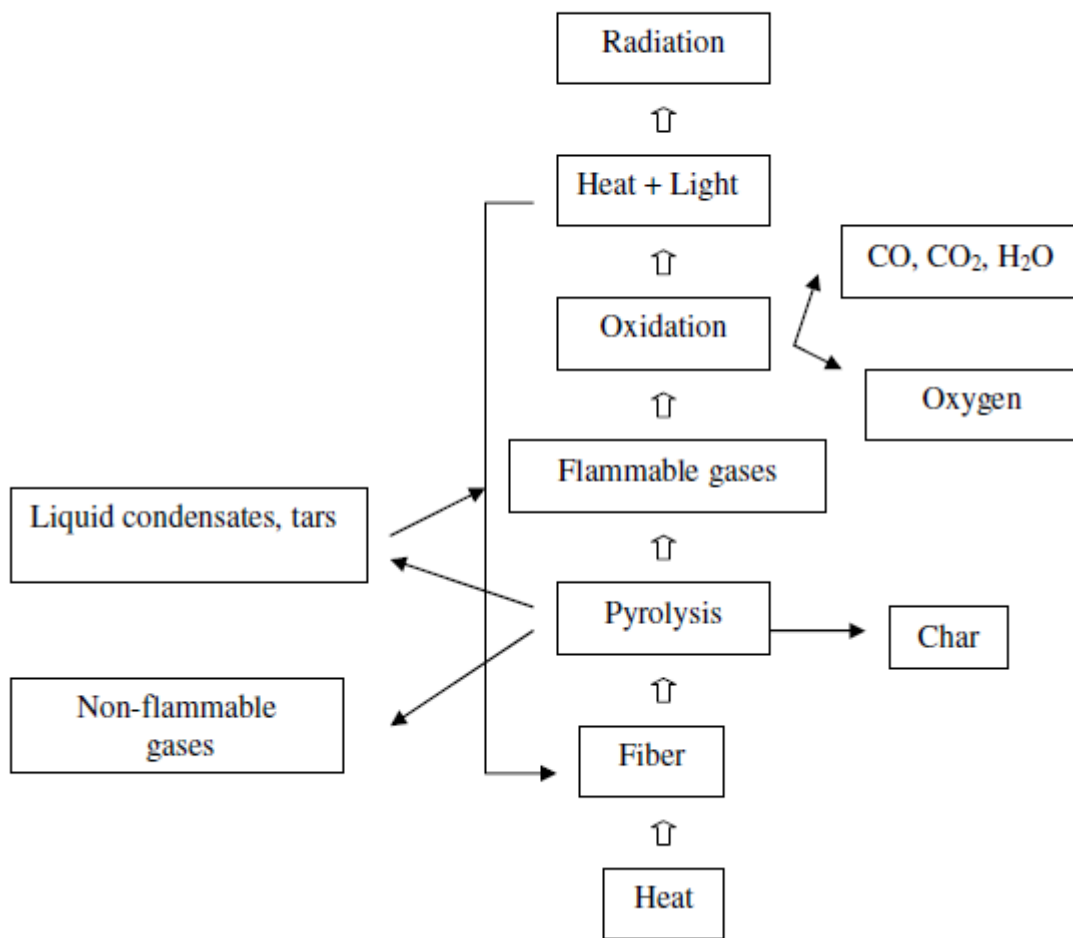


Figure 2.1: The combustion process

Illustrated in Figure 2.1 is the general combustion process for a textile substrate and its feedback mechanism. When an external heat source of sufficient energy is applied to a fiber, the fiber thermally decomposes, undergoes pyrolysis, and releases liquid condensates, non-flammable gases, and char. The liquid condensates mix with

oxygen in the air and provide fuel for combustion. As the liquid condensates are burned, non-flammable gases and heat are released. The heat now serves as a feedback mechanism to further the pyrolysis of the fabric and the combustion of flammable gases. Cotton is a natural fiber that burns readily when introduced to a heat source. In addition to burning readily, cotton combusts almost immediately when introduced to a heat source high enough to initiate pyrolysis. In contrast, many synthetic fibers such as polyester do not combust immediately upon pyrolysis, but instead melt and drip until temperatures are sufficient. Pyrolysis begins around 350°C for cotton and 430°C for polyester, but combustion does not begin for polyester until temperatures reach 480°C [38].

2.2.2 Flame Retardant Mechanisms

Much research has been done to develop and commercialize new flame retardants with increased properties. Most flame retardants achieve flame resistance through one or more of the following methods [38]:

1. Direct thermal degradation to low-fuel pyrolysis paths
2. Coat the substrate to exclude oxygen
3. Form an internal barrier to resist the release of combustible gases
4. Release inert gases to dilute combustible gases
5. Dissipate heat away from the flame

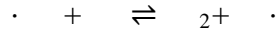
Flame retardants generally achieve these mechanisms in the condensed phase or the vapor phase.

2.2.2.1 Condensed Phase Mechanism

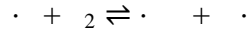
In general, condensed phase mechanisms work by altering the pyrolysis of a textile. By altering the pyrolytic path, pyrolysis temperature can be decreased, char formation can be promoted, and formation of non-volatile compounds can be increased [43]. Within the condensed phase, flame retardants serve to decrease the release of combustible products during pyrolysis, effectively reducing the fuel supply for combustion.

2.2.2.2 Vapor Phase Mechanism

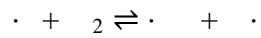
Vapor phase mechanisms work by altering the actual combustion process of the textile. Vapor phase flame retardants can alter the combustion process in multiple ways. Some flame retardants that work in the vapor phase interfere with combustion by reducing the availability of combustible gases. Other vapor phase based flame retardants actually interfere with the combustion reactions and reduce the heat given off by combustion. By reducing the heat of combustion, the feedback mechanism associated with the combustion of textiles can be partially or completely impeded. The main exothermic reaction of flame is illustrated in Equation 2.1, and is where the majority of the heat needed to sustain the flame is created. However, the primary reaction for flame is dependent upon two separate chain branching reactions illustrated in Equations 2.2 and 2.3. Thus, vapor phase based flame retardants reduce the combustion process by limiting the chain branching reactions [38,43,52].



Equation 2.1: Flame's primary exothermic reaction



Equation 2.2: Chain branching Reaction 1



Equation 2.3: Chain branching reaction 2

2.2.3 Types of Flame Retardants

All flame retardants fall into three general categories: inorganics, halogenated compounds, and organophosphates. Inorganic flame retardants include compounds such as metal oxides and nitrogen-based compounds, and are generally non-durable, and typically they are used as a synergist with another flame retardant. Organophosphorus and halogenated flame retardants are the most commercially utilized flame retardants and will be discussed further.

2.2.3.1 Halogenated Flame Retardants

The most common halogenated flame retardants are compounds based on either bromine or chlorine. Due to the chemical structure of the halogen within brominated

flame retardants, they tend to be more effective than chlorine based flame retardants [38]. Bromine based flame retardants are most common flame retardants used in industry, but they are also becoming controversial due to possible health risks associated with their use. Studies have found measurable levels of bromine residue in human tissue and breast milk, even in countries where the residents had no contact with the chemicals [49,52]. Compounds such as antimony are typically applied in conjunction with halogen based flame retardants; as they are known to have a synergistic relationship with halogen based flame retardants. A synergistic relationship is one where the two chemicals, when used in conjunction with one another, perform better than when used separately. Halogen based flame retardants typically work in the vapor phase by creating stable free radicals, which slow the chain branching reactions shown in Equations 2.2 and 2.3.

2.2.3.2 Phosphorus Flame Retardants

Phosphorus flame retardants are the second most used commercial flame retardant, and they are the main alternative to halogenated flame retardants. There are many different types of phosphorus based flame retardants including phosphines, red phosphorus, phosphonates, and phosphine oxides [38]. Typically working in the condensed phase, phosphorus based flame retardants release phosphoric and polyphosphoric acids, which serve to dehydrate the substrate and promote char formation. Due to the formation of char, phosphorus based flame retardants are known to be effective for oxygen rich polymers such as cellulose and some synthetics [3,11,19].

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) is one of the most successful phosphorus based flame retardants used on cellulose and some synthetics. The chemical structure of THPC is shown below in Figure 2.2. To achieve acceptable flame retardance, THPC is generally applied in conjunction with a phenol or amine, which allows polymerization of the flame retardant within and on the surface of the molecule. Furthermore, nitrogen compounds have been shown to increase the performance of THPC flame retardants [10,32,38,42]. When applying THPC flame retardants to fabrics, a high add-on % on weight of fabric is typically necessary to ensure sufficient phosphorus content. Typically, final phosphorus add-on % on weight of fabric is around 3-4% to ensure flame retardance.

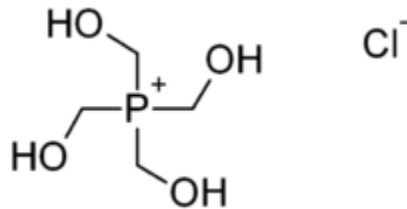


Figure 2.2: Chemical structure of THPC

Application of THPC based flame retardants onto cellulose is typically a pad, dry, cure, oxidize, and wash process. When applying THPC flame retardants onto cellulosic fabrics, ensuring adequate absorption of the flame retardant into the fiber is important for providing durability to laundering. As such, manufacturers of THPC based flame retardants may recommend using a double-dip-double-nip process to allow for migration of the flame retardant to the core of the fiber.

The application of phosphorus based flame retardants to synthetic fibers, such as polyester, is slightly different than for cellulose. Phosphorus based flame retardants are often applied using a pad-dry-cure-rinse or pad-thermosol-rinse process. By elevating the curing temperature to that of the thermosol temperature, the flame retardant is able to penetrate into the polymer itself. Upon cooling, the flame retardant is physically trapped within the fiber structure, thus giving the flame retardant durability until structural degradation of the polymer occurs.

Applying THPC based flame retardants to cotton/polyester blended fabrics has proven to be difficult. Due to the lower pyrolysis temperature of cotton, char will form prior to the temperature elevating high enough to reach the pyrolysis temperature of polyester. As such, “wicking” occurs, where molten polyester cannot flow away from the flame due to the char present [38]. Phosphorus flame retardants are useful when using cotton/polyester blends because they promote char formation of the polyester, thus reducing or eliminating the “wicking” effect associated with the blend. Commonly, THPC is used in combination with other flame retardants when applying durable finishes to cotton/polyester blended fabrics. For example, Jang et al. successfully applied a durable flame retardant finish to a 50/50 cotton/polyester blended fabric using 15% dichlorotribromophenyl phosphate (DCTBPP) and 30% THPC/Urea precondensate, which was durable to repeated laundering [24].

2.2.4 Flammability Test Methods

There are many different methods of testing textile flammability. Methods can be issued by companies, government groups, third party organizations, and scientific societies. Although there are many varieties of flammability testing, most methods are very similar. Most flammability tests involve placing a fabric of specific width and length vertically or horizontally in a holder, applying an open flame to the sample for a known length of time, and then measuring the burning characteristics of the sample. The most common characteristics measured include char length (measure of visible damage to the sample), afterflame time (measure of time the sample maintains a flame after the flame source has been removed), afterglow time (measure of time the sample glows after cessation of the flame). Visual observations of melting or dripping, in the case of synthetics, are also noted. The most common method for testing the flammability of textiles is ASTM D6413: Standard Test Method for Flame Resistance of Textiles.

2.3 Water Repellent Textiles

In order to understand how to functionalize a textile surface to impart water repellency, it is important to understand basic principles of wetting. Water repellent textiles, by definition, repel water from the surface of the fabric. However, there are multiple methods by which water can be repelled from the fabric surface. A fabric surface can repel water by resisting adsorption, absorption, or penetration of water.

When functionalizing a fabric for water repellency, it is important to keep in mind the end use of the textile. Rendering a textile water proof implies that the fabric will be repellent to water in both the liquid and vapor forms. The distinction between water proof and water repellent textiles becomes important when considering the end use of the textile. Water proof textiles are valuable when creating barriers to eliminate the penetration of water of all forms, such as tenting. In contrast, textiles that are both water repellent and breathable are necessary for end uses such as performance clothing.

When measuring the repellency of a textile, it is important to maintain differentiation of the terms: water repellency and contact angle. Water repellency describes how well a fabric resists the absorption, adsorption, and penetration of water on a fabric surface. The measurement of the contact angle of a liquid on the surface of a fabric is a method of quantitatively describing the surface energy of the substrate. Furthermore, factors such as fabric construction, basis weight, and repellent coating chemistry can have a direct effect on the repellency of a fabric.

2.3.1 Concept of Wettability

The contact angle of a liquid on the surface of a material is an indirect measurement of the wettability, and directly relates to the interactions of the solid, liquid, and gas phases. To understand the interactions of the three phases, Gibbs equation can be used. As illustrated in Equation 2.4, Gibbs' Equation gives the sum of the three

interfacial energies of a system, F , where A is the area and γ is the surface energy per unit area of the given phases [17].

$$F = A_S\gamma_{SV} + A_L\gamma_{LV} = \Sigma A\gamma$$

Equation 2.4: Gibbs' equation

Wetting occurs spontaneously when the change in free energy, ΔF , of the system becomes negative as a result of contact between the liquid and solid phases, presented in Equation 2.5 [17].

$$\Delta F = F_2 - F_1 = \Sigma(A\gamma)_2 - \Sigma(A\gamma)_1$$

Equation 2.5: Spontaneous wetting

When the liquid is introduced into the system, the solid-vapor interface is replaced with the solid-liquid interface. The change in energy of the system is a result of the work done on the surface by the liquid [17]. If a liquid is not immediately absorbed or adsorbed to the fabric, then an equilibrium will be met between the solid, liquid, and vapor interfaces of the system. Young's Equation, shown in Equation 2.6, makes a relation between the surface energies of the three phases shown in Gibbs' equation, and the contact angle that the liquid will make on the solid's surface.

$$\gamma_{LV} (\cos \theta) = \gamma_{SV} - \gamma_{SL}$$

Equation 2.6: Young's equation

Thus, the differences between the surface energies of the solid-vapor and solid-liquid phases strongly affect the resultant contact angle formed between the solid and liquid.

It should be noted that Young's Equation is based upon a perfect system where the solid surface is smooth and homogeneous. As textile surfaces are not smooth, and uniform application of finishes is extremely difficult, there is large variability in repellency data based upon fabrics [18]. Due to the nature of textiles surfaces, further work was done to enhance Young's Equation to take into account surface roughness. For example, Wenzel's Equation, shown by Equation 2.7, is a modification of Young's Equation, where r is Wenzel's roughness factor.

$$\gamma_{LV} (\cos \theta)' = r (\gamma_{SV} - \gamma_{SL})$$

Equation 2.7: Wenzel's equation

Wenzel's roughness factor, r , seen in Equation 2.7 is defined as the ratio of the actual area of rough surface to the geometrically projected area.

2.3.2 Contact Angle

The contact angle of a droplet on a substrate is the angle formed between the solid-liquid interface and the liquid-vapor interface, and is shown in Figure 2.3.

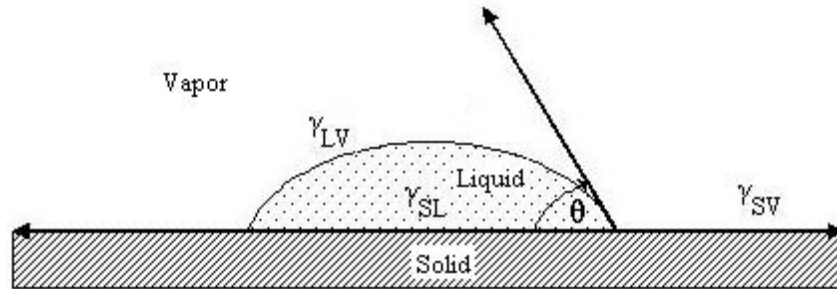


Figure 2.3: Contact angle measurement

When $\theta \leq 90^\circ$, the surface is said to be hydrophilic and the drop wets the surface. If the contact angle is 0° , then the solid-liquid interaction is greater than or equal to that of the liquid-liquid interaction. Conversely, if the contact angle is 180° , then there is no interaction between the solid and liquid phases. When the contact angle exceeds 90° , wetting of the substrate does not occur, and the substrate is said to be hydrophobic. In this case, the interaction between the liquid and gas phases is greater than the interaction between the solid and liquid phases. When surfaces have contact angles greater than 90° , the fluid and surface are unable to efficiently form secondary bonds.

However, hydrophobicity is possible without relying solely on surface energy. Increasing surface roughness has also been shown to positively impact the water repellency of smooth surfaces [7,8,36]. The lotus leaf, occurring naturally in nature, is an example of a system where surface roughness has a large effect on water repellency. The lotus leaf surface is covered in paraffin crystals on the scale of 1-10 micrometers, and can achieve contact angles greater than 155° [45]. The use of the sol-gel process is one

method that has been used to increase surface roughness through the introduction of nanoparticles [36,64,68].

2.3.3 Fluorinated Finishes

Within the textile industry, the use of chemicals and auxiliaries to achieve water repellency is common. Fluorocarbon based finishes are the most common repellent finishes used in industry, and are used to treat both natural and synthetic fabrics. Due to the high electronegativity of the fluorine molecule, fluorocarbon finishes are highly inert and serve as excellent repellent finishes. Due to the extremely low surface energy associated with fluorinated finishes, as low as 5 dynes/cm, they can render fabrics both repellent to water as well as oil [8,37]. Water repellency of fluorinated repellents is achieved by the presence of $-CF_3$ chains on the fabric surface. These perfluorinated chains provide a barrier on the fabric surface with a low surface energy, and sufficient chain length to reduce or eliminate any secondary bonding between the fabric and the liquid [22]. Fluorocarbon based finishes also have excellent chemical and thermal stability, which provides excellent durability to laundering [22].

Although fluorocarbon finishes provide the highest repellency, they are also the most expensive and difficult to process. High temperatures are typically required to process and cure the finish. Commonly, fluorochemicals are mixed with softeners and resins to lower the cost, and improve fabric hand. In addition to the high cost associated with fluorocarbon finishes, recent studies have also shown potential health risks

associated with these compounds [1,3,22]. Many fluorinated compounds are environmentally persistent and bioaccumulative [14]. In addition, little information is available as to the degradation and toxicity of these compounds in the environment. Furthermore, workers in processing plants that handle the organic fluorinated precursors used to make the repellent finishes have been found to have elevated levels of organic fluorine in their blood serum [18]. Due to the fact that some fluorinated compounds decompose into carcinogenic materials, it is desirable to find an alternative to these compounds.

2.4 Ceramic Nanoparticles

Research involving nanoscale particles and finishes is becoming of great interest within the scientific community. As the average particle size decreases, the specific surface area of a given mass of particles will increase. Thus, the use of nanoparticles offers a method of altering both the chemical and physical properties of a surface with a single finish. Generally, these particles are used as additives to a finish due to the fact that ceramic nanoparticles have no direct fixation mechanism when applied alone. This research uses silica and titania nanoparticles produced by Evonik Industries under the trade name Aerosil[®]. These ceramic nanoparticles are produced by continuous flame hydrolysis using either silicon tetrachloride, SiCl_4 , or titanium tetrachloride, TiCl_4 ,

known as the “Aerosil[®] Process” [12]. In the Aerosil[®] Process, the tetrachloride is converted to the gas phase and then reacted with an oxyhydrogen flame to produce a ceramic dioxide. The process diagram for silica dioxide is shown in Figure 2.4.

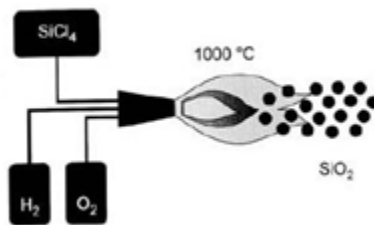


Figure 2.4: Process diagram of flame hydrolysis of silicon tetrachloride [11].

The Aerosil[®] Process is rather versatile, and varying process variables such as dwell time, temperature, and reactant concentration allow for the processing of nanoparticles with specific particle sizes, purities, size distributions, and surface properties [12,13]. Furthermore, post processing of ceramic nanoparticles is possible and can impart additional properties such as hydrophobicity. Due to the high concentration of hydroxyl groups on the surface of ceramic nanoparticles, silanes are commonly used for chemical after-treatment [12,13].

2.5 Properties of Ceramic Nanoparticles

Ceramic nanoparticles have been researched and commercially used for over 60 years. Chemically, the particles are metal oxides and contain an extremely high surface concentration of hydroxyl groups. The nanoparticles are available in a particles sizes ranging from 5 to 50 nanometers with BET specific surface areas of 600-50 m²/g [13]. General properties of Aerosil[®] nanoparticles can be seen in Table 2.1.

Table 2.1: General Properties of Aerosil[®] nanoparticles [12]

<i>Characteristics</i>		AEROSIL[®]
		Aero
1	Spec. surface according to BET ¹⁾	m ² /g 50 to 600
2	Primary particle size	nm 5 to 50
3	Aggregate or agglomerate size	µm ¹¹⁾
4	Density ²⁾	g/cm ³ 2.2
5	Compacted apparent volume ³⁾	ml/100 g 1000 to 2000
6	Drying loss ⁴⁾	% ≤ 2.5
7	Ignition loss ⁵⁾	% 1 to 3
8	pH value ⁶⁾	3.6 to 4.3
9	Predominant pore diameter	nm not porous to app. 300 m ² /g
10	Dibutyl phthalate adsorption ⁷⁾	ml/100 g 250 to 350
11	Pore diamete distribution	¹¹⁾
12	Proportion of the internal surface ⁹⁾	0
13	Structure of the aggregates and agglomerates	chain-like agglomerates
14	Tendency to have thickening effect	very strongly pronounced

As shown in Table 2.1, ceramic nanoparticles tend to form agglomerates when in solution, and as the size of the particle decreases, tendency of the particles to form agglomerates increases and the difficulty to break and disperse the agglomerates also increases. Orwa et al. noted that the use of a high shear mixer is sufficient to disperse agglomerates, and hydrophilic silicas (such as those used in this research) are much easier to disperse than are hydrophobic silicas [54]. Ceramic have a wide range of uses in industry:

- Increase abrasion resistance in films and plastics [3,6,13]
- Provide excellent water-repelling properties [13,48,52,62,64]
- Increase heat stability [9,13,23,13]
- Control rheological properties [13]
- Increase dielectric properties[13]
- Provide Lotus effect [13].

By increasing the surface roughness of a substrate, the addition of ceramic nanoparticles to finishes can augment both repellency and abrasion resistance. Makita et al. found that the addition of 4 mol% SiO₂ as an underlayer to a silane film increased the repellency and abrasion resistance of glass coatings [46]. Seono created silica films by dissolving 0.05 wt % SiO₂ into poly(allylamine hydrochloride) and found that the introduction of silica film onto silica wafers increased the contact angle of the sample by 50° as compared to samples treated with only dichlorodimethyl silane, and, as shown in Figure

2.5, as the surface roughness of the films increased, the average contact angle of the samples also increased.

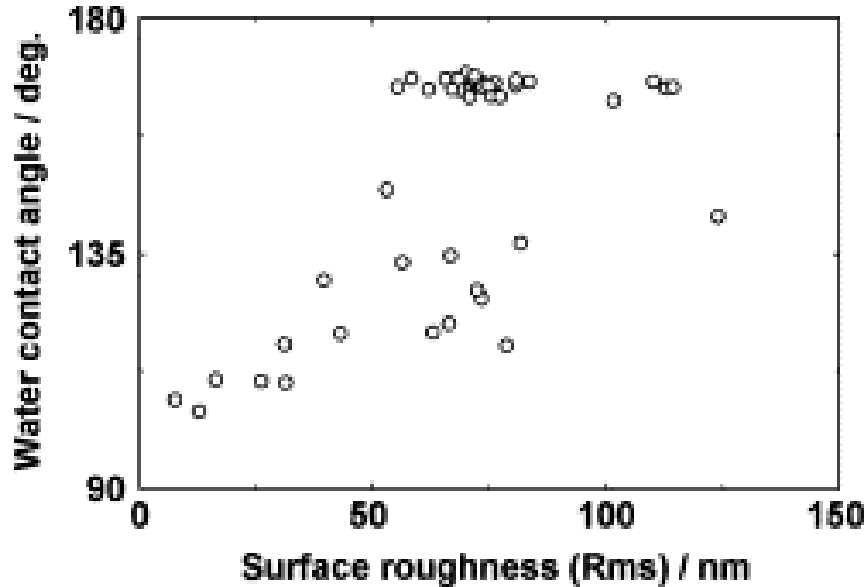


Figure 2.5: The relation between surface roughness (Rms) and water contact angle of prepared films[64].

Other work by Larmour et al. showed that increasing the etching time of a metal surface prior to treatment with a hydrophobic finish increased the contact angle of the final sample by more than 10° [36].

Research has also shown that ceramic nanoparticles can be used to alter the thermal degradation of polymers. Laachachi found that melt blending 5 wt % of metal oxides, such as TiO_2 , increased the thermal stability of poly(methylmethacrylate), PPMA, by about 70 [28,29,32,33]. The data also showed that as the loading content of

TiO₂ in the PMMA increased, the peak of heat release decreased and the time to ignition increased [32]. Other work by Laachachiet al. found that when metal oxides were melt blended into PMMA, there was a direct increase in the glass transition temperature and the limiting oxygen index (LOI), as can be seen in Figure 2.6 [33].

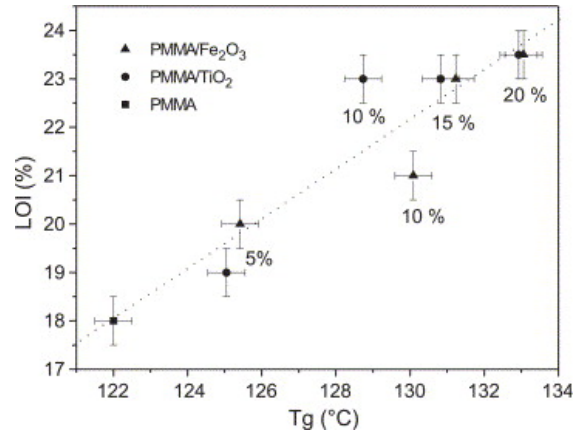


Figure 2.6: Effect of metal oxide content on Tg(°C) and LOI(%) of PMMA

PMMA polymers loaded with 20 wt % TiO₂ showed an increase in Tg of 6 °C. Chou et al. noted that the addition of silicon compounds showed synergistic effect on enhancing the thermal stability and char formation of phosphorus containing epoxy resins [10]. Ma et al. also found that the addition of silicon compounds into epoxies increased the char formation by a factor of 2 and resulted in higher thermal stability [45].

2.6 Sol-Gel Coatings

Coating textiles via the sol-gel process provides the textile substrate with a desired functionality while maintaining the physical properties of the textile. The application of sols containing metal oxides has the following benefits:

- 1) Use of particles with diameters < 50 nm form durable transparent oxide layers;
- 2) Heat, light, chemical and microbial stability;
- 3) Augmented properties such as mechanical strength, wear and abrasion resistance;
- 4) Oxide coatings can carry embedded functional additives such as biological compounds, inorganic particles, and polymers;
- 5) Application can be carried out at room temperature and atmospheric pressure, and applied using conventional textile processes such as padding, and dip-coating [20].

In addition to being able to apply these coatings at room temperature and atmospheric pressure, curing nanosol coatings can be carried out at temperatures as low as 120°C , which is lower than that of traditional fluorochemicals (as high as 180°C).

Thus, when applying a nanosol coating on a cotton fabric, which discolors at relatively high temperatures, the curing temperature can be lowered to avoid the negative impact on the performance of the coating. Silanes and other ceramic nanoparticles have been prepared in the sol gel process to create thin films that can be applied to surfaces such as natural fibers, synthetic fibers and solids, metals, wood, and glass [3,6,20,31,64,65,79,80]. Depending on the chemistry of the applied coating, surfaces can be modified to be hydrophilic or hydrophobic, and additional functionality can be added to a surface, such as flame resistance [27,28,62,63,64].

2.7 The Sol-Gel Process

The sol-gel process is a method of preparing ceramic or metal oxide coatings through the hydrolysis, application, and curing of silica or metal alkoxides. Sols are first created by the hydrolysis of one or more chemicals in water or other organic solvents, typically ethanol. When the sol is applied to a substrate, the nanoparticles form a lyogel-layer, which is a 3-dimensional network of solvent and nanoparticles maintained by secondary bonds [6,20]. During curing, a condensation reaction occurs, and the lyogel dehydrates to a xerogel. The silanol groups formed by hydrolysis react with available hydroxyl groups resulting in siloxane groups and water [19,20]. A diagram of the sol-gel process can be seen in Figure 2.7.

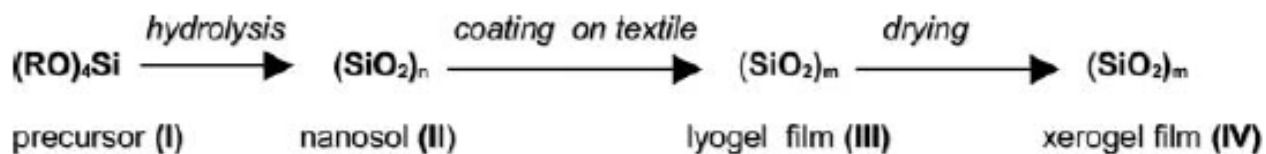


Figure 2.7: Preparation of nanosol coatings (sol-gel process) [20].

The xerogel has a porous structure, and silica-based xerogels can have very high surface areas. High surface area provides more active sites for interaction, which is desirable when creating functional surface coatings [7]. Physical and mechanical properties of the coating are governed by the hydrolysis and drying conditions used. Hydrolysis in acidic conditions forms weakly cross-linked condensation products with a dense condensation layer, whereas alkali hydrolysis results in particle aggregates with larger pores [20]. The presence of organic solvents during hydrolysis allows for shorter drying times and lower drying temperatures; however, aqueous hydrolysis is still desired because of the safety, environmental, and cost issues associated with organic solvents [7,20].

Physical modification of the formed oxide matrix, or xerogel, is often used to immobilize or bond additives such as pigments, dyes, bio-molecules, and oxides [20]. Additives can be added either before the hydrolysis of the sol, or after hydrolysis and prior to application on the textile [20]. Whether the additive, in this case a metal oxide, is

added before or after hydrolysis does not significantly affect the final composite structure, because the encapsulation or integration occurs during condensation of the lyogel. Mahtig et al. claim that xerogels are transparent, stable, nanosized dispersions with 4-20 wt. % solids with particle diameters of less than 50 nm.

2.8 Cotton and Polyester Fabrics

When using functional coatings to modify fabric properties, it is important to understand the surface chemistry available to use for chemical bonding. The structure of cellulose, which makes up the largest part of cotton, contains a large amount of hydroxyl groups. These groups are largely what make cotton a hydrophilic fabric, and they also provide sites for attaching functional coatings. The chemical structure of cellulose is shown in Figure 2.8.

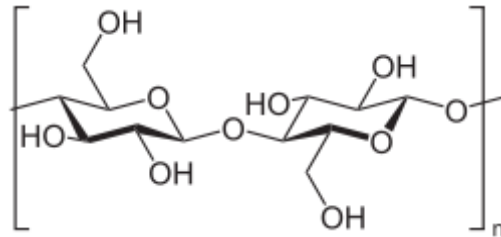


Figure 2.8: Chemical structure of cellulose

Poly(ethylene terephthalate), or PET, has available ester functional groups in its backbone. The chemical structure of PET is shown in Figure 2.9.

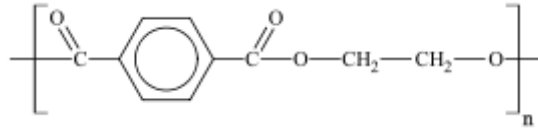


Figure 2.9: Chemical structure of PET

When applying finishes to PET and cotton blended fabrics, special attention must be used to carefully choose chemistries that will create strong bonds with the fabric substrate. Since each fiber type has different functionality, bonding to both fiber types may not be feasible with simple chemistries.

3 Methodology and Experimental Procedures

3.1 The Intent and Advantages of this Research

The approach of this research involves the use of ceramic nanoparticles, multi-functional silanes, and flame retardants to treat 50/50 PET/cotton blended fabrics to obtain hydrophobic, flame retardant finishes that are durable to home laundering. The main objective is to obtain a fabric finishing technology with the following advantages:

1. High flame resistance,
2. High hydrophobicity (as measured by water contact angle),
3. Good Durability to home laundering, and
4. Simple processing and application.

After treatment of the fabrics, hydrophobic and flame resistant properties were measured. Following initial analysis, fabrics were laundered and re-tested for hydrophobicity and flame resistance to assess the durability of the finish. To achieve a finish with the previously mentioned properties, ceramic nanoparticles, multi-functional silanes, and flame retardants were used to treat 50/50 PET/cotton blended fabrics.

Ceramic nanoparticles were chosen as an additive to the finish because they are known synergists with phosphorus-based flame retardants, can form large numbers of covalent bonds, and enhance the surface roughness of the applied finish. The use of ceramic nanoparticles can improve the flame resistance, repellency, and durability of the

finished fabrics due to their small diameter (< 25 nm), high surface hydroxyl content, and high specific surface area. Thus, the ceramic nanoparticles offer many more bonding sites per given mass than non-nanoscale additives. The ability of the nanoparticles to form large amounts of covalent bonds not only allows the nanoparticles to strongly attach to the fabric surface, but also provides bonding sites for the multi-functional silanes in the finish. In addition to ceramic nanoparticles, long chain alkyltrialkoxysilanes (such as hexadecyltriethoxysilane) were used to provide hydrophobicity. Crosslink enhancing silanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), were used to serve as crosslink centers to form a 3-dimensional network between the fabric surface, multi-functional silanes, flame retardants, and ceramic nanoparticles.

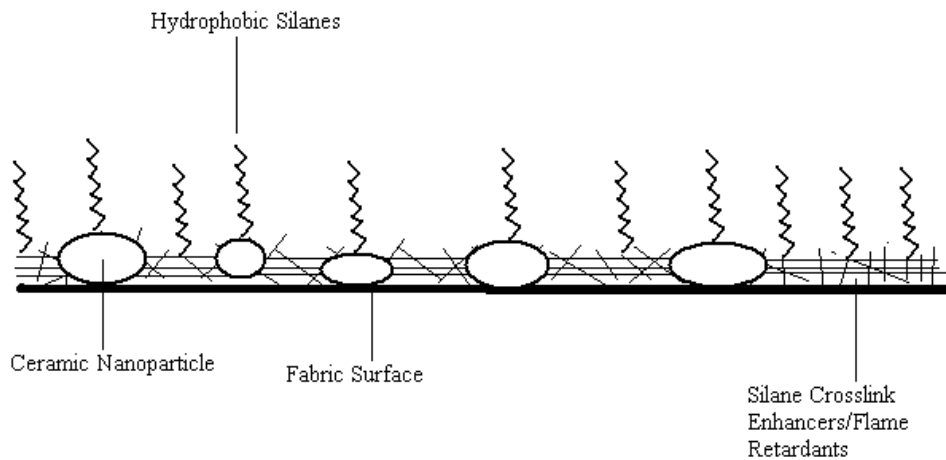


Figure 3.1: 3-Dimensional attachment of the proposed finish to cellulosic fabric surface

Figure 3.1 shows the representative 3-dimensional attachment of the finish to the fabric substrate. Although this is an idealized schematic describing the general attachment of the finish to the fabric surface, it does give a good representation of actual attachment. It is important to note that although it is possible for single nanoparticles to attach to the fabric surface, it is more common for the nanoparticles to attach to the surface in clusters at random intervals. Although the hydrophobic silanes are shown in Figure 3.1 to be bonded only to the surface of the finish, they can bond directly to the fabric and nanoparticles as well. As the hydrophobic silanes bond to the fabric surface, ceramic nanoparticles, and 3-dimensional silane network, a “forest” of long chain alkyltrialkoxysilanes is formed and provides hydrophobicity to the finish.

3.2 Fabric Selection

Due to the variability seen in flame retardant and repellent fabrics, and input from ITT sponsor companies, all treatment and testing was performed on a 50/50 PET/Cotton jersey fabric with a base weight of 6 oz/yd². Fabric was acquired from Judy Elson in the NCSU College of Textile Undergraduate Labs. When needed, 18in. x 18in. samples were cut and treated.

3.3 Finishing Variables

In order to maintain uniform finish application during all fabric treatment, equipment used for finishing was chosen so as to minimize any variability of finishing

parameters. Equipment used to mix, apply, dry, and cure fabrics in this research is given in Table 3.1.

Table 3.1: Machinery used for finish application

Equipment	Model	Manufacturer	Notes
Pad	HVF	Werner Mathis A.G.	Lab Scale
Curing Oven	CH-8155	Werner Mathis A.G.	Lab Scale
High Speed Mixer	Tissuemiser	Fisher Scientific	10,000 - 33,000 RPM

3.3.1 Padding Equipment

The Werner Mathis HVF is a lab scale pad that allows horizontal and vertical fabric introduction. The Werner Mathis HVF can be used to pad batches of fabric, or it can be set to work in tandem with the curing oven CH-8155. When used for batch padding, the instrumentation panel on the machine allows for the adjustment of nip pressure and drive speed (Figure 3.2).



Figure 3.2: Werner Mathis HVF pad

When in the vertical configuration, as seen in Figure 3.2, small batches of chemicals can be placed between the two rubber rollers to serve as a well. Once loaded with chemicals, the operator can choose a dwell time for the fabric in the bath by varying the roll speed while maintaining constant nip pressure.

3.3.2 Drying/Curing Equipment

Once samples were treated, they were air dried over night prior to curing. Curing of the treated samples was carried out using a Werner Mathis CH-8155 Horizontal Oven shown in Figure 3.3.



Figure 3.3: Werner Mathis CH-8155 Curing Oven

The Werner Mathis CH-8155 maintains curing temperatures from entry to exit by means of heated air vents that blow directly onto the fabric passing through the oven, which is the same as typical curing carried out in conventional textile processes. The fabric samples were pinned onto racks used for small sample testing, above the controls shown in Figure 3.3. Curing temperature, fabric roll speed, and velocity can be controlled and maintained by the control panel during the curing process.

3.3.3 High Speed Mixer

To properly disperse the ceramic nanoparticles in the finishing solution, a Fisher Scientific Tissuemiser High Speed Mixer, shown in Figure 3.4, was used. The high speed mixer has variable speed and can operate between 10,000 and 33,000 rpm. High speeds are necessary when dispersing nanoparticles because enough energy must be applied to the system to overcome the associative forces that cause agglomerates.



Figure 3.4: Fisher Scientific Tissuemiser high speed mixer

3.3.4 Chemical Components

At the onset of this research, numerous chemicals were acquired for testing. All chemicals pertain to one of the previously mentioned categories: ceramic nanoparticles, flame retardants, and multifunctional silanes. To clear ambiguity, multifunctional silanes are further categorized by hydrophobic silanes and silane crosslink enhancers. All chemicals used in this research are shown in **Table 3.2**.

Table 3.2: List of chemicals used for testing

Chemical Type	Chemical Name	Company
Ceramic Nanoparticles	SiO ₂ (Aerosil®90), TiO ₂ (Aeroxide P-25)	Evonik Industries
Crosslink Enhancing Silanes	Tetraethoxysilane, Tetramethoxysilane, Bis(triethoxysilyl)ethane, Bis(trimethoxysilyl)ethane, 3- Isocyanatopropyltriethoxysilane	Gelest
Hydrophobic Silanes	Propyltriethoxysilane, Octyltriethoxysilane, Dodecyltriethoxysilane,	Gelest

	Hexadecyltriethoxysilane	
Flame Retardants	Tetrakis(hydroxymethyl)- phosphonium-chloride/Urea precondensate	Emerald Performance Materials

It is important to note that the flame retardant used in this research was a commercially available THPC/Urea precondensate (Pyrosan[®] C-FR). This flame retardant provides durable flame resistance for 100% cotton fabrics and can be used to provide semi-durable flame resistance for cotton/synthetic blended fabrics [2,9,60]. Typical application of Pyrosan[®] C-FR calls for pad, dry, cure, ammonification, and washing; however, this research used a pad, dry, cure procedure because the flame retardant will be bound into the crosslinked silane/ceramic nanoparticle network on the fabric surface.

3.3.5 Chemical Structures and Properties

3.3.5.1 Ceramic Nanoparticles

Ceramic nanoparticles used in this research were Aerosil[®] 90 silica and Aeroxide[®] P-25 titania nanoparticles manufactured by Evonik Industries. The nanoparticles are manufactured according to the Aerosil[®] Process. Processing of the nanoparticles can result in either hydrophilic or hydrophobic particles with varying

diameters. In this work, both the Aerosil[®] 90 and Aeroxide[®] P-25 are hydrophilic. Table 3.3 shows the particle diameter and surface area of these two nanoparticles.

Table 3.3: Physio-chemical data for ceramic nanoparticles [11,12]

Nanoparticle Type	Particle Diameter (nm)	Surface Area (m ² /g)
Aerosil [®] 90	20	90 ± 15
Aeroxide [®] P-25	21	50 ± 15

3.3.5.2 *Hydrophobic Silanes*

Four hydrophobic silanes were used in this research to determine the effect of alkyl chain length on the hydrophobicity of the finish.

- Butyltrimethoxysilane, shown in Figure 3.5.

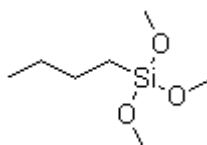


Figure 3.5: Chemical structure of butyltrimethoxysilane [2]

- N-octyltrimethoxysilane, shown in Figure 3.6.

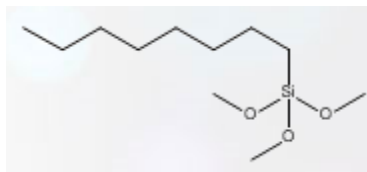


Figure 3.6: Chemical structure of n-octyltrimethoxysilane [2]

- Dodecyltrimethoxysilane, shown in Figure 3.7.

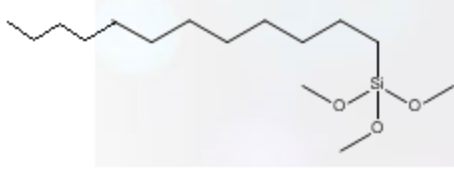


Figure 3.7: Chemical structure of dodecyltrimethoxysilane [2]

- Hexadecyltrimethoxysilane, shown in Figure 3.8.

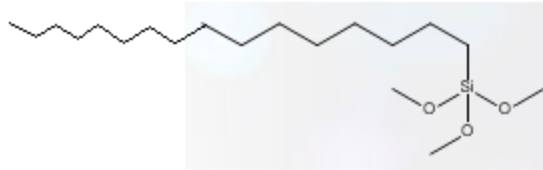


Figure 3.8: Chemical structure of hexadecyltrimethoxysilane [2]

3.3.5.3 Silane Crosslink Enhancers

Five different silanes were chosen as crosslink enhancers to determine the effects of crosslink enhancing silane on the durability and performance of the finish.

- Tetraethoxysilane, as shown in Figure 3.9.

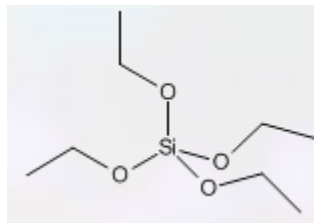


Figure 3.9: Chemical structure of tetraethoxysilane [2]

- Tetramethoxysilane, as shown in Figure 3.10.

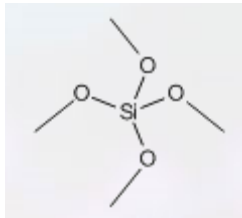


Figure 3.10: Chemical structure of tetramethoxysilane [2]

- Bis(triethoxysilyl)ethane, as shown in Figure 3.11.

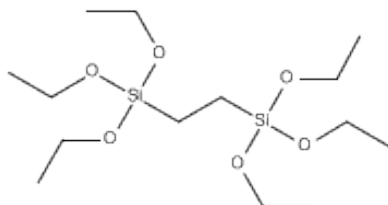


Figure 3.11: Chemical structure of bis(triethoxysilyl)ethane [2]

- Bis(trimethoxysilyl)ethane, as shown in Figure 3.11.

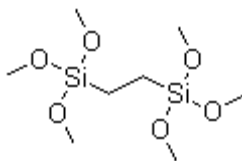


Figure 3.12: Chemical structure of bis(trimethoxysilyl)ethane [2]

- 3-Isocyanatopropyltriethoxysilane, as shown in Figure 3.13

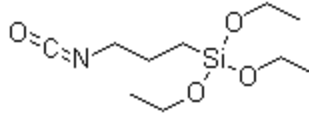


Figure 3.13: Chemical Structure of 3-Isocyanatopropyltriethoxysilane

3.3.5.4 Flame Retardants

A THPC and Urea precondensate (Pyrosan[®] C-FR) was chosen and used as the flame retardant in all experimentation.

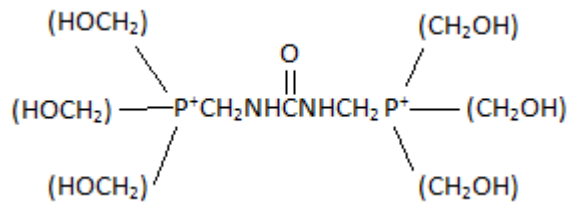


Figure 3.14: Chemical Structure of Pyrosan[®] C-FR

3.4 Design of Experiments

In order to determine the effects of the chemical variables mentioned in Section 3.3, multiple Design of Experiments (DOE's) were conducted to see how variation of a specific chemical variable will affect the flame resistance, repellency, and durability of the finish.

3.4.1 Hydrophobic Silane Type Experiments

The first set of experiments carried out was used to determine which hydrophobic silane created the most repellent finish. Fabrics were treated with different hydrophobic

silanes and then water contact angles were measured. The fabrics were treated according to the following formulas:

- 0% silane, 5% TEOS, 1% silica, 94% H₂O (control)
- 2% N-butyltrimethoxysilane, 5% TEOS, 1% silica, 92% H₂O
- 2% N-octyltrimethoxysilane, 5% TEOS, 1% silica, 92% H₂O
- 2% Dodecyltrimethoxysilane, 5% TEOS, 1% silica, 92% H₂O
- 2% Hexadecyltrimethoxysilane, 5% TEOS, 1% silica, 92% H₂O

Based upon the measured water contact angle, the silane that produced the most repellent finish was used in following experiments.

3.4.2 Hydrophobic Silane Concentration

After choosing the hydrophobic silane that produced the finished fabric with the highest contact angle, the concentration of the hydrophobic silane was varied to assess the effect of hydrophobic silane concentration on the performance of the finished fabric. Fabrics were treated with varying concentrations of hexadecyltriethoxysilane and then tested for repellency and flame resistance. The fabrics were treated according to the following formulas:

- 0% silane, 5% TEOS, 1% silica, 94% H₂O (control)
- 0.1% Hexadecyltrimethoxysilane, 5% TEOS, 1% silica, 92% H₂O
- 0.5% Hexadecyltrimethoxysilane, 5% TEOS, 1% silica, 92% H₂O

- 1% Hexadecyltrimethoxysilane, 5% TEOS, 1% silica, 93% H₂O
- 5% Hexadecyltrimethoxysilane, 5% TEOS, 1% silica, 89% H₂O
- 10% Hexadecyltrimethoxysilane, 5% TEOS, 1% silica, 84% H₂O

3.4.3 pH Experiments

Literature currently available on sol-gel technology states that the pH value at which hydrolysis of silanes occurs can have a large impact on the performance of the finish. Hydrolysis in acidic conditions (pH ~3) forms weak networks with large particle condensates, whereas hydrolysis in more basic conditions (pH 4.5-5.5) create more porous finishes. Thus experiments were carried out to test whether hydrolysis pH had an effect on the performance of the resultant finish. The formulas used for experimentation are given below:

- pH=3: 5% TEOS, 2% hexadecyltriethoxysilane, 1% silica, 92% H₂O
- pH=4.5: 5% TEOS, 2% hexadecyltriethoxysilane, 1% silica, 92% H₂O

3.4.4 Silane Crosslink Enhancer Type Experiments

Since the silane crosslink enhancers affect the crosslinking density of the 3-dimensional network created during curing, changing the type of crosslink enhancer should have a direct impact on the durability and performance of the finish. Experiments

were carried out by testing the effect of the crosslink enhancer on the repellency of the finish based upon the following formulas:

- 0% silane, 30% Pyrosan[®] C-FR, 1% silica, 2% hexadecyltriethoxysilane, 67% H₂O
- 5% TEOS, 30% Pyrosan[®] C-FR, 1% silica, 2% hexadecyltriethoxysilane, 62% H₂O
- 5% TMOS, 30% Pyrosan[®] C-FR, 1% silica, 2% hexadecyltriethoxysilane, 62% H₂O
- 5% BTESE, 30% Pyrosan[®] C-FR, 1% silica, 2% hexadecyltriethoxysilane, 62% H₂O
- 5% BTMSE, 30% Pyrosan[®] C-FR, 1% silica, 2% hexadecyltriethoxysilane, 62% H₂O

In this set of experiments, only the silane type was varied during the testing, and contact angles of the samples were measured before and after laundering to determine which silane imparted the most durable, repellent finish. Based upon repellency data before and after laundering, the silane that created the most durable finish with the best performance was chosen for all further experiments.

3.4.5 Silane Crosslink Enhancer Concentration Experiments

To further examine the effects of the silane crosslink enhancer on the performance of the finish, experiments were conducted with varying silane crosslink enhancer

concentration. Since the crosslink enhancer serves to form the 3-dimensional network containing the hydrophobes, ceramic nanoparticles, and flame retardants, varying the concentration of the crosslink enhancer should directly impact the performance of the finish. Silane crosslink enhancer concentration was varied between 0% and 10% using the following concentrations: 0%, 0.1%, 0.5%, 1%, 5%, 10%. The formulas used for these experiments are shown below:

- 0% silane, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 1% silica, 67% H₂O (control)
- 0.1% silane, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 1% silica, 67% H₂O
- 0.5% silane, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 1% silica, 67% H₂O
- 1% silane, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 1% silica, 67% H₂O
- 5% silane, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 1% silica, 62% H₂O
- 10% silane, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 1% silica, 57% H₂O

3.4.6 Hydrolysis Experiments

After all initial testing was completed, data showed that traditional crosslink enhancing silanes did not bond to the phosphorus based flame retardant, and as a result, little durability to laundering was seen in the flame retardancy of the finished fabrics. In order to increase bonding of flame retardant to the 3-dimensional silane network, 3-isocyanatopropyltriethoxysilane was used. Due to the high reactivity of 3-isocyanatopropyltriethoxysilane, the 12 hour hydrolysis time used in all other experiments was too long, resulting in the solution forming a solid byproduct during stirring. As a result, a set of experiments was carried out varying the hydrolysis time of the silanes. The silanes were hydrolyzed in separate containers for 6, 9, and 12 hours to see how different hydrolysis times would affect the final finish and its performance. The bath formula used for the three experiments was 5% 3-isocyanatopropyltriethoxysilane, 2% hexadecyltriethoxysilane, 1% TiO₂, 30% Pyrosan[®] C-FR, 62% H₂O.

3.4.7 Ceramic Nanoparticle Type and Concentration Experiments

In this research, both SiO₂ and TiO₂ nanoparticles were used as additives to the sol-gel process. In the literature, silica nanoparticles have been used as additives to increase the repellency of finishes, and titanium dioxide nanoparticles have been used to increase the flame resistance of finishes. In order to determine whether the type of ceramic nanoparticle used has an impact on finish performance and durability, the type and concentration of the ceramic nanoparticles were varied while keeping all other variables constant. An outline of the finishing formulas can be seen below.

- 0% ceramic nanoparticles, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 63% H₂O (control)
- 0.1% silica, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 63% H₂O
- 0.5% silica, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 63% H₂O
- 1% silica, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 62% H₂O
- 2% silica, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 61% H₂O
- 3% silica, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 60% H₂O
- 0.1% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 63% H₂O
- 0.5% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 63% H₂O
- 1% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 62% H₂O
- 2% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 61% H₂O

- 3% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan® C-FR, 60% H₂O

Initial experiments also include ceramic nanoparticle concentrations of 5% and 10%, however, samples prepared using 5% and 10% ceramic nanoparticles became overly viscous and did not have uniform application.

3.5 Solution Preparation

Solutions were prepared by hydrolyzing the multifunctional silanes in water for 12 hours using a magnetic stirrer. Two hours before application, a second solution was prepared by mixing the ceramic nanoparticles with the Pyrosan® C-FR flame retardant to begin the dispersion of the nanoparticles. Fifteen minutes before padding the finish onto the fabric, the hydrolyzed silanes were mixed into the ceramic nanoparticle/Pyrosan® C-FR mixture and stirred together for 10 minutes. Directly before padding of the finish onto the fabric, the solution was mixed using a Tissuemiser high speed mixer to ensure dispersion of the ceramic nanoparticles within the solution. It is important to note that the solution preparation changed slightly once 3-isocyanatopropyltriethoxysilane was used as the crosslink enhancer. For all solutions prepared using 3-isocyanatopropyltriethoxysilane, the two silanes were hydrolyzed in separate beakers, each with half of the total water. Also, the hydrolysis time had to be lowered because 12 hour hydrolysis resulted in solid byproducts.

3.6 Finish Application, Drying, and Curing

3.6.1 Finish Application

Application of the finish was carried out using the Werner Mathis HVF pad in vertical configuration. The nip pressure of the rolls was 1 bar, and the roll speed was set at 1 meter/minute. Since the vertical configuration of the pad creates a trough for the padding chemicals, the pad rolls were un-nipped, washed, and rinsed between applications of different chemical baths.

3.6.2 Fabric Preparation and Wet Pick-Up (WPU) Calculation

All fabrics were conditioned to standard temperature (20°C) and humidity (65% relative humidity) prior to treatment. Prior to, and after coating, fabrics were weighed and then the % WPU of the fabric was calculated according to Equation 3.1.

Equation 3.1: Calculation for % wet pick-up

WPU's of the 50/50 PET/cotton fabrics were measured on 5 different samples. The average wet pick-up of the fabric was 86.1% with a standard deviation of 2.5. Once WPU was calculated, % add-on of the various chemicals in the bath can be calculated as shown in Equation 3.2.

Equation 3.2: Calculation for % add-on

Table 3.4 shows add-on's of each chemical obtained from a typical bath, which includes 5% TEOS, 2% hexadecyltriethoxysilane, 1% titania, and 30% Pyrosan[®] C-FR.

Table 3.4: Typical chemical add-on of each chemical if finishing bath

Chemical	% Add-On
TEOS	4.31
hexadecyltriethoxysilane	1.77
titania	0.86
Pyrosan [®] C-FR	25.8

3.6.3 Drying and Curing

Drying and curing of the finish play a significant role in the final performance of the finished fabrics. Based upon recommendations by Gelest, which is the company supplying all silanes for this research, samples were dried overnight prior to curing to allow ample time for secondary bonding of the lyogel to the substrate and other

chemicals. The curing of the finish is when the solvent is evaporated from the finish and the condensation reaction converting hydrogen bonds to covalent bonds occurs. Silanes can be cured at a wide range of temperatures, and as the curing temperature increases, the curing rate and overall curing percentage increases. However, attention must be paid when curing cotton blended fabrics because cotton discolors at temperatures near 160°C. After speaking with a Gelest representative and reviewing the literature, a curing temperature of 150°C for 5 minutes was chosen in this work.

3.7 Fabric Laundering Process

In 1984, Standardization of Home Laundry Test Conditions was developed with the last revision occurring in 2005. The conditions set in the standard are set to imitate a vigorous wash cycle followed by drying. Below is a summary of the conditions set in the “Standardization of Home Laundering Conditions” by the AATCC:

- Water Level: 18 ± 1 gal (equivalent to a medium load)
- Agitation Speed: 179 ± 2 spm (equivalent to “Heavy Duty”)
- Wash Time: 12 min
- Water: Hot-Warm Cycle
- Spin Speed: 645 ± 15
- Final Spin Time: 6 min
- Detergent: 66g 1993 AATCC Standard Reference Detergent
- Ballast: Added to make a 2.7 kg load

Washing of fabrics was carried out using a General Electric Company home washing machine, model number WCSR2090DAWW, and drying was carried out using a matching General Electric Company dryer, model number DBXR463ED2WW. Drying was carried out at high heat for 45 minutes.

3.8 Testing Methods

3.8.1 Scanning Electron Microscope Characterization

Scanning electron microscopy was performed at North Carolina State's Analytical Instrumentation Facility (AIF). Select samples were taken and coated with gold-palladium. The SEM used was a Hitachi S-3200 Scanning Electron Microscope. Picture magnifications were 500x, 1000x, 5000x, and 10,000x.

3.8.2 Flame Resistance Testing

The method used for flame resistance testing was a modified version of the American Society for Testing and Materials (ASTM) Method D 6413-99: Standard Test Method for Flame Resistance of Textile (Vertical Test). AATCC Test Method 34-1969 is also a documented flame resistance test method but has been discontinued. According to the ASTM standard, 3 in. x 12 in. samples were taken from each fabric and a total of three different samples were collected from each fabric. The samples were taken as shown in Figure 3.15 (those labeled FR).

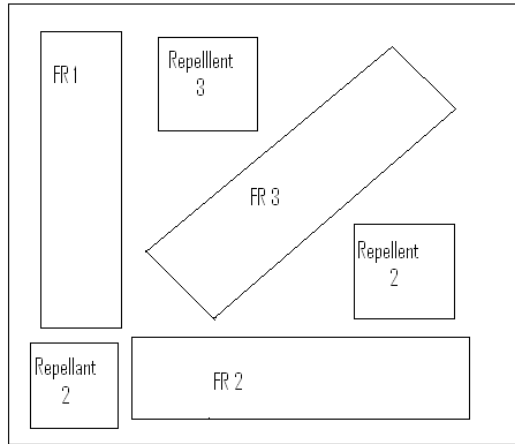


Figure 3.15: Fabric sampling for FR and ECA Tests

Once cut, fabrics were first mounted into brackets and then placed into a vertical flame chamber as shown in Figure 3.16. After the fabric was placed in the chamber, the burner was ignited, placed in the chamber, and adjusted to a flame length of 1.5 inches. For testing, the lower $\frac{3}{4}$ inch of the middle 2 inches of the fabric were introduced to the flame for a total of 8 seconds. The flame was then removed and the fabric was allowed to burn until cessation of the flame.

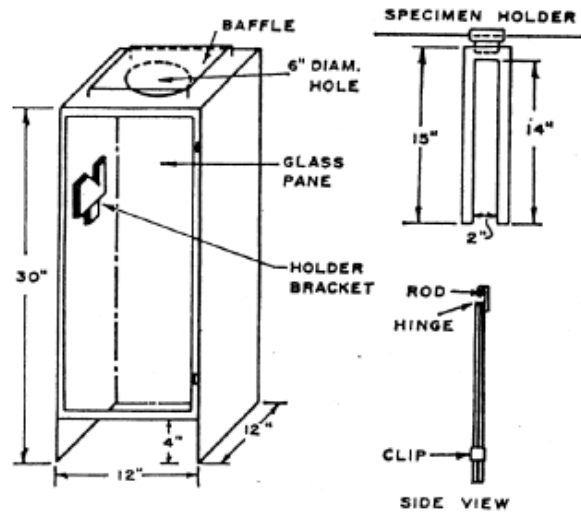


Figure 3.16: Schematic of vertical flame chamber and fabric holder

After the flame has been removed, data collected consisted of char length and after flame time. Char length is defined as the distance from the fabric edge to the furthest point of visible damage after a specified tearing force has been applied, and after flame time is defined as the time for which a material continues to flame after the ignition source has been removed. For a fabric weight of 60oz/yd^2 , the weight used for tearing is 100 grams, and measurement of char length can be visualized in Figure 3.17.

It should be noted that there are three possibilities for the outcome of the flame resistance testing:

- The fabric self extinguishes prior to combustion of the entire 12 inch sample with no afterflame time.

- The fabric self extinguishes prior to combustion of the entire 12 inch sample and has an afterflame time once the burner is removed.
- The fabric does not self extinguish once the burner is removed and burns its entire length.

In the case that the fabric self extinguishes once the burner has been removed and no afterflame is present, then the char length is the only measurement of flame resistance. Short char lengths imply that the treated fabric has high flame resistance. Increasing char length means that the fabric is less flame resistant.

Fabrics that self extinguish and have an afterflame time have two metrics relating to flame resistance. Just as with the first case, shorter char length means higher flame resistance, and longer char length means less flame resistance. Similarly, a short afterflame time means that the finished fabric was able to cessate the afterflame quickly, and longer afterflame times imply that the finished fabric was less flame resistant.

In the third case, where the fabric does not self extinguish, the context of afterflame time is slightly different. Afterflame time is now a measure of how long it takes the entire sample to combust, rather than how quickly the flame extinguishes. When the entire fabric is combusted during testing, shorter afterflame times correlate to lower flame resistance, because the treated fabric does not impede the combustion process. Thus, longer afterflame times would mean that although the treated fabric is not

flame resistant enough to self extinguish, enough flame retardant on the fabric is able to slow the progress of the flame to the entire sample length.

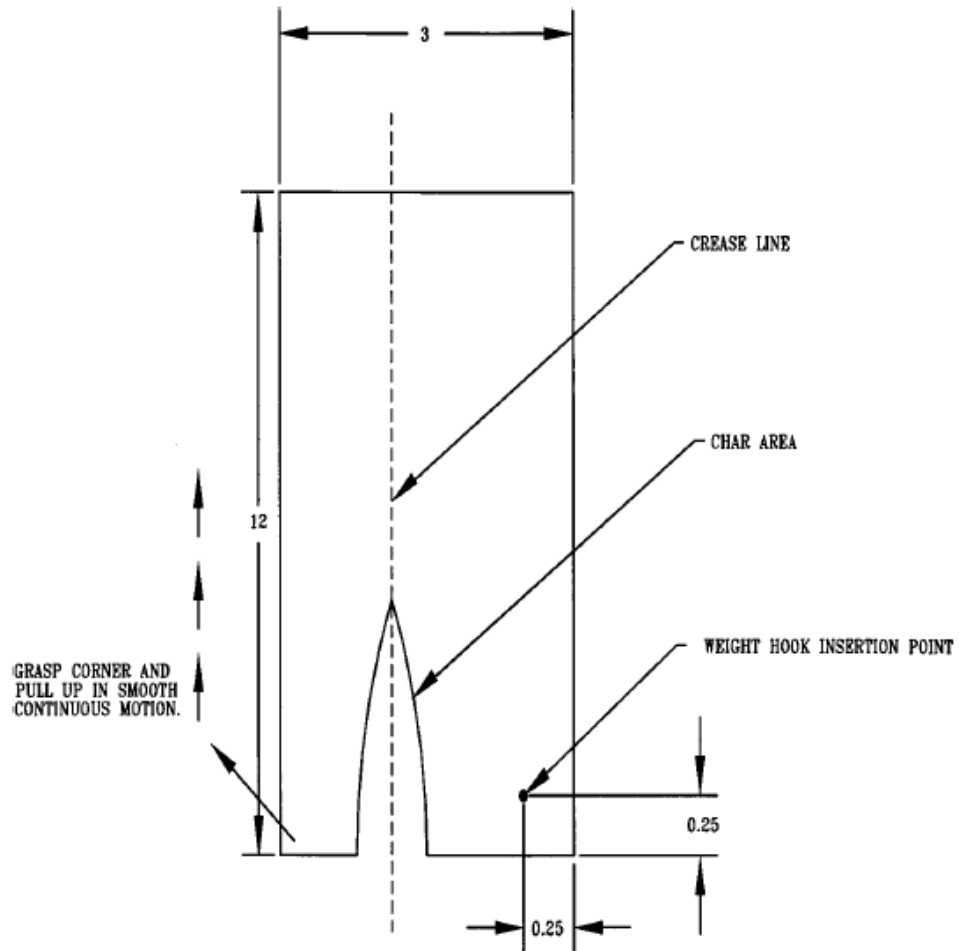


Figure 3.17: Schematic for char length measurement

Figure 3.17 shows an example of a self-extinguishing sample from vertical flame testing.

Data from flame resistance testing was collected and analyzed using Excel software.

3.9 Contact Angle Measurements

Contact angles were collected using an A-100 CA Goniometer made by Ramé-Hart, Inc. Samples used for testing were approximately 1 inch X 1 inch and were taken as shown in Figure 3.15 (labeled Repellency). The samples were placed on the sample platform of the goniometer. When using a goniometer, it is very important to have a flat fabric edge in order to get accurate data. A Gilmont Industries, 2 mL syringe was filled with high purity liquid chromatography (HPLC) water and then placed in the holder above the sample platform. The goniometer apparatus is shown in Figure 3.18.

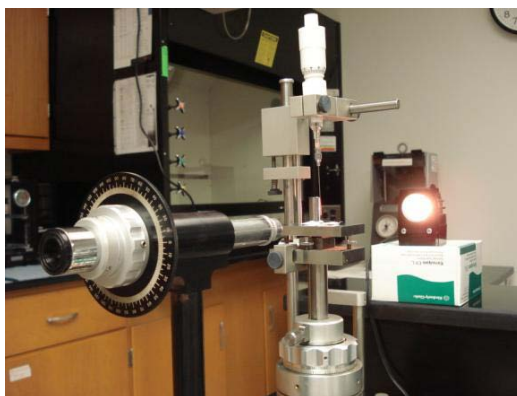


Figure 3.18: Goniometer apparatus

Once in place, a water droplet was placed onto the fabric for contact angle measurement. Average water volume necessary to form the water droplet was 0.016 mL of water. The sample was backlit using a Reichert Scientific Instruments No. 610 Illuminator. When the droplet was placed on the fabric sample, the goniometer was then manually adjusted so that the entire droplet was visible through the scope and the base

line of the scope was level with the fabric surface. The goniometer was then focused so that the water droplet edges could be easily seen. Two measurements were taken for each droplet, one on each side, by adjusting the two lines of the goniometer to form the contact angle between the droplet and the fabric line. Measurements for each sample were recorded and averaged.

4 Results and Discussion

4.1 Effects of Hydrophobic Silane Type

This study was carried out to compare the performance of fabrics treated with various hydrophobic silanes. Specifically, this study examines how the alkyl chain length of hydrophobic silane affects the performance of the treated fabric. The hydrophobic silanes used are n-butyltriethoxysilane, n-octyltriethoxysilane, dodecyltriethoxysilane, and hexadecyltriethoxysilane. Their chemical structures can be seen in Figures 3.5, 3.6, 3.7, and 3.8, respectively. All fabrics were treated with 2% hydrophobic silane, 5% TEOS, 1% silica, and 92% de-ionized water. Results from the water repellency testing are shown in Figure 4.1.

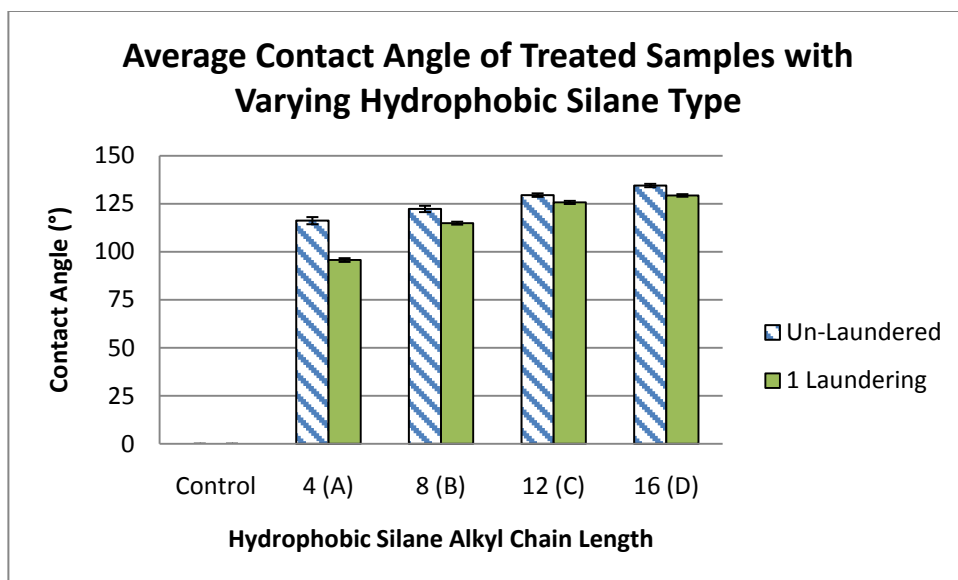


Figure 4.1: Contact Angles of samples treated with 2% hydrophobic silane, 5% TEOS, 30% THPC/Urea, 1% silica, 62% de-ionized water.

As shown in Figure 4.1, without the addition of hydrophobic silane (i.e., control), treated fabrics had no repellency. However, with the addition of hydrophobic silanes in finishing, the treated fabrics had water contact angles (WCA's) greater than 115 , indicating they are hydrophobic. In addition, when the alkyl length of the applied hydrophobic silane increased, the resulting WCA of the finished fabrics increased slightly. Specifically, an increase in the alkyl chain length from four carbons to sixteen carbons resulted in an 18.3° increase in the WCA of the treated fabric. Shown in Figure 4.2 are the control fabric and the fabric treated with hexadecyltriethoxysilane containing finish. Untreated fabrics readily absorb water, whereas samples treated with hydrophobic silane-containing finish repelled all droplets.

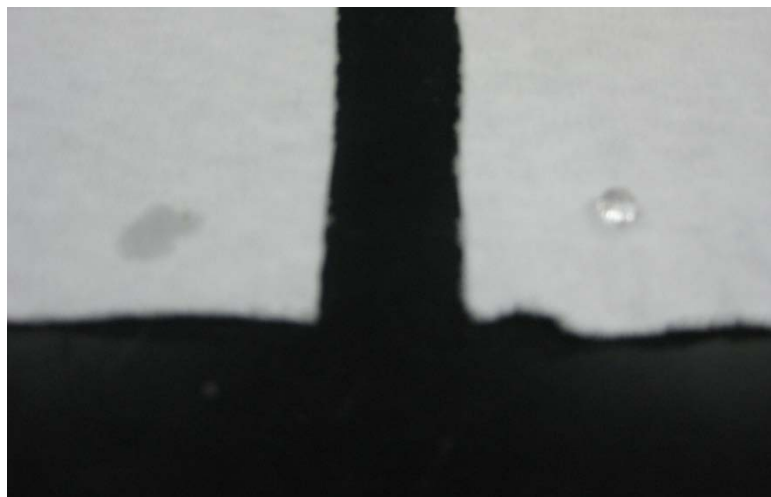


Figure 4.2: Droplets on 50/50 PET/cotton fabric treated with hexadecyltriethoxysilane (right) and control fabric (left)

From Figure 4.1, it is also seen that fabrics treated with hydrophobes with longer alkyl chain lengths provided higher durability to laundering. Fabrics treated with n-butyltriethoxysilane (4 carbons) showed a decrease in WCA of 20.5° after laundering, whereas fabrics treated with hexadecyltriethoxysilane (16 carbons) showed a decrease in WCA of only 5.2° . As the alkyl chain length of the hydrophobic silane increases, the distance between the water molecules and the surface of the fabric increases as well. By increasing the distance between the hydrophilic fabric surface and the water droplet, the interaction between the water droplet and the fabric decreases, resulting in higher repellency.

4.2 Effect of Hydrophobic Silane Concentration

This study was conducted to investigate the effect of varying hydrophobic silane concentration on the performance of the finished fabrics. Hexadecyltriethoxysilane was used as the hydrophobic silane since it gives the highest water repellency, as discussed above. Fabrics were treated with hydrophobic silane, 30% THPC/Urea , 5% BTESE, 1% silica, and de-ionized water. Hydrophobic silane concentrations were 0.1%, 0.5%, 1%, 5%, and 10%.

4.2.1 Effect of Hydrophobic Silane Concentration on Repellency

The results from water repellency testing are shown in Figure 4.3. The control fabric, which contained no hydrophobic silane, showed no repellency and all droplets were absorbed readily into the fabric. As shown in Figure 4.3, the addition of even 0.1% hexadecyltriethoxy silane was sufficient to render to the finished fabric hydrophobic. As the concentration of hexadecyltriethoxy silane was increased in the finishing bath, a slight increase in the WCA of the finished fabric is seen.

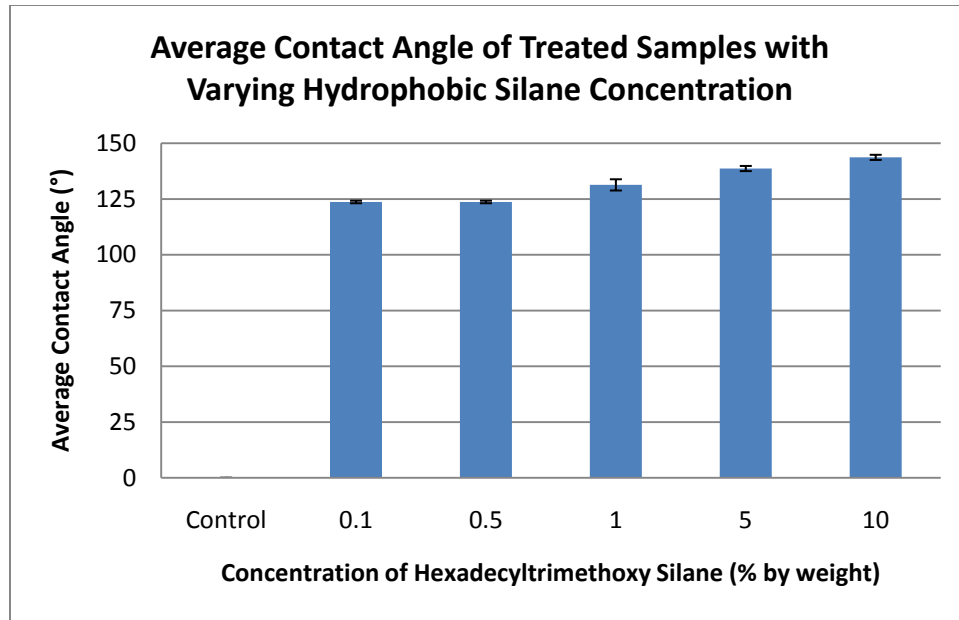


Figure 4.3: Contact Angles of samples treated with varying hexadecyltriethoxysilane concentration, 30% THPC/Urea, 5% BTESE, 1.0% silica, and 62% de-ionized water.

4.2.2 Effect of Hydrophobic Silane Concentration on Flame Resistance

Results from flame resistance testing are shown in Figure 4.4. The concentration of the hydrophobic silane did not have a significant effect on the flame resistance of the finished fabrics. As mentioned previously, shorter char lengths represent treated fabrics with higher flame resistance. All samples had average char lengths within one inch of each other, and the standard deviations of the average char lengths were all greater than a quarter inch.

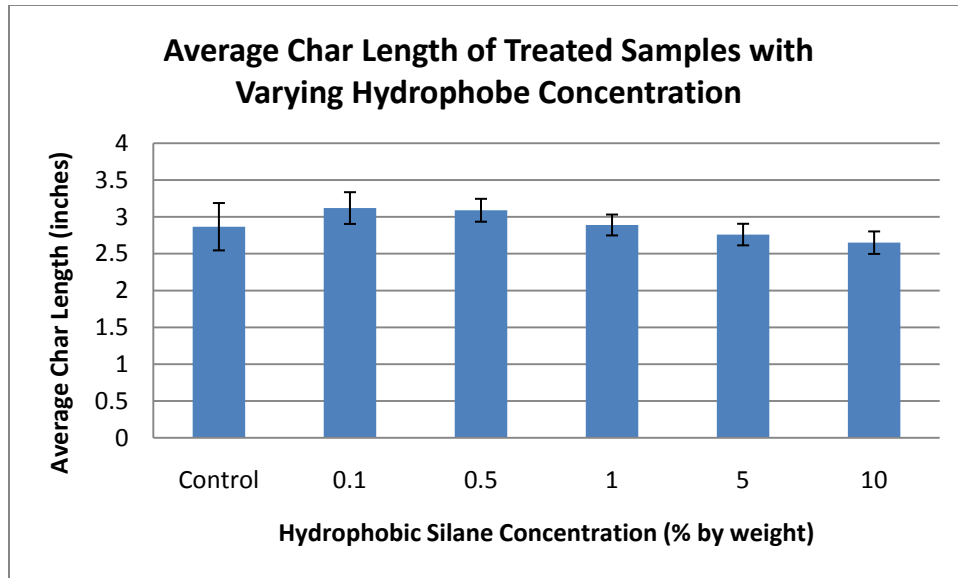


Figure 4.4: Char Lengths of samples with varying hexadecyltriethoxysilane concentration, 30% THPC/Urea, 5% BTESE, 1.0% silica, and 62% de-ionized water.

As shown in Figure 4.4, the samples treated with 10% hydrophobic silane did have the lowest average char length of 2.65 with a standard deviation of 0.3, but the control fabric with no hydrophobic silane had an average char length of 2.86 with a standard deviation of 0.64 inches, which is similar to that of the sample treated with 10% hydrophobic silane.

Since the hydrophobic silane serves only to maintain sufficient distance between water droplets and the fabric surface, it is not expected that the concentration of the hydrophobic silane would have an impact on the flame resistance of the treated fabric. If

the flame retardants applied in the finish worked via the vapor phase, byproducts from the combusted silanes may have had an interaction; however, phosphorus based flame retardants act in the condensed phase and hence no apparent difference is seen on the flame resistance when the hydrophobic silane is added.

4.3 Effect of Silane Crosslink Enhancer Type

This study was performed to understand whether or not the type of silane crosslink enhancer used to modify the 3-dimensional crosslinked network had any effect on the performance of the treated fabric. The silanes used for testing are TEOS, TMOS, BTESE, and BTMSE. After all initial data were gathered, 3-isocyanopropyltriethoxysilane was chosen as another possible silane crosslink enhancer and will be described in more detail in Section 4.6. All fabrics were treated with 5% silane crosslink enhancer, 30% THPC/Urea, 2% hexadecyltriethoxysilane, 1% silica, and 62% de-ionoized water.

4.3.1 Effect of Silane Crosslink Enhancer Type on Repellency

Due to the fact that the silane crosslink enhancer serves to enhance the durability of the finish on the fabric, treated fabrics were laundered and tested three times to more accurately assess the durability of each finish. The results from the repellency testing are shown in Figure 4.5. With respect to initial contact angle, the type of silane crosslink enhancer has little effect; even the control fabric with no crosslink enhancer had an initial

WCA of 128°. However, the addition of a crosslink enhancer does have a large effect on the durability of the finish.

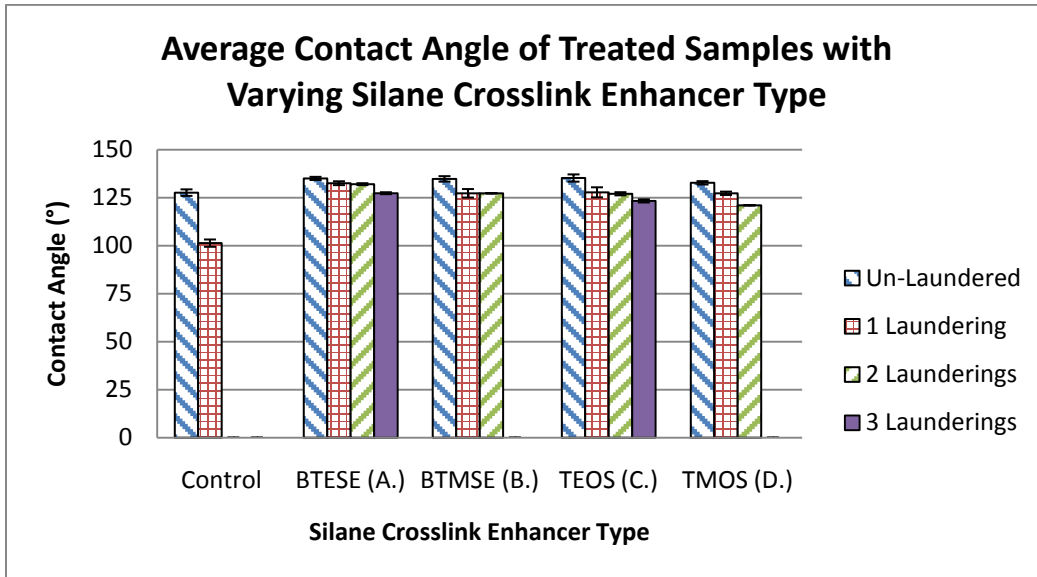


Figure 4.5: Contact Angles of samples treated with 5% silane crosslink enhancer with varying type, 30% THPC/Urea, 2%hexadecyltriethoxy silane, 1.0% silica, and 62% de-ionized water.

Among these four silane crosslink enhancers, methoxysilanes, such as TMOS and BTMSE, were unable to maintain repellency after three launderings. In contrast, ethoxysilanes, such as TEOS and BTESE, provide better durability to laundering, as they were able to withstand three launderings and still maintain a contact angle above 120°. Fabric treated with BTESE containing finish had the highest WCA of 127.3° after three launderings, which is 94.3% of the initial WCA. Since fabrics treated with BTESE-

containing finish provided the highest durability to laundering, this finish was chosen for use in all future tests.

4.3.2 Effect of pH on Repellency

Since it was noted that the pH value plays a role in the physical structure of the resultant 3-dimensional network formed by silanes, BTESE and TEOS were both hydrolyzed at two different pH values. Samples were hydrolyzed with no pH modification (pH ~3), and with the addition of 0.1 molar sodium bicarbonate to raise the pH value to 4.5. Samples were then laundered and tested twice to ensure accuracy.

Results from the repellency testing of samples with varying pH are shown in Figure 4.6. No apparent difference can be seen between samples with the same silane crosslink enhancer but different pH values. Initial contact angles of TEOS samples with a hydrolysis pH of 4.5 had higher initial WCA's, as opposed to BTESE treated samples, which had higher initial WCA's when the pH was not modified (i.e. pH = 3.0). Since the hydrophobic silanes extend off of the surface of the treated fabric (Figure 3.1), the morphology of the 3-dimensional network created has no apparent effect on the repellency of the treated fabric.

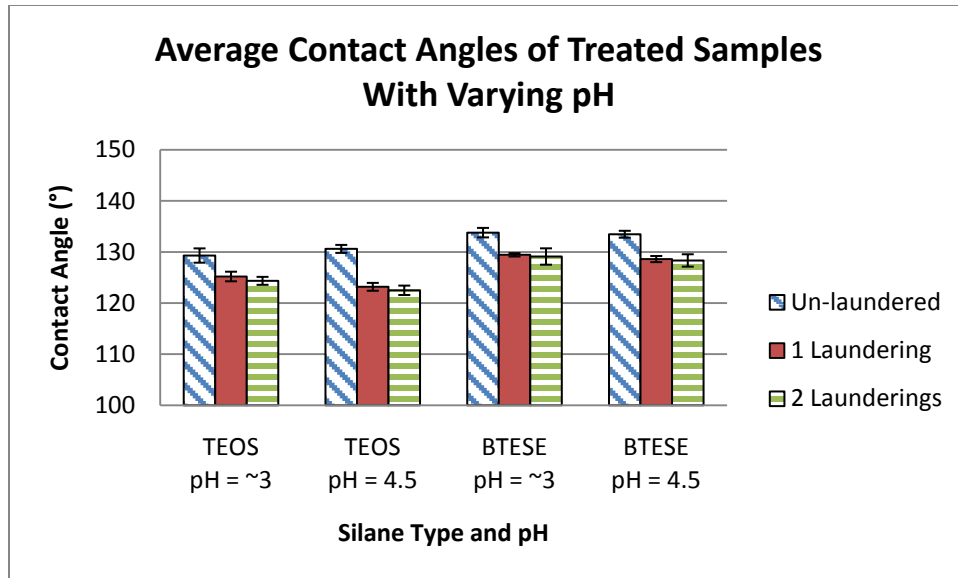


Figure 4.6: Contact Angles of samples treated with varying pH, 5% TEOS or BTESE, 30% THPC/Urea, 2%hexadecyltriethoxy silane, 1.0% silica, and 62% de-ionized water.

After laundering, samples that had the hydrolysis pH raised all had slightly lower WCA's, but the differences were small and insignificant. Since no real apparent difference was seen when the pH value was raised during hydrolysis, all following experiments were conducted without modifying the pH during hydrolysis.

4.3.3 Effect of Silane Crosslink Enhancer Type on Flame Resistance

After testing the repellency of the treated fabrics, only BTESE and TEOS were tested for flame resistance since they provided higher durability for the repellent performance.

Results for the flame resistance testing are shown in Figures 4.7 and 4.8 .

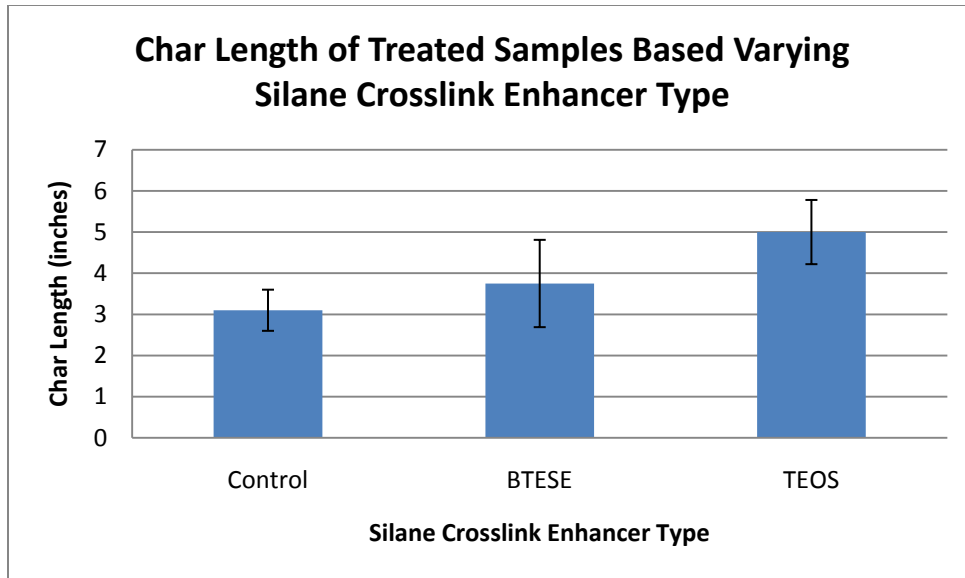


Figure 4.7: Char lengths of samples with 5% silane crosslink enhancer, 30% THPC/Urea, 2% hexadecyltriethoxysilane, 1% silica, 62% deionized water.

Testing of treated fabrics prior to laundering shows that the addition of a silane crosslink enhancer may have a small negative effect on the initial flame resistance of the finished fabric. Fabrics treated with BTESE had an average char length of 3.8 inches with a standard deviation of 1.1 inches, and fabrics treated with TEOS had an average char length of 5.0 inches with a standard deviation of 0.8 inches. But the control fabric provided the best flame resistance, i.e., an average char length of 3.1 inches with a standard deviation of 0.5 inches. However, it must be noted that the change in char length when silane crosslink enhancers were added was insignificant.

The crosslink enhancer serves to increase the crosslink density of the 3-dimensional network created during curing. If the crosslink enhancer has a higher affinity for bonding than the flame retardant, it may replace some of the flame retardant on the surface, reducing the overall content of flame retardant on the treated fabric, which in turn leads to lower flame resistance. However, that effect is minimal.

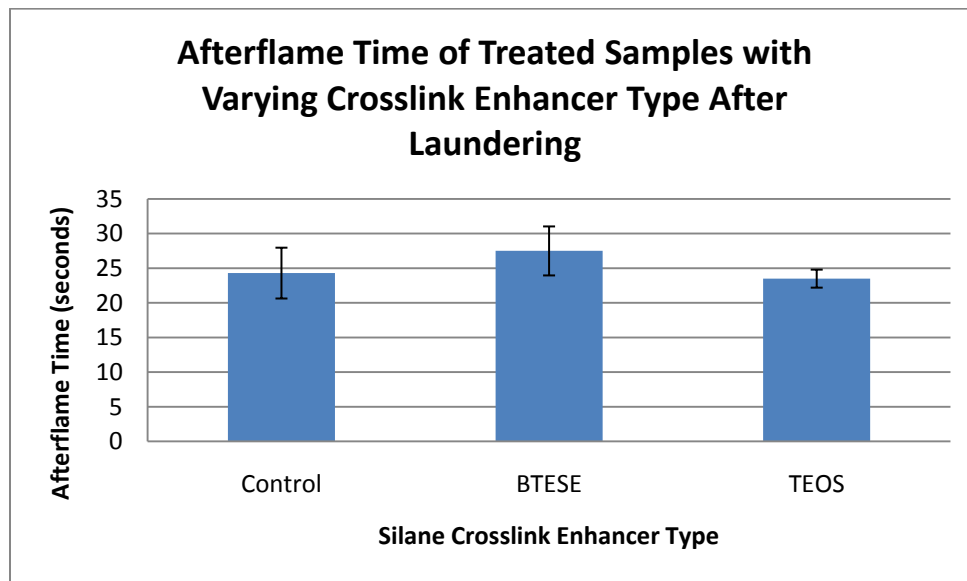


Figure 4.8: Afterflame Times of samples with 5% silane crosslink enhancer, 30% THPC/Urea, 2% hexadecyltriethoxysilane, 1% silica, 62% deionized water after laundering.

After laundering, no fabrics self extinguished, but fabrics treated with BTESE provided the best flame resistance and had an average afterflame time of 27.5 seconds with standard deviation of 3.5 seconds (Figure 4.8). Both control and TEOS fabrics

burned less than three seconds faster than the BTESE fabric. Although the difference may be small, data from flame resistance and repellency testing show that BTESE provided the most durable finish as compared to other silane crosslink enhancers.

4.4 Effect of Silane Crosslink Enhancer Concentration

This study was conducted to study how the concentration of the silane crosslink enhancer affects the performance of the finished fabrics. Samples were treated with varying BTESE concentration, 30% THPC/Urea, 2% hexadecyltriethoxysilane, 1% silica, and de-ionized water. The BTESE concentrations used were 0.1%, 0.5%, 1%, 5%, and 10%.

4.4.1 Effect of Silane Crosslink Enhancer Concentration on Repellency

The results from the repellency testing are shown in Figure 4.9. The concentration of BTESE applied to the fabrics does not have an apparent effect on the initial contact angle of the treated fabrics, and all samples had initial WCA's within 2° of 135°. However, the presence of a crosslink enhancer in the finishing bath has a positive impact on the durability of the finish. The fabric treated with 10% BTESE, which is 100 times more concentrated than the fabric treated with 0.1% BTESE, had a contact angle of 132° after laundering, whereas the sample treated with 0.1% BTESE had a contact angle of 128° after laundering. Thus, the presence of a crosslink enhancer in the bath does positively affect the durability of the finish, and increasing the concentration of the crosslink enhancer in the bath leads to a slight increase in finish durability.

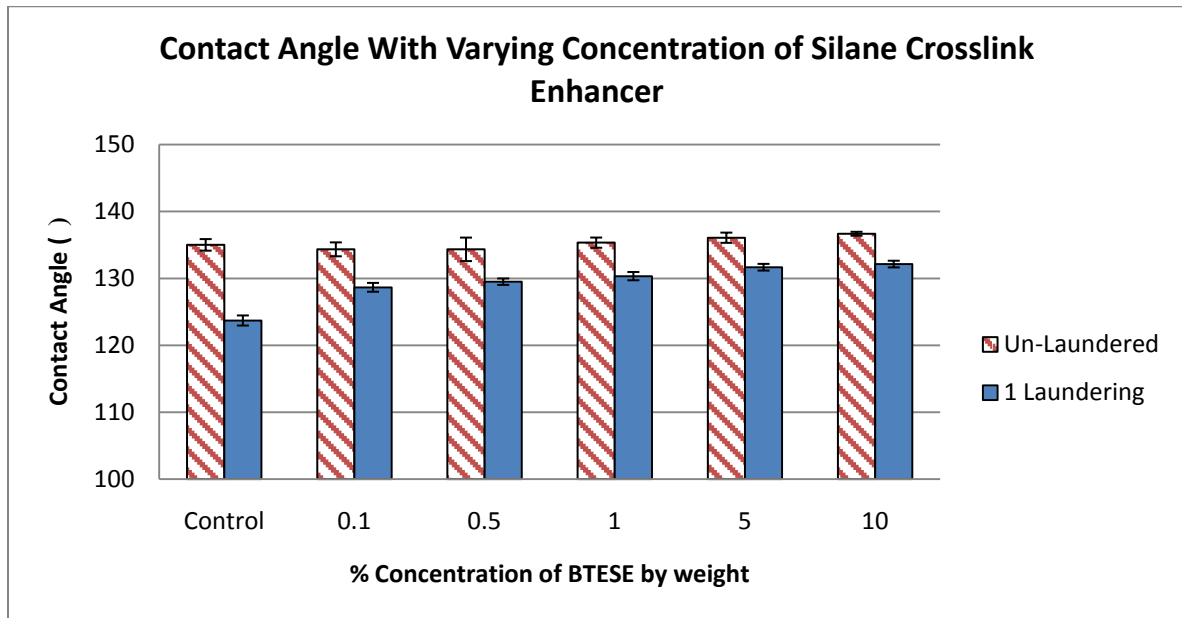


Figure 4.9: Contact Angles of samples treated with varying BTESE concentration, 30% THPC/Urea, 2% hexadecyltriethoxysilane, 1% silica, and de-ionized water.

4.4.2 Effect of Silane Crosslink Enhancer Concentration on Flame Resistance

The results from flame resistance testing are shown in Figures 4.10 and 4.11. With respect to the initial char length of the treated fabrics, the concentration of BTESE applied has no apparent effect on the initial flame resistance of the treated fabrics, which is similar to the repellency results. All fabrics self-extinguished after removal of the flame and had initial char lengths between 2.5 and 3.5 inches; most fabrics had standard deviations of about 0.5 inches. Fabrics treated with 10% BTESE did have the lowest average char length, 2.7 inches with a standard deviation of 0.5 inches, but fabrics treated

with 0.1% BTESE had an average char length of only 3.0 inches and a standard deviation of 0.5 inches. Since, the crosslink enhancing silanes primarily increase the crosslink density of the 3-dimensional network, initial flame resistance is not expected to change based upon the concentration of the silane crosslink enhancer.

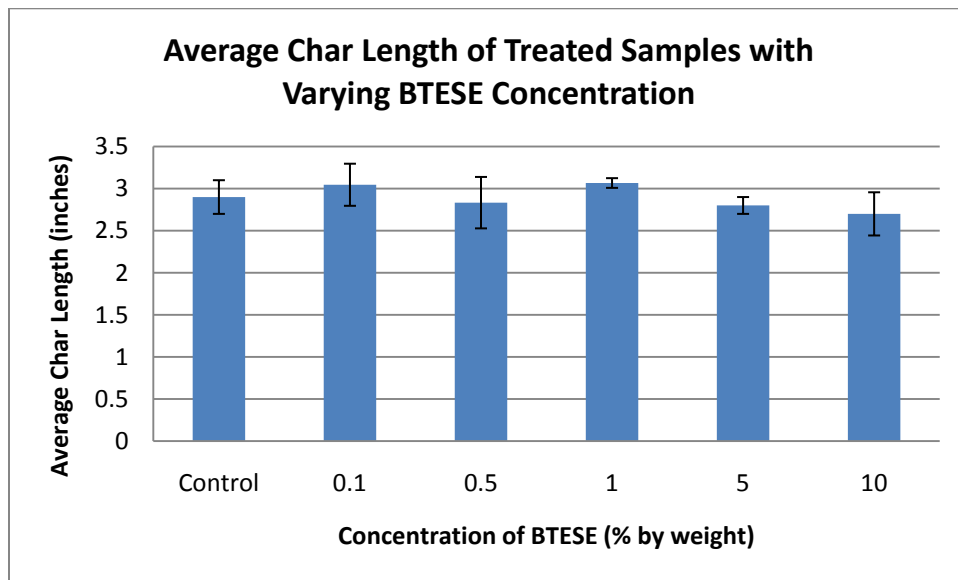


Figure 4.10: Char Lengths of samples treated with varying BTESE concentration, 30% THPC/Urea, 2% hexadecyltriethoxysilane, 1% silica, and de-ionized water.

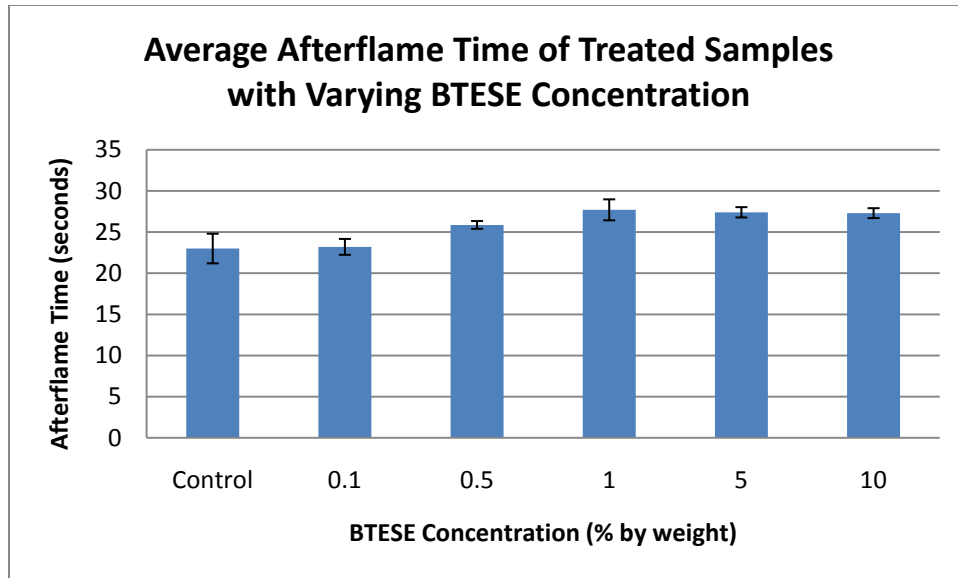


Figure 4.11: Afterflame Times of samples treated with varying BTESE concentration, 30% THPC/Urea, 2% hexadecyltriethoxysilane, 1% Silica, and de-ionized water after laundering.

Just as discussed in Section 4.4.1, results in Figure 4.11 appear to show that the concentration of BTESE applied to the fabric does have a positive impact on the durability of the finish. However, 0.1% BTESE treated fabrics showed no real increase in durability over control fabrics. Samples treated with 1% BTESE had the highest average afterflame time, 27.7 seconds with a standard deviation of 2.5 seconds, but samples treated with 5% and 10% BTESE were within 0.3 seconds of the 27.7 seconds and had comparable standard deviations.

Compared to results from Section 4.4.1, the concentration of crosslink enhancer had a similar impact on the flame resistance of the fabric as it did the repellency of the fabric. A reason for this trend is that the structure of the hydrophobic silanes are very similar to that of the crosslink enhancing silanes. Structurally, hexadecyltriethoxy silane is identical to TEOS, except that one of the hydrolysable ethoxy groups is replaced is a 16 carbon alkyl chain. Hexadecyltriethoxysilane has three hydrolysable groups to form crosslinks as opposed to the four available in TEOS; thus, even without a crosslink enhancer, the hydrophobic silane would create a similar 3-dimensional crosslinked network, but with less cross-linking density.

4.5 Effect of Ceramic Nanoparticles

Since the ceramic nanoparticles have synergistic relationships with both hydrophobic silanes and phosphorus based flame retardants, this research was conducted to understand how ceramic nanoparticle impact the performance of the finished fabric. Silica and titania nanoparticles were used in this research, and fabrics were treated with varying ceramic nanoparticle concentration, 40% THPC/Urea, 5% BTESE, 2% hexadecyltriethoxysilane, and de-ionoized water. The concentration of the THPC/Urea precondesate was also increased for this line of experiments after running the same experiment at the usual concentration of 30%. The reason for the increase in THPC/Urea concentration is because data at lower concentrations showed no apparent difference between either type of ceramic nanoparticle.

4.5.1 Effect of Ceramic Nanoparticles on Repellency

Results from repellency testing are shown in Figure 4.12. When comparing the performance of the finished fabrics with respect to ceramic nanoparticle type, no apparent difference is seen at any concentration. However, as the concentration of ceramic nanoparticles increased in the bath, the resultant WCA of the treated fabrics increased. The sample treated with 3% silica had the highest WCA of 139° with a standard deviation of 1.5° . Samples treated with 3% titania had an average WCA of 137° with a standard deviation of 1.7° . Even the addition of 0.1% silica or titania had a positive effect on the repellency of the finish. Samples treated with 0.1% ceramic nanoparticles had an average WCA increase of 5° . Since a low concentration of ceramic nanoparticles was sufficient to increase the contact angle of the treated samples, some repellency must be attributed to the lotus effect. Due to the hydrophilic nature of the ceramic nanoparticles used in this work, adding the nanoparticles to the finishing bath would result in lower repellency if the silanes were not present to help crosslink the ceramic nanoparticles into the 3-dimensional network. Thus, the surface roughness gained by the addition of ceramic nanoparticles must have a positive impact on the repellency of the treated fabrics.

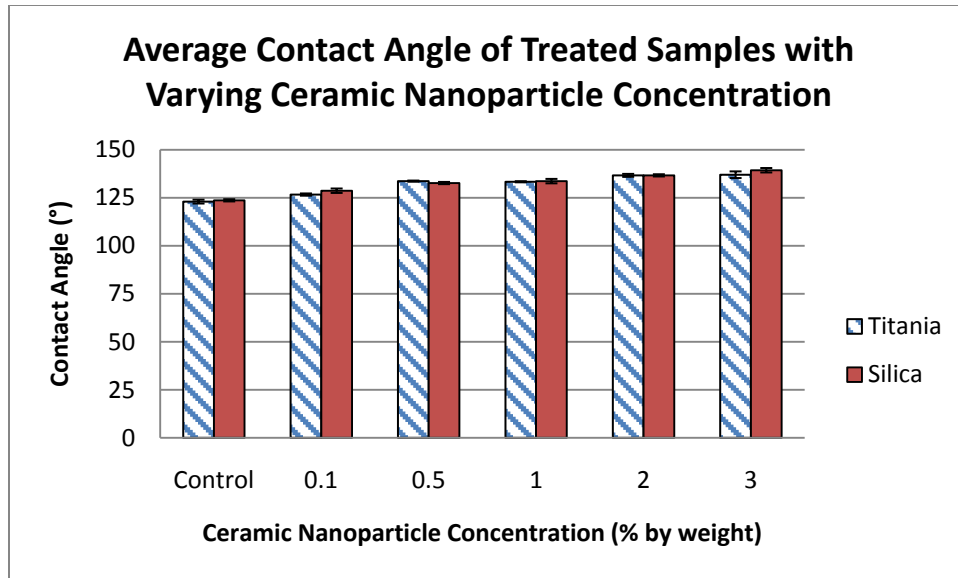


Figure 4.12: Contact Angles of samples treated with varying ceramic nanoparticle concentration, 40% THPC/Urea, 5% BTESE, 2% hexadecyltriethoxysilane, and de-ionized water.

4.5.2 Effect of Ceramic Nanoparticles on Flame Resistance

Results from flame resistance testing are shown in Figures 4.13 and 4.14. For the initial char length data, there is no apparent difference between titania and silica at any concentration. Furthermore, increasing the concentration of the ceramic nanoparticles in the bath does not have a large impact on the flame resistance of the finished fabrics. Samples treated with 3% ceramic nanoparticles did create finished fabrics with the lowest char lengths; samples treated with 3% silica had the lowest average char length of 3.0 inches with a standard deviation of 0.5 inches, and samples treated with 3% titania had an average char length of 3.1 inches, with a standard deviation of 0.25 inches.

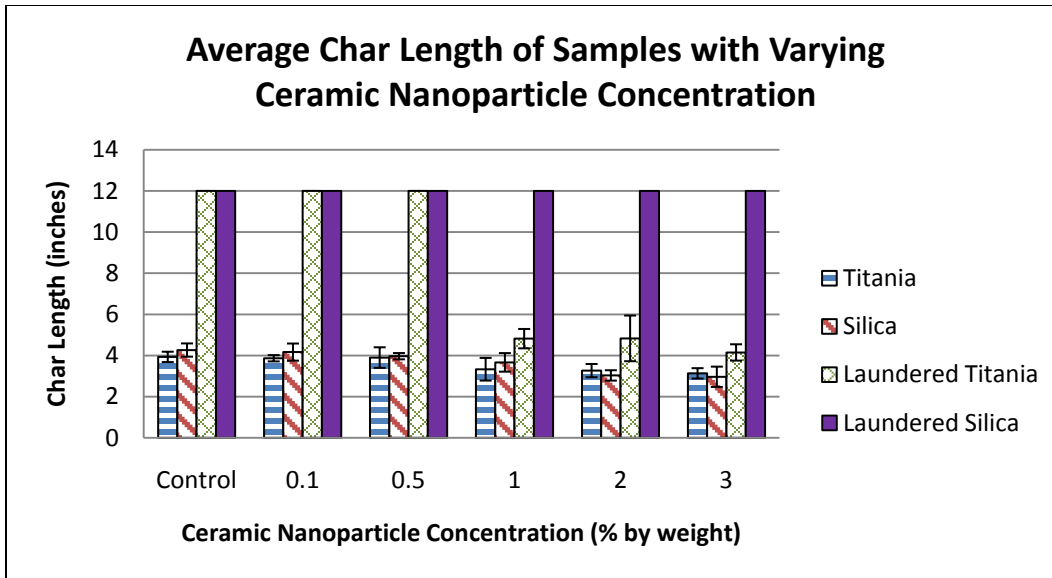


Figure 4.13: Char Lengths of samples treated with varying ceramic nanoparticle concentration, 40% THPC/Urea, 5% BTESE, 2% hexadecyltriethoxysilane, and de-ionized water.

However, after laundering, samples show drastically different char lengths. No samples treated with silica self extinguished after laundering, and only those samples treated with 1% titania or higher self extinguished after removal of the flame. Samples treated with 3% titania had the lowest average char length after laundering, 4.15 inches, with a standard deviation of 0.79 inches.

Even though no samples with silica self extinguished after laundering, they did tend to have slightly higher afterflame times than did samples with titania when the

concentration was below 1% (Figure 4.14). However, at concentrations of 1% and above, titania treated samples had no afterflame time.

The fact that titania provides better flame resistance has also been found by other researchers for different systems. For example, work by Laachachi et al. showed that the use of titania in place of silica increased the thermal stability of PMMA fabrics and reduced overall heat evolved [35]. As a result, fabrics treated with higher concentrations of titania were able to cessate the flame prior to the sample burning its entire length. Due to the fact that only fabrics treated with titania produced finishes durable to laundering, titania was used in all future experiments.

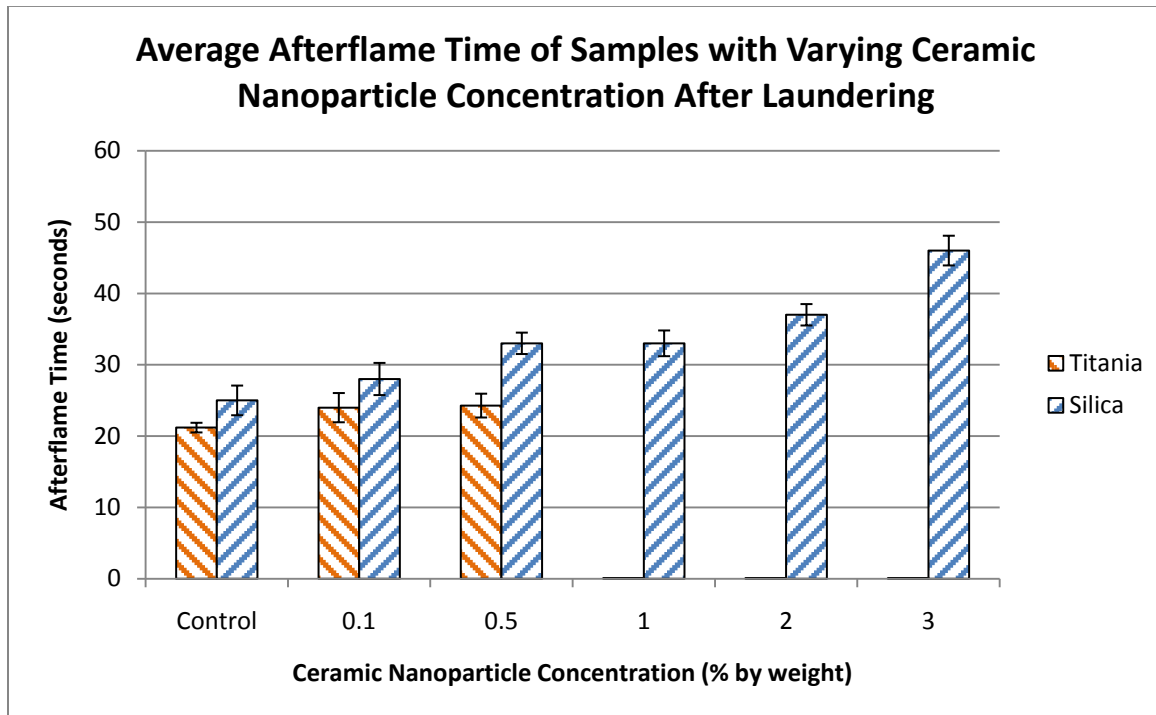


Figure 4.14: Afterflame times of samples treated with varying ceramic nanoparticle concentration, 30% THPC/Urea, 5% BTESE, 2% hexadecyltriethoxysilane, and de-ionized water after laundering.

4.6 Effect of Organofunctional Silane Crosslink Enhancer

Throughout the course of this research, all crosslink enhancing silanes had only functional methoxy or ethoxy hydrolysable groups to serve as crosslink points. Using these types of silanes, only fabrics treated with both high levels of flame retardants and titania particles showed good durability to laundering. In order to enhance the bonding of THPC/Urea flame retardant into the three dimensional silane network, an additional silane was chosen as a crosslink enhancer, 3-isocyanatopropyltriethoxysilane (IPTES). The structures of IPTES and TEOS can be seen in Figure 4.15. The only difference between IPTES and TEOS is that one ethoxy group is replaced with a non-hydrolyzable isocyanatopropyl group, which has extremely high reactivity. The idea behind using IPTES is that the organofunctional isocyanate group can bond with the available hydroxyl groups of both the THPC/Urea flame retardant and also the cellulosic fibers in the blended fabric.

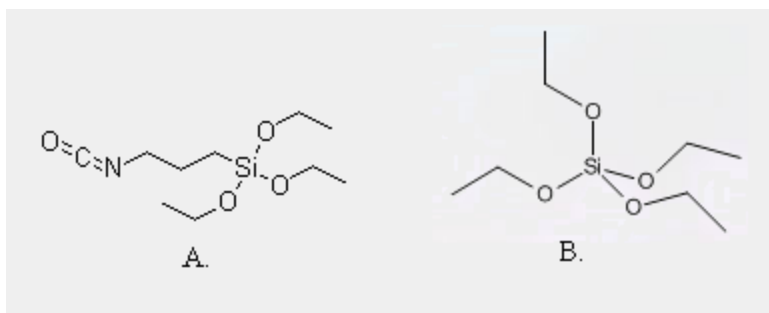


Figure 4.15: Chemical structures of (A): 3-isocyanatopropyltriethoxysilane (IPTES) and (B): tetraethoxysilane (TEOS)

Since IPTES is much more reactive than the silane crosslink enhancers described in previous sections, the hydrolysis process had to be modified to prevent the silane from reacting with other compounds. Throughout the rest of the research, IPTES and hexadecyltriethoxysilane were hydrolyzed in separate containers with half of the total de-ionized water each. The THPC/Urea flame retardant and titania nanoparticles were mixed in a separate container. Fifteen minutes prior to application of the finish onto the fabric, all three solutions were combined and mixed for 10 minutes prior to dispersion of the nanoparticles using the high speed mixer. Once mixed, application, drying, and curing were all performed in the same manner as all other samples.

4.6.1 Effect of Hydrolysis Time

Once IPTES was incorporated as a silane crosslink enhancer, the length of hydrolysis came into question because samples that were hydrolyzed for long periods of time became too viscous to apply to the fabrics. As such, a set of experiments were run to find

an optimal hydrolysis time for the silanes. Silanes were hydrolyzed for 6, 9, and 12 hours with 5% IPTES, 2% hexadecyltriethoxysilane, 30% THPC/Urea, 1% titania, and 62% de-ionized water.

4.6.1.1 Effect of Hydrolysis Time on Repellency

Results from repellency tests are shown in Figure 4.16.

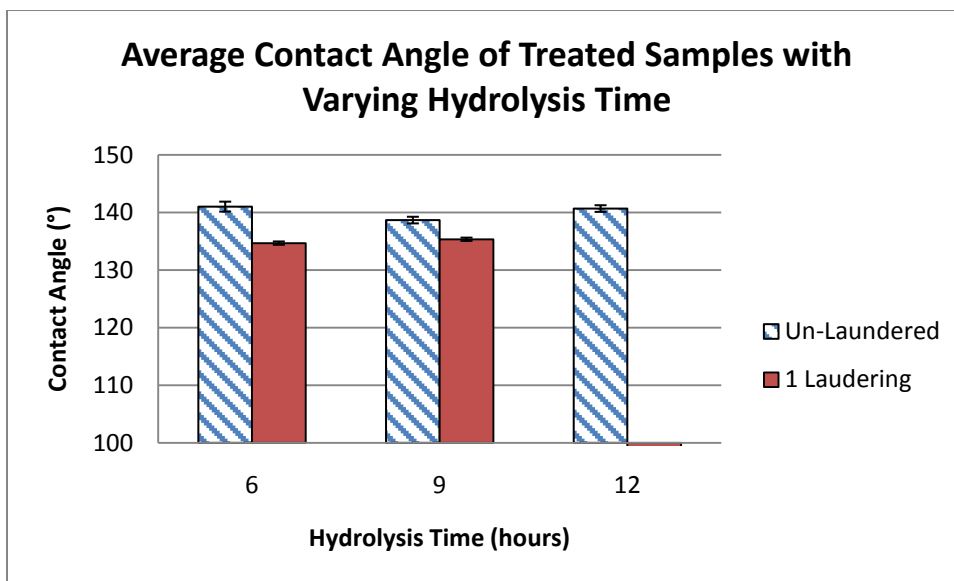


Figure 4.16: Contact Angles of samples treated with 5% IPTES, 2% hexadecyltriethoxysilane, 30% THPC/Urea, 1% titania, 62% de-ionized water and varying hydrolysis time.

The hydrolysis time of the silanes has no apparent effect on the initial contact angle of the treated fabrics. The sample hydrolyzed for 6 hours produced the most repellent finish, having an average WCA of 141° with a standard deviation of 1.73°. However, all other samples also had initial WCA's no less than 4° from 141°. After laundering the samples,

results show that increasing hydrolysis time of the silanes has a negative impact on the durability of the finish. Silanes hydrolyzed for 9 hours or less lead to fabrics that are durable to laundering, with those hydrolyzed for 9 hours having the highest average WCA after laundering, 135°, with a standard deviation of 0.57°. Samples with silanes hydrolyzed for 12 hours showed no durability to laundering.

One of the main reasons that hydrolysis time plays such an important role in the performance of the treated fabrics is because only de-ionized water was used for hydrolysis in this work. Commonly, ethanol is used to hydrolyze silanes because it can be used safely without running the risk of the bath prematurely polymerizing. When only water is used, long hydrolysis periods allow the sol to polymerize and the viscosity increases drastically. In addition, isocyanate containing compounds can react with water in a foaming reaction that releases CO₂. Thus, hydrolysis time must be carefully monitored to maximize the reactions of silanes prior to the application on the fabric substrate.

4.6.1.2 Effect of Hydrolysis Time on Flame Resistance

Results from flame resistance testing are shown in Figure 4.17. With respect to initial char length, the hydrolysis time of the silanes had no apparent impact on flame resistance. All samples had initial char lengths of less than 3.5 inches. After laundering, an interesting phenomenon occurred. As opposed to the results from repellency in Section 4.6.1.1, increasing the hydrolysis time of the silane IPTES appears to increase the durability of the finished fabric with respect to flame resistance. All samples hydrolyzed

for 12 hours self-extinguished after laundering with no afterflame time. Of the samples hydrolyzed for 9 hours, 60% of fabrics self extinguished, and 40% burned the entire 12 inches of fabric. However, no samples hydrolyzed for 6 hours showed any durability to laundering, and all samples burned the entire length.

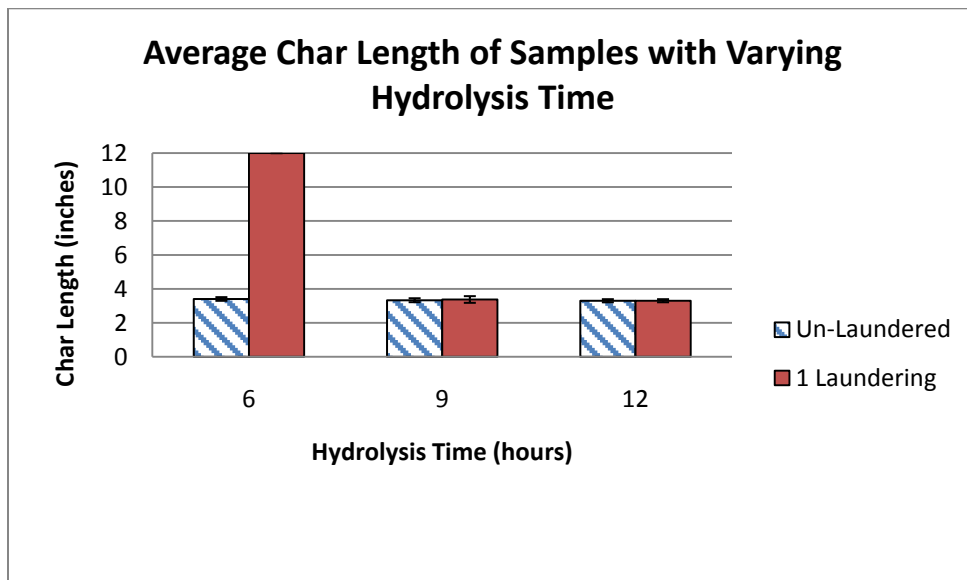


Figure 4.17: Char Lengths of samples treated with 5% IPTES, 2% hexadecyltriethoxysilane, 30% THPC/Urea, 1% titania, 62% de-ionized water and varying hydrolysis time.

As a result, it appears that hydrolysis of the silanes has a precise window, within which treated samples are able to maintain flame resistance and repellency after laundering. When samples are hydrolyzed for too short of a time, no durability of flame

resistance is maintained; while samples hydrolyzed for long periods of time (e.g., 12 hours) were unable to provide durable repellency. However, samples hydrolyzed for a period of 9 hours showed durability to laundering for both repellency and flame resistance.

4.6.2 Effect of Titania Nanoparticles on Flame Resistance

Previous data presented in Section 4.5.2 have shown to there is little effect of titania nanoparticles on the initial flame resistance of treated fabrics. As a result, another set of trials was run to further assess the effects of titania nanoparticles on flame resistance when IPTES was used. Since no apparent difference was seen between different concentrations of titania when the concentration of the THPC/Urea flame retardant was 30%, another set of fabrics were treated with various concentrations of titania, 20% THPC/Urea, 5% IPTES, 2% hexadecyltriethoxysilane, and de-ionized water. Results from flame resistance testing are shown in Figure 4.18 and Figure 4.19.

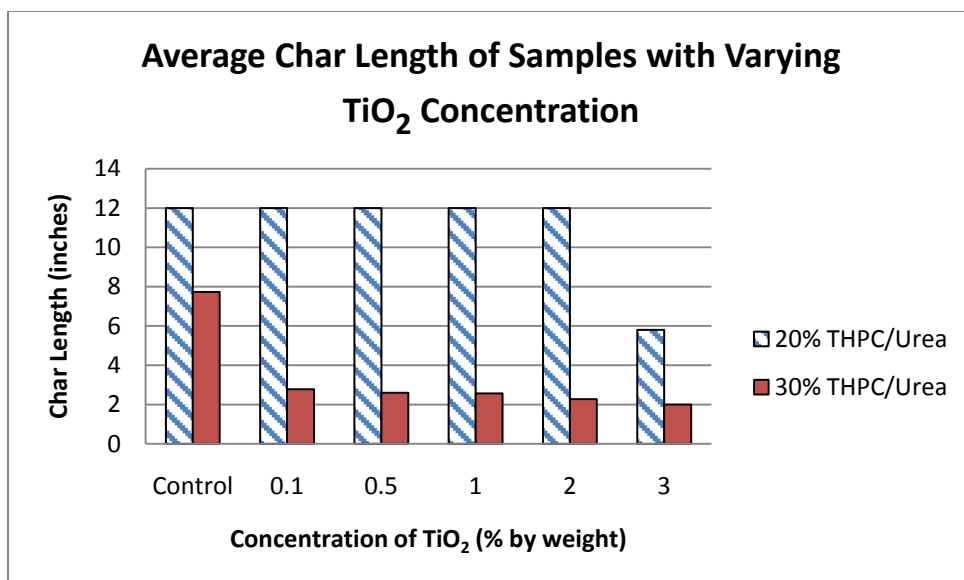


Figure 4.18: Char Length of samples treated with various concentrations of titania, two levels of THPC/Urea, 5% IPTES, 2% hexadecyltriethoxysilane, and de-ionized water.

Initial data for 30% THPC/Urea samples was very similar to those shown in Section 4.5.2, the addition of titania nanoparticles into the finish had a positive effect on flame resistance even at very low concentrations, however little difference was seen between samples as the concentration of titania increased. In contrast, when the concentration of THPC/Urea was 20%, only a treated fabrics with 3% titania self extinguished. Thus, the increase in titania concentration had a positive impact on the flame resistance of the treated fabrics. The addition of 3% titania in the finishing bath was able to render a fabric flame resistant. In addition, the afterflame time data further supported the beneficial effect that titania has on flame resistance (Figure 4.19). At a

THPC/Urea concentration of 20%, afterflame times of samples increased as the concentration of titania in the bath increased.

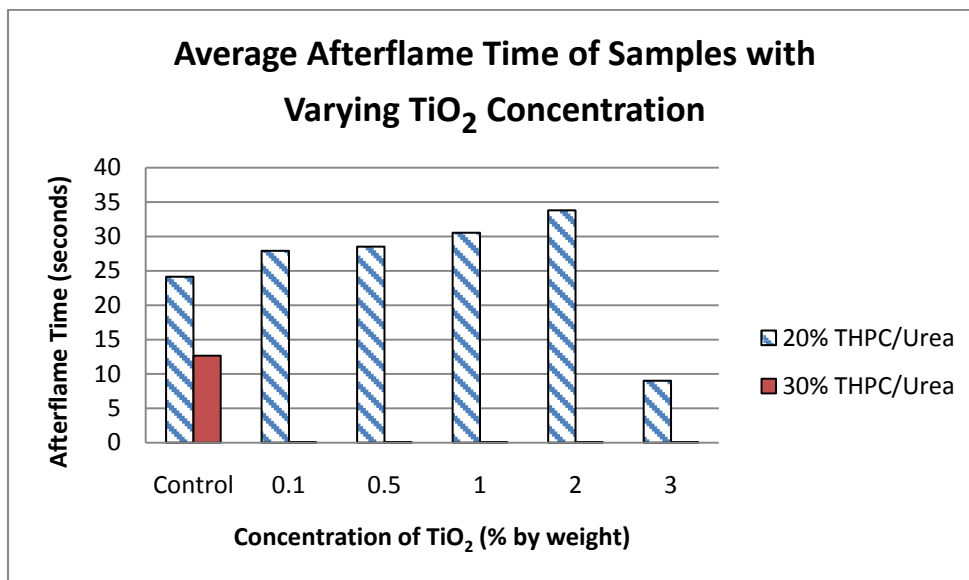


Figure 4.19: Afterflame time of samples treated with various concentrations of titania, two levels of THPC/Urea, 5% IPTES, 2% hexadecyltriethoxysilane, and de-ionized water.

4.7 SEM Characterization of Finished Fabrics

To understand the effect of laundering and titania concentration on the finished fabrics, surface morphology of selected treated fabrics was analyzed qualitatively using Scanning Electron Microscopy (SEM). Analyzed fabrics were prepared according to the following formulas:

- 0% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 63% de-ionized water
- 1% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 63% de-ionized water,
- 3% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% Pyrosan[®] C-FR, 63% de-ionized water

SEM images were gathered both pre- and post-laundering at 500x, 1000x, 5000x, and 10,000x magnification. Magnifications of 500x and 1000x offered the best representation of the treated fabrics as a whole. In order to view individual titania nanoparticles, a magnification of 20,000x or higher would be required, which is outside the ability of the SEM used for this research.

4.7.1 50/50 PET/cotton fabrics treated with 1% titania

The first image, Figure 4.20, is of untreated 50/50 PET/cotton fabric. From the image, it is obvious that the fabric is untreated, and no apparent damage is visible. As shown in Figure 4.20, the blend of lumen shaped (cotton) fibers and circular (PET) fibers implies an intimate blend of 50% cotton and 50% PET. Shown in Figure 4.21 is the same fabric treated with 1% titania, 5% BTESE, 2% hexadecyltriethoxysilane, and 30% THPC/Urea. The treated fabric has a rougher surface than does the untreated fabric, which is distinctly visible on the lumen shaped treated cotton fibers, implying successful and even coating of the fibers with the finish. The lack of agglomerations in Figure 4.21 shows that the

dispersion of titania particles was successful. However, a crack in the finish can be seen, which implies that the finish may coat multiple fibers into groups. When using water as a hydrolysis medium, long hydrolysis allows the solution to partially polymerize and the viscosity of the finishing bath will increase, which may cause coating of multiple fibers rather than single fibers.

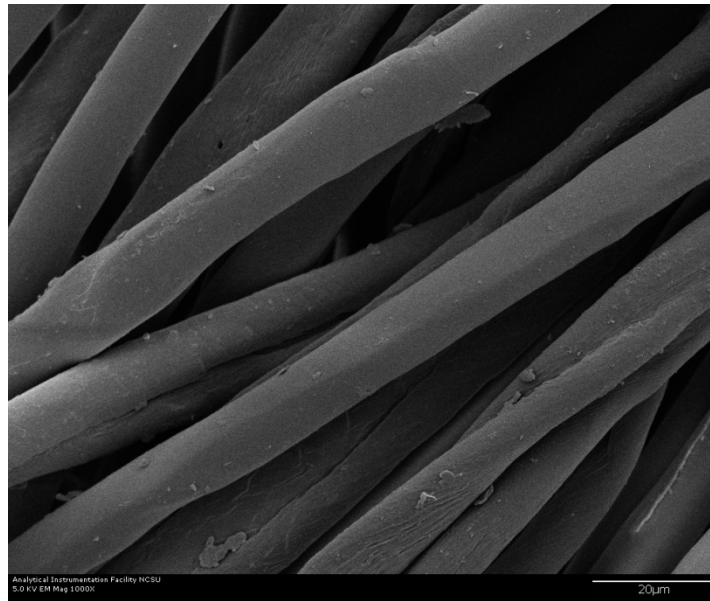


Figure 4.20: SEM image of untreated 50/50 PET/cotton fabric

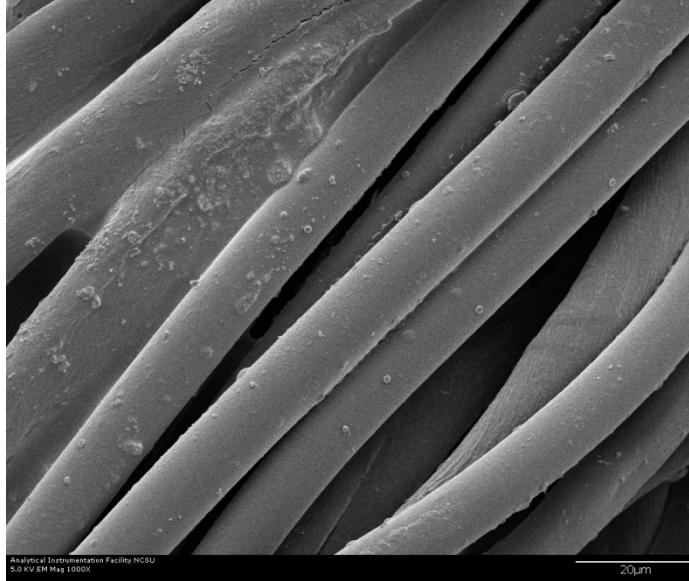


Figure 4.21: SEM image of 50/50 PET/cotton fabric treated with 1% titania, 5% BTESE, 2% hexadecyltriethoxysilane

SEM image of fabric treated with 1% titania after laundering is shown in Figure 4.22. Compared to treated fibers shown in Figure 4.21, the abrasion from laundering and drying has changed the morphology of the finish, but a significant amount of finish is still present. From Figure 4.22, the titania particles appear to bond more to the cotton fibers than the PET fibers, this is due to the surface hydroxyl groups on both the titania particles and the cotton surface.

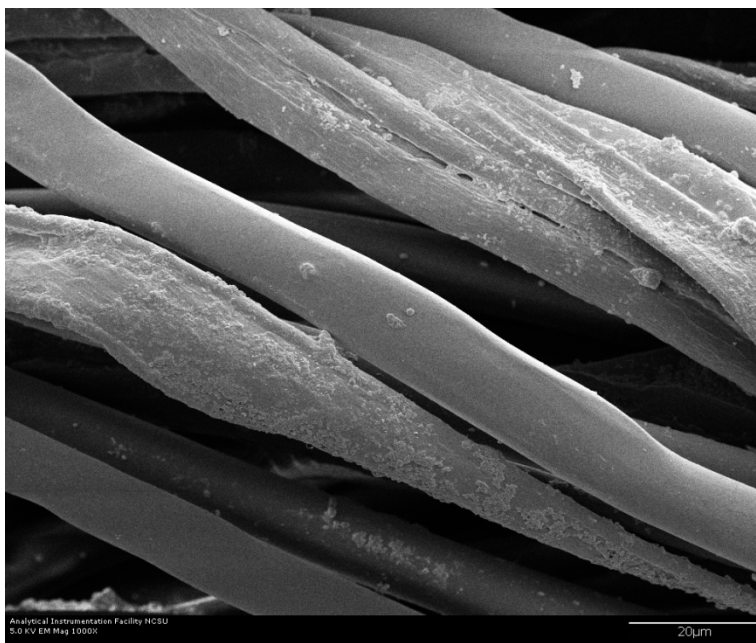


Figure 4.22: SEM image of PET/cotton fabric treated with 1% titania, 5% BTESE, 2% hexadecyltriethoxysilane, and 30% THPC/Urea after laundering.

4.7.2 50/50 PET/cotton fabrics treated with 3% titania

Samples treated with 3% titania showed different surface morphology than did fabrics treated with 1% titania. Figure 4.23 shows an SEM image of a fabric treated with 3% titania-containing finish. In contrast to fabrics treated with 1% titania, those treated with 3% titania have a rougher surface as a result of the higher titania content.

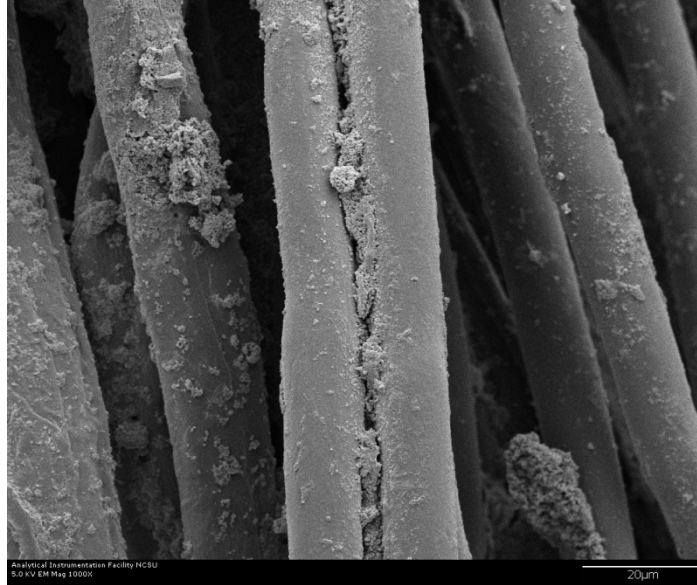


Figure 4.23: SEM image of PET/cotton fabric treated with 3% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% THPC/Urea

From Figure 4.23, it is also seen that samples treated with 3% titania tended to form agglomerations both on fiber surfaces and in between fibers, which did not occur in samples with 1% titania. Laundering of samples containing 3% titania yielded results similar to those of samples with 1% titania. An SEM image of fabric treated with 3% titania after laundering is shown in Figure 4.24. As a result of laundering, surface morphology is much less smooth and uniform, and the presence of titania on the fiber surface is much more pronounced.

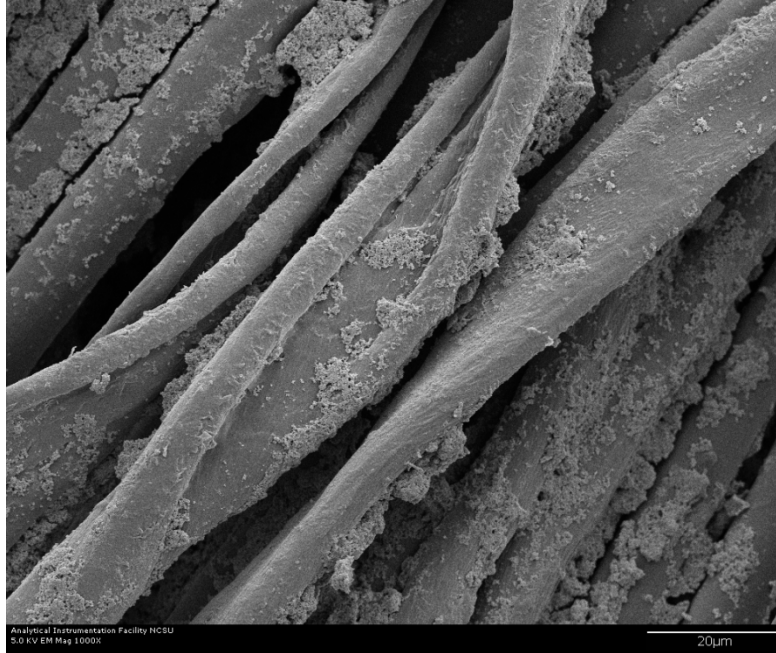


Figure 4.24: SEM image of PET/cotton fibers treated with 3% titania, 5% BTESE, 2% hexadecyltriethoxysilane, 30% THPC/Urea

4.8 Recommended Finishing Bath

After all treatment and testing, it was found that the finishing bath that created the treated fabrics with the best performance and durability was prepared according to the following formula:

- 30% Pyrosan[®] C-FR, 5% 3-isocyanatopropyltriethoxysilane, 2% hexadecyltriethoxysilane, 1% titania, 62% de-ionized water

The two silanes, 3-isocyanatopropyltriethoxysilane and hexadecyltriethoxysilane, were hydrolyzed in separate containers with half the total de-ionized water for 9 hours, and the

flame retardant and titania were mixed in a separate beaker until well mixed. After the hydrolysis, all three solutions were combined and mixed for 10 minutes prior to the dispersion of nanoparticles with the high speed mixer.

In addition to imparting durable repellency and flame resistance, the recommended finishing bath also uses a smaller concentration of flame retardant than do most current commercial flame retardant baths. Currently, most commercial phosphorus based flame retardants require a concentration of 40% or greater to achieve flame resistance. The recommended finish only uses a concentration of 30% by weight to achieve flame resistance.

5 Conclusions and Recommendations for Future Work

5.1 Summary of Results

The scope of this work was to determine if 50/50 PET/cotton fabrics treated with multifunctional silanes, ceramic nanoparticles, and phosphorus based flame retardants could present dual functionalities of water repellency and flame resistance. In addition, whether the treated fabrics were durable to laundering was investigated. The following are the main conclusions that were obtained from this work.

- Flame resistant and water repellent finishes can be produced on 50/50 PET/cotton blended fabrics using a combination of multifunctional silanes, ceramic nanoparticles, and phosphorus based flame retardants.
- Among all fabrics, those treated with 5% IPTES, 2% hexadecyltriethoxysilane, 30% THPC/Urea, and 1% titania showed the best results with respect to durable flame resistance and water repellency.
- The addition of either silica or titania nanoparticles has a positive effect on both flame resistance and repellency. As the concentration of silica or titania increases, both the flame resistance and repellency of the finished fabric increase. In addition, titania nanoparticles increase flame resistance of treated fabrics more than do silica nanoparticles. However, there was no apparent difference between the repellency of samples treated with silica or titania.

- As the alkyl chain length of the hydrophobic silane increases, the resultant water contact angle of the treated fabrics increases. In addition, increasing the concentration of hydrophobic silane increases both the repellency of the finished fabric and its durability to laundering. The type and concentration of hydrophobic silane had no apparent effect on the flame resistance of the treated fabric.
- Traditional silane crosslink enhancers (such as TEOS and BTESE) can be used to create fabrics exhibiting dual functions of flame resistance and water repellency, but these fabrics only maintain water repellency after laundering.
- Addition of an organofunctional silane (such as IPTES) allows for better bonding of the phosphorus based flame retardants into the crosslinked silane network. Some fabrics treated with IPTES were able to maintain both flame resistance and repellency after laundering.

5.2 Recommendations for Future Work

There are many different steps that could be taken to not only improve upon this research, but use the basis of this research to create different types of functional finishes.

- Future work should further investigate the use of IPTES to increase the durability of the treated fabrics to laundering. Data gathered in this research shows that IPTES is a viable silane to be used for the creation of durable finishes on 50/50 PET/cotton fabrics, but more detailed analysis of hydrolysis time should be performed to find an optimum.

- Experiments addressing drying and curing times should be performed to assess the effects of drying and curing on the performance of finished fabrics. Although drying and curing only serve to crosslink the silanes in a condensation reaction, there should be an optimal time and temperature for this finish. Furthermore, curing at elevated temperatures may degrade the cotton fibers, which may have undesired effects on the performance of the finished fabric.
- Due to the ease in manipulating the reactivity of the silane crosslink enhancers through the use of organofunctional groups, fabrics of different types should be researched to see if finishes very similar to this can be used to create repellent and flame resistant finishes on various synthetic fiber types.
- Testing should be performed on dyed fabrics to see if application of the finish has an impact on the visual characteristics of the fabric. In addition, the finish should be applied to fabrics dyed with different dye types. Fabrics dyed with reactive dyes may have fewer available hydroxyl groups do to bonding with the colorant. It is possible that application of this finish to dyed fabrics may result in color or hue change. For non-dyed fabrics, an evaluation of change in whiteness would be useful.
- Further testing of repellency should be conducted. AATCC tests such as the spray test and impact penetration test would provide valuable data as to the overall repellency of the finish. Using contact angles to measure repellency provides accurate data as to the affinity of the treated surface for water, but does

not fully represent how the treated fabric will perform when in contact with larger amounts of water.

- Evaluation of the hand of finished fabrics should be performed, as samples had a stiff hand after initial curing. In markets where the aesthetics of the fabric are important (such as clothing), post treatment of the treated fabrics may have to be conducted to increase the hand of the fabric.
- As this technology is relatively new in the scientific community, optimization of this finish should be investigated. An optimal combination of chemicals and processing parameters should be investigated to not only optimize the performance of the finished fabric, but also to optimize the aesthetic properties of the finished fabric as well.
- Due to the nature of application chemistry, this finish could be used with chemicals other than flame retardants to create dual function fabrics of other types. Based upon the current chemicals, any chemical with available hydroxyl groups for bonding could be added into the finish in place of THPC/Urea, and titania has shown efficacy in odor neutralization and antimicrobial applications.
- The possibility of creating finished fabrics with different functionalities should be investigated as well.

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